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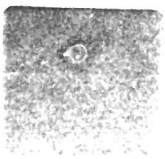

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II

STRUCTURAL STUDIES OF SOME POLYNUCLEAR CARBONYL CLUSTERS OF RUTHENIUM AND OSMIUM AND THEIR COMPLEXES WITH SMALL ORGANIC MOLECULES AND HYDROGEN

A thesis submitted to the
Council for National Academic Awards in partial
fulfilment of the requirements for the degree of
Doctor of Philosophy

By
William John Henry Nelson

The work described in this thesis was carried out in the Department of Chemistry, The Polytechnic of North London and in the University Chemical Laboratory, Cambridge.

October 1980

STRUCTURAL STUDIES OF SOME POLYNUCLEAR CARBONYL CLUSTERS OF RUTHENIUM AND OSMIUM AND THEIR COMPLEXES WITH SMALL ORGANIC MOLECULES AND HYDROGEN

W.J.H.NELSON

ABSTRACT

X-ray analyses of fifteen carbonyl clusters of ruthenium and osmium have been completed which demonstrate several new aspects of cluster structures.

Two isomers differing only in the disposition of their hydride ligands have been found for the anion in $[(Ph_3P)_2N]^+ [H_3Ru_4(CO)_{12}]^-$ confirming that such isomers can persist into the solid state. Two crystalline modifications of $[(Ph_3P)_2N]^+ [H_3Os_4(CO)_{12}]^-$ were studied but both contained the same isomer whose geometry is similar to that reported for the anion in the $[Me_4N]^+$ salt.

For pentanuclear clusters with seven skeletal electron pairs $Os_5C(CO)_{15}$ has the expected square pyramidal metal geometry but $[H_2Os_5(CO)_{15}I]^-$ and $H_2Os_5(CO)_{15}P(OMe)_3$ have alternative edge-bridged tetrahedral geometries. In $[Os_5C(CO)_{15}I]^-$, which has two more skeletal electrons, the Os atoms define five vertices of a pentagonal bipyramid. Thus on addition of I^- to $Os_5C(CO)_{15}$ a coordination site is provided *via* the breaking of an Os-Os bond; this flexibility of the metal framework suggests that these clusters may be of use as catalysts.

In $[Ph_4As]_2^+ [Ru_6C(CO)_{16}]^{2-}$ the dianion has a carbonyl distribution of C_{2v} symmetry unlike that reported for the $[Me_4N]^+$ salt. The complex $Ru_6C(CO)_{15}(C_6H_{10})$, which also has an octahedral Ru_6C unit, is a rare example of high nuclearity cluster with a hydrocarbon ligand. The dianion $[Ru_6(CO)_{18}]^{2-}$ has bridging as well as terminal CO ligands so it is not isostructural with $[Os_6(CO)_{18}]^{2-}$ which has only terminal CO's. An interstitial site has been confirmed for the hydride in $[Ru_6H(CO)_{18}]^-$; this is the first example of a carbonyl cluster with an H atom in such an environment.

The largest osmium cluster prepared to date, $[Os_{10}C(CO)_{24}]^{2-}$, has been isolated from the pyrolysis of $Os_3(CO)_{11}Py$. The Os atoms adopt a novel tetracapped octahedral geometry and the arrangement of CO's perpendicular to each Os_6 face may be the best model so far of carbon monoxide chemisorbed onto a metal surface.

PREFACE

While registered as a candidate for the degree for which submission is made the author has not been a registered candidate for another award of the CNAA or of a University during the research programme. The results and conclusions presented in this thesis represent original work by the author unless specific reference is made.

In partial fulfilment of the requirements of the degree the author completed a course in Fortran IV computer programming (30 hrs) and one on X-ray crystallography (10 hrs). He also attended the 1978 and 1979 Autumn meetings of the Chem. Soc. dealing with aspects of the chemistry of polynuclear clusters and several research seminars held by the carbonyl cluster group at Cambridge University (20 hrs).

W.J.H. Nelson

ACKNOWLEDGEMENTS

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The award of an S.R.C. Research Studentship for the duration of my studies is gratefully acknowledged.

ABBREVIATIONS

AO	atomic orbital
ARUPS	angle-resolved ultraviolet photoemission spectroscopy
b.c.c.	body-centred cubic
Bu	butyl
c.c.p	cubic close packed
EAN	effective atomic number
EH	extended Hückel
EHMO	" " molecular orbital
Et	ethyl
f.c.c.	face-centred cubic
F.t. n.m.r.	Fourier transform nuclear magnetic resonance
h.c.p.	hexagonal close packed
i.r.	infra red
LCAO	linear combination of atomic orbitals
LEED	low energy electron diffraction
Me	methyl
MO	molecular orbital
n.m.r.	nuclear magnetic resonance
Ph	phenyl
Py	pyridine
S	skeletal electron pairs
THF	tetrahydrofuran
t.l.c.	thin layer chromatography
UPS	ultra violet photoemission spectroscopy
VSEPR	valence shell electron pair repulsion
XPS	X-ray photoemission spectroscopy

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APPENDICES Containing the Fractional Atomic Coordinates and Thermal Parameters for the Compounds above & Copies of Papers Arising from the Work Subsequent Pages

SECTION 1

Introduction.

Section 1.1 The Importance of Cluster Compounds

In recent years great interest has been shown in the chemistry of transition metal clusters which has been motivated by the proposition that discrete molecular clusters (metal units in which each metal is bonded to at least two other metal atoms, thus forming a polyhedron) may be reasonable models of metal surfaces in chemisorption and catalysis. Clusters, microcrystallites, and macroscopic crystals have in common the faces [e.g. M_3 (triangular), M_4 (square planar) or M_4 (butterfly)] which they present on the outside surface, and it is conceivable that by studying their geometries and modes of reaction with simple molecules, mechanisms involved in heterogeneous catalysis on a metal surface will be elucidated. Recent advances in X-ray analysis, F.t. n.m.r., and mass spectrometry have enabled the geometries of clusters containing up to 30 metal atoms to be "routinely" determined, and their properties compared with those of the chemisorbed state obtained from techniques such as LEED, ARUPS, and UPS - XPS.

Metal clusters have also been shown to be effective catalysts in their own right[1] in reactions involving isomerization, hydrogenation, oligomerization, hydroformylation, oxidation, and in the Fischer-Tropsch and water gas shift reactions. The last two examples are of paramount importance in view of the rapidly declining oil reserves and the need to produce liquid and gaseous fuels from coal.[2] However at this stage it is important to note that most commercial heterogeneous catalysis takes place on oxide supported metals or on oxides, rather than on bare metal surfaces themselves.[3]

The most easily studied clusters are of the type $M_n L_x$ in which the transition metal unit M_n is surrounded by strong π - acceptor ligands L, commonly CO. Experimental observations reveal that the metal atoms are almost always in the zero oxidation state, the function of the ligands being to remove excess electron density

from the anti-bonding orbitals of the cluster (which would inevitably be occupied as a result of the many d-electrons donated to the cluster by each metal atom) and hence stabilize it. Few clusters are known containing metals of higher oxidation state, this is thought to be a consequence of poor overlapping between relatively contracted d-orbitals.[4]

Some aspects of the relationship between polynuclear carbonyl clusters and the bulk metal, and various methods that have been used to predict their structures (and reactivity) will be discussed in the following Sections.

Section 1.2 Comparisons between Clusters and the Bulk Metal[5]

The electronic structure of the cluster is an important parameter that determines chemical reactivity and structure. UPS studies on $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Os_6(CO)_{18}$ show their first ionization energies to be larger than the work function of the metal,[6] therefore their electronic characteristics differ from those of the bulk metal. However the UPS spectrum of $Rh_6(CO)_{16}$ is similar to that of Pd (III)/CO with respect to position and width of maxima inferring similar electronic properties.[7]

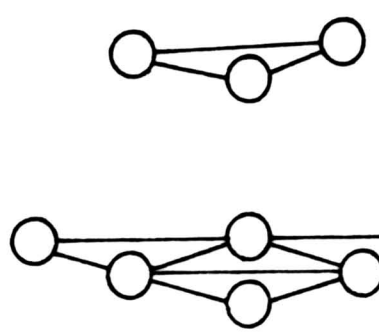
EHMO calculations show that as aggregates of metal atoms are built up the atomic orbitals combine to form molecular orbitals, and at the infinite limit these MO's evolve into the band structure of bulk metals.[8] Similar calculations carried out using the X_α-SW approximation also show that cluster properties converge to those of the metal as their size increases.[9]

In some of the larger clusters prepared the metal atoms adopt geometries closely related to the lattices found for bulk metals. For example the clusters $[Ni_{12}H_{4-n}(CO)_{21}]^{n-}$ (ref. 10) and $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (refs. 11 and 12) contain sections of an h.c.p. array of metals [Figures 1.1(a) and 1.1(b)], and in $[Rh_{14}(CO)_{25}]^{4-}$ a b.c.c. arrangement of metal atoms is found[13a] [Figure 1.1(c)]. The species $[Rh_{17}S_2(CO)_{32}]^{3-}$, which contains stacked squares of Rh atoms[14] [Figure 1.1(d)] is also reminiscent of a b.c.c. lattice. This example is particularly interesting because of the interstitial sites, which are present in all metal polyhedra, two are occupied by sulphur atoms. The occupation of interstitial sites in polyhedra by atoms such as H and C is exceedingly important in relation to processes such as the diffusion of gases in metals, and in relation to the structures and properties of alloys, and will be referred to in more detail in later Sections. In the rhodium trianion $[Rh_{14}H(CO)_{25}]^{3-}$ the metal

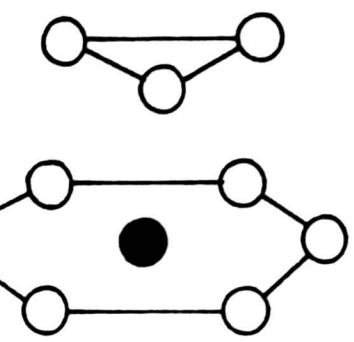
polyhedron is not so regular in structure but can still be described as an array intermediate between a c.c.p. arrangement and b.c.c. packing[13b] [Figure 1.1(e)]. The metal atoms in $[Rh_{15}(CO)_{27}]^{3-}$ also adopt an intermediate geometry, the polyhedron displaying elements of an h.c.p. array and b.c.c. packing[13a] [Figure 1.1(f)].

The geometries adopted by the metal atoms in other large clusters are not closely related to those of the bulk metal. For example $[Rh_{12}(CO)_{30}]^{2-}$ is composed of two linked octahedral Rh_6 units,[15] $Rh_{12}C_2(CO)_{25}$ has an irregular metal geometry which can nevertheless be described in terms of layer packing of atoms,[16] and in $[Rh_{15}C_2(CO)_{28}]^{-}$ the twelve coordination about the central Rh atom is not metal like,[17] i.e. not a close packing of atoms in which all the metal - metal contacts are equal in length. The Pt tetraanion $[Pt_{19}(CO)_{22}]^{4-}$ is also of interest. Although 5-fold axes cannot occur in crystals the cluster as a whole exhibits virtual fivefold symmetry (Figure 1.2),[18] and the CO : surface metal ratio (1.29) is the lowest found to date in a metal carbonyl cluster and may provide an excellent model for the chemisorption of carbon monoxide on a platinum surface. These examples imply, as pointed out by Chini,[19] that CO interactions tend to limit cluster size, and also modify the metal geometries to include more corner and edge atoms to minimize the CO repulsions. Therefore such clusters are intrinsically different from metal surfaces in catalytic activity, but a metal cluster - highly dispersed metal particle analogy would not be so seriously flawed.

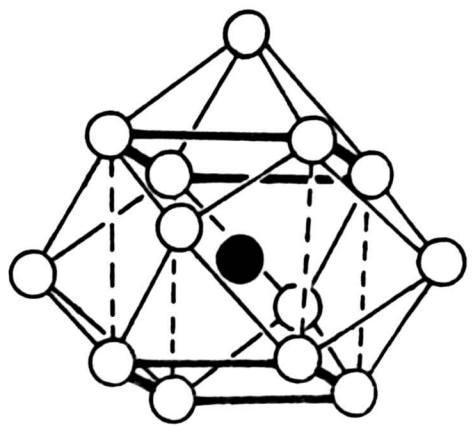
Figure 1.1 Analogues of metallic lattices in carbonyl clusters. The shaded metal atoms are completely encapsulated.



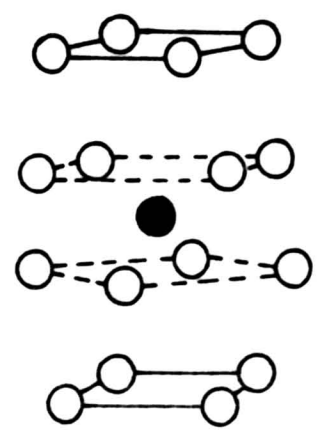
(a) $[Ni_{12}H_{4-n}(CO)_{21}]^{n-}$: h.c.p.



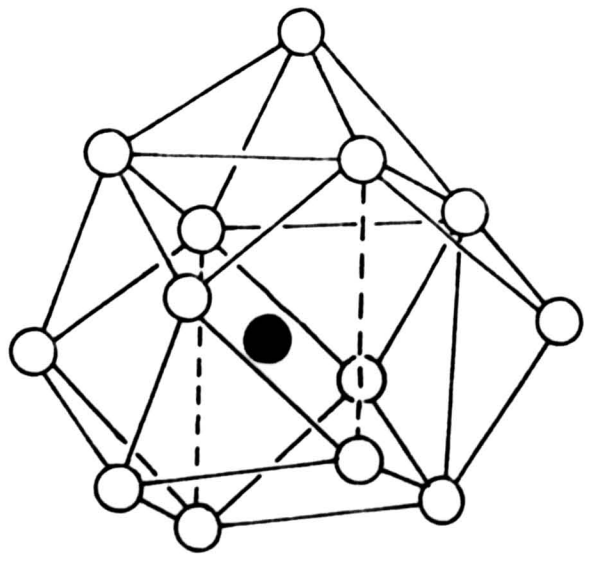
(b) $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$: h.c.p.



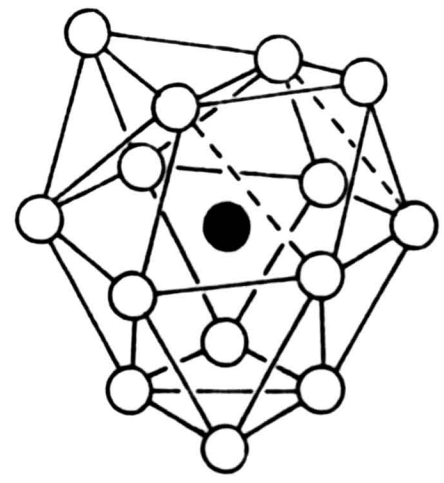
(c) $[Rh_{14}(CO)_{25}]^{4-}$: b.c.c.



(d) $[Rh_{17}S_2(CO)_{32}]^{3-}$: reminiscent of b.c.c. packing.

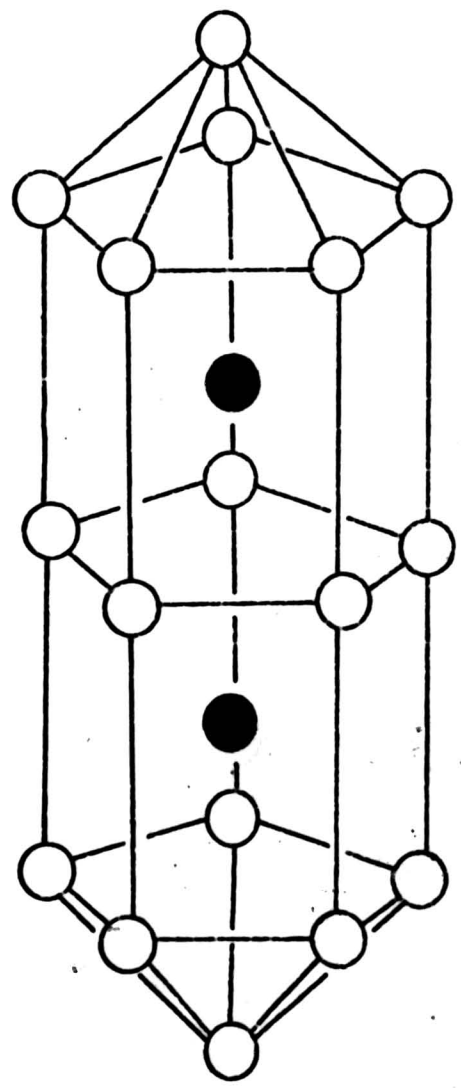


(e) $[Rh_{14}H(CO)_{25}]^{3-}$: b.c.c./ c.c.p.



(f) $[Rh_{15}(CO)_{27}]^{3-}$: b.c.c./ h.c.p.

Figure 1.2 The Pt_{19} core in the tetraanion $[Pt_{19}(CO)_{22}]^{4-}$ that has virtual 5-fold symmetry. The shaded atoms are internally sandwiched between the five-membered rings.



Section 1.3 The CO Ligand in Clusters

The CO ligand is by far the most ubiquitous in metal clusters. These ligands effectively shield the metal nucleus from attack so in many reactions the first step will be CO dissociation to expose the M_n unit.

Carbonyl ligands may bond in a number of different ways to the metals: terminal, doubly bridging (μ_2), triply briding (μ_3), and in a few clusters both the C and O atoms are bonded to the metals (vide infra).

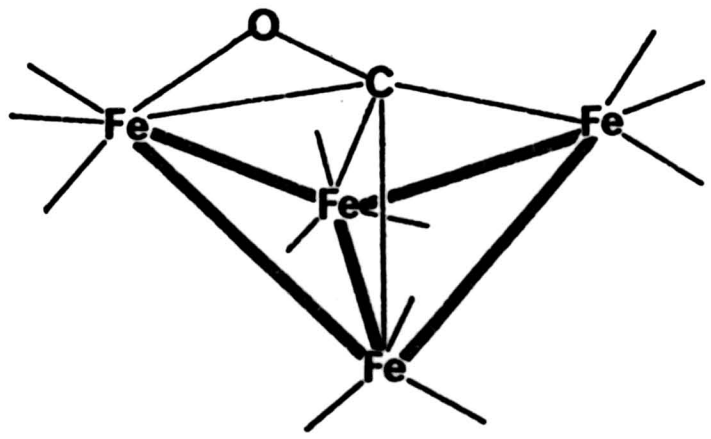
The terminal CO ligand is the most common ligand that is found in clusters. The synergic effect is responsible for the stability of the M-C bond,[20] and since the two π^* orbitals are not required by symmetry to interact equally with the metal d-orbitals[21] in most cases the M-C-O angle is not linear, but nearer 175°. Crystal packing forces would also tend to cause a distortion in the M-C-O angle from linearity.

There are three different types of μ_2 carbonyl; symmetrical, in which the two M-C bond lengths are not significantly different, asymmetric, in which the M-C bond lengths do differ significantly but the C-O vector is still approximately normal to the M-M axis, and semi-bridging (or incipient) in which the two M-C lengths are markedly different and the two M-C-O angles are also different such that the C-O vector is no longer at right angles to the M-M bond. These types are not distinct but merge into one another. It is well known that in solution facile exchange occurs between μ_2 bridging and terminal CO ligands, implying a low activation energy. Therefore in the solid intermediate bonding modes between symmetrically bridging and terminal, that are all very similar in energy, will be "frozen out". Often asymmetric bridges occur in compensating pairs[22] representing a single stage in the CO exchange process. A recent review by Colton and McCormick[23] discusses μ_2 carbonyl ligands in more detail.

Triply bridging carbonyls also occur in symmetric or asymmetric situations. Chini has suggested[24] that μ_3 carbonyls are more effective at withdrawing electron density than μ_2 carbonyls, which in turn are more effective than terminals CO's. This is consistent with the observation that the C-O distance in CO ligands increases in the order terminal $< \mu_2 < \mu_3$ implying an increasing occupation of the CO π^* orbitals, and the i.r. stretching frequency decreases concomitantly in the order terminal $> \mu_2 > \mu_3$. Bridging CO's are therefore most commonly found in highly charged clusters, for example although $H_4Ru_4(CO)_{12}$[25] and $[H_3Ru_4(CO)_{12}]^-$ (ref.26) contain only terminal CO ligands, bridging carbonyls are present[27] in the dianion $[H_2Ru_4(CO)_{12}]^{2-}$. Further, since the bridging CO ligands in clusters are more effective at withdrawing electron density, their distribution may be used as a guide to the distribution of negative charge in the molecule.[28]

In the iron cluster $[HFe_4(CO)_{13}]^-$ both the C and O atoms of one carbonyl ligand are bonded to metals[29] (Figure 1.3). Dissociative chemisorption is thought to be the first step in Fischer-Tropsch reactions catalysed by Fe, Co, Ni, and Ru,[30] and the unusual mode of bonding shown by this CO ligand is suggestive of an intermediate state in the conversion of CO to disjointed C and O atoms on a metal surface.

Figure 1.3 The η^2 4-electron donor CO ligand in $[HFe_4(CO)_{13}]^-$.



Section 1.4 Methods Used to Rationalize Cluster Structures

The structures of the majority of polynuclear carbonyls are based on triangular faced polyhedra (deltahedra). King has suggested[31] that this preference for deltahedra results because a triangle of metal atoms maximizes the number of bonding electrons per metal atom, and has the smallest maximum intermetallic distance thereby optimizing interactions between the M-M bonds. By joining triangles into polyhedral networks a delocalized system may be built up in much the same way that polycyclic aromatic systems are formed by the fusion of hexagonal subunits.

A number of qualitative and semi-quantitative bonding schemes have been used, with varying success, to interpret the structures of carbonyl clusters. Several of these schemes are discussed below with emphasis being placed on their uses and limitations.

1.4.1 The Effective Atomic Number (EAN) Rule

This rule is based on the assumption that polyhedral edges represent two-centre two-electron M-M bonds, and that each metal attains an inert gas configuration by forming the appropriate number of M-M bonds with its neighbours. The EAN rule is most useful for rationalizing the structures of triangular clusters, for example in $Os_3(CO)_{12}$[32] each $Os(CO)_4$ fragment has 16 valance electrons (therefore the cluster as a whole has 3 x 16 = 48 valence electrons), so an inert gas configuration is obtained for each Os by forming an M-M bond to each of the other two $Os(CO)_4$ fragments. The EAN rule in this form may be used to place negative charge in anionic clusters, for example in $[H_2Ir_4(CO)_{10}]^{2-}$ (ref.33) the two Ir atoms that are bonded to a terminal hydride ligand each have only 17 valence electrons, so unit negative charge may be considered to reside on these atoms.

Consideration of the electronic requirements of the cluster as

a whole, rather than the requirements of each metal atom individually, allows the structures of other clusters to be rationalized. Assuming each metal utilizes all of its 9 valence orbitals, the number of M-M bonds required is given by $1/2(18N_1-N_2)$ where N_1 = number of metal atoms and N_2 = the total number of valence electrons in the cluster. Therefore triangular clusters require 48 valence electrons, tetrahedral clusters 60 valence electrons, and so on. The dihydride $H_2Os_3(CO)_{11}$[32] has 48 valence electrons so obeys the EAN rule overall, but the presence of a doubly bridging H ligand which effectively donates half an electron to each of two Os atoms, means each Os individually does not.

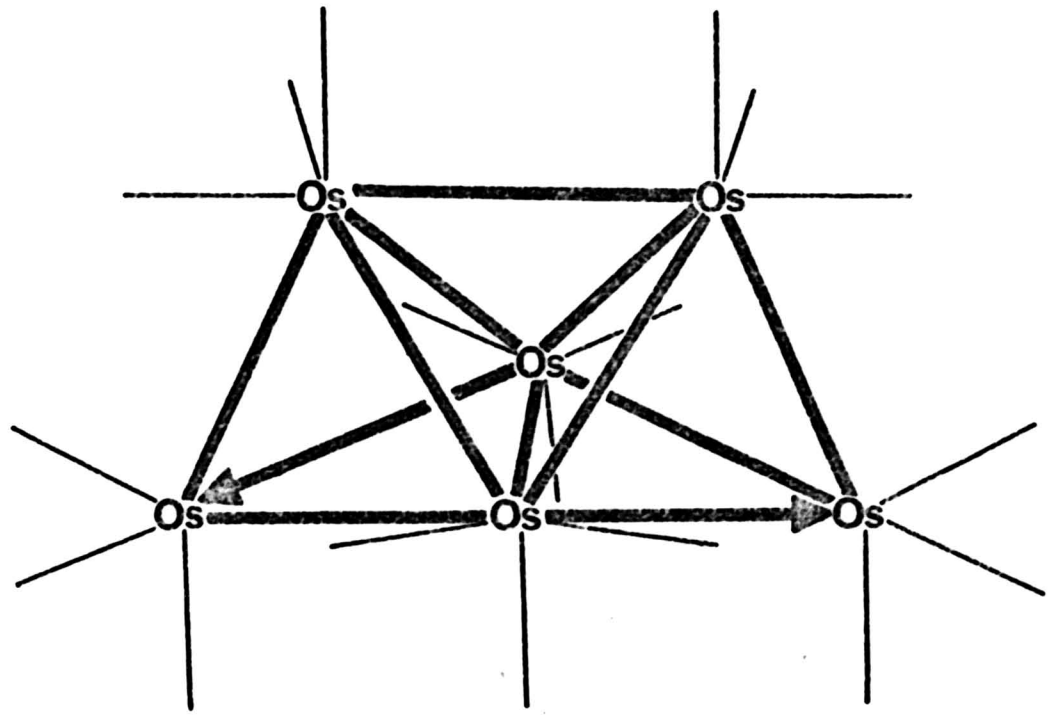
The trinuclear clusters $[H_3Re_3(CO)_{10}]^{2-}$ (ref.34) and $H_2Os_3(CO)_{10}$[35,36] only have 46 valence electrons, so in each a double bond is required between two metals to allow these molecules to obey the EAN rule overall. This is consistent with the chemistry of the latter cluster which readily adds on a two-electron donor such as CO or PPh_3 to give a saturated 48 electron species.

Electrons in excess of the count required by the EAN rule are considered to cause rupture of the appropriate number of M-M bonds[37] which suggests that each edge has a well defined bonding and anti-bonding MO associated with it. In the dianion $[H_4Re_4(CO)_{15}]^{2-}$ there are 3 electron pairs in excess of the 6 required for a tetrahedral metal geometry, so 3 bonds of the "parent" tetrahedron are ruptured.[38]

The EAN rule is less satisfactory for predicting the structures of larger clusters. For example the hexanuclear cluster $Os_6(CO)_{18}$, which has 84 valence electrons, was confidently predicted[39] to have an octahedral metal geometry (12 M-M bonds) similar to that found in the isoelectronic species $H_6Cu_6L_6$.[40] In addition with three terminal CO's per metal, each Os would <u>individually</u> obey the EAN rule. However octahedral carbonyl clusters are found to require 86 rather than 84 valence electrons for a closed shell configuration (see Subsection 1.4.3) and an alternative capped trigonal bipyramidal metal geometry is found for $Os_6(CO)_{18}$.[41] This structure also has

12 M-M bonds, so obeys the EAN overall, but dative bonds are necessary for each metal atom to achieve an inert gas configuration (Figure 1.4). This approach nevertheless explains the observation that nucleophiles attack the molecule at the "electron deficient" capping groups.[42]

Figure 1.4 The capped-trigonal bipyramidal structure of $Os_6(CO)_{18}$



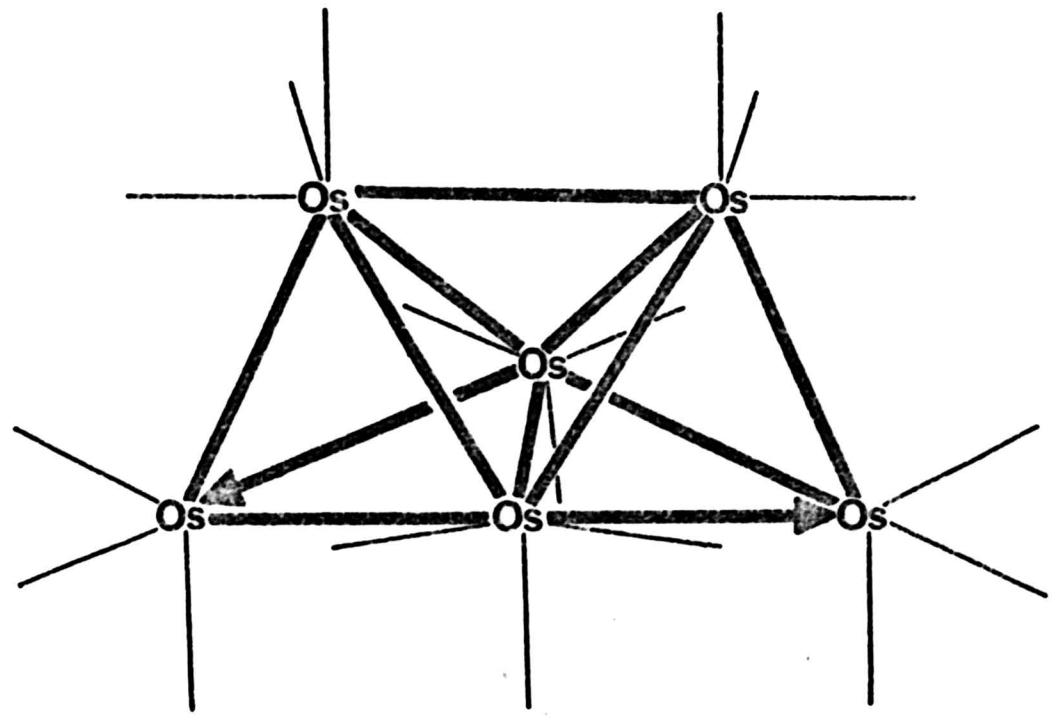
1.4.2 Close Packing of Electron Pairs or CO Ligands

Gillespie has suggested that the valence electron pairs in clusters will constitute one overall close packed arrangement,[43] which is a logical extension of the VSEPR theory for AL_x molecules. The metal atoms then occupy appropriate holes in the polyhedron of localized electron pairs.

For octahedral clusters with 84 valence electrons, the 12 electron pairs define a cubo-octahedron and correspond to M-M edge bonds [Figure 1.5(a)]. The 86 electron octahedral clusters, which were not conveniently explained by the EAN rule, may be

12 M-M bonds, so obeys the EAN overall, but dative bonds are necessary for each metal atom to achieve an inert gas configuration (Figure 1.4). This approach nevertheless explains the observation that nucleophiles attack the molecule at the "electron deficient" capping groups.[42]

Figure 1.4 The capped-trigonal bipyramidal structure of $Os_6(CO)_{18}$



1.4.2 Close Packing of Electron Pairs or CO Ligands

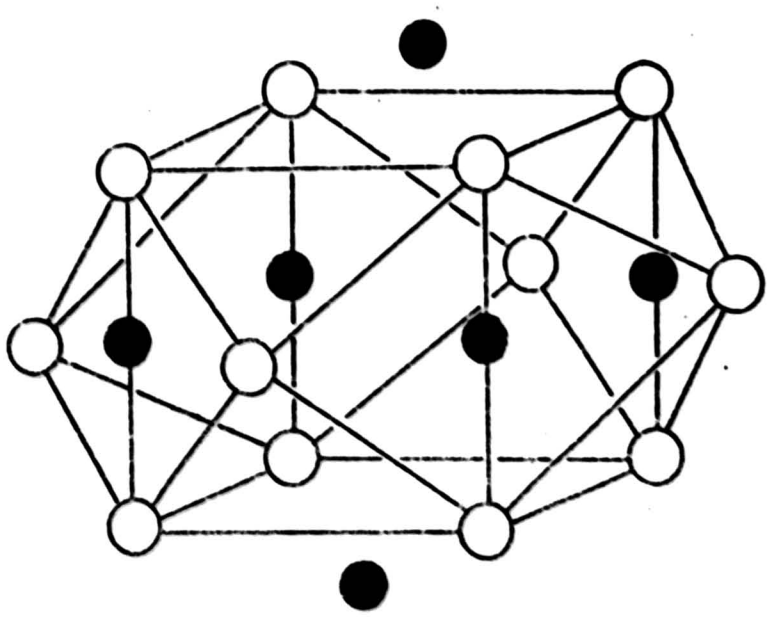
Gillespie has suggested that the valence electron pairs in clusters will constitute one overall close packed arrangement,[43] which is a logical extension of the VSEPR theory for AL_x molecules. The metal atoms then occupy appropriate holes in the polyhedron of localized electron pairs.

For octahedral clusters with 84 valence electrons, the 12 electron pairs define a cubo-octahedron and correspond to M-M edge bonds [Figure 1.5(a)]. The 86 electron octahedral clusters, which were not conveniently explained by the EAN rule, may be

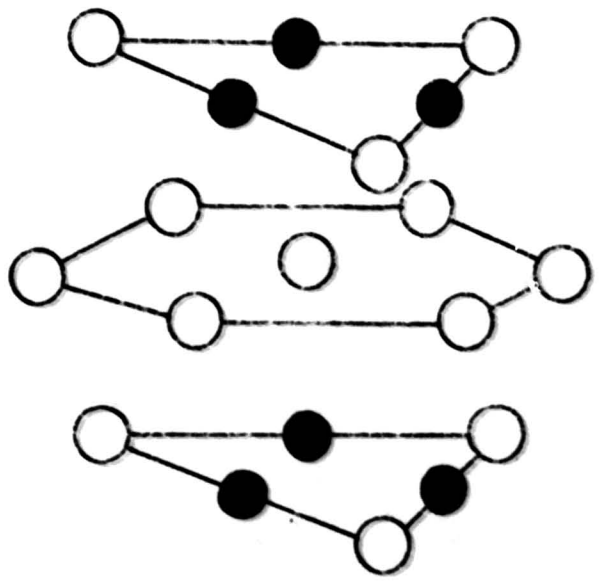
Figure 1.5 (a) Cubo-octahedral arrangement of 12 electron pairs with six nuclei occupying four-coordinate holes and having an octahedral arrangement. The 86 electron octahedral clusters, for example $[Ni_6(CO)_{12}]^{2-}$, have an extra electron pair placed at the centre of the cubo-octahedron giving a c.c.p. stack of 13 electron pairs;

(b) Hexagonal close packed arrangement of 13 electron pairs which gives rise to a trigonal prismatic M_6 unit as in $[Pt_6(CO)_{12}]^{2-}$.

(a)



(b)



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The 86 electron
$(CO)_{12}]^{2-}$, have
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13 electron
riematic M_6

rationalized by placing the extra electron pair at the centre of the cubo-octahedron giving a c.c.p. stack of 13 electron pairs. The dianion $[Ni_6(CO)_{12}]^{2-}$ is such an example.[44] The Pt analogue has an alternative trigonal prismatic metal geometry;[45] in this case the 13 electron pairs adopt an alternative h.c.p. geometry [Figure 1.5(b)].

Although this theory is good for rationalizing many cluster structures, like others to follow it is unreliable for <u>predicting</u> their geometries.

An alternative approach suggested by Johnson[46] assumes that the CO ligands rather than valence electron pairs are close packed. The shape and orientation of the M_n unit may then be deduced from a combination of Wade theory (see following Subsection) and consideration of the space and sites available within the CO polyhedron. In $Fe_3(CO)_{12}$ the molecule is based on the favourable icosahedral arrangement of CO groups[47] which gives rise to two μ_2 carbonyls, but in $Ru_3(CO)_{12}$[48] and $Os_3(CO)_{12}$[31] the larger Ru_3 or Os_3 triangles cannot be accomodated within an icosahedron so the CO's adopt an alternative cubo-octahedral arrangement that requires no bridging carbonyls. The differing geometries of $[Ni_6(CO)_{12}]^{2-}$ (ref.44) and $[Pt_6(CO)_{12}]^{2-}$ (ref.45) may also be rationalized using this theory; in the former the octahedral Ni_6 unit is accomodated within a puckered bihexagonal arrangement of carbonyl ligands, but in the latter the greater size of the Pt_6 trigonal prismatic unit means the CO's adopt the eclipsed bihexagonal arrangement.

The positions of hydride ligands in clusters may be inferred from a consideration of the vacant sites in the CO polyhedron. For example in $[H_2Ir_4(CO)_{10}]^{2-}$ the carbonyl ligands define a cubo-octahedron which has two vertices missing, if these were occupied by the hydrogens they would be terminally bonded to the metal atoms.[32]

Fluxional behaviour in carbonyl clusters may also be explained by this theory in terms of a change of orientation of the M_n unit within the CO polyhedron.[49]

The wider applicability of this approach for rationalizing cluster structure and fluxionality in larger systems is currently being examined.[50]

1.4.3 Wade Theory[51]

This theory is a logical extension of localized schemes in small clusters to large clusters in which the MO's are delocalized. Hence the metal units are considered *in toto* rather than as individual metal atoms.

By analogy with the boron hydride series the following assumptions and rules are made:-

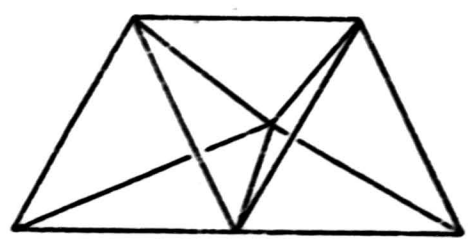
(1) Only 3 hybrid orbitals are used by each metal carbonyl fragment for cluster bonding, primarily of s and p character. The remaining 6 orbitals of the initial 9 (s + 5d + 3p) are used for ligand bonding and housing non-bonding electrons.

(2) The orbitals available for ligand bonding and non-bonding electrons are filled first, requiring a total of 12n electrons where n = number of metal atoms.

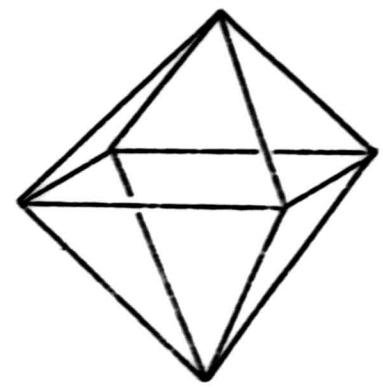
(3) The remaining electrons are involved in skeletal bonding. The fundamental metal polyhedron, which must have triangulated faces, is established from the number of skeletal electron pairs, S [= 1/2 (N-12n) where N is the number of valence electrons in the cluster], thus:- S = 6, trigonal bipyramid; S = 7, octahedron; S = 8, pentagonal bipyramid; S = 9, dodecahedron, etc. These values of S correspond to 72, 86, 100 and 114 valence electrons respectively.

Closo - structures have S = (n+1) and the n metal atoms define the n vertices of the appropriate polyhedron above.

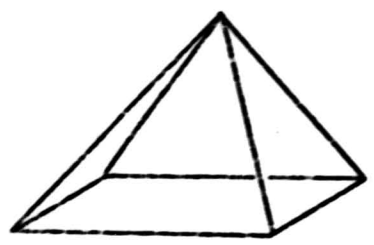
Figure 1.6 The metal geometry in some polynuclear carbonyl clusters. The number of skeletal electron pairs (S) is given in parentheses.



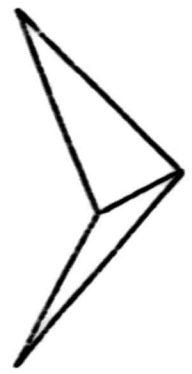
(a) $Os_6(CO)_{18}$ (S = 6)



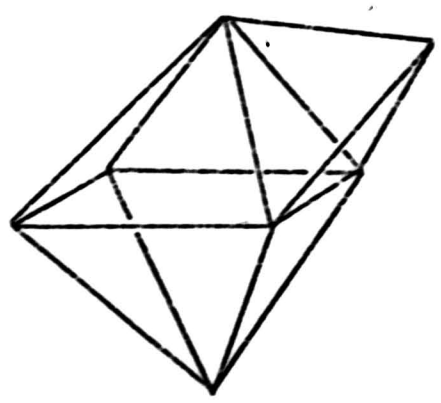
(b) $[Os_6(CO)_{18}]^{2-}$ (S = 7)



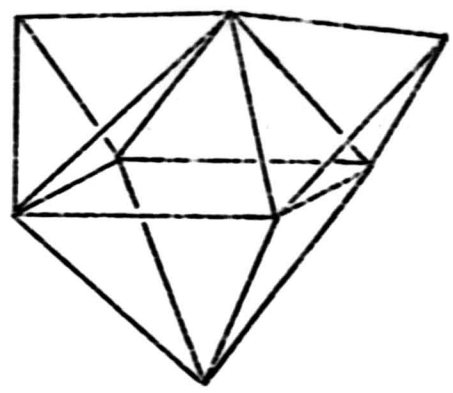
(c) $Fe_5C(CO)_{15}$ (S = 7)



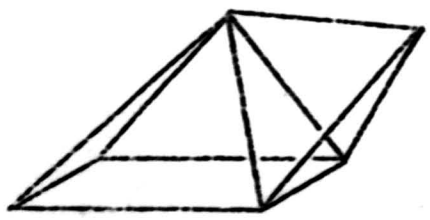
(d) $H_3Os_4(CO)_{12}I$ (S = 7)



(e) $Os_7(CO)_{21}$ (S = 7)



(f) $[Os_8(CO)_{22}]^{2-}$ (S = 7)



(g) $H_2Os_6(CO)_{18}$ (S = 7)

yl
rs

(S = 7)

(S = 7)

(S = 7)

)

Nido - structures have S = (n+2) and one vertex of the parent n vertex polyhedron is missing.

Arachno - structures have S = (n+3) and two vertices are missing from the fundamental polyhedron.

It is fundamental to Wade theory that closo - nido - and arachno - versions of the same polyhedron require the same number of skeletal electron pairs.

(4) This rule is an extension of Wade theory suggested by Mason and Mingos,[40] and Lewis et al.[52] to include clusters in which S = n or (n-1) by taking the basic polyhedron derived from the value of S, and for S = n capping it once, whilst for S = (n-1) capping it twice.

Therefore capped structures, or those with vertices removed all require the same number of skeletal electron pairs as the parent polyhedron from which they are derived. Several examples will now be used to illustrate the use of Wade theory for rationalizing cluster structures (see also Figure 1.6).

(i) $Os_6(CO)_{18}$,[41] S = 6, fund. polyhedron: trigonal bipyramid, this must be capped once since S = n.

(ii) $[Os_6(CO)_{18}]^{2-}$,[53] S = 7, fund. polyhedron: octahedron, closo - version since S = (n+1).

(iii) $Fe_5C(CO)_{15}$,[54] S = 7, fund. polyhedron: octahedron, nido - version since S = (n+2) so a square pyramidal metal geometry.

(iv) $H_3Os_4(CO)_{12}I$,[55] S = 7, fund. polyhedron: octahedron, arachno - version since S = (n+3) so a butterfly metal geometry.

(v) $Os_7(CO)_{21}$,[56] S = 7, fund. polyhedron: octahedron, this must be capped once since S = n.

(vi) $[Os_8(CO)_{22}]^{2-}$,[57] S = 7, fund. polyhedron: octahedron, this must be capped twice since S = (n-1).

Although Wade theory may be successfully used to rationalize the geometries of many clusters, no account is taken of the requirements of the ligands attached to the metal unit. For example,

although $[Os_6(CO)_{18}]^{2-}$ has the octahedral geometry expected from Wade theory, $H_2Os_6(CO)_{18}$, which has the same number of skeletal electron pairs, has an alternative monocapped square pyramidal metal geometry[53] [Figure 1.6(g)]. In this case the extra hydrogen atoms have altered the favoured structure of the metal unit from an octahedron to a polyhedron having a square face.[58]

Wade theory allows structural changes to be predicted involving addition or loss of electron pairs. Thus, on reduction, the metal geometry changes from a capped trigonal bipyramid in $Os_6(CO)_{18}$ (S = 6), to an octahedron in $[Os_6(CO)_{18}]^{2-}$ (S = 7).

The assumptions inherent in Wade theory need justification since it is perhaps surprising that a bonding scheme derived for electron-deficient boranes is applicable to electron-rich metal clusters. Some theoretical contributions supporting these emperical rules will be now presented.

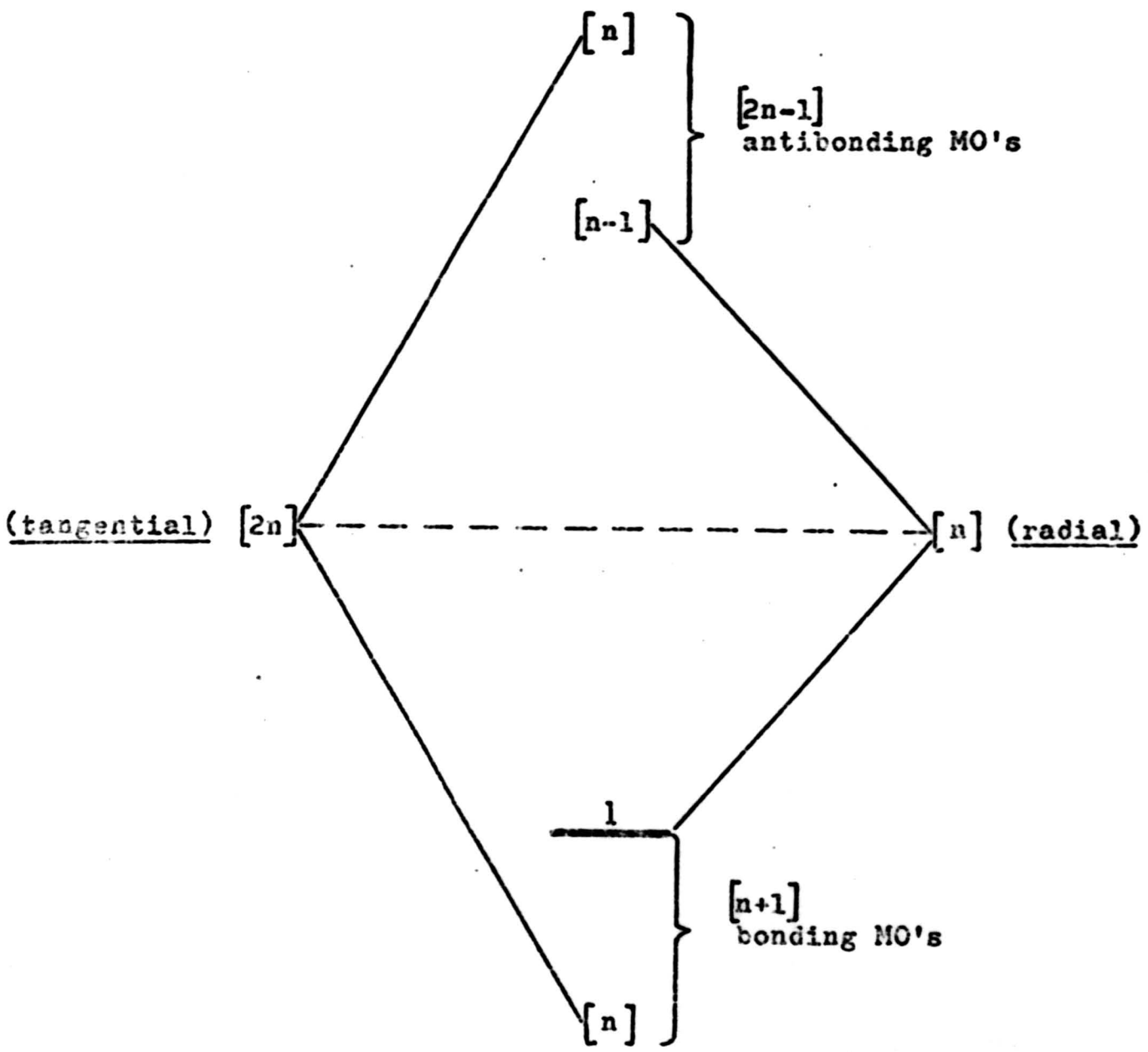
(a) Each Skeletal Atom Provides 3 AO's

Hoffmannhas considered the symmetry properties of a series of $M(CO)_x$ fragments.[59,60] For $Fe(CO)_3$, which is regarded by Wade theory to be analogous to the BH fragment in its bonding capabilities, there are three high-lying orbitals occupied by two electrons, these may be used for cluster bonding. Thus $Fe(CO)_3$ and BH fragments have similar symmetries, similar extents in space, and similar energies for their frontal orbitals, and both donate two electrons for skeletal bonding.

(b) <u>Closo</u> - Polyhedra Require (n+1) Skeletal Electron Pairs

Several workers have used MO calculations to show that <u>closo</u>-polyhedra have symmetries appropriate to generate (n+1) bonding

Figure 1.7 Combination of 3n AO's (2n tangential, n radial) to give (n+1) bonding and (2n-1) antibonding MO's.



) to

AO's

radial)

MO's.[61-67] The same conclusion has been reached by King using an alternative graph theoretical approach.[68]

The original 3n AO's may be divided into a set of 2n orbitals tangential to the cluster surface, and a set of n orbitals pointing towards the cluster centre. The 2n orbitals interact pairwise to give n bonding and n antibonding MO's, the n radial orbitals interact to form only one new bonding MO but (n-1) antibonding MO's (Figure 1.7). Thus there are a total of (n+1) bonding and (2n-1) antibonding MO's.

The calculations by Mingos[65] on the 86 electron species $[Co_6(CO)_{14}]^{4-}$ suggest that Wade's analogy with the boranes is better expressed in terms of the number and symmetry of the antibonding MO's. Both $[Co_6(CO)_{14}]^{4-}$ and its borane analogue $[B_6H_6]^{2-}$ have 11 (2n-1) antibonding MO's with the same symmetries and a lot of s and p character, but Mingos points out that for electron counting procedures (n+1) bonding MO's or (2n-1) antibonding MO's are indistinguishable. His calculations on the cobalt tetraanion also confirm that the M-L orbitals are at lower energy than the cluster bonding orbitals.

(c) Capped and Uncapped Polyhedra Require the Same Number of Skeletal Electron Pairs.

This principle has been shown by Mingos[69] to have a quite general quantum mechanical basis. All the orbital combinations presented by the capping groups give rise to antibonding MO's and therefore the capped polyhedron is characterized by the same number of bonding MO's as the parent polyhedron. However for a large number of capping groups, new bonding MO's may be created, for example a trigonal prism requires 9, but a tricapped trigonal prism 10 skeletal electron pairs.[70]

(d) The Bonding Electrons are Delocalized

Observations on the paramagnetic anion $[B_8H_8]^-$ indicate that all boron and hydrogen atoms are equally coupled with the odd electron implying that the MO containing this electron is delocalized over the entire polyhedron.[71]

However in $[Co_6C(CO)_{14}]^-$ the unpaired electron appears to be located over one edge of the metal octahedron,[72] and in $[Rh_7(CO)_{16}I]^-$ the extra electron pair is thought to be delocalized in the capping group only.[73]

Some Additional Comments Regarding Wade Theory

(1) In systems that have all vertices of order 3, the three hybrid orbitals may be directed along the polyhedral edges, i.e. the MO's reflect the topology in a simple way and global delocalization is not necessary.[68] Therefore the EAN rule can almost always be successfully applied to tetrahedral, trigonal prismatic and cubic clusters.

In terms of Wade theory a tetrahedron is a nido- trigonal bipyramid requiring 6 skeletal electron pairs, rather than a fundamental polyhedron in its own right that would require (n+1), i.e. 5 skeletal electron pairs.

(2) Wade theory predicts the thermodynamically most stable geometry, but other easily accessible geometries may be stabilized by kinetic or other factors. For example Evans,[70] Grimes,[74,75] and Lipscomb[76] have pointed out that the energy difference between alternative 8-vertex polyhedra is small. Not surprisingly therefore the clusters $[Co_8C(CO)_{18}]^{2-}$,[77] $Rh_8C(CO)_{19}$,[78] and $Cu_2Rh_6C(CO)_{15}(NCMe)_2$[79] do not contain the

same metal polyhedron despite all having 9 skeletal electron pairs. In solution metal polyhedral non-rigidity has been observed in several large clusters, for example $[Rh_9P(CO)_{21}]^{2-}$,[80] $[Rh_{15}(CO)_{27}]^{3-}$,[13] and $[Pt_n(CO)_{2n}]^{2-}$,[81] also implying a low energy barrier to rearrangement.

Grimes also suggests that in the metallacarboranes the method of synthesis plays a major role in determining cage geometry.[82] On heating nido- polyhedra that have been synthesized from various synthetic routes, the appropriate closo- polyhedron is produced that was originally predicted by the presence of (n+1) skeletal electron pairs.[83]

(3) In summary Wade theory is very successful for rationalizing the structures of polynuclear carbonyl clusters, but cannot be used at present to predict the metal geometry with certainty because the additional requirements of the ligands and other factors are neglected.

1.4.4 The Use of MO Calculations for Predicting Cluster Geometries

The use of this method for explaining cluster geometries is obviously restricted to an expert in the field, and is far from convenient since a separate calculation must usually be performed by computer for each alternative geometry considered.

Recently, in an evaluation of skeletal electron counting procedures, Evans used EHMO calculations to estimate the energies of alternative n-vertexed structures for different overall charges on the molecule.[70] He also performed EHMO calculations on some trinuclear metal carbonyl species of Fe, Co, and Ni to identify their bonding properties, and differences between the structural forms and rigidity of complexes containing $[Ni_3(CO)_6]^{2-}$ or $M_3(CO)_9$ [M = Fe,Co] fragments were rationalized on the basis of

the frontier-orbital properties.[84] Lauher[62] also explored the electronic properties of a wide range of isolated metal polyhedra containing up to 15 atoms, and predicted the number of cluster valence orbitals which are energetically accessible for metal-metal and metal-ligand bonding.

In general the results obtained using MO calculations are in agreement with the geometries predicted by Wade theory, but the latter method is much more convenient for rationalizing the structures of polynuclear carbonyl clusters.

Section 1.5 Scope of the Research

The aim of the work presented in this thesis was to investigate the structures of some polynuclear carbonyl clusters of Ru and Os and their complexes with small organic molecules and hydrogen, and to use the information obtained to predict the geometries of new clusters of these metals (and the geometrical changes that may be brought about by reacting species) with more reliability. This knowledge is fundamental to an understanding of heterogeneous catalysis. Emphasis was placed on extending the methods currently available for conveniently rationalizing the metal geometries in clusters, in particular Wade theory which is very successful for explaining the structure of the metal unit in polynuclear carbonyls of the iron triad. Where appropriate however, interesting features associated with the carbonyl ligands in the clusters have been highlighted.

More extensive reviews relating to specific areas of the research will be referenced in the relevant Section, but some comprehensive reviews of a more general nature are listed below.

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SECTION 2

The Structures of Some Pentanuclear Osmium Clusters and the Geometrical Changes that may be Brought About by Reaction with Simple Nucleophilic Reagents.

Section 2.1 Introduction

Although the EAN rule may be successfully used to explain the structures of small clusters (see Subsection 1.4.1) the delocalized bonding scheme suggested by Wade (Subsection 1.4.3) is most suitable for rationalizing the geometries of clusters with more than four metal atoms. For M_5 species a trigonal bipyramidal metal geometry is predicted for 6 skeletal electron pairs and a square pyramidal (i.e. a nido-octahedral) geometry is predicted for 7 skeletal electron pairs. However no account is taken of the source of these electrons. It is the purpose of this Section to examine the structures of various pentanuclear osmium clusters, and their complexes with simple nucleophilic reagents, to find out whether the additional requirements of the ligands influence the preferred geometry, and if so to see whether Wade theory can be modified to accommodate these requirements.

Section 2.2 The Structures of the Dihydrides $[H_2Os_5(CO)_{15}I]^-$ and $H_2Os_5(CO)_{15}P(OMe)_3$

2.2.1 Preamble

These dihydrides were prepared by Dr. G.R. John, University of Cambridge, using the nucleophilic attack of I^- or $P(OMe)_3$ on the cluster $H_2Os_5(CO)_{15}$.[1] Each have 7 skeletal electron pairs available for bonding so a square pyramidal metal geometry (i.e. a nido-octahedron) is predicted by Wade theory.

2.2.2 Data Collection

Crystals of $[Bu_4N]^+ [H_2Os_5(CO)_{15}I]^-$ (I) and $H_2Os_5(CO)_{15}P(OMe)_3$ (II) suitable for X-ray analysis were grown by slow evaporation from CH_2Cl_2. The crystal selected for data collection was of dimensions 0.16 x 0.07 x 0.07 mm (I) and 0.21 x 0.10 x 0.09 mm (II); this was mounted on a thin quartz fibre held by a brass pin and placed on a eucentric goniometer. The goniometer was attached to a Philips PW1100 automated diffractometer and the crystal accurately centred by eye.

The initial unit-cell dimensions were determined using the PW1100 peak-search routine: an area of reciprocal space is systematically scanned until a radiation intensity is sensed that exceeds a preset discrimination level, the peak is then centred, measured and the relevant information stored. This process continues until 25 peaks or the whole of the selected area of reciprocal space have been explored. After printing the peak information (θ angle, χ angle, ϕ angle, and intensity for each reflection) the computer analyses these results in order to find

the three shortest reciprocal lattice vectors not lying in one plane (a^*, b^*, and c^*). Simple instructions to the computer initiate refinement of the results and calculation of the direct lattice constants. Accurate unit cell dimensions were derived from a least squares fit of the angular measurements of 25 strong high angle ($25 < 2\theta < 35^\circ$) reflections. Crystal data for (I) and (II) are given in Table 2.1.

Table 2.1 Crystal data for $[Bu_4N]^+ [H_2Os_5(CO)_{15}I]^-$ (I) and $H_2Os_5(CO)_{15}P(OMe)_3$ (II).

	(I)	(II)
M_r	1742.6	1497.2
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	16.915	15.015
b/Å	17.532	12.084
c/Å	14.584	8.494
$\alpha/^\circ$	90	100.73
$\beta/^\circ$	98.55	97.57
$\gamma/^\circ$	90	94.65
$U/Å^3$	4276.8	1492.2
D_c/g cm^{-3}	2.71	3.33
Z	4	2

Intensity data were collected† at 296 K in the range $3 < \theta < 30^\circ$ using an $\omega - 2\theta$ scan technique and graphite-

† In this and subsequent structure analyses reflections measured were $\pm h \pm k$ l for triclinic, $\pm$ hkl for monoclinic, and hkl for orthorhombic crystal systems.

monochromatized Mo-Kα radiation (λ = 0.71069 Å). Weak reflections which gave $I_t - 2(I_t)^{1/2} < I_b$ on the first scan were not further examined where I_t = the count rate at the top of the reflection peak and I_b = the mean count rate of two preliminary 5 s background measurements on either side of the peak. Of the remaining reflections, those for which the total intensity recorded in the first scan of the peak (I_i) was < 250 were scanned twice to increase their accuracy. A constant scan speed of 0.05 $^{\circ}s^{-1}$ and scan widths of 0.80 $^{\circ}$(I) and 1.00 $^{\circ}$(II) were used, with a background measuring time proportional to I_b/I_i. Three standard reflections were measured every 5 h during data collection and no significant ($> 3\sigma$) variations in intensity were observed from the average values.

Following data collection several strong reflections were measured at 20° intervals of rotation about their diffraction vector. These Ψ scans were used for correcting the data for absorption (vide infra).

The raw data were converted to intensities using the programme DRED written for the PW1100 diffractometer.[2] The intensity (I) is given by I = CT - tB where CT = the total number of counts recorded in the peak scan, B = the total of the two background counts either side of the peak, and t = the ratio of peak to background measuring times. Estimated errors $[\sigma(I)]$ are calculated from the expression $\sigma(I) = [\sigma_c^2(I) + (0.04I)^2]^{1/2}$ where $\sigma_c^2(I)$ is the variance due to counting statistics and the term in I^2 is an "ignorance" factor which was introduced to allow for other sources of error.[3] The I and $\sigma(I)$ values were corrected for Lorentz and polarization factors.

Empirical absorption corrections were applied to both data sets using the program EMPABS[4] based on a pseudo-ellipsoid model in which 6 parameters are refined to obtimise the agreement between equivalent reflections measured at various azimuthal angles, i.e. the Ψ scans measured after data collection. This gave relative transmission coefficients which ranged from 0.630 to 0.997 for the

full data set in (I) [μ = 149.5 cm^{-1}] and 0.331 to 0.845 for the full data set in (II) [μ = 205.0 cm^{-1}]. Laue equivalent reflections were averaged yielding 4171 and 5698 independent observed data [$I \geqslant 3\sigma(I)$] for (I) and (II) respectively.

2.2.3 Structure Solution and Refinement

The atomic scattering factors for all non-hydrogen atoms were taken from ref.5 and included both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[6] The scattering factors used for hydrogen were those given by Stewart.[7]

The function minimized during least - squares refinement was $\sum \underline{w}(|F_o| - |F_c|)^2$ where the weight assigned to each reflection is given by $\underline{w} = k/[\sigma^2 F + gF^2]$. The value of g is refined after each set of structure factor calculations, or if the weight refinement does not converge well various fixed values of g are tried to see which gives the smallest variation of $\sum \underline{w}(|F_o| - |F_c|)^2$ as a function of $|F_o|$, $\sin\theta$, and hkl values. The value of k (which cancels in all calculations) is redetermined at the same time as g and should be near unity if there are no serious systematic errors.

Discrepency indices used in the text are defined by the equations:-

$$R = \Sigma|F_o - F_c| / \Sigma F_o$$
$$R_W = \Sigma(|F_o - F_c| . \underline{w}^{\frac{1}{2}}) / \Sigma(F_o . \underline{w}^{\frac{1}{2}})$$
$$R_G = [\Sigma(|F_o - F_c|^2 . \underline{w}) / \Sigma(F_o^2 . \underline{w})]^{\frac{1}{2}}$$

Systematic absences (0k0 for k = 2n + 1 and h0l for l = 2n +1) uniquely indicated the space group $P2_1/c$ for $[Bu_4N]^+[H_2Os_5(CO)_{15}I]^-$ (I) but the unit cell was transformed into one containing a smaller β angle for data collection. This alternative setting, which corresponds to the non-standard space group $P2_1/n$, was chosen to avoid correlations during refinement of the structure. The diffraction

data for $H_2Os_5(CO)_{15}P(OMe)_3$ (II) showed only $\bar{1}$ Laue symmetry; the centric triclinic space group $P\bar{1}$ was assumed and confirmed by the satisfactory solution and refinement of the structure.

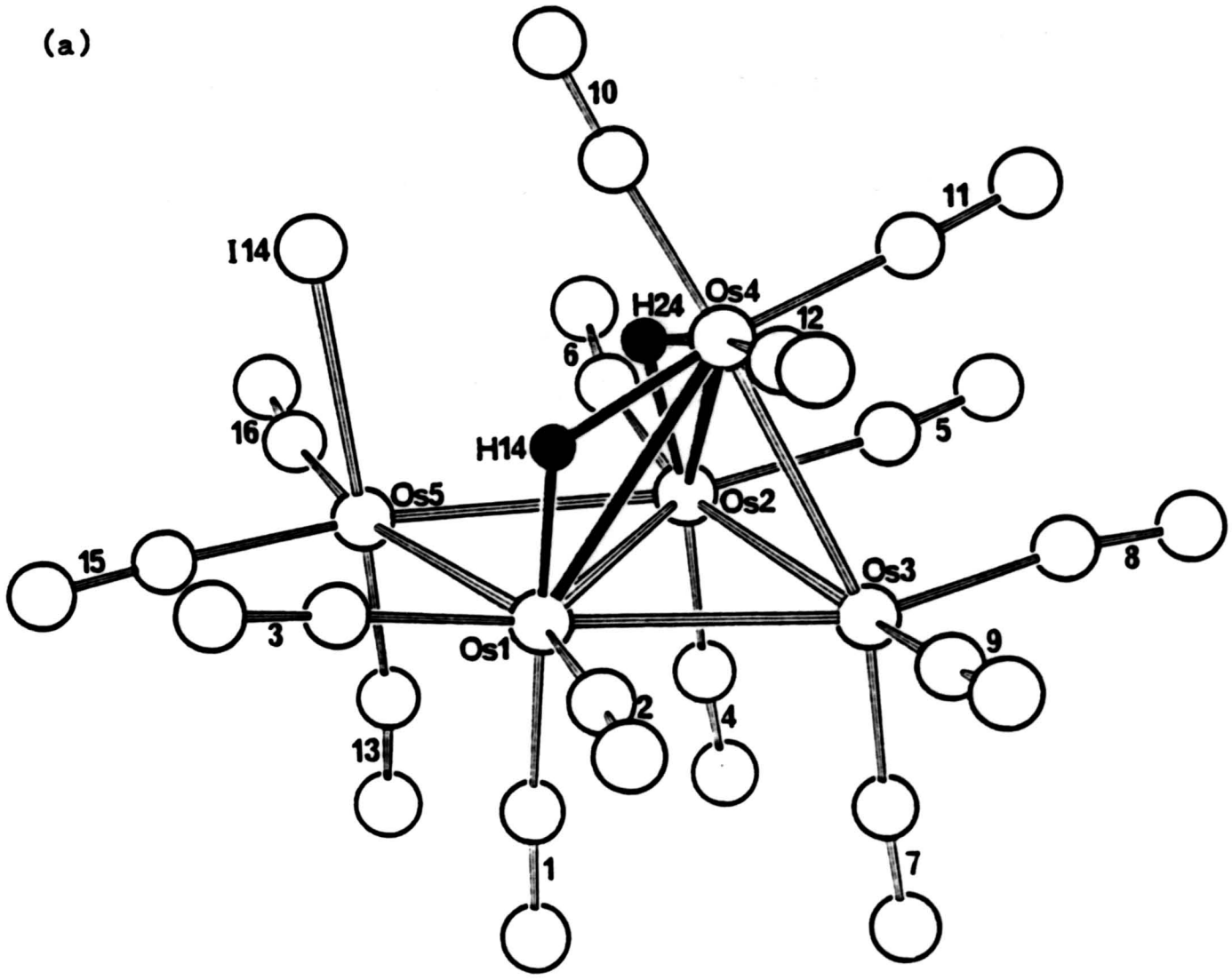
The metal atoms in (I) and (II) were located by direct methods using multisolution Σ_2 sign expansion, and the remaining non-hydrogen atoms were located from subsequent difference - Fourier syntheses.

The methylene hydrogen atoms of the $[Bu_4N]^+$ cation in (I) were placed in geometrically calculated positions [d(C-H) = 1.08 Å] with the hydrogens given a common temperature factor. The methyl groups were refined as rigid groups [d(C-H = 1.08 Å, H-C-H = 109.5°], with the H atoms again given a common temperature factor. Blocked full-matrix refinement was carried out with the atoms grouped together as follows: block 1, the osmium atoms; block 2, the other atoms of the $[H_2Os_5(CO)_{15}I]^-$ anion; block 3, the atoms of the $[Bu_4N]^+$ cation. Refinement converged at R = 0.0543 using anisotropic thermal parameters for the Os and I atoms of the anion. At this stage a difference - Fourier synthesis calculated using only those reflections with $(\sin\theta)/\lambda < 0.3$ revealed suitable maxima for the two hydride ligands in the $[H_2Os_5(CO)_{15}I]^-$ anion, the peaks having heights of ~0.3 eÅ^{-3}. The coordinates of these hydrogens were included in the model, but not subsequently refined, and their isotropic thermal parameters were fixed at 0.05 Å^2. Refinement of the structure resulted in slightly lower residuals ($R = 0.0542$, $R_w = 0.0569$, $R_G = 0.0699$) than refinement with the hydride locations omitted from the structure factor calculation ($R = 0.0543$, $R_w = 0.0571$, $R_G = 0.0702$). Weights were assigned to reflections as $\underline{w} = 1.0462/[\sigma^2F + 0.000540F^2]$ (*vide supra*). A final difference - Fourier synthesis for (I) revealed a few residual maxima in the region of the osmium atoms, the largest of which had a height of 1.7 eÅ^{-3}.

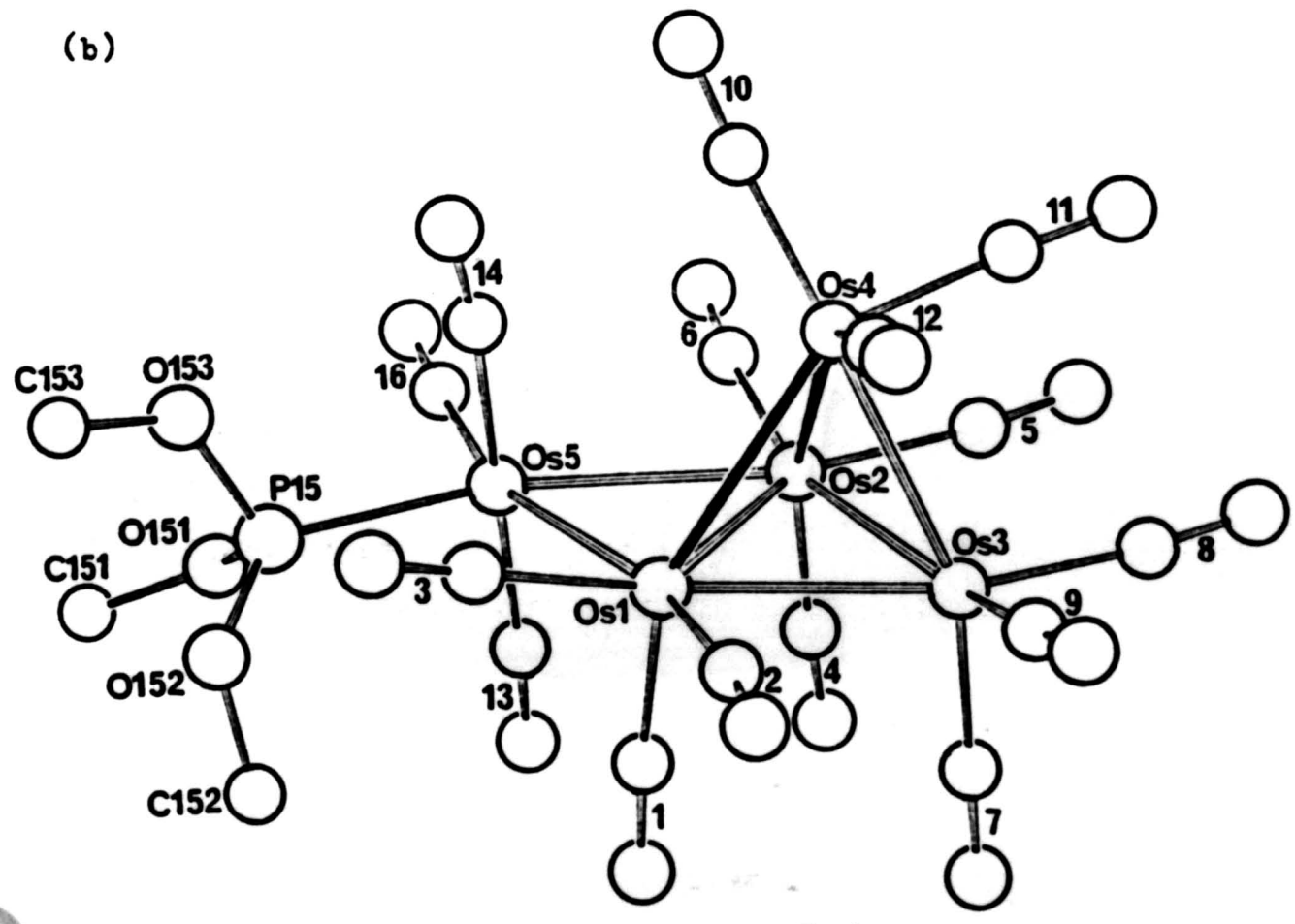
The atoms in $H_2Os_5(CO)_{15}P(OMe)_3$ (II) were divided into three groups for blocked full - matrix refinement, block 1 contained the Os atoms, block 2 half of the CO ligands attached to the cluster and block 3 the remaining atoms. Refinement converged at R = 0.0447,

Figure 2.1 The structures of (a) $[H_2Os_5(CO)_{15}I]^-$
(b) $H_2Os_5(CO)_{15}P(OMe)_3$.

(a)



(b)



R_W = 0.0484, and R_G = 0.0618 with all the non-hydrogen atoms assigned anisotropic thermal parameters. Weights were assigned to reflections as $\underline{w} = 1.5642/[\sigma^2 F + 0.001767\ F^2]$ (vide supra). Attempts to locate the hydride ligands in (II) from difference - Fourier syntheses calculated using various $(\sin\theta)/\lambda$ cutoffs were unsuccessful. A final difference - Fourier synthesis calculated using all the data showed several residual maxima in the region of the osmium atoms, none of which had a height greater than 2.4 $eÅ^{-3}$.

Final positional and thermal parameters for $[Bu_4N]^+$ $[H_2Os_5(CO)_{15}I]^-$ (I) and $H_2Os_5(CO)_{15}P(OMe)_3$ (II) are given in Appendices 1 and 2 respectively.

2.2.4 Discussion

The structures of the $[H_2Os_5(CO)_{15}I]^-$ anion in (I) and $H_2Os_5(CO)_{15}P(OMe)_3$ (II) are shown in Figure 2.1 and the bond distances and angles are given in Tables 2.2 - 2.4.

In both dihydrides four of the osmium atoms Os(1), Os(2), Os(3), and Os(4) define a tetrahedron and the fifth osmium bridges the Os(1) - Os(2) edge. Three terminal carbonyl ligands are attached to each of the osmium atoms and in addition Os(5) is bonded to a terminal iodide ligand in (I) and a terminal $P(OMe)_3$ ligand in (II). These geometries are derived from that of the dihydride $H_2Os_5(CO)_{16}$,[8] which also has 7 skeletal electron pairs, by replacement of an axial carbonyl ligand on Os(5) by I^- in $[H_2Os_5(CO)_{15}I]^-$, or by replacement of an equatorial CO ligand on the same osmium by $P(OMe)_3$ in $H_2Os_5(CO)_{15}P(OMe)_3$. The preference of the iodide ligand for an axial site in (I), and $P(OMe)_3$ for an equatorial site in (II), is simply explained in terms of the much greater steric demands of the phosphite ligand.

It is perhaps surprising that the metal atoms in these dihydrides do not adopt the square pyramidal geometry predicted by

Wade theory because hydride ligands have been shown to have a strong preference for bridging the edges of square faces, so much so that they may alter the favoured cluster geometry to one containing a square face.[9] However with hindsight the alternative edge-bridged tetrahedral geometry may still be rationalized by Wade theory. Two principles that are fundamental to skeletal electron counting procedures are:-

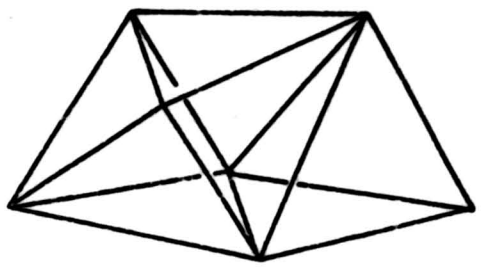
(1) Polyhedra with vertices removed require the same number of skeletal electron pairs (S) as the parent closo- polyhedron and

(2) Capped and uncapped variants of the same polyhedron are characterized by the same value of S.

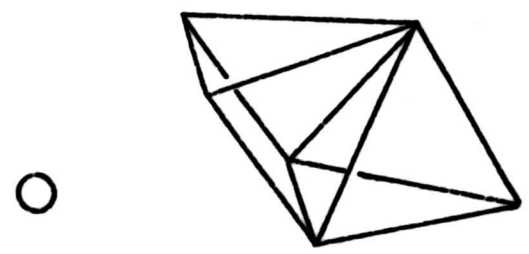
By applying these principles simultaneously cluster geometries may be rationalized that are derived by removing vertices from capped polyhedra. Thus the unexpected nido- capped octahedral metal skeleton observed in $H_2Os_6(CO)_{18}$[10] (Figure 2.2) is a suitable alternative geometry for 6 metal atoms and S =7. By analogy the structure of the dihydrides in (I), (II), and $H_2Os_5(CO)_{16}$ may be regarded as an arachno- capped octahedron which is a valid alternative geometry for 5 metal atoms and S = 7 (Figure 2.2). It is consistent with this description that the structure forms part of a close-packed array and the four osmium atoms Os(1), Os(2), Os(3), and Os(5) are coplanar to within 0.06 Å (Table 2.5) whereas a more symmetrical situation might have been expected in which the Os(5), Os(1), Os(2) plane was perpendicular to the Os(3) - Os(4) bond.

The only other cluster with a similar metal geometry is $Co_5(CO)_{11}[P(Me)_2]_3$[11] which has 8 skeletal electron pairs. Although the structure could not be explained by conventional skeletal electron counting procedures, it may be looked upon as a capped pentagonal bipyramid with 3 vertices removed which is an appropriate structure for 5 metal atoms and S = 8. Although details of the structure of $Co_5(CO)_{11}[P(Me)_2]_3$ have not appeared, it is consistent with this description that the edge-bridging cobalt atom is apparently not coplanar with a triangular

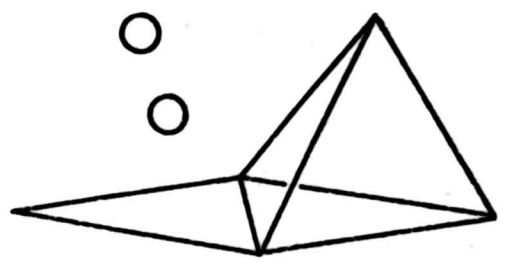
Figure 2.2 Removal of vertices from a capped octahedron to give capped square pyramidal and edge-bridged tetrahedral metal geometries.



Capped octahedron (S=7).

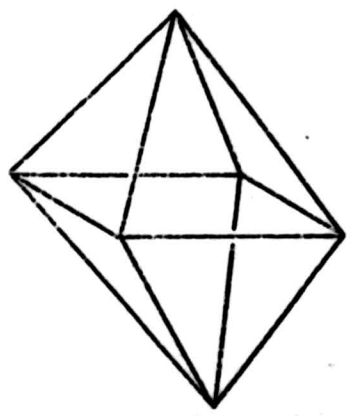


Nido- capped octahedron.

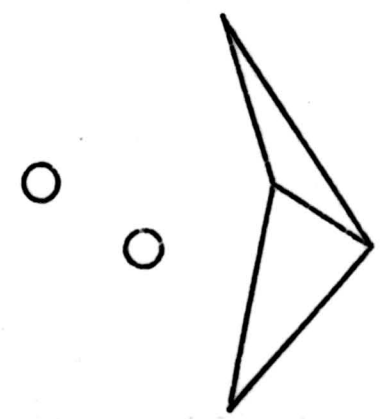


Arachno- capped octahedron.

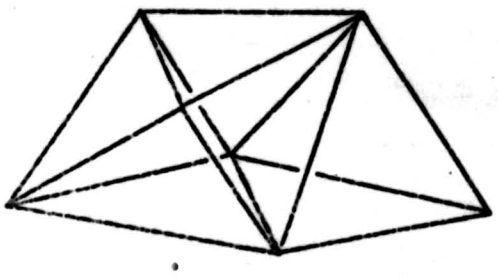
Figure 2.3 Removal of vertices from an octahedron and capped octahedron to give a butterfly and a planar triangulated rhomboidal metal geometry respectively.



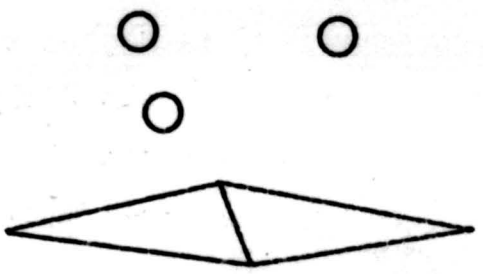
Octahedron (S=7).



Arachno- octahedron.



Capped octahedron (S=7).



Capped octahedron with 3 vertices removed.

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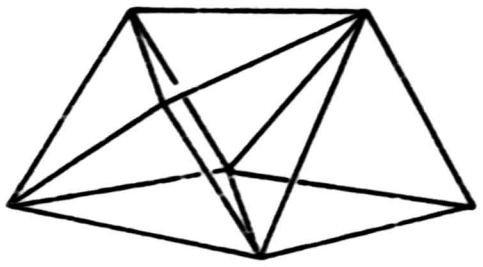
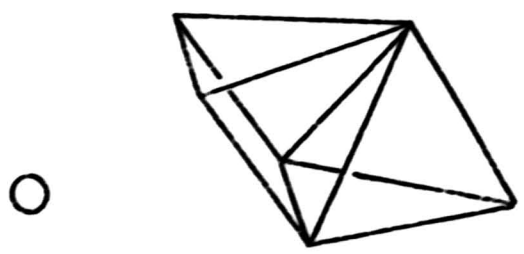
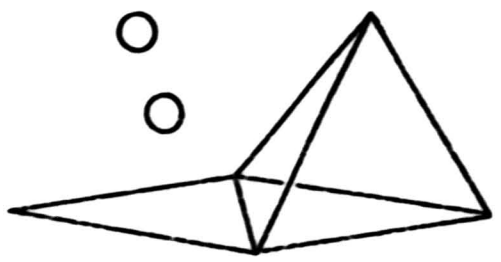
Figure 2.2 Removal of vertices from a capped octahedron to give capped square pyramidal and edge-bridged tetrahedral metal geometries.



Capped octahedron (S=7).



Nido- capped octahedron.

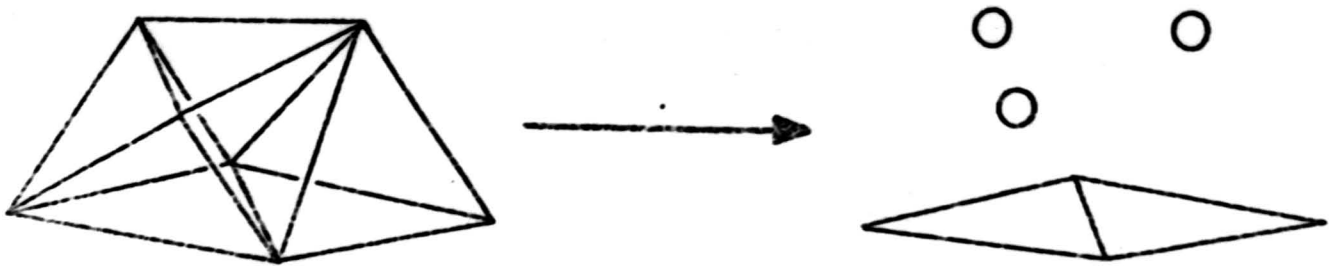


Arachno- capped octahedron.

Figure 2.3 Removal of vertices from an octahedron and capped octahedron to give a butterfly and a planar triangulated rhomboidal metal geometry respectively.

Octahedron (S=7).

Arachno- octahedron.



Capped octahedron (S=7).

Capped octahedron with 3 vertices removed.

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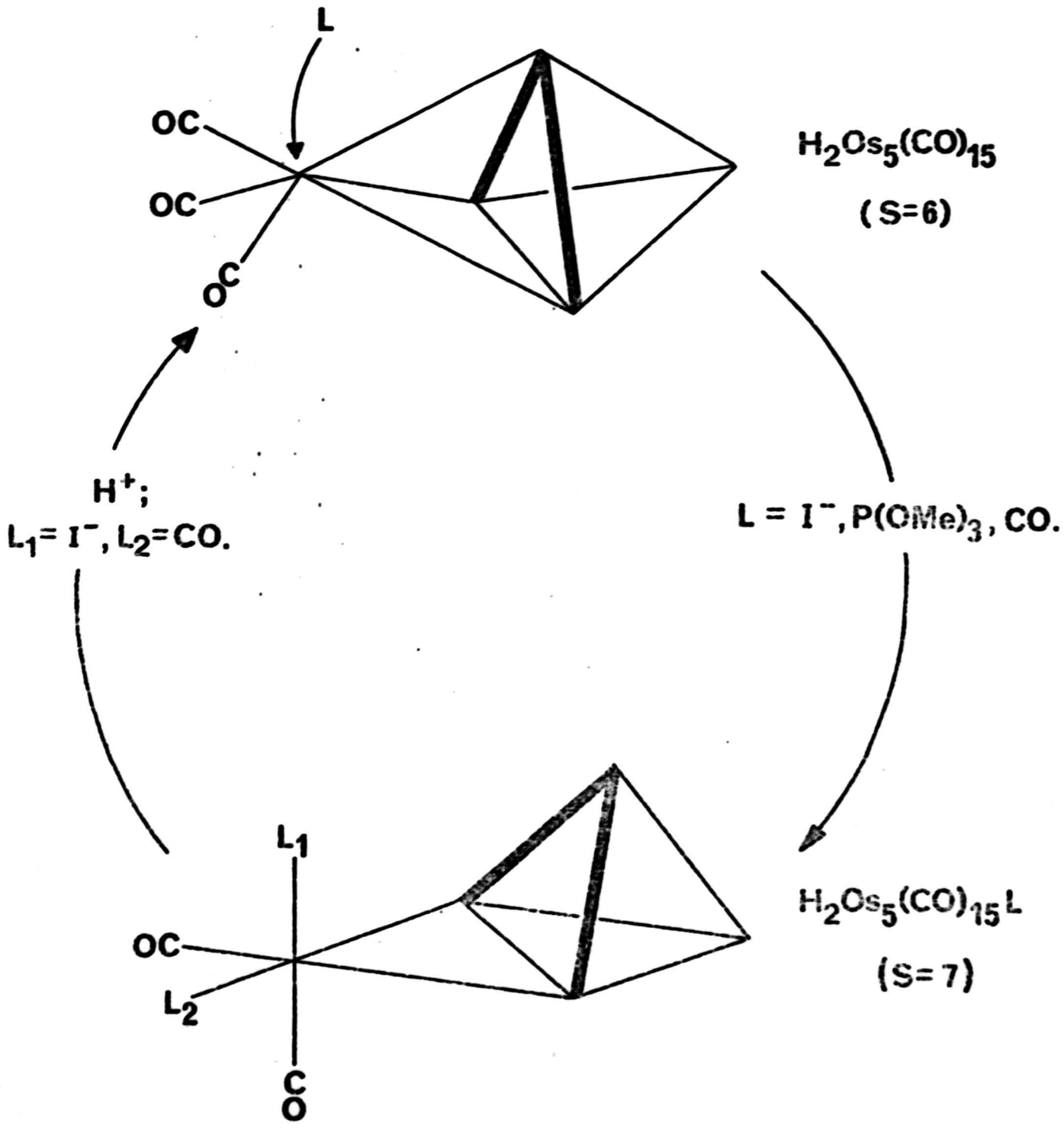
face of the Co_4 tetrahedron. Therefore a particular geometry is not necessarily characteristic of a particular number of skeletal electron pairs (S), and some type of edge-bridged tetrahedral structure could arise from any capped polyhedron.

Alternatively, clusters with the same value of S need not contain the same metal polyhedron. For example $H_3Os_4(CO)_{12}I$, which has S = 7, has a butterfly geometry[12] which is an arachno-octahedron (Figure 2.3) but in $[Re_4(CO)_{16}]^{2-}$, which has the same number of skeletal electron pairs, the metals define a planar triangulated rhombus[13] which may be obtained by removing 3 vertices from a capped octahedron (Figure 2.3). The clusters $[Ni_5(CO)_{12}]^{2-}$,[14] $[Rh_5(CO)_{14}I]^{-}$,[15] $[Rh_5(CO)_{15}]^{-}$,[16] and $[M_2Ni_3(CO)_{16}]^{3-}$ (ref.17) have the same number of skeletal electron pairs (8) as $Co_5(CO)_{11}[P(Me)_2]_3$ but possess trigonal bipyramidal metal geometries which cannot be rationalized by Wade theory. Alternative approaches using LCAO[17] and EH[18] molecular orbital calculations have been successfully used to explain the structures of these species.

It is of interest that clusters with disimilar geometries (that can nevertheless be rationalized by Wade theory) possess the same number of skeletal electron pairs (S), or that clusters with the same geometry may have differing values of S. This suggests that factors other than just the number of skeletal electrons determine the preferred metal geometry, for example the number and type of ligands present.

In $H_2Os_5(CO)_{16}$ the hydride ligands are thought to bridge the long Os - Os bonds Os(1) - Os(4) and Os(2) - Os(4). In the $[H_2Os_5(CO)_{15}I]^{-}$ anion in (I) the hydrogens were located directly from the X-ray analysis and bridge the same Os - Os bonds, the Os - H distances being Os(1) - H(14) = 1.65, Os(4) - H(14) = 1.75, Os(2) - H(24) = 1.76, and Os(4) - H(24) = 1.71 Å. The hydride H(14) is coplanar with the Os(1), Os(3), Os(4) face to within 0.34 Å, and H(24) is coplanar with Os(2), Os(3), Os(4) to within 0.01 Å (Table 2.5). In $H_2Os_5(CO)_{15}P(OMe)_3$ although the hydrides were not located directly from the X-ray analysis, the corresponding bonds Os(1) - Os(4) and Os(2) - Os(4) are significantly longer

Figure 2.4 The reaction of $H_2Os_5(CO)_{15}$ with some nucleophilic reagents. The number of skeletal electron pairs (S) is given in parentheses; shaded Os-Os bonds are bridged by hydrogen atoms.



$L_1 = L_2 = CO;$

$L_1 = I^-, L_2 = CO;$

$L_1 = CO, L_2 = P(OMe)_3.$

cleophilic
n pairs (S)
nds are

$Os_5(CO)_{15}$

(S=6)

$^-$, $P(OMe)_3$, CO.

$H_2Os_5(CO)_{15}L$

(S=7)

[mean 2.965(12) Å] than the rest [mean 2.850(55) Å] as has previously been found for M - M distances bridged by H atoms.[19] The disposition of the carbonyl ligands is also consistent with this assignment, i.e. in the other portions of the molecule the CO contacts are too close to allow H coordination.[19]

Since all three dihydrides (I), (II) and $H_2Os_5(CO)_{16}$ are synthesized from $H_2Os_5(CO)_{15}$,[1] for which a trigonal bipyramidal metal geometry is predicted by Wade theory (S = 6), it is likely that the two hydrides occupy adjacent equatorial edge bridging sites in the $H_2Os_5(CO)_{15}$ molecule (Figure 2.4). On reaction with weak nucleophiles such as I^-, $P(OMe)_3$, or even CO, cleavage of an Os - Os bond occurs to yield the appropriate edge-bridged tetrahedral arrangement (Figure 2.4). Further evidence in support of this proposition is provided by the monoanion $[HOs_5(CO)_{15}]^-$, which may be obtained by deprotonation of $H_2Os_5(CO)_{15}$, which has been shown to contain the H atom in an equatorial edge bridging position.[20] Interestingly on addition of H^+ to $[H_2Os_5(CO)_{15}I]^-$ the iodide ligand is removed[1] and the anion reverts back to $H_2Os_5(CO)_{15}$ demonstrating a facile reversible structural transformation that may lead to catalysis by these systems.

There is no apparent reason why two resonances appear in the ^1H n.m.r. spectrum of $[H_2Os_5(CO)_{15}I]^-$ (ref.1) since the hydrogens are related by the approximate non-crystallographic mirror plane that passes through Os(3), Os(4) and Os(5). It seems probable therefore that in solution either a completely different metal geometry exists, which is unlikely, or that a mixture of isomers are present differing only in the disposition of the H or I ligands. For example an equatorial rather than axially bound iodide would give rise to two signals in the ^1H n.m.r. spectrum.

The Os-I distance in $[H_2Os_5(CO)_{15}I]^-$, 2.651(3) Å, is much shorter than that observed in $[Os_5(CO)_{15}I]^-$, 2.740(5) Å,[21] implying that less negative charge is localized on the I atom in the former leading to a stronger Os - I bond.

In $H_2Os_5(CO)_{15}P(OMe)_3$ the metal bond Os(5) - Os(2) <u>trans</u> to

the phosphite ligand is significantly longer [2.934(1) Å] than the corresponding distance Os(5) - Os(1) <u>trans</u> to a carbonyl ligand [2.893(1) Å]. This indicates that $P(OMe)_3$ is a better π - acceptor ligand than CO.

Table 2.2

Selected Interatomic Distances (Å) for (I) and (II). E.s.d's are given in parentheses.

(a) Metal-Metal Bonds

	(I)	(II)
Os(1)-Os(2)	2.807(1)	2.818(1)
Os(1)-Os(3)	2.829(1)	2.828(1)
Os(1)-Os(4) †	2.959(1)	2.973(1)
Os(1)-Os(5)	2.916(1)	2.893(1)
Os(2)-Os(3)	2.833(1)	2.840(1)
Os(2)-Os(4) †	2.942(1)	2.956(1)
Os(2)-Os(5)	2.909(1)	2.934(1)
Os(3)-Os(4)	2.797(1)	2.784(1)
† Mean M-M, hydrogen bridged	2.951(12)[a]	2.965(12)[a]
Mean M-M, non-bridged	2.849(51)[a]	2.850(55)[a]

(b) Metal-Hydrogen Distances in (I)[b]

Os(1)-H(14)	1.654
Os(4)-H(14)	1.753
Os(2)-H(24)	1.757
Os(4)-H(24)	1.711
Mean Os-H	1.719(48)[a]

(c) Metal-Ligand Distances in (I) and (II)

(i) Metal-Carbon Distances

	(I)	(II)
Os(1)-C(1)	1.843(28)	1.867(15)
Os(1)-C(2)	1.876(29)	1.932(15)
Os(1)-C(3)	1.832(26)	1.920(10)
Os(2)-C(4)	1.903(30)	1.908(14)
Os(2)-C(5)	1.967(30)	1.921(14)
Os(2)-C(6)	1.868(27)	1.955(14)
Os(3)-C(7)	1.820(38)	1.906(19)
Os(3)-C(8)	1.852(33)	1.878(14)
Os(3)-C(9)	1.854(32)	1.868(17)
Os(4)-C(10)	1.836(32)	1.911(15)
Os(4)-C(11)	1.835(28)	1.898(14)
Os(4)-C(12)	1.794(37)	1.907(13)
Os(5)-C(13)	1.865(32)	1.937(13)
Os(5)-C(14)	-	1.953(13)
Os(5)-C(15)	1.852(27)	-
Os(5)-C(16)	1.828(36)	1.916(13)
Mean Os-C	1.855(40)[a]	1.912(27)[a]

(ii) Os-I Distance in (I)

Os(5)-I(4)	2.651(3)

(iii) Os-P Distance in (II)

Os(5)-P(15)	2.293(3)

(d) Intraligand Distances in (I) and (II)

(i) Carbon-Oxygen Distances in CO Ligands

	(I)	(II)
C(1)-O(1)	1.198(37)	1.166(20)
C(2)-O(2)	1.188(37)	1.139(19)
C(3)-O(3)	1.195(33)	1.118(14)
C(4)-O(4)	1.145(38)	1.122(19)
C(5)-O(5)	1.075(38)	1.145(16)
C(6)-O(6)	1.182(35)	1.108(17)
C(7)-O(7)	1.189(47)	1.151(26)
C(8)-O(8)	1.180(42)	1.143(19)
C(9)-O(9)	1.166(39)	1.142(22)
C(10-O(10)	1.175(40)	1.151(20)
C(11)-O(11)	1.172(37)	1.166(17)
C(12)-O(12)	1.241(44)	1.133(17)
C(13)-O(13)	1.139(41)	1.142(18)
C(14)-O(14)	-	1.108(17)
C(15)-O(15)	1.154(34)	-
C(16)-O(16)	1.207(48)	1.096(17)
Mean C-O	1.174(37)[a]	1.135(21)[a]

(ii) Carbon-Oxygen Distances in $P(OMe)_3$ Ligand in (II)

C(151)-O(151)	1.448(21)
C(152)-O(152)	1.415(24)
C(153)-O(153)	1.375(21)

(iii) Phosphorus-Oxygen Distances in $P(OMe)_3$ Ligand in (II)

P(15)-O(151)	1.585(11)
P(15)-O(152)	1.549(11)
P(15)-O(153)	1.602(14)

a E.s.d's on mean bond lengths and angles are calculated from the equation

$$\sigma = \sqrt{\{[\sum_{1}^{n}(x_i - \bar{x})^2]/(n-1)\}}$$

where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

b H(14) and H(24) were included in fixed positions.

Table 2.3

Selected Intramolecular Angles (°) in (I) and (II)

E.s.d's are given in parentheses.

(a) M-C-O Angles

	(I)	(II)
Os(1)-C(1)-O(1)	173.6(22)	175.3(12)
Os(1)-C(2)-O(2)	174.6(24)	170.7(12)
Os(1)-C(3)-O(3)	168.0(24)	170.4(11)
Os(2)-C(4)-O(4)	175.4(24)	177.1(12)
Os(2)-C(5)-O(5)	170.1(29)	168.7(14)
Os(2)-C(6)-O(6)	167.9(22)	172.9(11)
Os(3)-C(7)-O(7)	176.1(29)	179.8(6)
Os(3)-C(8)-O(8)	169.9(33)	172.7(16)
Os(3)-C(9)-O(9)	177.5(30)	178.0(17)
Os(4)-C(10)-O(10)	173.2(26)	175.0(13)
Os(4)-C(11)-O(11)	175.2(25)	176.2(14)
Os(4)-C(12)-O(12)	175.7(30)	177.1(13)

cont...

Os(5)-C(13)-O(13)	172.6(25)	177.1(11)
Os(5)-C(14)-O(14)	-	172.8(12)
Os(5)-C(15)-O(15)	176.5(27)	-
Os(5)-C(16)-O(16)	172.5(29)	175.0(12)
Mean Os-C-O	173.3(31) [a]	174.6(31) [a]

(b) Angles Involving Hydrides in (I) [b]

H(14)-Os(1)-Os(2)	83.5
H(14)-Os(1)-Os(3)	86.4
H(14)-Os(1)-Os(4)	30.7
H(14)-Os(1)-Os(5)	91.7
H(14)-Os(1)-C(1)	178.7
H(14)-Os(1)-C(2)	88.9
H(14)-Os(1)-C(3)	85.4
H(14)-Os(4)-Os(1)	28.8
H(14)-Os(4)-Os(2)	77.9
H(14)-Os(4)-Os(3)	85.6
H(14)-Os(4)-C(10)	91.1
H(14)-Os(4)-C(11)	173.4
H(14)-Os(4)-C(12)	90.5

cont...

H(24)-Os(2)-Os(1)	75.9
H(24)--Os(2)-Os(3)	89.4
H(24)-Os(2)-Os(4)	31.5
H(24)-Os(2)--Os(5)	81.2
H(24)-Os(2)-C(4)	170.2
H(24)-Os(2)-C(5)	97.1
H(24)-Os(2)-C(6)	85.5
H(24)-Os(4)-Os(1)	72.1
H(24)-Os(4)-Os(2)	32.5
H(24)-Os(4)-Os(3)	91.6
H(24)-Os(4)-C(10)	85.7
H(24)-Os(4)-C(11)	100.1
H(24)-Os(4)-C(12)	169.6
H(14)-Os(4)-H(24)	79.1
Os(1)-H(14)-Os(4)	120.5
Os(2)-H(24)-Os(4)	116.0

(c) Angles Involving Iodine in (I)

I(14)-Os(5)-Os(1)	96.4(1)
I(14)-Os(5)-Os(2)	94.9(1)
I(14)-Os(5)-C(13)	173.9(9)
I(14)-Os(5)-C(15)	87.6(10)
I(14)-Os(5)-C(16)	82.0(12)

cont...

(d) Angles Involving $P(OMe)_3$ Ligand in (II)

P(15)-Os(5)-Os(1)	110.9(1)
P(15)-Os(5)-Os(2)	167.0(1)
P(15)-Os(5)-C(13)	88.2(4)
P(15)-Os(5)-C(14)	91.8(4)
P(15)-Os(5)-C(16)	85.7(3)
O(151)-P(15)-Os(5)	107.2(3)
O(152)-P(15)-Os(5)	122.4(5)
O(153)-P(15)-Os(5)	111.6(5)
C(151)-O(151)-P(15)	127.3(9)
C(152)-O(152)-P(15)	125.1(10)
C(153)-O(153)-P(15)	127.8(14)
O(152)-P(15)-O(151)	106.6(6)
O(153)-P(15)-O(151)	108.8(7)
O(153)-P(15)-O(152)	99.5(6)

(e) Angles Between Metal Atoms in (I) and (II)

	(I)	(II)
Os(3)-Os(1)-Os(2)	60.3(1)	60.4(1)
Os(4)-Os(1)-Os(2)	61.3(1)	61.3(1)
Os(4)-Os(1)-Os(3)	57.7(1)	57.3(1)
Os(5)-Os(1)-Os(2)	61.1(1)	61.8(1)
Os(5)-Os(1)-Os(3)	121.2(1)	122.1(1)
Os(5)-Os(1)-Os(4)	97.3(1)	97.2(1)
Os(3)-Os(2)-Os(1)	60.2(1)	60.0(1)
Os(4)-Os(2)-Os(1)	61.9(1)	61.9(1)
Os(4)-Os(2)-Os(3)	57.9(1)	57.4(1)
Os(5)-Os(2)-Os(1)	61.3(1)	60.3(1)
Os(5)-Os(2)-Os(3)	121.4(1)	120.2(1)
Os(5)-Os(2)-Os(4)	97.9(1)	96.7(1)
Os(2)-Os(3)-Os(1)	59.4(1)	59.6(1)
Os(4)-Os(3)-Os(1)	63.5(1)	64.0(1)
Os(4)-Os(3)-Os(2)	63.0(1)	63.4(1)
Os(2)-Os(4)-Os(1)	56.8(1)	56.8(1)
Os(3)-Os(4)-Os(1)	58.8(1)	58.7(1)
Os(3)-Os(4)-Os(2)	59.1(1)	59.2(1)
Os(2)-Os(5)-Os(1)	57.6(1)	57.8(1)

(f) M-M-CO Angles in (I) and (II)

	(I)	(II)
Os(2)-Os(1)-C(1)	95.7(8)	96.6(4)
Os(3)-Os(1)-C(1)	92.4(8)	94.6(4)
Os(4)-Os(1)-C(1)	148.1(8)	149.8(4)
Os(5)-Os(1)-C(1)	88.8(8)	88.6(4)
Os(2)-Os(1)-C(2)	136.3(9)	132.3(4)
Os(3)-Os(1)-C(2)	76.2(9)	72.0(4)
Os(4)-Os(1)-C(2)	92.1(10)	91.7(5)
Os(5)-Os(1)-C(2)	162.5(9)	165.9(4)
Os(2)-Os(1)-C(3)	130.9(9)	135.1(4)
Os(3)-Os(1)-C(3)	165.0(9)	158.5(3)
Os(4)-Os(1)-C(3)	115.8(9)	112.8(4)
Os(5)-Os(1)-C(3)	71.6(9)	76.1(3)
Os(1)-Os(2)-C(4)	94.7(8)	97.6(4)
Os(3)-Os(2)-C(4)	88.6(8)	91.6(4)
Os(4)-Os(2)-C(4)	145.1(8)	148.1(4)
Os(5)-Os(2)-C(4)	91.6(8)	92.8(4)
Os(1)-Os(2)-C(5)	137.0(9)	136.8(5)
Os(3)-Os(2)-C(5)	77.5(9)	77.2(5)
Os(4)-Os(2)-C(5)	89.9(10)	91.2(4)
Os(5)-Os(2)-C(5)	160.9(9)	162.4(5)

cont...

Os(1)-Os(2)-C(6)	130.2(8)	131.5(3)
Os(3)-Os(2)-C(6)	166.3(8)	163.5(4)
Os(4)-Os(2)-C(6)	116.3(9)	114.4(4)
Os(5)-Os(2)-C(6)	70.4(8)	73.2(3)
Os(1)-Os(3)-C(7)	95.8(10)	94.8(5)
Os(2)-Os(3)-C(7)	99.6(11)	98.2(5)
Os(4)-Os(3)-C(7)	157.4(10)	156.6(5)
Os(1)-Os(3)-C(8)	158.6(11)	163.4(5)
Os(2)-Os(3)-C(8)	102.0(11)	104.6(5)
Os(4)-Os(3)-C(8)	99.8(11)	105.6(6)
Os(1)-Os(3)-C(9)	106.9(9)	107.7(4)
Os(2)-Os(3)-C(9)	161.3(10)	161.0(5)
Os(4)-Os(3)-C(9)	100.1(10)	98.8(5)
Os(1)-Os(4)-C(10)	117.6(9)	119.0(4)
Os(2)-Os(4)-C(10)	118.1(9)	114.6(4)
Os(3)-Os(4)-C(10)	176.1(9)	173.8(4)
Os(1)-Os(4)-C(11)	144.8(10)	143.3(5)
Os(2)-Os(4)-C(11)	97.9(9)	96.3(4)
Os(3)-Os(4)-C(11)	87.9(10)	86.9(5)
Os(1)-Os(4)-C(12)	98.3(12)	98.9(4)
Os(2)-Os(4)-C(12)	144.1(13)	147.9(5)
Os(3)-Os(4)-C(12)	86.5(12)	91.0(5)
Os(1)-Os(5)-C(13)	89.7(9)	92.9(4)
Os(2)-Os(5)-C(13)	87.9(9)	86.2(4)

cont ..

Os(1)-Os(5)-C(14)	-	83.1(4)
Os(2)-Os(5)-C(14)	-	92.9(4)
Os(1)-Os(5)-C(15)	106.1(9)	-
Os(2)-Os(5)-C(15)	163.7(9)	-
Os(1)-Os(5)-C(16)	167.7(10)	162.9(3)
Os(2)-Os(5)-C(16)	110.2(10)	106.2(3)

(g) OC-M-CO Angles in (I) and (II)

	(I)	(II)
C(2)-Os(1)-C(1)	91.0(13)	89.2(6)
C(3)-Os(1)-C(1)	95.9(12)	97.4(5)
C(3)-Os(1)-C(2)	91.0(12)	90.4(5)
C(5)-Os(2)-C(4)	91.8(13)	88.7(6)
C(6)-Os(2)-C(4)	98.5(12)	97.5(6)
C(6)-Os(2)-C(5)	90.5(12)	89.3(6)
C(8)-Os(3)-C(7)	97.9(15)	92.6(7)
C(9)-Os(3)-C(7)	94.3(15)	96.9(8)
C(9)-Os(3)-C(8)	88.4(14)	86.0(7)
C(11)-Os(4)-C(10)	95.4(13)	93.7(6)
C(12)-Os(4)-C(10)	95.7(15)	95.1(6)
C(12)-Os(4)-C(11)	90.0(14)	93.6(6)
C(14)-Os(5)-C(13)	-	175.7(6)
C(15)-Os(5)-C(13)	91.1(13)	-
C(16)-Os(5)-C(13)	91.9(15)	91.9(6)
C(15)-Os(5)-C(14)	-	-
C(16)-Os(5)-C(14)	-	92.4(6)
C(16)-Os(5)-C(15)	86.1(13)	-

[a] See Table 2.2. footnote a.

[b] See Table 2.2. footnote b.

Table 2.4

Selected Bond lengths (Å) and Angles (°) in the $[Bu_4N]^+$ Cation* in (I).

E.s.d's are given in parentheses.

N-C(17)	1.500(39)	C(21)-N-C(17)	114.6(20)
N-C(21)	1.553(33)	C(25)-N-C(17)	103.8(21)
N-C(25)	1.563(35)	C(25)-N-C(21)	109.1(19)
N-C(29)	1.516(34)	C(29)-N-C(17)	110.8(20)
		C(29)-N-C(21)	106.3(19)
C(17)-C(18)	1.434(42)	C(29)-N-C(25)	112.3(19)
C(18)-C(19)	1.553(46)		
C(19)-C(20)	1.459(48)	N--C(17)-C(18)	118.1(26)
		N-C(21)-C(22)	113.6(23)
C(21)-C(22)	1.500(42)	N-C(25)-C(26)	110.1(23)
C(22)-C(23)	1.441(48)	N-C(29)-C(30)	117.0(24)
C(23)-C(24)	1.395(69)		
		C(17)-C(18)-C(19)	111.0(26)
C(25)-C(26)	1.680(47)	C(18)-C(19)-C(20)	107.5(28)
C(26)-C(27)	1.589(48)		
C(27)-C(28)	1.393(51)	C(21)-C(22)-C(23)	106.9(28)
		C(22)-C(23)-C(24)	116.4(35)
C(29)-C(30)	1.510(41)		
C(30)-C(31)	1.613(60)	C(25)-C(26)-C(27)	103.4(26)
C(31)-C(32)	1.513(67)	C(26)-C(27)-C(28)	117.9(32)
		C(29)-C(30)-C(31)	108.1(29)
		C(30)-C(31)-C(32)	106.7(36)

* One limb of the cation has a trans configuration [C(17), C(18), C(19), C(20)], the other three limbs adopt a gauche configuration.

Table 2.5 Least-squares planes in direct space for $[Bu_4N]^+[H_2Os_5(CO)_{15}I]^-$ (I) and $H_2Os_5(CO)_{15}P(OMe)_3$ (II). Only atoms marked with an asterisk were included in calculation of the plane.

(a) $[Bu_4N]^+ [H_2Os_5(CO)_{15}I]^-$

atom	dev./Å
Plane 1:-13.1281x + 4.2907y + 10.0645_3 = 1.6794	
Os(1)*	0.0555
Os(2)*	0.0557
Os(3)*	-0.0566
Os(4)	2.3983
Os(5)*	-0.0545
H(14)	1.6965
H(24)	1.7542
Plane 2:-1.3784x + 17.4432y - 0.6721_3 = 7.4365	
Os(1)*	-
Os(3)*	-
Os(4)*	-
H(14)	0.3362
Plane 3:13.2611x + 8.3024y + 4.0885_3 = 7.1517	
Os(2)*	-
Os(3)*	-
Os(4)*	-
H(24)	-0.0136

(b) $H_2Os_5(CO)_{15}P(OMe)_3$

atom	dev./Å
Plane :11.0753x + 4.0732y - 5.9929_3 = 2.0762	
Os(1)*	0.0408
Os(2)*	0.0393
Os(3)*	-0.0408
Os(4)	2.3981
Os(5)*	-0.0393

Section 2.3 The Structures of $Os_5C(CO)_{15}$ and $[Os_5C(CO)_{15}I]^-$

2.3.1 Preamble

Much interest has recently been shown in polynuclear carbonyl clusters that contain interstitial atoms, but little is known about the chemistry of the atoms in these sites since they are usually completely surrounded by the metals and are therefore shielded from attack.

Both $Os_5C(CO)_{15}$ and $[Os_5C(CO)_{15}I]^-$ have more skeletal electron pairs than the 6 required for the appropriate closed metal polyhedron (a trigonal bipyramid), so opened out structures are expected in which the carbido atom occupies a more exposed position. The exciting potential of carbido clusters as catalysts has recently been demonstrated by Bradley *et al.*[22] who showed that a partially encapsulated carbon atom exhibits a chemistry conducive to C - C bond formation and suceeded in synthesizing methyl acetate from CO and H_2 only.

Crystals of $Os_5C(CO)_{15}$(III) and $[(Ph_3P)_2N]^+ [Os_5C(CO)_{15}I]^-$ (IV) suitable for X-ray analysis were provided by Dr. P.F. Jackson, University of Cambridge. The neutral cluster $Os_5C(CO)_{15}$ was fractionally crystallized from an ethyl acetate solution containing several polynuclear species formed by the pyrolysis of $Os_3(CO)_{12}$;[23] reaction of $Os_5C(CO)_{15}$ in tetrahydrofuran with iodide followed by addition of $(Ph_3P)_2NCl$ in methanol, leads to the precipitation of $[(Ph_3P)_2N]^+ [Os_5C(CO)_{15}I]^-$ which was recrystallized from CH_2Cl_2 - MeOH.

2.3.2 Data Collection

The crystal selected for data collection was of dimensions

0.26 x 0.16 x 0.12 mm (III) and 0.38 x 0.29 x 0.10 mm (IV). Unit cell parameters were determined, and data was collected and processed by the methods described in Subsection 2.2.2. Crystal data for (III) and (IV) are given in Table 2.6.

Table 2.6 Crystal data for $Os_5C(CO)_{15}$ (III) and $[(Ph_3P)_2N]^+$ $[Os_5C(CO)_{15}I]^-$ (IV).

	(III)	(IV)
M_r	1383.2	2048.7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	16.404	34.337
b/Å	14.170	10.042
c/Å	20.798	16.382
α/°	90	90
β/°	91.71	101.77
γ/°	90	90
U/Å^3	4832.2	5529.9
D_c/g cm^{-3}	3.80	2.46
Z	8	4

Scan widths of 0.70 and 0.50 ° were used for (III) and (IV) respectively, empirical absorption corrections were applied to both data sets which gave relative transmission coefficients which ranged from 0.323 to 0.953 for the full data set in (III) [μ = 232.5 cm^{-1}] and from 0.512 to 0.995 for the full data set in (IV) [μ = 116.3 cm^{-1}]. Laue equivalent reflections were averaged to give 5946 and 6134 unique observed data [$I \geqslant 3\sigma(I)$] for (III) and (IV) respectively.

2.3.3 Structure Solution and Refinement

The scattering factors used, the function minimized during least - squares refinement, and definitions of the discrepancy indices quoted in the text are given in Subsection 2.2.3.

Systematic absences (0k0 for k = 2n + 1, h0l for l = 2n + 1) uniquely defined the centrosymmetric space group $P2_1/c$ for both (III) and (IV), but the unit cell in (IV) was transformed into one containing a smaller β angle for data collection. This alternative setting, which corresponds to the non-standard space group $P2_1/n$, was chosen to avoid correlations during refinement of the structure.

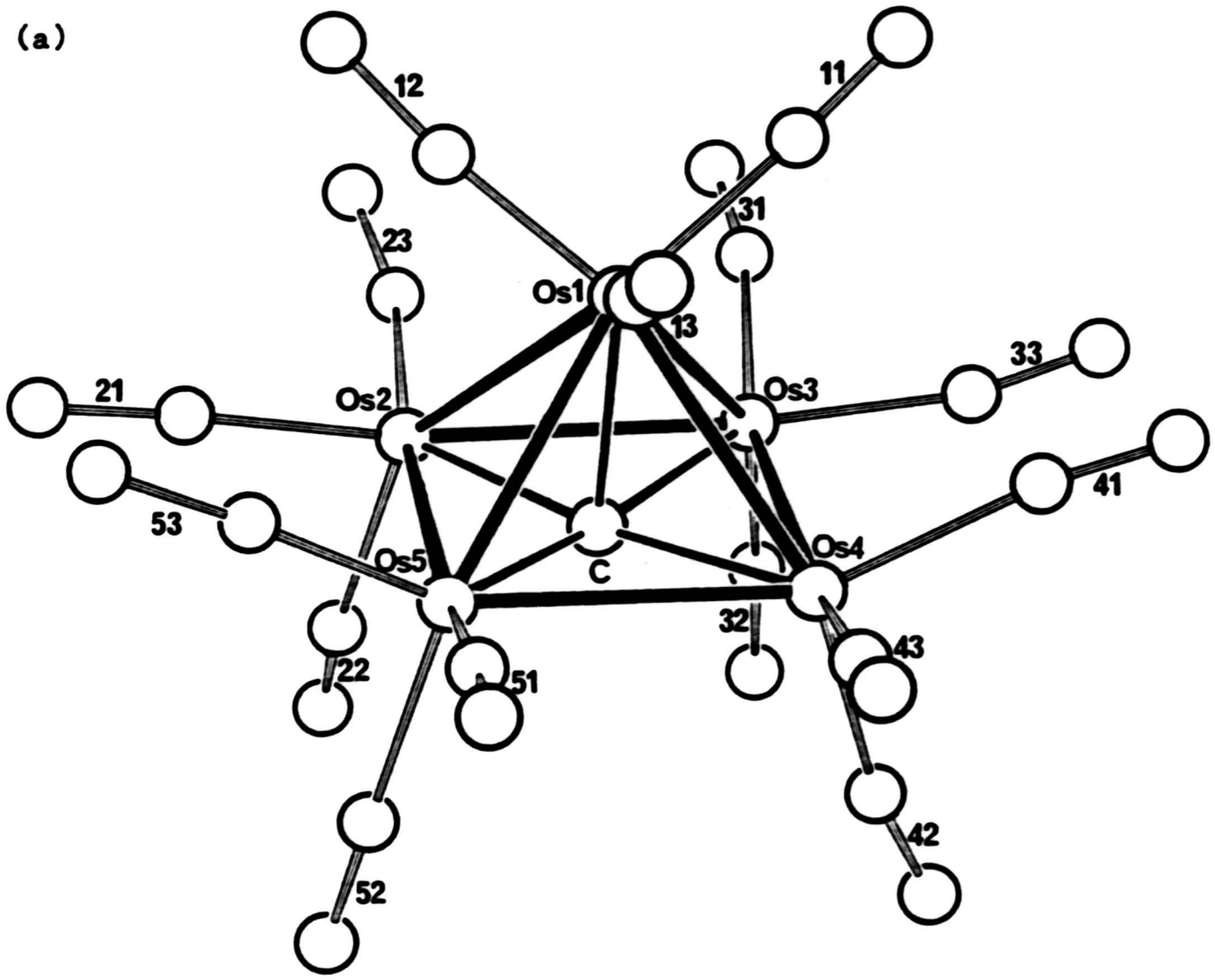
The metal atoms in (III) and (IV) were located by direct methods using multisolution Σ_2 sign expansion, and the remaining non-hydrogen atoms were located from subsequent difference - Fourier syntheses.

There are two independent molecules in the asymmetric unit for $Os_5C(CO)_{15}$ (III) but the two molecules have similar overall geometries. Blocked full -matrix refinement was performed with the atoms grouped as follows: block 1, the osmium atoms of cluster 1; block 2, the other atoms of cluster 1; block 3, the Os atoms of cluster 2; block 4, the rest of the atoms of cluster 2. Refinement converged at R = 0.0499, R_w = 0.0499, and R_G = 0.0575 using anisotropic thermal parameters for the osmium atoms. Weights were assigned to reflections as $\underline{w} = 0.6747/\sigma^2 F$ (see Subsection 2.2.3). A final difference - Fourier map showed several residual maxima in the region of the osmium atoms, none of which had a height greater than 2.9 $e\text{Å}^{-3}$.

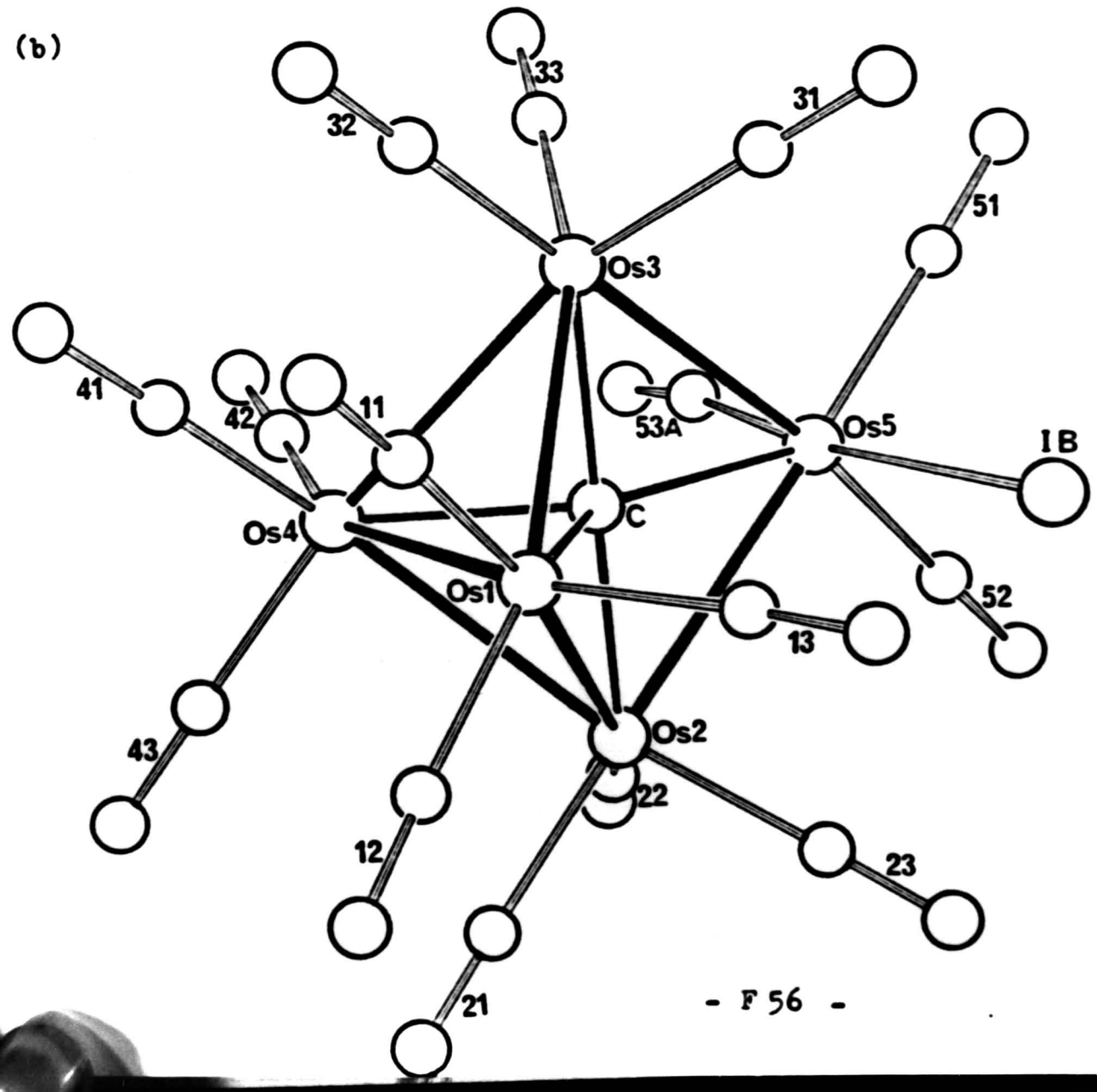
The anion in $[(Ph_3P)_2N]^+ [Os_5C(CO)_{15}I]^-$ (IV) is disordered having two orientations of equal occupancy that are approximately related by a non-crystallographic two fold axis that contains Os(5) and passes through the midpoint of the Os(1) - Os(4) bond (Figure 2.6). This operation results in I and CO(53)

Figure 2.5 The structures of (a) $Os_5C(CO)_{15}$ (Cluster 1)
(b) $[Os_5C(CO)_{15}I]^-$ (One orientation).

(a)

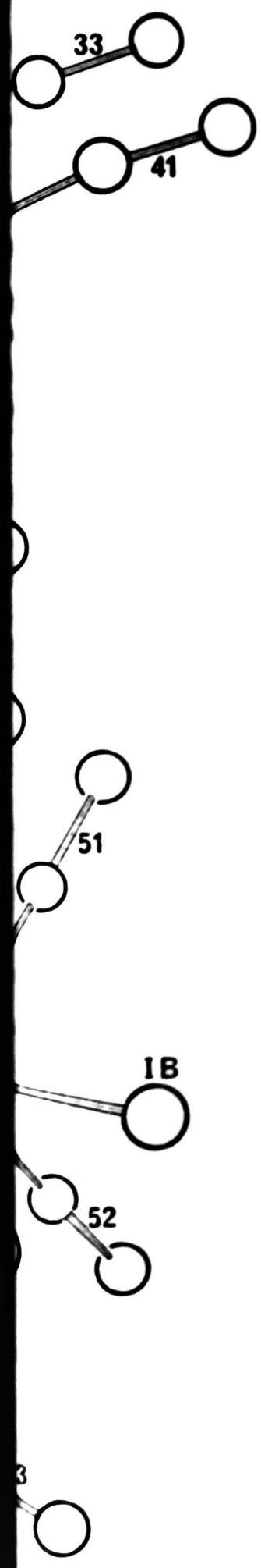


(b)



luster 1)

(One orientation).



exchanging positions, therefore there are two sites for the carbon atom [C(53A) and C(53B)] which were set to have 0.5 occupancy, but since the Os - I distance is approximately equal to an Os ... O distance the I and O(53) sites coincide. Since the atomic number of iodine is much larger than that of oxygen these two sites were assigned as 1/2 I atoms [I(A) and I(B)], no allowance being made for O(53) in the structure factor calculations. Blocked full matrix refinement was used with the atoms grouped as follows: block 1, the osmium atoms; block 2, half of the CO ligands of the $[Os_5C(CO)_{15}I]^-$ anion; block 3, the remaining atoms of the anion; block 4, the atoms of the $[(Ph_3P)_2N]^+$ cation. Refinement converged at R = 0.0399, R_w = 0.0435 and R_c = 0.0533 using anisotropic thermal parameters for all atoms of the anion, except for C(53), and the N and P atoms of the $[(Ph_3P)_2N]^+$ cation. The phenyl rings were treated as rigid groups [d(C-C) = 1.395 Å], no allowance was made for the phenyl hydrogens in the structure factor calculations. Weights were assigned to reflections as $w = 0.8767/[\sigma^2F + 0.000694\ F^2]$ (see Subsection 2.2.3). A final difference - Fourier synthesis for (IV) revealed a few residual maxima in the region of the osmium atoms, the largest of which had a height of 1.9 $eÅ^{-3}$.

Final positional and thermal parameters for $Os_5C(CO)_{15}$ (III) and $[(Ph_3P)_2N]^+[Os_5C(CO)_{15}I]^-$ (IV) are given in Appendices 3 and 4 respectively.

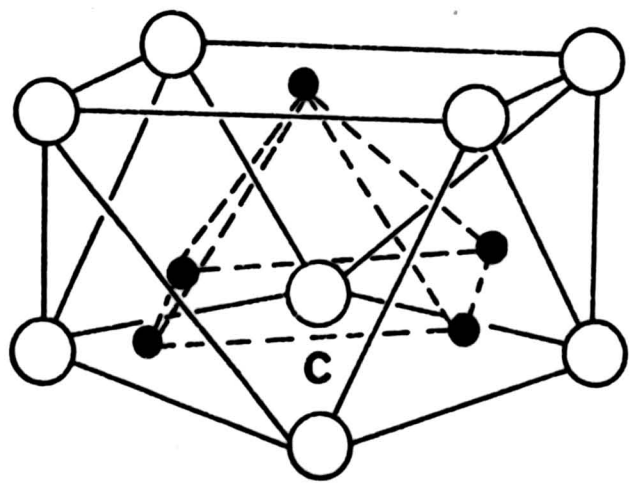
2.3.4 Discussion

The structures of $Os_5C(CO)_{15}$(III) and the anion in $[(Ph_3P)_2N]^+[Os_5C(CO)_{15}I]^-$ (IV) are shown in Figures 2.5 and 2.6 and the bond distances and angles are given in Tables 2.7 - 2.11.

As inferred from the similarity of the i.r. spectrum of $Os_5C(CO)_{15}$[24] to that of $Fe_5C(CO)_{15}$,[25] $Os_5C(CO)_{15}$ is isostructural

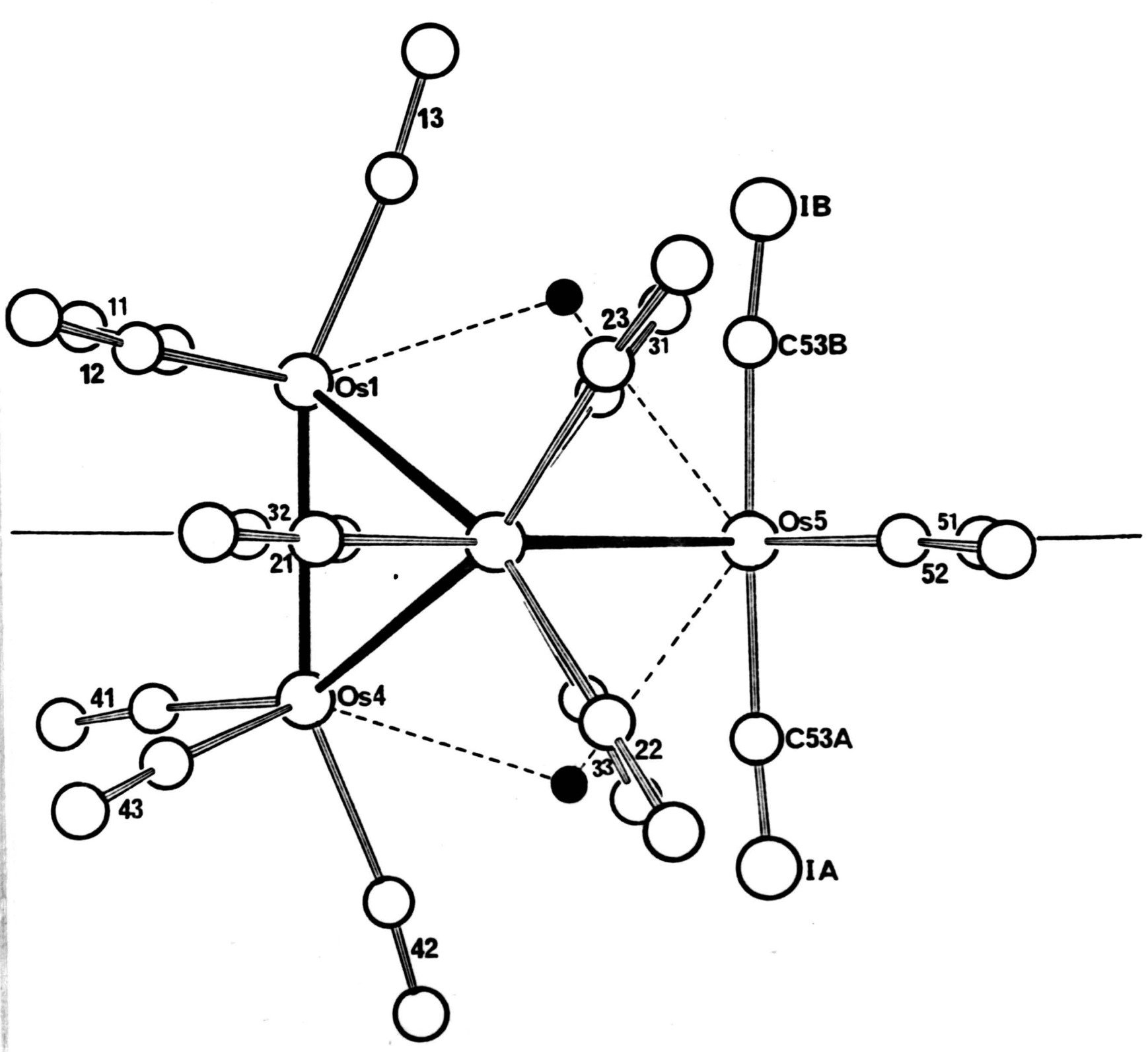
(but not isomorphous) with its iron analogue consisting of a square pyramid of osmium atoms with three terminal carbonyls per Os atom. The carbido atom sits slightly below the square face in both independent clusters of $Os_5C(CO)_{15}$ (0.11 Å in cluster 1 and 0.13 Å in cluster 2, Table 2.12) as it does in $Fe_5C(CO)_{15}$;[26] in the square pyramidal heterometallic cluster $[Fe_4RhC(CO)_{14}]^-$ the carbido atom is also located just below (0.19 Å) the basal (Fe_3Rh) plane.[27] Since the $M_{apical} - M_{basal}$ distances are slightly shorter than the $M_{basal} - M_{basal}$ bond lengths in these clusters [mean values being 2.85(3) and 2.88(2) Å respectively for $Os_5C(CO)_{15}$] the position of the carbido atom just below the tetragonal face probably equalizes the five Os - C interactions. Gillespie has explained the position of the carbido atom using his close-packed valence electron pair theory of cluster structures[28] (see Subsection 1.4.2): the C is located in the base of a square antiprism of electron pairs (Figure 2.7) which means it sits slightly below the four basal metal atoms occupying four of the eight trigonal holes in the square antiprismatic arrangement of electron pairs.

Figure 2.7 **Square antiprism arrangement of eight electron pairs in square pyramidal clusters.**



In contrast to the dihydrides $[H_2Os_5(CO)_{15}I]^-$, $H_2Os_5(CO)_{15}P(OMe)_3$, and $H_2Os_5(CO)_{16}$, which also have 7 skeletal electron pairs (S), $Os_5C(CO)_{15}$ does have the square pyramidal (*i.e.* *nido* - octahedral) geometry predicted by Wade theory. Significantly in all but one osmium cluster that has a square pyramidal subunit,

Figure 2.6 The anion $[Os_5C(CO)_{15}I]^-$ viewed down Os_2-C-Os_3 to illustrate the arachno-pentagonal metal geometry and the two orientations of the molecule that are approximately related by a non-crystallographic two fold axis that contains Os(5) and passes through the midpoint of the Os(1)-Os(4) bond (see Subsection 2.3.3).



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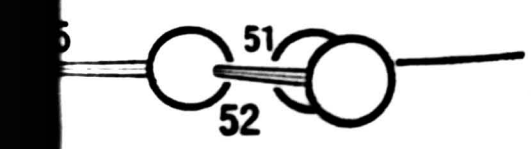
B

BB



3A

A

the tetragonal face is bridged by a 3 or 4 electron donor atom or group, the only exception being $H_2Os_6(CO)_{18}$ whose structure has been discussed in Subsections 1.4.3 and 2.2.4. For example in $Fe_5C(CO)_{15}$,[26] $M_4M'C$,[27] and $Os_6C(CO)_{16}(MeC{:}CMe)$[29] C atoms are inserted into the square hole, and in $Os_6(CMe)(CO)_{16}(CMe)$[29] and $Os_5P(OMe)(CO)_{15}$[30] the tetragonal face is capped by MeC and P(OMe) respectively. This supports King's contention that square faces should be regarded as "insulators" that interrupt electron delocalization in clusters, and their presence will not be favoured unless they are suitably plugged by an atom or group.[31]

Iodide adds to (III) to give $[Os_5C(CO)_{15}I]^-$, in a similar manner to that in which it adds to $H_2Os_5(CO)_{15}$ to give $[H_2Os_5(CO)_{15}I]^-$, and an appropriate change in the metal polyhedron occurs from a square pyramid (S = 7) to an arachno - pentagonal bipyramid (S = 8) [Figures 2.5 and 2.6] which is consistent with the predictions of Wade theory. The carbido atom is contained in this polyhedron and lies in the plane of the three equatorial osmium atoms Os(1), Os(4), and Os(5) [Table 2.12] and is equidistant from the apical osmiums, Os(2) and Os(3) [mean Os - C, 1.99(1) Å] (Table 2.9). The other three Os - C bond lengths are significantly different and range from 2.11(1) to 2.17(1) Å. In contrast to $[H_2Os_5(CO)_{15}I]^-$ which reverts back to $H_2Os_5(CO)_{15}$ on addition of H^+, protonation of $[Os_5C(CO)_{15}I]^-$ yields the neutral complex $HOs_5C(CO)_{15}I$.[32] By analogy to the monohydrides $HOs_5C(CO)_{13}[OP(OMe)CP(OMe)_2]$[33] and $HOs_5C(CO)_{14}[OP(OMe)_2]$,[34] which have a similar Os_5C unit, the hydride in $HOs_5C(CO)_{15}I$ probably bridges the Os(1) - Os(4) bond. Unlike the phosphorus containing species the iodide complexes have only simple ligands present so the chemistry of a "semi-interstitial" carbon atom in such an environment may now be conveniently investigated for the first time.

The mean Os - I distance of 2.84(3) Å in $[Os_5C(CO)_{15}I]^-$ is much larger than the values of 2.651(3) and 2.740(5) Å found in $[H_2Os_5(CO)_{15}I]^-$ (Subsection 2.2.4) and $[Os_5(CO)_{15}I]^-$ (ref. 21) respectively. Although disorder of the I atom (see previous Subsection) limits the accuracy of this bond length, the very long

distance indicates that more negative charge is localized on the terminal I in $\left[Os_5C(CO)_{15}I\right]^-$ than in the other two clusters, thereby weakening the Os - I bond.

Table 2.7

Selected Interatomic Distances (Å) for (III).

E.s.d's are given in parentheses.

(a) Metal-Metal Bonds

	Cluster 1	Cluster 2
Os(1)-Os(2)	2.872(1)	2.834(1)
Os(1)-Os(3)	2.850(1)	2.892(1)
Os(1)-Os(4)	2.827(1)	2.820(1)
Os(1)-Os(5)	2.825(1)	2.869(1)
Os(2)-Os(3)	2.864(1)	2.865(1)
Os(2)-Os(5)	2.867(1)	2.875(1)
Os(3)-Os(4)	2.889(1)	2.889(1)
Os(4)-Os(5)	2.910(1)	2.905(1)
Mean Os(apical)-Os(basal)	2.849(26)[a]	
Mean Os(basal)-Os(basal)	2.883(18)[a]	

(b) Metal-Carbide Distances

	Cluster 1	Cluster 2
Os(1)-C	2.091(21)	2.131(23)
Os(2)-C	2.004(19)	2.083(23)
Os(3)-C	2.071(23)	2.026(20)
Os(4)-C	2.081(19)	2.016(23)
Os(5)-C	2.009(23)	2.047(20)
Mean Os-carbide	2.056(42)[a]	

(c) Metal-Carbon Distances

	Cluster 1	Cluster 2
Os(1)-C(11)	1.857(29)	1.864(36)
Os(1)-C(12)	1.917(21)	1.877(31)
Os(1)-C(13)	1.800(31)	1.903(25)
Os(2)-C(21)	1.877(30)	1.899(27)
Os(2)-C(22)	1.841(34)	1.846(26)
Os(2)-C(23)	1.921(34)	1.887(24)
Os(3)-C(31)	1.905(33)	1.919(24)
Os(3)-C(32)	1.922(26)	1.877(24)
Os(3)-C(33)	1.945(34)	1.877(25)
Os(4)-C(41)	1.827(28)	1.872(25)
Os(4)-C(42)	1.863(35)	1.868(30)
Os(4)-C(43)	1.845(40)	1.900(25)
Os(5)-C(51)	1.922(29)	1.932(24)
Os(5)-C(52)	1.895(30)	1.862(30)
Os(5)-C(53)	1.939(28)	1.866(29)
Mean Os-C	1.884(35) [a]	

(d) Carbon-Oxygen Distances

	Cluster 1	Cluster 2
C(11)-O(11)	1.186(37)	1.178(43)
C(12)-O(12)	1.184(27)	1.142(43)
C(13)-O(13)	1.207(39)	1.135(32)
C(21)-O(21)	1.150(38)	1.148(35)
C(22)-O(22)	1.171(40)	1.162(34)
C(23)-O(23)	1.139(41)	1.148(31)
C(31)-O(31)	1.180(41)	1.152(31)
C(32)-O(32)	1.171(34)	1.115(34)
C(33)-O(33)	1.109(43)	1.149(33)
C(41)-O(41)	1.186(36)	1.152(32)
C(42)-O(42)	1.209(43)	1.161(38)
C(43)-O(43)	1.170(53)	1.113(31)
C(51)-O(51)	1.150(39)	1.152(33)
C(52)-O(52)	1.170(37)	1.146(39)
C(53)-O(53)	1.122(36)	1.175(37)
Mean C-O	1.158(25)[a]	

[a] E.s.d's on mean bond lengths and angles are calculated from the equation $\sigma = \sqrt{\{[\sum_{1}^{n}(x_i-\bar{x})^2]/(n-1)\}}$ where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

Table 2.8

Selected Intramolecular Angles (°) in (III).
E.s.d's are given in parentheses.

(a) M-C-O Angles

	Cluster 1	Cluster 2
Os(1)-C(11)-O(11)	178.1(21)	171.1(31)
Os(1)-C(12)-O(12)	174.6(21)	174.0(27)
Os(1)-C(13)-O(13)	176.7(27)	177.8(25)
Os(2)-C(21)-O(21)	175.8(25)	174.8(25)
Os(2)-C(22)-O(22)	174.7(27)	173.6(24)
Os(2)-C(23)-O(23)	168.1(31)	176.9(22)
Os(3)-C(31)-O(31)	176.5(30)	174.8(22)
Os(3)-C(32)-O(32)	176.2(20)	177.0(22)
Os(3)-C(33)-O(33)	168.7(29)	177.5(20)
Os(4)-C(41)-O(41)	171.2(25)	176.5(20)
Os(4)-C(42)-O(42)	170.7(32)	175.9(24)
Os(4)-C(43)-O(43)	178.6(35)	176.7(25)
Os(5)-C(51)-O(51)	177.2(27)	177.6(23)
Os(5)-C(52)-O(52)	176.3(26)	171.6(25)
Os(5)-C(53)-O(53)	176.1(26)	175.0(25)
Mean Os-C-O	175.0(28)[a]	

(b) Angles Involving Carbide in (I II)

	Cluster 1	Cluster 2
C-Os(1)-Os(2)	44.3(5)	47.0(6)
C-Os(1)-Os(3)	46.5(6)	44.4(5)
C-Os(1)-Os(4)	47.2(5)	45.5(6)
C-Os(1)-Os(5)	45.3(6)	45.4(5)
C-Os(2)-Os(1)	46.7(6)	48.5(6)
C-Os(2)-Os(3)	46.3(7)	45.0(6)
C-Os(2)-Os(5)	44.5(7)	45.4(5)
C-Os(3)-Os(1)	47.1(6)	47.4(7)
C-Os(3)-Os(2)	44.4(5)	46.6(7)
C-Os(3)-Os(4)	46.0(5)	44.3(6)
C-Os(4)-Os(1)	47.5(6)	48.9(7)
C-Os(4)-Os(3)	45.8(6)	44.5(6)
C-Os(4)-Os(5)	43.7(6)	44.8(6)
C-Os(5)-Os(1)	47.7(6)	47.9(7)
C-Os(5)-Os(2)	44.3(5)	46.4(6)
C-Os(5)-Os(4)	45.6(5)	43.9(6)
C-Os(1)-C(11)	124.6(11)	121.4(12)
C-Os(1)-C(12)	118.3(9)	123.0(11)
C-Os(1)-C(13)	119.5(11)	119.7(11)

cont...

	Cluster 1	Cluster 2
C-Os(2)-C(21)	135.2(11)	134.9(9)
C-Os(2)-C(22)	104.3(11)	105.6(11)
C-Os(2)-C(23)	133.4(12)	132.2(9)
C-Os(3)-C(31)	134.9(12)	138.3(10)
C-Os(3)-C(32)	101.7(10)	101.4(9)
C-Os(3)-C(33)	133.1(11)	132.7(9)
C-Os(4)-C(41)	132.3(10)	132.1(10)
C-Os(4)-C(42)	105.2(12)	103.9(11)
C-Os(4)-C(43)	132.0(14)	133.9(10)
C-Os(5)-C(51)	134.7(10)	133.3(10)
C-Os(5)-C(52)	103.7(11)	103.6(10)
C-Os(5)-C(53)	130.0(10)	132.5(11)
Os(1)-C-Os(2)	89.0(7)	84.5(9)
Os(1)-C-Os(3)	86.4(8)	88.1(9)
Os(1)-C-Os(4)	85.3(8)	85.6(8)
Os(1)-C-Os(5)	87.1(9)	86.7(8)
Os(2)-C-Os(3)	89.3(8)	88.4(8)
Os(2)-C-Os(4)	174.0(12)	170.1(13)
Os(2)-C-Os(5)	91.2(9)	88.2(9)
Os(3)-C-Os(4)	88.2(8)	91.2(9)
Os(3)-C-Os(5)	173.5(12)	174.1(13)
Os(4)-C-Os(5)	90.7(8)	91.3(8)

(c) Angles Between Metal Atoms

	Cluster 1	Cluster 2
Os(3)-Os(1)-Os(2)	60.1(1)	60.0(1)
Os(4)-Os(1)-Os(2)	91.4(1)	92.5(1)
Os(4)-Os(1)-Os(3)	61.2(1)	60.7(1)
Os(5)-Os(1)-Os(2)	60.4(1)	60.5(1)
Os(5)-Os(1)-Os(3)	91.7(1)	89.8(1)
Os(5)-Os(1)-Os(4)	62.0(1)	61.4(1)
Os(3)-Os(2)-Os(1)	59.6(1)	61.0(1)
Os(5)-Os(2)-Os(1)	59.0(1)	60.3(1)
Os(5)-Os(2)-Os(3)	90.6(1)	90.2(1)
Os(2)-Os(3)-Os(1)	60.3(1)	59.0(1)
Os(4)-Os(3)-Os(1)	59.0(1)	58.4(1)
Os(4)-Os(3)-Os(2)	90.3(1)	90.4(1)
Os(3)-Os(4)-Os(1)	59.8(1)	60.9(1)
Os(5)-Os(4)-Os(1)	59.0(1)	60.1(1)
Os(5)-Os(4)-Os(3)	89.3(1)	89.2(1)
Os(2)-Os(5)-Os(1)	60.6(1)	59.1(1)
Os(4)-Os(5)-Os(1)	59.1(1)	58.5(1)
Os(4)-Os(5)-Os(2)	89.8(1)	89.9(1)

(d) Carbon-Metal-Metal Angles

	Cluster 1	Cluster 2
C(11)-Os(1)-Os(2)	126.9(9)	124.6(10)
C(11)-Os(1)-Os(3)	80.3(9)	79.4(10)
C(11)-Os(1)-Os(4)	99.2(8)	99.1(12)
C(11)-Os(1)-Os(5)	161.0(7)	160.5(12)
C(12)-Os(1)-Os(2)	74.9(7)	76.4(9)
C(12)-Os(1)-Os(3)	117.2(7)	117.8(8)
C(12)-Os(1)-Os(4)	163.2(7)	166.5(9)
C(12)-Os(1)-Os(5)	102.2(7)	105.9(9)
C(13)-Os(1)-Os(2)	138.5(10)	138.2(8)
C(13)-Os(1)-Os(3)	145.3(9)	146.1(9)
C(13)-Os(1)-Os(4)	86.4(9)	87.1(9)
C(13)-Os(1)-Os(5)	82.5(10)	83.3(9)
C(21)-Os(2)-Os(1)	113.4(9)	104.9(8)
C(21)-Os(2)-Os(3)	170.2(9)	162.3(8)
C(21)-Os(2)-Os(5)	91.0(9)	91.3(8)
C(22)-Os(2)-Os(1)	151.0(9)	153.7(9)
C(22)-Os(2)-Os(3)	102.2(10)	105.6(8)
C(22)-Os(2)-Os(5)	102.4(10)	99.6(8)
C(23)-Os(2)-Os(1)	107.5(10)	107.0(7)
C(23)-Os(2)-Os(3)	88.1(10)	88.1(7)
C(23)-Os(2)-Os(5)	164.5(10)	165.9(7)

cont ...

	Cluster 1	Cluster 2
C(31)-Os(3)-Os(1)	107.1(10)	108.5(7)
C(31)-Os(3)-Os(2)	92.2(10)	92.9(7)
C(31)-Os(3)-Os(4)	161.8(10)	161.5(7)
C(32)-Os(3)-Os(1)	148.7(8)	148.7(7)
C(32)-Os(3)-Os(2)	96.9(8)	99.4(7)
C(32)-Os(3)-Os(4)	103.5(7)	103.5(7)
C(33)-Os(3)-Os(1)	106.9(10)	110.8(7)
C(33)-Os(3)-Os(2)	165.5(10)	167.9(8)
C(33)-Os(3)-Os(4)	88.0(10)	88.7(7)
C(41)-Os(4)-Os(1)	100.3(8)	100.1(8)
C(41)-Os(4)-Os(3)	89.8(8)	90.6(7)
C(41)-Os(4)-Os(5)	156.0(8)	157.1(8)
C(42)-Os(4)-Os(1)	152.1(10)	152.7(9)
C(42)-Os(4)-Os(3)	98.4(11)	99.1(8)
C(42)-Os(4)-Os(5)	107.4(11)	104.4(8)
C(43)-Os(4)-Os(1)	109.1(12)	106.1(8)
C(43)-Os(4)-Os(3)	167.6(12)	164.9(8)
C(43)-Os(4)-Os(5)	88.9(12)	90.2(8)
C(51)-Os(5)-Os(1)	109.8(9)	110.8(8)
C(51)-Os(5)-Os(2)	168.7(8)	167.9(8)
C(51)-Os(5)-Os(4)	89.5(9)	89.5(8)
C(52)-Os(5)-Os(1)	150.5(9)	151.4(8)
C(52)-Os(5)-Os(2)	94.9(9)	101.2(8)
C(52)-Os(5)-Os(4)	108.6(9)	104.8(9)

cont .

	Cluster 1	Cluster 2
C(53)-Os(5)-Os(1)	98.1(9)	104.1(9)
C(53)-Os(5)-Os(2)	89.7(8)	87.4(8)
C(53)-Os(5)-Os(4)	153.5(9)	160.5(9)

(e) OC-M-CO Angles

	Cluster 1	Cluster 2
C(12)-Os(1)-C(11)	96.9(11)	93.6(15)
C(13)-Os(1)-C(11)	94.2(13)	96.6(13)
C(13)-Os(1)-C(12)	97.4(11)	96.0(12)
C(22)-Os(2)-C(21)	87.0(14)	91.5(11)
C(23)-Os(2)-C(21)	87.8(14)	86.1(11)
C(23)-Os(2)-C(22)	93.0(14)	94.3(11)
C(32)-Os(3)-C(31)	94.1(13)	93.9(10)
C(33)-Os(3)-C(31)	85.0(14)	84.2(10)
C(33)-Os(3)-C(32)	97.4(12)	92.6(10)
C(42)-Os(4)-C(41)	96.5(12)	98.2(12)
C(43)-Os(4)-C(41)	87.0(15)	84.1(10)
C(43)-Os(4)-C(42)	93.9(16)	95.7(12)
C(52)-Os(5)-C(51)	96.0(12)	90.6(11)
C(53)-Os(5)-C(51)	85.9(12)	89.1(11)
C(53)-Os(5)-C(52)	97.9(12)	94.7(13)

[a] See footnote to Table 2.7

Table 2.9 Selected Interatomic Distances (Å) for (IV). Esd's are given in parentheses.

(a) Metal-Metal Bonds

Os(2)-Os(1)	2.903(1)	
Os(3)-Os(1)	2.921(1)	
Os(4)-Os(1)	2.748(1)	
Os(4)-Os(2)	2.899(1)	
Os(5)-Os(2)	2.933(1)	
Os(4)-Os(3)	2.896(1)	
Os(5)-Os(3)	2.934(1)	
Mean Os-Os	2.891(65) [a]	including Os(4)-Os(1)
Mean Os-Os	2.914(17) [a]	excluding Os(4)-Os(1)

(b) Metal-Iodine Distances [b]

Os(5)-I(A)	2.809(3)
Os(5)-I(B)	2.870(3)

(c) Metal - Carbide Distances

Os(1)-C	2.108(11)
Os(2)-C	1.978(10)
Os(3)-C	1.995(10)
Os(4)-C	2.108(12)
Os(5)-C	2.174(10)
Mean Os-C	2.073(83)[a]

(d) Metal - Carbon and Carbon-Oxygen Distances[b]

Os(1)-C(11)	1.849(15)	C(11)-O(11)	1.184(19)
Os(1)-C(12)	1.911(14)	C(12)-O(12)	1.163(17)
Os(1)-C(13)	1.916(18)	C(13)-O(13)	1.146(23)
Os(2)-C(21)	1.926(14)	C(21)-O(21)	1.118(17)
Os(2)-C(22)	1.913(19)	C(22)-O(22)	1.133(24)
Os(2)-C(23)	1.914(19)	C(23)-O(23)	1.138(23)
Os(3)-C(31)	1.892(17)	C(31)-O(31)	1.147(22)
Os(3)-C(32)	1.907(13)	C(32)-O(32)	1.151(17)
Os(3)-C(33)	1.877(13)	C(33)-O(33)	1.164(17)
Os(4)-C(41)	1.868(16)	C(41)-O(41)	1.185(20)
Os(4)-C(42)	1.917(18)	C(42)-O(42)	1.070(22)
Os(4)-C(43)	1.859(16)	C(43)-O(43)	1.176(22)

cont ...

Os(5)-C(51)	1.930(14)	C(51)-O(51)	1.127(17)
Os(5)-C(52)	1.860(15)	C(52)-O(52)	1.138(18)
Mean Os-C	1.896(28)[a]	Mean C-O	1.146(30)[a]
Os(5)-C(53A)	1.707(1)		
Os(5)-C(53B)	1.718(1)		

a

Esd's on mean bond lengths and angles are calculated from the equation $\sigma = \sqrt{\left\{\left[\sum_{1}^{n} (x_i - \bar{x})^2\right]/(n-1)\right\}}$ where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

b

In the anion the I atom and CO(53) are disordered. These ligands are related in position by an approximate non-crystallographic two-fold axis that contains Os(5) and passes through the midpoint of the Os(1) - Os(4) bond; the site occupation factors for the two alternative iodine sites [I(A) and I(B)] and the two alternative carbon sites [C(53A) and C(53B), which were placed in fixed positions] were set to 0.5. The Os-I distance is approximately equaly to an Os...O distance so the two alternative sites for O(53) are masked by the two I sites. Since the atomic no. of I is much larger than that of O, no allowance was made for this oxygen in the structure factor calculations.

Table 2.10 Selected Intramolecular Angles (°) in (IV).
Esd's are given in parentheses.

(a) M-C-O Angles

Os(1)-C(11)-O(11)	176.7(12)	Os(4)-C(41)-O(41)	175.3(16)
Os(1)-C(12)-O(12)	176.3(14)	Os(4)-C(42)-O(42)	172.2(19)
Os(1)-C(13)-O(13)	173.8(17)	Os(4)-C(43)-O(43)	176.7(17)
Os(2)-C(21)-O(21)	178.1(16)	Os(5)-C(51)-O(51)	177.6(12)
Os(2)-C(22)-O(22)	178.7(12)	Os(5)-C(52)-O(52)	175.3(21)
Os(2)-C(23)-O(23)	174.2(18)		
Os(3)-C(31)-O(31)	178.5(14)		
Os(3)-C(32)-O(32)	177.9(15)		
Os(3)-C(33)-O(33)	177.0(13)		
Mean Os-C-O	176.3(19)[a]		

(b) Angles Involving Iodine[b]

I(A)-Os(5)-Os(2)	92.4(1)	I(B)-Os(5)-Os(2)	92.6(1)
I(A)-Os(5)-Os(3)	92.4(1)	I(B)-Os(5)-Os(3)	91.0(1)

cont ...

I(A)-Os(5)-C	93.7(3)	I(B)-Os(5)-C	92.1(4)
I(A)-Os(5)-C(51)	87.6(7)	I(B)-Os(5)-C(51)	87.5(7)
I(A)-Os(5)-C(52)	88.4(8)	I(B)-Os(5)-C(52)	88.9(8)
I(A)-Os(5)-C(53B)	175.1(1)	I(B)-Os(5)-C(53A)	172.8(1)
I(A)-C(53A)-Os(5)	168.5(1)	I(B)-C(53B)-Os(5)	166.7(1)

(c) Angles Involving Carbide

Os(2)-C-Os(1)	90.5(4)	Os(4)-C-Os(3)	89.8(4)
Os(3)-C-Os(1)	90.7(5)	Os(5)-C-Os(3)	89.4(4)
Os(4)-C-Os(1)	81.4(4)		
Os(5)-C-Os(1)	139.9(7)		
		Os(5)-C-Os(4)	138.7(6)
Os(3)-C-Os(2)	178.8(7)		
Os(4)-C-Os(2)	90.3(5)		
Os(5)-C-Os(2)	89.8(4)		

(d) Angles Between Metal Atoms

Os(3)-Os(1)-Os(2)	86.0(1)	Os(4)-Os(2)-Os(1)	56.5(1)
Os(4)-Os(1)-Os(2)	61.7(1)	Os(5)-Os(2)-Os(1)	87.2(1)
Os(4)-Os(1)-Os(3)	61.4(1)	Os(5)-Os(2)-Os(4)	86.8(1)

cont ...

Os(4)-Os(3)-Os(1)	56.4(1)	Os(2)-Os(4)-Os(1)	61.8(1)
Os(5)-Os(3)-Os(1)	86.8(1)	Os(3)-Os(4)-Os(1)	62.3(1)
Os(5)-Os(3)-Os(4)	86.8(1)	Os(3)-Os(4)-Os(2)	86.5(1)
		Os(3)-Os(5)-Os(2)	85.2(1)

(e) Carbon-Metal-Metal Angles [b]

C(11)-Os(1)-Os(2)	161.5(5)	C(31)-Os(3)-Os(1)	106.3(4)
C(11)-Os(1)-Os(3)	87.5(4)	C(31)-Os(3)-Os(4)	162.2(4)
C(11)-Os(1)-Os(4)	100.1(5)	C(31)-Os(3)-Os(5)	87.8(4)
C(12)-Os(1)-Os(2)	89.3(5)	C(32)-Os(3)-Os(1)	92.7(4)
C(12)-Os(1)-Os(3)	158.7(5)	C(32)-Os(3)-Os(4)	93.0(4)
C(12)-Os(1)-Os(4)	98.2(5)	C(32)-Os(3)-Os(5)	179.5(4)
C(13)-Os(1)-Os(2)	101.1(5)	C(33)-Os(3)-Os(1)	157.6(5)
C(13)-Os(1)-Os(3)	104.1(5)	C(33)-Os(3)-Os(4)	101.4(5)
C(13)-Os(1)-Os(4)	156.6(6)	C(33)-Os(3)-Os(5)	89.9(4)
C(21)-Os(2)-Os(1)	92.0(5)	C(41)-Os(4)-Os(1)	93.6(5)
C(21)-Os(2)-Os(4)	93.3(4)	C(41)-Os(4)-Os(2)	154.1(5)
C(21)-Os(2)-Os(5)	178.9(5)	C(41)-Os(4)-Os(3)	88.5(6)
C(22)-Os(2)-Os(1)	158.5(5)	C(42)-Os(4)-Os(1)	157.3(6)
C(22)-Os(2)-Os(4)	102.2(5)	C(42)-Os(4)-Os(2)	109.5(6)
C(22)-Os(2)-Os(5)	88.4(4)	C(42)-Os(4)-Os(3)	97.5(6)
C(23)-Os(2)-Os(1)	102.3(6)	C(43)-Os(4)-Os(1)	104.8(5)
C(23)-Os(2)-Os(4)	158.6(6)	C(43)-Os(4)-Os(2)	86.7(5)
C(23)-Os(2)-Os(5)	88.8(5)	C(43)-Os(4)-Os(3)	167.1(5)

cont...

C(51)-Os(5)-Os(2)	177.8(4)	C(53A)-Os(5)-Os(2)	94.5(1)
C(51)-Os(5)-Os(3)	92.5(4)	C(53A)-Os(5)-Os(3)	88.6(1)
C(52)-Os(5)-Os(2)	86.9(4)	C(53B)-Os(5)-Os(2)	87.6(1)
C(52)-Os(5)-Os(3)	172.2(4)	C(53B)-Os(5)-Os(3)	92.5(1)

(f) OC-M-CO Angles[b]

C(12)-Os(1)-C(11)	90.5(6)	C(42)-Os(4)-C(41)	96.3(8)
C(13)-Os(1)-C(11)	97.2(8)	C(43)-Os(4)-C(41)	92.8(8)
C(13)-Os(1)-C(12)	97.2(7)	C(43)-Os(4)-C(42)	95.1(8)
C(22)-Os(2)-C(21)	92.7(7)	C(52)-Os(5)-C(51)	95.3(6)
C(23)-Os(2)-C(21)	90.7(7)	C(53A)-Os(5)-C(51)	85.4(7)
C(23)-Os(2)-C(22)	98.6(8)	C(53B)-Os(5)-C(51)	92.6(7)
		C(53A)-Os(5)-C(52)	92.5(8)
C(32)-Os(3)-C(31)	92.2(7)	C(53B)-Os(5)-C(52)	86.7(8)
C(33)-Os(3)-C(31)	95.6(6)	C(53B)-Os(5)-C(53A)	177.7(0)
C(33)-Os(3)-C(32)	90.6(6)		

[a] See Table 2.9 footnote a.

[b] See Table 2.9 footnote b.

Table 2.11 Selected Bond Lengths (Å) and Angles (°) for the $\left[(Ph_3P)_2N\right]^+$ Cation[a] in (IV). Esd's are given in parentheses.

P(1)-N	1.580(9)	P(1)-N-P(2)	142.4(6)
P(2)-N	1.587(9)		
		N-P(1)-C(111)	115.6(5)
P(1)-C(111)	1.781(10)	N-P(1)-C(121)	112.2(5)
P(1)-C(121)	1.798(11)	N-P(1)-C(131)	108.8(5)
P(1)-C(131)	1.819(11)	N-P(2)-C(211)	108.7(5)
P(2)-C(211)	1.794(10)	N-P(2)-C(221)	115.1(4)
P(2)-C(221)	1.788(9)	N-P(2)-C(231)	110.2(5)
P(2)-C(231)	1.810(9)		
		C(111)-P(1)-C(121)	107.1(5)
		C(111)-P(1)-C(131)	107.0(4)
		C(121)-P(1)-C(131)	105.6(5)
		C(211)-P(2)-C(221)	107.1(4)
		C(211)-P(2)-C(231)	108.3(4)
		C(221)-P(2)-C(231)	107.3(4)

[a] The cation is in the usual bent form (R.D. Wilson and R. Bau, J. Am. Chem. Soc. 1974, 96, 7601 and refs. therein.)

Table 2.12 Least-squares planes in direct space for $Os_5C(CO)_{15}$ (III) and $[(Ph_3P)_2N]^+[Os_5C(CO)_{15}I]^-$ (IV). Only atoms marked with an asterisk were included in calculation of the plane.

(a) $Os_5C(CO)_{15}$

atom	dev./Å
Plane 1: $1.8923x + 12.8175y + 8.4613_3 = 5.4802$	
Os(11)	1.9822
Os(12)*	-0.0075
Os(13)*	0.0075
Os(14)*	-0.0073
Os(15)*	0.0074
C(1)	-0.1075
Plane 2: $12.5920x - 8.1427y + 5.4236_3 = -4.3180$	
Os(21)	1.9975
Os(22)*	0.0431
Os(23)*	-0.0429
Os(24)*	0.0423
Os(25)*	-0.0426
C(2)	-0.1336

(b) $[(Ph_3P)_2N]^+[Os_5C(CO)_{15}I]^-$

atom	dev./A°
Plane : $33.3204x + 2.0609y - 1.2005_3 = 12.7222$	
Os(1)*	-0.0010
Os(2)	1.9815
Os(3)	-1.9909
Os(4)*	-0.0010
Os(5)*	-0.0015
C	0.0036

*(See facing page)

In the monohydride $HOs_5(CO)_{13}(PhNC_6H_4N)$, which has only six electron pairs available for skeletal bonding, the five Os atoms have also been shown to adopt an edge-bridged tetrahedral geometry. The apparent electron deficiency in this novel complex is thought to be relieved by the formation of Os-Os bonds of multiple character; two Os-Os distances are, at 2.60 Å, the shortest yet reported in a carbonyl cluster (Z.Dawoodi, M.J.Mays, and P.R.Raithby, J.Chem.Soc., Chem. Commun., 1980, 712).

*(See facing page)

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Section 2.4 Conclusions

(1) For M_5 osmium clusters with 7 skeletal electron pairs (S) the preferred geometry is determined not just by the value of S alone, but also by the ligands attached to the metal unit. Thus although $Os_5C(CO)_{15}$ and $Os_5P(OMe)(CO)_{15}$ have the square pyramidal geometry predicted by Wade theory, $[H_2Os_5(CO)_{15}I]^-$, $H_2Os_5(CO)_{15}P(OMe)_3$ and $H_2Os_5(CO)_{16}$ have an alternative edge-bridged tetrahedral metal geometry. Significantly there are no square pyramidal M_5 clusters in which the square face is not bridged, and there are no edge-bridged tetrahedral species without two hydride ligands. Therefore there appear to be two explanations:-

(i) A square pyramidal metal geometry is favoured only when a 4 (or 3) electron donor atom or group is present to "plug" the tetragonal face.

(ii) An edge-bridged tetrahedral (i.e. an arachno - capped octahedral) metal geometry is preferred when two hydrogen atoms are present.

Many more structures need to be examined to assess the relative importance of these two factors in determining the preferred cluster geometry.

(2) The clusters $H_2Os_5(CO)_{15}$ and $Os_5C(CO)_{15}$ can add on weak nucleophiles due to their ability to undergo an appropriate change in metal polyhedron (which may be rationalized by Wade theory) to accommodate the extra electrons. Thus in these complexes, owing to the unexpected flexibility of the metal framework, it is possible to generate a new coordination site via the breaking of a M - M bond. The reversibility of $[H_2Os_5(CO)_{15}I]^-$ to $H_2Os_5(CO)_{15}$ also suggests that these clusters may be of use as catalysts.

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SECTION 3

The Structures of Some Ruthenium and Osmium clusters that contain completely encapsulated carbon atoms.

Section 3.1 Introduction

In the previous Section the structures of some clusters containing a partially encapsulated carbon atom were discussed. However, there are few other examples of complexes of this type, in most polynuclear carbonyls the interstitial atoms are completely surrounded by metal atoms. To date H,[1] C,[2] N,[3] P,[4] and S[5] have been found embedded in the interstices of metal polyhedra; the enhanced stability of such clusters has been attributed to the presence of additional bonds with the interstitial atoms.[5,6]

The chemistry of carbide clusters in the cobalt sub-group is well developed[2] but the structures and reactivity of carbido clusters of Ru and Os are not well known although $Ru_6C(CO)_{14}(C_6H_3Me_3)$ was the first polynuclear carbonyl to have a completely encapsulated carbon atom confirmed by X-ray analysis.[7] In carbides of the Fe triad the interstitial carbon atom appears to be derived exclusively from reduction of a CO ligand[8,9] in contrast to other transition metal clusters where the carbido atom can arise from other sources. For example CCl_4, the solvent used for the reaction, is the source of the carbon atom in $[Co_6C(CO)_{15}]^{2-}$ (ref. 6), and in $Co_6C(CO)_{12}S_2$ the carbido atom arises from CS_2.[10]

These complexes may be good models for studying the structures and properties of alloys, and it is hoped that they will be good catalysts in their own right. However it should be pointed out that recent work has indicated that for rhodium clusters, those <u>without</u> interstitial atoms are much more effective catalysts than those that contain embedded atoms.[11]

Section 3.2 The Structures of $[Ru_6C(CO)_{16}]^{2-}$ and $Ru_6C(CO)_{15}(C_6H_{10})$

3.2.1. Preamble

In contrast to the hexanuclear osmium cluster $Os_6(CO)_{18}$ which can undergo fragmentation to smaller clusters on reaction with $[OH]^-$, [12] reaction of $Ru_6C(CO)_{17}$ with base leaves the Ru_6C unit intact and ultimately yields the dianion $[Ru_6C(CO)_{16}]^{2-}$ (ref.13). This dianion has the same number of CO ligands and the same number of valence electrons as $[Fe_6C(CO)_{16}]^{2-}$ (ref.14) and $Rh_6(CO)_{16}$.[15]

The complex $Ru_6C(CO)_{15}(C_6H_{10})$, which was isolated from the reaction of $Ru_3(CO)_{12}$ with ethylene, is a rare example of a high order cluster containing a hydrocarbon ligand. Previous examples include the arene derivatives $Ru_6C(CO)_{14}$(arene) [8,9,16] of which the mesitylene and $\eta^6 - \mu_3$-bitropyl [17] clusters have been structurally characterized, the compounds formulated as $Rh_6(CO)_{14}$(diene), [18] $[Rh_6(CO)_{14}(\eta^3 - C_3H_5)]^-$, [19] the osmium clusters $Os_6(CMe)(CO)_{16}(CMe)$ and $Os_6C(CO)_{16}(MeC{:}CMe)$, [20] and $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$. [21] This family of compounds may be critical in the assessment of the cluster - surface analogy in that they are potential models of hydrocarbon interactions with metal surfaces, processes of great importance in the chemical and petrochemical industries. A study of such hydrocarbon complexes could provide some understanding of isomerization, oligomerization, polymerization, hydrogenation and dehydrogenation processes.

3.2.2 Data Collection

Crude samples of $[Ph_4As]_2^+[Ru_6C(CO)_{16}]^{2-}$ (V) and

$Ru_6C(CO)_{15}(C_6H_{10})$ (VI) were provided from the University of Cambridge by Dr. K. Wong and G.J. Will respectively. The dianion was recrystallized from CH_2Cl_2 - C_6H_{12} and $Ru_6C(CO)_{15}(C_6H_{10})$ was recrystallized from $CHCl_3$- MeOH. The crystal selected for data collection was of dimensions 0.48 x 0.40 x 0.40 mm (V) and 0.43 x 0.26 x 0.19 mm (VI). Unit cell parameters were determined and data was collected and processed by the methods described in Subsection 2.2.2. Crystal data for (V) and (VI) are given in Table 3.1.

Table 3.1 Crystal data for $[Ph_4As]_2^+ [Ru_6C(CO)_{16}]^{2-}$ (V) and $Ru_6C(CO)_{15}(C_6H_{10})$ (VI).

	(V)	(VI)
M_r	1833.3	1120.9
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	19.329	10.592
b/Å	14.958	32.953
c/Å	11.498	16.746
α/°	90	90
β/°	101.33	96.34
γ/°	90	90
U/Å^3	3259.5	5809.2
$D_c(D_m)$/g cm^{-3}	1.87 (1.86)	2.56
Z	2	8

Scan widths of 0.64 and 0.62 °were used for (V) and (VI) respectively.

For (V) and (VI) following data collection several relatively intense reflections were measured at 20° intervals of rotation

about their diffraction vector (Ψ). The variation in intensity was not significant ($\not> 3\sigma$) for $[Ph_4As]_2^+ [Ru_6C(CO)_{16}]^{2-}$ (V); this and the small value of μ (22.62 cm^{-1}) indicated that absorption corrections could be reasonably neglected. The Ψ scans for $Ru_6C(CO)_{15}(C_6H_{10})$ (VI) showed a small but significant variation in intensity, empirical absorption corrections were therefore applied to the data which gave relative transmission coefficients which ranged from 0.814 to 1.171 [μ = 28.44 cm^{-1}].

Laue equivalent reflections were averaged to give 4520 and 7887 unique observed data [$I \geqslant 3\sigma(I)$] for (V) and (VI) respectively.

3.2.3 Structure Solution and Refinement

The scattering factors used, the function minimized during least-squares refinement, and definitions of the discrepancy indices quoted in the text are given in Subsection 2.2.3.

Systematic absences (0 k 0 for k = 2n + 1 and h 0 l for l = 2n + 1) indicated the centric space group $P2_1/c$ for $[Ph_4As_2]^+ [Ru_6C(CO)_{16}]^{2-}$ (V), but the unit cell was transformed into one containing a smaller β angle for data collection. This alternative setting, which corresponds to the non-standard space group $P2_1/n$, was chosen to avoid correlations during refinement. The measured density (1.86 $g\ cm^{-3}$) was consistent with the presence of two molecules of (V) in the unit cell which required the dianion to lie on a centre of symmetry. The three Ru atoms in the asymmetric unit were located from a Patterson map, but the first difference - Fourier synthesis showed a distribution of maxima that could be rationalized in two alternative ways:-

(1) The space group is wrong and the correct space group is Pn (non-centric) but the atoms have a near centric distribution.

(2) The centric space group $P2_1/n$ is correct but there is massive disorder of the structure.

To investigate the first possibility a difference - Fourier map was calculated in the non-centric space group Pn; the phases were calculated using the positions of the Ru atoms that are centrosymmetrically related, therefore a map was obtained with imposed centric symmetry. However a suitable geometry for the $[Ru_6C(CO)_{16}]^{2-}$ dianion was resolved from the centrosymmetric image. The overall geometry approximated to C_{2v} symmetry and of the sixteen carbonyl ligands twelve were terminally bonded to the cluster, the remaining four were asymmetrically edge-bridging [Figure 3.1(a)]. The only alternative geometry has the four edge-bridging carbonyls all bonded to the same Ru atom and was thought to be very unlikely. Refinement in this non-centric space group posed great difficulty due to parameter correlations between atoms that were approximately centrosymmetrically related [Ru(1), Ru(6); Ru(2), Ru(5); Ru(3), Ru(4); CO(21), CO(51); CO(22), CO(52); CO(31), CO(41); CO(32), CO(42); and the atoms of the two $[Ph_4As]^+$ cations]. These atoms were therefore refined in separate cycles and equivalent bond lengths were constrained to be equal. Refinement converged satisfactorily at R = 0.0805 using anisotropic thermal parameters for the arsenic and ruthenium atoms. The phenyl rings of the $[Ph_4As]^+$ cations were treated as rigid groups [d(C-C) = 1.395 Å] and the phenyl hydrogens were included in geometrically calculated positions [d(C-H) = 1.08 Å]. A final difference - Fourier synthesis revealed no electron density $>1\ e\text{Å}^{-3}$ except in the region of the Ru atoms. Thus the overall geometry of the $[Ru_6C(CO)_{16}]^{2-}$ dianion was clearly established. Refinement of the structure was then attempted using the disordered model in the centric space group $P2_1/n$. The disordered image of the $[Ru_6C(CO)_{16}]^{2-}$ dianion is shown in Figure 3.1(b) and may be explained in terms of statistical disorder between two centrosymmetrically related orientations of the cluster, one of which is shown in Figure 3.1(a), the other orientation is obtained by translating the bridging CO's, and the terminal carbonyls attached to Ru(1) and Ru(6) [i.e. Ru(1')], across the centre of symmetry. The sites of these carbonyl ligands are therefore only of 0.5 occupancy. The remaining CO groups are

common to the two orientations of the dianion (the atoms are related in pairs *via* the centre of symmetry) so the sites for the atoms of these ligands are of unit occupancy. Refinement of the structure yielded large thermal parameters for the eight centrosymmetrically related terminal CO ligands, and half of the phenyl carbon atoms. The common isotropic thermal parameter for the phenyl hydrogens also assumed an unrealistically large value (30 $Å^2$) consistent with some disorder of the phenyl rings of the cation. For each of the terminal carbonyls originally of full occupancy, the peaks for the C and O atoms were resolved into separate maxima separated by approximately 0.5 and 0.7 Å respectively. The occupation factor for these sites was fixed at 0.5 and the C atoms in these groups were placed in calculated positions such that d(Ru - C)/d(Ru-O) = 0.615 and Ru - C - O = 180°. Refinement was continued for the oxygen atoms, the C positions were recalculated if large shifts were observed for the oxygen atoms to which they were attached. The disorder of the cation was compensated for by assigning the phenyl carbons anisotropic thermal parameters, no allowance now being made for the phenyl hydrogen atoms in the structure factor calculations. Blocked full matrix refinement was used with the atoms grouped as follows: block 1, the ruthenium atoms; block 2, half of the CO ligands of the $[Ru_6C(CO)_{16}]^{2-}$ dianion; block 3, the remaining atoms of the dianion; block 4, the atoms of the $[Ph_4As]^+$ cation. Refinement converged at R = 0.0615, R_w = 0.0661, and R_G = 0.0786 using anisotropic thermal parameters for all atoms except those of the centrosymmetrically related terminal CO ligands, and with the phenyl rings treated as rigid groups. Weights were assigned to reflections as $\underline{w} = 4.9429/\sigma^2 F$ (see Subsection 2.2.3). A final difference-Fourier synthesis revealed a few residual maxima in the region of the ruthenium atoms, the largest of which had a height of 1.0 $eÅ^{-3}$. The overall geometry of the $[Ru_6C(CO)_{16}]^{2-}$ dianion was therefore established beyond question from the two alternative refinements. The data/parameter ratio was very similar for the two models, but the bond lengths and angles quoted in the text (*vide infra*) are those obtained from the disordered model refined in the centric space group.

In $Ru_6C(CO)_{15}(C_6H_{10})$ (VI) the ruthenium atoms in the asymmetric

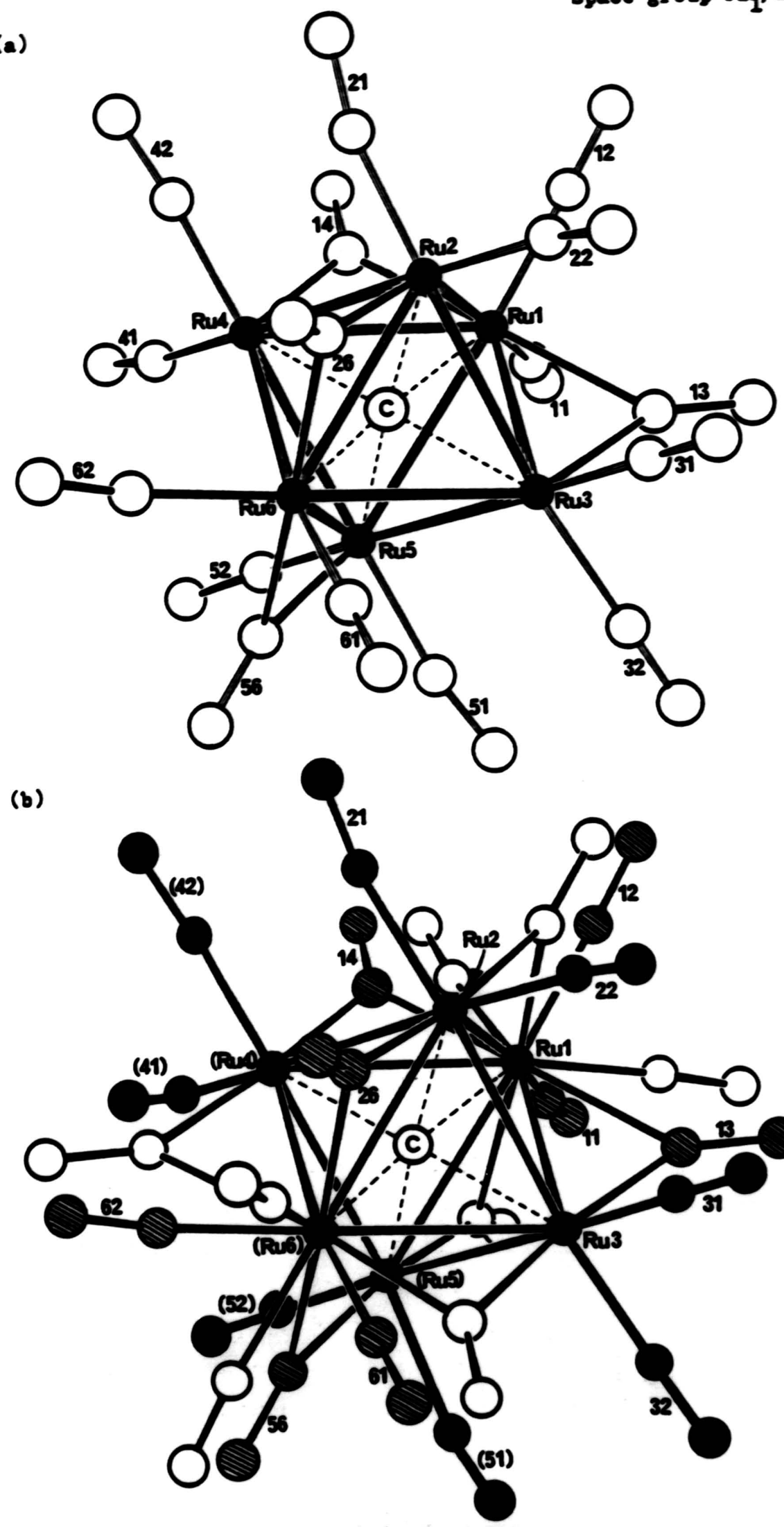
unit were located as two distinct Ru_6 octahedra by direct methods using multisolution Σ_2 sign expansion. The remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. The two independent clusters are not identical (Figures 3.3 and 3.4). Firstly the CO's attached to Ru(5) are rotated by 60° in the second cluster relative to those in the first. Secondly the C_6 hydrocarbon unit in cluster 2 is partially disordered; the peaks due to carbon atoms C(2) and C(5) were each resolved into two separate maxima (A and B) approximately 1 Å apart, and although their positional and thermal parameters were allowed to refine freely the site occupation factors of the two components were fixed at 0.5. The positions of C(2B) and C(5B) in the C_6 unit in cluster 2 correspond to the same relative positions as C(2) and C(5) in cluster 1. Blocked full matrix refinement was used with the atoms grouped as follows: block 1, the ruthenium atoms of cluster 1; block 2, the other atoms of cluster 1; block 3, the Ru atoms of cluster 2; block 4, the remaining atoms of cluster 2. The hydrogen atoms attached to the hydrocarbon ligand in cluster 1 were included in geometrically calculated positions [d(C-H) = 1.08 Å] based upon the assumptions that C(1) and C(6) were methyl groups (H - C - H = 109.5°) and that C(2), C(3), C(4), and C(5) were using sp^2 hybrid orbitals with one H attached. This was consistent with the C-C-C angles observed within the C_6 ligand. Refinement converged at R = 0.0418, R_w = 0.0481 and R_G = 0.0580 using anisotropic thermal parameters for the ruthenium atoms. Weights were assigned to reflections as $\underline{w} = 1.6842/\sigma^2 F$ (see Subsection 2.2.3). A final difference-Fourier synthesis revealed several maxima in the region of the oxygen atoms, the largest of which had a height of 1.2 $e\text{Å}^{-3}$.

Final positional and thermal parameters for $[Ph_4As]_2^+ [Ru_6C(CO)_{16}]^{2-}$ (V) ($P2_1/n$ refinement) and $Ru_6C(CO)_{15}(C_6H_{10})$ (VI) are given in Appendices 5 and 6 respectively.

3.2.4 Discussion

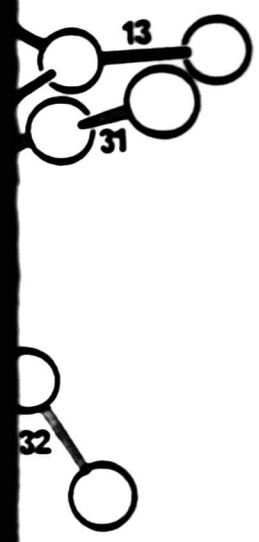
The structures of the dianion in $[Ph_4As]_2^+ [Ru_6C(CO)_{16}]^{2-}$

Figure 3.1 (a)The overall geometry of $[Ru_6C(CO)_{16}]^{2-}$
(b)The disordered image of the dianion in the centric space group $P2_1/n$.



]$^{2-}$

in the centric
ce group $P2_1/n$.

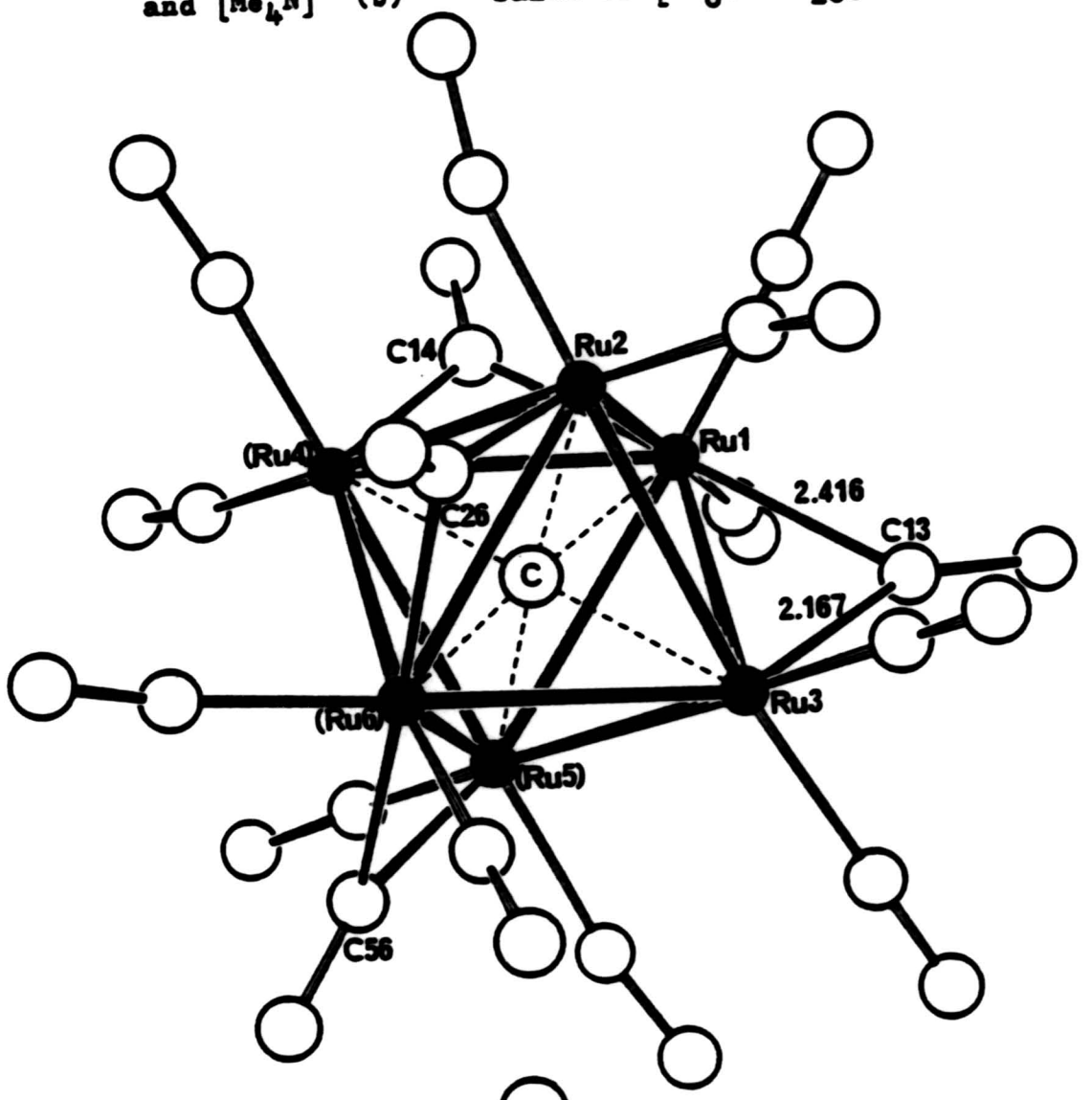


(V) and $Ru_6(C(CO)_{15}(C_6H_{10})$ (VI) are shown in Figures 3.1 - 3.4 and the bond distances and angles are given in Tables 3.2 - 3.6.

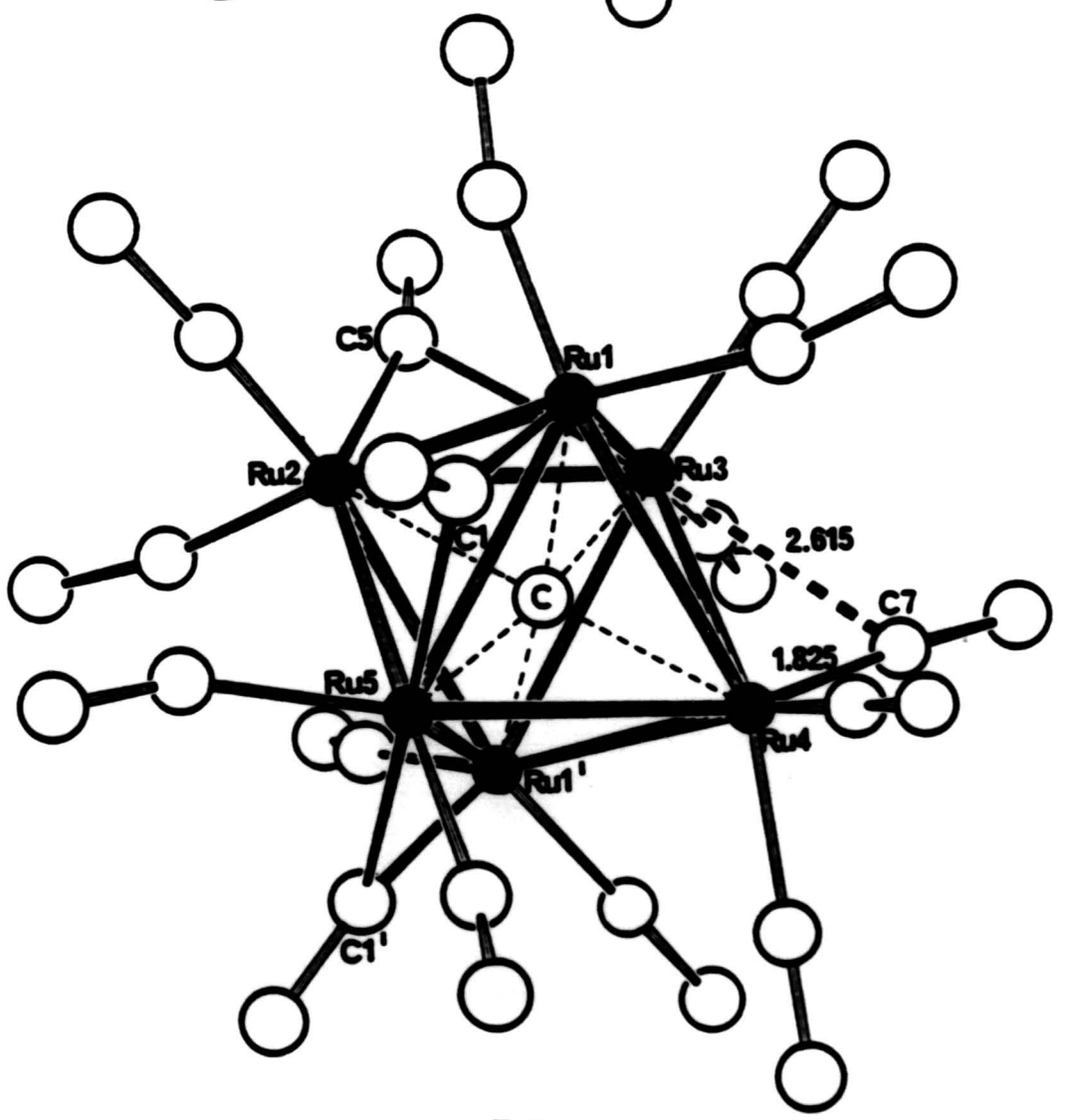
Although a space group ambiguity exists for (V) [see previous Subsection], the overall geometry of the $[Ru_6C(CO)_{16}]^{2-}$ dianion has been established unequivocally. The carbido atom is situated at the centre of an octahedral array of ruthenium atoms [mean Ru -- C, 2.05(1) Å, Ru - C - Ru angles in the range 178.8 - 179.9°] and of the sixteen carbonyl ligands twelve are terminal and four are asymmetrically edge-bridging. This arrangement contrasts with that in $Rh_6(CO)_{16}$ where four CO's are face rather than edge-bridging.[15] Surprisingly this carbonyl distribution is also different from that recently reported[22] for the dianion in $[Me_4N]_2^+ [Ru_6C(CO)_{16}]^{2-}$, which is isomorphous and isostructural with its iron analogue (ref. 14), and has only <u>three</u> edge-bridging carbonyls, the remaining thirteen being terminal. Although isomeric forms differing only in their carbonyl distribution have been postulated for several polynuclear clusters in solution[23] the $[Ph_4As]^+$ and $[Me_4N]^+$ salts of $[Ru_6C(CO)_{16}]^{2-}$ appear to be the first example of such isomerism persisting into the solid state. However comparison of their structures (Figure 3.2) shows that the only gross difference in the overall arrangement of the carbonyls is that the bridging carbonyl CO(13) in the $[Ph_4As]^+$ salt corresponds to the apparently terminal carbonyl CO(7) in the $[Me_4N]^+$ salt of $[Ru_6C(CO)_{16}]^{2-}$ and in its isomorphous iron analogue $[Me_4N]_2^+ [Fe_6C(CO)_{16}]^{2-}$. Significantly in these $[Me_4N]^+$ salts this terminal carbonyl is close to a second metal atom so that the M(3) ... C(7) contacts (2.615 and 2.65 Å respectively for the mean of two independent molecules in each case) are considerably shorter than any other non-bonded contact within the dianion. Additionally in the ruthenium species the Ru(4) - C(7) - O(7) angle is markedly non-linear (mean 159.9°) and the atoms of the ligand have large thermal parameters probably indicative of disorder. As the three bridging carbonyls are very asymmetric in the $[Me_4N]^+$ salts of $[Fe_6C(CO)_{16}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$ with M-C bond length ranges of 1.78 - 2.33 and 1.933 - 2.303 Å respectively, it is possible that the CO(7) ligand in these dianions should be regarded as a fourth asymmetric edge-

Figure 3.2 Comparison of the geometries of the $[Ph_4As]^+$ (a) and $[Me_4N]^+$ (b) salts of $[Ru_6C(CO)_{16}]^{2-}$.

(a)



(b)



bridge. The marked similarity in distribution of the rest of the CO ligands to that observed in the $[Ph_4As]^+$ salt supports this conclusion. However the Ru dianion is fluxional in solution[9,24] implying a low energy barrier to rearrangement, so it would not be surprising if slightly different carbonyl arrangements possessing similar energies were "frozen out" in the solid state with different counterions. Fluxionality, which is often observed in charged species, has been explained by Chini as a means of delocalizing the charge over the whole cluster.[25]

The two independent clusters in the asymmetric unit of $Ru_6C(CO)_{15}(C_6H_{10})$ (VI) are shown in Figures 3.3 and 3.4. Their structures may be considered as derived from that of $Ru_6C(CO)_{17}$[26] by replacement of the two carbonyl ligands on adjacent metal atoms by the hydrocarbon group. A μ_2 - bridging carbonyl group is retained bridging the Ru(4) - Ru(6) bond [Ru(4) - C(46) 2.044(9), 2.018(9); Ru(6) - C(46) 2.111(9), 2.128(9)], and an incipient carbonyl bridge is also observed on an adjacent edge of the octahedron, Ru(3) - Ru(6) [Ru(3) - C(32) 1.879(11), 1.937(11); Ru(6) - C(32) 2.692(11), 2.495(11) Å; Ru(3) - C(32) - O(32) 162.4(9), 156.9(9) °]. Cotton and Troupe suggest that asymmetric carbonyl bridges often occur in compensating pairs representing intermediate stages in the CO exchange process.[27] The pair of bridging carbonyls in $Ru_6C(CO)_{15}(C_6H_{10})$, which show differing degrees of asymmetry in the two independent clusters, may be related to the other geometric differences between the clusters and suggests that the molecule is fluxional in solution. The Ru - C and C - C bond parameters associated with the hydrocarbon ligand suggest that Ru(1) and Ru(2) are coordinated to C(4) - C(5) and C(2) - C(3) respectively [Figures 3.3 and 3.4] by π - interactions, while the other C - C bonds are predominantly single. Thus in the ordered hydrocarbon ligand in cluster 1 the bond lengths alternate long [C(11) - C(12) 1.51(2)], short [C(12) - C(13) 1.37(1)], long [C(13) - C(14) 1.42(1)], short [C(14) - C(15) 1.34(2)], long [C(15) - C(16) 1.49(2) Å] although the differences between these distances are of low significance. The partial disorder of the C_6 chain in cluster 2 makes a full analysis of the bonding difficult; however the trans, trans isomer of the 2, 4 - hexadiene ligand occurs in both molecules. A six carbon atom chain bound to a metal polyhedron has not

Figure 3.3 $Ru_6C(CO)_{15}(C_6H_{10})$ Cluster 1.

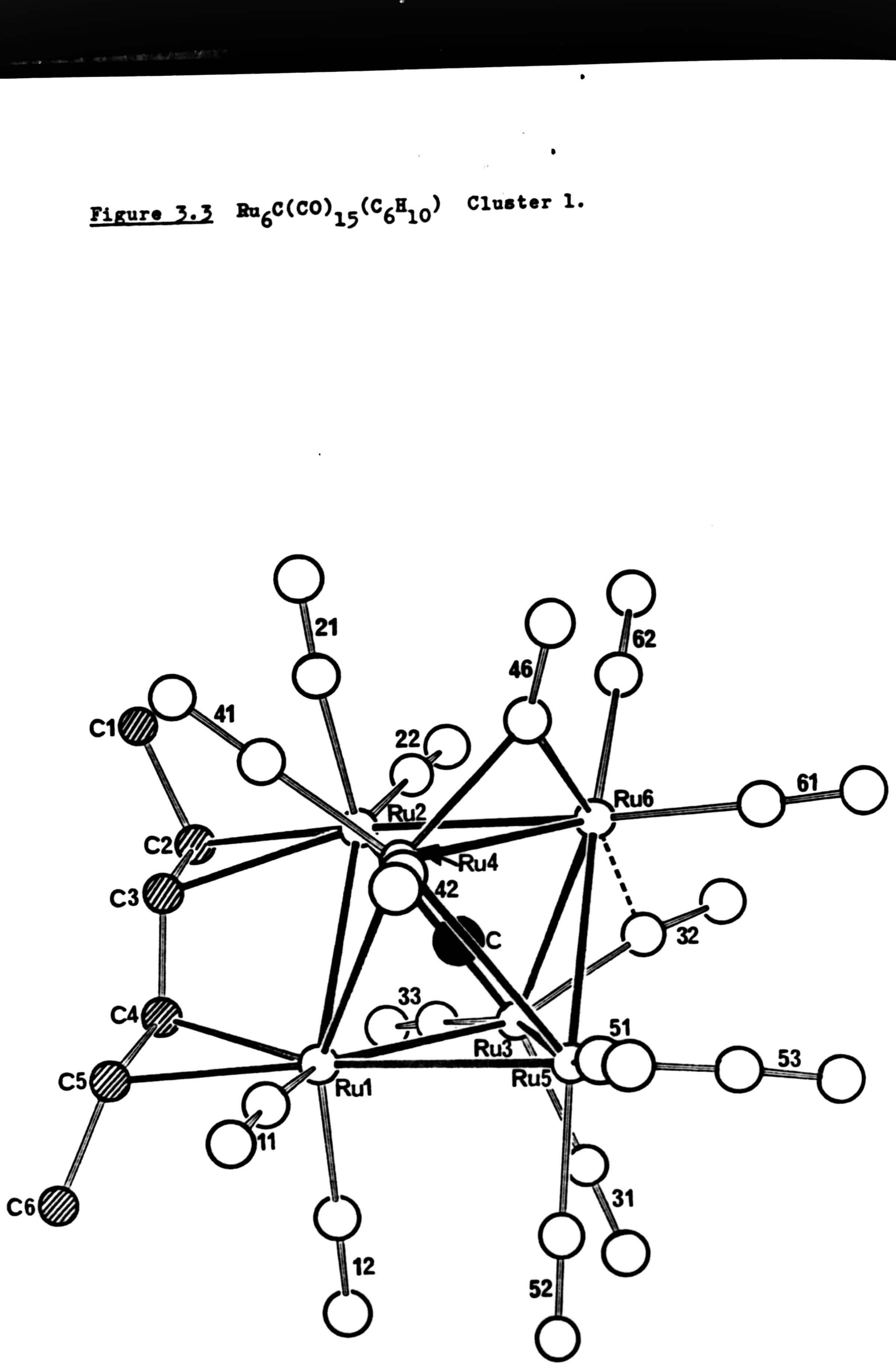
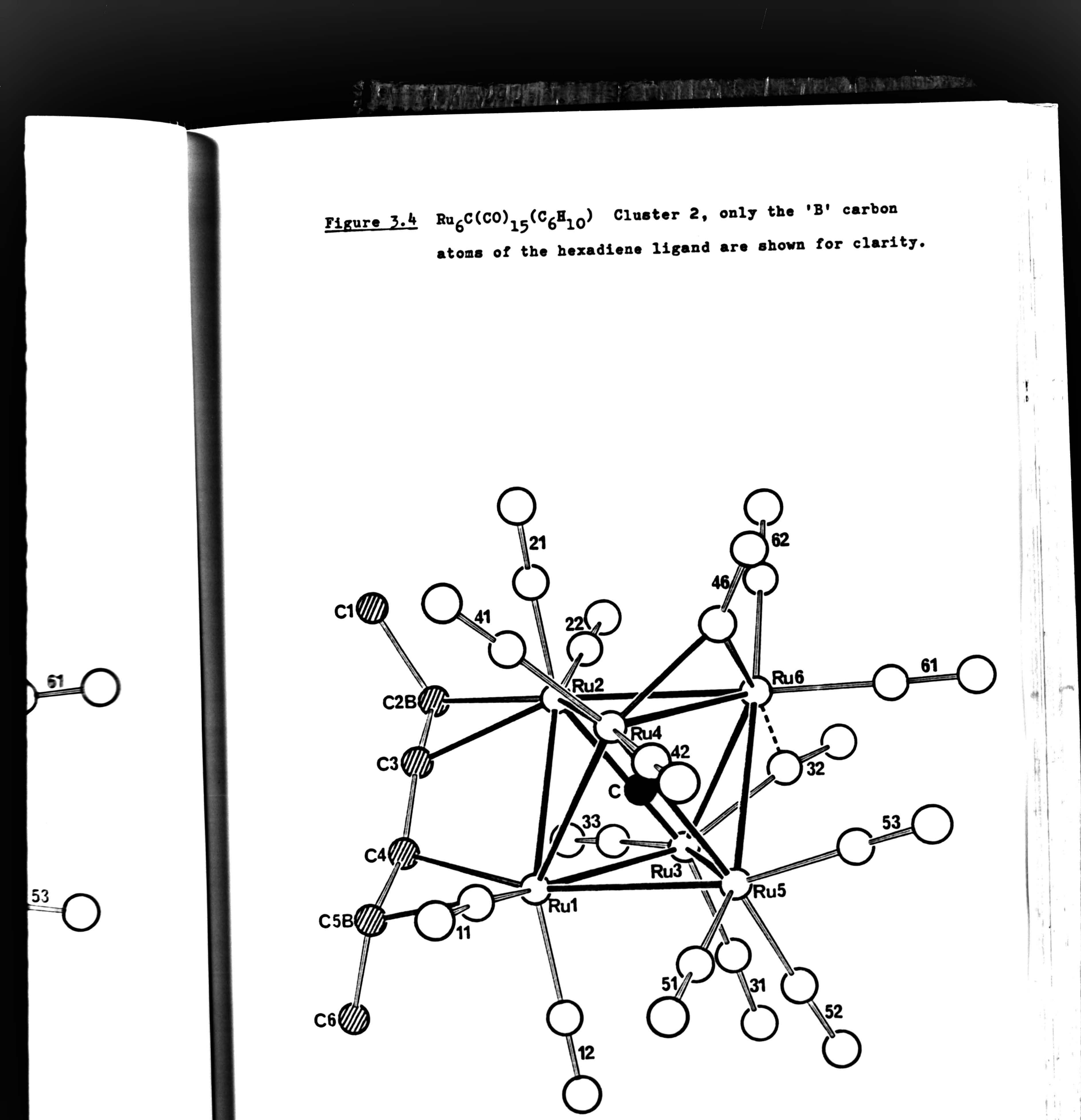


Figure 3.4 $Ru_6C(CO)_{15}(C_6H_{10})$ Cluster 2, only the 'B' carbon atoms of the hexadiene ligand are shown for clarity.



previously been observed but in $Os_3(CO)_{10}$ (s-trans - C_4H_6)[28] a four carbon atom chains span an edge of the metal triangle. In cluster 1 of $Ru_6C(CO)_{15}(C_6H_{10})$, as in the Os_3 species, the M - M distance spanned by the organic ligand is the largest in the molecule [Ru(11) - Ru(12) 2.982(1), mean Ru-Ru 2.907(51) Å] . In cluster 2 the hexadiene group bridges the third largest M-M bond in the molecule [Ru(21) - Ru(22)=2.943(1), mean Ru - Ru 2.902(46) Å]. The presence of the symmetrically bound interstitial carbide [mean Ru - C distances in the two independent clusters are 2.056(11) and 2.053(31) Å respectively] is of importance because coordination of large ligands to clusters is hindered by steric interactions with the large number of carbonyl groups present. The carbido atom donates four electrons reducing the number of CO ligands required by two, and this makes the bonding of the bulky hexadiene group to the Ru_6 core more sterically favourable. The isolation of $Ru_6C(CO)_{15}(C_6H_{10})$ indicates that oligomerization of ethylene has occured in the reaction with $Ru_3(CO)_{12}$, and such compounds may be important intermediates in the catalytic polymerization of ethylene by transition metal clusters to give (ultimately) polyethylenes.

Table 3.2 Selected Interatomic Distances (Å) for (V).[a]
E.s.d's are given in parentheses.

(a) Metal-Metal Bonds

Ru(1) - Ru(2)	2.895(1)	Ru(3) - Ru(5)	2.886(1)
Ru(1) - Ru(3)	2.948(1)	Ru(3) - Ru(6)	2.860(1)
Ru(1) - Ru(4)	2.860(1)		
Ru(1) - Ru(5)	2.910(1)	Ru(4) - Ru(5)	2.883(1)
		Ru(4) - Ru(6)	2.948(1)
Ru(2) - Ru(3)	2.883(1)		
Ru(2) - Ru(4)	2.886(1)	Ru(5) - Ru(6)	2.895(1)
Ru(2) - Ru(6)	2.910(1)		

(b) Metal-Carbide Distances

Ru(1) - C	2.066(1)	
Ru(2) - C	2.039(1)	
Ru(3) - C	2.041(1)	Mean Ru - C,
Ru(4) - C	2.041(1)	
Ru(5) - C	2.039(1)	2.049(13)[b]
Ru(6) - C	2.066(1)	

(c) Metal-carbon Distances

(i) Terminal CO's [c]

Ru(1) - C(11)	1.817(22)	Ru(6) - C(61)	1.906(21)
Ru(1) - C(12)	1.949(22)	Ru(6) - C(62)	1.805(19)

(ii) μ_2 - CO's

Ru(1) - C(13)	2.416(18)	Ru(2) - C(26)	2.092(18)
Ru(3) - C(13)	2.167(19)	Ru(6) - C(26)	2.251(19)
Ru(1) - C(14)	2.081(17)	Ru(5) - C(56)	2.021(19)
Ru(4) - C(14)	2.150(18)	Ru(6) - C(56)	2.124(16)

cont...

(d) Carbon-Oxygen Distances

(i) Terminal CO's [c]

C(11) - O(11)	1.123(28)	C(61) - O(61)	1.166(27)
C(12) - O(12)	1.145(27)	C(62) - O(62)	1.145(25)

(ii) μ_2 - CO's

C(13) - O(13)	1.092(22)	C(26) - O(26)	1.174(22)
C(14) - O(14)	1.163(24)	C(56) - O(56)	1.155(24)

[a] Where appropriate, symmetry related bond lengths and angles have been quoted separately; Ru(4) = Ru(3'), Ru(5) = Ru(2'), Ru(6) = Ru(1'), CO(51) = CO(21'), CO(52) = CO(22'), CO(41) = CO(31') and CO(42) = CO(32').

[b] E.s.d's on mean bond lengths and angles are calculated from the equation $\sigma = \sqrt{\left\{ \left[\sum_{1}^{n} (x_i - \bar{x})^2 \right] / (n-1) \right\}}$ where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

[c] In carbonyl ligands CO(21), CO(22), CO(31) and CO(32) the two components [(A) and (B)] of the C atoms were placed in fixed positions such that d(Ru - C)/d (Ru...O) = 0.615, these positions were recalculated after each cycle of refinement if large shifts were observed for the oxygen atoms to which they were attached [O(nA) and O(nB) respectively].

Table 3.3 Selected Intramolecular Angles (°) in (V).[a]
E.s.d's are given in parentheses.

(a) Angles Between Metal Atoms

Ru(3) - Ru(1) - Ru(2)	59.1(1)	Ru(2) - Ru(4) - Ru(1)	60.5(1)
Ru(4) - Ru(1) - Ru(2)	60.2(1)	Ru(5) - Ru(4) - Ru(1)	60.9(1)
Ru(4) - Ru(1) - Ru(3)	89.3(1)	Ru(5) - Ru(4) - Ru(2)	89.9(1)
Ru(5) - Ru(1) - Ru(2)	89.2(1)	Ru(6) - Ru(4) - Ru(1)	90.7(1)
Ru(5) - Ru(1) - Ru(3)	59.0(1)	Ru(6) - Ru(4) - Ru(2)	59.8(1)
Ru(5) - Ru(1) - Ru(4)	60.0(1)	Ru(6) - Ru(4) - Ru(5)	59.5(1)
Ru(3) - Ru(2) - Ru(1)	61.4(1)	Ru(3) - Ru(5) - Ru(1)	61.1(1)
Ru(4) - Ru(2) - Ru(1)	59.3(1)	Ru(4) - Ru(5) - Ru(1)	59.2(1)
Ru(4) - Ru(2) - Ru(3)	90.1(1)	Ru(4) - Ru(5) - Ru(3)	90.1(1)
Ru(6) - Ru(2) - Ru(1)	90.8(1)	Ru(6) - Ru(5) - Ru(1)	90.8(1)
Ru(6) - Ru(2) - Ru(3)	59.2(1)	Ru(6) - Ru(5) - Ru(3)	59.3(1)
Ru(6) - Ru(2) - Ru(4)	61.1(1)	Ru(6) - Ru(5) - Ru(4)	61.4(1)
Ru(2) - Ru(3) - Ru(1)	59.5(1)	Ru(3) - Ru(6) - Ru(2)	60.0(1)
Ru(5) - Ru(3) - Ru(1)	59.8(1)	Ru(4) - Ru(6) - Ru(2)	59.0(1)
Ru(5) - Ru(3) - Ru(2)	89.9(1)	Ru(4) - Ru(6) - Ru(3)	89.3(1)
Ru(6) - Ru(3) - Ru(1)	90.7(1)	Ru(5) - Ru(6) - Ru(2)	89.2(1)
Ru(6) - Ru(3) - Ru(2)	60.9(1)	Ru(5) - Ru(6) - Ru(3)	60.2(1)
Ru(6) - Ru(3) - Ru(5)	60.5(1)	Ru(5) - Ru(6) - Ru(4)	59.1(1)

(b) Angles Involving Carbide

Ru(1) - C - Ru(6)	179.9(1)
Ru(2) - C - Ru(5)	179.8(1)
Ru(3) - C - Ru(4)	179.8(1)

(c) M - C - O Angles

(i) Terminal CO's [b]

Ru(1) - C(11) - O(11)	174.3(19)	Ru(6) - C(61) - O(61)	175.2(16)
Ru(1) - C(12) - O(12)	172.2(20)	Ru(6) - C(62) - O(62)	168.1(19)

cont. .

(ii) μ_2 - CO's

Ru(1) - C(13) - O(13)	131.4(16)	Ru(2) - C(26) - O(26)	144.1(13)
Ru(3) - C(13) - O(13)	148.6(17)	Ru(6) - C(26) - O(26)	131.9(13)
Ru(1) - C(14) - O(14)	132.8(13)	Ru(5) - C(56) - O(56)	138.6(14)
Ru(4) - C(14) - O(14)	140.9(15)	Ru(6) - C(56) - O(56)	132.8(14)

(d) M - C(O) - M Angles

Ru(1) - C(13) - Ru(3)	79.9(5)	Ru(2) - C(26) - Ru(6)	84.0(6)
Ru(1) - C(14) - Ru(4)	85.0(6)	Ru(5) - C(56) - Ru(6)	88.6(7)

(e) OC - M - M Angles

(i) Terminal CO's [b]

C(11) - Ru(1) - Ru(2)	174.6(6)	C(61) - Ru(6) - Ru(2)	115.7(5)
C(11) - Ru(1) - Ru(3)	117.4(7)	C(61) - Ru(6) - Ru(3)	82.8(6)
C(11) - Ru(1) - Ru(4)	124.9(6)	C(61) - Ru(6) - Ru(4)	172.1(6)
C(11) - Ru(1) - Ru(5)	92.1(7)	C(61) - Ru(6) - Ru(5)	116.7(5)
C(12) - Ru(1) - Ru(2)	85.3(7)	C(62) - Ru(6) - Ru(2)	120.1(6)
C(12) - Ru(1) - Ru(3)	113.9(7)	C(62) - Ru(6) - Ru(3)	176.0(6)
C(12) - Ru(1) - Ru(4)	120.6(6)	C(62) - Ru(6) - Ru(4)	94.1(7)
C(12) - Ru(1) - Ru(5)	172.8(6)	C(62) - Ru(6) - Ru(5)	123.6(7)

	CO 'A'	CO 'B'
C(21) - Ru(2) - Ru(1)	116.9(1)	128.4(1)
C(21) - Ru(2) - Ru(3)	175.3(1)	169.9(1)
C(21) - Ru(2) - Ru(4)	92.6(1)	93.5(1)
C(21) - Ru(2) - Ru(6)	125.5(1)	114.8(1)
C(22) - Ru(2) - Ru(1)	125.7(1)	108.3(1)
C(22) - Ru(2) - Ru(3)	88.2(1)	89.9(1)
C(22) - Ru(2) - Ru(4)	172.4(1)	165.4(1)
C(22) - Ru(2) - Ru(6)	111.8(1)	130.2(1)
C(31) - Ru(3) - Ru(1)	125.7(1)	116.5(1)
C(31) - Ru(3) - Ru(2)	89.4(1)	94.4(1)
C(31) - Ru(3) - Ru(5)	172.5(1)	171.5(1)
C(31) - Ru(3) - Ru(6)	112.8(1)	128)(1)

cont...

C(32) - Ru(3) - Ru(1)	129.5(1)		116.0(1)
C(32) - Ru(3) - Ru(2)	166.3(1)		175.5(1)
C(32) - Ru(3) - Ru(5)	87.8(1)		87.5(1)
C(32) - Ru(3) - Ru(6)	106.6(1)		120.7(1)
C(41) - Ru(4) - Ru(1)	112.8(1)		128.0(1)
C(41) - Ru(4) - Ru(2)	172.5(1)		171.5(1)
C(41) - Ru(4) - Ru(5)	89.4(1)		94.4(1)
C(41) - Ru(4) - Ru(6)	125.7(1)		116.5(1)
C(42) - Ru(4) - Ru(1)	106.6(1)		120.7(1)
C(42) - Ru(4) - Ru(2)	87.8(1)		87.5(1)
C(42) - Ru(4) - Ru(5)	166.3(1)		175.5(1)
C(42) - Ru(4) - Ru(6)	129.5(1)		116.0(1)
C(51) - Ru(5) - Ru(1)	125.5(1)		114.8(1)
C(51) - Ru(5) - Ru(3)	92.6(1)		93.5(1)
C(51) - Ru(5) - Ru(4)	175.3(1)		169.9(1)
C(51) - Ru(5) - Ru(6)	116.9(1)		128.4(1)
C(52) - Ru(5) - Ru(1)	111.8(1)		130.2(1)
C(52) - Ru(5) - Ru(3)	172.4(1)		165.4(1)
C(52) - Ru(5) - Ru(4)	88.2(1)		89.9(1)
C(52) - Ru(5) - Ru(6)	125.7(1)		108.3(1)

(ii) μ_2 - CO's

C(13) - Ru(1) - Ru(2)	89.8(1)	C(26) - Ru(2) - Ru(1)	140.7(1)
C(13) - Ru(1) - Ru(3)	46.4(1)	C(26) - Ru(2) - Ru(3)	89.5(1)
C(13) - Ru(1) - Ru(4)	135.7(1)	C(26) - Ru(2) - Ru(4)	98.1(1)
C(13) - Ru(1) - Ru(5)	90.5(1)	C(16) - Ru(2) - Ru(6)	50.3(1)
C(13) - Ru(3) - Ru(1)	53.8(1)	C(26) - Ru(6) - Ru(2)	45.7(1)
C(13) - Ru(3) - Ru(2)	95.3(1)	C(26) - Ru(6) - Ru(3)	87.1(1)
C(13) - Ru(3) - Ru(5)	96.4(1)	C(26) - Ru(6) - Ru(4)	92.9(1)
C(13) - Ru(3) - Ru(6)	144.5(1)	C(26) - Ru(6) - Ru(5)	134.6(1)
C(14) - Ru(1) - Ru(2)	90.1(1)	C(56) - Ru(5) - Ru(1)	137.8(1)
C(14) - Ru(1) - Ru(3)	137.6(1)	C(56) - Ru(5) - Ru(3)	88.6(1)
C(14) - Ru(1) - Ru(4)	48.5(1)	C(56) - Ru(5) - Ru(4)	95.2(1)

cont...

C(14) - Ru(1) - Ru(5)	95.5(1)	C(56) - Ru(5) - Ru(6)	47.2(1)
C(14) - Ru(4) - Ru(1)	46.5(1)	C(56) - Ru(6) - Ru(2)	133.4(1)
C(14) - Ru(4) - Ru(2)	89.0(1)	C(56) - Ru(6) - Ru(3)	87.3(1)
C(14) - Ru(4) - Ru(5)	94.7(1)	C(56) - Ru(6) - Ru(4)	91.1(1)
C(14) - Ru(4) - Ru(6)	136.9(1)	C(56) - Ru(6) - Ru(5)	44.3(1)

(f) OC - M - CO Angles [b]

C(11) - Ru(1) - C(12)	92.9(10)	C(22A) - Ru(2) - C(26)	74.5(4)
C(11) - Ru(1) - C(13)	85.0(8)		
C(11) - Ru(1) - C(14)	95.0(8)	C(22B) - Ru(2) - C(26)	96.5(4)
C(12) - Ru(1) - C(13)	84.8(7)	C(31A) - Ru(3) - C(32A)	91.0
C(12) - Ru(1) - C(14)	89.3(7)	C(31A) - Ru(3) - C(32B)	93.6
		C(31A) - Ru(3) - C(13)	91.2(5)
C(13) - Ru(1) - C(14)	174.1(7)		
C(13) - Ru(3) - C(31A)	91.2(5)	C(31B) - Ru(3) - C(32A)	89.6
C(13) - Ru(3) - C(31B)	76.0(5)	C(31B) - Ru(3) - C(32B)	87.6
C(13) - Ru(3) - C(32A)	98.4(5)	C(31B) - Ru(3) - C(13)	76.0(5)
C(13) - Ru(3) - C(32B)	81.4(5)		
		C(56) - Ru(6) - C(61)	89.2(6)
C(21A) - Ru(2) - C(22A)	89.7	C(56) - Ru(6) - C(62)	94.8(7)
C(21A) - Ru(2) - C(22B)	86.6		
C(21A) - Ru(2) - C(26)	94.0(5)	C(61) - Ru(6) - C(62)	93.8(6)
C(21B) - Ru(2) - C(22A)	87.0		
C(21B) - Ru(2) - C(22B)	89.0		
C(21B) - Ru(2) - C(26)	80.7(4)		

[a] See Table 3.2 footnote a.

[b] See Table 3.2 footnote c.

Table 3.4 Selected Bond Lengths (Å) and Angles (°) in the $[Ph_4 As]^+$ cation in (V). E.s.d's are given in parentheses.

As - C(111)	1.902(5)
As - C(121)	1.890(7)
As - C(131)	1.889(7)
As - C(141)	1.888(7)

C(111) - As - C(121)	110.8(3)
C(111) - As - C(131)	106.8(3)
C(121) - As - C(131)	111.8(3)
C(111) - As - C(141)	109.9(3)
C(121) - As - C(141)	108.3(3)
C(131) - As - C(141)	109.3(3)

Table 3.5 Selected Interatomic Distances (Å) for (VI). E.s.d's are given in parentheses.

(a) Metal - Metal Distances.

	Cluster 1	Cluster 2
Ru(1)-Ru(2)	2.982(1)	2.943(1)
Ru(1)-Ru(3)	2.913(1)	2.901(1)
Ru(1)-Ru(4)	2.911(1)	2.971(1)
Ru(1)-Ru(5)	2.881(1)	2.844(1)
Ru(2)-Ru(3)	2.895(1)	2.921(1)
Ru(2)-Ru(4)	2.943(1)	2.924(1)
Ru(2)-Ru(6)	2.842(1)	2.853(1)
Ru(3)-Ru(5)	2.829(1)	2.924(1)
Ru(3)-Ru(6)	2.964(1)	2.887(1)
Ru(4)-Ru(5)	2.966(1)	2.839(1)
Ru(4)-Ru(6)	2.842(1)	2.858(1)
Ru(5)-Ru(6)	2.915(1)	2.960(1)
Mean Ru-Ru	2.907(51)[a]	2.902(46)[a]

(b) Metal - Ligand Distances

(i) Metal - Terminal CO

	Cluster 1	Cluster 2
Ru(1)-C(11)	1.879(9)	1.878(10)
Ru(1)-C(12)	1.846(9)	1.882(10)
Ru(2)-C(21)	1.873(9)	1.882(10)
Ru(2)-C(22)	1.874(9)	1.886(11)
Ru(3)-C(31)	1.864(11)	1.872(11)
Ru(3)-C(33)	1.900(10)	1.828(10)
Ru(4)-C(41)	1.832(10)	1.884(10)
Ru(4)-C(42)	1.861(10)	1.850(10)
Ru(5)-C(51)	1.899(10)	1.901(12)
Ru(5)-C(52)	1.890(10)	1.898(10)
Ru(5)-C(53)	1.837(11)	1.859(10)
Ru(6)-C(61)	1.848(11)	1.864(10)
Ru(6)-C(62)	1.870(10)	1.832(11)
Mean Ru-C	1.867(22)[a]	1.870(23)[a]

(ii) Metal - μ_2 CO

	Cluster 1	Cluster 2
Ru(4)-C(46)	2.044(9)	2.018(9)
Ru(6)-C(46)	2.111(9)	2.128(9)

(iii) Metal - Incipient μ_2 CO

	Cluster 1	Cluster 2
Ru(3)-C(32)	1.879(11)	1.937(11)
Ru(6)-C(32)	2.692(11)	2.495(11)

(iv) Metal - Hexadiene Ligand[b]

	Cluster 1	Cluster 2
Ru(2)-C(2)	2.307(11)	C(2A) 2.313(17)
		C(2B) 2.285(21)
Ru(2)-C(3)	2.307(10)	2.280(11)
Ru(1)-C(4)	2.271(10)	2.252(12)
Ru(1)-C(5)	2.297(12)	C(5A) 2.298(17)
		C(5B) 2.350(19)
Mean Ru-C	2.296(17)[a]	2.296(33)[a]

(c) Metal - Carbide Distances

	Cluster 1	Cluster 2
Ru(1)-C	2.040(7)	2.007(8)
Ru(2)-C	2.047(8)	2.033(8)
Ru(3)-C	2.054(7)	2.062(8)
Ru(4)-C	2.064(7)	2.053(8)
Ru(5)-C	2.064(8)	2.066(8)
Ru(6)-C	2.066(7)	2.099(8)
Mean Ru - Carbide	2.056(11)[a]	2.053(31)[a]

(d) Intraligand Distances

(i) CO Ligands

	Cluster 1	Cluster 2
C(11)-O(11)	1.157(12)	1.169(13)
C(12)-O(12)	1.173(12)	1.149(13)
C(21)-O(21)	1.140(12)	1.140(12)
C(22)-O(22)	1.155(12)	1.142(14)
C(31)-O(31)	1.167(14)	1.184(14)
C(33)-O(33)	1.138(13)	1.151(13)

cont...

	Cluster 1	Cluster 2
C(41)-O(41)	1.169(13)	1.152(13)
C(42)-O(42)	1.173(13)	1.161(13)
C(51)-O(51)	1.171(13)	1.152(15)
C(52)-O(52)	1.150(13)	1.143(13)
C(53)-O(53)	1.192(14)	1.160(14)
C(61)-O(61)	1.173(14)	1.160(13)
C(62)-O(62)	1.148(13)	1.164(15)
Mean C-O (terminal CO's)	1.162(16)[a]	1.156(13)[a]
C(32)-O(32)	1.178(14)	1.152(15)
C(46)-O(46)	1.168(11)	1.180(11)

(iii) Hexadiene Ligand[b]

	Cluster 1		Cluster 2
C(1)-C(2)	1.510(15)	C(2A)	1.562(22)
		C(2B)	1.579(25)
C(2)-C(3)	1.365(14)	C(2A)	1.275(21)
		C(2B)	1.228(26)
C(3)-C(4)	1.422(14)		1.386(18)

cont...

	Cluster 1		Cluster 2
C(4)-C(5)	1.336(15)	C(5A)	1.255(21)
		C(5B)	1.241(24)
C(5)-C(6)	1.491(15)	C(5A)	1.498(21)
		C(5B)	1.471(22)

[a] E.s.d's on mean bond lengths and angled are calculated from the equation $\sigma = \sqrt{\left\{\left[\sum_{1}^{n}(x_i-\bar{x})^2\right]/(n-1)\right\}}$ where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

[b] The hydrocarbon ligand in cluster 2 is partially disordered, the peaks due to C(2) and C(5) were each resolved into two sites (A and B) approximately 1 Å apart of 0.5 occupancy. The positions of C(2B) and C(5B) in cluster 2 correspond to the same relative positions as C(2) and C(5) in cluster 1.

Table 3.6 Selected Intramolecular Angles (°) for (VI). E.s.d's are given in parentheses.

(a) M-M-M Angles.

	Cluster 1	Cluster 2
Ru(3)-Ru(1)-Ru(2)	58.8(1)	60.0(1)
Ru(4)-Ru(1)-Ru(2)	59.9(1)	59.3(1)
Ru(4)-Ru(1)-Ru(3)	90.0(1)	88.8(1)
Ru(5)-Ru(1)-Ru(2)	88.9(1)	90.1(1)
Ru(5)-Ru(1)-Ru(3)	58.5(1)	61.2(1)
Ru(5)-Ru(1)-Ru(4)	61.6(1)	58.4(1)
Ru(3)-Ru(2)-Ru(1)	59.4(1)	59.3(1)
Ru(4)-Ru(2)-Ru(1)	58.8(1)	60.8(1)
Ru(4)-Ru(2)-Ru(3)	89.7(1)	89.3(1)
Ru(6)-Ru(2)-Ru(1)	89.6(1)	90.2(1)
Ru(6)-Ru(2)-Ru(3)	62.2(1)	60.0(1)
Ru(6)-Ru(2)-Ru(4)	58.8(1)	59.3(1)
Ru(2)-Ru(3)-Ru(1)	61.8(1)	60.7(1)
Ru(5)-Ru(3)-Ru(1)	60.2(1)	58.4(1)
Ru(5)-Ru(3)-Ru(2)	91.7(1)	89.0(1)
Ru(6)-Ru(3)-Ru(1)	88.6(1)	90.3(1)
Ru(6)-Ru(3)-Ru(2)	58.0(1)	58.8(1)
Ru(6)-Ru(3)-Ru(5)	60.4(1)	61.2(1)

cont...

	Cluster 1	Cluster 2
Ru(2)-Ru(4)-Ru(1)	61.3(1)	59.9(1)
Ru(5)-Ru(4)-Ru(1)	58.7(1)	58.6(1)
Ru(5)-Ru(4)-Ru(2)	88.1(1)	90.6(1)
Ru(6)-Ru(4)-Ru(1)	91.1(1)	89.5(1)
Ru(6)-Ru(4)-Ru(2)	58.8(1)	59.1(1)
Ru(6)-Ru(4)-Ru(5)	60.2(1)	62.6(1)
Ru(3)-Ru(5)-Ru(1)	61.3(1)	60.4(1)
Ru(4)-Ru(5)-Ru(1)	59.7(1)	63.0(1)
Ru(4)-Ru(5)-Ru(3)	90.5(1)	90.9(1)
Ru(6)-Ru(5)-Ru(1)	90.2(1)	90.0(1)
Ru(6)-Ru(5)-Ru(3)	62.1(1)	58.8(1)
Ru(6)-Ru(5)-Ru(4)	57.8(1)	59.0(1)
Ru(3)-Ru(6)-Ru(2)	59.8(1)	61.2(1)
Ru(4)-Ru(6)-Ru(2)	62.4(1)	61.6(1)
Ru(4)-Ru(6)-Ru(3)	90.3(1)	91.3(1)
Ru(5)-Ru(6)-Ru(2)	91.0(1)	89.6(1)
Ru(5)-Ru(6)-Ru(3)	57.5(1)	60.0(1)
Ru(5)-Ru(6)-Ru(4)	62.0(1)	58.4(1)

(b) M-C-O and M-C-M Angles[a]

	Cluster 1	Cluster 2
Ru(1)-C(11)-O(11)	173.3(8)	172.5(8)
Ru(1)-C(12)-O(12)	175.8(8)	177.2(10)
Ru(2)-C(21)-O(21)	175.4(9)	175.4(9)
Ru(2)-C(22)-O(22)	178.5(8)	178.4(9)
Ru(3)-C(31)-O(31)	177.3(9)	174.5(10)
Ru(3)-C(33)-O(33)	177.7(9)	178.1(10)
Ru(4)-C(41)-O(41)	178.1(8)	177.4(9)
Ru(4)-C(42)-O(42)	177.8(10)	178.6(9)
Ru(5)-C(51)-O(51)	174.1(9)	178.8(10)
Ru(5)-C(52)-O(52)	179.6(6)	172.1(9)
Ru(5)-C(53)-O(53)	176.2(9)	177.9(10)
Ru(6)-C(61)-O(61)	177.6(9)	177.7(9)
Ru(6)-C(62)-O(62)	177.2(8)	178.4(9)
Mean Ru-C-O (terminal CO's)	176.8(18)[b]	176.7(23)[b]
Ru(3)-C(32)-O(32)	162.4(9)	156.9(9)
Ru(6)-C(32)-O(32)	118.9(8)	122.8(8)
Ru(3)-C(32)-Ru(6)	78.6(4)	80.2( )

cont...

	Cluster 1	Cluster 2
Ru(4)-C(46)-O(46)	138.7(7)	140.0(7)
Ru(6)-C(46)-O(46)	134.9(7)	132.8(7)
Ru(4)-C(46)-Ru(6)	86.3(3)	87.1(3)

(c) Angles Involving Carbide

	Cluster 1	Cluster 2
Ru(2)-C-Ru(1)	93.7(3)	93.5(3)
Ru(3)-C-Ru(1)	90.7(3)	91.0(3)
Ru(3)-C-Ru(2)	89.8(3)	91.0(3)
Ru(4)-C-Ru(1)	90.3(3)	94.1(3)
Ru(4)-C-Ru(2)	91.5(3)	91.4(3)
Ru(4)-C-Ru(3)	178.3(4)	174.2(4)
Ru(5)-C-Ru(1)	89.2(3)	88.6(3)
Ru(5)-C-Ru(2)	175.6(4)	177.5(4)
Ru(5)-C-Ru(3)	86.8(3)	90.2(3)
Ru(5)-C-Ru(4)	91.9(3)	87.2(3)
Ru(6)-C-Ru(1)	177.1(4)	178.6(4)
Ru(6)-C-Ru(2)	87.4(3)	87.3(3)
Ru(6)-C-Ru(3)	92.0(3)	87.9(3)
Ru(6)-C-Ru(4)	86.9(3)	87.0(3)
Ru(6)-C-Ru(5)	89.8(3)	90.6(3)

(d) OC-M-M Angles[a]

	Cluster 1	Cluster 2
C(11)-Ru(1)-Ru(2)	128.3(3)	116.8(3)
C(11)-Ru(1)-Ru(3)	147.5(3)	156.9(3)
C(11)-Ru(1)-Ru(4)	74.1(3)	72.1(3)
C(11)-Ru(1)-Ru(5)	89.1(3)	97.0(3)
C(12)-Ru(1)-Ru(2)	131.0(3)	143.7(3)
C(12)-Ru(1)-Ru(3)	80.7(3)	85.6(3)
C(12)-Ru(1)-Ru(4)	153.1(3)	137.0(3)
C(12)-Ru(1)-Ru(5)	92.3(3)	81.9(3)
C(21)-Ru(2)-Ru(1)	132.3(3)	128.1(3)
C(21)-Ru(2)-Ru(3)	155.7(3)	152.1(3)
C(21)-Ru(2)-Ru(4)	83.4(3)	76.4(3)
C(21)-Ru(2)-Ru(6)	94.6(3)	92.1(3)
C(22)-Ru(2)-Ru(1)	137.0(3)	138.2(3)
C(22)-Ru(2)-Ru(3)	83.1(3)	85.9(3)
C(22)-Ru(2(-Ru(4)	147.9(3)	148.1(3)
C(22)-Ru(2)-Ru(6)	90.6(3)	91.5(3)
C(31)-Ru(3)-Ru(1)	106.6(3)	110.3(4)
C(31)-Ru(3)-Ru(2)	167.4(3)	164.3(3)
C(31)-Ru(3)-Ru(5)	85.7(3)	96.8(4)
C(31)-Ru(3)-Ru(6)	129.5(3)	136.5(3)
C(32)-Ru(3)-Ru(1)	151.5(3)	148.5(3)
C(32)-Ru(3)-Ru(2)	98.6(3)	96.2(3)
C(32)-Ru(3)-Ru(5)	103.0(3)	103.5(3)
C(32)-Ru(3)-Ru(6)	62.9(3)	58.4(3)

cont...

	Cluster 1	Cluster 2
C(32)-Ru(6)-Ru(2)	83.3(2)	86.6(3)
C(32)-Ru(6)-Ru(3)	38.4(2)	41.4(3)
C(32)-Ru(6)-Ru(4)	128.8(2)	132.7(3)
C(32)-Ru(6)-Ru(5)	83.4(2)	89.9(3)
C(41)-Ru(4)-Ru(1)	107.0(3)	112.2(3)
C(41)-Ru(4)-Ru(2)	86.6(3)	95.1(3)
C(41)-Ru(4)-Ru(5)	165.5(3)	164.2(3)
C(41)-Ru(4)-Ru(6)	126.9(3)	132.6(3)
C(42)-Ru(4)-Ru(1)	117.9(3)	114.9(3)
C(42)-Ru(4)-Ru(2)	170.8(3)	174.0(3)
C(42)-Ru(4)-Ru(5)	99.2(3)	83.9(3)
C(42)-Ru(4)-Ru(6)	129.9(3)	119.7(3)
C(46)-Ru(4)-Ru(1)	138.3(2)	137.5(2)
C(46)-Ru(4)-Ru(2)	86.5(2)	90.3(2)
C(46)-Ru(4)-Ru(5)	97.3(3)	95.6(3)
C(46)-Ru(4)-Ru(6)	47.8(2)	48.0(2)
C(46)-Ru(6)-Ru(2)	88.0(2)	90.1(2)
C(46)-Ru(6)-Ru(3)	135.6(2)	136.2(2)
C(46)-Ru(6)-Ru(4)	45.9(2)	44.8(2)
C(46)-Ru(6)-Ru(5)	97.2(2)	89.9(2)
C(51)-Ru(5)-Ru(1)	115.1(3)	86.5(3)
C(51)-Ru(5)-Ru(3)	169.0(3)	140.7(3)
C(51)-Ru(5)-Ru(4)	79.1(3)	91.9(3)
C(51)-Ru(5)-Ru(6)	108.6(3)	148.5(3)
C(52)-Ru(5)-Ru(1)	86.8(3)	107.6(3)
C(52)-Ru(5)-Ru(3)	99.9(3)	79.5(3)
C(52)-Ru(5)-Ru(4)	134.4(3)	169.3(3)
C(52)-Ru(5)-Ru(6)	160.5(3)	118.2( )

cont...

	Cluster 1	Cluster 2
C(53)-Ru(5)-Ru(1)	151.3(3)	161.0(3)
C(53)-Ru(5)-Ru(3)	91.0(3)	125.8(4)
C(53)-Ru(5)-Ru(4)	133.4(3)	98.1(3)
C(53)-Ru(5)-Ru(6)	82.4(3)	81.0(3)
C(61)-Ru(6)-Ru(2)	175.0(3)	173.3(3)
C(61)-Ru(6)-Ru(3)	120.7(3)	117.7(3)
C(61)-Ru(6)-Ru(4)	122.2(3)	125.0(3)
C(61)-Ru(6)-Ru(5)	93.2(3)	95.3(3)
C(62)-Ru(6)-Ru(2)	88.0(3)	88.2(3)
C(62)-Ru(6)-Ru(3)	114.5(3)	118.0(3)
C(62)-Ru(6)-Ru(4)	125.0(3)	121.2(3)
C(62)-Ru(6)-Ru(5)	170.8(3)	177.6(3)

(e) OC-M-CO Angles[a]

	Cluster 1	Cluster 2
C(12)-Ru(1)-C(11)	100.7(4)	99.4(4)
C(22)-Ru(2)-C(21)	90.5(4)	93.6(4)
C(32)-Ru(3)-C(31)	93.9(5)	96.6(5)
C(33)-Ru(3)-C(31)	93.2(4)	86.6(5)
C(33)-Ru(3)-C(32)	96.4(4)	97.8(5)

cont...

	Cluster 1	Cluster 2
C(42)-Ru(4)-C(41)	85.0(4)	89.7(4)
C(46)-Ru(4)-C(41)	95.9(4)	99.0(4)
C(46)-Ru(4)-C(42)	98.0(4)	92.6(4)
C(52)-Ru(5)-C(51)	90.1(4)	92.6(5)
C(53)-Ru(5)-C(51)	93.5(5)	92.4(5)
C(53)-Ru(5)-C(52)	91.1(5)	91.4(4)
C(46)-Ru(6)-C(32)	171.3(4)	176.6(3)
C(61)-Ru(6)-C(32)	94.5(4)	88.9(4)
C(61)-Ru(6)-C(46)	94.2(4)	94.5(4)
C(62)-Ru(6)-C(32)	87.5(4)	89.0(4)
C(62)-Ru(6)-C(46)	91.9(4)	91.1(4)
C(62)-Ru(6)-C(61)	87.4(4)	86.8(5)

(f) Angles involving Hexadiene Ligand[c]

(i) C-M-M Angles

	Cluster 1		Cluster 2
C(2)-Ru(2)-Ru(1)	95.4(3)	C(2A)	94.5(4)
		C(2B)	97.2(6)
C(2)-Ru(2)-Ru(3)	110.4(3)	C(2A)	133.2(4)
		C(2B)	111.5(5)
C(2)-Ru(2)-Ru(4)	133.8(3)	C(2A)	112.1(4)
		C(2B)	137.2(6)
C(2)-Ru(2)-Ru(6)	167.0(3)	C(2A)	166.1(4)
		C(2B)	163.3(6)

cont...

	Cluster 1	Cluster 2	
C(3)-Ru(2)-Ru(1)	66.7(2)		67.6(3)
C(3)-Ru(2)-Ru(3)	107.9(2)		102.1(3)
C(3)-Ru(2)-Ru(4)	100.5(2)		110.1(3)
C(3)-Ru(2)-Ru(6)	155.2(2)		157.2(3)
C(4)-Ru(1)-Ru(2)	71.3(2)		72.0(3)
C(4)-Ru(1)-Ru(3)	102.0(3)		102.6(3)
C(4)-Ru(1)-Ru(4)	112.8(2)		114.6(3)
C(4)-Ru(1)-Ru(5)	158.2(3)		160.9(3)
C(5)-Ru(1)-Ru(2)	99.6(3)	C(2A)	98.7(4)
		C(2B)	101.8(5)
C(5)-Ru(1)-Ru(3)	134.4(3)	C(2A)	102.1(4)
		C(2B)	127.2(5)
C(5)-Ru(1)-Ru(4)	114.6(3)	C(2A)	146.3(4)
		C(2B)	126.2(5)
C(5)-Ru(1)-Ru(5)	167.1(3)	C(2A)	153.6(4)
		C(2B)	167.8(5)

(ii) C-M-CO Angles[a]

	Cluster 1	Cluster 2	
C(2)-Ru(2)-C(21)	90.9(4)	C(2A)	74.7(5)
		C(2B)	94.9(6)
C(2)-Ru(2)-C(22)	77.6(4)	C(2A)	93.7(5)
		C(2B)	73.0(6)
C(3)-Ru(2)-C(21)	96.3(4)		105.3(4)
C(3)-Ru(2)-C(22)	111.5(4)		101.8(4)

cont...

	Cluster 1		Cluster 2
C(4)-Ru(1)-C(11)	110.2(4)		97.2(4)
C(4)-Ru(1)-C(12)	93.9(4)		108.2(4)
C(5)-Ru(1)-C(11)	78.0(4)	C(5A)	101.0(5)
		C(5B)	75.7(6)
C(5)-Ru(1)-C(12)	89.4(4)	C(5A)	76.3(5)
		C(5B)	89.6(6)

(iii) Intraligand Angles

	Cluster 1		Cluster 2
C(1)-C(2)-C(3)	122.8(9)	C(2A)	127.4(14)
		C(2B)	129.8(18)
C(2)-C(3)-C(4)	126.8(9)	C(2A)	150.9(14)
		C(2B)	154.7(15)
C(3)-C(4)-C(5)	127.3(9)	C(5A)	151.7(14)
		C(5B)	156.4(15)
C(4)-C(5)-C(6)	128.3(9)	C(5A)	126.8(15)
		C(5B)	130.4(17)

[a] The carbonyl ligands associated with Ru(5) in cluster 2 are rotated by 60° with respect to those in cluster 1.

[b] See Table 3.5 footnote a.

[c] See Table 3.5 footnote b.

Section 3.3 The Synthesis and Structure of $[Os_{10}C(CO)_{24}]^{2-}$

3.3.1 Preamble

The pyrolysis of dodecacarbonyl triosmium and its substituted derivatives provides the only means at present of synthesizing high-nuclearity clusters of osmium. Thus $Os_3(CO)_{12}$ itself is known to undergo pyrolysis to form a mixture of cluster carbonyls based on Os_5, Os_6, Os_7, and Os_8 units[8] but pyrolyses of $Os_3(CO)_{11}P(OMe)_3$[29] and $Os_3(CO)_{12-n}(CNR)_n$[30] lead exclusively to the formation of Os_5 and Os_6 clusters respectively. Few other systems have been investigated, but an elegant high yield route to substituted derivatives of $Os_3(CO)_{12}$ has recently been developed[31] (see following Subsection) enabling the further potential of this route to high clusters of osmium to be examined.

3.3.2 Synthesis of $[Os_{10}C(CO)_{24}]^{2-}$

The $Os_3(CO)_{12}$ derivative $Os_3(CO)_{11}Py$ was prepared by the method of Pippard,[31] *viz* Me_3NO in MeOH was added to a solution of $Os_3(CO)_{12}$ (1 g) and Py (1 cm^3) in CH_2Cl_2 (200 cm^3) until the strong band at 2067 cm^{-1} in the i.r. spectrum of $Os_3(CO)_{12}$ disappeared. The product was isolated by evaporation of the solvent to near dryness under vacuum, followed by filtration (yield 60%), and was characterized by i.r. spectroscopy [ν (CO) (CH_2Cl_2) 2104w, 2050s, 2034vs, 2004m, 2000 m sh, 1973w and 1960 vw sh cm^{-1}].

Pyrolysis of $Os_3(CO)_{11}Py$ (0.5 g) *in vacuo* at 250°C for 24 h gave a red-brown crystalline solid which was extracted with portions of ethyl acetate (total volume used, 100 cm^3); a small quantity (8 mg) of insoluble material, light brown in colour, remained in

the Carius tube [ν (CO)(CH_2Cl_2) 2056s, 2018m, 2008s cm^{-1}]. Evaporation of the ethyl acetate solution to 30 cm^3 followed by addition of diethyl ether caused precipitation of the major product of the reaction (ca. 80%, 250 mg), a pink-red solid, leaving in solution mainly $[HOs_5(CO)_{15}]^-$ which was identified by i.r. spectroscopy [ν(CO)(CH_2Cl_2) 2035s, 2022s, 2005m, 2000 m sh, and 1960 w cm^{-1}] . Very small amounts of $H_4Os_4(CO)_{12}$ and some neutral Os_3 clusters were also obtained from the ether fraction, these were separated by t.l.c. (1:1 cyclohexane-acetone eluent) and identified by i.r.[ν (CO)] and mass spectroscopy.

The pink-red solid, which was purified by t.l.c. using 1:1 cyclohexane-acetone as eluent, exhibited i.r. vibrational frequencies at 2033 and 1986 cm^{-1} of approximately equal intensity indicative of an anionic species of very high symmetry. No bands due to bridging carbonyls were observed in the i.r. spectrum although in some cases this type of absorption is known to be very weak and broad. The cation in this new compound has yet to be identified but the $[Bu_4N]^+$ salt was prepared by metathesis. A species that displayed an i.r. spectrum identical to that of the new anion was later isolated as one of the products of the pyrolysis of $Os_3(CO)_{12}$ by Dr. P.F. Jackson, University of Cambridge, using acetone for extraction rather than the usual cyclohexane-ethyl acetate mixture.[8] He detected no resonance characteristic of an M-H linkage in the ^1H n.m.r. spectrum of the $[Ph_4As]^+$ salt of this compound (- 40 to + 100 τ) indicating that it was not protonated and therefore probably dianionic. Since ionic species are not usually the product of these pyrolysis reactions it is likely that a neutral hydrido carbonyl is originally formed; this then dissociates in the polar solvents used for extraction to give the charged cluster. This idea is supported by the fact that much higher yields are obtained from the pyrolysis of $Os_3(CO)_{11}Py$, where the pyridine ligand can function as a hydrogen source, than from the pyrolysis of $Os_3(CO)_{12}$ where the hydrogen must come from minute quantities of water present on the glass of the Carius tube itself. Further, careful acidification of the dianion by Dr. Jackson gave initially a brown solution which had an i.r.[ν (CO)] spectrum identical to that of the ethyl acetate insoluble compound isolated

from the pyrolysis of $Os_3(CO)_{11}Py$ (*vide supra*). This compound is probably the mono-protonated derivative of the dianion. Continued addition of H^+ yielded a totally insoluble compound as the final product (the neutral dihydride).

An X-ray structural analysis was necessary to establish the molecular formula of the dianion (*vide infra*).

3.3.3 The Structure of $[Os_{10}C(CO)_{24}]^{2-}$

3.3.31 Data Collection

Crystals of the $[Bu_4N]^+$ salt of the dianion decomposed on exposure to air by loss of solvent of crystallization (THF). A crystal was therefore mounted inside a Lindemann tube with some of the mother liquor and unit cell dimensions were obtained (Table 3.7). However repeated movement of the crystal precluded data collection.

At this stage stable crystals of the $[(Ph_3P)_2N]^+$ salt (VII) were provided by Dr. Jackson. The crystal selected for data collection was of dimensions 0.26 x 0.21 x 0.07 mm; unit cell dimensions were determined and data was collected and processed by the methods described in Subsection 2.2.2. Crystal data for (VII) is given in Table 3.7.

Table 3.7 Crystal data for the $[Bu_4N]^+$ and $[(Ph_3P)_2N]^+$ (VII) salts of the osmium dianion.

	$[Bu_4N]^+$salt	(VII)
M_r	-	3663.4
Crystal system	Monoclinic	Triclinic
Space group	I2/c or Ic	$P\bar{1}$
a/Å	17.870	27.157
b/Å	28.692	17.535
c/Å	17.864	10.470
o/°	90	96.37
/°	113.05	100.71
o/°	90	85.92
$U/Å^3$	8427.8	4862.2
$D_c(D_m)$/g cm^{-3}	-	2.50(2.49)
Z	-	2

A scan width of 0.80° was used for data collection.

Empirical absorption corrections were applied which gave relative transmission coefficient which ranged from 0.307 to 2.023 [μ = 126.2 cm^{-1}].

Laue equivalent reflections were averaged to give 8942 unique observed data [$I \geqslant 3\sigma(I)$] for (VII).

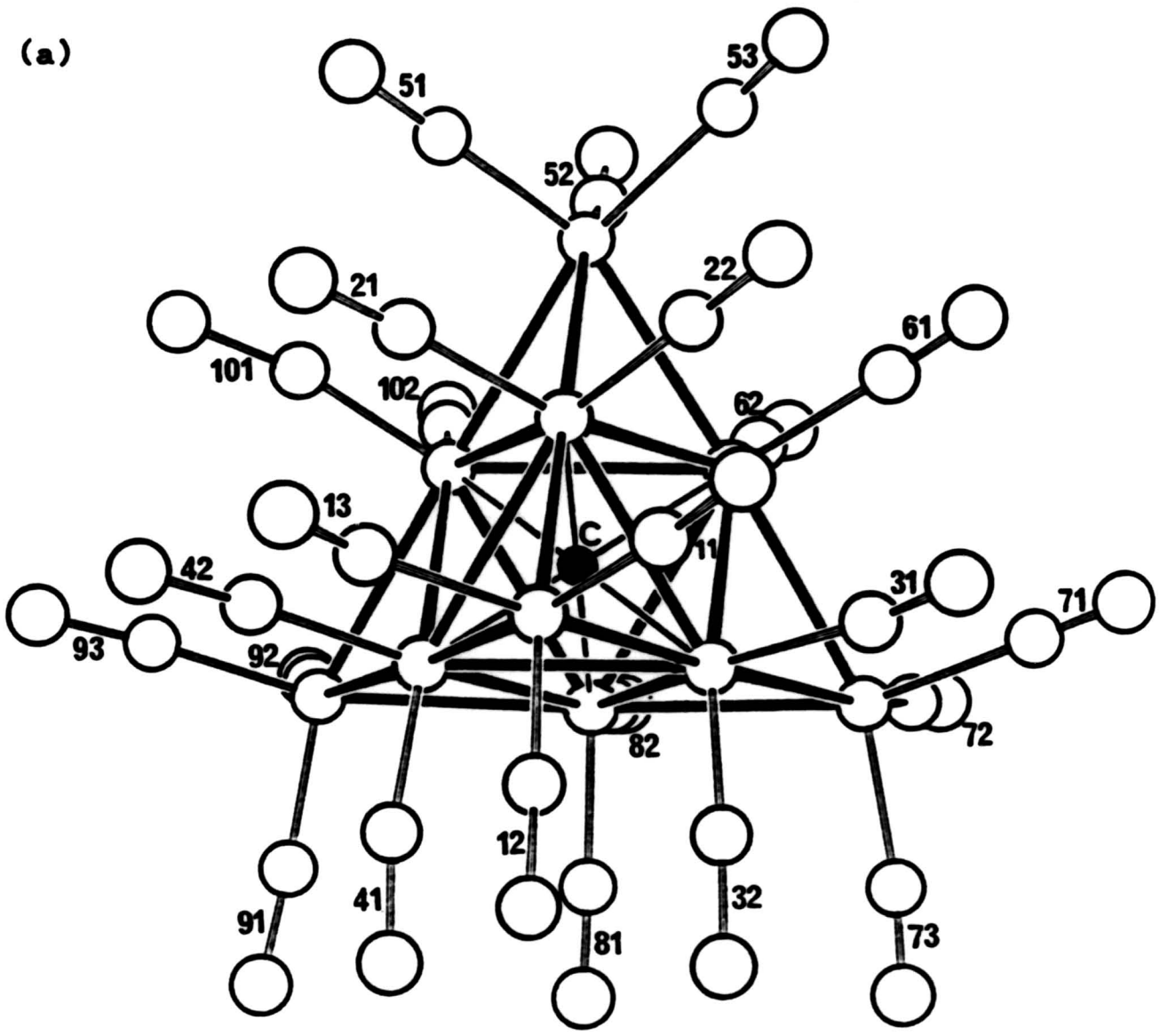
3.3.32 Structure Solution and Refinement

The scattering factors used, the function minimized during least-squares refinement, and definitions of the discrepancy indices quoted in the text are given in Subsection 2.2.3.

The diffraction data showed only $\bar{1}$ Laue symmetry; the triclinic space group $P\bar{1}$ was assumed and confirmed by the satis-

Figure 3.5 The structure of the $[Os_{10}C(CO)_{24}]^{2-}$ dianion (a); the $Os_{10}C$ unit without the carbonyl ligands (b).

(a)



(b)

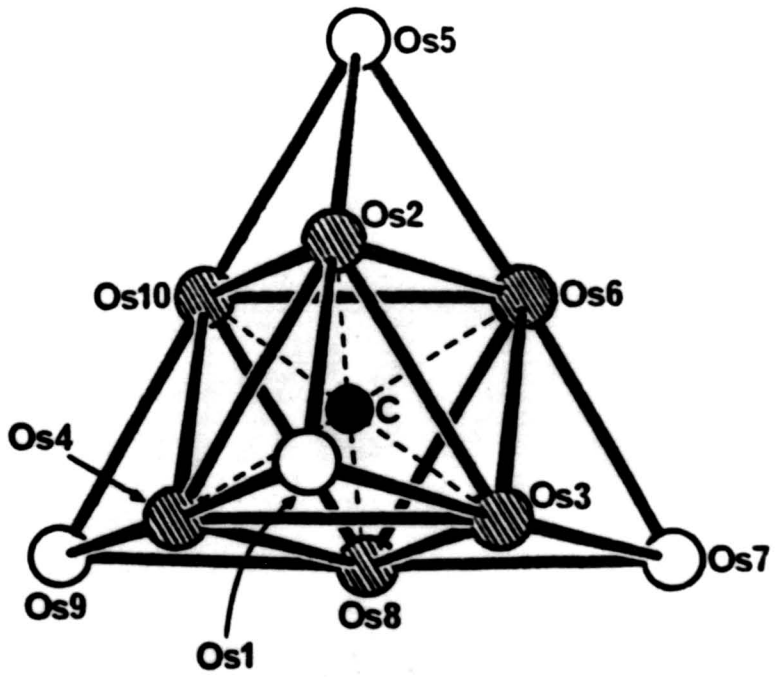
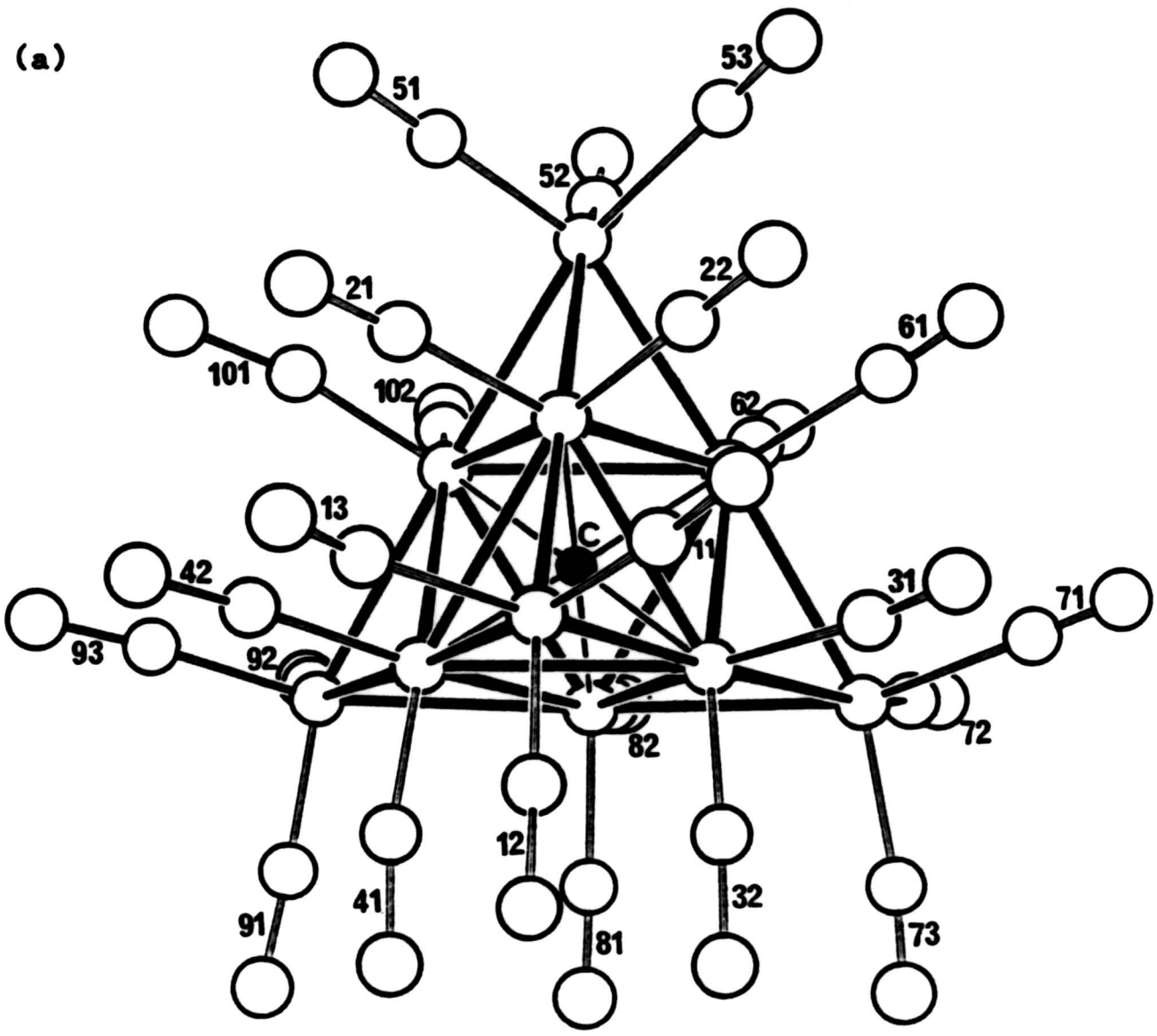
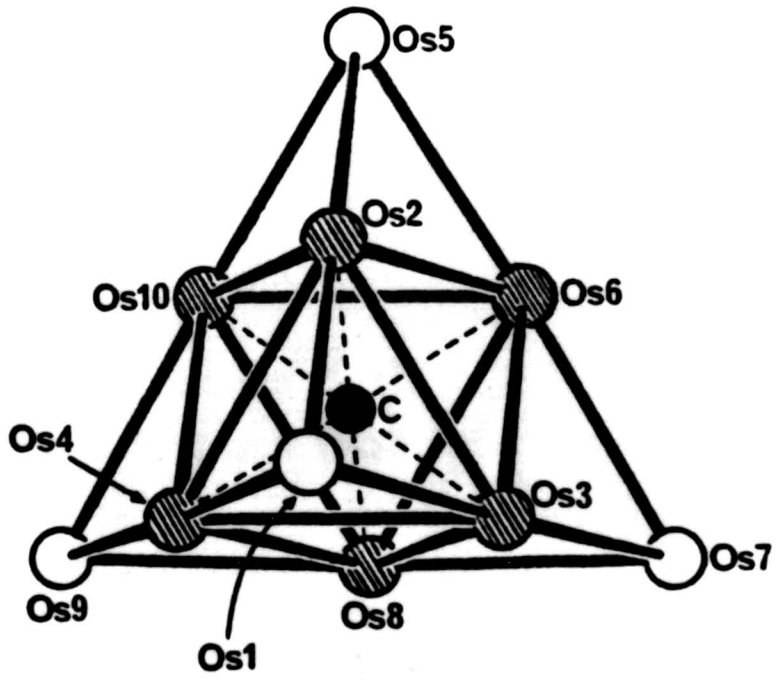


Figure 3.5 The structure of the $[Os_{10}C(CO)_{24}]^{2-}$ dianion (a); the $Os_{10}C$ unit without the carbonyl ligands (b).

(a)

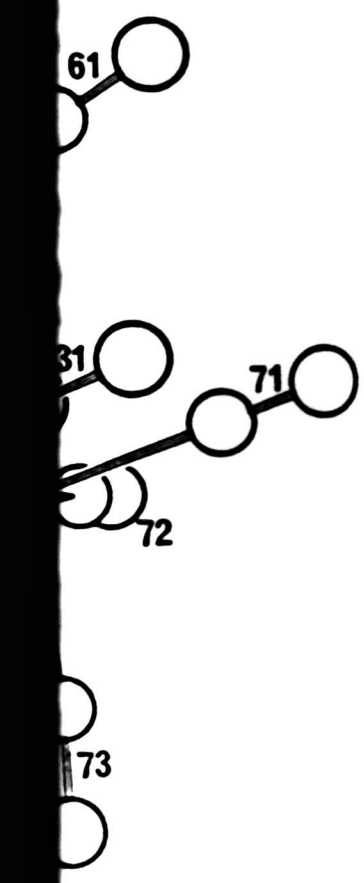


(b)



dianion (a);

ligands (b).



factory solution and refinement of the structure. The positions of six osmium atoms (defining an octahedron) were obtained from a Patterson map, four more Os atoms and the non-hydrogen atoms were located from subsequent difference-Fourier synthesis establishing the molecular formula for (VII) to be $\left[(Ph_3P)_2N\right]_2^+ \left[Os_{10}C(CO)_{24}\right]^{2-}$. Blocked full matrix refinement was carried out on the structure with the atoms grouped as follows: block 1, the osmium atoms; block 2, the other atoms of the dianion; block 3, the atoms of the first $\left[(Ph_3P)_2N\right]^+$ cation; block 4, the atoms of the second cation. Refinement converged at $R = 0.0553$, $R_w = 0.0581$, and $R_G = 0.0699$ using anisotropic thermal parameters for the Os, N, and P atoms. The phenyl rings were treated as rigid groups $\left[d(C-C) = 1.395\ \text{Å}\right]$, no allowance was made for the phenyl hydrogens in the structure factor calculations. Weights were assigned to reflections a $\underline{w} = 1.6995/\left[\sigma^2F + 0.000458\,F^2\right]$ (see Subsection 2.2.3). A final difference-Fourier synthesis showed several residual maxima in the region of the osmium atoms, none of which were greater than 2.5 $e\text{Å}^{-3}$ in height.

Final positional and thermal parameters for $\left[(Ph_3P)_2N\right]_2^+ \left[Os_{10}C(CO)_{24}\right]^{2-}$ (VII) are given in Appendix 7.

3.3.4 Discussion

The structure of the dianion in $\left[(Ph_3P)_2N\right]_2^+ \left[Os_{10}C(CO)_{24}\right]^{2-}$ (VII) is shown in Figures 3.5 and 3.6 and the bond distances and angles are given in Tables 3.8 - 3.10.

The dianion has approximate overall T_d symmetry and may be described as a carbido-centred Os_6 octahedron, with two terminal carbonyls per osmium, capped on four tetrahedrally related faces by $Os(CO)_3$ groups. There are thus only two different environments for the 24 carbonyl ligands (12 of each type) which is completely consistent with the i.r. pattern of this species [ν(CO) 2033s, 1986s cm^{-1}]. Interestingly this structure is closely related to

that found for $Rh_6(CO)_{16}$ in which an $M_6(CO)_{12}$ unit is this time capped on four tetrahedrally related faces by triply bridging CO ligands.[15]

Although many carbido-centred octahedral Ru_6 clusters are known (see Section 3.2), this is the first osmium cluster to be shown by X-ray analysis to have a completely encapsulated carbon atom, although the stability of $[Os_nC]^+$ fragments has been noted in the mass spectrum of several carbido osmium clusters.[8] There is a marked difference between the Os-Os bond lengths of the octahedron [2.88(1) Å, mean] and those from the capping groups [2.79(1) Å, mean]. In the bicapped octahedral osmium unit of $[Os_8(CO)_{22}]^{2-}$, which does not contain an interstitial carbon atom, this trend is not observed.[32] Therefore the expansion of the octahedron in the Os_{10} dianion must be attributed to the central carbon atom. The mean Os-carbido distance is 2.04(2) Å similar to that observed in the Ru_6C species discussed in Section 3.2.

The metal skeleton in the $[Os_{10}C(CO)_{24}]^{2-}$ dianion is a fragment of a c.c.p. array and corresponds to a face-centred cubic unit cell with four tetrahedrally related faces removed (Figure 3.7).

Figure 3.7

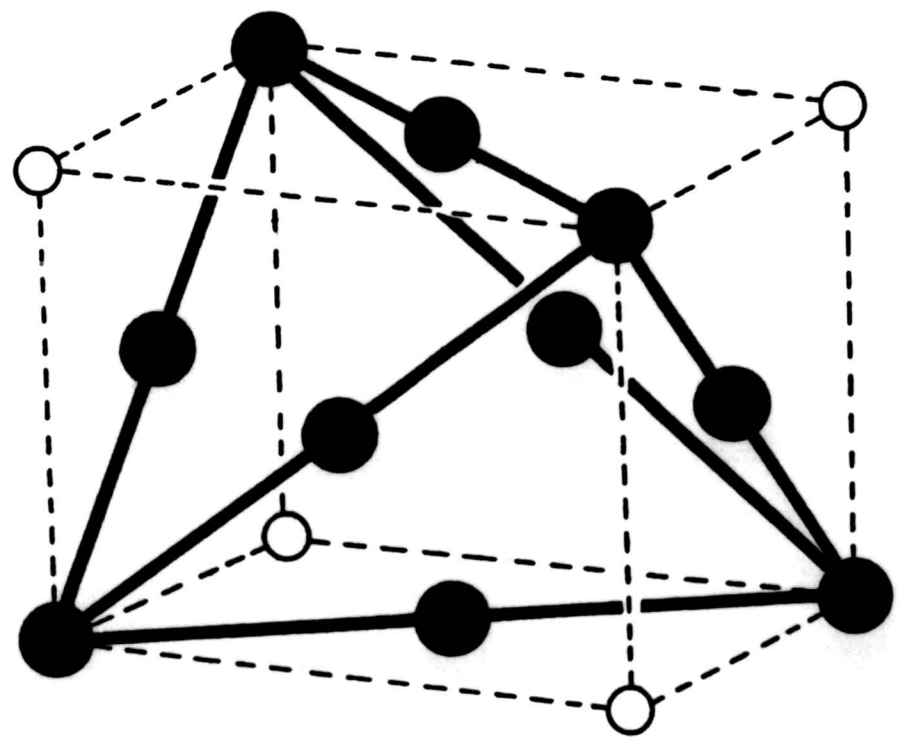
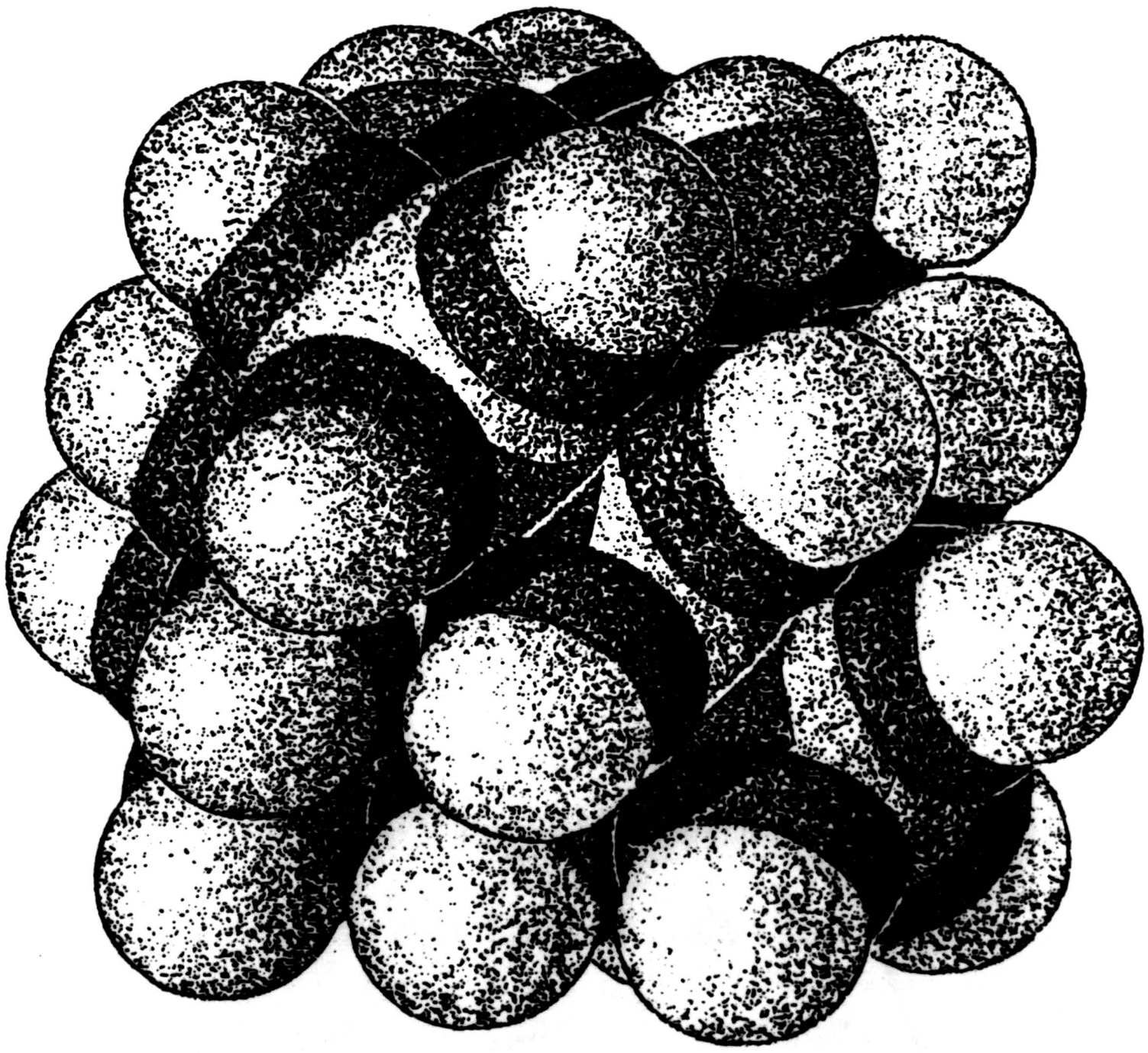


Figure 3.6 Space-filling drawing of the $[Os_{10}C(CO)_{24}]^{2-}$ dianion portraying the arrangement of CO ligands perpendicular to each face of the Os_{10} tetrahedron.



Although large Rh and Ni clusters that contain h.c.p. arrangements of metal are known (see Section 1.2) a c.c.p. array has not previously been observed in a metal carbonyl cluster. Several examples have been reported which indicate that cluster geometries differ from those of the bulk metal,[33] and indeed osmium metal has a h.c.p. rather than a c.c.p. lattice. Interestingly rhodium metal has a c.c.p. lattice rather than the h.c.p. geometry that some of the large clusters display.

The metal core in $[Os_{10}C(CO)_{24}]^{2-}$ has the largest planar surfaces observed to date in a carbonyl cluster and the arrangement of CO ligands approximately perpendicular to each face (Figure 3.6) may provide the best analogy so far of a monolayer of carbon monoxide chemisorbed onto a metal surface. In this connection Chini has suggested that CO interactions are an important parameter in determining cluster structures, these being at a maximum on flat surfaces.[34] The largest OC-Os-CO angle in the $[Os_{10}C(CO)_{24}]^{2-}$ dianion is only 98.5° [the mean value being 94(3)°] so the Os_{10} metal unit might be expected to open out on reaction with incoming molecules, thereby reducing the carbonyl repulsions. However addition of bridging hydrogens would probably leave the metal unit intact, these atoms being accommodated by a slight change in the configuration of the CO ligands.

The dianion has 134 valence electrons, so using Wade's skeletal electron counting scheme (see Subsection 1.4.3) the fundamental polyhedron should be an octahedron (7 skeletal electron pairs). Since capped and uncapped versions of the same polyhedron require the same number of skeletal electron pairs the remaining four osmium atoms may be accommodated in face-capping positions, thus giving the observed structure. Other approaches are less successful for rationalizing the structure. For example, although Lauher envisaged a tetrahedral arrangement for 10 metal atoms, his EHMO calculations indicated that it would require 140 valence electrons[35] which would correspond to the incorrect formulation $[Os_{10}C(CO)_{27}]^{2-}$.

Table 3.8 Selected Interatomic Distances (Å) in (VII). Esd's are given in parentheses.

(a) Metal-Metal Distances

(i) Within Octahedron		(ii) Involving Capping Osmiums	
Os(2)-Os(3)	2.875(1)	Os(1)-Os(2)	2.782(1)
Os(2)-Os(4)	2.868(1)	Os(1)-Os(3)	2.799(1)
Os(2)-Os(6)	2.877(1)	Os(1)-Os(4)	2.781(1)
Os(2)-Os(10)	2.861(1)		
		Os(5)-Os(2)	2.789(1)
Os(3)-Os(4)	2.863(1)	Os(5)-Os(6)	2.798(1)
Os(3)-Os(6)	2.902(1)	Os(5)-Os(10)	2.776(1)
Os(3)-Os(8)	2.883(1)		
		Os(7)-Os(3)	2.785(1)
Os(4)-Os(8)	2.889(1)	Os(7)-Os(6)	2.782(1)
Os(4)-Os(10)	2.900(1)	Os(7)-Os(8)	2.787(1)
Os(6)-Os(8)	2.890(1)	Os(9)-Os(4)	2.783(1)
Os(6)-Os(10)	2.886(1)	Os(9)-Os(8)	2.814(1)
		Os(9)-Os(10)	2.761(1)
Os(8)-Os(10)	2.903(1)		
Mean Os-Os	2.883(15)[a]		2.786(13)[a]

(b) Metal-Carbide Distances

Os(2)-C	2.032(18)
Os(3)-C	2.018(15)
Os(4)-C	2.040(16)
Os(6)-C	2.045(16)
Os(8)-C	2.033(18)
Os(10)-C	2.065(15)

Mean Os-Carbide	2.039(16)[a]

(c) Metal-Carbon and Carbon-Oxygen Distances

Os(1)-C(11)	1.871(32)	C(11)-O(11)	1.133(39)
Os(1)-C(12)	1.907(24)	C(12)-O(12)	1.159(29)
Os(1)-C(13)	1.821(32)	C(13)-O(13)	1.193(41)
Os(2)-C(21)	1.819(26)	C(21)-O(21)	1.239(31)
Os(2)-C(22)	1.811(23)	C(22)-O(22)	1.221(30)
Os(3)-C(31)	1.869(25)	C(31)-O(31)	1.199(32)
Os(3)-C(32)	1.830(21)	C(32)-O(32)	1.210(27)
Os(4)-C(41)	1.840(22)	C(41)-O(41)	1.145(28)
Os(4)-C(42)	1.809(32)	C(42)-O(42)	1.213(42)
Os(5)-C(51)	1.861(23)	C(51)-O(51)	1.215(29)
Os(5)-C(52)	1.841(29)	C(52)-O(52)	1.161(35)
Os(5)-C(53)	1.919(26)	C(53)-O(53)	1.129(34)

cont ...

Os(6)-C(61)	1.836(25)	C(61)-O(61)	1.152(33)
Os(6)-C(62)	1.818(28)	C(62)-O(62)	1.200(36)
Os(7)-C(71)	1.854(26)	C(71)-O(71)	1.131(32)
Os(7)-C(72)	1.829(27)	C(72)-O(72)	1.196(34)
Os(7)-C(73)	1.875(18)	C(73)-O(73)	1.141(23)
Os(8)-C(81)	1.833(21)	C(81)-O(81)	1.190(27)
Os(8)-C(82)	1.771(33)	C(82)-O(82)	1.231(42)
Os(9)-C(91)	1.874(25)	C(91)-O(91)	1.130(31)
Os(9)-C(92)	1.835(28)	C(92)-O(92)	1.174(37)
Os(9)-C(93)	1.886(27)	C(93)-O(93)	1.211(34)
Os(10)-C(101)	1.817(21)	C(101)-O(101)	1.214(28)
Os(10)-C(102)	1.854(23)	C(102)-O(102)	1.166(30)
Mean Os-C	1.845(34)[a]	Mean C-O	1.181(35)[a]

[a] Esd's on mean bond lengths and angles are calculated from the equation $\sigma = \sqrt{\left\{ \left[\sum_{i}^{n} (x_i - \bar{x})^2 \right] / (n-1) \right\}}$ where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

Table 3.9 Selected Intramolecular Angles (°) in **(VII)**. Esd's are given in parentheses.

(a) M-C-O Angles

Os(1)-C(11)-O(11)	172.1(27)	Os(6)-C(61)-O(61)	175.8(24)
Os(1)-C(12)-O(12)	177.9(22)	Os(6)-C(62)-O(62)	177.4(20)
Os(1)-C(13)-O(13)	175.7(24)		
		Os(7)-C(71)-O(71)	178.6(24)
Os(2)-C(21)-O(21)	177.6(26)	Os(7)-C(72)-O(72)	178.3(20)
Os(2)-C(22)-O(22)	173.7(20)	Os(7)-C(73)-O(73)	176.2(21)
Os(3)-C(31)-O(31)	179.2(20)	Os(8)-C(81)-O(81)	173.2(20)
Os(3)-C(32)-O(32)	177.2(23)	Os(8)-C(82)-O(82)	177.9(24)
Os(4)-C(41)-O(41)	175.4(22)	Os(9)-C(91)-O(91)	172.5(26)
Os(4)-C(42)-O(42)	177.1(33)	Os(9)-C(92)-O(92)	176.2(20)
		Os(9)-C(93)-O(93)	164.9(26)
Os(5)-C(51)-O(51)	174.6(23)		
Os(5)-C(52)-O(52)	174.7(23)	Os(10)-C(101)-O(101)	172.0(19)
Os(5)-C(53)-O(53)	175.7(24)	Os(10)-C(102)-O(102)	176.8(17)
Mean Os-C-O	175.4(31)[a]		

(b) M-Carbide-M Angles

Os(3)-C-Os(2)	90.4(7)	Os(8)-C-Os(4)	90.4(6)
Os(4)-C-Os(2)	89.6(7)	Os(8)-C-Os(6)	90.3(7)
Os(4)-C-Os(3)	89.7(6)	Os(10)-C-Os(2)	88.6(6)
Os(6)-C-Os(2)	89.8(6)	Os(10)-C-Os(3)	178.9(10)
Os(6)-C-Os(3)	91.1(6)	Os(10)-C-Os(4)	89.9(6)
Os(6)-C-Os(4)	178.9(8)	Os(10)-C-Os(6)	89.2(6)
Os(8)-C-Os(2)	178.8(8)	Os(10)-C-Os(8)	90.2(7)
Os(8)-C-Os(3)	90.8(6)		

(c) Angles Between Metal Atoms

Os(3)-Os(1)-Os(2)	62.0(1)	Os(2)-Os(3)-Os(1)	58.7(1)
Os(4)-Os(1)-Os(2)	62.1(1)	Os(4)-Os(3)-Os(1)	58.8(1)
Os(4)-Os(1)-Os(3)	61.7(1)	Os(4)-Os(3)-Os(2)	60.0(1)
		Os(6)-Os(3)-Os(1)	118.5(1)
		Os(6)-Os(3)-Os(2)	59.7(1)
Os(3)-Os(2)-Os(1)	59.3(1)	Os(6)-Os(3)-Os(4)	90.2(1)
Os(4)-Os(2)-Os(1)	58.9(1)	Os(7)-Os(3)-Os(1)	176.8(1)
Os(4)-Os(2)-Os(3)	59.8(1)	Os(7)-Os(3)-Os(2)	118.3(1)
Os(5)-Os(2)-Os(1)	178.5(1)	Os(7)-Os(3)-Os(4)	119.2(1)
Os(5)-Os(2)-Os(3)	119.8(1)	Os(7)-Os(3)-Os(6)	58.5(1)
Os(5)-Os(2)-Os(4)	119.7(1)	Os(8)-Os(3)-Os(1)	119.2(1)
Os(6)-Os(2)-Os(1)	119.9(1)	Os(8)-Os(3)-Os(2)	89.8(1)
Os(6)-Os(2)-Os(3)	60.6(1)	Os(8)-Os(3)-Os(4)	60.4(1)
Os(6)-Os(2)-Os(4)	90.6(1)	Os(8)-Os(3)-Os(6)	59.9(1)
Os(6)-Os(2)-Os(5)	59.2(1)	Os(8)-Os(3)-Os(7)	58.9(1)
Os(10)-Os(2)-Os(1)	119.8(1)		
Os(10)-Os(2)-Os(3)	90.8(1)		
Os(10)-Os(2)-Os(4)	60.8(1)		
Os(10)-Os(2)-Os(5)	58.9(1)		
Os(10)-Os(2)-Os(6)	60.4(1)		

cont...

Os(2)-Os(4)-Os(1)	59.0(1)
Os(3)-Os(4)-Os(1)	59.4(1)
Os(3)-Os(4)-Os(2)	60.2(1)
Os(8)-Os(4)-Os(1)	119.6(1)
Os(8)-Os(4)-Os(2)	89.8(1)
Os(8)-Os(4)-Os(3)	60.2(1)
Os(9)-Os(4)-Os(1)	176.5(1)
Os(9)-Os(4)-Os(2)	117.5(1)
Os(9)-Os(4)-Os(3)	119.6(1)
Os(9)-Os(4)-Os(8)	59.5(1)
Os(10)-Os(4)-Os(1)	118.4(1)
Os(10)-Os(4)-Os(2)	59.5(1)
Os(10)-Os(4)-Os(3)	90.2(1)
Os(10)-Os(4)-Os(8)	60.2(1)
Os(10)-Os(4)-Os(9)	58.1(1)

Os(6)-Os(5)-Os(2)	62.0(1)
Os(10)-Os(5)-Os(2)	61.9(1)
Os(10)-Os(5)-Os(6)	62.3(1)

Os(3)-Os(6)-Os(2)	59.7(1)
Os(5)-Os(6)-Os(2)	58.8(1)
Os(5)-Os(6)-Os(3)	118.5(1)
Os(7)-Os(6)-Os(2)	118.3(1)
Os(7)-Os(6)-Os(3)	58.6(1)
Os(7)-Os(6)-Os(5)	176.7(1)
Os(8)-Os(6)-Os(2)	89.6(1)
Os(8)-Os(6)-Os(3)	59.7(1)
Os(8)-Os(6)-Os(5)	118.8(1)
Os(8)-Os(6)-Os(7)	58.8(1)
Os(10)-Os(6)-Os(2)	59.5(1)
Os(10)-Os(6)-Os(3)	89.7(1)
Os(10)-Os(6)-Os(5)	58.5(1)
Os(10)-Os(6)-Os(7)	119.2(1)
Os(10)-Os(6)-Os(8)	60.3(1)

Os(6)-Os(7)-Os(3)	62.8(1)
Os(8)-Os(7)-Os(3)	62.3(1)
Os(8)-Os(7)-Os(6)	62.5(1)

Os(4)-Os(8)-Os(3)	59.5(1)
Os(6)-Os(8)-Os(3)	60.3(1)
Os(6)-Os(8)-Os(4)	90.0(1)
Os(7)-Os(8)-Os(3)	58.8(1)
Os(7)-Os(8)-Os(4)	118.2(1)
Os(7)-Os(8)-Os(6)	58.6(1)
Os(9)-Os(8)-Os(3)	117.8(1)
Os(9)-Os(8)-Os(4)	58.4(1)
Os(9)-Os(8)-Os(6)	117.5(1)
Os(9)-Os(8)-Os(7)	175.5(1)
Os(10)-Os(8)-Os(3)	89.7(1)
Os(10)-Os(8)-Os(4)	60.1(1)
Os(10)-Os(8)-Os(6)	59.8(1)
Os(10)-Os(8)-Os(7)	118.4(1)
Os(10)-Os(8)-Os(9)	57.7(1)

Os(8)-Os(9)-Os(4)	62.2(1)
Os(10)-Os(9)-Os(4)	63.1(1)
Os(10)-Os(9)-Os(8)	62.8(1)

Os(4)-Os(10)-Os(2)	59.7(1)
Os(5)-Os(10)-Os(2)	59.3(1)
Os(5)-Os(10)-Os(4)	119.0(1)
Os(6)-Os(10)-Os(2)	60.1(1)
Os(6)-Os(10)-Os(4)	89.8(1)
Os(6)-Os(10)-Os(5)	59.2(1)
Os(8)-Os(10)-Os(2)	89.7(1)
Os(8)-Os(10)-Os(4)	59.7(1)
Os(8)-Os(10)-Os(5)	119.1(1)
Os(8)-Os(10)-Os(6)	59.9(1)
Os(9)-Os(10)-Os(2)	118.5(1)
Os(9)-Os(10)-Os(4)	58.8(1)
Os(9)-Os(10)-Os(5)	177.7(1)
Os(9)-Os(10)-Os(6)	119.4(1)
Os(9)-Os(10)-Os(8)	59.5(1)

(d) Carbon-Metal-Metal Angles

C(11)-Os(1)-Os(2)	98.7(8)	C(32)-Os(3)-Os(1)	90.2(8)
C(11)-Os(1)-Os(3)	102.4(9)	C(32)-Os(3)-Os(2)	147.2(7)
C(11)-Os(1)-Os(4)	158.8(9)	C(32)-Os(3)-Os(4)	96.6(7)
		C(32)-Os(3)-Os(6)	149.4(8)
		C(32)-Os(3)-Os(7)	92.6(8)
C(12)-Os(1)-Os(2)	159.3(9)	C(32)-Os(3)-Os(8)	97.9(9)
C(12)-Os(1)-Os(3)	99.5(8)		
C(12)-Os(1)-Os(4)	101.9(9)		
		C(41)-Os(4)-Os(1)	90.9(8)
		C(41)-Os(4)-Os(2)	148.3(8)
C(13)-Os(1)-Os(2)	101.9(9)	C(41)-Os(4)-Os(3)	97.3(7)
C(13)-Os(1)-Os(3)	160.4(10)	C(41)-Os(4)-Os(8)	97.9(8)
C(13)-Os(1)-Os(4)	101.7(11)	C(41)-Os(4)-Os(9)	92.5(8)
		C(41)-Os(4)-Os(10)	149.0(9)
C(21)-Os(2)-Os(1)	87.3(8)		
C(21)-Os(2)-Os(3)	143.3(8)	C(42)-Os(4)-Os(1)	89.5(12)
C(21)-Os(2)-Os(4)	91.1(8)	C(42)-Os(4)-Os(2)	97.7(10)
C(21)-Os(2)-Os(5)	93.3(8)	C(42)-Os(4)-Os(3)	147.7(12)
C(21)-Os(2)-Os(6)	148.7(9)	C(42)-Os(4)-Os(8)	149.1(12)
C(21)-Os(2)-Os(10)	93.7(10)	C(42)-Os(4)-Os(9)	90.9(12)
		C(42)-Os(4)-Os(10)	98.2(10)
C(22)-Os(2)-Os(1)	91.1(7)		
C(22)-Os(2)-Os(3)	100.0(6)	C(51)-Os(5)-Os(2)	101.1(8)
C(22)-Os(2)-Os(4)	149.1(6)	C(51)-Os(5)-Os(6)	158.8(7)
C(22)-Os(2)-Os(5)	90.2(7)	C(51)-Os(5)-Os(10)	99.1(8)
C(22)-Os(2)-Os(6)	99.3(7)		
C(22)-Os(2)-Os(10)	148.3(7)		
		C(52)-Os(5)-Os(2)	155.7(8)
		C(52)-Os(5)-Os(6)	99.2(8)
C(31)-Os(3)-Os(1)	89.4(8)	C(52)-Os(5)-Os(10)	96.5(8)
C(31)-Os(3)-Os(2)	97.8(6)		
C(31)-Os(3)-Os(4)	147.1(7)		
C(31)-Os(3)-Os(6)	98.9(7)	C(53)-Os(5)-Os(2)	105.2(7)
C(31)-Os(3)-Os(7)	92.1(8)	C(53)-Os(5)-Os(6)	102.7(6)
C(31)-Os(3)-Os(8)	149.7(8)	C(53)-Os(5)-Os(10)	163.1(8)

cont...

C(61)-Os(6)-Os(2)	98.1(8)	C(82)-Os(8)-Os(3)	149.8(9)
C(61)-Os(6)-Os(3)	99.4(7)	C(82)-Os(8)-Os(4)	148.2(8)
C(61)-Os(6)-Os(5)	89.7(7)	C(82)-Os(8)-Os(6)	99.1(9)
C(61)-Os(6)-Os(7)	92.3(7)	C(82)-Os(8)-Os(7)	92.1(9)
C(61)-Os(6)-Os(8)	149.8(6)	C(82)-Os(8)-Os(9)	90.7(9)
C(61)-Os(6)-Os(10)	147.0(7)	C(82)-Os(8)-Os(10)	98.5(8)
C(62)-Os(6)-Os(2)	149.1(7)	C(91)-Os(9)-Os(4)	100.6(9)
C(62)-Os(6)-Os(3)	147.0(7)	C(91)-Os(9)-Os(8)	98.9(8)
C(62)-Os(6)-Os(5)	92.2(7)	C(91)-Os(9)-Os(10)	159.2(8)
C(62)-Os(6)-Os(7)	90.3(7)		
C(62)-Os(6)-Os(8)	96.3(8)		
C(62)-Os(6)-Os(10)	97.5(8)	C(92)-Os(9)-Os(4)	159.9(7)
		C(92)-Os(9)-Os(8)	101.3(7)
		C(92)-Os(9)-Os(10)	100.0(7)
C(71)-Os(7)-Os(3)	97.3(9)		
C(71)-Os(7)-Os(6)	95.6(7)		
C(71)-Os(7)-Os(8)	154.7(8)	C(93)-Os(9)-Os(4)	94.4(10)
		C(93)-Os(9)-Os(8)	153.3(10)
		C(93)-Os(9)-Os(10)	96.3(10)
C(72)-Os(7)-Os(3)	160.8(7)		
C(72)-Os(7)-Os(6)	101.3(7)		
C(72)-Os(7)-Os(8)	101.5(7)		
		C(101)-Os(10)-Os(2)	98.5(9)
		C(101)-Os(10)-Os(4)	101.0(7)
C(73)-Os(7)-Os(3)	98.6(7)	C(101)-Os(10)-Os(5)	88.3(7)
C(73)-Os(7)-Os(6)	158.3(6)	C(101)-Os(10)-Os(6)	146.7(8)
C(73)-Os(7)-Os(8)	99.6(6)	C(101)-Os(10)-Os(8)	151.3(7)
		C(101)-Os(10)-Os(9)	92.8(7)
C(81)-Os(8)-Os(3)	95.7(8)		
C(81)-Os(8)-Os(4)	97.3(8)	C(102)-Os(10)-Os(2)	148.9(6)
C(81)-Os(8)-Os(6)	146.6(7)	C(102)-Os(10)-Os(4)	149.1(6)
C(81)-Os(8)-Os(7)	89.7(7)	C(102)-Os(10)-Os(5)	90.7(6)
C(81)-Os(8)-Os(9)	93.7(7)	C(102)-Os(10)-Os(6)	99.3(6)
C(81)-Os(8)-Os(10)	149.5(7)	C(102)-Os(10)-Os(8)	99.7(6)
		C(102)-Os(10)-Os(9)	91.4(6)

(e) OC-M-CO Angles

C(12)-Os(1)-C(11)	94.4(12)	C(72)-Os(7)-C(71)	95.0(11)
C(13)-Os(1)-C(11)	90.5(14)	C(73)-Os(7)-C(71)	98.2(9)
C(13)-Os(1)-C(12)	94.0(12)	C(73)-Os(7)-C(72)	94.1(10)
C(22)-Os(2)-C(21)	95.1(11)	C(82)-Os(8)-C(81)	91.8(12)
C(32)-Os(3)-C(31)	91.4(10)	C(92)-Os(9)-C(91)	93.0(11)
		C(93)-Os(9)-C(91)	97.7(11)
		C(93)-Os(9)-C(92)	98.5(12)
C(42)-Os(4)-C(41)	91.3(12)		
		C(102)-Os(10)-C(101)	87.4(10)
C(52)-Os(5)-C(51)	92.9(11)		
C(53)-Os(5)-C(51)	93.9(10)		
C(53)-Os(5)-C(52)	93.5(11)		
C(62)-Os(6)-C(61)	91.9(12)		

[a] See footnote to Table 3.8.

Table 3.10. Selected Bond Lengths (Å) and Angles (°) the two $[(Ph_3P)_2N]^+$ cations [a] in (VII). Esd's are given in parentheses.

P(1)-N(1)	1.607(20)	P(1)-N(1)-P(2)	144.0(11)
P(2)-N(1)	1.556(20)		
		P(3)-N(2)-P(4)	137.4(13)
P(3)-N(2)	1.575(16)		
P(4)-N(2)	1.603(15)		
		N(1)-P(1)-C(111)	107.2(8)
		N(1)-P(1)-C(121)	113.0(9)
P(1)-C(111)	1.823(16)	N(1)-P(1)-C(131)	114.8(9)
P(1)-C(121)	1.834(19)	N(1)-P(2)-C(211)	107.7(8)
P(1)-C(131)	1.792(13)	N(1)-P(2)-C(221)	112.9(9)
P(2)-C(211)	1.779(15)	N(1)-P(2)-C(231)	115.3(9)
P(2)-C(221)	1.770(17)		
P(2)-C(231)	1.830(14)		
		N(2)-P(3)-C(311)	115.9(8)
		N(2)-P(3)-C(321)	110.7(8)
P(3)-C(311)	1.806(15)	N(2)-P(3)-C(331)	105.6(9)
P(3)-C(321)	1.790(14)	N(2)-P(4)-C(411)	108.3(8)
P(3)-C(331)	1.809(15)	N(2)-P(4)-C(421)	108.5(8)
P(4)-C(411)	1.797(14)	N(2)-P(4)-C(431)	114.5(8)
P(4)-C(421)	1.803(15)		
P(4)-C(431)	1.774(16)		
		C(111)-P(1)-C(121)	107.1(8)
		C(111)-P(1)-C(131)	108.2(7)
		C(121)-P(1)-C(131)	106.2(7)
		C(211)-P(2)-C(221)	104.5(8)
		C(211)-P(2)-C(231)	109.3(7)
		C(221)-P(2)-C(231)	106.6(7)
		C(311)-P(3)-C(321)	108.1(7)
		C(311)-P(3)-C(331)	109.7(7)
		C(321)-P(3)-C(331)	106.4(7)
		C(411)-P(4)-C(421)	109.3(7)
		C(411)-P(4)-C(431)	106.1(7)
		C(421)-P(4)-C(431)	110.0(7)

[a] The $[(Ph_3P)_2N]^+$ cations are in the usual bent form (R.D.Wilson and R.Bau, J. Am. Chem. Soc., 1974, 96, 7601 and refs therein).

Section 3.4 Conclusions

(1) The carbonyl distribution observed in the dianion in $[Ph_4As]_2^+ [Ru_6C(CO)_{16}]^{2-}$ is apparently different from that recently reported for the dianion in the $[Me_4N]^+$ salt, although both structural determinations were problematic (see Section 3.2). There are two possible explanations for the differing geometries:-

(i) Discrete isomers of $[Ru_6C(CO)_{16}]^{2-}$ exist in the solid state containing 4($[Ph_4As]^+$ salt) or 3 $[Me_4N]^+$ salt) edge-bridging CO's, the remaining carbonyls being terminal.

(ii) Both the $[Ph_4As]^+$ and $[Me_4N]^+$ salts of the dianion have 4 edge-bridging CO's, but the degree of asymmetry of these carbonyls differs markedly in the two salts.

The close similarity in distribution of the CO ligands in the $[Ph_4As]^+$ and $[Me_4N]^+$ salts of $[Ru_6C(CO)_{16}]^{2-}$ supports the second possibility.

(2) Bulky ligands are not commonly found in large clusters because coordination of the ligand to the metal core is sterically unfavourable. An interstitial carbon atom donates four electrons to the cluster reducing the number of CO groups required by two, this enables large ligands to bond to the cluster. Carbido clusters of ruthenium may therefore be better catalysts for the polymerization of small molecules than those with no interstial atoms. For rhodium clusters recent work has indicated that the reverse is true and those <u>without</u> interstitial atoms are more effective catalysts than those that contain embedded

atoms.[11] The coordination of the diene in $Ru_6C(CO)_{15}(C_6H_{10})$ to an edge of the Ru_6 octahedron may represent a more adequate model of diene (or polyene) interactions with a metal surface than those in which the hydrocarbon unit is bonded to one metal atom only.

(3) The largest osmium cluster prepared to date has been isolated in high yield from the pyrolysis of the Py derivative of $Os_3(CO)_{12}$ again demonstrating the utility of this route to high osmium clusters.

The mechanism of formation of polynuclear metal carbonyls under pyrolysis conditions is of interest. The generation of coordinately unsaturated species must be an important initial step in the reaction, combination of these with the parent carbonyl or with each other then leads to the formation of high clusters. Complexes of the type $Os_3(CO)_{11}L$, where L is a labile ligand (e.g. Py), were expected to be good candidates for pyrolysis since a vacant coordination site could be provided by loss of the labile ligand. The synthesis of the $[Os_{10}C(CO)_{24}]^{2-}$ dianion by the pyrolysis of $Os_3(CO)_{11}Py$ fulfils this expectation. The tetranuclear cluster $H_4Os_4(CO)_{12}$ has been postulated as an important intermediate in the production of large hydrido osmium clusters,[36] and it may be significant that small yields of this tetrahydride were isolated from the pyrolysis of $Os_3(CO)_{11}Py$ where the parent Os_{10} species produced is thought to be the neutral hydrido cluster $H_2Os_{10}C(CO)_{24}$ (see Subsection 3.3.2).

(4) In clusters containing Ru_6C and Os_6C units the M-carbido distance is approximately the same ($\sim$2.05 Å) and in the $[Os_{10}C(CO)_{24}]^{2-}$ dianion the interstitial carbon atom has been shown to cause expansion of the octahedral portion of the metal polyhedron. This observation contrasts with the conclusion of Mason and Mingos that in octahedral clusters

the metal polyhedron is neither distorted nor expanded to accommodate the carbon atom.[37] However the M-carbido distance in clusters tends to reflect the environment of the encapsulated carbon atom; a value of ~2.05 Å is observed in octahedral (antiprismatic) cavities whilst in prismatic arrangements of metal atoms a value nearer 2.13 Å is found.[13]

(5) The capping principle, which was introduced to extend the application of Wade theory (see Subsection 1.4.3), has been found to hold for 4 capping atoms in $[Os_{10}C(CO)_{24}]^{2-}$. It is interesting to speculate that an octahedron can accommodate four more capping osmium groups (see Figure 3.7) which would correspond to a complete face-centred cubic unit cell of Os atoms, i.e. an Os_{14} species.

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SECTION 4

The Structures of Some Hydrido Clusters of Ruthenium and Osmium and the Structure of $[Ru_6(CO)_{18}]^{2-}$.

Section 4.1 Introduction

Since the majority of chemical compounds contain hydrogen it is inevitable that hydrido metal cluster compounds should occupy a position of importance both as products and as intermediates in the chemistry of cluster complexes.

Structural and spectroscopic studies indicate that in small clusters the hydrogen atoms are in bridging positions between metal atoms and, in some, they are also involved in tautomerism. There is a similarity between this behaviour and the mobility of hydrogen chemisorbed onto metallic phases.

A few large hydride clusters have been synthesized whose cores resemble fragments of the bulk metal with H atoms embedded in interstitial sites. These systems should be better models for hydrogen interaction with a close-packed metal lattice.

Several reports have also appeared in the literature in which hydrido-metal clusters have either been employed as catalysts or have been observed to arise in catalytic systems. For example the anion $[H_3Ru_4(CO)_{12}]^-$ has been identified as the principal constituent in the alkaline solution of $Ru_3(CO)_{12}$ found to be catalytically active in the water-gas shift reaction.[1] Thus clusters containing hydrogen atoms may provide an important link between the study of soluble molecular complexes (and the problems of homogeneous catalysis), and that of the solid state and surface phenomena (in connection with the problems of heterogeneous catalysis).

A comprehensive review of hydrido-transition metal cluster complexes has recently appeared by A.P. Humphries and H.D. Kaesz (Prog.Inorg.Chem., 1979, 25, 145).

Section 4.2 The Structures of the $[H_3M_4(CO)_{12}]^-$ Anions (M = Ru,Os) in the Solid State

4.2.1. Preamble

Relatively few polynuclear carbonyl hydrides containing more than four metal atoms are available in high yields, so the many tetrahedral species, which represent the simplest closed polyhedron, provide the most convenient model for investigating the reactions of H with a core of metal atoms. Tetranuclear carbonyl clusters have been prepared containing up to six hydride ligands and the hydrogens have been observed in a number of bonding modes.

Fluxional molecules have also been characterized and the existence of definite structural isomers has been suggested for $H_2Ru_4(CO)_{13}$,[2] $H_4Ru_4(CO)_{12}$,[3] $H_4Os_4(CO)_{12}$,[4] and $[H_3M_4(CO)_{12}]^-$ (M = Ru,Os)[5,6] (*vide infra*).

The i.r. spectrum of $[H_3M_4(CO)_{12}]^-$ (M = Ru,Os) indicates only terminal carbonyl groups,[5,6] and the complexity of the pattern indicates that either a species of low symmetry or more than one species is present. From the ^1H n.m.r. spectrum of $[H_3Ru_4(CO)_{12}]^-$ Koepke *et al.* deduced that two structural isomers are present in solution,[6] one having C_2 (or C_{2v}) and one having C_{3v} symmetry of the metal-hydrogen framework. Crude samples of $[(Ph_3P)_2N]^+$ $[H_3Ru_4(CO)_{12}]^-$ and $[(Ph_3P)_2N]^+$ $[H_3Os_4(CO)_{12}]^-$ were provided from the University of Cambridge by Dr. P.F. Jackson and G.J. Will respectively. In order to examine the solid state structure of these salts crystals suitable for X-ray analysis were grown from CH_2Cl_2 - MeOH.

4.2.2 Data Collection

4.2.21 $[(Ph_3P)_2N]^+[H_3Ru_4(CO)_{12}]^-$

For this salt the habit of all the crystals grown from the first recrystallization appeared to be the same, i.e. parallelpipeds with diamond shaped faces (VIII). The crystal selected for data collection was of dimensions 0.29 x 0.25 x 0.13 mm. Unit cell parameters were determined, and data collected by the methods described in Subsection 2.2.2 using a scan width of 0.90°.

From a later recrystallization as well as the "diamond shaped" crystals many were present which possessed rectangular faces. A triclinic unit cell was obtained for one of these crystals (IX), which was of dimensions 0.35 x 0.20 x 0.20 mm, and Delaunay reduction showed it was unrelated to the triclinic cell found for the "diamond shaped" crystal obtained from the first recrystallization (VIII); the unit cell volume was ca. 26 $Å^3$ smaller than that of the original crystal. Data collection and processing was carried out as in Subsection 2.2.2 using a scan width of 0.80°.

For the two independent crystals of $[(Ph_3P)_2N]^+[H_3Ru_4(CO)_{12}]^-$ {(VIII) and (IX) respectively} several relatively intense reflections were measured after data collection at 20 intervals around their diffraction vector (ψ). The variation in intensity was, in each case, not significant ($\not> 3\sigma$). This and the small value of μ (12.00 cm^{-1}) indicated that absorption corrections could be reasonably neglected.

Laue equivalent reflections were averaged to give 7210 and 10945 unique data $[I \geq 3\sigma(I)]$ for (VIII) and(IX) respectively. Crystal data for (VIII) and (IX) are given in Table 4.1.

4.2.22 $[(Ph_3P)_2N]^+ [H_3Os_4(CO)_{12}]^-$

Careful examination showed that two different crystalline forms were also present for this salt. The first (10) had characteristic "diamond shaped" faces and was found to be isomorphous with one form of the ruthenium salt, (VIII). Data was therefore not collected. The second form (X) had rectangular faces and these crystals were found to be orthorhombic. It seemed likely that this orthorhombic modification would correspond to a different isomer of the $[H_3Os_4(CO)_{12}]^-$ anion, so data was collected and processed as in Subsection 2.2.2 using a crystal of dimensions 0.26 x 0.19 x 0.14 mm and a scan width of 0.74 °. During data collection the intensity of the reference reflections dropped progressively to final values ca. 8% lower than their initial values. No correction was made for this slight crystal decomposition. Empirical absorption corrections were applied to the data set which gave relative transmission coefficients which ranged from 0.804 to 1.131 for the full data set. Laue equivalent reflections were averaged to give 3347 unique data $[I \geqslant 3\sigma(I)]$ for (X). Crystal data for (10) and (X) are given in Table 4.1.

Table 4.1 Crystal data for the two crystalline forms of $[(Ph_3P)_2N]^+ [H_3Ru_4(CO)_{12}]^-$ (VIII) and (IX) and $[(Ph_3P)_2N]^+ [H_3Os_4(CO)_{12}]^-$ (10) and (X)

	(VIII)	(IX)	(10)	(X)
M_r	1282.0	1282.0	1638.5	1681.0
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$
a/Å	17.361	15.608	17.378	17.648
b/Å	11.735	15.370	11.691	19.597
c/Å	12.321	11.219	12.308	15.429
α/°	94.61	99.26	94.40	90

Table 4.1 (Continued)

	(VIII)	(IX)	(10)	(X)
β/°	98.44	103.27	98.62	90
γ/°	88.52	105.72	88.41	90
U/Å^3	2474.7	2449.0	2491.4	5336.1
D_c/g cm^{-3}	1.72	1.74	2.18	2.09
Z	2	2	2	4

4.2.3 Structure Solution and Refinement

The scattering factors used, the function minimized during least-square refinement, and definitions of the discrepancy indices quoted in the text are given in Subsection 2.2.3.

4.2.31 $[(Ph_3P)_2N]^+[H_3Ru_4(CO)_{12}]^-$

The intensity data showed $\bar{1}$ Laue symmetry only for the two independent crystals [(XIII) and (IX)] of $[(Ph_3P)_2N]^+$ $[H_3Ru_4(CO)_{12}]^-$. The centric triclinic space group $P\bar{1}$ was assumed in each case and confirmed by the satisfactory solution and refinement of the structure. The Ru atoms in(XIII) and (IX) were found from Patterson maps, the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses.

After several cycles of refinement a difference-Fourier map calculated for (VIII) showed four pronounced peaks in positions capping the faces of the metal tetrahedron. These features, which were *ca.* 3 eÅ^{-3} in height, were interpreted in terms of a second

orientation of the cluster of low occupancy (Figure 4.3). Similar cluster disorder was found in the neutral tetrahydride $H_4Ru_4(CO)_{12}$.[7] Thus the original four ruthenium atoms were designated Ru(1A), Ru(2A), Ru(3A), and Ru(4A) and their occupancies were coupled in the least-squares refinement to a free variable p_A, which refined to 0.9386(10). The common occupation factor of the ruthenium sites of minor occupancy, Ru(1B), Ru(2B), Ru(3B), and Ru(4B) was set to $1-p_A$. No allowance was made in the structure factor calculations for the CO ligands associated with the second orientation of the cluster. Blocked full matrix refinement was used with the atoms grouped as follows: block 1, the ruthenium atoms; block 2, the carbonyl ligands; block 3, the $[(Ph_3P)_2N]^+$ cation. Refinement converged at R = 0.0480, R_w = 0.0519, and R_G = 0.0629 using anisotropic thermal parameters for all atoms of the anion, except the 'B' Ru atoms, and the N and P atoms of the $[(Ph_3P)_2N]^+$ cation. The phenyl rings of the cation were treated as rigid groups [d(C-C) = 1.395 Å] and the phenyl hydrogens were included in geometrically calculated positions [d(C-H) = 1.08 Å]. At this stage a difference-Fourier synthesis calculated using only those data for which $(\sin\theta)/\lambda < 0.3$ revealed the positions of the three hydride ligands associated with the 'A' ruthenium atoms, the peaks having an average height of 0.2 $eÅ^{-3}$. The occupation factors of these atoms were tied to that of the 'A' Ru atoms (p_A), and their positional and thermal parameters were successfully optimized <u>via</u> least-squares refinement. This gave the following final discrepancy indices for (VIII) : R = 0.0473, R_w = 0.0508, and R_G = 0.0607. Weights were assigned to reflections as $\underline{w} = 2.4041/[\sigma^2F + 0.000099F^2]$ (see Subsection 2.2.3). A final difference-Fourier synthesis showed a few residual maxima in the region of the ruthenium atoms, the largest of which had a height of 1.3 $eÅ^{-3}$.

For (IX), the second crystalline form of $[(Ph_3P)_2N]^+[H_3Ru_4(CO)_{12}]^-$, blocked full matrix refinement (the atoms were grouped as for (VIII), and the phenyl rings were treated similarly) converged at R = 0.0446, R_w = 0.0509, and R_G = 0.0621 using anisotropic thermal parameters for all atoms of the anion, and the N and P atoms of the cation. A difference-Fourier synthesis calculated at

this stage using all the data revealed the positions of the three hydride ligands, the peaks having an average height of 0.31 $e\text{Å}^{-3}$. Inclusion of these ligands in the model, and refinement of their positional and isotropic thermal parameters gave final discrepancy indices of R = 0.0432, R_w = 0.0489, and R_G = 0.0592. Weights were assigned to reflections a $\underline{w} = 1.0000/[\sigma^2 F + 0.0004 F^2]$ (see Subsection 2.2.3). A final difference-Fourier synthesis revealed a few residual maxima in the region of the ruthenium atoms, none of which had a height greater than 1.2 $e\text{Å}^{-3}$.

Final positional and thermal parameters for the two crystalline forms of $[(Ph_3P)_2N]^+ [H_3Ru_4(CO)_{12}]^-$ (VIII) and (IX) are given in Appendices 8 and 9 respectively.

4.2.32 $[(Ph_3P)_2N]^+ [H_3Os_4(CO)_{12}]^-$

For the orthorhombic modification, (X), systematic absences (0kl for k + l = 2n + 1, h0l for h = 2n + 1, h00 for h = 2n + 1, 0k0 for k = 2n + 1, and 00l for l = 2n + 1) were consistent with either the non-centric space group $Pna2_1$, or the centric alternative Pnam (a non-standard setting of Pnma). Direct methods failed to solve the structure in the centric space group, but a suitable solution for the osmium atom positions was obtained in the non-centric space group $Pna2_1$ from a Patterson map. The remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. Blocked full matrix refinement was used with the atoms grouped as follows: block 1, the osmium atoms; block 2, the carbonyl ligands of the anion; block 3, the atoms of the $[(Ph_3P)_2N]^+$ cation. Refinement converged at R = 0.0528, R_w = 0.0547, and R_G = 0.0680 using anisotropic thermal parameters for the Os, N, and P atoms. The phenyl rings were treated as rigid groups [d(C-C) = 1.395 Å] and the phenyl hydrogens were included in geometrically calculated positions [d(C-H) = 1.08 Å]. A difference-Fourier synthesis calculated at this stage revealed two

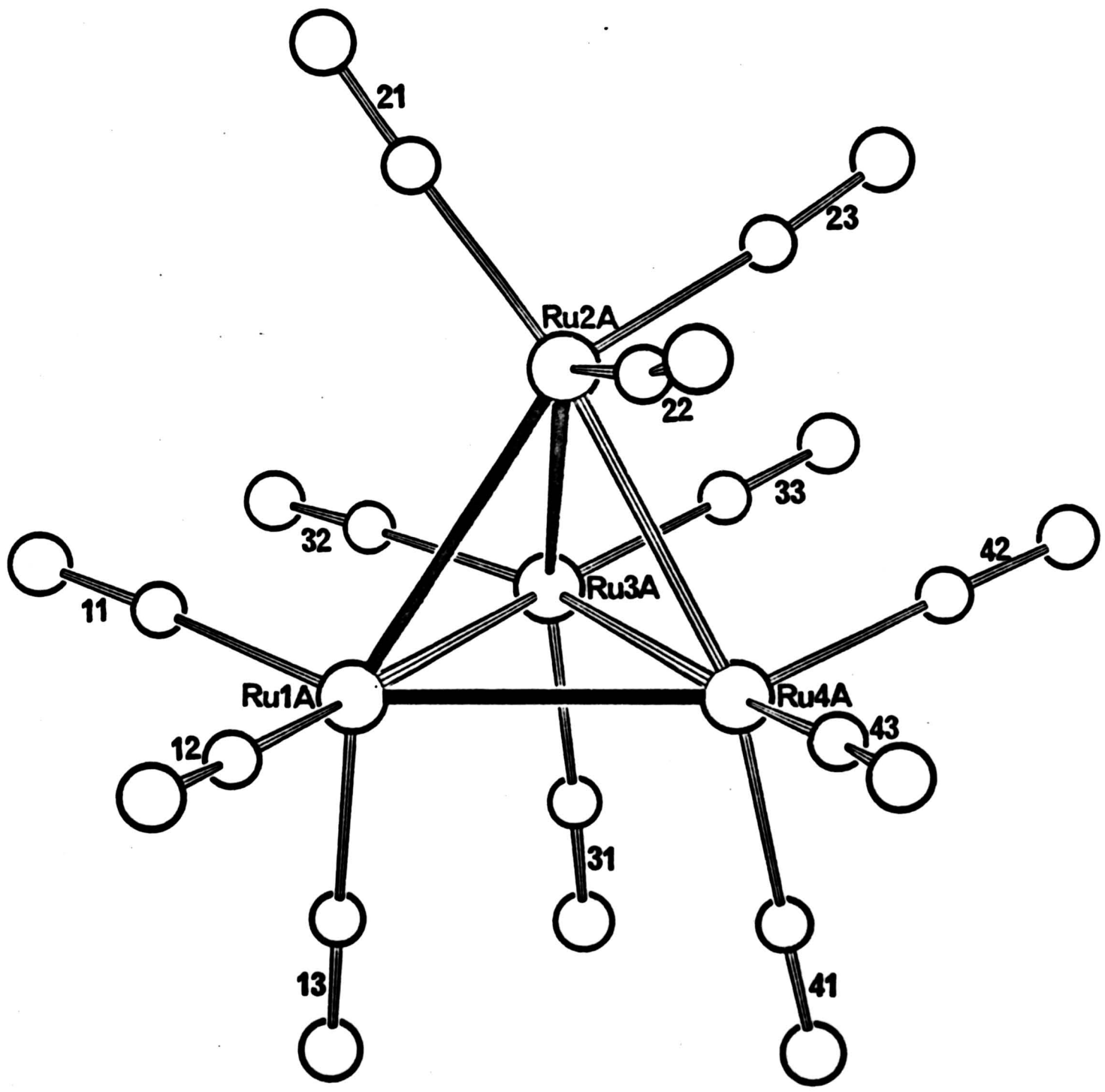
prominent peaks, approximately 3 $e\text{Å}^{-3}$ in height, that were well separated from the anion and cation and were ca. 2.8 Å apart. These features were interpreted as Cl atoms of partial occupancy associated with a CH_2Cl_2 solvent molecule. Refinement of their occupation factors yielded values of ~0.5; these were fixed at exactly 0.5 for the final cycles of refinement which converged at $R = 0.0454$, $R_w = 0.0477$, and $R_G = 0.0568$. Since the scattering factors used included the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion (see Subsection 2.2.3) it was necessary to investigate the absolute configuration. Thus the other enantiomorph was obtained by changing the sign of all three coordinates (x to -x, y to -y, z to -z) for all the atoms; refinement now converged at $R = 0.0426$, $R_w = 0.0435$, and $R_G = 0.0503$. These values of the discrepancy indices are significantly lower than before, so this configuration for the atoms is the correct one. Weights were assigned to reflections as $\underline{w} = 0.8923/\sigma^2F$ (see Subsection 2.2.3). Attempts to locate the hydridic H atoms from difference-Fourier syntheses calculated using various low angle portions of the data [$(\sin\theta)/\lambda$ cutoffs of 0.30, 0.27, 0.24, and 0.21 were tried] were unsuccessful. A final difference-Fourier map calculated using all the data showed a few residual maxima in the region of the osmium atoms, none of which had a height greater than 1.4 $e\text{Å}^{-3}$.

Final positional and thermal parameters for the orthorhombic crystal form of $[(Ph_3P)_2N]^+ [H_3Os_4(CO)_{12}]^-$ (X) are given in Appendix 10.

4.2.4 Discussion

The structures of the $[H_3Ru_4(CO)_{12}]^-$ anions in the two crystal forms of $[(Ph_3P)_2N]^+ [H_3Ru_4(CO)_{12}]^-$ {(VIII) and (IX)} are shown in Figures 4.1 - 4.5 and the bond distances and angles are given in Tables 4.1 - 4.4.

Figure 4.1 The isomer of $[H_3Ru_4(CO)_{12}]^-$ having C_2 symmetry of the M-H core. The solid Ru-Ru bonds are bridged by hydrogen atoms; 'B' Ru atoms have been omitted for clarity.



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have

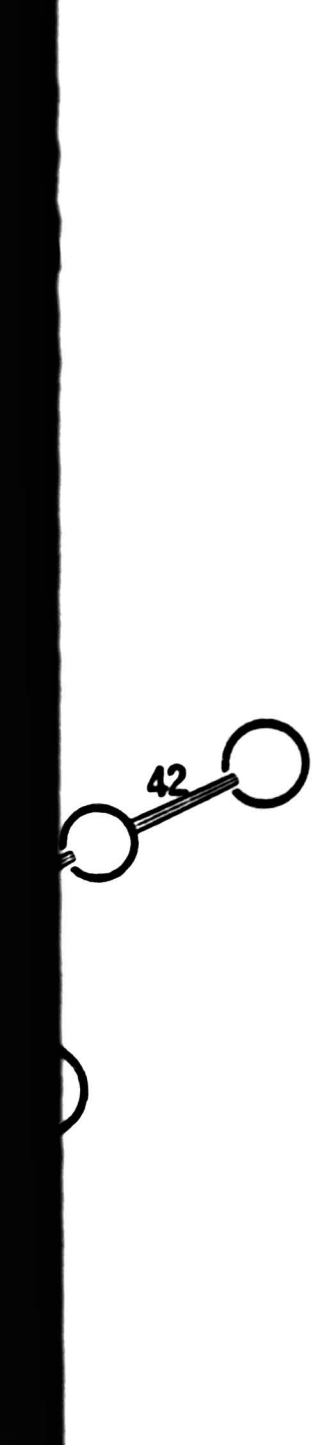


Figure 4.2 The isomer of $[H_3Ru_4(CO)_{12}]^-$ having C_{3v} symmetry of the M-H core. The solid Ru-Ru bonds are bridged by hydrogen atoms.

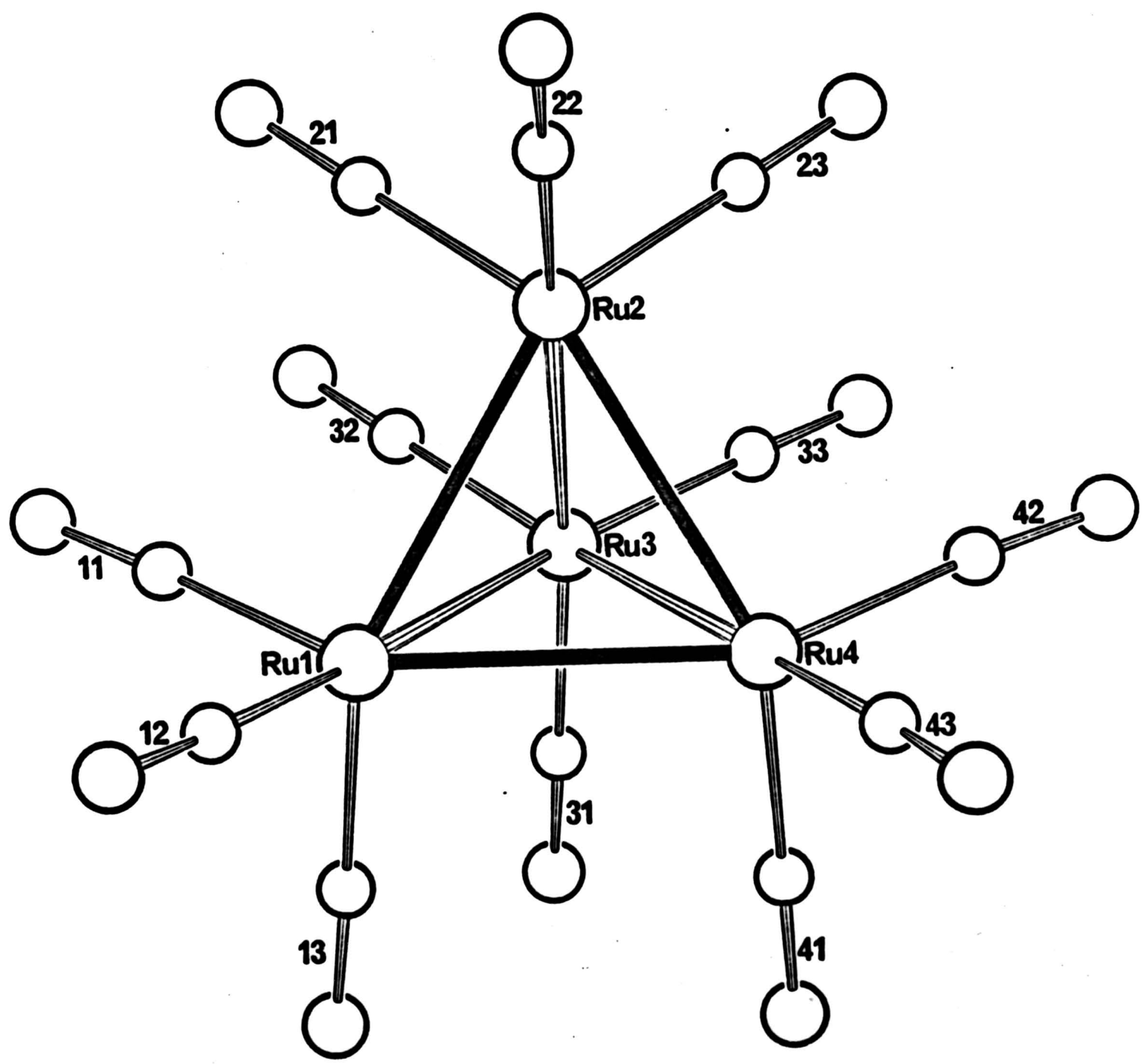


Figure 4.3 Configuration of the metal core in the isomer of $[H_3Ru_4(CO)_{12}]^-$ having C_2 symmetry portraying the disordering of the molecules. Solid Ru-Ru bonds are bridged by hydrogen atoms.

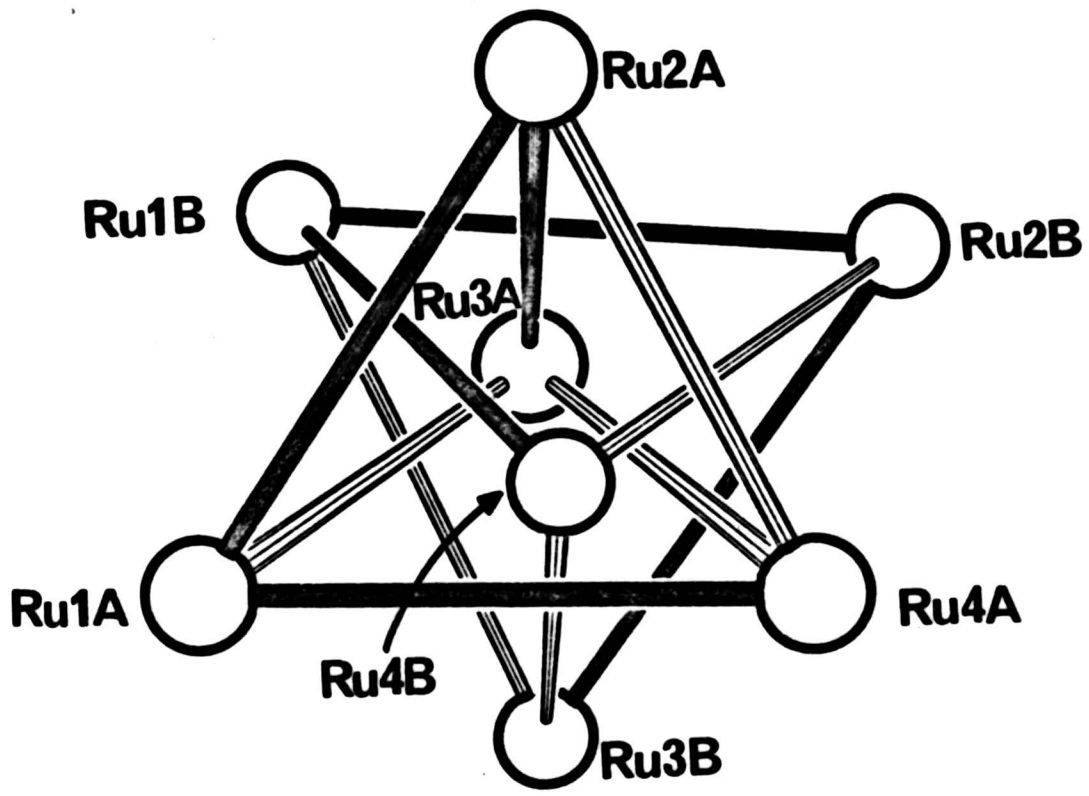
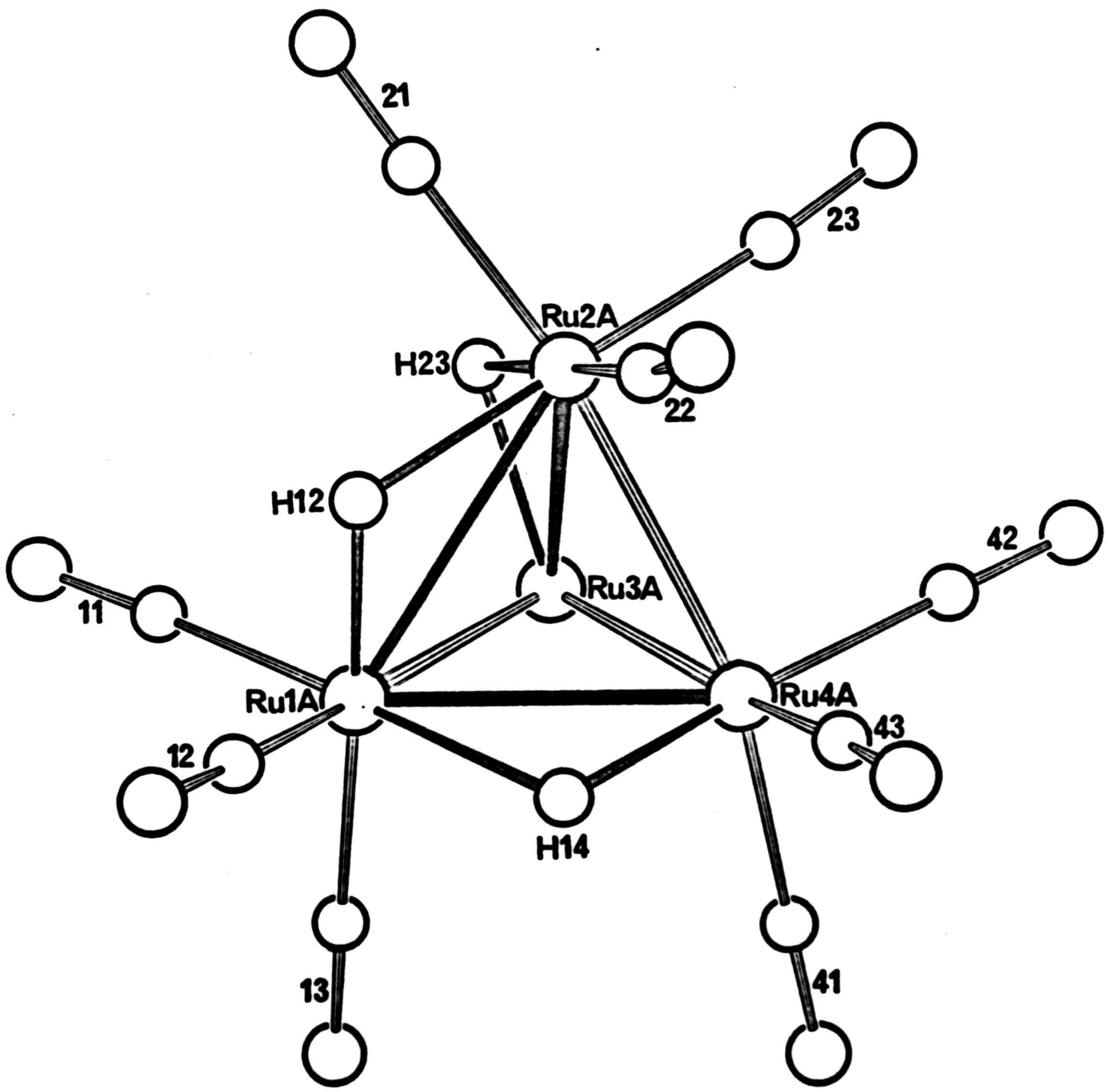


Figure 4.4 View of the isomer of $[H_3Ru_4(CO)_{12}]^-$ having C_2 symmetry of the M-H core showing the distribution of the hydride ligands. 'B' Ru atoms and the CO's attached to Ru(3A) have been omitted for clarity.



aving C_2
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nd the CO's
or clarity.

42

Figure 4.5 View of the isomer of $[H_3Ru_4(CO)_{12}]^-$ having C_{3v} symmetry of the M-H core showing the distribution of the hydride ligands. The CO's attached to Ru(3) have been omitted for clarity.

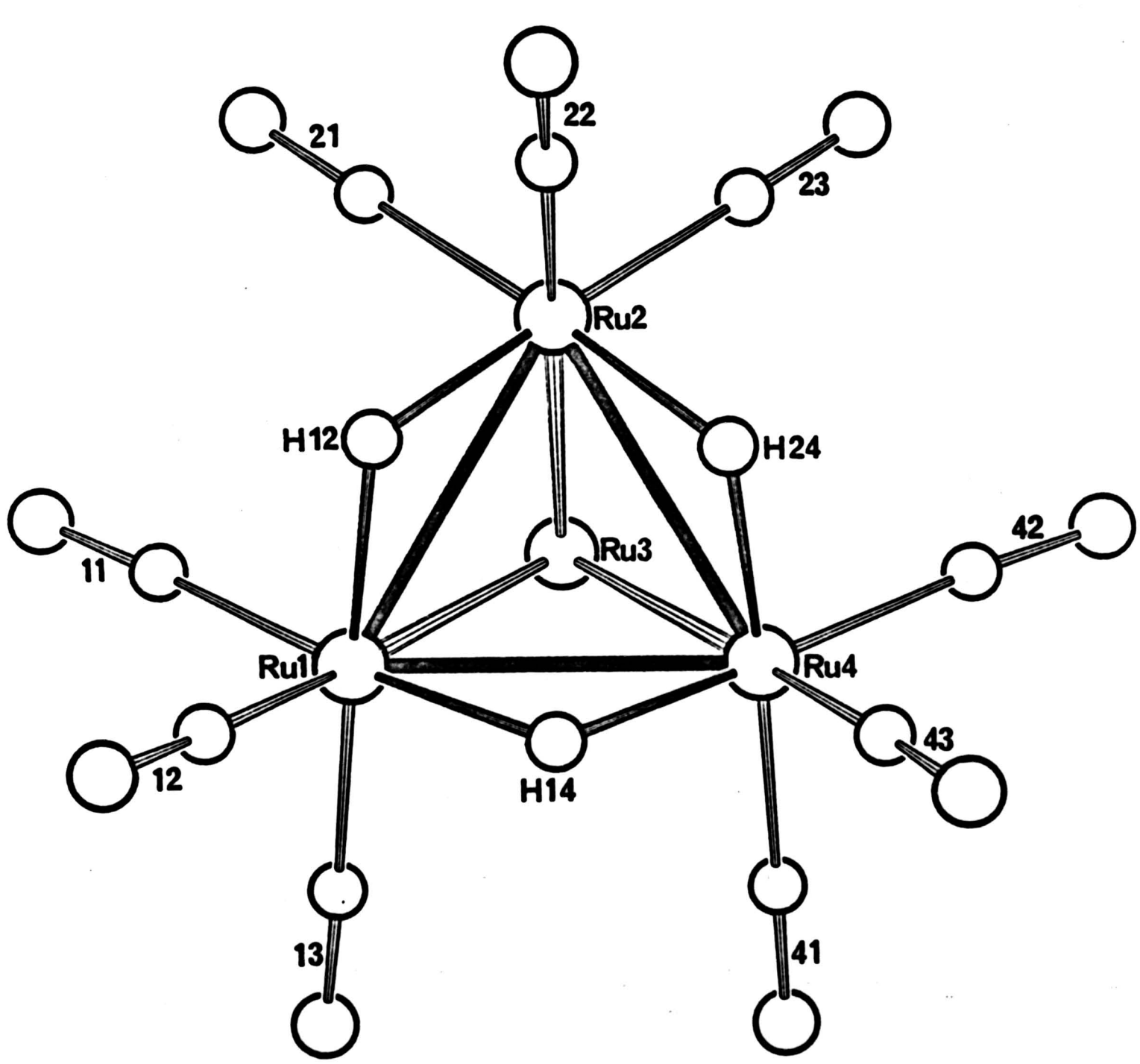
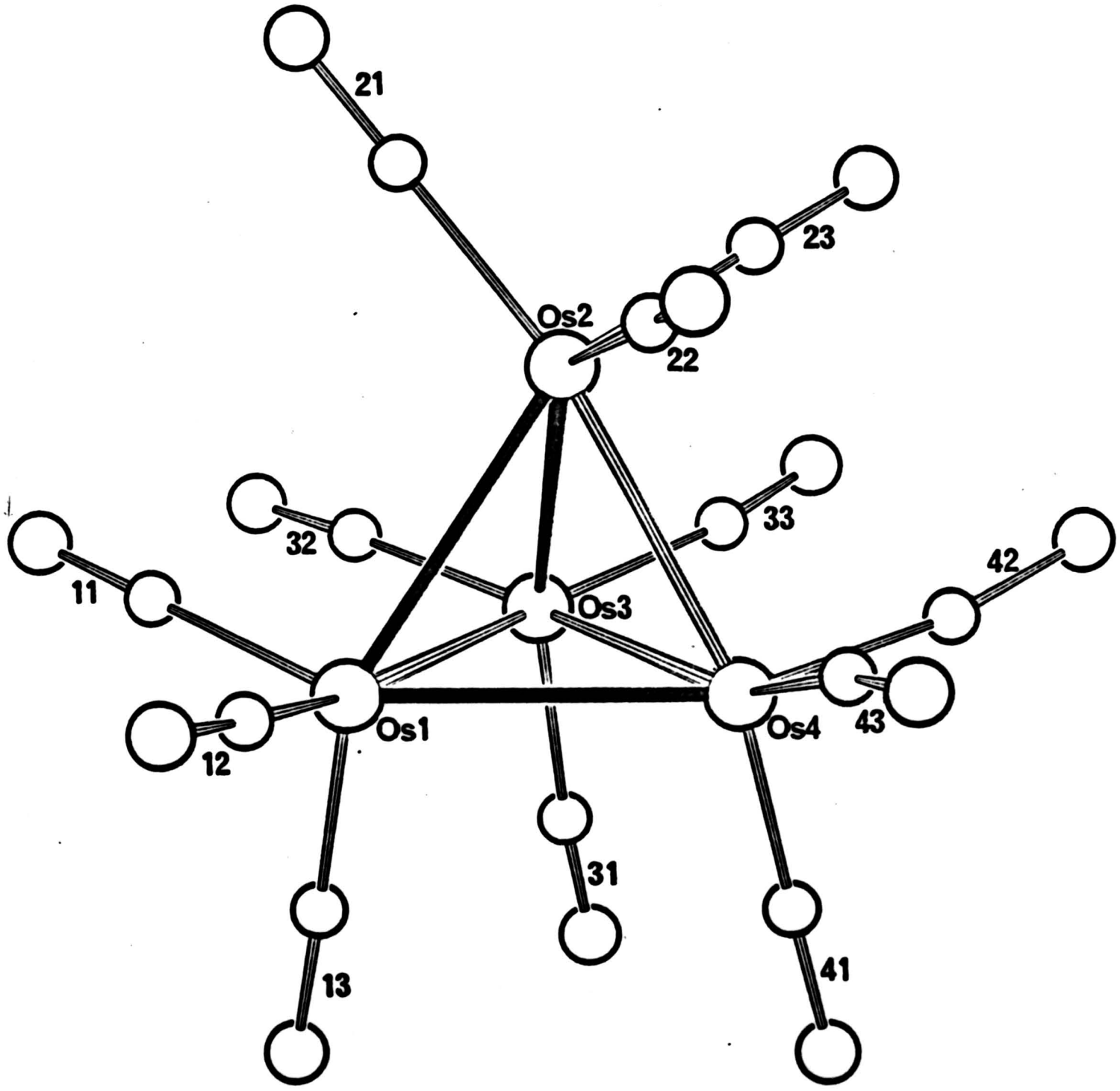


Figure 4.6 The structure of the anion in $[(Ph_3P)_2N]^+$ $[H_3Os_4(CO)_{12}]^-$ 0.5 CH_2Cl_2. The M-H core has approximate C_2 symmetry: solid Os-Os bonds are bridged by hydrogen atoms.



X-ray analysis has shown that $[(Ph_3P)_2N]^+$ $[H_3Ru_4(CO)_{12}]^-$ crystallizes in two different forms, (VIII) and (IX), which correspond to two different structural isomers of the anion. These have metal-hydrogen geometries approximating to C_2 (VIII) and C_{3v} (IX) symmetry respectively and this provides the first confirmation of the existence of such isomers in the solid state. For the $[H_3Os_4(CO)_{12}]^-$ anion two crystalline forms of the $[(Ph_3P)_2N]^+$ salt were analysed, (10) and (X), but in both the metal-hydrogen geometry approximates to C_2 symmetry as had previously been found for the $[Me_4N]^+$ salt.[8] In all the anions each metal atom is bonded to three terminal carbonyl ligands with each $M(CO)_3$ unit adopting a staggered conformation relative to the three M-M bonds. This is usually observed when edge-bridging hydrogens are present. In contrast in $H_4Re_4(CO)_{12}$ where the hydrides bridge the four faces of the Re_4 tetrahedron, the carbonyls adopt the eclipsed configuration.[9]

In the isomer of the $[H_3M_4(CO)_{12}]^-$ anion with C_2 symmetry (Figures 4.1, 4.4, and 4.6) three tetrahedral edges M(1) - M(2), M(1) - M(4), and M(2) - M(3) are significantly longer [M = Ru, mean Ru - Ru = 2.922(34); M = Os, mean Os - Os = 2.944(29) Å] than the rest [M = Ru, mean Ru - Ru = 2.802(3); M = Os, mean Os - Os = 2.816(14) Å] consistent with these longer edges being identified as the M(μH)M two-electron three-centre bonds. For the Ru anion the hydrogen atoms bridging these edges were located directly from the X-ray analysis and their positional and thermal parameters successfully optimized <u>via</u> least-squares refinement giving Ru - H (mean) = 1.93(15) Å and Ru - H - Ru (mean) = 99(9)°. In the isomer of $[H_3Os_4(CO)_{12}]^-$ of C_2 symmetry for which data was collected (X) the hydrogens were not located directly from the X-ray analysis. However, the carbonyls <u>cis</u> to the long apparently H-bridged Os - Os bonds have larger Os - Os - C angles [mean 105°] than those <u>cis</u> to the other Os - Os bonds [mean 93°]; the widening of these angles, which is often a more important criterion than bond lengths for identifying the position of bridging hydrides,[10] supports the conclusion that the longer edges are bridged by the hydrogen atoms.

The isomer of $[H_3Ru_4(CO)_{12}]^-$ of C_{3v} symmetry has three Ru-Ru bonds, in this case forming the triangular face Ru(1), Ru(2), Ru(4), which are significantly longer [mean 2.937(3) Å] than the others [mean 2.787(11) Å]. The hydrides were located directly from the X-ray analysis bridging the long Ru-Ru bonds, and they lie ca. 1 Å above the Ru(1), Ru(2), Ru(4) plane (Figure 4.5, Table 4.5). The Ru(μH)Ru bridges are symmetrical [mean Ru-H = 1.85(3) Å, mean Ru-H-Ru = 105.6(3)°] so are similar in this respect to those found for example in $H_4Ru_4(CO)_{10}$ (diphos)[11] and $H_4Ru_4(CO)_{10}$ (μ-diphos).[12] H(12), H(14), and H(24) are coplanar to within 0.26 Å with the Ru(1), Ru(2), Ru(3); Ru(1), Ru(4), Ru(3); and Ru(2), Ru(4), Ru(3) faces respectively (Table 4.5). As might be expected the carbonyl distribution in this isomer of the $[H_3Ru_4(CO)_{12}]^-$ anion closely resembles that found for the isoelectronic neutral cluster $H_3CoOs_3(CO)_{12}$ where the three hydrogen atoms are also thought to bridge the edges of one triangular face.[13]

Although $[H_3Os_4(CO)_{12}]^-$ exhibits i.r. and n.m.r. properties consistent with two isomers being present in solution[5] only one isomer has been characterized to date for the $[(Ph_3P)_2N]^+$ salt in the solid state, the metal-hydrogen geometry approximating to C_2 symmetry, despite many crystals being examined from several recrystallizations. An independent X-ray analysis of the $[Me_4N]^+$ salt also showed this same isomer to be present.[8] The most likely explanation for this is that the polarity of the solvent systems used for recrystallization did not favour crystallization of the other isomer; for $[H_3Ru_4(CO)_{12}]^-$ the isomer having C_{3v} metal-hydrogen symmetry is favoured in polar solvents.[6]

Conclusions derived from n.m.r. data indicate that in solution the hydride ligands in $H_4Ru_4(CO)_{12-n}L_n$,[14] $H_4Ru_4(CO)_{10}$(diphos),[11] $H_4Ru_4(CO)_{10}$ (μ-diphos),[12] and $H_3Os_3W(CO)_{11}(h^5\text{-}C_5H_5)$[15] scramble over the metal framework implying a low energy barrier to rearrangement. In the solid the tetrahydrides $H_4Ru_4(CO)_{11}P(OMe)_3$,[16] $H_4Ru_4(CO)_{10}(PPh_3)_2$,[7,17] and $H_4Ru_4(CO)_{12}$[7] all have metal-hydrogen geometries approximating to D_{2d} symmetry, but in $H_4Ru_4(CO)_{10}$ (diphos)[11] and $H_4Ru_4(CO)_{10}$(μ-diphos)[12] the H_4Ru_4 core possesses only C_s symmetry. This also suggests that the alternative metal-hydrogen

arrangements differ little in energy. Theoretical calculations by Hoffmann *et al.*[18] on the staggered and eclipsed conformations of $H_nM_4(CO)_{12}$ also lead to the same conclusion that there is relatively little energy difference between the possible H bridging positions. However the anion $[H_3Ru_4(CO)_{12}]^-$ is the only example so far for which definite structural isomers have been confirmed to exist in the solid state different only in the disposition of the bridging hydride ligands.

Table 4.2

Selected Interatomic Distances (Å) for the $[H_3M_4(CO)_{12}]^-$ anions.[a]

E.s.d's are given in parentheses.

(a) Metal-Metal Bonds

	(VIII)		(IX)	(X)
	Cluster(A)	Cluster(B)		
M(1)-M(2)	2.959(1)	2.90(2)	2.935(1)	2.968(1)
M(1)-M(3)	2.799(1)	2.87(2)	2.799(1)	2.826(1)
M(1)-M(4)	2.892(1)	2.89(2)	2.941(1)	2.951(1)
M(2)-M(3)	2.916(1)	2.94(2)	2.777(1)	2.912(2)
M(2)-M(4)	2.803(1)	2.80(2)	2.936(1)	2.821(1)
M(3)-M(4)	2.805(1)	2.81(2)	2.786(1)	2.800(2)
Mean M-M "long"	2.922(34)[b]	2.91(3)[b]	2.937(3)[b]	2.944(29)[b]
" " "short"	2.802(3)[b]	2.83(4)[b]	2.787(11)[b]	2.816(14)[b]

(b) Ruthenium-Hydrogen Distances in the $[H_3Ru_4(CO)_{12}]^-$ anions.

	(VIII)	(IX)
Ru(1)-H(12)	1.71(7)	1.83(4)
Ru(2)-H(12)	1.91(7)	1.87(5)
Ru(1)-H(14)	2.10(8)	1.83(4)
Ru(4)-H(14)	1.98(8)	1.86(4)
Ru(2)-H(23)	1.80(8)	-
Ru(3)-H(23)	2.07(8)	-
Ru(2)-H(24)	-	1.88(5)
Ru(4)-H(24)	-	1.80(4)
Mean Ru-H	1.93(15)[b]	1.85(3)[b]

(c) Metal-Carbon Distances

	(VIII)	(IX)	(X)
M(1)-C(11)	1.891(7)	1.882(5)	1.882(30)
M(1)-C(12)	1.929(8)	1.910(5)	1.904(27)
M(1)-C(13)	1.878(7)	1.898(4)	1.909(28)
M(2)-C(21)	1.916(6)	1.885(5)	1.920(24)
M(2)-C(22)	1.894(8)	1.911(4)	1.926(38)
M(2)-C(23)	1.889(7)	1.891(5)	1.905(27)
M(3)-C(31)	1.901(7)	1.893(4)	1.895(30)
M(3)-C(32)	1.899(8)	1.880(5)	1.929(28)
M(3)-C(33)	1.890(9)	1.893(7)	1.884(23)
M(4)-C(41)	1.893(7)	1.909(4)	1.790(28)
M(4)-C(42)	1.867(8)	1.904(6)	1.895(32)
M(4)-C(43)	1.895(10)	1.936(5)	1.811(33)
Mean M-C	1.895(16)[b]	1.899(16)[b]	1.888(44)[b]

(d) Carbon-Oxygen Distances

	(VIII)	(IX)	(X)
C(11)-O(11)	1.138(9)	1.136(7)	1.194(38)
C(12)-O(12)	1.132(10)	1.142(7)	1.156(35)
C(13)-O(13)	1.146(9)	1.136(6)	1.162(35)
C(21)-O(21)	1.119(8)	1.142(6)	1.124(33)
C(22)-O(22)	1.145(10)	1.133(5)	1.162(44)
C(23)-O(23)	1.116(10)	1.140(7)	1.129(34)
C(31)-O(31)	1.125(10)	1.138(5)	1.087(36)
C(32)-O(32)	1.148(11)	1.145(7)	1.138(35)
C(33)-O(33)	1.157(12)	1.139(9)	1.144(30)
C(41)-O(41)	1.133(9)	1.118(5)	1.255(35)
C(42)-O(42)	1.120(11)	1.132(7)	1.171(40)
C(43)-O(43)	1.161(12)	1.116(7)	1.238(41)
Mean C-O	1.137(15)[b]	1.135(9)[b]	1.163(47)[b]

[a] Bond lengths and angles quoted for (VIII) that involve ruthenium refer to the Ru sites of major (0.94) occupation unless stated otherwise.

[b] E.s.d's on mean bond lengths and angles are calculated from the equation $\sigma = \sqrt{\{[\sum_{1}^{n}(x_i-\bar{x})^2]/(n-1)\}}$ where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

Table 4.3

Selected Intramolecular Angles (°) in the $[H_3M_4(CO)_{12}]^-$ anions with e.s.d's.[a]

(a) M-C-O Angles

	(VIII)	(IX)	(X)
M(1)-C(11)-O(11)	176.2(6)	175.7(5)	174.8(26)
M(1)-C(12)-O(12)	176.5(8)	175.5(5)	176.3(25)
M(1)-C(13)-O(13)	178.3(6)	175.8(6)	178.6(27)
M(2)-C(21)-O(21)	175.7(7)	176.9(4)	175.5(27)
M(2)-C(22)-O(22)	172.6(7)	175.2(4)	174.6(29)
M(2)-C(23)-O(23)	174.8(7)	175.8(4)	173.9(23)
M(3)-C(31)-O(31)	175.6(7)	177.1(6)	174.6(27)
M(3)-C(32)-O(32)	175.3(7)	177.4(5)	176.9(24)
M(3)-C(33)-O(33)	178.7(9)	175.7(5)	174.8(20)
M(4)-C(41)-O(41)	178.5(7)	175.7(5)	176.9(24)
M(4)-C(42)-O(42)	178.8(7)	177.1(5)	176.6(29)
M(4)-C(43)-O(43)	174.7(8)	177.3(5)	171.9(29)
Mean M-C-O	176.3(19)[b]	176.3(8)[b]	175.5(17)[b]

(b) Angles Involving Hydrides in (VIII) and (IX)

	(VIII)	(IX)
H(12)-Ru(1)-Ru(2)	37.5(21)	37.8(15)
H(12)-Ru(1)-Ru(3)	94.5(20)	95.3(15)
H(12)-Ru(1)-Ru(4)	87.5(22)	82.4(15)
H(12)-Ru(2)-Ru(1)	32.9(19)	36.9(12)
H(12)-Ru(2)-Ru(3)	86.6(19)	95.1(12)
H(12)-Ru(2)-Ru(4)	86.4(19)	82.0(13)
Ru(1)-H(12)-Ru(2)	109.5(32)	105.3(24)
H(12)-Ru(1)-C(11)	86.2(22)	91.4(15)
H(12)-Ru(1)-C(12)	78.8(20)	79.7(15)
H(12)-Ru(1)-C(13)	175.8(20)	174.8(15)
H(12)-Ru(2)-C(21)	85.1(19)	92.5(15)
H(12)-Ru(2)-C(22)	85.0(19)	82.7(12)
H(12)-Ru(2)-C(23)	176.8(19)	175.2(14)
H(14)-Ru(1)-Ru(2)	82.1(22)	83.2(10)
H(14)-Ru(1)-Ru(3)	101.8(20)	95.1(14)
H(14)-Ru(1)-Ru(4)	43.2(21)	37.5(14)
H(14)-Ru(4)-Ru(1)	46.5(23)	36.8(13)
H(14)-Ru(4)-Ru(2)	88.4(22)	82.7(11)
H(14)-Ru(4)-Ru(3)	104.9(23)	94.8(13)
Ru(1)-H(14)-Ru(4)	90.2(29)	105.6(21)
H(14)-Ru(1)-C(11)	171.5(20)	174.9(10)
H(14)-Ru(1)-C(12)	72.1(20)	81.1(14)
H(14)-Ru(1)-C(13)	88.9(22)	92.1(10)
H(14)-Ru(4)-C(41)	90.8(23)	91.2(10)
H(14)-Ru(4)-C(42)	160.6(24)	175.0(10)
H(14)-Ru(4)-C(43)	66.0(24)	80.6(13)

cont...

	(VIII)	(IX)
H(23)-Ru(2)-Ru(1)	78.5(26)	-
H(23)-Ru(2)-Ru(3)	44.8(25)	-
H(23)-Ru(2)-Ru(4)	103.5(25)	-
H(23)-Ru(3)-Ru(1)	78.7(21)	-
H(23)-Ru(3)-Ru(2)	37.7(21)	-
H(23)-Ru(3)-Ru(4)	96.3(22)	-
Ru(2)-H(23)-Ru(3)	97.6(34)	-
H(23)-Ru(2)-C(21)	72.7(25)	-
H(23)-Ru(2)-C(22)	172.4(24)	-
H(23)-Ru(2)-C(23)	93.3(26)	-
H(23)-Ru(3)-C(31)	168.0(24)	-
H(23)-Ru(3)-C(32)	77.1(23)	-
H(23)-Ru(3)-C(33)	94.6(22)	-
H(24)-Ru(2)-Ru(1)	-	83.3(11)
H(24)-Ru(2)-Ru(3)	-	93.6(12)
H(24)-Ru(2)-Ru(4)	-	36.1(11)
H(24)-Ru(4)-Ru(1)	-	84.5(15)
H(24)-Ru(4)-Ru(2)	-	38.0(15)
H(24)-Ru(4)-Ru(3)	-	95.1(15)
Ru(2)-H(24)-Ru(4)	-	105.9(21)
H(24)-Ru(2)-C(21)	-	177.3(15)
H(24)-Ru(2)-C(22)	-	81.9(12)
H(24)-Ru(2)-C(23)	-	90.6(14)
H(24)-Ru(4)-C(41)	-	177.4(15)
H(24)-Ru(4)-C(42)	-	89.1(15)
H(24)-Ru(4)-C(43)	-	80.6(15)
H(12)-Ru(1)-H(14)	90.1(31)	83.6(18)
H(12)-Ru(2)-H(23)	89.9(32)	-
H(12)-Ru(2)-H(24)	-	84.9(20)
H(14)-Ru(4)-H(24)	-	86.2(18)

cont...

(c) Angles Between Metal Atoms

	(VIII)	(XI)	(X)
M(3)-M(1)-M(2)	60.8(1)	57.9(1)	60.3(1)
M(4)-M(1)-M(2)	57.2(1)	60.0(1)	56.9(1)
M(4)-M(1)-M(3)	59.0(1)	58.0(1)	57.9(1)
M(3)-M(2)-M(1)	56.9(1)	58.6(1)	57.4(1)
M(4)-M(2)-M(1)	60.2(1)	60.1(1)	61.2(1)
M(4)-M(2)-M(3)	58.7(1)	58.3(1)	58.4(1)
M(2)-M(3)-M(1)	62.3(1)	63.5(1)	62.3(1)
M(4)-M(3)-M(1)	62.1(1)	63.6(1)	63.3(1)
M(4)-M(3)-M(2)	58.6(1)	63.7(1)	59.1(1)
M(2)-M(4)-M(1)	62.6(1)	59.9(1)	61.8(1)
M(3)-M(4)-M(1)	58.8(1)	58.4(1)	58.8(1)
M(3)-M(4)-M(2)	62.7(1)	58.0(1)	62.4(1)

(d) Carbon-Metal-Metal Angles

	(VIII)	(XI)	(X)
C(11)-M(1)-M(2)	99.4(2)	93.5(1)	96.8(10)
C(11)-M(1)-M(3)	86.2(2)	86.4(2)	87.2(9)
C(11)-M(1)-M(4)	144.0(2)	142.8(2)	143.0(9)
C(12)-M(1)-M(2)	110.9(3)	116.8(1)	110.1(9)
C(12)-M(1)-M(3)	170.8(3)	174.0(1)	169.8(9)
C(12)-M(1)-M(4)	113.8(3)	117.5(2)	114.8(9)
C(13)-M(1)-M(2)	146.2(2)	144.6(2)	148.2(9)
C(13)-M(1)-M(3)	89.7(2)	87.9(2)	90.6(8)
C(13)-M(1)-M(4)	94.6(2)	95.9(2)	97.9(9)
C(21)-M(2)-M(1)	110.5(2)	95.0(1)	107.6(8)
C(21)-M(2)-M(3)	116.9(2)	87.4(1)	112.7(9)
C(21)-M(2)-M(4)	170.7(2)	144.2(1)	168.0(9)
C(22)-M(2)-M(1)	99.9(2)	118.8(1)	99.5(10)
C(22)-M(2)-M(3)	140.0(2)	175.1(1)	143.9(9)
C(22)-M(2)-M(4)	81.8(2)	116.9(1)	86.7(10)
C(23)-M(2)-M(1)	148.6(2)	140.7(1)	147.8(8)
C(23)-M(2)-M(3)	96.0(2)	83.3(1)	93.7(8)
C(23)-M(2)-M(4)	93.4(2)	93.4(1)	92.7(8)

cont...

	(VIII)	(XI)	(X)
C(31)-M(3)-M(1)	95.9(2)	97.9(2)	95.6(9)
C(31)-M(3)-M(2)	147.5(2)	159.9(2)	147.3(9)
C(31)-M(3)-M(4)	90.5(2)	102.1(2)	90.1(9)
C(32)-M(3)-M(1)	99.9(2)	101.0(2)	100.0(9)
C(32)-M(3)-M(2)	112.9(2)	97.5(1)	109.7(8)
C(32)-M(3)-M(4)	161.9(2)	159.2(2)	162.5(9)
C(33)-M(3)-M(1)	159.4(3)	161.0(2)	158.4(7)
C(33)-M(3)-M(2)	100.6(3)	103.1(1)	100.2(7)
C(33)-M(3)-M(4)	99.8(3)	98.9(2)	97.4(7)
C(41)-M(4)-M(1)	100.8(2)	93.5(2)	100.7(9)
C(41)-M(4)-M(2)	156.9(2)	141.7(2)	157.9(9)
C(41)-M(4)-M(3)	95.4(2)	85.2(2)	97.6(9)
C(42)-M(4)-M(1)	148.2(2)	144.1(2)	147.3(9)
C(42)-M(4)-M(2)	92.9(2)	94.6(1)	94.0(9)
C(42)-M(4)-M(3)	92.8(3)	87.2(2)	91.3(9)
C(43)-M(4)-M(1)	110.0(3)	116.4(2)	110.4(10)
C(43)-M(4)-M(2)	104.7(3)	117.1(1)	98.4(11)
C(43)-M(4)-M(3)	165.5(3)	173.8(1)	160.4(10)

(e) OC - M - CO Angles

	(VIII)	(IX)	(X)
C(12)-M(1)-C(11)	99.6(3)	97.1(2)	97.9(12)
C(13)-M(1)-C(11)	94.2(3)	92.9(2)	94.3(13)
C(13)-M(1)-C(12)	97.0(3)	96.8(2)	97.8(12)
C(22)-M(2)-C(21)	101.2(3)	97.1(2)	100.2(13)
C(23)-M(2)-C(21)	95.3(3)	92.0(2)	96.1(11)
C(23)-M(2)-C(22)	91.8(3)	98.5(2)	97.3(13)
C(32)-M(3)-C(31)	93.4(3)	93.5(2)	97.1(12)
C(33)-M(3)-C(31)	94.0(4)	92.8(2)	94.1(12)
C(33)-M(3)-C(32)	97.6(4)	93.9(3)	97.9(11)
C(42)-M(4)-C(41)	95.5(3)	93.5(2)	95.8(13)
C(43)-M(4)-C(41)	95.9(4)	98.8(2)	100.6(14)
C(43)-M(4)-C(42)	95.1(4)	97.1(2)	93.9(14)

[a] See Table 4.2 footnote a .

[b] See Table 4.2 footnote b .

Table 4.4

Selected bond lengths (Å) and angles (°) for the $[(Ph_3P)_2N]^+$ cations [a] in (VIII), (IX), and (X) with e.s.d's.

	(VIII)	(IX)	(X)
P(1)-N	1.565(5)	1.571(3)	1.604(18)
P(2)-N	1.549(5)	1.575(3)	1.579(18)
P(1)-N-P(2)	164.9(4)	147.6(3)	134.8(12)
P(1)-C(111)	1.805(4)	1.792(3)	1.817(17)
P(1)-C(121)	1.793(5)	1.796(3)	1.808(16)
P(1)-C(131)	1.790(4)	1.798(3)	1.788(16)
P(2)-C(211)	1.802(4)	1.804(3)	1.807(17)
P(2)-C(221)	1.804(5)	1.795(3)	1.788(18)
P(2)-C(231)	1.797(4)	1.786(3)	1.835(17)
N-P(1)-C(111)	112.6(3)	107.9(2)	109.1(8)
N-P(1)-C(121)	110.0(2)	115.7(2)	107.4(9)
N-P(1)-C(131)	111.6(2)	111.3(2)	115.9(9)
N-P(2)-C(211)	113.3(2)	114.5(2)	112.5(9)
N-P(2)-C(221)	110.0(3)	106.8(2)	115.7(9)
N-P(2)-C(231)	110.3(2)	113.2(2)	106.0(8)
C(111)-P(1)-C(121)	106.8(2)	107.6(1)	108.7(8)
C(111)-P(1)-C(131)	108.5(2)	107.7(1)	107.3(7)
C(121)-P(1)-C(131)	107.0(2)	106.3(1)	108.2(7)
C(211)-P(2)-C(221)	107.1(2)	107.3(1)	109.7(8)
C(211)-P(2)-C(231)	107.3(2)	107.4(2)	104.6(7)
C(221)-P(2)-C(231)	108.7(2)	107.2(1)	107.5(8)

[a] The cations are in the usual bent form in (IX) and (X) (R.D. Wilson and R. Bau, J.Am. Chem.Soc., 1974, 96, 7601 and refs. therein), but in (VIII) the P-N-P angle is nearer 180° (G. Longoni, M. Manassero and M. Sansoni, J.Organomet. Chem., 1979, 174, C41).

Table 4.5 Least-squares planes in direct space for the isomer of $[H_3Ru_4(CO)_{12}]^-$ having C_{3v} symmetry of the M-H framework. Only atoms marked with an asterisk were included in calculation of the plane.

atom	dev./Å
Plane 1 : -9.2978x + 13.9124y + 1.8515z = 11.4051	
Ru(1)*	-
Ru(2)*	-
Ru(3)	2.2118
Ru(4)*	-
H(12)	-0.9721
H(14)	-0.9477
H(24)	-0.9160
Plane 2 : 0.8844x - 9.6924y + 9.6501z = -2.2559	
Ru(1)*	-
Ru(2)*	-
Ru(3)*	-
H(12)	-0.1695
Plane 3 : 5.2832x + 6.0671y + 6.2325z = 11.9606	
Ru(1)*	-
Ru(3)*	-
Ru(4)*	-
H(14)	0.2042
Plane 4 : 14.4453x + 0.8411y - 5.4006z = -0.3679	
Ru(2)*	-
Ru(3)*	-
Ru(4)*	-
H(24)	-0.2594

Section 4.3 The Structures of $[Ru_6(CO)_{18}]^{2-}$ and $[Ru_6H(CO)_{18}]^-$

4.3.1 Preamble

The dihydride $H_2Ru_6(CO)_{18}$ was one of the first clusters with 86 valence electrons to be prepared and X-ray structural analysis showed an octahedral metal geometry with three terminal carbonyls per metal, and the H-ligands bridge two opposite faces of the metal polyhedron. The structure of the dianion $[Ru_6(CO)_{18}]^{2-}$ was assumed to be derived from that of $H_2Ru_6(CO)_{18}$, and this model with 3 terminal CO's per Ru has been widely used to illustrate the fundamentals of skeletal electron counting.[19] This geometry with only terminal carbonyl ligands has recently been found in the osmium anions $[Os_6(CO)_{18}]^{2-}$ and $[HOs_6(CO)_{18}]^-$,[20] and also in $[Ru_6H(CO)_{18}]^-$ (*vide infra*). However the i.r. $[\nu(CO)]$ spectrum of $[Ru_6(CO)_{18}]^{2-}$ is quite unlike that of its Os analogue suggesting that they are not isostructural.[21]

The monoanion $[Ru_6H(CO)_{18}]^-$ is obtained on acidification of $[Ru_6(CO)_{18}]^{2-}$ or $[HRu_3(CO)_{11}]^-$,[22] and the combined evidence of ^1H n.m.r. studies, i.r. $[\nu(CO)]$ spectra, variable-temperature ^{13}C n.m.r. and incomplete X-ray analyses of two modifications of the $[(Ph_3P)_2N]^+$ salt, were only consistent with the hydrogen atom occupying a novel environment within the Ru_6 octahedron.[21]

4.3.2 Data Collection

4.3.21 $[Ph_3MeP]_2^+ [Ru_6(CO)_{18}]^{2-}$

Crystals of $[Ph_3MeP]_2^+ [Ru_6(CO)_{18}]^{2-}$ (XI) suitable for X-ray analysis were provided by Dr. P.F. Jackson, University of

Cambridge. The crystal selected for data collection was of dimensions 0.24 x 0.15 x 0.13 mm. Unit cell dimensions were determined and data collected and processed by the methods described in Subsection 2.2.2 using a scan width of 0.90°. The unit cell dimensions and crystal system were not the same as those found for the $[Ph_3MeP]^+$ salt of $[Os_6(CO)_{18}]^{2-}$ (ref.20) so the compounds are not isomorphous.

Table 4.6 Crystal data for the $[Ph_3MeP]^+$ salts of $[Ru_6(CO)_{18}]^{2-}$ (XI) and $[Os_6(CO)_{18}]^{2-}$

	(XI)	$[Os_6(CO)_{18}]^{2-}$
M_r	1665.3	2200.0
Crystal system	Triclinic	Trigonal
Space group	$P\bar{1}$	$P\bar{3}1c$
a/Å	25.084	12.045
b/Å	11.296	12.045
c/Å	10.663	24.767
α/°	79.44	90
β/°	102.57	90
γ/°	93.61	120
U/Å^3	2898.1	3111.8
D_c/g cm^{-3}	1.91	2.35
Z	2	2

Following data collection several relatively intense reflections were measured at 20° intervals around their diffraction vector (Ψ). The variation in intensity was not significant ($\not> 3\sigma$); this and the small value of μ (14.87 cm^{-1}) indicated that absorption corrections could be reasonably neglected.

Laue equivalent reflections were averaged to give 7799 unique data [$I \geqslant 3\sigma(I)$] for (XI).

4.3.22 $[(Ph_3P)_2N]^+ [Ru_6H(CO)_{18}]^-$

Data collection and processing was performed on a crystal of $[(Ph_3P)_2N]^+ [Ru_6H(CO)_{18}]^-$ {triclinic modification, (XII)} by Dr. M.McPartlin, Polytechnic of North London, using the methods described in Subsection 2.2.2. No absorption corrections were applied (μ = 14.95 cm^{-1}). Laue equivalent reflections were averaged to give 9165 unique data [$I \geqslant 3\sigma(I)$].

Crystal data for(XII) is given in Table 4.7.

4.3.23 $[Ph_4As]^+ [Ru_6H(CO)_{18}]^-$

Crystals of $[Ph_4As]^+ [Ru_6H(CO)_{18}]^-$ (XIII) suitable for X-ray analysis were provided by Dr. P.F. Jackson, University of Cambridge. The crystal selected for data collection was of dimensions 0.32 x 0.26 x 0.16 mm. Unit cell dimensions were determined, and data collected by the methods described in Subsection 2.2.2 using a scan width of 1.00°.

Although Ψ scans performed after data collection showed very small variations in intensity for each reflection examined (μ = 24.45 cm^{-1}), absorption corrections were applied to the data. This was necessary because a combined refinement of a single set of positional and thermal parameters was to be carried out for (XIII) (see Subsection 4.3.33) using the X-ray data and neutron data collected as described below. For this combined refinement technique it is desirable to minimize all systematic errors in the data.

Laue equivalent reflections were averaged to give 7344 unique data [$I \geqslant 3\sigma(I)$]. Crystal data for (XIII) is given in Table 4.7.

Table 4.7 Crystal data for the $[(Ph_3P)_2N]^+$ (XII) and $[Ph_4As]^+$ (XIII) salts of $[Ru_6H(CO)_{18}]^-$

	(XII)	(XIII)
M_r	1650.2	1495.0
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	18.083	16.393
b/Å	19.101	19.426
c/Å	19.238	15.023
α/°	117.70	90
β/°	78.13	100.64
γ/°	97.05	90
U/Å^3	5767.0	4701.8
D_c/g cm^{-3}	1.90	2.11
Z	4	4

Neutron data were collected with a larger crystal of the $[Ph_4As]^+$ salt (2.5 x 1.5 x 1.0 mm) on the D8 - facility at the I.L.L., Grenoble. The crystal was initially aligned about the b axis by photographic means, then the goniometer was transferred to the four circle neutron diffractometer and the crystal accurately centred by eye. The orientation matrix was determined from a least-squares fit of the angular measurements of 15 strong high angle reflections. Intensity data were recorded in the range $0 < \theta < 45°$ at 296 K using neutrons of wavelength 1.2641(4) Å [a Cu (200) reflection]. Due to a slight defect in the monochromator the peaks had an unusually wide non-Gaussian profile. The $\Delta\omega/\Delta\theta$ relationship for several strong reflections suggested the use of the ω-scan technique in the range $0 < \theta < 12°$, an ω-θ scan mode in the range $12 < \theta < 16°$ and a ω- 2θ scan mode for θ angles greater than 16°. Variable scan and step widths were used; these were chosen initially from an inspection of the profiles of a few reflections, but as more data were collected better values were obtained from the resolution curve (peak width plotted

against θ) to optimize the peak/background ratio for successive data. Three standard reflections were measured after every 100 reflections during data collection and no significant variations ($> 3\sigma$) in intensity were observed from the average values. Values for the intensity of each reflection were obtained using the minimal $\sigma(I)/I$ method for step scan measured data,[23] but no effort was made to optimize the peak/background ratio. No absorption ($\mu = 0.65\ cm^{-1}$) or extinction corrections have been applied to the neutron data, and no allowance has been made for the $\lambda/2$ component of the beam which is estimated to be 0.4% on I. Laue equivalent reflections were averaged to give 2261 independent observed neutron data $[I \geqslant 2.5\sigma(I)]$.

4.3.3 Structure Solution and Refinement

The scattering factors used, the function minimized during least-squares refinement, and definitions of the discrepancy indices quoted in the text are given in Subsection 2.2.3.

4.3.31 $[Ph_3MeP]^+_2\,[Ru_6(CO)_{18}]^{2-}$

The intensity data for $[Ph_3MeP]_2^+\,[Ru_6(CO)_{18}]^{2-}$ (XI) showed only $\bar{1}$ Laue symmetry; the centric triclinic space group $P\bar{1}$ was assumed and confirmed by the satisfactory solution and refinement of the structure. The metal atoms were found from a Patterson map, the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. Blocked full matrix refinement was used with the atoms grouped as follows: block 1, the ruthenium atoms; block 2, the carbonyl ligands; block 3, the first $[Ph_3MeP]^+$ cation; block 4, the second cation. Refinement converged at $R = 0.0476$, $R_w = 0.0551$, and $R_G = 0.0647$ using anisotropic thermal parameters for the ruthenium and phosphorus

atoms. The phenyl rings of the $[Ph_3PMe]^+$ cations were treated as rigid groups [d(C-C) = 1.395 Å] and the phenyl hydrogens were included in geometrically calculated positions [d(C-H) = 1.08 Å]. The methyl groups were also refined as rigid groups [d(C-H) = 1.08 Å, H-C-H = 109.5°]. Weights were assigned to reflections as $w = 2.6651/\sigma^2 F$ (see Subsection 2.2.3). A final difference-Fourier synthesis revealed several residual maxima in the region of the oxygen atoms, none of which had a height greater than 1.2 $eÅ^{-3}$.

Final positional and thermal parameters for $[Ph_3MeP]_2^+ [Ru_6(CO)_{18}]^{2-}$ are given in Appendix 11.

4.3.32 $[(Ph_3P)_2N]^+ [Ru_6H(CO)_{18}]^-$

The intensity data for $[(Ph_3P)_2N]^+ [Ru_6H(CO)_{18}]^-$ (XII) showed $\bar{1}$ Laue symmetry only; the centric triclinic space group $P\bar{1}$ was assumed* and confirmed by the satisfactory solution and refinement of the structure. The 12 ruthenium atoms of the asymmetric unit were located by direct methods using Σ_2 sign expansion as discrete Ru_6 octahedra. Least-squares refinement of their positional and isotropic thermal parameters gave R = 0.28. Four of the Ru atoms within one octahedron showed relatively large isotropic thermal parameters, indicative of disorder. Subsequent difference-Fourier syntheses revealed the atoms of the two independent $[(Ph_3P)_2N]^+$ cations and all the carbonyl ligands associated with cluster (1) of the anion, but only six carbonyl groups of cluster (2) could be conclusively identified although

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* The primitive cell had a large α angle (Table 4.7), so it was converted into a centred cell to avoid correlations during refinement ($C\bar{1}$ cell: a = 19.248, b = 33.912, c = 18.081 Å, α = 91.23, β = 101.86, γ = 92.53°).

all the oxygen atoms appeared to be present. At this stage a difference-Fourier map was computed in the region of the apparently disordered Ru atoms, these ruthenium atoms being omitted from the structure factor calculations. This revealed that each peak, originally assigned as ruthenium sites of full occupancy, could be resolved into two components ca. 1 Å apart. Thus the four most intense independent maxima were designated Ru(1A), Ru(2A), Ru(5A), and Ru(6A), the remaining four high peaks Ru(1B), Ru(2B), Ru(5B), and Ru(6B). The isotropic thermal parameter for each of these sites was initially constrained to be equal to the same free variable; refinement of their population parameters yielded values in the range 0.58 - 0.60 for the 'A' set and 0.40 - 0.42 for the 'B' set of atoms. Subsequent difference-Fourier syntheses utilizing this model revealed suitable maxima for the missing disordered carbon atoms of cluster (2) of the anion. The component pairs of these carbon atoms were too close to one another to be refined independently, so they were placed in calculated positions [d(Ru-C)/d(Ru-O) = 0.615, Ru-C-O = 180 °], but their atomic coordinates were recalculated after each cycle of refinement if large shifts were observed for the oxygen atoms to which they were attached. The disorder of cluster (2) apparently arises from two different orientations [(2A) and (2B), having occupancies of ca. 0.6 and 0.4 respectively] that are approximately related by a non-crystallographic two-fold axis which lies in the plane of the disordered atoms, and passes through the midpoints of Ru(2A) ... Ru(2B) and Ru(5A) ... Ru(5B) (Figure 4.8). Under this operation Ru(3C) and its associated carbonyl ligands would exchange position with Ru(4C) and its CO groups, therefore the sites of these atoms are of full occupancy. Significantly, the remaining oxygen atoms also coincide in position for the two orientations, indicating that the packing is effectively determined by these peripheral oxygen atoms and is independent of the arrangement of the internal atoms of the cluster. A similar type of disorder has been observed for several other smaller polynuclear carbonyl clusters.[24] Crucially, clusters (1), (2A), and (2B) appear to be stereochemically equivalent (Figure 4.9) within the accuracy limits imposed by the disorder. The structure was further refined with the occupancy (p_A) of the disordered atoms

of orientation (2A) allowed to vary between 0 and 1, and the occupancy of the disordered (2B) set of atoms was set to $1-p_A$. The isotropic temperature factors of the disordered part of cluster (2) were constrained to be equal to two independent free variables. Similarly the isotropic temperature factors of each pair of disordered Ru atoms were constrained to be equal to a separate free variable. In the final cycles of blocked full-matrix least-squares refinement the Ru atoms of full occupancy were assigned anisotropic thermal parameters. The phenyl rings of the $[(Ph_3P)_2N]^+$ cations were treated as rigid groups [d(C-C) = 1.395 Å], no allowance being made for the H atoms in the structure factor calculations. This resulted in R = 0.0681 and R_w = 0.0687 and weights were assigned to reflections as $\underline{w} = 1.0000/\sigma^2 F$ (see Subsection 2.2.3). A final difference-Fourier map showed several residual maxima in the region of the disordered ruthenium atoms, none of which had a height greater than 1.7 $eÅ^{-3}$.

Final positional and thermal parameters for $[(Ph_3P)_2N]^+ [Ru_6H(CO)_{18}]^-$ (XII) are given in Appendix 12.

4.3.33 $[Ph_4As]^+ [Ru_6H(CO)_{18}]^-$

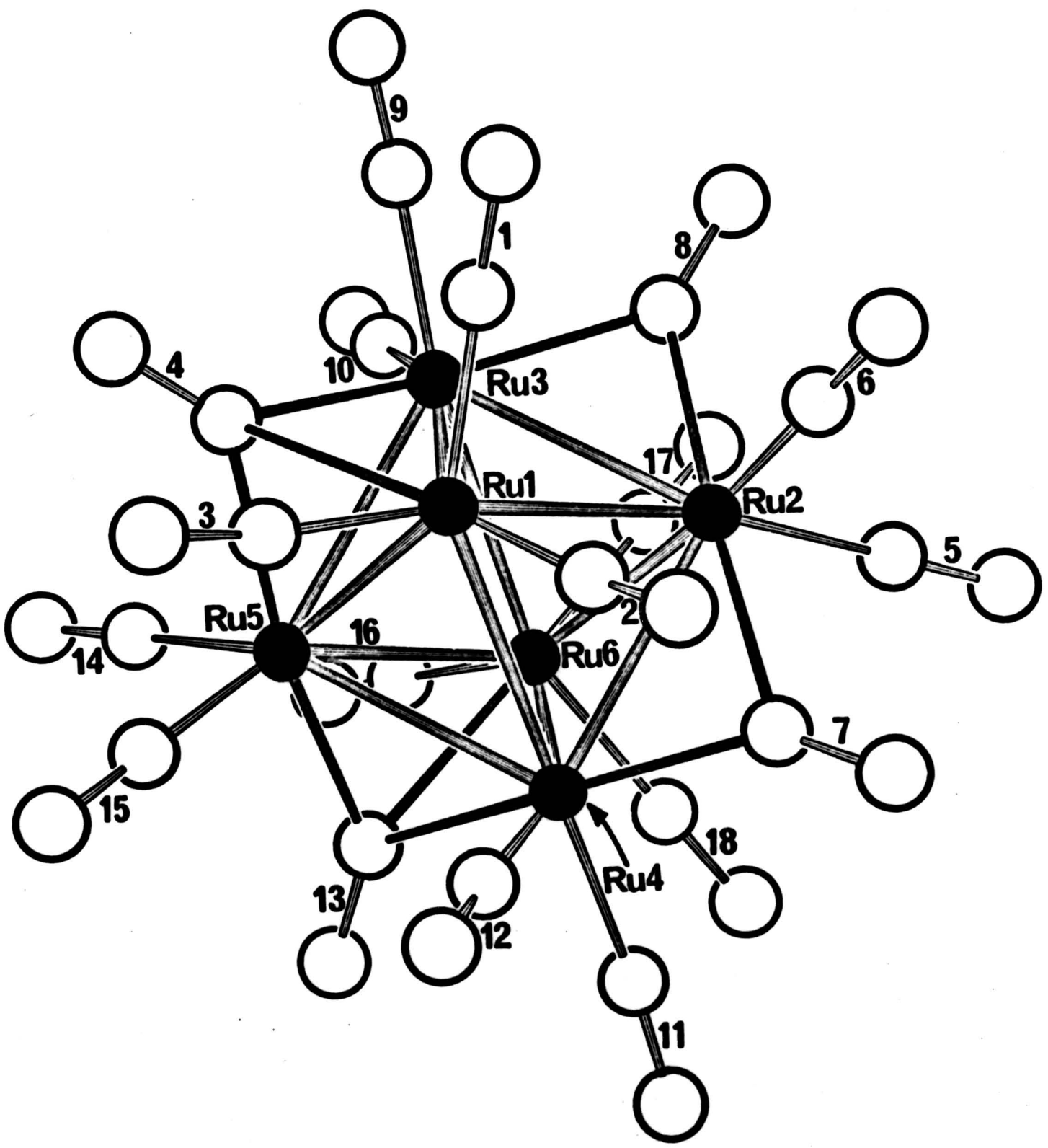
Systematic absences (0k0 for k = 2n + 1 and h0l for l = 2n + 1) uniquely indicated the space group $P2_1/c$ for $[Ph_4As]^+ [Ru_6H(CO)_{18}]^-$ (XIII) but the unit cell was transformed into one containing a smaller β angle for data collection. This alternative setting, which corresponds to the non-standard space group $P2_1/n$, was chosen to avoid correlations during refinement of the structure. The ruthenium atoms were located by direct methods using Σ_2 sign expansion, the remaining non-hydrogen atoms were located from subsequent difference-Fourier synthesis. After several cycles of refinement a difference-Fourier map calculated for (XIII) showed a pronounced peak close to four of the ruthenium atoms Ru(1), Ru(2), Ru(5), and Ru(6). These features, which were ca. 4 $eÅ^{-3}$ in height, wete interpreted in terms of a second orientation of

the cluster of low occupancy. Thus these four original ruthenium atoms were redesignated Ru(1A), Ru(2A), Ru(5A), and Ru(6A) and their occupancies were coupled in the least-squares refinement to a free variable p_A which refined to 0.9015(11). The common occupation factor of the ruthenium sites of minor occupancy, Ru(1B), Ru(2B), Ru(5B), and Ru(6B) was set to $1-p_A$. The other ruthenium positions, Ru(3) and Ru(4), were of full occupancy. The disorder of the cluster was therefore assumed to be of a similar nature to that observed for one independent cluster of the $[(Ph_3P)_2N]^+$ salt (see previous Subsection). Therefore the carbonyl positions associated with Ru(3) and Ru(4) were assigned occupation factors of unity, as were the remaining O atoms of the cluster. The occupation factors of the carbon atoms attached to the 'A' set of ruthenium atoms was set to $1-p_A$ by analogy to the $[(Ph_3P)_2N]^+$ salt of the anion. Blocked full matrix refinement was carried out with the atoms grouped as follows: block 1, the ruthenium atoms; block 2, half of the carbonyl ligands; block 3, the remainder of the CO ligands; block 4, the atoms of the $[Ph_4As]^+$ cation. Refinement converged at $R = 0.0446$, $R_w = 0.0495$, and $R_G = 0.0581$ using anisotropic thermal parameters for all atoms of the anion and the As atom of the cation. The phenyl rings were treated as rigid groups [d(C-C) = 1.395 Å] with the phenyl hydrogens included in geometrically calculated positions [d(C-H) = 1.08 Å]. At this stage a difference-Fourier synthesis calculated using all the data unexpectedly revealed the position of the hydride ligand at the centre of the Ru_6 octahedron, the peak having a height of 0.50 $eÅ^{-3}$. Its location was included in the model and its positional and thermal parameters successfully optimized <u>via</u> least-squares refinement. This yielded the following final discrepancy indices: $R = 0.0446$, $R_w = 0.0495$, and $R_G = 0.0580$. Weights were assigned to reflections as $\underline{w} = 1.2869/\sigma^2F$ (see Subsection 2.2.3). A final difference-Fourier synthesis showed a few residual maxima in the region of the ruthenium atoms, the largest of which had a height of 1.6 $eÅ^{-3}$.

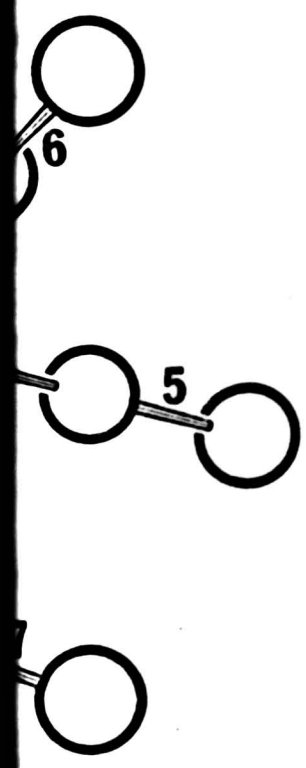
Final positional and thermal parameters for $[Ph_4As]^+ [Ru_6H(CO)_{18}]^-$ (XIII) are given in Appendix 13.

Subsequently a combined refinement of the structure was carried out in collaboration with Dr. P.R. Raithby, University of Cambridge, using the X-ray data and neutron data collected and processed as described in Subsection 4.3.23. The method of refinement was that of Sheldrick,[25] the results of which are given in the following Subsection.

Figure 4.7 The structure of the dianion $[Ru_6(CO)_{18}]^{2-}$.



$_6(CO)_{18}]^{2-}$.



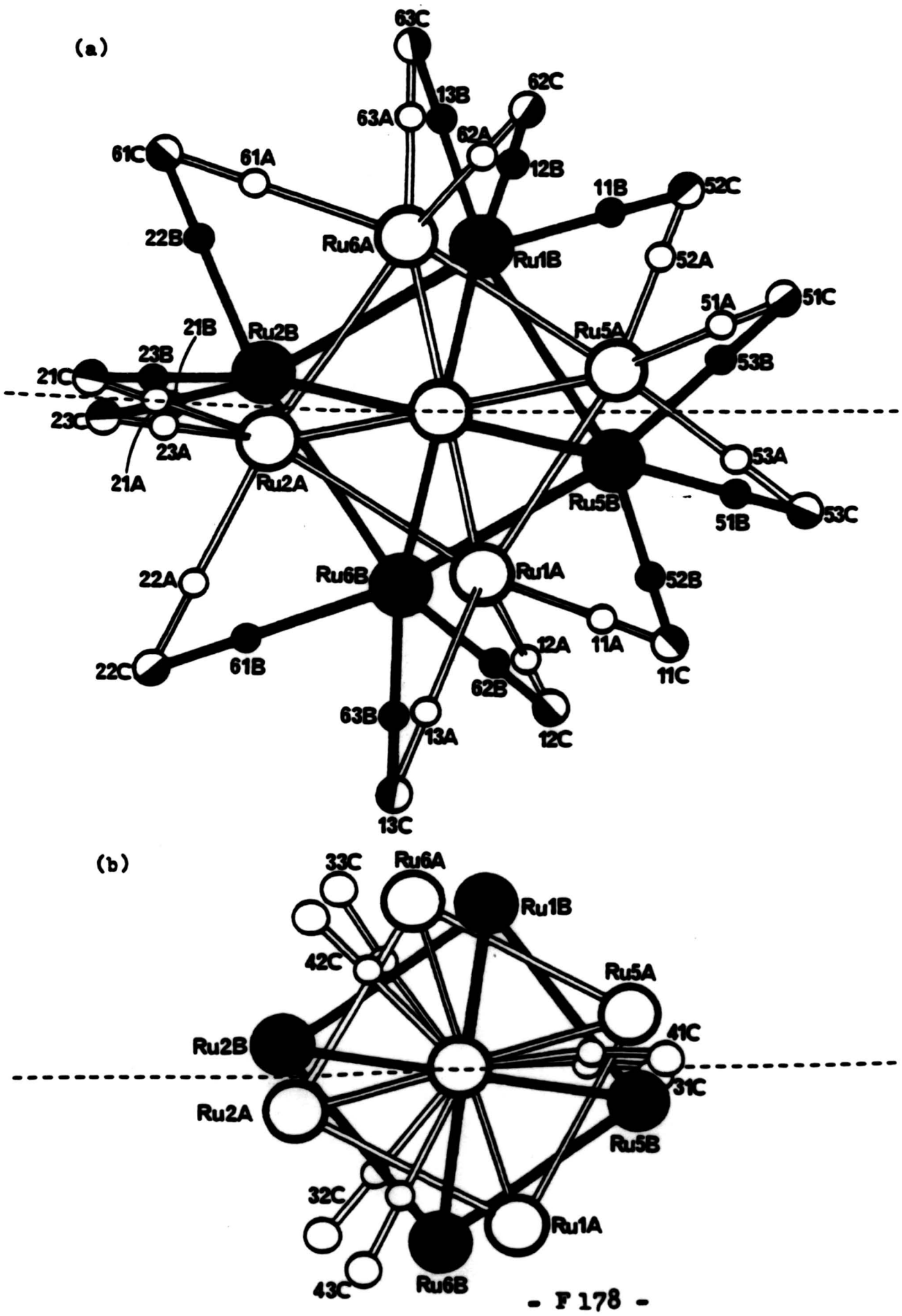
4.3.4 Discussion

The structure of the dianion in $[Ph_3MeP]_2^+ [Ru_6(CO)_{18}]^{2-}$ (XI) is shown in Figure 4.7 and the bond distances and angles are given in Tables 4.8 - 4.10. Although the M_6 core is octahedral, similar to that found in the osmium analogue $[Os_6(CO)_{18}]^{2-}$,[20] the carbonyl distribution is quite unlike that of $[Os_6(CO)_{18}]^{2-}$ which has only terminal CO's [Figure 4.9(a)]. Thus of the eighteen carbonyl ligands two are asymmetrically edge bridging [Ru(2) - C(7) = 2.201(7), Ru(4) - C(7) = 1.996(7); Ru(2) - C(8) = 2.059(8), Ru(3) - C(8) = 2.110(7) Å], two are asymmetrically face bridging [Ru(1) - C(4) = 2.576(7), Ru(3) - C(4) = 2.109(8), Ru(5) - C(4) = 2.124(7); Ru(4) - C(13) = 2.334(7), Ru(5) - C(13) = 2.008(7), Ru(6) - C(13) = 2.452(8) Å], while the remaining 14 CO groups are terminal. Although it is valid for electron counting procedures to consider all carbonyls as terminal,[19] their precise disposition is of interest in the light of recent arguments present by Johnson (see Subsection 1.4.2) to rationalize the geometry of simple binary carbonyls. Indeed in the $[M_6(CO)_{18}]^{2-}$ dianions (M = Ru,Os) the CO polyhedra appear to be similar and the differences in structure are the result of a small rotation of the M_6 unit within this polyhedron.[26]

The structure of the monoanion in $[(Ph_3P)_2N]^+ [Ru_6H(CO)_{18}]^-$ (XII) is shown in Figures 4.9(b) - 4.9(d) and the bond distances and angles are given in Tables 4.11 - 4.13. Despite disordering of one of the independent clusters (see Subsection 4.3.32) the structure of $[Ru_6H(CO)_{18}]^-$ is established unambiguously; the anion has approximate non-crystallographic D_3 symmetry with three terminal CO's per metal atom, and the carbonyl distribution bears a marked resemblance to that found in $[Os_6(CO)_{18}]^{2-}$ which has an overall structure of exact D_3 symmetry[28] [Figure 4.9(a)]. The Ru_6 core has two equivalent parallel faces that are approximately equilateral

Figure 4.8 (a) The disordered cluster (2) of $[Ru_6H(CO)_{18}]^-$ ($[(Ph_3P)_2N]^+$ salt) viewed down the ordered Ru atoms Ru(4C),Ru(3C). The two components (2A) and (2B) are related by a pseudo two fold axis passing through the midpoints of Ru(2A)..Ru(2B) and Ru(5A)..Ru(5B). All of the O atoms are common to both orientations so they have been labelled (C) and numbered to correspond to the C atoms of the major component (2A). For clarity the six ordered CO's bonded to Ru(3C) and Ru(4C) have been omitted.

(b) The orientation of the six ordered CO's in cluster (2).



$(CO)_{18}]^-$ ($[(Ph_3P)_2N]^+$
ms Ru(4C),Ru(3C). The
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ordered CO's bonded
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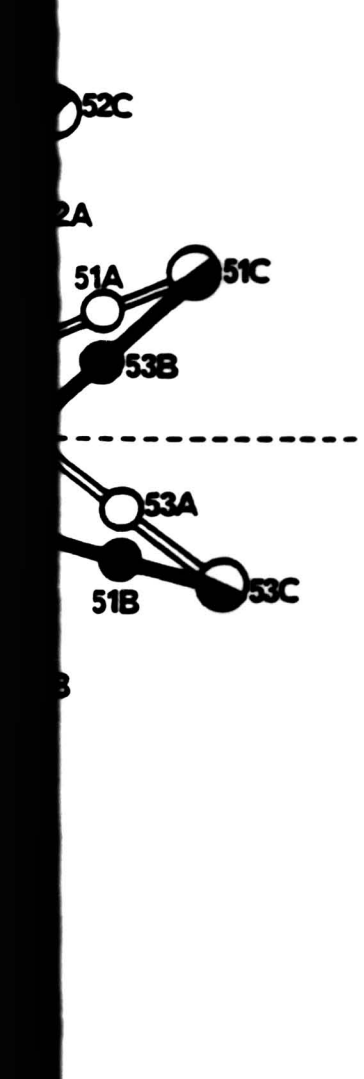
CO's in cluster (2).



[mean Ru-Ru, * 2.877(13) Å], these are slightly twisted from O_h symmetry so that the remaining bond lengths* are alternately long [mean 2.924(3) Å] and short [mean 2.839(6) Å]. The structure of $[Ru_6H(CO)_{18}]^-$ is quite unlike that of $[HOs_6(CO)_{18}]^-$ where the carbonyl ligands on one face are pushed back to accommodate the external H ligand;[20] this confirmed the evidence of the solution and solid i.r. [ν(CO)] spectra which showed just one broad band consistent with the presence of six equivalent $Ru(CO)_3$ groups.[21] These spectra were significantly different from that of $[HOs_6(CO)_{18}]^-$, but closely resembled (in pattern) that of the highly symmetrical $[Os_6(CO)_{18}]^{2-}$ dianion.[21] Thus there was no crystallographic or spectroscopic evidence for an external H atom in $[Ru_6H(CO)_{18}]^-$. Furthermore no $^{13}C-^1H$ n.m.r. coupling could be detected, and the unusual low field signal (-6.41 τ) in the ^1H n.m.r. spectrum was attributed to a novel hydrogen environment <u>within</u> the Ru_6 octahedron.[21] This assignment proved to be controversial. Recent neutron diffraction studies of $[Ni_{12}H_n(CO)_{21}]^{(4-n)-}$ (n = 1 or 2)[27] showed that the hydrogen ligands are also interstitial, being located in distorted octahedral cavities, but the ^1H spectra show the normal high field shifts (n = 1, 34.0 τ; n = 2, 28.0 τ). This promoted the conclusion, in a review published by Chini <u>et al.</u>,[28] that the hydrogen atom in $[Ru_6H(CO)_{18}]^-$ was not interstitial but associated with a carbonyl ligand. The authors made a similar assignment for $[Co_6H(CO)_{15}]^-$ (-13.2 τ) and proposed that a particularly low field ^1H n.m.r. shift is diagnostic of a new class of cluster hydrides with direct carbonyl-hydrogen linkages. (A recent neutron analysis has shown that this anion also contains an interstitial hydrogen atom[29]). In addition, from consideration of the weakening effect of H ligands on M-M bonds, they concluded that interstitial hydrides would not occur in M_6 clusters, except in the presence of μ_2 - or μ_3- carbonyl ligands .

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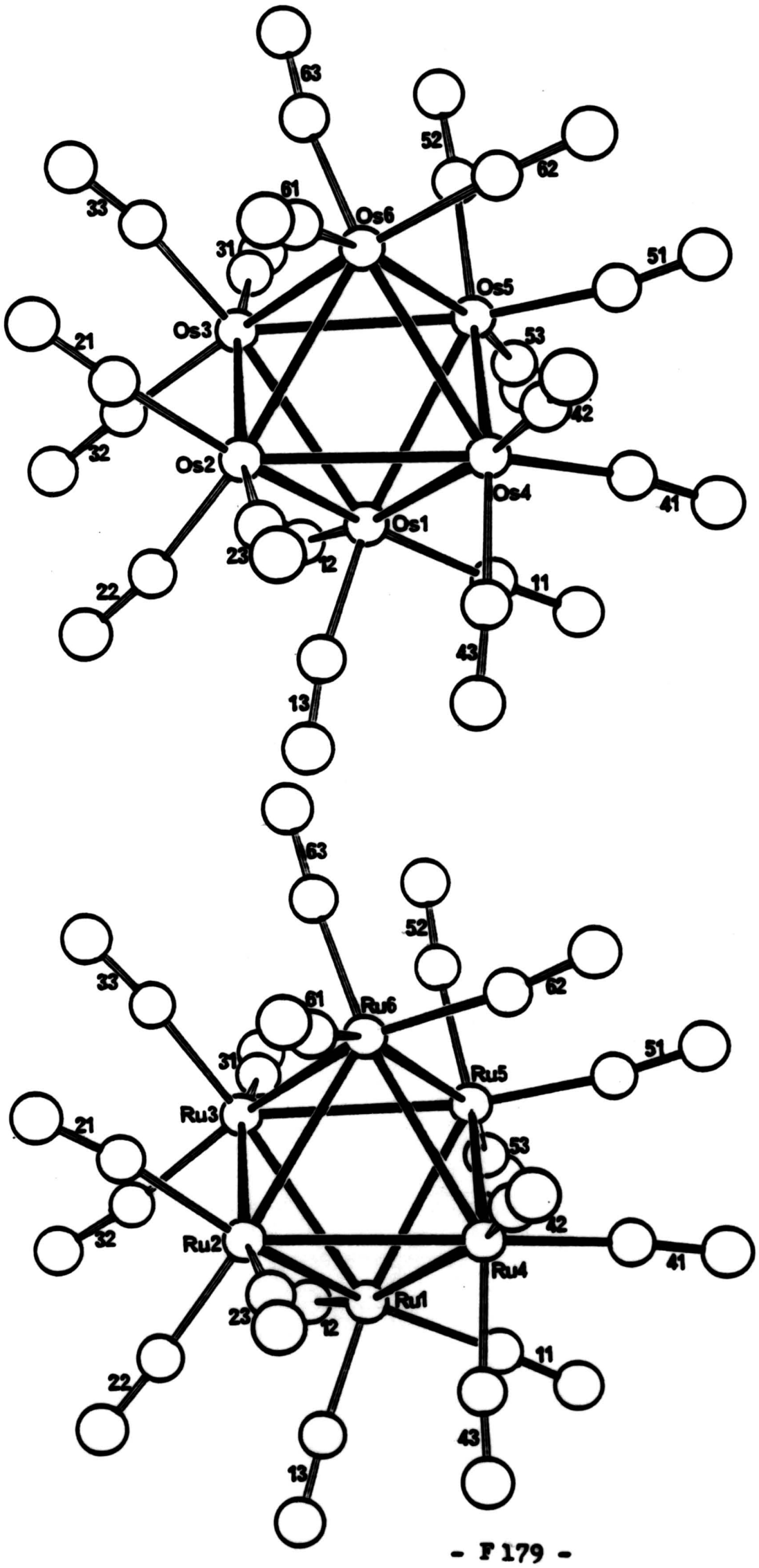
* The bond lengths refer to the ordered cluster (1), but the same pattern is observed in the disordered cluster (2).

Figure 4.9 (a) $[Os_6(CO)_{18}]^{2-}$ (b) $[Ru_6H(CO)_{18}]^{-}$ cluster 1

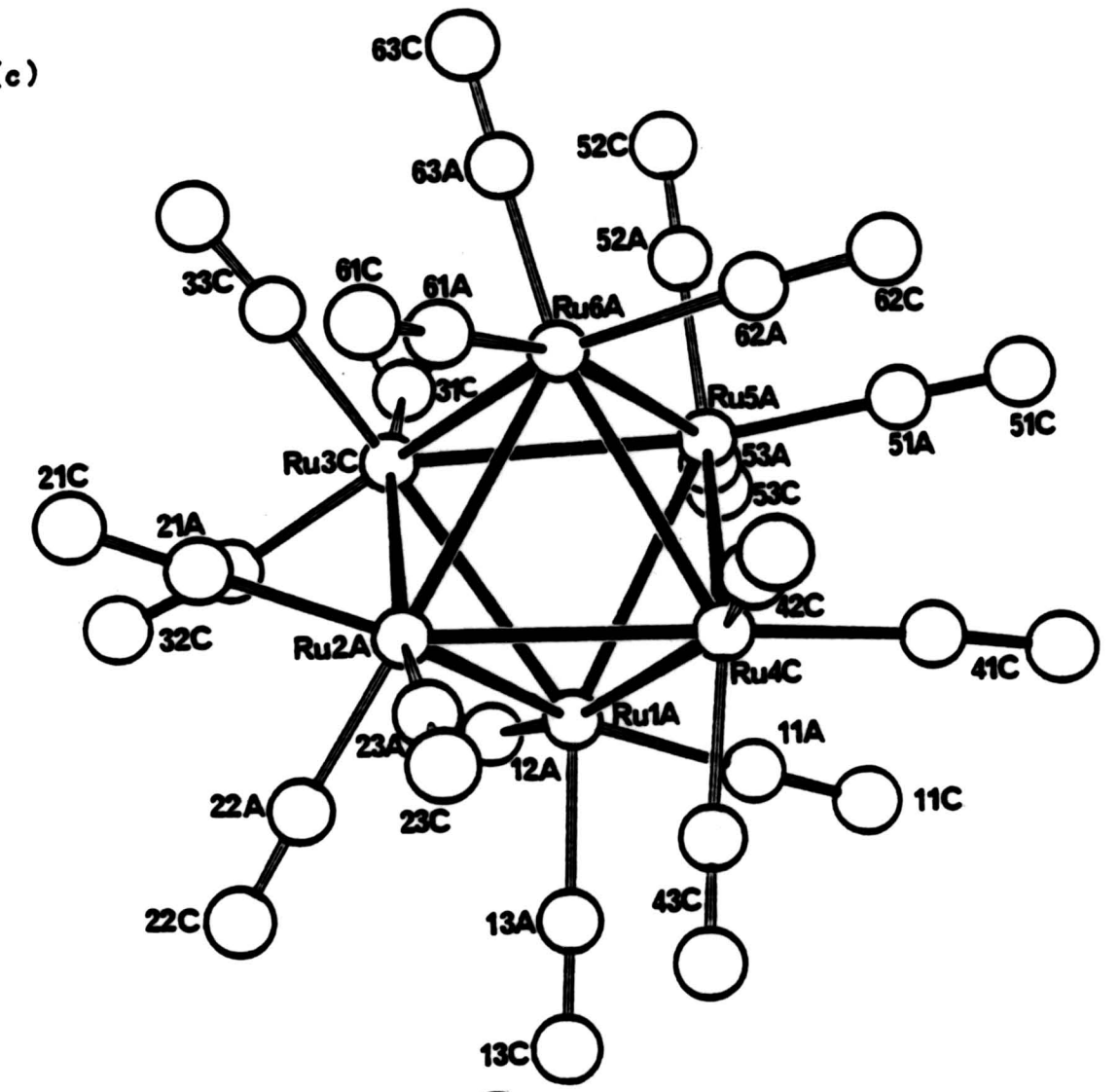
(a)



(b)

Figure 4.9(cont.) $[Ru_6H(CO)_{18}]^-$: (c) Cluster 2A (d) Cluster 2B, see Figure 4.8 for labelling scheme.

(c)



(d)

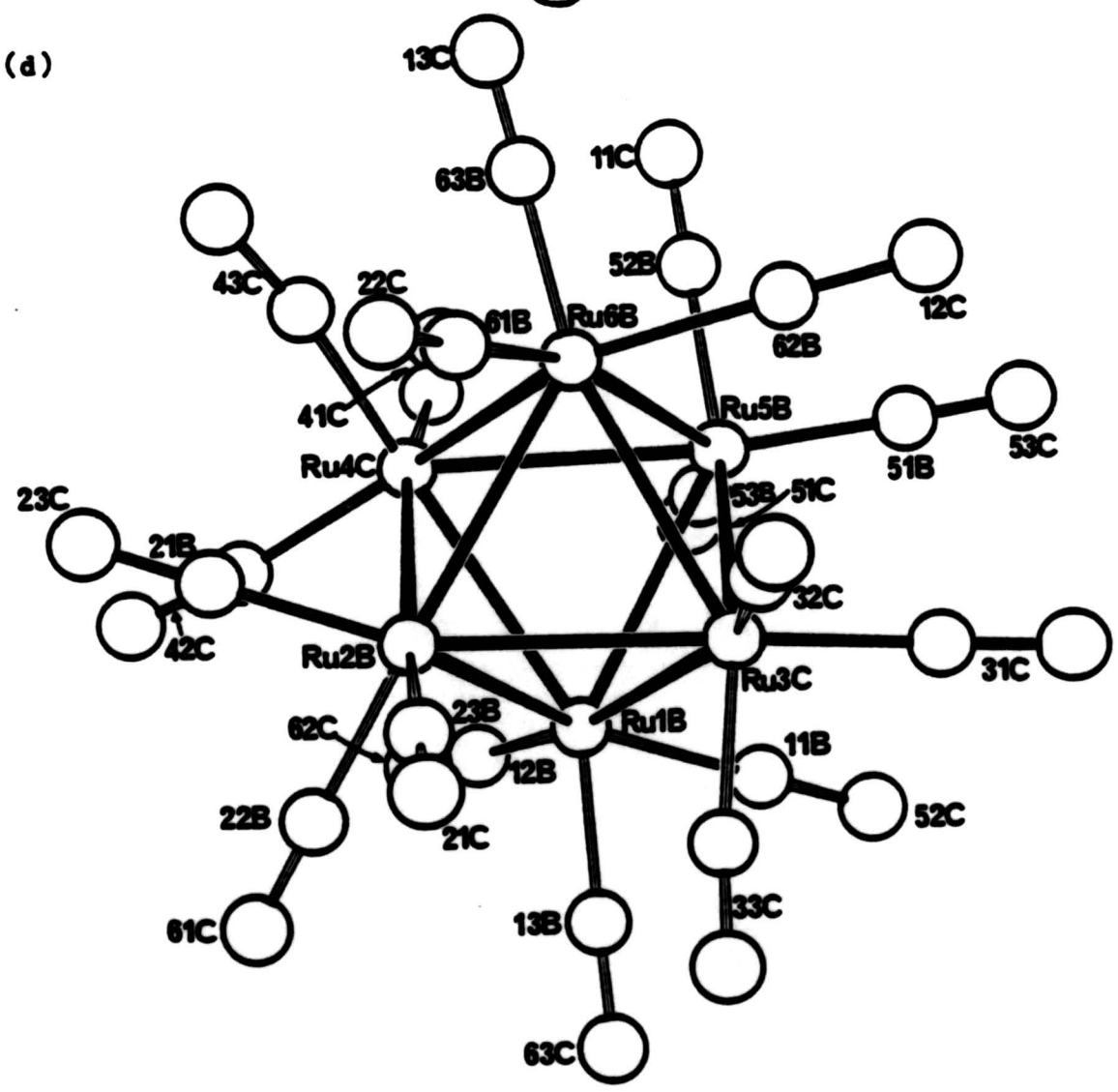
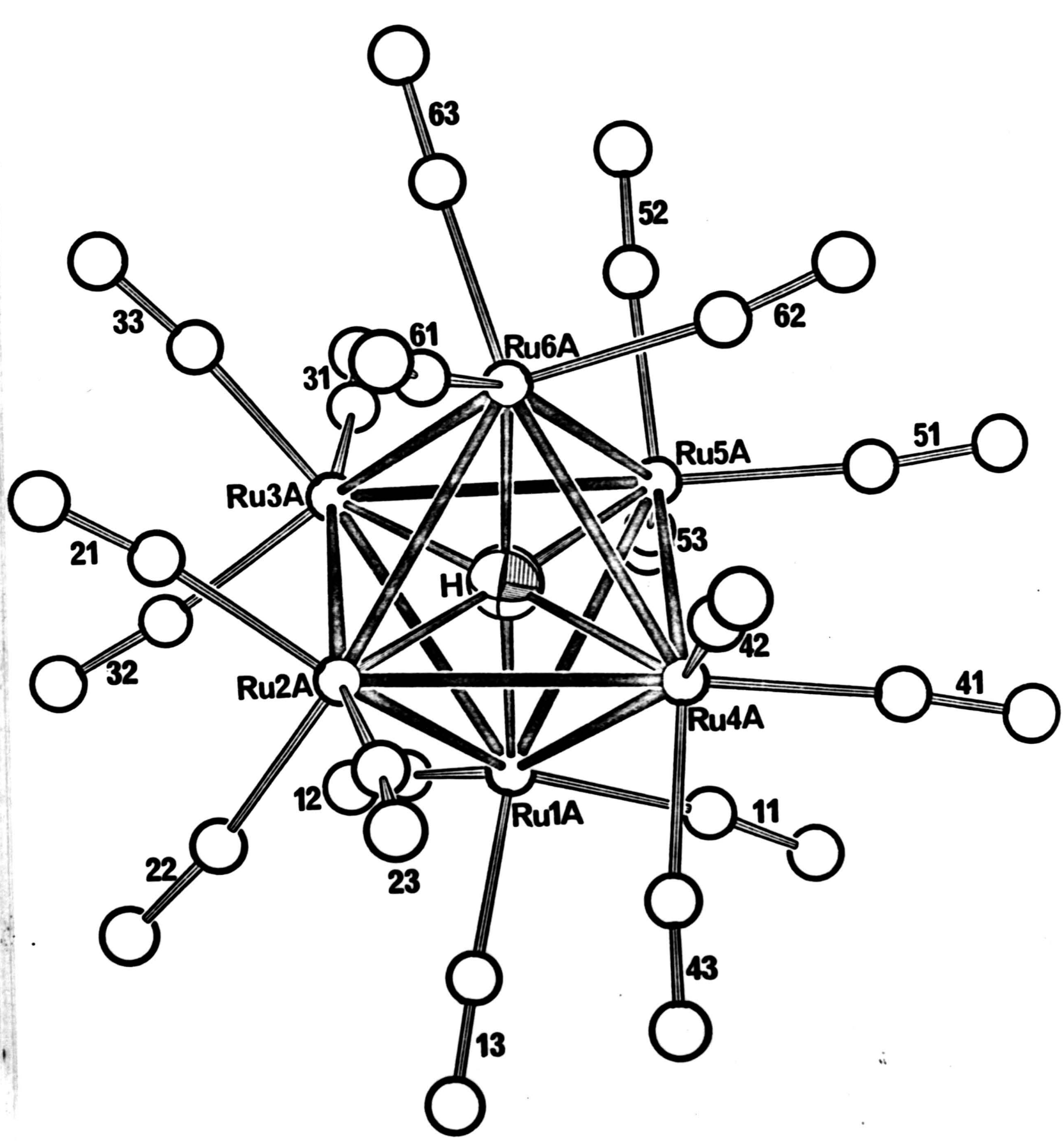


Figure 4.10 The structure of the anion in $[Ph_4As]^+[Ru_6H(CO)_{18}]^-$. Mean Ru-H = 2.04 Å, the probability ellipsoid for the hydrogen atom was obtained from the combined X-ray/neutron refinement. The 'B' Ru atoms have been omitted for clarity.



$_4As]^+[Ru_6H(CO)_{18}]^-$.
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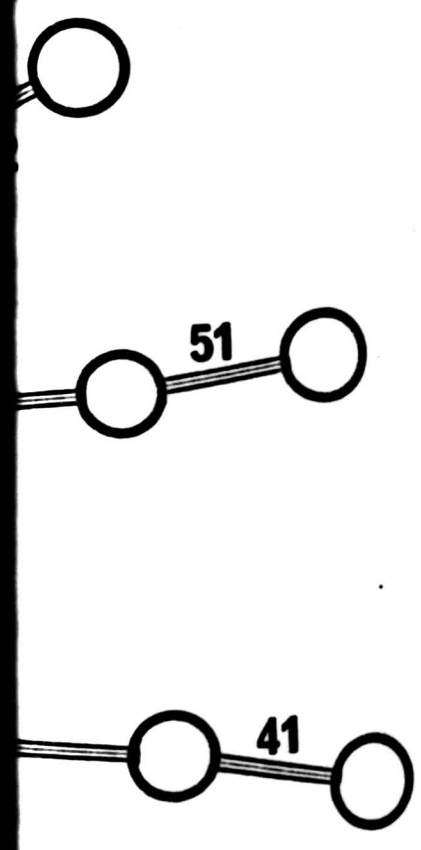

Recently with accurate X-ray data hydrogen atoms have occasionally been located directly in carbonyl clusters with up to four metal atoms. The $[Ph_4As]^+$ salt of the $[Ru_6H(CO)_{18}]^-$ anion (XIII) gave very good X-ray data which afforded ready location of the hydride at the centre of the Ru_6 octahedron (Figure 4.10). The positional and isotropic thermal parameters were successfully refined giving a mean Ru-H distance of 2.04(17) Å; thus the interstitial site of the hydrogen ligand is confirmed unequivocally. The other bond distances and angles for (XIII) are given in Tables 4.14 - 4.16. As in the $[(Ph_3P)_2N]^+$ salt, (XII), the anion has approximate D_3 symmetry [mean Ru-Ru "long" = 2.920(35), mean Ru-Ru "short" = 2.840(31), mean Ru-Ru "parallel faces" = 2.878(18) Å] with only terminal carbonyl ligands present (Figure 4.10), so clearly octahedral clusters containing interstitial H atoms are <u>not</u> too unstable to exist without the presence of μ_2- or μ_3- CO groups. Indeed the $[Ru_6H(CO)_{18}]^-$ anion is the first hexanuclear Ru species to be obtained with no external bridging ligands so the role of the interstitial hydrogen ligand may be to stabilize an otherwise unfavourable geometry for this metal. Significantly the stability of polynuclear carbonyl clusters of other metals seems to be enhanced if interstitial atoms are present.[30,31]

In view of the very large difference in the ^1H n.m.r. shifts observed for the interstitial hydride in the octahedral clusters compared to those for the embedded hydrogen atoms in the larger Ni clusters, it was important to obtain a more accurate location of the H atom within the Ru_6 octahedron of $[Ru_6H(CO)_{18}]^-$. A combined refinement of a single set of positional and thermal parameters was therefore carried out using the X-ray data and neutron data (See Subsection 4.3.23). The method used was that described by Sheldrick;[25] the results together with data reported for other interstitial hydrides are shown in Table 4.17.

Table 4.17 The M-H distances in $[Ru_6H(CO)_{18}]^-$ (from X-ray/neutron refinement) together with those reported for the other interstitial hydrides.

Interstitial hydride	d(M-H)/Å	^{1}H n.m.r.shift/τ
$[Co_6H(CO)_{15}]^-$	1.80-1.87(2)[a]	- 13.2[a]
$[Ru_6H(CO)_{18}]^-$	2.03-2.06(1)	-6.4
$[Ni_{12}H_2(CO)_{21}]^{2-}$	long 2.00(av.)[b]	28.0[b]
	short 1.84(av.)	
$[Ni_{12}H(CO)_{21}]^{3-}$	long 2.22(av.)[b]	34.0[b]
	short 1.72(av.)	

[a] Ref. 29 [b] Ref. 27

It should be noted that in $[Rh_{13}H_2(CO)_{24}]^{3-}$ and $[Rh_{13}H_3(CO)_{24}]^{2-}$ that H - atoms occupy square pyramidal sites on the cluster surface (as deduced from n.m.r.[32] and X-ray[33] analyses) and exhibit ^{1}H n.m.r. shifts of 36.7 and 39.3 τ respectively. The range of ^{1}H n.m.r. shifts for the four truly interstitial carbonyl cluster hydrides (Table 4.17) varies from -13.2 to 34 τ, a wide range compared to that of the hundreds of other reported compounds of the later transition metals where, in spite of a variety of modes of hydrogen bonding, this shift lies in the range 10-69 τ with very few exceptions.[34] Clearly interstitial hydrides are very sensitive to the exact symmetry of their surroundings so ^{1}H n.m.r. spectroscopy alone cannot be used alone as a diagnostic test for the position of an H-atom. In $[Ru_6H(CO)_{18}]^-$ and $[Co_6H(CO)_{15}]^-$ a nearly O_h symmetry is observed for the metals together with almost equal M-H distances; this environment is associated with large downfield shifts of the ^{1}H n.m.r. resonances. However the hydride ligands in the Ni_{12} clusters are in less symmetrical positions being much closer to the central hexa-metal plane than to the outer triangular metal set (Table 4.17), so that the hydrides may be considered as internally

face bridging three nickel atoms and only being weakly bonded to the other three.[27] This unsymmetrical bonding of the H-atoms is accompanied by ^{1}H n.m.r. signals in the normal upfield region (Table 4.17). It seems consistent with this trend that the "interstitial" hydride ligands in $[Rh_{13}H_n(CO)_{24}]^{(5-n)-}$ (n = 2 or 3), which are in incomplete octahedral (i.e. square pyramidal) sites on the surface of the clusters have ^{1}H n.m.r. shifts at even higher τ values of 36.7 and 39.3.[32]

Many transition metals absorb hydrogen to produce non-stoichiometric hydrides in which the hydrogen atoms occupy octahedral sites within the close-packed metal array. This is always accompanied by an expansion of the metal lattice; for example an octahedral site in the c.c.p. structure of palladium metal has a radius of 1.94 Å, but the radius of this site increases to 2.04 Å in $PdH_{0.7}$.[35] Of the polynuclear carbonyl species $[H_nRu_6(CO)_{18}]^{n-2}$ (n = 0,1,2) the dianion, with no hydride ligands, has an octahedral site radius of 2.02 Å. The introduction of an interstitial hydride ligand increases this to 2.04 Å in $[Ru_6H(CO)_{18}]^-$; significantly this value is close to the octahedral site radius observed in Ru_6(carbido) species (2.05 Å) and $[Os_{10}C(CO)_{24}]^{2-}$ (2.04 Å) (Section 3) and casts doubt on any assumption that increase in the M-M distances is merely a reflection of the size of the interstitial atom. From the limited data available for external Ru-H bond lengths it seems that a value of ca. 1.8 Å is typical, for example the eight μ_2-H-Ru lengths in $H_4Ru_4(CO)_{10}$ (diphos) average 1.76(5) Å.[11] This supports the conclusion that the space available in an "unexpanded" Ru_6 octahedral hole of radius 2.02 Å would be more than adequate to accommodate an interstitial H-atom. Thus it seems probable that the expansion in M-M bond lengths produced by external μ-H ligands and those produced by interstitial H (and C) atoms are related and are electronic in origin. It is consistent with this idea that on protonation of $[Ru_6H(CO)_{18}]^-$ to give $H_2Ru_6(CO)_{18}$, where the two hydrogen atoms are on the outside of the cluster,[36] their is a further expansion of the octahedral hole from 2.04 to 2.05 Å.

The clusters $[Ru_6(CO)_{18}]^{2-}$ and $[Ru_6H(CO)_{18}]^-$ are the

last members of the series $[H_nM_6(CO)_{18}]^{n-2}$ (n = 0,1,2; M = Ru or Os) to be structurally characterized, and interestingly no two analogous clusters have the same overall geometry although formally they have identical numbers of electrons for bonding. In the interstitial hydride $[Co_6H(CO)_{15}]^-$ the arrangement of CO's is also grossly different from that found in the parent $[Co_6(CO)_{15}]^{2-}$ dianion.[29] These observations suggest that the preferred structure depends on very subtle factors, and simple electronic arguments cannot be used to predict the overall geometry of the cluster with certainty, especially if hydride ligands are present.[20,37]

Table 4.8 Selected Interatomic Distances (Å) for (XI). E.s.d's are given in parentheses.

(a) Metal-Metal Bonds

Ru(1)-Ru(2)	2.862(1)
Ru(1)-Ru(3)	2.857(1)
Ru(1)-Ru(4)	2.886(1)
Ru(1)-Ru(5)	2.821(1)
Ru(2)-Ru(3)	2.818(1)
Ru(2)-Ru(4)	2.813(1)
Ru(2)-Ru(6)	2.891(1)
Ru(3)-Ru(5)	2.799(1)
Ru(3)-Ru(6)	2.889(1)
Ru(4)-Ru(5)	2.817(1)
Ru(4)-Ru(6)	2.860(1)
Ru(5)-Ru(6)	2.816(1)
Mean Ru-Ru	2.844(34)[a]

(b) Metal-Carbon and Carbon-Oxygen Distances

(i) Terminal CO's.

Ru(1)-C(1)	1.860(8)	C(1)-O(1)	1.173(10)
Ru(1)-C(2)	1.847(8)	C(2)-O(2)	1.166(10)
Ru(1)-C(3)	1.852(10)	C(3)-O(3)	1.170(13)

cont...

Ru(2)-C(5)	1.866(8)	C(5)-O(5)	1.147(11)
Ru(2)-C(6)	1.854(8)	C(6)-O(6)	1.156(10)
Ru(3)-C(9)	1.872(8)	C(9)-O(9)	1.152(10)
Ru(3)-C(10)	1.869(9)	C(10)-O(10)	1.154(11)
Ru(4)-C(11)	1.854(7)	C(11)-O(11)	1.163(10)
Ru(4)-C(12)	1.876(9)	C(12)-O(12)	1.147(12)
Ru(5)-C(14)	1.854(8)	C(14)-O(14)	1.161(10)
Ru(5)-C(15)	1.857(9)	C(15)-O(15)	1.169(12)
Ru(6)-C(16)	1.878(8)	C(16)-O(16)	1.170(11)
Ru(6)-C(17)	1.854(9)	C(17)-O(17)	1.180(12)
Ru(6)-C(18)	1.869(8)	C(18)-O(18)	1.169(11)
Mean Ru-C	1.862(10)[a]	Mean C-O	1.163(10)[a]

(ii) μ_2-CO's.

Ru(2)-C(7)	2.201(7)	C(7)-O(7)	1.169(9)
Ru(4)-C(7)	1.996(7)		
Ru(2)-C(8)	2.059(8)	C(8)-O(8)	1.183(11)
Ru(3)-C(8)	2.110(7)		

(iii) μ_3-CO's.

Ru(1)-C(4)	2.576(7)		
Ru(3)-C(4)	2.109(8)	C(4)-O(4)	1.199(8)
Ru(5)-C(4)	2.124(7)		
Ru(4)-C(13)	2.334(7)		
Ru(5)-C(13)	2.008(7)	C(13)-O(13)	1.194(9)
Ru(6)-C(13)	2.452(8)		

a E.s.d's on mean bond lengths and angles are calculated from the equation $\sigma = \sqrt{\left\{\left[\sum_{1}^{n} (x_i - \bar{x})^2\right] / (n-1)\right\}}$ where

x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

Table 4.9 Selected Intramolecular Angles (^{o}) in (XI). E.s.d's are given in parentheses.

(a) M-C-O Angles.

(i) Terminal CO's.

Ru(1)-C(1)-O(1)	174.8(8)	Ru(5)-C(14)-O(14)	176.7(7)
Ru(1)-C(2)-O(2)	171.5(7)	Ru(5)-C(15)-O(15)	176.2(8)
Ru(1)-C(3)-O(3)	172.7(8)		
		Ru(6)-C(16)-O(16)	177.0(8)
Ru(2)-C(5)-O(5)	174.5(8)	Ru(6)-C(17)-O(17)	173.0(7)
Ru(2)-C(6)-O(6)	177.8(8)	Ru(6)-C(18)-O(18)	175.0(9)
Ru(3)-C(9)-O(9)	177.5(7)		
Ru(3)-C(10)-O(10)	177.2(7)		
Ru(4)-C(11)-O(11)	174.2(8)		
Ru(4)-C(12)-O(12)	177.0(6)		

Mean Ru-C-O 175.4(20)[a]

(ii) μ_2-CO's

Ru(2)-C(7)-O(7)	131.8(6)	Ru(2)-C(8)-O(8)	138.1(6)
Ru(4)-C(7)-O(7)	144.1(6)	Ru(3)-C(8)-O(8)	136.7(6)

(iii) μ_3-CO's

Ru(1)-C(4)-O(4)	125.2(6)	Ru(4)-C(13)-O(13)	129.1(5)
Ru(3)-C(4)-O(4)	137.6(6)	Ru(5)-C(13)-O(13)	143.5(5)
Ru(5)-C(4)-O(4)	136.2(6)	Ru(6)-C(13)-O(13)	126.7(6)

(b) M-C-M Angles Associated with Bridging CO ligands

(i) μ_2-CO's

Ru(2)-C(7)-Ru(4)	84.0(3)	Ru(2)-C(8)-Ru(3)	85.0(3)

(iii) μ_3-CO's

Ru(1)-C(4)-Ru(3)	74.4(2)	Ru(4)-C(13)-Ru(5)	80.5(3)
Ru(1)-C(4)-Ru(5)	73.1(2)	Ru(4)-C(13)-Ru(6)	73.4(2)
Ru(3)-C(4)-Ru(5)	82.8(3)	Ru(5)-C(13)-Ru(6)	77.6(3)

(c) Angles between Metal Atoms

Ru(3)-Ru(1)-Ru(2)	59.0(1)	Ru(2)-Ru(4)-Ru(1)	60.3(1)
Ru(4)-Ru(1)-Ru(2)	58.6(1)	Ru(5)-Ru(4)-Ru(1)	59.3(1)
Ru(4)-Ru(1)-Ru(3)	88.7(1)	Ru(5)-Ru(4)-Ru(2)	88.8(1)
Ru(5)-Ru(1)-Ru(2)	87.8(1)	Ru(6)-Ru(4)-Ru(1)	91.4(1)
Ru(5)-Ru(1)-Ru(3)	59.1(1)	Ru(6)-Ru(4)-Ru(2)	61.3(1)
Ru(5)-Ru(1)-Ru(4)	59.2(1)	Ru(6)-Ru(4)-Ru(5)	59.5(1)
Ru(3)-Ru(2)-Ru(1)	60.4(1)	Ru(3)-Ru(5)-Ru(1)	61.1(1)
Ru(4)-Ru(2)-Ru(1)	61.1(1)	Ru(4)-Ru(5)-Ru(1)	61.6(1)
Ru(4)-Ru(2)-Ru(3)	90.9(1)	Ru(4)-Ru(5)-Ru(3)	91.2(1)
Ru(6)-Ru(2)-Ru(1)	91.2(1)	Ru(6)-Ru(5)-Ru(1)	93.7(1)
Ru(6)-Ru(2)-Ru(3)	60.8(1)	Ru(6)-Ru(5)-Ru(3)	61.9(1)
Ru(6)-Ru(2)-Ru(4)	60.2(1)	Ru(6)-Ru(5)-Ru(4)	61.0(1)
Ru(2)-Ru(3)-Ru(1)	60.6(1)	Ru(3)-Ru(6)-Ru(2)	58.4(1)
Ru(5)-Ru(3)-Ru(1)	59.8(1)	Ru(4)-Ru(6)-Ru(2)	58.6(2)
Ru(5)-Ru(3)-Ru(2)	89.1(1)	Ru(4)-Ru(6)-Ru(3)	88.5(1)
Ru(6)-Ru(3)-Ru(1)	91.4(1)	Ru(5)-Ru(6)-Ru(2)	87.3(1)
Ru(6)-Ru(3)-Ru(2)	60.9(1)	Ru(5)-Ru(6)-Ru(3)	58.7(1)
Ru(6)-Ru(3)-Ru(5)	59.3(1)	Ru(5)-Ru(6)-Ru(4)	59.5(1)

(d) Carbon-Metal-Metal angles

C(1)-Ru(1)-Ru(2)	93.7(2)	C(5)-Ru(2)-Ru(1)	167.2(3)
C(1)-Ru(1)-Ru(3)	81.9(3)	C(5)-Ru(2)-Ru(3)	130.8(3)
C(1)-Ru(1)-Ru(4)	151.3(2)	C(5)-Ru(2)-Ru(4)	109.2(3)
C(1)-Ru(1)-Ru(5)	133.2(3)	C(5)-Ru(2)-Ru(6)	90.5(3)
C(2)-Ru(1)-Ru(2)	84.7(2)	C(6)-Ru(2)-Ru(1)	85.3(2)
C(2)-Ru(1)-Ru(3)	142.5(2)	C(6)-Ru(2)-Ru(3)	113.9(2)
C(2)-Ru(1)-Ru(4)	78.9(2)	C(6)-Ru(2)-Ru(4)	121.1(3)
C(2)-Ru(1)-Ru(5)	134.4(2)	C(6)-Ru(2)-Ru(6)	174.7(2)
C(3)-Ru(1)-Ru(2)	171.5(3)	C(7)-Ru(2)-Ru(1)	84.9(2)
C(3)-Ru(1)-Ru(3)	123.4(3)	C(7)-Ru(2)-Ru(3)	134.8(2)
C(3)-Ru(1)-Ru(4)	112.9(3)	C(7)-Ru(2)-Ru(4)	44.9(2)
C(3)-Ru(1)-Ru(5)	87.2(3)	C(7)-Ru(2)-Ru(6)	94.9(2)
C(4)-Ru(1)-Ru(2)	103.1(2)	C(7)-Ru(4)-Ru(1)	88.0(2)
C(4)-Ru(1)-Ru(3)	45.3(2)	C(7)-Ru(4)-Ru(2)	51.1(2)
C(4)-Ru(1)-Ru(4)	104.0(2)	C(7)-Ru(4)-Ru(5)	138.6(2)
C(4)-Ru(1)-Ru(5)	46.1(2)	C(7)-Ru(4)-Ru(6)	100.7(2)
C(4)-Ru(3)-Ru(1)	60.3(2)	C(8)-Ru(2)-Ru(1)	96.4(2)
C(4)-Ru(3)-Ru(2)	119.1(2)	C(8)-Ru(2)-Ru(3)	48.2(2)
C(4)-Ru(3)-Ru(5)	48.8(2)	C(8)-Ru(2)-Ru(4)	138.4(2)
C(4)-Ru(3)-Ru(6)	107.8(2)	C(8)-Ru(2)-Ru(6)	88.3(2)
C(4)-Ru(5)-Ru(1)	60.9(2)	C(8)-Ru(3)-Ru(1)	95.4(3)
C(4)-Ru(5)-Ru(3)	48.4(2)	C(8)-Ru(3)-Ru(2)	46.7(2)
C(4)-Ru(5)-Ru(4)	120.7(2)	C(8)-Ru(3)-Ru(5)	135.2(2)
C(4)-Ru(5)-Ru(6)	110.0(2)	C(8)-Ru(3)-Ru(6)	87.4(2)

cont...

C(9)-Ru(3)-Ru(1)	100.3(3)	C(14)-Ru(5)-Ru(1)	148.7(2)
C(9)-Ru(3)-Ru(2)	118.7(2)	C(14)-Ru(5)-Ru(3)	99.0(2)
C(9)-Ru(3)-Ru(5)	133.6(3)	C(14)-Ru(5)-Ru(4)	147.9(2)
C(9)-Ru(3)-Ru(6)	166.0(3)	C(14)-Ru(5)-Ru(6)	97.3(2)
C(10)-Ru(3)-Ru(1)	162.1(2)	C(15)-Ru(5)-Ru(1)	93.3(3)
C(10)-Ru(3)-Ru(2)	126.5(2)	C(15)-Ru(5)-Ru(3)	145.0(3)
C(10)-Ru(3)-Ru(5)	102.6(2)	C(15)-Ru(5)-Ru(4)	96.9(2)
C(10)-Ru(3)-Ru(6)	80.8(2)	C(15)-Ru(5)-Ru(6)	149.4(2)
C(11)-Ru(4)-Ru(1)	170.9(3)	C(16)-Ru(6)-Ru(2)	160.2(2)
C(11)-Ru(4)-Ru(2)	123.5(3)	C(16)-Ru(6)-Ru(3)	103.3(2)
C(11)-Ru(4)-Ru(5)	126.9(2)	C(16)-Ru(6)-Ru(4)	133.8(3)
C(11)-Ru(4)-Ru(6)	97.6(3)	C(16)-Ru(6)-Ru(5)	88.7(3)
C(12)-Ru(4)-Ru(1)	82.1(2)	C(17)-Ru(6)-Ru(2)	78.1(3)
C(12)-Ru(4)-Ru(2)	131.3(2)	C(17)-Ru(6)-Ru(3)	79.5(2)
C(12)-Ru(4)-Ru(5)	97.8(2)	C(17)-Ru(6)-Ru(4)	134.4(3)
C(12)-Ru(4)-Ru(6)	155.9(2)	C(17)-Ru(6)-Ru(5)	137.1(2)
C(13)-Ru(4)-Ru(1)	103.9(2)	C(18)-Ru(6)-Ru(2)	99.6(3)
C(13)-Ru(4)-Ru(2)	113.9(2)	C(18)-Ru(6)-Ru(3)	157.4(3)
C(13)-Ru(4)-Ru(5)	44.7(2)	C(18)-Ru(6)-Ru(4)	82.7(3)
C(13)-Ru(4)-Ru(6)	55.2(2)	C(18)-Ru(6)-Ru(5)	130.6(3)
C(13)-Ru(5)-Ru(1)	116.3(2)		
C(13)-Ru(5)-Ru(3)	119.8(2)		
C(13)-Ru(5)-Ru(4)	54.8(2)		
C(13)-Ru(5)-Ru(6)	58.3(2)		
C(13)-Ru(6)-Ru(2)	107.7(2)		
C(13)-Ru(6)-Ru(3)	102.6(2)		
C(13)-Ru(6)-Ru(4)	51.4(2)		
C(13)-Ru(6)-Ru(5)	44.1(2)		

(e) OC-M-CO angles

C(2)-Ru(1)-C(1)	92.2(3)
C(3)-Ru(2)-C(1)	94.8(4)
C(3)-Ru(1)-C(2)	93.9(4)
C(4)-Ru(1)-C(1)	88.5(3)
C(4)-Ru(1)-C(2)	172.1(3)
C(4)-Ru(1)-C(3)	78.2(3)
C(6)-Ru(2)-C(5)	93.8(3)
C(7)-Ru(2)-C(5)	82.3(3)
C(7)-Ru(2)-C(6)	88.8(3)
C(8)-Ru(2)-C(5)	96.4(4)
C(8)-Ru(2)-C(6)	88.1(3)
C(8)-Ru(2)-C(7)	176.6(3)
C(8)-Ru(3)-C(4)	150.7(3)
C(9)-Ru(3)-C(4)	84.8(3)
C(9)-Ru(3)-C(8)	83.9(3)
C(10)-Ru(3)-C(4)	106.7(3)
C(10)-Ru(3)-C(8)	100.2(3)
C(10)-Ru(3)-C(9)	90.0(4)
C(11)-Ru(4)-C(7)	89.1(3)
C(12)-Ru(4)-C(7)	102.2(3)
C(12)-Ru(4)-C(11)	90.1(4)
C(13)-Ru(4)-C(7)	152.6(3)
C(13)-Ru(4)-C(11)	82.4(3)
C(13)-Ru(4)-C(12)	103.8(3)
C(13)-Ru(5)-C(4)	168.2(3)
C(14)-Ru(5)-C(4)	87.9(3)
C(14)-Ru(5)-C(13)	94.2(3)
C(15)-Ru(5)-C(4)	99.5(3)
C(15)-Ru(5)-C(13)	92.1(3)
C(15)-Ru(5)-C(14)	92.0(4)
C(16)-Ru(6)-C(13)	82.3(3)
C(17)-Ru(6)-C(13)	174.1(3)
C(17)-Ru(6)-C(16)	91.9(4)
C(18)-Ru(6)-C(13)	88.1(3)
C(18)-Ru(6)-C(16)	97.8(4)
C(18)-Ru(6)-C(17)	91.9(4)

[a] See footnote to Table 4.8.

Table 4.10

Selected bond lengths (Å) and angles (°) for the $[Ph_3 Me P]^+$ cations in (XI). E.s.d's are given in parentheses.

P(1)-C(111)	1.791(5)	C(121)-P(1)-C(111)	109.7(2)
P(1)-C(121)	1.795(4)	C(131)-P(1)-C(111)	110.6(2)
P(1)-C(131)	1.780(4)	C(131)-P(1)-C(121)	108.8(2)
P(1)-C(19)	1.788(9)	C(19)-P(1)-C(111)	108.7(3)
		C(19)-P(1)-C(121)	110.4(3)
		C(19)-P(1)-C(131)	108.7(3)
P(2)-C(211)	1.787(6)		
P(2)-C(221)	1.778(5)	C(221)-P(2)-C(211)	110.5(3)
P(2)-C(231)	1.783(5)	C(231)-P(2)-C(211)	110.6(2)
P(2)-C(20)	1.789(9)	C(231)-P(2)-C(221)	108.4(2)
		C(20)-P(2)-C(211)	109.2(3)
		C(20)-P(2)-C(221)	109.8(3)
		C(20)-P(2)-C(231)	108.3(3)

Table 4.11 Selected Interatomic Distances (Å){E.s.d's in parentheses} for (XII).[a]

(a) Metal-Metal Bonds

$[HRu_6(CO)_{18}]^-$

	Cluster (1)	Cluster (2A)	Cluster (2B)	$[Os_6(CO)_{18}]^{2-}$
M(1)-M(2)	2.927(2)	2.931(4)	2.917(5)	= 2.884(3)
M(3)-M(6)	2.921(2)	2.934(3)	2.951(3)	
M(4)-M(5)	2.924(2)	2.950(3)	2.936(4)	
M(1)-M(4)	2.841(2)	2.812(3)	2.793(3)	= 2.816(3)
M(2)-M(3)	2.843(2)	2.867(3)	2.928(4)	
M(5)-M(6)	2.832(2)	2.835(4)	2.847(5)	
M(1)-M(3)	2.863(2)	2.890(3)	2.869(4)	= 2.876(2)
M(1)-M(5)	2.865(2)	2.872(4)	2.856(5)	
M(2)-M(4)	2.878(2)	2.800(3)	2.829(4)	
M(2)-M(6)	2.900(2)	2.870(4)	2.883(5)	
M(3)-M(5)	2.881(2)	2.890(3)	2.838(3)	
M(4)-M(6)	2.876(2)	2.871(3)	2.858(4)	

(b) Metal-Carbon Distances [b]

	Cluster(1)	Cluster(2)
Ru(1)-C(11)	1.856(19)	
Ru(1)-C(12)	1.872(20)	-
Ru(1)-C(13)	1.828(19)	
Ru(2)-C(21)	1.843(19)	
Ru(2)-C(22)	1.838(18)	-
Ru(2)-C(23)	1.841(19)	
Ru(3)-C(31)	1.886(17)	1.830(21)
Ru(3)-C(32)	1.850(19)	1.808(26)
Ru(3)-C(33)	1.852(17)	1.861(23)
Ru(4)-C(41)	1.838(21)	1.863(17)
Ru(4)-C(42)	1.846(20)	1.858(20)
Ru(4)-C(43)	1.875(18)	1.858(21)
Ru(5)-C(51)	1.833(21)	
Ru(5)-C(52)	1.863(18)	-
Ru(5)-C(53)	1.865(20)	
Ru(6)-C(61)	1.853(17)	
Ru(6)-C(62)	1.838(19)	-
Ru(6)-C(63)	1.846(18)	
Mean Ru-C	1.850(17) [c]	

(c) Carbon-Oxygen Distances [b]

	Cluster(1)	Cluster(2)
C(11)-O(11)	1.136(24)	
C(12)-O(12)	1.158(25)	-
C(13)-O(13)	1.157(24)	
C(21)-O(21)	1.146(24)	
C(22)-O(22)	1.162(22)	-
C(23)-O(23)	1.161(23)	
C(31)-O(31)	1.154(21)	1.149(26)
C(32)-O(32)	1.145(24)	1.195(32)
C(33)-O(33)	1.188(22)	1.129(28)
C(41)-O(41)	1.180(27)	1.156(23)
C(42)-O(42)	1.181(25)	1.155(24)
C(43)-O(43)	1.129(22)	1.154(25)
C(51)-O(51)	1.183(26)	
C(52)-O(52)	1.170(21)	-
C(53)-O(53)	1.144(25)	
C(61)-O(61)	1.151(21)	
C(62)-O(62)	1.173(24)	-
C(63)-O(63)	1.184(23)	
Mean C-O	1.160(18) [c]	

a The occupation factors of the disordered 'A' atoms in cluster (2) were coupled in the least-squares refinement to a free variable p_A which refined to 0.5840(11). The occupancies of the disordered 'B' atoms in this cluster was set to $1-p_A$.

In Figure 4.9(d) cluster (2B) has been rotated about the pseudo two-fold axis to obtain a view that corresponds to those of cluster (1) and (2A) in Figures 4.9(b) and 4.9(c) respectively. Under this operation Ru(3C) and its associated carbonyl ligands exchange position with Ru(4C) and its carbonyl groups, but in order to allow ease of comparison of their geometries, the bond lengths and angles for cluster (2B) have been listed next to those in cluster (1) and (2A) to which they are equivalent. The correct labels for cluster (2B) may be obtained by simply interchanging those involving M(3) and M(4).

b Disordered carbon atoms associated with the two orientations [(2A) and (2B)] of cluster (2) were placed in fixed positions such that d(M-C)/d(M...O) = 0.615 and M-C-O = 180°.

c E.s.d's on mean bond lengths and angles are calculated from the equation

$\sigma = \sqrt{\{[\sum_{1}^{n}(x_i-\bar{x})^2]/(n-1)\}}$, where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

Table 4.12

Selected Intramolecular Angles (°) for (XII) with e.s.d.'s.[a]

(a) Ru-C-O Angles

	Cluster(1)	Cluster(2)
Ru(1)-C(11)-O(11)	176.8(16)	
Ru(1)-C(12)-O(12)	174.0(16)	-
Ru(1)-C(13)-O(13)	174.3(18)	
Ru(2)-C(21)-O(21)	173.0(16)	
Ru(2)-C(22)-O(22)	174.4(17)	-
Ru(2)-C(23)-O(23)	174.0(16)	
Ru(3)-C(31)-O(31)	175.2(15)	175.2(17)
Ru(3)-C(32)-O(32)	172.9(17)	172.4(24)
Ru(3)-C(33)-O(33)	173.1(15)	173.9(17)
Ru(4)-C(41)-O(41)	173.1(18)	175.3(17)
Ru(4)-C(42)-O(42)	174.1(15)	173.9(18)
Ru(4)-C(43)-O(43)	174.5(19)	171.0(16)
Ru(5)-C(51)-O(51)	172.5(17)	
Ru(5)-C(52)-O(52)	174.1(14)	-
Ru(5)-C(53)-O(53)	172.7(15)	
Ru(6)-C(61)-O(61)	172.8(14)	
Ru(6)-C(62)-O(62)	172.2(15)	-
Ru(6)-C(63)-O(63)	175.2(17)	
Mean Ru-C-O	173.8(13)[b]	

(b) Angles Between Metal Atoms

	Cluster(1)	Cluster(2A)	Cluster(2B)
Ru(2)-Ru(1)-Ru(3)	58.8(1)	59.0(1)	60.8(1)
Ru(2)-Ru(1)-Ru(4)	59.8(1)	58.3(1)	59.3(1)
Ru(2)-Ru(1)-Ru(5)	89.6(1)	89.1(1)	90.2(1)
Ru(3)-Ru(1)-Ru(4)	90.9(1)	90.9(1)	91.7(1)
Ru(3)-Ru(1)-Ru(5)	60.4(1)	60.2(1)	59.4(1)
Ru(4)-Ru(1)-Ru(5)	61.7(1)	62.5(1)	62.6(1)
Ru(1)-Ru(2)-Ru(3)	59.5(1)	59.8(1)	58.8(1)
Ru(1)-Ru(2)-Ru(4)	58.6(1)	58.7(1)	58.2(1)
Ru(1)-Ru(2)-Ru(6)	88.4(1)	89.0(1)	88.4(1)
Ru(3)-Ru(2)-Ru(4)	90.6(1)	91.6(1)	89.8(1)
Ru(3)-Ru(2)-Ru(6)	61.1(1)	61.5(1)	61.0(1)
Ru(4)-Ru(2)-Ru(6)	59.7(1)	60.8(1)	60.0(1)
Ru(1)-Ru(3)-Ru(2)	61.7(1)	61.2(1)	60.4(1)
Ru(1)-Ru(3)-Ru(5)	59.8(1)	59.6(1)	60.1(1)
Ru(1)-Ru(3)-Ru(6)	89.3(1)	88.6(1)	88.0(1)
Ru(2)-Ru(3)-Ru(5)	91.0(1)	90.0(1)	90.3(1)
Ru(2)-Ru(3)-Ru(6)	60.4(1)	59.3(1)	58.7(1)
Ru(5)-Ru(3)-Ru(6)	58.4(1)	58.3(1)	58.9(1)
Ru(1)-Ru(4)-Ru(2)	61.6(1)	63.0(1)	62.5(1)
Ru(1)-Ru(4)-Ru(5)	59.6(1)	59.7(1)	59.7(1)
Ru(1)-Ru(4)-Ru(6)	90.6(1)	91.4(1)	91.4(1)
Ru(2)-Ru(4)-Ru(5)	89.4(1)	90.1(1)	90.3(1)
Ru(2)-Ru(4)-Ru(6)	60.5(1)	60.8(1)	60.9(1)
Ru(5)-Ru(4)-Ru(6)	58.4(1)	58.3(1)	58.9(1)
Ru(1)-Ru(5)-Ru(3)	59.8(1)	60.2(1)	60.5(1)
Ru(1)-Ru(5)-Ru(4)	58.8(1)	57.7(1)	57.6(1)
Ru(1)-Ru(5)-Ru(6)	91.0(1)	90.9(1)	90.3(1)
Ru(3)-Ru(5)-Ru(4)	88.9(1)	88.2(1)	89.5(1)
Ru(3)-Ru(5)-Ru(6)	61.5(1)	61.6(1)	62.5(1)
Ru(4)-Ru(5)-Ru(6)	59.9(1)	59.5(1)	59.2(1)

cont...

Ru(2)-Ru(6)-Ru(3)	58.5(1)	59.2(1)	60.2(1)
Ru(2)-Ru(6)-Ru(4)	59.8(1)	58.4(1)	59.0(1)
Ru(2)-Ru(6)-Ru(5)	90.8(1)	91.0(1)	91.0(1)
Ru(3)-Ru(6)-Ru(4)	89.1(1)	88.9(1)	88.8(1)
Ru(3)-Ru(6)-Ru(5)	60.1(1)	60.1(1)	58.6(1)
Ru(4)-Ru(6)-Ru(5)	61.6(1)	62.2(1)	61.9(1)

(c) Carbon-Metal-Metal Angles

	Cluster(1)	$[Os_6(CO)_{18}]^{2-}$
C(11)-M(1)-M(2)	137.8(6)	147.5
C(11)-M(1)-M(3)	142.0(5)	141.8
C(11)-M(1)-M(4)	80.6(6)	90.1
C(11)-M(1)-M(5)	83.4(5)	87.5
C(12)-M(1)-M(2)	124.2(6)	122.4
C(12)-M(1)-M(3)	79.4(6)	83.5
C(12)-M(1)-M(4)	162.5(5)	169.3
C(12)-M(1)-M(5)	100.8(5)	108.4
C(13)-M(1)-M(2)	86.2(6)	81.2
C(13)-M(1)-M(3)	127.7(7)	126.3
C(13)-M(1)-M(4)	104.3(7)	99.4
C(13)-M(1)-M(5)	165.3(7)	160.2
C(21)-M(2)-M(1)	140.0(6)	147.5
C(21)-M(2)-M(3)	83.7(6)	90.1
C(21)-M(2)-M(4)	143.5(6)	141.8
C(21)-M(2)-M(6)	86.5(5)	87.5
C(22)-M(2)-M(1)	85.0(6)	81.2
C(22)-M(2)-M(3)	106.0(6)	99.4
C(22)-M(2)-M(4)	124.5(6)	126.3
C(22)-M(2)-M(6)	167.2(6)	160.2
C(23)-M(2)-M(1)	124.1(5)	122.4
C(23)-M(2)-M(3)	164.2(5)	169.3
C(23)-M(2)-M(4)	80.5(5)	83.5
C(23)-M(2)-M(6)	103.1(5)	108.4
C(31)-M(3)-M(1)	100.8(5)	108.4
C(31)-M(3)-M(2)	162.1(5)	169.3
C(31)-M(3)-M(5)	82.4(5)	83.5
C(31)-M(3)-M(6)	127.1(5)	122.4
C(32)-M(3)-M(1)	83.8(6)	87.5
C(32)-M(3)-M(2)	79.9(6)	90.1
C(32)-M(3)-M(5)	142.0(6)	141.8
C(32)-M(3)-M(6)	137.7(6)	147.5

cont...

	Cluster(1)	$[Os_6(CO)_{18}]^{2-}$		Cluster(1)	$[Os_6(CO)_{18}]^{2-}$
C(33)-M(3)-M(1)	164.0(5)	160.2	C(51)-M(5)-M(1)	128.9(6)	126.3
C(33)-M(3)-M(2)	102.3(5)	99.4	C(51)-M(5)-M(3)	169.2(6)	160.2
C(33)-M(3)-M(5)	124.3(5)	126.3	C(51)-M(5)-M(4)	91.3(6)	81.2
C(33)-M(3)-M(6)	81.9(6)	81.2	C(51)-M(5)-M(6)	109.5(6)	99.4
C(41)-M(4)-M(1)	108.5(7)	99.4	C(52)-M(5)-M(1)	138.7(6)	141.8
C(41)-M(4)-M(2)	169.8(7)	160.2	C(52)-M(5)-M(3)	80.7(5)	87.5
C(41)-M(4)-M(5)	82.9(6)	81.2	C(52)-M(5)-M(4)	137.5(6)	147.5
C(41)-M(4)-M(6)	119.8(6)	126.3	C(52)-M(5)-M(6)	79.2(5)	90.1
C(42)-M(4)-M(1)	158.3(6)	169.3	C(53)-M(5)-M(1)	76.6(5)	83.5
C(42)-M(4)-M(2)	97.6(6)	108.4	C(53)-M(5)-M(3)	97.7(6)	108.4
C(42)-M(4)-M(5)	130.8(5)	122.4	C(53)-M(5)-M(4)	123.3(6)	122.4
C(42)-M(4)-M(6)	83.2(6)	83.5	C(53)-M(5)-M(6)	159.2(6)	169.3
C(43)-M(4)-M(1)	78.4(7)	90.1	C(61)-M(6)-M(2)	78.3(5)	83.5
C(43)-M(4)-M(2)	88.8(6)	87.5	C(61)-M(6)-M(3)	124.0(5)	122.4
C(43)-M(4)-M(5)	132.6(6)	147.5	C(61)-M(6)-M(4)	98.8(5)	108.4
C(43)-M(4)-M(6)	148.8(6)	141.8	C(61)-M(6)-M(5)	160.4(5)	169.3

cont...

	Cluster(1)	$[Os_6(CO)_{18}]^{2-}$		Cluster(1)	$[Os_6(CO)_{18}]^{2-}$
C(62)-M(6)-M(2)	135.3(5)	141.8	C(63)-M(6)-M(2)	130.0(6)	126.3
C(62)-M(6)-M(3)	139.9(6)	147.5	C(63)-M(6)-M(3)	89.8(6)	81.2
C(62)-M(6)-M(4)	78.0(5)	87.5	C(63)-M(6)-M(4)	166.3(5)	160.2
C(62)-M(6)-M(5)	80.6(6)	90.1	C(63)-M(6)-M(5)	106.2(6)	99.4

(d) OC-M-CO Angles

	Cluster(1)	$[Os_6(CO)_{18}]^{2-}$
C(11)-M(1)-C(12)	98.0(8)	89.1
C(11)-M(1)-C(13)	90.2(8)	91.2
C(12)-M(1)-C(13)	93.1(9)	91.3
C(21)-M(2)-C(22)	91.5(8)	91.2
C(21)-M(2)-C(23)	95.7(8)	89.1
C(22)-M(2)-C(23)	89.7(8)	91.3
C(31)-M(3)-C(32)	95.1(8)	89.1
C(31)-M(3)-C(33)	95.2(7)	91.3
C(32)-M(3)-C(33)	93.7(8)	91.2
C(41)-M(4)-C(42)	92.5(9)	91.3
C(41)-M(4)-C(43)	91.4(8)	91.2
C(42)-M(4)-C(43)	96.3(8)	89.1
C(51)-M(5)-C(52)	91.9(8)	91.2
C(51)-M(5)-C(53)	91.2(9)	91.3
C(52)-M(5)-C(53)	99.0(8)	89.1
C(61)-M(6)-C(62)	95.7(8)	89.1
C(61)-M(6)-C(63)	93.2(8)	91.3
C(62)-M(6)-C(63)	94.3(8)	91.2

a See Table 4.11 footnote a.

b See Table 4.11 footnote c.

Table 4.13

Selected bond lengths (Å) and angles (°) in the two $[(Ph_3P)_2N]^+$ cations [a] in (XII). [a] E.s.d.'s are given in parentheses.

P(1)-N(1)	1.577(14)	P(1)-N(1)-P(2)	138.1(9)
P(2)-N(1)	1.577(13)	P(3)-N(2)-P(4)	138.8(9)
P(3)-N(2)	1.591(14)		
P(4)-N(2)	1.561(13)		
		N(1)-P(1)-C(111)	109.1(6)
P(1)-C(111)	1.802(11)	N(1)-P(1)-C(121)	115.2(6)
P(1)-C(121)	1.799(11)	N(1)-P(1)-C(131)	110.1(6)
P(1)-C(131)	1.788(10)	N(1)-P(2)-C(211)	114.2(6)
P(2)-C(211)	1.812(10)	N(1)-P(2)-C(221)	111.8(6)
P(2)-C(221)	1.799(10)	N(1)-P(2)-C(231)	107.5(7)
P(2)-C(231)	1.777(13)	N(2)-P(3)-C(311)	107.9(6)
P(3)-C(311)	1.790(10)	N(2)-P(3)-C(321)	115.1(6)
P(3)-C(321)	1.792(11)	N(2)-P(3)-C(331)	110.7(7)
P(3)-C(331)	1.794(12)	N(2)-P(4)-C(411)	106.5(6)
P(4)-C(411)	1.798(12)	N(2)-P(4)-C(421)	114.6(6)
P(4)-C(421)	1.803(10)	N(2)-P(4)-C(431)	110.6(7)
P(4)-C(431)	1.787(14)		
		C(111)-P(1)-C(121)	108.9(5)
		C(111)-P(1)-C(131)	105.7(5)
		C(121)-P(1)-C(131)	107.4(5)
		C(211)-P(2)-C(221)	108.9(5)
		C(211)-P(2)-C(231)	106.5(6)
		C(221)-P(2)-C(231)	107.6(5)
		C(311)-P(3)-C(321)	107.9(5)
		C(311)-P(3)-C(331)	107.9(5)
		C(321)-P(3)-C)331)	107.0(5)
		C(411)-P(4)-C(421)	108.0(5)
		C(411)-P(4)-C(431)	109.2(6)
		C(421)-P(4)-C(431)	107.7(6)

[a] The $[(Ph_3P)_2N]^+$ cations are in the usual bent form (R.D. Wilson and R. Bau, J. Am. Chem. Soc., 1974, 96, 7601)

Table 4.14 Selected Interatomic Distances (Å) for (XIII).[a] E.s.d's are given in parentheses

(a) Metal - Metal Bonds[b]

	Cluster (A)	Cluster (B)
Ru(1)-Ru(2)	2.907(1)	2.920(8)
Ru(3)-Ru(6)	2.893(1)	2.907(6)
Ru(4)-Ru(5)	2.959(1)	3.032(6)
Ru(1)-Ru(4)	2.843(1)	3.241(6)
Ru(2)-Ru(3)	2.837(1)	2.727(5)
Ru(5)-Ru(6)	2.839(1)	2.868(8)
Ru(1)-Ru(3)	2.896(1)	2.655(5)
Ru(1)-Ru(5)	2.869(1)	2.859(7)
Ru(2)-Ru(4)	2.879(1)	3.005(5)
Ru(2)-Ru(6)	2.880(1)	2.878(7)
Ru(3)-Ru(5)	2.848(1)	2.802(5)
Ru(4)-Ru(6)	2.898(1)	2.713(5)

(b) Ruthenium - Hydrogen Distances

Ru(1)-H	2.178(69)
Ru(2)-H	2.155(73)
Ru(3)-H	1.945(83)
Ru(4)-H	2.164(82)
Ru(5)-H	1.914(73)
Ru(6)-H	1.898(70)
Mean Ru-H	2.04(17)[c]

(c) Metal - Carbon and Carbon - Oxygen Distances.

Ru(1)-C(11)	1.895(9)	C(11)-O(11)	1.114(11)
Ru(1)-C(12)	1.872(10)	C(12)-O(12)	1.138(13)
Ru(1)-C(13)	1.891(8)	C(13)-O(13)	1.126(10)
Ru(2)-C(21)	1.903(8)	C(21)-O(21)	1.123(10)
Ru(2)-C(22)	1.884(7)	C(22)-O(22)	1.137(9)
Ru(2)-C(23)	1.873(8)	C(23)-O(23)	1.143(9)
Ru(3)-C(31)	1.906(8)	C(31)-O(31)	1.132(10)
Ru(3)-C(32)	1.892(9)	C(32)-O(32)	1.142(12)
Ru(3)-C(33)	1.876(9)	C(33)-O(33)	1.145(11)
Ru(4)-C(41)	1.897(11)	C(41)-O(41)	1.137(14)
Ru(4)-C(42)	1.888(9)	C(42)-O(42)	1.145(11)
Ru(4)-C(43)	1.915(9)	C(43)-O(43)	1.115(11)
Ru(5)-C(51)	1.861(10)	C(51)-O(51)	1.149(12)
Ru(5)-C(52)	1.875(8)	C(52)-O(52)	1.141(10)
Ru(5)-C(53)	1.935(8)	C(53)-O(53)	1.106(11)
Ru(6)-C(61)	1.892(8)	C(61)-O(61)	1.134(10)
Ru(6)-C(62)	1.896(10)	C(62)-O(62)	1.122(13)
Ru(6)-C(63)	1.865(9)	C(63)-O(63)	1.148(11)
Mean Ru-C	1.890(18)[c]	Mean C-O	1.133(13)[c]

[a] Bond lengths and angles quoted that involve ruthenium refer to the Ru sites of major (0.90) occupation unless stated otherwise.

[b] To obtain an orientation of cluster (B) that corresponds to that of cluster (A) the former must be rotated about the pseudo two-fold axis that passes through the midpoints of Ru(2A)···Ru(2B) and Ru(5A)···Ru(5B). Under this

cont...

operation Ru(3) exchanges position with Ru(4), but in order to allow ease of comparison of their geometries the bond lengths for cluster (B) have been listed next to those in cluster (A) to which they are equivalent. The correct labels for cluster (B) may be obtained by simply interchanging those labels involving Ru(3) and Ru(4).

c

E.s.d's on mean bond lengths and angles are calculated from the equation $\sigma = \sqrt{\left\{\left[\sum_{1}^{n}(x_i-\bar{x})^2\right]/(n-1)\right\}}$ where x_i is the i'th measurement and $\bar{x}$ is the mean of n equivalent measurements.

Table 4.15 Selected Intramolecular Angles (°) in (XIII). [a] E.s.d's are given in parentheses.

(a) Angles Between Metal Atoms

Ru(3)-Ru(1)-Ru(2)	58.5(1)	Ru(3)-Ru(5)-Ru(1)	60.9(1)
Ru(4)-Ru(1)-Ru(2)	60.1(1)	Ru(4)-Ru(5)-Ru(1)	58.4(1)
Ru(4)-Ru(1)-Ru(3)	90.8(1)	Ru(4)-Ru(5)-Ru(3)	89.4(1)
Ru(5)-Ru(1)-Ru(2)	89.3(1)	Ru(6)-Ru(5)-Ru(1)	90.8(1)
Ru(5)-Ru(1)-Ru(3)	59.2(1)	Ru(6)-Ru(5)-Ru(3)	61.1(1)
Ru(5)-Ru(1)-Ru(4)	62.4(1)	Ru(6)-Ru(5)-Ru(4)	59.9(1)
Ru(3)-Ru(2)-Ru(1)	60.5(1)	Ru(3)-Ru(6)-Ru(2)	58.9(1)
Ru(4)-Ru(2)-Ru(1)	58.9(1)	Ru(4)-Ru(6)-Ru(2)	59.8(1)
Ru(4)-Ru(2)-Ru(3)	91.3(1)	Ru(4)-Ru(6)-Ru(3)	89.8(1)
Ru(6)-Ru(2)-Ru(1)	89.2(1)	Ru(5)-Ru(6)-Ru(2)	90.5(1)
Ru(6)-Ru(2)-Ru(3)	60.8(1)	Ru(5)-Ru(6)-Ru(3)	59.6(1)
Ru(6)-Ru(2)-Ru(4)	60.4(1)	Ru(5)-Ru(6)-Ru(4)	62.1(1)
Ru(2)-Ru(3)-Ru(1)	60.9(1)		
Ru(5)-Ru(3)-Ru(1)	59.9(1)		
Ru(5)-Ru(3)-Ru(2)	91.2(1)		
Ru(6)-Ru(3)-Ru(1)	89.2(1)		
Ru(6)-Ru(3)-Ru(2)	60.3(1)		
Ru(6)-Ru(3)-Ru(5)	59.3(1)		
Ru(2)-Ru(4)-Ru(1)	61.1(1)		
Ru(5)-Ru(4)-Ru(1)	59.2(1)		
Ru(5)-Ru(4)-Ru(2)	88.1(1)		
Ru(6)-Ru(4)-Ru(1)	90.1(1)		
Ru(6)-Ru(4)-Ru(2)	59.8(1)		
Ru(6)-Ru(4)-Ru(5)	58.0(1)		

(b) Angles involving Interstitial Hydride

Ru(2)-H-Ru(1)	84.3(25)	Ru(6)-H-Ru(1)	171.3(43)
Ru(3)-H-Ru(1)	89.0(31)	Ru(6)-H-Ru(2)	90.3(29)
Ru(3)-H-Ru(2)	87.4(31)	Ru(6)-H-Ru(3)	97.6(33)
Ru(4)-H-Ru(1)	81.8(25)	Ru(6)-H-Ru(4)	90.8(33)
Ru(4)-H-Ru(2)	83.6(26)	Ru(6)-H-Ru(5)	96.3(32)
Ru(4)-H-Ru(3)	167.8(39)		
Ru(5)-H-Ru(1)	88.8(28)		
Ru(5)-H-Ru(2)	172.6(39)		
Ru(5)-H-Ru(3)	95.1(33)		
Ru(5)-H-Ru(4)	92.8(33)		

(c) Ru-C-O Angles

Ru(1)-C(11)-O(11)	171.9(8)	Ru(4)-C(41)-O(41)	172.6(9)
Ru(1)-C(12)-O(12)	174.5(9)	Ru(4)-C(42)-O(42)	175.5(7)
Ru(1)-C(13)-O(13)	174.6(8)	Ru(4)-C(43)-O(43)	172.9(9)
Ru(2)-C(21)-O(21)	173.5(7)	Ru(5)-C(51)-O(51)	173.9(8)
Ru(2)-C(22)-O(22)	171.3(6)	Ru(5)-C(52)-O(52)	171.1(7)
Ru(2)-C(23)-O(23)	176.1(7)	Ru(5)-C(53)-O(53)	175.5(8)
Ru(3)-C(31)-O(31)	175.4(7)	Ru(6)-C(61)-O(61)	171.9(7)
Ru(3)-C(32)-O(32)	174.3(8)	Ru(6)-C(62)-O(62)	173.5(9)
Ru(3)-C(33)-O(33)	172.1(9)	Ru(6)-C(63)-O(63)	175.9(9)

Mean Ru-C-O 173.7(16)[b]

(d) Carbon-Metal-Metal Angles

C(11)-Ru(1)-Ru(2)	143.0(3)	C(31)-Ru(3)-Ru(1)	108.3(2)
C(11)-Ru(1)-Ru(3)	132.1(2)	C(31)-Ru(3)-Ru(2)	169.2(2)
C(11)-Ru(1)-Ru(4)	83.2(3)	C(31)-Ru(3)-Ru(5)	81.6(3)
C(11)-Ru(1)-Ru(5)	76.4(3)	C(31)-Ru(3)-Ru(6)	121.2(2)
C(12)-Ru(1)-Ru(2)	117.7(3)	C(32)-Ru(3)-Ru(1)	86.5(3)
C(12)-Ru(1)-Ru(3)	77.0(3)	C(32)-Ru(3)-Ru(2)	83.2(3)
C(12)-Ru(1)-Ru(4)	165.4(3)	C(32)-Ru(3)-Ru(5)	143.7(2)
C(12)-Ru(1)-Ru(5)	103.9(3)	C(32)-Ru(3)-Ru(6)	140.0(2)
C(13)-Ru(1)-Ru(2)	90.2(3)	C(33)-Ru(3)-Ru(1)	159.1(3)
C(13)-Ru(1)-Ru(3)	134.8(3)	C(33)-Ru(3)-Ru(2)	98.2(3)
C(13)-Ru(1)-Ru(4)	101.1(3)	C(33)-Ru(3)-Ru(5)	127.0(3)
C(13)-Ru(1)-Ru(5)	160.9(3)	C(33(-Ru(3)-Ru(6)	80.8(3)
C(21)-Ru(2)-Ru(1)	141.5(2)	C(41)-Ru(4)-Ru(1)	109.5(4)
C(21)-Ru(2)-Ru(3)	84.1(2)	C(41)-Ru(4)-Ru(2)	170.5(4)
C(21)-Ru(2)-Ru(4)	142.9(2)	C(41)-Ru(4)-Ru(5)	87.0(3)
C(21)-Ru(2)-Ru(6)	85.7(2)	C(41)-Ru(4)-Ru(6)	123.4(3)
C(22)-Ru(2)-Ru(1)	78.2(2)	C(42)-Ru(4)-Ru(1)	156.5(3)
C(22)-Ru(2)-Ru(3)	97.7(2)	C(42)-Ru(4)-Ru(2)	95.9(3)
C(22)-Ru(2)-Ru(4)	123.8(2)	C(42)-Ru(4)-Ru(5)	129.1(2)
C(22)-Ru(2)-Ru(6)	158.5(2)	C(42)-Ru(4)-Ru(6)	80.7(3)
C(23)-Ru(2)-Ru(1)	122.2(2)	C(43)-Ru(4)-Ru(1)	31.1(3)
C(23)-Ru(2)-Ru(3)	165.8(2)	C(43)-Ru(4)-Ru(2)	86.7(3)
C(23)-Ru(2)-Ru(4)	80.2(2)	C(43)-Ru(4)-Ru(5)	136.8(3)
C(23)-Ru(2)-Ru(6)	105.1(2)	C(43)-Ru(4)-Ru(6)	145.0(3)

cont...

C(51)-Ru(5)-Ru(1)	120.2(3)	C(61)-Ru(6)-Ru(2)	78 2(2)
C(51)-Ru(5)-Ru(3)	175.9(3)	C(61)-Ru(6)-Ru(3)	122.3(3)
C(51)-Ru(5)-Ru(4)	88.1(3)	C(61)-Ru(6)-Ru(4)	100.7(3)
C(51)-Ru(5)-Ru(6)	114.7(3)	C(61)-Ru(6)-Ru(5)	162.7(3)
C(52)-Ru(5)-Ru(1)	146.8(3)	C(62)-Ru(6)-Ru(2)	135.0(3)
C(52)-Ru(5)-Ru(3)	86.3(3)	C(62)-Ru(6)-Ru(3)	138.9(3)
C(52)-Ru(5)-Ru(4)	131.1(3)	C(62)-Ru(6)-Ru(4)	77.3(3)
C(52)-Ru(5)-Ru(6)	75.8(2)	C(62)-Ru(6)-Ru(5)	80.1(3)
C(53)-Ru(5)-Ru(1)	80.4(2)	C(63)-Ru(6)-Ru(2)	131.2(3)
C(53)-Ru(5)-Ru(3)	91.4(3)	C(63)-Ru(6)-Ru(3)	89.7(3)
C(53)-Ru(5)-Ru(4)	131.6(2)	C(63)-Ru(6)-Ru(4)	165.2(3)
C(53)-Ru(5)-Ru(6)	151.7(3)	C(63)-Ru(6)-Ru(5)	105.2(3)

(e) OC-M-CO Angles

C(12)-Ru(1)-C(11)	98.9(4)	C(42)-Ru(4)-C(41)	93.5(4)
C(13)-Ru(1)-C(11)	92.8(4)	C(43)-Ru(4)-C(41)	91.3(4)
C(13)-Ru(1)-C(12)	93.3(4)	C(43)-Ru(4)-C(42)	94.1(4)
C(22)-Ru(2)-C(21)	93.3(3)	C(52)-Ru(5)-C(51)	92.9(4)
C(23)-Ru(2)-C(21)	95.9(3)	C(53)-Ru(5)-C(51)	92.7(4)
C(23)-Ru(2)-C(22)	96.4(3)	C(53)-Ru(5)-C(52)	97.1(4)
C(32)-Ru(3)-C(31)	97.8(4)	C(62)-Ru(6)-C(61)	98.6(4)
C(33)-Ru(3)-C(31)	92.6(4)	C(63)-Ru(6)-C(61)	92.0(4)
C(33)-Ru(3)-C(32)	89.3(4)	C(63).Ru(6)-C(62)	93.5(4)

[a] See Table 4.14 footnote a.

[b] See Table 4.14 footnote c.

Table 4.16 Selected bond lengths (Å) and angles (°) for the $[Ph_4As]^+$ cation in (XIII).
E.s.d's are given in parenthesis.

As-C(111)	1.900(5)	C(121)-As-C(111)	111.4(2)
As-C(121)	1.903(5)	C(131)-As-C(111)	109.0(2)
As-C(131)	1.889(5)	C(131)-As-C(121)	110.0(2)
As-C(141)	1.890(6)	C(141)-As-C(111)	109.1(2)
		C(141)-As-C(121)	107.5(2)
		C(141)-As-C(131)	109.8(2)

Section 4.4 Conclusions

(1) Definite structural isomers of the $[H_3Ru_4(CO)_{12}]^-$ anion, differing only in the disposition of their bridging hydrogens, have been identified by X-ray analysis. This is the first time such isomers have been shown to exist in the solid state, and their isolation implies a very low energy barrier to tautomerism in this and related systems.

(2) Preliminary evidence[21] indicated that the monoanion $[Ru_6H(CO)_{18}]^-$ was the first authentic example of a polynuclear carbonyl compound containing an H atom within the metal polyhedron. This has now been confirmed by direct location of the hydride ligand at the centre of the Ru_6 core by both X-ray and neutron analyses of the $[Ph_4As]^+$ salt. Therefore in addition to the three well documented types of bonding for hydrogen attached to metal clusters (terminal, edge-bridging, and face-bridging) a fourth class has now been established in which the hydrogen atom is embedded inside the metal polyhedron. Such complexes may be useful models for the interaction of hydrogen with the bulk metal.

(3) Insertion of an H atom into the "unexpanded" Ru_6 octahedron in $[Ru_6(CO)_{18}]^{2-}$ causes an increase in size of the interstitial hole from 2.02 to 2.04 Å. The M-C distance is approximately the same in octahedral Ru_6C and Os_6C units (see Section 3); this implies that the expansion of the metal octahedron in these systems is not related to the size of the interstitial atom, but is electronic in origin.

(4) No two analogous members of the series $[H_nM_6(CO)_{18}]^{n-2}$

(n = 0,1,2; M = Ru or Os) have the same overall structure so clearly the preferred overall geometry is not just dictated by the number of valence electrons and other factors such as the number and type of ligands present are important.

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SECTION 5

Overall Conclusions.

In previous Sections the structures of several clusters containing from four to ten metal atoms have been discussed. Significantly in all these clusters the metal geometry may be rationalized by Wade theory using the extensions that capped polyhedra require the same number of skeletal electron pairs (S) as the parent polyhedron, and that capped polyhedra with vertices removed are also characterized by the same value of S as the parent polyhedron. The latter extension to Wade theory, which has only previously been used to explain the metal geometry in one cluster ($H_2Os_6(CO)_{18}$, see Subsection 2.2.4), means that a wider range of alternative geometries may be observed for a given value of S and a given number of metal atoms than was previously supposed, depending on the associated requirements of the ligands. For example $Os_5C(CO)_{15}$ has a square pyramidal (i.e. nido-octahedral) metal geometry which is expected for five metal atoms and S = 7, but $[H_2Os_5(CO)_{15}I]^-$, $H_2Os_5(CO)_{15}P(OMe)_3$, and $H_2Os_5(CO)_{16}$,[1] which have the same number of skeletal electron pairs, have alternative edge-bridged tetrahedral (i.e. arachno-capped octahedral) metal geometries. Thus although Wade theory is very successful for rationalizing the metal geometries in clusters of the iron triad, before geometries can be predicted with more confidence many more structures need to be examined to assess the relative importance of various ligands in determining the preferred geometry. Hydride ligands in particular appear to have a marked effect in determining the favoured structure, for example $H_2Ru_6(CO)_{18}$ has an octahedral metal geometry,[2] but the metal atoms in $H_2Os_6(CO)_{18}$ adopt an alternative capped square pyramidal geometry.[3] Significantly in the series $[H_nM_6(CO)_{18}]^{n-2}$ (n = 1, 2; M = Ru or Os) no two analogous clusters have the same overall geometry although they have identical numbers of electrons for bonding. This emphasises the fact that although Wade theory may be used to explain the metal geometry in clusters, it gives no information as to the precise disposition of the ligands.

For the anion $[H_3Ru_4(CO)_{12}]^-$ structural isomers have been isolated differing only in the disposition of the bridging hydrogens, and for $[Ru_6H(CO)_{18}]^-$ an interstitial mode of bonding has been confirmed for the hydride ligand. These clusters are the

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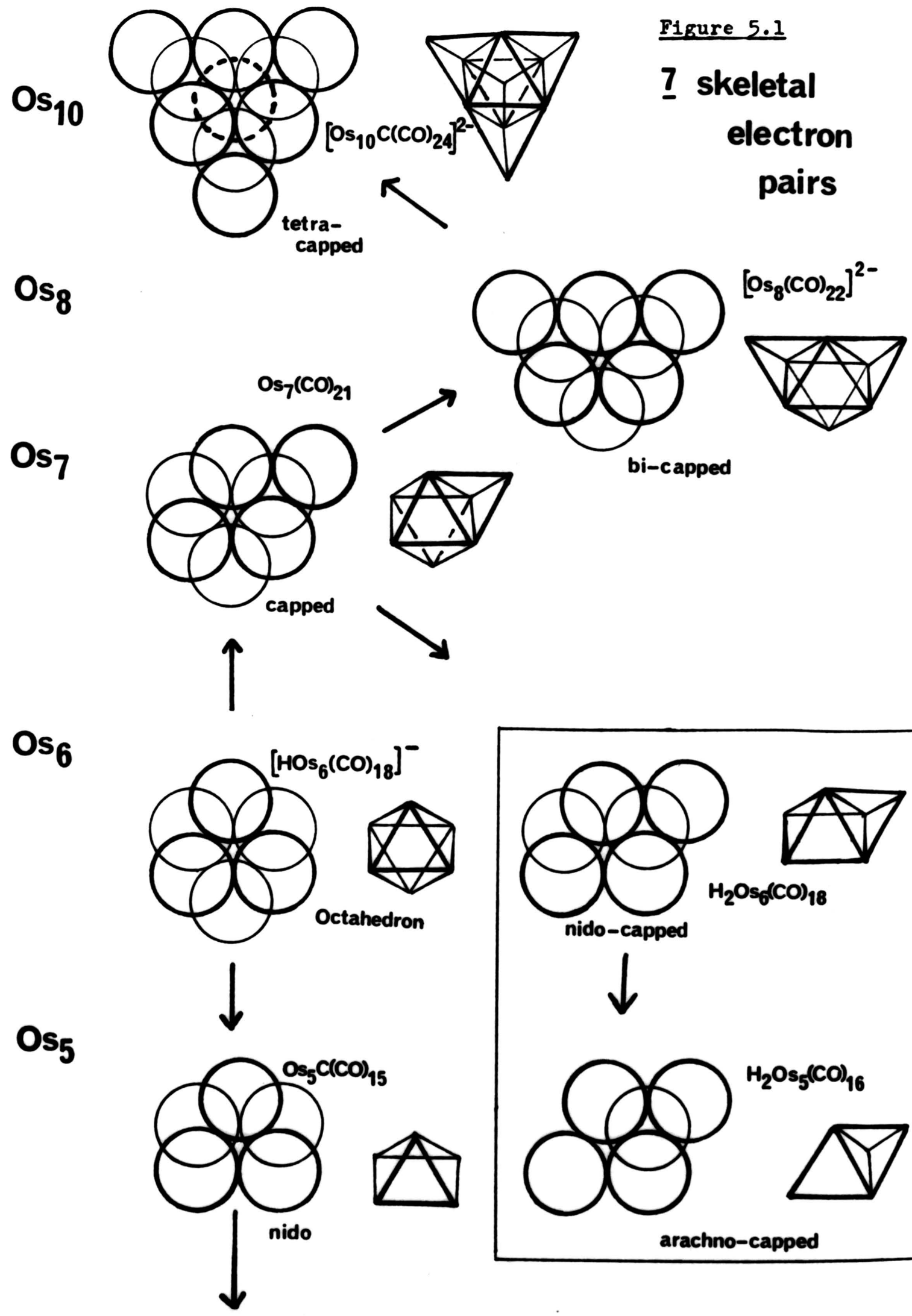
For the anion $[H_3Ru_4(CO)_{12}]^-$ structural isomers have been isolated differing only in the disposition of the bridging hydrogens, and for $[Ru_6H(CO)_{18}]^-$ an interstitial mode of bonding has been confirmed for the hydride ligand. These clusters are the

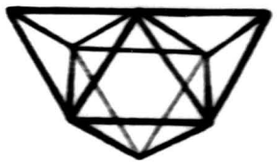
Figure 5.1


7 skeletal electron pairs
Os10
[Os10C(CO)24]2-
tetra-capped
Os8
[Os8(CO)22]2-
bi-capped
Os7(CO)21
Os7
capped
Os6
[HOs6(CO)18]-
Octahedron
H2Os6(CO)18
nido-capped
Os5
Os5C(CO)15
nido
H2Os5(CO)16
arachno-capped
Os4
H3Os4(CO)12I
arachno

igure 5.1

skeletal electron pairs

$[Os_8(CO)_{22}]^{2-}$



apped

$H_2Os_6(CO)_{18}$

d

$H_2Os_5(CO)_{16}$

achno-capped

first of their type and they may be good models for hydrogen interaction with a metal surface, a process of great importance in heterogeneous catalysis. The interstitial site for the hydrogen atom in $[Ru_6H(CO)_{18}]^-$ illustrates a fundamental difference between clusters of ruthenium and osmium, i.e. the former almost always contain interstitial atoms, but for Os the dianion $[Os_{10}C(CO)_{24}]^{2-}$ is the first cluster to be shown by X-ray analysis to contain a completely encapsulated (C) atom. Only two ruthenium clusters are known that do not contain interstitial atoms, $H_2Ru_6(CO)_{18}$[2] and $[Ru_6(CO)_{18}]^{2-}$, but these appear to be relatively unstable. Thus on gentle warming the dihydride is converted into the carbido cluster $Ru_6C(CO)_{17}$,[4] and indirect evidence suggests that on heating $[Ru_6(CO)_{18}]^{2-}$[17] is transformed into the carbide dianion $[Ru_6C(CO)_{16}]^{2-}$ (ref.5). The carbido ruthenium clusters might be expected to be better catalysts than clusters of osmium because the interstitial carbon atom, in donating four electrons to the cluster, reduces the number of carbonyl ligands required by two and hence coordination of reactants is more sterically favourable. For example $Ru_6C(CO)_{15}(C_6H_{10})$, which was isolated from the reaction of $Ru_3(CO)_{12}$ with ethylene, may be an important intermediate in the catalytic polymerization of ethylene to give (ultimately) poly-ethylenes. However the pentanuclear osmium clusters studied exhibit an unexpected flexibility of the metal framework on addition or loss of electrons. In this case a coordination site is made available via the breaking of an M-M bond which suggests that these clusters may also be of use as catalysts. Interestingly recent work has shown[4] that the dianion $[Os_{10}C(CO)_{24}]^{2-}$ reacts reversibly with I_2 also via the breaking or making of M-M bonds to the capping $Os(CO)_3$ groups.

For osmium metal it may be significant that there are a preponderance of clusters having 7 skeletal electron pairs (S), some of which are shown in Figure 5.1, as this produces a close packed array of metals. However the structures of these clusters are not related to that of the bulk metal (h.c.p.) and in $[Os_{10}C(CO)_{24}]^{2-}$ the largest osmium cluster prepared to date the metal skeleton

corresponds to a face centred cubic unit cell with four tetrahedrally related faces removed. Therefore, significantly, only four more capping groups can be added to the Os_{10} dianion which would give an Os_{14} species comprising a complete f.c.c. unit cell of metal atoms. This hypothetical cluster may represent the largest possible osmium cluster based on an octahedral subunit (S = 7), and larger clusters might be expected to exhibit geometries related to that of the bulk metal.

References

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APPENDIX 1.

Fractional Atomic Coordinates and Thermal Parameters for

$[Bu_4N]^+ [H_2Os_5(CO)_{15}I]^-$ (I).

Table 1 Fractional Atomic Coordinates (x 10^4) and Isotropic Temperature Factors ($Å^2$ x 10^3) for (I). E.s.d 's are given in parentheses.

atom[a]	x	y	z	U[b]	
Os (1)	3083 (1)	4652 (1)	3763 (1)	c	
Os (2)	2324 (1)	3241 (1)	3374 (1)	c	
Os (3)	1905 (1)	4498 (1)	2180 (1)	c	
Os (4)	1360 (1)	4521 (1)	3899 (1)	c	
Os (5)	3624 (1)	3340 (1)	491.7 (1)	c	
C (1)	3902 (16)	4473 (14)	3086 (18)	44 (7)	
O (1)	4407 (13)	4416 (12)	2595 (15)	73 (6)	
C (2)	2956 (18)	5648 (17)	3292 (20)	58 (8)	
O (2)	2920 (13)	6297 (13)	3055 (15)	76 (7)	
C (3)	3723 (17)	4997 (16)	4805 (19)	49 (7)	
O (3)	4093 (12)	5349 (11)	5427 (14)	67 (6)	
C (4)	3034 (17)	2911 (16)	2557 (19)	51 (7)	
O (4)	3417 (13)	2694 (12)	2027 (15)	75 (6)	
C (5)	1389 (20)	2853 (18)	2540 (21)	64 (9)	
O (5)	871 (14)	2571 (13)	2178 (16)	80 (7)	
C (6)	2340 (16)	2362 (15)	4101 (18)	49 (7)	
O (6)	2217 (13)	1782 (13)	4468 (15)	76 (6)	
C (7)	2605 (21)	4352 (19)	1361 (24)	76 (10)	
O (7)	3026 (16)	4241 (15)	791 (18)	101 (8)	
C (8)	993 (21)	4144 (20)	1441 (23)	73 (10)	
O (8)	489 (17)	3893 (16)	875 (20)	113 (9)	
C (9)	1627 (19)	5476 (18)	1767 (21)	66 (9)	
O (9)	1428 (13)	6089 (13)	1525 (15)	80 (7)	
C (10)	1072 (18)	4516 (17)	5064 (21)	61 (8)	
O (10)	847 (13)	4580 (12)	5784 (15)	77 (6)	
C (11)	385 (18)	4201 (16)	3301 (20)	53 (8)	
O (11)	-228 (14)	3948 (13)	2953 (16)	86 (7)	

cont...

atom	x	y	z	U
C(12)	1080(22)	5494(21)	3642(25)	83(11)
O(12)	893(14)	6175(14)	3529(16)	83(7)
C(13)	4322(18)	3079(16)	4029(21)	57(8)
O(13)	4809(15)	2906(14)	3671(16)	86(7)
I(14)	2681(2)	3575(2)	6188(2)	c
C(15)	4466(18)	3684(16)	5776(20)	54(8)
O(15)	5005(13)	3919(12)	6275(15)	73(6)
C(16)	3771(21)	2420(21)	5508(24)	79(10)
O(16)	3787(18)	1787(18)	5837(21)	126(11)
H(14)	2334	4808	4349	50
H(24)	1789	3659	4197	50
N	1911(12)	709(11)	7008(14)	42(5)
C(17)	2576(18)	468(17)	6497(21)	67(9)
C(18)	3003(18)	-217(17)	6788(21)	64(9)
C(19)	3663(18)	-382(17)	6180(21)	67(9)
C(20)	4107(24)	-1050(22)	6566(27)	99(12)
C(21)	2183(17)	935(16)	8037(18)	54(7)
C(22)	2823(19)	1533(17)	8162(21)	68(9)
C(23)	3035(24)	1653(23)	9145(26)	101(13)
C(24)	2474(30)	2035(31)	9587(35)	146(19)
C(25)	1547(18)	1424(17)	6460(21)	67(9)
C(26)	805(19)	1791(18)	6970(22)	73(9)
C(27)	593(23)	2566(21)	6423(25)	97(12)
C(28)	319(26)	2522(24)	5475(26)	106(13)
C(29)	1305(16)	73(15)	7019(18)	51(7)
C(30)	850(20)	-169(19)	6095(23)	81(10)
C(31)	267(29)	-864(26)	6274(34)	139(18)
C(32)	800(29)	-1521(29)	6646(35)	146(19)
H(171)	3007(18)	926(17)	6560(21)	136(28)
H(172)	2324(18)	396(17)	5777(21)	136(28)
H(181)	3279(18)	-157(17)	7502(21)	136(28)
H(182)	2587(18)	-688(17)	6730(21)	136(28)

cont...

atom	x	y	z	U
H(191)	4058(18)	103(17)	6189(21)	136(28)
H(192)	3391(18)	-496(17)	5475(21)	136(28)
H(201)	4364(24)	-1416(22)	6092(27)	139(39)
H(202)	3732(24)	-1384(22)	6950(27)	139(39)
H(203)	4580(24)	-788(22)	7042(27)	139(39)
H(211)	2407(17)	431(16)	8415(18)	136(28)
H(212)	1671(17)	1151(16)	8319(18)	136(28)
H(221)	2604(19)	2057(17)	7826(21)	136(28)
H(222)	3339(19)	1339(17)	7872(21)	136(28)
H(231)	3586(24)	1972(23)	9257(26)	136(28)
H(232)	3128(24)	1098(23)	9466(26)	136(28)
H(241)	2815(30)	1838(31)	10228(35)	139(39)
H(242)	2117(30)	1572(31)	9259(35)	139(39)
H(243)	2086(30)	2496(31)	9730(35)	139(39)
H(251)	2007(18)	1849(17)	6446(21)	136(28)
H(252)	1312(18)	1258(17)	5760(21)	136(28)
H(261)	1005(19)	1902(18)	7696(22)	136(28)
H(262)	296(19)	1412(18)	6900(22)	136(28)
H(271)	1127(23)	2911(21)	6505(25)	136(28)
H(272)	137(23)	2850(21)	6743(25)	136(28)
H(281)	-34(26)	3037(24)	5366(26)	139(39)
H(282)	-22(26)	2046(24)	5156(26)	139(39)
H(283)	858(26)	2588(24)	5169(26)	139(39)
H(291)	873(16)	257(15)	7448(18)	136(28)
H(292)	1619(16)	-422(15)	7326(18)	136(28)
H(301)	503(20)	305(19)	5780(23)	136(28)
H(302)	1263(20)	-355(19)	5643(23)	136(28)
H(311)	-101(29)	-1023(26)	5632(34)	136(28)
H(312)	-111(29)	-697(26)	6775(34)	136(28)
H(321)	569(29)	-2065(29)	6832(35)	139(39)
H(322)	1339(29)	-1389(29)	7114(35)	139(39)
H(323)	933(29)	-1548(29)	5945(35)	139(39)

[a] H(14) and H(24) were placed in fixed positions with their isotropic temperature factors set at 0.05 $\AA^2$.

[b] Methylene and methyl hydrogen atoms had their isotropic temperature factors tied to separate common free variables.

[c] Anisotropic thermal parameters.

Table 2 Anisotropic Temperature Factors* ($Å^2 \times 10^3$) for (I).
E.s.d's in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	28.3(5)	27.8(5)	45.2(5)	3.7(5)	11.4(5)	-1.5(4)
Os(2)	37.0(6)	29.2(5)	45.6(6)	-4.0(5)	15.9(5)	-2.4(5)
Os(3)	39.4(7)	54.6(7)	40.2(7)	6.6(6)	8.8(5)	-2.4(6)
Os(4)	29.1(5)	33.9(5)	45.2(6)	0.7(5)	12.4(5)	2.5(5)
Os(5)	31.6(6)	39.8(6)	53.8(7)	11.7(5)	11.7(5)	3.6(5)
I(14)	104(2)	117(2)	100(2)	-11(2)	28(2)	1(2)

* Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\right]$$

APPENDIX 2

Fractional Atomic Coordinates and Thermal Parameters for $H_2Os_5(CO)_{15}P(OMe)_3$ (II).

Table 1 Fractional Atomic Coordinates ($x10^4$) for (II).
E.s.d 's are given in parentheses.

atom	x	y	z
Os (1)	3099 (1)	8351 (1)	7870 (1)
Os (2)	1819 (1)	7664 (1)	5040 (1)
Os (3)	2927 (1)	6085 (1)	6148 (1)
Os (4)	3756 (1)	7700 (1)	4708 (1)
Os (5)	1924 (1)	9975 (1)	6936 (1)
C (1)	2328 (9)	8048 (11)	9328 (16)
O (1)	1852 (8)	7781 (11)	10204 (14)
C (2)	3998 (10)	7568 (12)	8932 (18)
O (2)	4554 (7)	7241 (10)	9709 (14)
C (3)	3680 (7)	9779 (10)	9107 (15)
O (3)	4120 (7)	10534 (9)	9855 (13)
C (4)	844 (8)	7135 (11)	6034 (18)
O (4)	274 (8)	6779 (10)	6587 (16)
C (5)	1521 (9)	6346 (13)	3332 (18)
O (5)	1262 (9)	5676 (9)	2186 (13)
C (6)	1135 (8)	8535 (11)	3675 (15)
O (6)	734 (6)	8932 (8)	2783 (11)
C (7)	2151 (12)	5517 (13)	7488 (22)
O (7)	1683 (10)	5171 (11)	8295 (21)
C (8)	2652 (12)	4769 (12)	4525 (22)
O (8)	2476 (10)	4044 (10)	3422 (18)
C (9)	3950 (12)	5431 (12)	6869 (20)
O (9)	4588 (9)	5043 (12)	7279 (17)
C (10)	4198 (9)	8865 (12)	3677 (17)
O (10)	4492 (8)	9507 (11)	2985 (13)
C (11)	3603 (9)	6566 (12)	2791 (18)
O (11)	3466 (9)	5843 (11)	1640 (13)

cont ...

atom	x	y	z
C(12)	4921 (8)	7323 (12)	5476 (17)
O(12)	5611 (7)	7126 (14)	5995 (16)
C(13)	954 (8)	9402 (11)	7961 (16)
O(13)	378 (7)	9111 (9)	8594 (13)
C(14)	2964 (8)	10500 (11)	6007 (16)
O(14)	3531 (7)	10906 (9)	5531 (13)
P(15)	2104 (2)	11592 (3)	8902 (4)
O(151)	1145 (6)	12049 (8)	8924 (12)
C(151)	909 (12)	12999 (16)	10045 (23)
O(152)	2498 (8)	11612 (11)	10687 (12)
C(152)	2122 (15)	10955 (16)	11702 (22)
O(153)	2800 (10)	12549 (11)	8521 (15)
C(153)	3348 (13)	13395 (16)	9610 (28)
C(16)	1121 (9)	10759 (11)	5701 (14)
O(16)	705 (7)	11209 (9)	4923 (12)

Table 2 Anisotropic Temperature Factors * ($Å^2 \times 10^3$) for (II)
E.s.d's are given in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	32.8(2)	32.9(2)	36.5(2)	9.0(2)	5.0(2)	8.4(2)
Os(2)	30.2(2)	29.0(2)	39.0(2)	3.7(2)	5.3(2)	3.9(2)
Os(3)	48.3(3)	29.1(2)	58.0(3)	12.5(2)	13.2(2)	10.8(2)
Os(4)	33.6(2)	36.4(2)	44.2(4)	7.1(2)	11.5(2)	8.0(2)
Os(5)	29.5(2)	27.9(2)	35.3(2)	5.8(2)	5.7(2)	5.6(2)
C(1)	56(7)	42(7)	53(7)	18(6)	16(6)	22(6)
O(1)	78(7)	78(8)	81(7)	23(6)	49(6)	8(6)
C(2)	53(8)	41(7)	66(8)	11(6)	14(7)	9(6)
O(2)	58(6)	81(8)	78(7)	32(6)	-6(5)	24(6)
C(3)	29(5)	33(6)	50(6)	11(5)	1(5)	6(4)
O(3)	55(6)	55(6)	73(6)	-5(5)	-10(5)	7(5)
C(4)	37(6)	40(6)	71(9)	17(6)	22(6)	2(5)
O(4)	76(8)	56(7)	106(9)	19(7)	36(7)	4(6)
C(5)	49(7)	56(8)	64(8)	-16	2(6)	23(7)
O(5)	103(9)	43(6)	58(6)	-7(5)	-2(6)	10(6)
C(6)	34(6)	50(7)	47(7)	4(6)	14(5)	2(5)
O(6)	51(5)	56(6)	51(5)	13(4)	0(4)	27(5)

cont ...

C(7)	69(10)	48(8)	95(12)	30(8)	32(9)	24(7)
O(7)	116(11)	67(8)	164(14)	47(9)	91(11)	13(8)
C(8)	80(11)	33(7)	87(11)	-3(7)	14(9)	14(7)
O(8)	115(11)	48(7)	114(10)	-14(7)	-6(9)	18(7)
C(9)	82(11)	30(6)	79(10)	2(7)	12(9)	25(7)
O(9)	89(9)	84(9)	115(10)	42(8)	-1(8)	45(8)
C(10)	47(7)	46(7)	61(8)	16(6)	13(6)	16(6)
O(10)	78(8)	86(9)	69(7)	43(6)	21(6)	-2(6)
C(11)	51(7)	53(8)	66(9)	5(7)	23(7)	19(6)
O(11)	117(11)	76(8)	54(6)	-14(6)	30(7)	6(7)
C(12)	37(6)	53(8)	69(9)	9(7)	12(6)	16(6)
O(12)	35(5)	152(13)	108(9)	59(10)	10(6)	28(7)
C(13)	41(6)	39(6)	53(7)	6(6)	6(5)	8(5)
O(13)	58(6)	56(6)	76(7)	7(5)	31(5)	-9(5)
C(14)	35(6)	44(7)	58(7)	3(6)	17(5)	-7(5)
O(14)	58(6)	67(7)	77(7)	33(6)	30(5)	11(5)
P(15)	42(2)	35(2)	43(2)	-1(1)	5(1)	5(1)
O(151)	55(6)	49(6)	66(6)	-14(5)	-6(5)	17(5)
C(151)	62(10)	80(13)	89(12)	-28(10)	19(9)	3(9)
O(152)	73(7)	81(8)	54(6)	13(6)	9(5)	24(6)
C(152)	117(16)	68(11)	70(11)	30(9)	32(11)	-12(11)
(153)	110(10)	67(8)	78(8)	-4(6)	37(7)	-23(7)
C(153)	73(11)	60(11)	132(17)	14(12)	-30(12)	-17(9)

cont...

C(16)	52(7)	45(7)	33(6)	2(5)	6(5)	12(6)
O(16)	64(6)	62(6)	62(6)	15(5)	-4(5)	30(5)

* Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2(\underline{U}_{11}h^2a^{*2} + \underline{U}_{22}k^2b^{*2} + \underline{U}_{33}l^2c^{*2} + 2\underline{U}_{23}klb^*c^* + 2\underline{U}_{13}hla^*c^* + 2\underline{U}_{12}hka^*b^*)\right]$$

APPENDIX 3

Fractional Atomic Coordinates and Thermal Parameters for $Os_5C(CO)_{15}$ (III).

Table 1 Fractional Atomic Coordinates (x 10^4) and Isotropic Temperature Factors ($Å^2$ x 10^3) for (III).
E.s.d's are given in parentheses.

atom	x	y	z	U
Os(11)	3249(1)	3586(1)	2661(1)	a
Os(12)	3263(1)	1699(1)	3165(1)	a
Os(13)	1870(1)	2390(1)	2447(1)	a
Os(14)	2899(1)	2916(1)	1402(1)	a
Os(15)	4309(1)	2229(1)	2145(1)	a
C(111)	2418(18)	4469(20)	2721(11)	49(7)
O(111)	1886(14)	5034(15)	2741(9)	72(6)
C(112)	3666(16)	3704(17)	3528(10)	37(6)
O(112)	3917(13)	3856(13)	4057(8)	56(5)
C(113)	3942(20)	4396(22)	2296(13)	59(8)
O(113)	4375(16)	4957(16)	2033(10)	82(7)
C(121)	4170(20)	1445(21)	3710(13)	57(8)
O(121)	4744(14)	1256(15)	4013(9)	69(6)
C(122)	3171(21)	414(24)	3053(14)	44(9)
O(122)	3064(13)	-388(15)	2946(8)	65(6)
C(123)	2607(23)	1693(24)	3915(15)	72(9)
O(123)	2320(17)	1790(18)	4402(11)	94(8)
C(131)	1233(22)	2457(24)	3197(15)	75(10)
O(131)	872(16)	2524(17)	3677(10)	88(7)
C(132)	1444(17)	1181(18)	2186(10)	42(6)
O(132)	1172(14)	437(16)	2062(9)	71(6)
C(133)	1014(22)	3163(23)	2050(14)	66(9)
O(133)	482(17)	3470(18)	1783(11)	91(8)
C(141)	2137(18)	3781(19)	1131(11)	47(7)
O(141)	1730(15)	4419(16)	940(10)	79(7)
C(142)	2589(24)	1969(26)	824(15)	80(10)
O(142)	2280(16)	1368(18)	483(11)	91(7)
C(143)	3600(26)	3482(28)	841(17)	89(12)

cont ...

atom	x	y	z	U	
O(143)	4033(23)	3836(25)	475(15)	143(12)	
C(151)	5012(19)	2823(20)	1542(12)	53(7)	
O(151)	5460(17)	3164(18)	1197(11)	95(8)	
C(152)	4528(19)	974(21)	1887(12)	54(7)	
O(152)	4620(14)	197(15)	1715(9)	69(6)	
C(153)	5207(19)	2371(20)	2764(12)	53(7)	
O(153)	5750(15)	2416(15)	3104(10)	74(6)	
C(1)	3100(14)	2231(15)	2277(9)	28(5)	
Os(21)	2686(1)	7112(1)	164(1)	a	
Os(22)	2551(1)	8946(1)	-373(1)	a	
Os(23)	1765(1)	7400(1)	-1027(1)	a	
Os(24)	980(1)	6861(1)	142(1)	a	
Os(25)	1699(1)	8500(1)	777(1)	a	
C(211)	2977(23)	6037(26)	-291(15)	78(10)	
O(211)	3088(15)	5296(17)	-530(10)	79(7)	
C(212)	3758(19)	7575(21)	218(12)	54(7)	
O(212)	4429(18)	7790(19)	219(11)	101(8)	
C(213)	2705(18)	6541(20)	992(12)	51(7)	
O(213)	2702(14)	6223(15)	1493(9)	69(6)	
C(221)	3325(18)	9685(19)	101(11)	44(6)	
O(221)	3837(14)	10095(15)	365(9)	70(6)	
C(222)	1981(17)	10010(18)	-631(11)	43(6)	
O(222)	1563(14)	10623(15)	-812(9)	68(6)	
C(223)	3286(16)	9006(17)	-1053(10)	39(6)	
O(223)	3715(13)	9009(14)	-1479(8)	59(5)	
C(231)	2512(16)	7431(17)	-1720(10)	37(6)	
O(231)	2927(14)	7505(15)	-2154(9)	70(6)	
C(232)	949(16)	8066(17)	-1488(10)	36(6)	
O(232)	472(15)	8494(16)	-1746(10)	80(7)	
C(233)	1439(16)	6242(18)	-1389(10)	38(6)	
O(233)	1234(14)	5520(16)	-1588(9)	70(6)	
C(241)	910(16)	5609(18)	-141(10)	39(6)	
O(241)	880(13)	4854(14)	-346(8)	60(5)	
C(242)	-85(19)	7233(20)	-76(12)	50(7)	
O(242)	-728(14)	7499(16)	-240(9)	71(6)	
C(243)	728(17)	6338(19)	954(11)	46(7)	
O(243)	551(13)	6061(14)	1430(9)	61(5)	cont ...

atom	x	y	z	U
C(251)	1326(17)	8038(19)	1591(11)	44(6)
O(251)	1112(15)	7793(16)	2085(10)	80(7)
C(252)	877(19)	9407(21)	752(12)	52(7)
O(252)	428(16)	10021(17)	683(10)	82(7)
C(253)	2452(19)	9264(21)	1222(12)	55(7)
O)253)	2894(15)	9730(16)	1543(10)	77(7)
C(2)	1669(15)	7958(16)	-136(9)	31(5)

[a] Anisotropic thermal parameters.

Table 2 Anisotropic Temperature Factors *($Å^2 \times 10^3$) for (III).

E.s.d's in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(11)	26.6(5)	30.1(5)	32.8(4)	-2.7(4)	0.1(4)	-1.3(5)
Os(12)	32.4(6)	33.6(5)	29.9(4)	2.6(4)	2.0(4)	-2.4(5)
Os(13)	18.7(5)	38.0(6)	47.6(5)	-7.0(4)	2.3(4)	-1.9(5)
Os(14)	32.3(6)	40.1(6)	29.4(4)	0.9(4)	-4.8(4)	4.9(5)
Os(15)	20.6(5)	42.1(6)	34.3(5)	1.9(4)	2.8(4)	3.7(5)
Os(21)	21.3(5)	27.9(5)	31.2(4)	2.8(4)	-0.7(4)	1.6(4)
Os(22)	23.6(5)	25.4(5)	33.9(4)	2.1(4)	1.7(4)	-1.9(4)
Os(23)	21.9(5)	30.6(5)	25.8(4)	-1.3(3)	0.7(3)	0.2(4)
Os(24)	21.0(5)	30.2(5)	32.3(4)	0.7(4)	3.5(4)	-4.8(4)
Os(25)	28.5(5)	33.2(5)	26.8(4)	-4.7(4)	0.7(4)	-0.8(5)

* Anisotropic temperature factor defined as:

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\right]$$

APPENDIX 4

Fractional Atomic Coordinates and Thermal Parameters for

$[(Ph_3P)_2N]^+ [Os_5C(CO)_{15}I]^-$ (IV).

Table 1 Fractional Atomic Coordinates (x 10^4) and Isotropic Temperature Factors ($Å^2$ x 10^3) for (IV). Esd's are given in parentheses.

atom[a]	x	y	z	U	
Os(1)	3967(1)	2741(1)	8853(1)		b
Os(2)	4414(1)	4716(1)	8132(1)		b
Os(3)	3260(1)	3909(1)	7803(1)		b
Os(4)	3906(1)	2740(1)	7154(1)		b
Os(5)	3706(1)	6417(1)	7927(1)		b
C(11)	3659(4)	1269(15)	8968(11)		b
O(11)	4378(3)	295(12)	9061(9)		b
C(12)	4440(4)	1694(14)	9150(10)		b
O(12)	4727(3)	1070(11)	9375(8)		b
C(13)	3979(4)	3493(19)	9933(10)		b
O(13)	3999(5)	3836(19)	10608(9)		b
C(21)	4877(4)	3589(15)	8288(11)		b
O(21)	5147(3)	2938(11)	8401(9)		b
C(22)	4586(4)	5749(15)	7290(12)		b
O(22)	4695(3)	6354(12)	6798(9)		b
C(23)	4650(4)	5757(17)	9083(14)		b
O(23)	4801(4)	6449(13)	9603(10)		b
C(31)	2959(4)	4656(14)	8536(11)		b
O(31)	2775(4)	5134(12)	8970(12)		b
C(32)	2973(3)	2273(14)	7730(11)		b
O(32)	2805(3)	1277(10)	7711(10)		b
C(33)	2926(4)	4518(14)	6821(9)		b
O(33)	2732(3)	4883(11)	6193(7)		b
C(41)	3620(5)	1145(15)	7005(11)		b
O(41)	3439(4)	141(12)	6852(11)		b

cont ...

atom	x	y	z	U
C(42)	3745(6)	3355(19)	6028(11)	b
O(42)	3630(6)	3581(17)	5386(9)	b
C(43)	4371(4)	1929(19)	6990(10)	b
O(43)	4667(4)	1466(15)	6861(10)	b
C(51)	3228(4)	7474(12)	7787(14)	b
O(51)	2941(3)	8055(10)	7693(11)	b
C(52)	4052(4)	7863(14)	8033(16)	b
O(52)	4251(3)	8771(11)	8043(12)	b
C(53A)	3630	6447	6864	73(9)
C(53B)	3773	6444	8995	66(8)
I(A)	3639(1)	6566(2)	6191(2)	b
I(B)	3740(1)	6531(3)	9690(2)	b
C	3841(3)	4300(10)	7978(8)	b
N	3469(3)	2034(9)	2966(7)	b
P(1)	3935(1)	1846(3)	3121(2)	b
P(2)	3129(1)	3125(3)	2747(2)	b
C(111)	4222(3)	3319(10)	3385(6)	53(3)
C(112)	4365(3)	3648(10)	4220(6)	67(4)
C(113)	4540(3)	4889(10)	4428(6)	85(5)
C(114)	4572(3)	5799(10)	3802(6)	90(6)
C(115)	4429(3)	5469(10)	2968(6)	82(5)
C(116)	4254(3)	4229(10)	2759(6)	69(4)
C(121)	4091(2)	1114(9)	2239(6)	47(3)
C(122)	3821(2)	285(9)	1723(6)	56(4)
C(123)	3937(3)	-399(9)	1071(6)	68(4)
C(124)	4322(2)	-256(9)	934(6)	87(5)
C(125)	4593(2)	573(9)	1449(6)	79(5)
C(126)	4477(2)	1258(9)	2102(6)	65(4)
C(131)	4086(2)	676(10)	3975(7)	52(3)
C(132)	3843(2)	482(10)	4551(7)	67(4)
C(133)	3962(2)	-388(10)	5220(7)	91(6)
C(134)	4323(3)	-1063(10)	5312(7)	90(5)
C(135)	4566(2)	-869(10)	4735(7)	78(5)
C(136)	4448(2)	1(10)	4067(7)	75(5)
C(211)	2795(2)	2942(6)	3450(6)	43(3)
C(212)	2579(2)	4022(6)	3658(6)	52(3)

cont ...

atom	x	y	z	U
C(213)	2343(2)	3873(6)	4251(6)	64(4)
C(214)	2323(2)	2643(6)	4638(6)	74(5)
C(215)	2540(2)	1564(6)	4430(6)	74(4)
C(216)	2776(2)	1713(6)	3837(6)	50(3)
C(221)	3300(2)	4812(8)	2826(8)	42(3)
C(222)	3460(2)	5320(8)	3616(5)	49(3)
C(223)	3608(2)	6617(8)	3700(5)	54(4)
C(224)	3596(2)	7407(8)	2995(5)	68(4)
C(225)	3435(2)	6899(8)	2205(5)	78(5)
C(226)	3288(2)	5601(8)	2121(5)	59(4)
C(231)	2850(2)	2886(9)	1694(6)	43(3)
C(232)	3063(2)	2675(9)	1066(6)	58(4)
C(233)	2862(2)	2555(9)	239(6)	71(4)
C(234)	2448(2)	2645(9)	40(6)	73(5)
C(235)	2235(2)	2855(9)	668(6)	64(4)
C(236)	2436(2)	2976(9)	1495(6)	54(3)

a In the anion the I atom and CO(53) are disordered. These ligands are related in position by an approximate non-crystallographic two-fold axis that contains Os(5) and passes through the midpoint of the Os(1) - Os(4) bond; the site occupation factors for the two alternative iodine sites /I(A) and I(B)/ and the two alternative carbon sites /C(53A) and C(53B), which were placed in fixed positions/ were set to 0.5. The Os-I distance is approximately equal to an Os...O distance so the two alternative sites for O(53) are masked by the two I sites. Since the atomic no. of I is much larger than that of O, no allowance was made for this oxygen in the structure factor calculations.

b Anisotropic thermal parameters.

Table 2

Anisotopic Temperature Factors * ($Å^2$ x 10^3) for (IV).
Esd's in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	46.1(3)	40.1(3)	36.1(3)	7.1(3)	11.9(2)	6.3(2)
Os(2)	35.7(2)	37.8(3)	60.4(4)	9.0(3)	6.7(3)	1.0(2)
Os(3)	36.1(2)	28.6(2)	40.1(3)	0.7(2)	11.4(2)	1.3(2)
Os(4)	48.7(3)	37.5(3)	37.1(3)	-0.5(3)	16.6(2)	6.0(2)
Os(5)	42.4(3)	24.8(2)	75.6(5)	-0.9(3)	5.5(3)	1.2(2)
C(11)	60(8)	58(9)	72(12)	28(9)	-4(8)	-3(7)
O(11)	104(9)	80(9)	98(11)	27(8)	17(8)	-6(7)
C(12)	66(9)	54(8)	58(10)	16(8)	31(8)	9(7)
O(12)	67(6)	75(7)	101(10)	23(8)	17(7)	23(6)
C(13)	71(10)	109(14)	44(10)	-27(10)	18(8)	8(9)
O(13)	207(17)	187(19)	69(10)	-33(12)	53(11)	9(13)
C(21)	51(8)	70(10)	80(12)	35(10)	17(8)	11(7)
O(21)	56(6)	85(8)	136(12)	62(9)	22(7)	29(6)
C(22)	49(8)	51(9)	108(15)	26(10)	16(9)	20(7)
O(22)	86(8)	100(10)	146(13)	80(10)	62(8)	21(7)

cont...

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(23)	59(9)	62(10)	115(17)	0(12)	-9(10)	-3(8)
O(23)	117(10)	82(9)	132(14)	-43(10)	-39(9)	-9(8)
C(31)	64(9)	53(9)	69(11)	2(9)	29(8)	4(7)
O(31)	130(10)	95(10)	84(10)	4(8)	62(8)	19(8)
C(32)	32(6)	48(8)	99(14)	3(9)	4(8)	7(6)
O(32)	63(6)	57(7)	163(14)	17(8)	19(8)	-17(5)
C(33)	57(8)	61(9)	39(8)	11(8)	16(7)	10(7)
O(33)	101(8)	87(9)	53(7)	15(7)	-3(6)	8(7)
C(41)	116(13)	51(9)	66(11)	-14(9)	59(10)	-9(9)
O(41)	158(12)	75(9)	167(16)	-47(10)	90(12)	-44(9)
C(42)	149(17)	91(14)	41(11)	22(11)	24(11)	44(12)
O(42)	293(21)	142(14)	54(9)	53(10)	49(11)	89(14)
C(43)	60(9)	110(14)	60(11)	-48(11)	-2(8)	18(9)
O(43)	105(10)	148(14)	155(16)	-67(12)	54(10)	15(9)
C(51)	59(8)	24(7)	158(20)	-8(10)	14(11)	-18(6)
O(51)	44(5)	49(6)	258(21)	-12(10)	16(9)	16(5)
C(52)	55(8)	35(8)	205(26)	0(12)	24(12)	-1(7)
O(52)	66(7)	56(7)	248(21)	-11(11)	-5(10)	-8(6)
I(A)	77(1)	65(1)	76(2)	17(1)	15(1)	1(1)
I(B)	108(2)	75(2)	93(2)	-37(2)	10(2)	18(1)

cont ...

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C	38(6)	20(5)	49(8)	12(6)	4(6)	6(4)
N	45(5)	32(5)	53(7)	8(6)	18(5)	3(4)
P(1)	48(2)	39(2)	42(2)	-2(2)	10(2)	1(1)
P(2)	43(2)	34(2)	39(2)	4(2)	11(2)	-3(1)

* Anisotropic temperature factor defined as:-

$$T = \exp -\left[2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\right]$$

APPENDIX 5

Fractional Atomic Coordinates and Thermal Parameters for

$[Ph_4As]_2^+ [Ru_6C(CO)_{16}]^{2-}$ (V).

Table 1 Fractional Atomic Coordinates (x 10^4) and Isotropic Temperature Factors ($Å^2$ x 10^3) for (V).
E.s.d's are given in parentheses.

atom [a]	x	y	z	U
Ru(1)	192(1)	-311(1)	-1658(1)	b
Ru(2)	597(1)	-1067(1)	695(1)	b
Ru(3)	-881(1)	-785(1)	-262(1)	b
C(11)	-120(11)	77(13)	-3168(20)	b
O(11)	-278(12)	376(14)	-4077(16)	b
C(12)	674(9)	-1339(15)	-2173(22)	b
O(12)	1006(8)	-1939(11)	-2351(19)	b
C(13)	-838(10)	-1262(12)	-2026(16)	b
O(13)	-1076(6)	-1656(10)	-2801(12)	b
C(14)	1135(9)	400(11)	-1407(15)	b
O(14)	1518(7)	583(10)	-2034(12)	b
C(21A)	1560	-1327	1228	107(7)
O(21A)	2146(8)	-1554(11)	1577(14)	105(5)
C(21B)	1505	-1274	1571	76(5)
O(21B)	2092(8)	-1355(11)	2159(14)	100(5)
C(22A)	376	-2165	1129	86(5)
O(22A)	252(8)	-2933(10)	1357(14)	116(5)
C(22B)	456	-2300	585	78(5)
O(22B)	360(8)	-3053(11)	452(15)	120(5)
C(26)	396(7)	-925(10)	2408(16)	b
O(26)	486(7)	-1250(9)	3355(11)	b
C(31A)	-1073	-1950	226	65(4)
O(31A)	-1166(6)	-2700(8)	561(13)	86(4)
C(31B)	-1111	-1967	-224	88(6)
O(31B)	-1262(8)	-2718(10)	-231(15)	112(5)
C(32A)	-1816	-498	-517	76(5)
O(32A)	-2408(7)	-299(9)	-670(13)	89(4)
C(32B)	-1808	-571	-982	69(4)
O(32B)	-2397(8)	-432(10)	-1419(15)	107(5)
C(56')	853(9)	-1374(11)	-880(15)	b
O(56')	1210(8)	-1872(10)	-1255(12)	b
C(61')	937(10)	105(12)	-2386(18)	b

cont...

O(61')	1420(7)	306(12)	-2798(14)	b
C(62')	-223(10)	-947(14)	-2941(18)	b
O(62')	-510(9)	-1454(11)	-3612(14)	b
C	0	0	0	b
As	3773(1)	267(1)	-2216(1)	b
C(111)	3680(3)	-898(3)	-1600(6)	b
C(112)	3077(3)	-1106(3)	-1157(6)	b
C(113)	2981(3)	-1971(3)	763(6)	b
C(114)	3487(3)	-2627(3)	-811(6)	b
C(115)	4090(3)	-2418(3)	-1254(6)	b
C(116)	4186(3)	-1554(3)	-1648(6)	b
C(121)	4704(3)	462(5)	-2438(7)	b
C(122)	4968(3)	-58(5)	-3259(7)	b
C(123)	5651(3)	85(5)	-3445(7)	b
C(124)	6070(3)	749(5)	-2810(7)	b
C(125)	5807(3)	1270(5)	-1989(7)	b
C(126)	5124(3)	1127(5)	-1803(7)	b
C(131)	3517(4)	1084(4)	-1122(5)	b
C(132)	3014(4)	1743(4)	-1515(5)	b
C(133)	2848(4)	2373(4)	-719(5)	b
C(134)	3185(4)	2345(4)	470(5)	b
C(135)	3688(4)	1687(4)	863(5)	b
C(136)	3854(4)	1057(4)	67(5)	b
C(141)	3154(4)	397(5)	-3696(6)	b
C(142)	3301(4)	1022(5)	-4516(6)	b
C(143)	2860(4)	1090(5)	-5629(6)	b
C(144)	2273(4)	533(5)	-5922(6)	b
C(145)	2126(4)	-91(5)	-5103(6)	b
C(146)	2567(4)	-159(5)	-3989(6)	b

a

All atoms have a site occupation factor of 0.5 except for Ru(1), Ru(2), Ru(3), and the atoms of the $[Ph_4As]^+$ cation whose sites are of full occupancy; in carbonyl liqands CO(21), CO(22), CO(31), and CO(32) the two components [(A) and (B)] of the C atoms were placed in fixed positions such that d(Ru-C)/d(Ru..O)= 0.615, these positions were recalculated after each cycle of refinement if large shifts were observed for the oxygen atoms to which they were attached [O(nA) and O(nB) respectively].

b

Anisotropic thermal parameters.

Table 2 Anisotropic temperature factors * ($Å^2 \times 10^3$) for (V).

E.s.d's are given in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	54.4(3)	67.0(4)	56.9(4)	0.4(3)	19.6(3)	5.4(3)
Ru(2)	53.6(3)	53.3(4)	73.2(4)	2.2(3)	16.6(3)	8.8(3)
Ru(3)	49.4(3)	66.1(4)	83.8(5)	9.7(4)	14.0(3)	-9.6(3)
C(11)	104(15)	80(12)	86(15)	-6(11)	30(13)	-3(11)
O(11)	209(21)	184(19)	85(12)	40(13)	11(13)	-9(15)
C(12)	65(11)	100(15)	176(23)	-57(15)	36(13)	8(10)
O(12)	115(12)	104(12)	257(22)	-54(13)	84(13)	19(9)
C(13)	93(12)	69(11)	63(11)	4(9)	-12(10)	18(9)
O(13)	72(7)	130(11)	85(9)	-33(9)	-2(7)	-4(7)
C(14)	93(12)	67(10)	62(11)	-11(8)	30(10)	-2(9)
O(14)	108(9)	126(11)	92(9)	-4(8)	77(8)	-17(8)
C(26)	52(8)	72(10)	74(12)	2(9)	22(8)	16(7)
O(26)	95(9)	118(10)	72(8)	33(8)	16(8)	27(8)
C(56')	79(10)	58(9)	80(12)	-1(9)	25(9)	13(8)
O(56')	171(14)	98(10)	97(10)	-3(8)	56(10)	53(10)
C(61')	89(12)	70(11)	101(15)	34(10)	37(12)	15(9)
O(61')	93(10)	175(16)	131(13)	33(11)	74(10)	20(10)
C(62')	72(11)	108(15)	84(14)	-14(12)	0(10)	17(10)
O(62')	153(14)	111(12)	119(13)	-46(11)	-38(11)	26(10)
C	37(4)	54(5)	55(6)	3(5)	14(4)	-1(4)
As	93.7(6)	64.1(6)	70.9(6)	-16.5(4)	2.8(5)	7.7(4)

cont...

C(111)	70(5)	68(5)	82(6)	-16(5)	9(5)	-3(4)
C(112)	126(9)	79(7)	108(9)	1(6)	16(7)	5(6)
C(113)	142(10)	103(9)	128(10)	-9(8)	29(8)	-29(8)
C(114)	126(9)	82(7)	115(9)	-13(6)	13(8)	22(7)
C(115)	142(11)	78(8)	229(16)	-36(9)	72(11)	4(7)
C(116)	128(9)	64(6)	133(10)	-11(6)	40(8)	8(6)
C(121)	98(7)	76(6)	81(7)	10(5)	24(6)	-6(5)
C(122)	156(11)	99(8)	173(14)	-33(9)	90(11)	-25(8)
C(123)	153(12)	150(12)	163(14)	-36(11)	101(11)	-10(10)
C(124)	120(10)	142(12)	115(11)	-1(9)	23(8)	15(8)
C(125)	110(9)	123(10)	163(14)	3(10)	-7(10)	-12(8)
C(126)	95(7)	92(7)	121(9)	-9(7)	2(7)	-5(6)
C(131)	110(7)	63(5)	85(7)	-15(5)	16(6)	13(5)
C(132)	124(9)	74(7)	144(11)	2(7)	47(8)	21(6)
C(133)	143(10)	86(8)	141(11)	4(8)	69(9)	19(7)
C(134)	226(16)	94(9)	100(9)	-10(7)	58(10)	33(9)
C(135)	115(9)	143(11)	109(9)	-55(8)	30(7)	-3(8)
C(136)	103(7)	132(9)	76(7)	-45(7)	8(6)	-4(7)
C(141)	129(9)	89(7)	68(7)	-19(6)	-5(6)	27(6)
C(142)	196(14)	107(9)	69(7)	-4(6)	12(8)	56(9)
C(143)	256(21)	172(15)	75(9)	-9(9)	11(11)	110(14)
C(144)	211(18)	136(13)	122(13)	-26(11)	-40(13)	56(12)
C(145)	233(20)	122(12)	163(16)	-20(11)	-81(15)	-5(12)
C(146)	138(11)	134(11)	112(11)	-16(8)	-28(9)	-2(9)

* Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2 \left(\underline{U}_{11}h^2a^{*2} + \underline{U}_{22}k^2b^{*2} + \underline{U}_{33}l^2c^{*2} + 2\underline{U}_{23}klb^*c^* + 2\underline{U}_{13}hla^*c^* + 2\underline{U}_{12}hka^*b^*\right)\right]$$

APPENDIX 6

Fractional Atomic Coordinates and Thermal Parameters for $Ru_6C(CO)_{15}(C_6H_{10})$ (VI).

Table 1 Fractional Atomic Coordinator ($x10^4$) and Isotropic Temperature Factors ($Å^2 x10^3$) for (VI). E.s.d's are given in parentheses.

atom [a]	x	y	z	U[b]
Ru(11)	600(1)	1530(1)	3299(1)	c
Ru(12)	-685(1)	724(1)	3279(1)	c
Ru(13)	2047(1)	778(1)	3304(1)	c
Ru(14)	-988(1)	1262(1)	1867(1)	c
Ru(15)	1820(1)	1280(1)	1925(1)	c
Ru(16)	390(1)	523(1)	1848(1)	c
C(111)	51(9)	2005(3)	2745(6)	46(2)
O(111)	-189(8)	2316(2)	2447(5)	69(2)
C(112)	2113(9)	1706(3)	3841(6)	46(2)
O(112)	3079(7)	1835(2)	4147(4)	66(2)
C(121)	-2328(9)	555(3)	2889(5)	43(2)
O(121)	-3289(7)	433(2)	2623(4)	65(2)
C(122)	-310(9)	204(3)	3692(5)	45(2)
O(122)	-54(7)	-113(2)	3956(4)	63(2)
C(131)	3757(10)	925(3)	3416(6)	54(3)
O(131)	4826(8)	1017(3)	3519(5)	79(2)
C(132)	2349(11)	263(3)	2884(6)	60(3)
O(132)	2791(8)	-59(3)	2782(5)	79(2)
C(133)	2093(9)	611(3)	4393(6)	49(2)
O(133)	2146(8)	522(2)	5053(5)	70(2)
C(141)	-2643(9)	1323(3)	2068(6)	44(2)
O(141)	-3709(8)	1359(2)	2174(5)	70(2)
C(142)	-1395(10)	1638(3)	1050(6)	52(3)
O(142)	-1672(9)	1883(3)	553(5)	85(3)
C(146)	-1282(9)	746(3)	1193(5)	39(2)
O(146)	-2037(7)	614(2)	701(4)	57(2)

cont...

atom	x	y	z	U
C(151)	1345(10)	1579(3)	969(6)	51(3)
O(151)	1150(8)	1752(2)	357(5)	72(2)
C(152)	3083(10)	1670(3)	2247(6)	47(2)
O(152)	3853(8)	1907(2)	2438(5)	69(2)
C(153)	2975(10)	967(3)	1460(6)	55(3)
O(153)	3778(9)	774(3)	1188(5)	81(3)
C(161)	1085(10)	345(3)	946(6)	52(3)
O(161)	1484(8)	233(3)	357(5)	84(3)
C(162)	-312(9)	5(3)	1913(6)	47(2)
O(162)	-771(8)	-310(2)	1922(5)	70(2)
C(11)	-2444(10)	545(3)	4725(6)	52(3)
C(12)	-1260(10)	772(3)	4564(6)	56(3)
C(13)	-1290(9)	1156(3)	4253(6)	45(2)
C(14)	-375(10)	1467(3)	4435(6)	50(2)
C(15)	-477(11)	1858(3)	4227(7)	59(3)
C(16)	164(10)	2215(3)	4643(6)	54(3)
H(111)	-2153(10)	239(3)	4880(6)	150(21)
H(112)	-3126(10)	541(3)	4195(6)	150(21)
H(113)	-2873(10)	680(3)	5218(6)	150(21)
H(12)	-349(10)	626(3)	4698(6)	104(20)
H(13)	-2098(9)	1230(3)	3827(6)	104(20)
H(14)	505(10)	1377(3)	4778(6)	104(20)
H(15)	-1108(11)	1925(3)	3692(7)	104(20)
H(161)	-92(10)	2484(3)	4294(6)	150(21)
H(162)	1164(10)	2224(3)	4855(6)	150(21)
H(163)	-382(10)	2202(3)	5150(6)	150(21)
C(1)	519(7)	1021(2)	2602(4)	27(2)

Ru(21)	3074(1)	8648(1)	2033(1)	c
Ru(22)	5661(1)	8944(1)	1891(1)	c
Ru(23)	4892(1)	8128(1)	1356(1)	c
Ru(24)	4933(1)	8753(1)	3482(1)	c
Ru(25)	4089(1)	7972(1)	2943(1)	c
Ru(26)	6695(1)	8253(1)	2757(1)	c

cont ...

atom	x	y	z	U
C(211)	2217(9)	8883(3)	2842(6)	47(2)
O(211)	1564(8)	9009(2)	3305(5)	70(2)
C(212)	1853(10)	8261(3)	1642(6)	52(3)
O(212)	1070(8)	8037(2)	1406(5)	72(2)
C(221)	6646(10)	9303(3)	2575(6)	50(3)
O(221)	7311(7)	9513(2)	2965(5)	68(2)
C(222)	6886(10)	8906(3)	1157(6)	50(3)
O(222)	7647(8)	8880(2)	728(5)	72(2)
C(231)	4061(11)	7685(4)	833(7)	62(3)
O(231)	3466(9)	7427(3)	471(5)	87(3)
C(232)	6589(11)	7902(3)	1431(6)	58(3)
O(232)	7442(9)	7733(3)	1217(5)	85(3)
C(233)	4871(10)	8358(3)	361(6)	54(3)
O(233)	4822(8)	8503(3)	-268(5)	82(3)
C(241)	5013(9)	9293(3)	3851(6)	48(2)
O(241)	5012(8)	9265(3)	4067(5)	80(3)
C(242)	4357(9)	8592(3)	4437(6)	46(2)
O(242)	3991(7)	8500(2)	5039(5)	68(2)
C(246)	6733(8)	8582(3)	3853(5)	37(2)
O(246)	7538(7)	8641(2)	4386(4)	61(2)
C(251)	2630(11)	8005(3)	3506(6)	57(3)
O(251)	1742(9)	8019(3)	3845(5)	81(3)
C(252)	3491(10)	7494(3)	2390(6)	53(3)
O(252)	3103(8)	7190(3)	2142(5)	77(2)
C(253)	4977(10)	7667(3)	3755(6)	55(3)
O(253)	5505(9)	7482(3)	4277(6)	93(3)
C(261)	7502(10)	7797(3)	3233(6)	52(3)
O(261)	8021(8)	7521(3)	3552(5)	76(2)
C(262)	8281(10)	8438(3)	2606(6)	53(3)
O(262)	9276(9)	8562(3)	2494(5)	88(3)
C(21)	5975(11)	9811(4)	983(7)	63(3)
C(22A)	5010(17)	9586(5)	1468(10)	37(4)
C(22B)	5132(21)	9415(7)	909(13)	58(5)
C(23)	4144(11)	9337(4)	1199(7)	64(3)
C(24)	2926(12)	9182(4)	1188(7)	69(3)

cont ...

atom	x	y	x	U
C(25A)	2047(17)	8950(5)	907(10)	36(4)
C(25B)	1823(19)	9162(6)	1371(12)	47(5)
C(26)	649(11)	9022(3)	900(7)	55(3)
C(2)	4849(7)	8462(2)	2393(5)	29(2)

[a] The disordered carbon atoms of the hexadiene ligand in cluster 2 [C(22A), C(22B); C(25A), C(25B)] had their site occupation factors fixed at 0.5.

[b] sp^3 and sp hydrogen atoms had their isotropic temperature factors tied to separate common free variable.

[c] Anisotropic thermal parameters.

Table 2 Anisotropic Thermal Parameters *($Å^2 \times 10^3$) for (VI).
E.s.d's are given in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(11)	29.8(4)	27.6(3)	31.0(3)	0.7(3)	3.7(3)	2.2(3)
Ru(12)	27.4(3)	28.7(4)	31.6(3)	3.0(3)	5.8(3)	0.9(3)
Ru(13)	26.8(3)	32.0(4)	34.6(4)	1.0(3)	1.4(3)	5.4(3)
Ru(14)	31.7(4)	33.1(4)	31.1(4)	3.8(3)	0.3(3)	5.5(3)
Ru(15)	33.1(4)	33.9(4)	33.9(4)	1.3(3)	10.1(3)	-2.3(3)
Ru(16)	36.0(4)	29.5(4)	35.2(4)	-2.9(3)	9.1(3)	0.8(3)
Ru(21)	22.1(3)	34.3(4)	33.0(4)	-1.7(3)	0.4(3)	-1.5(3)
Ru(22)	25.5(3)	31.8(4)	31.3(3)	0.7(3)	2.7(3)	-4.3(3)
Ru(23)	35.8(4)	33.2(4)	33.0(4)	-6.6(3)	5.6(3)	-0.8(3)
Ru(24)	30.2(4)	36.4(4)	28.4(3)	-3.5(3)	2.4(3)	2.0(3)
Ru(25)	31.8(4)	33.5(4)	37.9(4)	4.6(3)	6.0(3)	-3.3(3)
Ru(26)	23.9(3)	37.0(4)	39.0(4)	1.9(3)	2.6(3)	3.8(3)

*Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2 \left(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*\right)\right]$$

Table 2 Anisotropic Thermal Parameters *($Å^2$ x 10^3) for (VI).
E.s.d's are given in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(11)	29.8(4)	27.6(3)	31.0(3)	0.7(3)	3.7(3)	2.2(3)
Ru(12)	27.4(3)	28.7(4)	31.6(3)	3.0(3)	5.8(3)	0.9(3)
Ru(13)	26.8(3)	32.0(4)	34.6(4)	1.0(3)	1.4(3)	5.4(3)
Ru(14)	31.7(4)	33.1(4)	31.1(4)	3.8(3)	0.3(3)	5.5(3)
Ru(15)	33.1(4)	33.9(4)	33.9(4)	1.3(3)	10.1(3)	-2.3(3)
Ru(16)	36.0(4)	29.5(4)	35.2(4)	-2.9(3)	9.1(3)	0.8(3)
Ru(21)	22.1(3)	34.3(4)	33.0(4)	-1.7(3)	0.4(3)	-1.5(3)
Ru(22)	25.5(3)	31.8(4)	31.3(3)	0.7(3)	2.7(3)	-4.3(3)
Ru(23)	35.8(4)	33.2(4)	33.0(4)	-6.6(3)	5.6(3)	-0.8(3)
Ru(24)	30.2(4)	36.4(4)	28.4(3)	-3.5(3)	2.4(3)	2.0(3)
Ru(25)	31.8(4)	33.5(4)	37.9(4)	4.6(3)	6.0(3)	-3.3(3)
Ru(26)	23.9(3)	37.0(4)	39.0(4)	1.9(3)	2.6(3)	3.8(3)

*Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2 \left(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*\right)\right]$$

APPENDIX 7

Fractional Atomic Coordinates and Thermal Parameters for

$[(Ph_3P)_2N]_2^+ [Os_{10}C(CO)_{24}]^{2-}$ (VII).

Table 1 Fractional Atomic Coordinates (x 10^4) and Isotropic Temperature Factors ($Å^2$ x 10^3) for (VII). Esd's are given in parentheses.

atom	x	y	z	U
Os(1)	3505(1)	1472(1)	-1419(1)	a
Os(2)	3180(1)	2483(1)	532(1)	a
Os(3)	2499(1)	2013(1)	-1826(1)	a
Os(4)	2867(1)	934(1)	34(1)	a
Os(5)	2834(1)	3474(1)	2485(1)	a
Os(6)	2151(1)	3062(1)	203(1)	a
Os(7)	1504(1)	2575(1)	-2082(1)	a
Os(8)	1831(1)	1503(1)	-290(1)	a
Os(9)	2231(1)	482(1)	1578(1)	a
Os(10)	2526(1)	1976(1)	2079(1)	a
C(11)	3808(12)	2171(16)	-2214(25)	74(8)
O(11)	3940(9)	2639(12)	-2714(19)	100(7)
C(12)	3480(11)	693(15)	-2850(24)	65(7)
O(12)	3470(8)	203(10)	-3693(17)	79(6)
C(13)	4117(13)	1127(17)	-592(27)	83(9)
O(13)	4518(10)	864(13)	-118(22)	120(8)
C(21)	3747(11)	2184(15)	1621(24)	66(8)
O(21)	4123(7)	1965(10)	2385(16)	72(5)
C(22)	3456(9)	3276(12)	0(19)	42(5)
O(22)	3596(7)	3844(10)	-377(15)	71(5)
C(31)	2655(10)	2733(13)	-2859(20)	50(6)
O(31)	2749(8)	3194(10)	-3533(17)	83(6)
C(32)	2360(10)	1305(13)	-3248(21)	53(6)
O(32)	2256(8)	821(10)	-4159(16)	77(5)
C(41)	2779(10)	56(13)	-1103(21)	52(6)
O(41)	2693(8)	-470(11)	-1844(17)	88(6)
C(42)	3404(14)	486(18)	1023(29)	93(10)
O(42)	3777(12)	210(15)	1673(25)	143(10)
C(51)	3359(11)	3366(14)	3886(22)	58(7)
O(51)	3726(7)	3274(10)	4725(16)	71(5)
C(52)	2388(11)	3850(14)	3557(23)	65(7)

cont.

atom	x	y	z	U	
O(52)	2108(8)	4143(10)	4197(17)	81(6)	
C(53)	3009(10)	4478(14)	2216(21)	55(6)	
O(53)	3138(8)	5048(11)	2036(17)	88(6)	
C(61)	2232(10)	3979(13)	-403(21)	54(6)	
O(61)	2312(8)	4538(11)	-795(17)	89(6)	
C(62)	1619(11)	3464(14)	931(23)	61(7)	
O(62)	1258(8)	3734(11)	1362(17)	87(6)	
C(71)	1567(10)	3418(14)	-2951(22)	59(7)	
O(71)	1616(7)	3931(10)	-3472(15)	69(5)	
C(72)	894(10)	2907(13)	-1666(21)	53(6)	
O(72)	491(8)	3106(10)	-1408(16)	76(5)	
C(73)	1229(9)	1914(11)	-3532(18)	40(5)	
O(73)	1087(6)	1511(8)	-4438(14)	54(4)	
C(81)	1572(10)	737(13)	-1515(21)	52(6)	
O(81)	1442(7)	190(10)	-2247(16)	74(5)	
C(82)	1267(12)	1635(15)	346(25)	72(8)	
O(82)	872(10)	1750(12)	767(20)	105(7)	
C(91)	2016(11)	-440(15)	621(23)	64(7)	
O(91)	1941(8)	-1018(11)	49(18)	90(6)	
C(92)	1732(10)	534(13)	2553(21)	53(6)	
O(92)	1393(9)	579(11)	3115(19)	96(7)	
C(93)	2755(12)	57(16)	2781(25)	74(8)	
O(93)	3017(9)	-351(12)	3521(19)	102(7)	
C(101)	2994(10)	1755(13)	3489(20)	50(6)	
O(101)	3328(8)	1537(10)	4329(17)	79(6)	
C(102)	2077(9)	2218(11)	3216(18)	36(5)	
O(102)	1779(7)	2381(10)	3882(16)	72(5)	
C	2505(7)	1994(9)	101(14)	16(4)	
N(1)	6067(7)	2864(10)	5494(15)	a	
P(1)	6425(2)	2769(3)	4419(5)	a	
P(2)	5511(2)	2927(3)	5684(5)	a	
C(111)	7007(6)	2272(9)	5131(10)	47(6)	
C(112)	7244(6)	1700(9)	4386(10)	52(6)	
C(113)	7687(6)	1323(9)	4949(10)	69(7)	
C(114)	7895(6)	1519(9)	6257(10)	71(8)	
C(115)	7659(6)	2091(9)	7001(10)	84(9)	cont.

atom	x	y	z	U
C(116)	7215(6)	2467(9)	6438(10)	63(7)
C(121)	6592(6)	3691(9)	3988(16)	45(6)
C(122)	7063(6)	3794(9)	3703(16)	78(8)
C(123)	7160(6)	4487(9)	3283(16)	90(9)
C(124)	6787(6)	5076(9)	3147(16)	87(9)
C(125)	6316(6)	4972(9)	3432(16)	111(12)
C(126)	6218(6)	4280(9)	3852(16)	76(8)
C(131)	6174(6)	2232(8)	2910(12)	34(5)
C(132)	6032(6)	1488(8)	2961(12)	60(7)
C(133)	5803(6)	1066(8)	1825(12)	79(8)
C(134)	5716(6)	1387(8)	637(12)	96(10)
C(135)	5858(6)	2130(8)	586(12)	70(8)
C(136)	6087(6)	2553(8)	1722(12)	46(6)
C(211)	5486(5)	3451(9)	7227(14)	46(6)
C(212)	5907(5)	3808(9)	7948(14)	58(7)
C(213)	5888(5)	4186(9)	9184(14)	60(7)
C(214)	5449(5)	4207(9)	9699(14)	57(6)
C(215)	5028(5)	3850(9)	8978(14)	60(7)
C(216)	5046(5)	3472(9)	7743(14)	54(6)
C(221)	5276(6)	2025(8)	5797(13)	52(6)
C(222)	4767(6)	1890(8)	5406(13)	48(6)
C(223)	4587(6)	1196(8)	5609(13)	78(8)
C(224)	4915(6)	637(8)	6204(13)	86(9)
C(225)	5424(6)	773(8)	6595(13)	95(10)
C(226)	5604(6)	1466(8)	6392(13)	81(9)
C(231)	5068(6)	3381(8)	4415(11)	43(5)
C(232)	4812(6)	4078(8)	4711(11)	62(7)
C(233)	4500(6)	4441(8)	3718(11)	75(8)
C(234)	4444(6)	4107(8)	2430(11)	70(8)
C(235)	4700(6)	3410(8)	2134(11)	63(7)
C(236)	5012(6)	3047(8)	3127(11)	49(6)
N(2)	8882(6)	2543(9)	3348(14)	a
P(3)	8845(2)	2750(3)	1905(5)	a
P(4)	9269(2)	2651(3)	4702(5)	a
C(311)	9181(6)	3571(6)	1718(13)	45(6)
C(312)	9640(6)	3457(6)	1290(13)	52(6)

cont.

atom	x	y	z	U
C(313)	9907(6)	4087(6)	1165(13)	50(6)
C(314)	9716(6)	4831(6)	1469(13)	55(6)
C(315)	9257(6)	4945(6)	1896(13)	75(8)
C(316)	8989(6)	4315(6)	2021(13)	45(6)
C(321)	9052(6)	1945(8)	896(9)	40(5)
C(322)	9240(6)	1267(8)	1435(9)	53(6)
C(323)	9381(6)	631(8)	633(9)	55(6)
C(324)	9336(6)	674(8)	-707(9)	52(6)
C(325)	9149(6)	1352(8)	-1245(9)	54(6)
C(326)	9007(6)	1987(8)	-444(9)	43(5)
C(331)	8182(6)	2919(7)	1294(13)	40(5)
C(332)	8013(6)	3425(7)	349(13)	49(6)
C(333)	7506(6)	3472(7)	-220(13)	67(7)
C(334)	7169(6)	3015(7)	156(13)	60(7)
C(335)	7339(6)	2509(7)	1102(13)	71(8)
C(336)	7845(6)	2461(7)	1671(13)	49(6)
C(411)	9417(5)	1725(7)	5301(12)	37(5)
C(412)	9872(5)	1583(7)	6130(12)	47(6)
C(413)	9991(5)	857(7)	6564(12)	57(6)
C(414)	9656(5)	273(7)	6168(12)	58(7)
C(415)	9201(5)	415(7)	5339(12)	49(6)
C(416)	9082(5)	1141(7)	4905(12)	39(5)
C(421)	8972(5)	3274(8)	5856(13)	41(5)
C(422)	9216(5)	3449(8)	7139(13)	52(6)
C(423)	8980(5)	3942(8)	8006(13)	53(6)
C(424)	8499(5)	4260(8)	7590(13)	65(7)
C(425)	8254(5)	4085(8)	6307(13)	90(9)
C(426)	8491(5)	3592(8)	5440(13)	69(7)
C(431)	9851(5)	3012(7)	4580(13)	37(5)
C(432)	9957(5)	3773(7)	5026(13)	50(6)
C(433)	10395(5)	4070(7)	4812(13)	57(6)
C(434)	10725(5)	3607(7)	4152(13)	56(6)
C(435)	10619(5)	2847(7)	3706(13)	72(8)
C(436)	10181(5)	2549(7)	3920(13)	45(6)

[a] Anisotropic thermal parameters

Table 2 Anisotropic Thermal Parameters* ($Å^2 \times 10^3$) for (VII). Esd's are given in parentheses.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	28.1(6)	58.8(6)	44.8(5)	9.0(4)	3.9(4)	1.4(5)
Os(2)	28.3(6)	40.7(5)	32.6(4)	7.3(4)	-5.0(4)	-9.2(4)
Os(3)	27.1(5)	37.5(5)	29.6(4)	4.4(3)	-2.2(4)	-2.8(4)
Os(4)	35.2(6)	35.4(5)	37.5(4)	7.4(4)	0.4(4)	0.4(4)
Os(5)	44.1(6)	37.0(5)	34.4(4)	0.7(4)	-6.2(4)	-13.7(5)
Os(6)	30.7(6)	34.7(5)	33.6(4)	2.0(3)	-4.6(4)	-3.2(4)
Os(7)	27.2(6)	44.9(5)	34.4(4)	5.8(4)	-7.0(4)	0.4(4)
Os(8)	33.4(6)	37.8(5)	33.1(4)	5.0(3)	-1.5(4)	-9.8(4)
Os(9)	57.8(7)	37.4(5)	40.3(5)	8.6(4)	1.3(5)	-19.1(5)
Os(10)	33.2(6)	36.0(5)	28.9(4)	4.5(3)	-2.1(4)	-10.3(4)
N(1)	31(12)	68(13)	42(10)	-2(9)	4(9)	-15(10)
P(1)	32(4)	52(4)	44(3)	-1(3)	1(3)	-4(3)
P(2)	31(4)	53(4)	38(3)	7(3)	-3(3)	2(3)
N(2)	26(11)	57(12)	34(9)	-2(8)	7(8)	-10(9)
P(3)	29(4)	39(3)	33(3)	4(2)	-1(2)	-3(3)
P(4)	35(4)	38(3)	31(3)	5(2)	-3(2)	-1(3)

* Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2 \left(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*\right)\right]$$

APPENDIX 8

Fractional Atomic Coordinates and Thermal Parameters for

$[(Ph_3P)_2N]^+ [H_3Ru_4(CO)_{12}]^-$ (VIII) - " C_2 isomer ".

Table 1 Fractional Atomic Coordinates (x 10^4) and isotropic Temperature Factors ($Å^2$ x 10^3) for (VIII), e.s.d 's in parentheses.

atom[a]	x	y	z	U^b	
Ru(1A)	1759(1)	3862(1)	2864(1)	c	
Ru(2A)	3165(1)	4016(1)	1787(1)	c	
Ru(3A)	3035(1)	5103(1)	3967(1)	c	
Ru(4A)	2215(1)	5956(1)	2061(1)	c	
Ru(1B)	3038(7)	3772(9)	3437(10)	79(3)	
Ru(2B)	3361(6)	5918(9)	2588(9)	76(3)	
Ru(3B)	1982(6)	5668(9)	3681(9)	73(3)	
Ru(4B)	2077(7)	4655(10)	1559(10)	87(3)	
H(12)	2279(36)	3142(54)	1946(54)	83(21)	
H(14)	1297(44)	4959(66)	1661(66)	146(28)	
H(23)	3587(45)	3766(66)	3170(66)	147(28)	
C(11)	2096(4)	2700(5)	3810(6)	c	
O(11)	2259(3)	1973(4)	4363(5)	c	
C(12)	942(4)	3062(7)	1890(7)	c	
O(12)	453(4)	2569(6)	1363(6)	c	
C(13)	1123(4)	4598(6)	3821(6)	c	
O(13)	720(3)	5050(5)	4383(5)	c	
C(21)	3701(4)	2570(5)	1728(6)	c	
O(21)	4003(3)	1723(4)	1625(5)	c	
C(22)	2694(4)	4071(6)	304(7)	c	
O(22)	2485(3)	4060(5)	-622(5)	c	
C(23)	4019(4)	4880(6)	1546(7)	c	
O(23)	4547(3)	5317(5)	1375(6)	c	
C(31)	2452(4)	6082(6)	4858(7)	c	
O(31)	2140(3)	6644(5)	5442(5)	c	
C(32)	3373(4)	4136(6)	5113(7)	c	
O(32)	3581(4)	3618(6)	5856(6)	c	
C(33)	3909(5)	6065(8)	4188(8)	c	
O(33)	4438(4)	6668(6)	4337(7)	c	
C(41)	1621(4)	7046(5)	2814(6)	c	cont ...

O(41)	1261(3)	7710(4)	3243(5)	c
C(42)	3011(5)	6955(6)	1931(8)	c
O(42)	3479(5)	7570(5)	1852(8)	c
C(43)	1663(6)	6138(8)	639(8)	c
O(43)	1340(5)	6338(7)	-220(6)	c
N	-2369(3)	-309(4)	2617(5)	c
P(1)	-3225(1)	84(1)	2721(1)	c
P(2)	-1569(1)	-551(1)	2224(1)	c
C(111)	-3413(2)	1554(3)	2423(3)	48(1)
C(112)	-3002(2)	2033(3)	1685(3)	69(2)
C(113)	-3124(2)	3178(3)	1472(3)	86(2)
C(114)	-3657(2)	3845(3)	1998(3)	87(2)
C(115)	-4068(2)	3367(3)	2737(3)	74(2)
C(116)	-3946(2)	2222(3)	2949(3)	65(2)
C(121)	-3414(2)	-29(3)	4100(3)	46(1)
C(122)	-2979(2)	652(3)	4939(3)	67(2)
C(123)	-3120(2)	630(3)	6022(3)	81(2)
C(124)	-3696(2)	-74	6268(3)	86(2)
C(125)	-4131(2)	-755(3)	5430(3)	80(2)
C(126)	-3990(2)	-733(3)	4346(3)	62(2)
C(131)	-3918(2)	-795(2)	1833(3)	45(1)
C(132)	-4661(2)	-364(2)	1479(3)	58(2)
C(133)	-5220(2)	-1075(2)	856(3)	70(2)
C(134)	-5035(2)	-2217(2)	586(3)	69(2)
C(135)	-4292(2)	-2648(2)	940(3)	72(2)
C(136)	-3734(2)	-1937(2)	1563(3)	60(2)
C(211)	-1554(2)	-219(3)	824(3)	46(1)
C(212)	-1013(2)	527(3)	552(3)	66(2)
C(213)	-1017(2)	753(3)	-544(3)	82(2)
C(214)	-1563(2)	232(3)	-1366(3)	79(2)
C(215)	-2104(2)	-514(3)	-1094(3)	83(2)
C(216)	-2100(2)	-740(3)	2(3)	71(2)
C(221)	-1310(3)	-2044(4)	2298(4)	54(1)
C(222)	-788(3)	-2576(4)	1654(4)	76(2)
C(223)	-582(3)	-3723(4)	1756(4)	95(3)
C(224)	-899(3)	-4339(4)	2502(4)	101(3)
C(225)	-1421(3)	-3807(4)	3147(4)	98(3)
C(226)	-1627(3)	-2659(4)	3044(4)	72(2)
C(231)	-828(2)	286(3)	3079(3)	47(1)

cont ...

C(232)	-67(2)	-129(3)	3321(3)	56(2)
C(233)	498(2)	555(3)	3964(3)	66(2)
C(234)	303(2)	1653(3)	4366(3)	66(2)
C(235)	-458(2)	2068(3)	4124(3)	69(2)
C(236)	-1024(2)	1384(3)	3480(3)	64(2)
H(112)	-2590(2)	1516(3)	1277(3)	127(5)
H(113)	-2806(2)	3548(3)	900(3)	127(5)
H(114)	-3752(2)	4732(3)	1833(3)	127(5)
H(115)	-4481(2)	3883(3)	3144(3)	127(5)
H(116)	-4264(2)	1851(3)	3521(3)	127(5)
H(122)	-2532(2)	1197(3)	4748(3)	127(5)
H(123)	-2783(2)	1158(3)	6671(3)	127(5)
H(124)	-3805(2)	-91(3)	7107(3)	127(5)
H(125)	-4577(2)	-1300(3)	5620(3)	127(5)
H(126)	-4327(2)	-1260(3)	3697(3)	127(5)
H(132)	-4804(2)	520(2)	1688(3)	127(5)
H(133)	-5795(2)	-741(2)	582(3)	127(5)
H(134)	-5468(2)	-2767(3)	104(3)	127(5)
H(135)	-4149(2)	-3532(2)	731(3)	127(5)
H(136)	-3159(2)	-2270(2)	1837(3)	127(5)
H(212)	-591(2)	930(3)	1189(3)	127(5)
H(213)	-598(2)	1331(3)	-755(3)	127(5)
H(214)	-1566(2)	407(3)	-2214(3)	127(5)
H(215)	-2526(2)	-917(3)	-1731(3)	127(5)
H(216)	-2519(2)	-1318(3)	213(3)	127(5)
H(222)	-542(3)	-2099(4)	1076(4)	127(5)
H(223)	-177(3)	-4135(4)	1257(4)	127(5)
H(224)	-739(3)	-5227(4)	2582(4)	127(5)
H(225)	-1667(3)	-4283(4)	3725(4)	127(5)
H(226)	-2032(3)	-2247(4)	3543(4)	127(5)
H(232)	85(2)	-979(3)	3010(3)	127(5)
H(233)	1088(2)	234(3)	4152(3)	127(5)
H(234)	740(2)	2182(3)	4865(3)	127(5)
H(235)	-610(2)	2918(3)	4435(3)	127(5)
H(236)	-1613(2)	1705(3)	3293(3)	127(5)

[a] Occupancies of the Ru atoms labelled (A) in the disordered sites were coupled in the least squares refinement to a free variable p_A which refined

cont...

to 0.9386 (10). The occupancies of the H's attached to the cluster were tied to this free variable. The occupancy of the (B) Ru atoms was set to $1-p_A$; the rest of the atoms are of unit occupancy.

[b] Phenyl hydrogen atoms had their isotropic temperature factors tied to the same free variable.

[c] Anisotropic thermal parameters.

Table 2 Anisotropic Temperature Factors * ($Å^2$ x 10^3) for (VIII).

E.s.d's in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1A)	40.8(3)	44.0(3)	62.8(4)	12.3(2)	17.4(2)	3.9(2)
Ru(2A)	40.6(3)	40.5(3)	59.1(3)	5.8(2)	18.3(2)	5.4(2)
Ru(3A)	51.7(3)	47.8(3)	62.2(4)	1.9(2)	16.6(3)	1.8(2)
Ru(4A)	50.1(3)	37.4(2)	66.0(4)	10.8(2)	21.3(3)	7.7(2)
C(11)	53(4)	56(4)	78(5)	18(4)	12(3)	1(3)
O(11)	83(4)	75(3)	144(6)	50(4)	19(4)	15(3)
C(12)	59(4)	92(6)	90(6)	6(5)	12(4)	-1(4)
O(12)	87(4)	151(6)	129(6)	-9(5)	-10(4)	-25(4)
C(13)	51(4)	68(4)	70(5)	14(4)	17(3)	11(3)
O(13)	70(3)	121(5)	94(4)	-1(4)	36(3)	20(3)
C(21)	62(4)	51(4)	82(5)	12(3)	36(4)	11(3)
O(21)	99(4)	64(3)	142(5)	25(3)	48(4)	33(3)
C(22)	63(4)	63(4)	79(6)	-2(4)	17(4)	9(3)
O(22)	108(5)	121(5)	67(4)	-5(4)	-1(3)	21(4)
C(23)	55(4)	60(4)	109(6)	14(4)	24(4)	4(3)
O(23)	74(4)	95(4)	212(8)	44(5)	59(4)	-11(3)
C(31)	64(4)	57(4)	88(6)	-1(4)	9(4)	5(3)
O(31)	82(4)	94(4)	118(5)	-34(4)	33(3)	17(3)
C(32)	81(5)	61(4)	78(6)	6(4)	7(4)	1(4)
O(32)	139(6)	110(5)	102(5)	26(4)	-13(4)	26(4)
C(33)	86(6)	123(7)	99(7)	-23(6)	30(5)	-35(6)
O(33)	112(5)	148(7)	139(8)	-31(6)	53(6)	-65(5)

cont...

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(41)	66(4)	51(4)	83(5)	16(4)	21(4)	11(3)
O(41)	100(4)	72(3)	110(4)	9(3)	51(4)	32(3)
C(42)	88(5)	51(4)	150(8)	-19(5)	70(6)	-7(4)
O(42)	176(7)	81(4)	271(10)	-27(5)	156(7)	-50(5)
C(43)	122(8)	96(6)	85(7)	-3(5)	4(6)	46(6)
O(43)	173(7)	145(6)	105(6)	8(5)	-9(5)	51(6)
N	43(3)	70(3)	75(4)	10(3)	13(3)	4(2)
P(1)	35.4(7)	46.5(8)	49.1(9)	6.9(7)	7.5(6)	0.7(6)
P(2)	35.7(7)	49.0(8)	51.0(9)	1.1(7)	6.7(7)	2.5(6)

* Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2(\underline{U}_{11}h^2a^{*2} + \underline{U}_{22}k^2b^{*2} + \underline{U}_{33}l^2c^{*2} + 2\underline{U}_{23}klb^*c^* + 2\underline{U}_{13}hla^*c^* + 2\underline{U}_{12}hka^*b^*)\right]$$

APPENDIX 9

Fractional Atomic Coordinates and Thermal Parameters for

$[(Ph_3P)_2N]^+ [H_3Ru_4(CO)_{12}]^-$ (IX) - " C_{3v} isomer ".

Table 1 Fractional Atomic Coordinates (x 10^4) and Isotropic Temperature Factors ($Å^2$ x 10^3) for (IX).

E.s.d.s are given in parentheses.

atom	x	y	z	U[a]
Ru(1)	3439(1)	9570(1)	6959(1)	b
Ru(2)	1485(1)	8397(1)	5960(1)	b
Ru(3)	2012(1)	10116(1)	7638(1)	b
Ru(4)	2467(1)	8697(1)	8633(1)	b
H(12)	2669(28)	8512(29)	5792(41)	53(12)
H(14)	3487(25)	8781(25)	8015(37)	37(10)
H(24)	1817(27)	7791(28)	7234(39)	48(12)
C(11)	3337(3)	10286(3)	5754(5)	b
O(11)	3285(3)	10676(3)	4976(4)	b
C(12)	4333(3)	9066(3)	6471(5)	b
O(12)	4882(3)	8811(3)	6142(4)	b
C(13)	4299(3)	10602(4)	8238(5)	b
O(13)	4853(3)	11216(3)	8964(5)	b
C(21)	1199(3)	8998(3)	4655(4)	b
O(21)	1015(3)	9324(3)	3826(3)	b
C(22)	1190(3)	7184(3)	4912(4)	b
O(22)	952(3)	6461(2)	4273(4)	b
C(23)	321(3)	8268(3)	6270(5)	b
O(23)	-402(2)	8142(3)	6400(4)	b
C(31)	2764(4)	11189(3)	8922(5)	b
O(31)	3193(4)	11854(3)	9672(4)	b
C(32)	1736(3)	10804(3)	6445(4)	b
O(32)	1552(3)	11240(2)	5748(4)	b
C(33)	941(4)	10081(4)	8176(6)	b
O(33)	313(4)	10118(4)	8510(5)	b
C(41)	3206(4)	9664(3)	10095(4)	b
O(41)	3671(3)	10194(3)	10970(3)	b
C(42)	1372(4)	8508(4)	9169(4)	b
O(42)	722(3)	8359(3)	9493(4)	b
C(43)	2811(3)	7669(3)	9157(4)	b
O(43)	2996(3)	7082(2)	9497(3)	b

...ont...

atom	x	y	z	U
N	-2906(2)	4871(2)	8193(3)	b
P(1)	-3497(1)	3948(1)	7166(1)	b
P(2)	-2140(1)	5854(1)	8540(1)	b
C(111)	-4662(2)	3644(2)	7281(2)	40(1)
C(112)	-4796(2)	3903(2)	8458(2)	61(1)
C(113)	-5688(2)	3639(2)	8600(2)	77(2)
C(114)	-6446(2)	3117(2)	7567(2)	64(1)
C(115)	-6313(2)	2858(2)	6390(2)	59(1)
C(116)	-5421(2)	3121(2)	6247(2)	51(1)
C(121)	-3549(2)	4000(2)	5564(3)	39(1)
C(122)	-3277(2)	3375(2)	4810(3)	52(1)
C(123)	-3314(2)	3426(2)	3570(3)	65(1)
C(124)	-3623(2)	4103(2)	3084(3)	62(1)
C(125)	-3896(2)	4729(2)	3839(3)	60(1)
C(126)	-3859(2)	4677(2)	5079(3)	51(1)
C(131)	-3064(2)	3004(2)	7439(3)	42(1)
C(132)	-2108(2)	3178(2)	7891(3)	54(1)
C(133)	-1760(2)	2441(2)	8015(3)	67(1)
C(134)	-2367(2)	1531(2)	7687(3)	68(1)
C(135)	-3322(2)	1357(2)	7235(3)	64(1)
C(136)	-3671(2)	2094(2)	7111(3)	53(1)
C(211)	-1130(2)	5856(2)	8016(2)	46(1)
C(212)	-1195(2)	5803(2)	6744(2)	60(1)
C(213)	-428(2)	5792(2)	6310(2)	67(1)
C(214)	404(2)	5835(2)	7148(2)	68(1)
C(215)	468(2)	5888(2)	8420(2)	75(1)
C(216)	-299(2)	5899(2)	8854(2)	60(1)
C(221)	-1756(2)	6226(1)	10229(3)	42(1)
C(222)	-1988(2)	5588(1)	10952(3)	55(1)
C(223)	-1682(2)	5872(1)	12265(3)	71(1)
C(224)	-1144(2)	6793(1)	12856(3)	71(1)
C(225)	-913(2)	7430(1)	12133(3)	69(1)
C(226)	-1219(2)	7147(1)	10820(3)	58(1)
C(231)	-2568(2)	6717(2)	7961(3)	44(1)
C(232)	-3510(2)	6619(2)	7752(3)	50(1)
C(233)	-3848(2)	7312(2)	7367(3)	61(1)
C(234)	-3244(2)	8103(2)	7191(3)	67(1)
C(235)	-2303(2)	8201(2)	7400(3)	71(1)
C(236)	-1965(2)	7508(2)	7785(3)	60(1)

cont..

atom	x	y	z	U
H(112)	-4208(2)	4307(2)	9258(2)	103(4)
H(113)	-5791(2)	3840(2)	9511(2)	103(4)
H(114)	-7137(2)	2913(2)	7677(2)	103(4)
H(115)	-6900(2)	2454(2)	5590(2)	103(4)
H(116)	-5317(2)	2921(2)	5337(2)	103(4)
H(122)	-3037(2)	2851(2)	5186(3)	103(4)
H(123)	-3103(2)	2942(2)	2986(3)	103(4)
H(124)	-3652(2)	4143(2)	2124(3)	103(4)
H(125)	-4135(2)	5253(2)	3463(3)	103(4)
H(126)	-4070(2)	5161(2)	5663(3)	103(4)
H(132)	-1639(2)	3882(2)	8145(3)	103(4)
H(133)	-1020(2)	2576(2)	8365(3)	103(4)
H(134)	-2097(2)	961(2)	7782(3)	103(4)
H(135)	-3792(2)	652(2)	6981(3)	103(4)
H(136)	-4411(2)	1959(2)	6761(3)	103(4)
H(212)	-1838(2)	5770(2)	6095(2)	103(4)
H(213)	-477(2)	5751(2)	5325(2)	103(4)
H(214)	997(2)	5826(2)	6812(2)	103(4)
H(215)	1111(2)	5921(2)	9069(2)	103(4)
H(216)	-249(2)	5940(2)	9839(2)	103(4)
H(222)	-2404(2)	4875(1)	10495(3)	103(4)
H(223)	-1861(2)	5378(1)	12824(3)	103(4)
H(224)	-907(2)	7012(1)	13872(3)	103(4)
H(225)	-497(2)	8143(1)	12590(3)	103(4)
H(226)	-1040(2)	7641(1)	10261(3)	103(4)
H(232)	-3977(2)	6007(2)	7888(3)	103(4)
H(233)	-4576(2)	7236(2)	7205(3)	103(4)
H(234)	-3506(2)	8639(2)	6893(3)	103(4)
H(235)	-1836(2)	8813(2)	7264(3)	103(4)
H(236)	-1236(2)	7585(2)	7947(3)	103(4)

[a]Phenyl hydrogens had their isotropic temperature factors tied to the same free variable.

[b]Anisotropic thermal parameters.

Table 2 Anisotropic Temperature Factors* ($Å^2 \times 10^3$) for (IX). E.s.d's in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	36.4(1)	38.3(1)	41.9(2)	10.1(1)	12.6(1)	7.6(1)
Ru(2)	35.3(1)	38.2(1)	34.1(1)	9.4(1)	7.3(1)	9.0(1)
Ru(3)	53.1(2)	38.2(1)	41.0(2)	11.9(1)	16.7(1)	20.3(1)
Ru(4)	47.2(2)	43.1(2)	32.7(1)	14.5(1)	11.5(1)	16.6(1)
C(11)	62(3)	44(2)	60(3)	18(2)	27(2)	16(2)
O(11)	116(3)	77(3)	93(3)	52(2)	54(3)	39(2)
C(12)	44(2)	57(2)	55(3)	10(2)	11(2)	13(2)
O(12)	60(2)	105(3)	98(3)	11(3)	29(2)	40(2)
C(13)	58(3)	61(3)	65(3)	-3(3)	16(3)	-1(2)
O(13)	85(3)	97(3)	97(4)	-28(3)	13(3)	-24(2)
C(21)	53(2)	48(2)	44(2)	13(2)	4(2)	11(2)
O(21)	93(3)	71(2)	52(2)	24(2)	1(2)	24(2)
C(22)	45(2)	47(2)	49(2)	11(2)	11(2)	6(2)
O(22)	84(3)	49(2)	82(3)	-6(2)	24(2)	9(2)
C(23)	47(2)	73(3)	54(3)	25(2)	15(2)	23(2)
O(23)	52(2)	122(3)	95(3)	47(3)	33(2)	35(2)
C(31)	94(4)	52(3)	48(3)	12(2)	19(3)	28(3)
O(31)	158(4)	63(2)	54(2)	-8(2)	9(3)	28(3)
C(32)	61(3)	46(2)	49(2)	11(2)	17(2)	22(2)

cont...

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(32)	95(3)	63(2)	64(2)	26(2)	16(2)	36(2)
C(33)	80(3)	66(3)	81(4)	33(3)	43(3)	41(3)
O(33)	125(4)	138(4)	137(5)	68(4)	90(4)	84(4)
C(41)	81(3)	54(2)	43(2)	17(2)	17(2)	28(2)
O(41)	127(4)	67(2)	43(2)	-2(2)	-6(2)	22(2)
C(42)	69(3)	77(3)	48(3)	30(2)	23(2)	41(3)
O(42)	78(3)	121(3)	95(3)	59(3)	53(2)	49(3)
C(43)	56(2)	58(2)	40(2)	20(2)	17(2)	19(2)
O(43)	101(3)	65(2)	68(2)	35(2)	28(2)	46(2)

N	47(2)	40(2)	49(2)	-1(2)	12(2)	-1(1)
P(1)	34.9(4)	34.1(4)	36.8(5)	5.5(4)	9.6(4)	7.7(3)
P(2)	33.6(4)	36.5(4)	44.9(5)	6.6(4)	10.1(4)	7.4(3)

* Anisotropic temperature factor defined as:-

$$T = \exp[-2\pi^2(\underline{U}_{11}h^2a^{*2} + \underline{U}_{22}k^2b^{*2} + \underline{U}_{33}l^2c^{*2} + 2\underline{U}_{23}klb^*c^* + 2\underline{U}_{13}hla^*c^* + 2\underline{U}_{12}hka^*b^*)]$$

APPENDIX 10

Fractional Atomic Coordinates and Thermal Parameters for

$[(Ph_3P)_2N]^+ [H_3Os_4(CO)_{12}]^- 0.5\ CH_2Cl_2$ (X).

Table 1 Fractional Atomic Coordinates (x 10^4) and Isotropic Temperature Factors ($Å^2$ x 10^3) for (X).
E.s.d's are given in parentheses.

atom[a]	x	y	z	U[b]	
Os(1)	-1023(1)	-1402(1)	0	c	
Os(2)	-592(1)	-378(1)	-1329(1)	c	
Os(3)	24(1)	-363(1)	422(1)	c	
Os(4)	499(1)	-1339(1)	-786(1)	c	
C(11)	-1766(15)	-869(17)	555(21)	c	
O(11)	-2193(12)	-514(12)	952(17)	c	
C(12)	-1681(15)	-2067(13	-492(20)	c	
O(12)	-2113(13)	-2454(11)	-769(16)	c	
C(13)	-757(18)	-1893(12)	1024(19)	c	
O(13)	-608(14)	-2187(9)	1655(13)	c	
C(21)	-1432(14)	235(12)	-1467(20)	c	
O(21)	-1932(13)	574(10)	-1599(18)	c	
C(22)	-705(19)	-926(13)	-2357(27)	c	
O(22)	-723(16)	-1232(11)	-3002(14)	c	
C(23)	159(17)	228(13)	-1768(17)	c	
O(23)	593(13)	622(11)	-1966(14)	c	
C(31)	512(17)	-857(16)	1319(19)	c	
O(31)	837(11)	-1145(9)	1793(14)	c	
C(32)	-600(18)	201(14)	1156(16)	c	
O(32)	-949(12)	526(10)	1619(14)	c	
C(33)	834(14)	253(11)	274(14)	c	
O(33)	1308(12)	650(9)	241(13)	c	
C(41)	1022(16)	-1870(13)	-56(19)	c	
O(41)	1420(13)	-2227(10)	443(15)	c	
C(42)	1333(19)	-788(13)	-1117(21)	c	
O(42)	1842(14)	-458(11)	-1365(19)	c	
C(43)	532(18)	-1852(19)	-1762(20)	c	
O(43)	603(17)	-2263(13)	-2366(14)	c	
N	957(10)	3771(8)	-908(13)	c	
P(1)	1093(3)	3010(3)	-557(4)	c	cont...

P(2)	252(4)	4265(3)	-959(4)	c
C(111)	1580(9)	3050(6)	479(10)	39(5)
C(112)	1894(9)	3671(6)	737(10)	53(6)
C(113)	2307(9)	3711(6)	1506(10)	71(8)
C(114)	2406(9)	3131(6)	2017(10)	85(9)
C(115)	2092(9)	2510(6)	1759(10)	87(10)
C(116)	1679(9)	2469(6)	990(10)	60(7)
C(121)	1698(9)	2580(6)	-1330(10)	42(5)
C(122)	2092(9)	2969(6)	-1938(10)	63(7)
C(123)	2563(9)	2650(6)	-2540(10)	61(7)
C(124)	2640(9)	1942(6)	-2535(10)	70(8)
C(125)	2246(9)	1552(6)	-1927(10)	59(7)
C(126)	1774(9)	1871(6)	-1325(10)	63(7)
C(131)	261(8)	2504(8)	-406(8)	40(5)
C(132)	-89(8)	2251(8)	-1150(8)	49(6)
C(133)	-780(8)	1910(8)	-1088(8)	66(8)
C(134)	-1122(8)	1821(8)	-280(8)	63(7)
C(135)	-773(8)	2074(8)	464(8)	65(7)
C(136)	-81(8)	2415(8)	402(8)	59(6)
C(211)	-230(8)	4217(7)	-1991(10)	37(5)
C(212)	16(8)	3757(7)	-2620(10)	53(6)
C(213)	-354(8)	3722(7)	-3418(10)	75(8)
C(214)	-970(8)	4148(7)	-3586(10)	76(9)
C(215)	-1216(8)	4608(7)	-2957(10)	69(8)
C(216)	-846(8)	4643(7)	-2159(10)	64(7)
C(221)	-421(8)	4187(8)	-99(12)	61(7)
C(222)	-179(8)	4343(8)	739(12)	61(7)
C(223)	-642(8)	4196(8)	1447(12)	94(10)
C(224)	-1348(8)	3892(8)	1317(12)	104(11)
C(225)	-1590(8)	3735(8)	480(12)	97(10)
C(226)	-1127(8)	3883(8)	-228(12)	69(8)
C(231)	638(7)	-4866(9)	-920(11)	47(6)
C(232)	180(7)	-4294(9)	-788(11)	69(8)
C(233)	487(7)	-3641(9)	-863(11)	86(9)
C(234)	1251(7)	-3559(9)	-1070(11)	68(8)
C(235)	1709(7)	-4130(9)	-1202(11)	71(8)
C(236)	1402(7)	-4784(9)	-1127(11)	54(7)
H(112)	1818(9)	4120(6)	341(10)	115(19)
H(113)	2550(9)	4192(6)	1706(10)	115(19)
H(114)	2726(9)	3163(6)	2613(10)	115(19)
H(115)	2169(9)	2061(6)	2155(10)	115(19)
H(116)	1436(9)	1989(6)	790(10)	115(19)

cont

P(2)	252(4)	4265(3)	-959(4)	c
C(111)	1580(9)	3050(6)	479(10)	39(5)
C(112)	1894(9)	3671(6)	737(10)	53(6)
C(113)	2307(9)	3711(6)	1506(10)	71(8)
C(114)	2406(9)	3131(6)	2017(10)	85(9)
C(115)	2092(9)	2510(6)	1759(10)	87(10)
C(116)	1679(9)	2469(6)	990(10)	60(7)
C(121)	1698(9)	2580(6)	-1330(10)	42(5)
C(122)	2092(9)	2969(6)	-1938(10)	63(7)
C(123)	2563(9)	2650(6)	-2540(10)	61(7)
C(124)	2640(9)	1942(6)	-2535(10)	70(8)
C(125)	2246(9)	1552(6)	-1927(10)	59(7)
C(126)	1774(9)	1871(6)	-1325(10)	63(7)
C(131)	261(8)	2504(8)	-406(8)	40(5)
C(132)	-89(8)	2251(8)	-1150(8)	49(6)
C(133)	-780(8)	1910(8)	-1088(8)	66(8)
C(134)	-1122(8)	1821(8)	-280(8)	63(7)
C(135)	-773(8)	2074(8)	464(8)	65(7)
C(136)	-81(8)	2415(8)	402(8)	59(6)
C(211)	-230(8)	4217(7)	-1991(10)	37(5)
C(212)	16(8)	3757(7)	-2620(10)	53(6)
C(213)	-354(8)	3722(7)	-3418(10)	75(8)
C(214)	-970(8)	4148(7)	-3586(10)	76(9)
C(215)	-1216(8)	4608(7)	-2957(10)	69(8)
C(216)	-846(8)	4643(7)	-2159(10)	64(7)
C(221)	-421(8)	4187(8)	-99(12)	61(7)
C(222)	-179(8)	4343(8)	739(12)	61(7)
C(223)	-642(8)	4196(8)	1447(12)	94(10)
C(224)	-1348(8)	3892(8)	1317(12)	104(11)
C(225)	-1590(8)	3735(8)	480(12)	97(10)
C(226)	-1127(8)	3883(8)	-228(12)	69(8)
C(231)	638(7)	-4866(9)	-920(11)	47(6)
C(232)	180(7)	-4294(9)	-788(11)	69(8)
C(233)	487(7)	-3641(9)	-863(11)	86(9)
C(234)	1251(7)	-3559(9)	-1070(11)	68(8)
C(235)	1709(7)	-4130(9)	-1202(11)	71(8)
C(236)	1402(7)	-4784(9)	-1127(11)	54(7)
H(112)	1818(9)	4120(6)	341(10)	115(19)
H(113)	2550(9)	4192(6)	1706(10)	115(19)
H(114)	2726(9)	3163(6)	2613(10)	115(19)
H(115)	2169(9)	2061(6)	2155(10)	115(19)
H(116)	1436(9)	1989(6)	790(10)	115(19)

cont.

H(122)	2033(9)	3518(6)	-1942(10)	115(19)
H(123)	2869(9)	2952(6)	-3011(10)	115(19)
H(124)	3005(9)	1695(6)	-3001(10)	115(19)
H(125)	2305(9)	1004(6)	-1923(10)	115(19)
H(126)	1469(9)	1570(6)	-854(10)	115(19)
H(132)	176(8)	2320(8)	-1775(8)	115(19)
H(133)	-1051(8)	1714(8)	-1664(8)	115(19)
H(134)	-1658(8)	1557(8)	-232(8)	115(19)
H(135)	-1037(8)	2005(8)	1089(8)	115(19)
H(136)	189(8)	2611(8)	978(8)	115(19)
H(212)	493(8)	3427(7)	-2490(10)	115(19)
H(213)	-164(8)	3365(7)	-3905(10)	115(19)
H(214)	-1257(8)	4121(7)	-4204(10)	115(19)
H(215)	-1693(8)	4938(7)	-3087(10)	115(19)
H(216)	-1036(8)	5000(7)	-1672(10)	115(19)
H(222)	368(8)	4579(8)	839(12)	115(19)
H(223)	-455(8)	4317(8)	2095(12)	115(19)
H(224)	-1707(8)	3778(8)	1865(12)	115(19)
H(225)	-2137(8)	3500(8)	379(12)	115(19)
H(226)	-1314(8)	3762(8)	-877(12)	115(19)
H(232)	-411(7)	-4358(9)	-628(11)	115(19)
H(233)	133(7)	-3199(9)	-760(11)	115(19)
H(234)	1489(7)	-3053(9)	-1128(11)	115(19)
H(235)	2300(7)	-4067(9)	-1362(11)	115(19)
H(236)	1756(7)	-5226(9)	-1229(11)	115(19)
Cl(1)	2336(12)	4510(10)	-3410(15)	123(7)
Cl(2)	1677(14)	3815(11)	-4721(18)	154(9)

[a] The site occupation factor of the Cl atoms was fixed at 0.5.

[b] Phenyl hydrogens had their isotropic temperature factors tied to the same free variable.

[c] Anisotropic thermal parameters.

Table 2 Anisotropic Temperature Factors * ($Å^2 \times 10^3$) for (X).
E.s.d's in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	54.1(6)	46.2(5)	41.7(5)	9.8(5)	7.1(5)	-0.3(5)
Os(2)	55.0(6)	41.5(5)	35.6(4)	7.3(5)	-1.8(5)	1.4(5)
Os(3)	57.6(6)	43.3(5)	33.8(4)	0.2(5)	1.2(5)	5.3(5)
Os(4)	56.1(6)	42.9(5)	39.2(5)	1.6(5)	6.2(5)	7.0(5)
C(11)	39(16)	121(26)	80(21)	38(22)	13(16)	-46(18)
O(11)	72(15)	131(19)	135(22)	-24(17)	78(16)	4(14)
C(12)	49(16)	55(17)	82(21)	28(16)	17(15)	3(15)
O(12)	93(17)	96(16)	120(19)	-28(17)	-14(17)	-35(14)
C(13)	90(23)	31(13)	71(20)	14(15)	-8(18)	16(14)
O(13)	155(23)	39(10)	69(13)	30(10)	3(15)	12(12)
C(21)	39(15)	49(15)	85(22)	26(15)	-16(15)	15(12)
O(21)	92(17)	68(14)	164(27)	37(15)	-4(18)	27(13)
C(22)	81(24)	22(13)	146(35)	32(18)	-22(24)	10(15)
O(22)	162(25)	84(16)	56(13)	-27(12)	-16(15)	-28(16)
C(23)	76(20)	44(16)	46(15)	17(12)	-11(14)	-18(15)
O(23)	91(16)	73(14)	74(14)	9(12)	-15(13)	-43(13)
C(31)	64(20)	95(23)	53(17)	13(17)	-28(16)	9(18)
O(31)	67(13)	64(12)	75(14)	-4(11)	-15(12)	24(11)

cont...

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(32)	83(21)	63(17)	33(13)	20(13)	2(14)	24(16)
O(32)	81(15)	83(15)	78(15)	-25(12)	14(12)	30(13)
C(33)	49(15)	42(14)	35(13)	-7(11)	-14(11)	-1(12)
O(33)	80(14)	70(12)	87(17)	1(12)	-11(13)	-24(12)
C(41)	71(19)	54(16)	65(18)	-41(16)	21(17)	12(15)
O(41)	107(19)	84(14)	81(14)	-2(14)	15(15)	34(13)
C(42)	103(25)	38(15)	84(23)	29(16)	25(20)	5(16)
O(42)	117(19)	78(15)	117(19)	-14(16)	7(19)	-17(15)
C(43)	75(23)	120(29)	56(18)	18(20)	6(18)	-18(22)
O(43)	204(32)	109(20)	42(12)	-12(13)	13(16)	11(19)

N	49(12)	34(10)	67(13)	-4(10)	14(11)	13(9)
P(1)	41(3)	39(3)	47(4)	1(3)	-1(3)	-2(3)
P(2)	48(4)	37(3)	44(3)	-1(3)	-3(3)	-4(3)

* Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2(\underline{U}_{11}h^2a^{*2} + \underline{U}_{22}k^2b^{*2} + \underline{U}_{33}l^2c^{*2} + 2\underline{U}_{23}klb^*c^* + 2\underline{U}_{13}hla^*c^* + 2\underline{U}_{12}hka^*b^*)\right]$$

APPENDIX 11

Fractional Atomic Coordinates and Thermal Parameters for

$[Ph_3MeP]_2^+ [Ru_6(CO)_{18}]^{2-}$ (XI).

Table 1 Fractional Atomic Coordinates (x 10^4) and Isotropic Temperature Factors (Å ^{2} x 10^3) for (XI). E.s.d's are given in parentheses.

atom	x	y	z	U[a]
Ru(1)	1947(1)	4170(1)	1362(1)	b
Ru(2)	1870(1)	4600(1)	-1401(1)	b
Ru(3)	2600(1)	2876(1)	209(1)	b
Ru(4)	2357(1)	6385(1)	36(1)	b
Ru(5)	3081(1)	4650(1)	1645(1)	b
Ru(6)	3033(1)	5093(1)	-1063(1)	b
C(1)	1522(3)	2761(7)	1350(8)	48(2)
O(1)	1222(3)	1922(6)	1353(6)	77(2)
C(2)	1339(3)	5118(7)	971(7)	45(2)
O(2)	927(3)	5599(5)	817(6)	67(2)
C(3)	2048(4)	4116(8)	3145(9)	64(2)
O(3)	2085(3)	3961(7)	4275(8)	105(3)
C(4)	2799(3)	2865(6)	2237(7)	43(2)
O(4)	2874(2)	2132(5)	3221(5)	53(1)
C(5)	1774(3)	5222(7)	-3179(8)	54(2)
O(5)	1682(3)	5657(6)	-4260(7)	80(2)
C(6)	1140(3)	4155(7)	-1504(7)	46(2)
O(6)	686(2)	3855(5)	-1597(6)	65(2)
C(7)	1665(3)	6445(6)	-1315(7)	42(2)
O(7)	1290(3)	7037(5)	-1857(6)	60(2)
C(8)	2015(3)	2860(7)	-1541(8)	51(2)
O(8)	1835(3)	2148(6)	-2219(6)	73(2)
C(9)	2336(3)	1304(7)	667(8)	51(2)
O(9)	2190(3)	330(6)	986(7)	87(2)
C(10)	3200(3)	2270(7)	-221(7)	45(2)
O(10)	3556(2)	1864(5)	-513(6)	65(2)
C(11)	2537(3)	7926(7)	-728(8)	49(2)
O(11)	2660(3)	8917(6)	-1101(7)	79(2)
C(12)	2146(3)	7012(7)	1361(8)	49(2)
O(12)	2006(3)	7436(5)	2130(6)	69(2)

cont...

atom	x	y	z	U
C(13)	3304(3)	6253(7)	716(7)	46(2)
O(13)	3643(2)	7043(5)	786(5)	53(1)
C(14)	3787(3)	4085(7)	2161(7)	47(2)
O(14)	4225(3)	3719(6)	2546(6)	76(2)
C(15)	3136(3)	5237(7)	3187(8)	55(2)
O(15)	3202(3)	5620(6)	4158(7)	83(2)
C(16)	3787(3)	4831(7)	-712(8)	52(2)
O(16)	4255(3)	4676(6)	-554(7)	83(2)
C(17)	2904(3)	4204(7)	-2402(8)	53(2)
O(17)	2876(3)	3676(6)	-3273(6)	73(2)
C(18)	3028(3)	6543(8)	-2236(9)	58(2)
O(18)	3045(3)	7406(6)	-3023(7)	87(2)
P(1)	436(1)	8341(2)	3482(2)	b
C(111)	12(2)	7532(4)	4518(4)	35(2)
C(112)	-545(2)	7762(4)	4276(4)	50(2)
C(113)	-873(2)	7099(4)	5067(4)	57(2)
C(114)	-646(2)	6207(4)	6100(4)	55(2)
C(115)	-90(2)	5977(4)	6342(4)	59(2)
C(116)	239(2)	6640(4)	5550(4)	47(2)
C(121)	49(2)	9491(4)	2312(4)	38(2)
C(122)	130(2)	10692(4)	2469(4)	44(2)
C(123)	--215(2)	11570(4)	1658(4)	58(2)
C(124)	-640(2)	11246(4)	691(4)	59(2)
C(125)	-721(2)	10044(4)	534(4)	58(2)
C(126)	-376(2)	9166(4)	1345(4)	47(2)
C(131)	1006(2)	9032(4)	4418(4)	41(2)
C(132)	1008(2)	9163(4)	5695(4)	41(2)
C(133)	1435(2)	9801(4)	6375(4)	54(2)
C(134)	1858(2)	10309(4)	5778(4)	59(2)
C(135)	1855(2)	10178(4)	4501(4)	65(2)
C(136)	1429(2)	9540(4)	3820(4)	58(2)
C(19)	683(3)	7303(7)	2673(8)	52(2)
P(2)	3916(1)	10510(2)	6108(2)	b
C(211)	3844(2)	10109(4)	4533(5)	43(2)

cont...

atom	x	y	z	U
C(212)	4132(2)	10745(4)	3631(5)	47(2)
C(213)	4056(2)	10450(4)	2389(5)	56(2)
C(214)	3693(2)	9519(4)	2048(5)	60(2)
C(215)	3405(2)	8883(4)	2950(5)	68(2)
C(216)	3481(2)	9178(4)	4192(5)	62(2)
C(221)	4300(2)	11881(4)	6194(6)	41(2)
C(222)	4869(2)	11868(4)	6550(6)	61(2)
C(223)	5168(2)	12940(4)	6668(6)	79(3)
C(224)	4898(2)	14027(4)	6430(6)	79(3)
C(225)	4329(2)	14041(4)	6073(6)	82(3)
C(226)	4030(2)	12968(4)	5955(6)	60(2)
C(231)	4259(2)	9364(5)	7346(4)	45(2)
C(232)	4450(2)	8335(5)	7054(4)	60(2)
C(233)	4704(2)	7449(5)	8058(4)	75(3)
C(234)	4768(2)	7591(5)	9354(4)	68(2)
C(235)	4577(2)	8620(5)	9647(4)	70(3)
C(236)	4322(2)	9507(5)	8643(4)	59(2)
C(20)	3253(3)	10672(7)	6411(8)	56(2)
H(112)	-721(2)	8452(4)	3476(4)	115(7)
H(113)	-1304(2)	7277(4)	4880(4)	115(7)
H(114)	-901(2)	5694(4)	6712(4)	115(7)
H(115)	86(2)	5287(4)	7141(4)	115(7)
H(116)	670(2)	6462(4)	5738(4)	115(7)
H(122)	459(2)	10943(4)	3217(4)	115(7)
H(123)	-152(2)	12501(4)	1779(4)	115(7)
H(124)	-907(2)	11926(4)	63(4)	115(7)
H(125)	-1050(2)	9793(4)	-215(4)	115(7)
H(126)	-439(2)	8236(4)	1224(4)	115(7)
H(132)	681(2)	8770(4)	6157(4)	115(7)
H(133)	1437(2)	9902(4)	7364(4)	115(7)
H(134)	2188(2)	10803(4)	6305(4)	115(7)
H(135)	2183(2)	10572(4)	4038(4)	115(7)
H(136)	1427(2)	9439(4)	2832(4)	115(7)
H(191)	365(3)	6903(7)	2010(8)	77(11)
H(192)	881(3)	6607(7)	3436(8)	77(11)
H(193)	980(3)	7764(7)	2147(8)	77(11)

cont...

atom	x	y	z	U
H(212)	4414(2)	11466(4)	3895(5)	115(7)
H(213)	4279(2)	10943(4)	1691(5)	115(7)
H(214)	3634(2)	9291(4)	1086(5)	115(7)
H(215)	3123(2)	8162(4)	2686(5)	115(7)
H(216)	3258(2)	8685(4)	4890(5)	115(7)
H(222)	5078(2)	11027(4)	6735(6)	115(7)
H(223)	5608(2)	12930(4)	6944(6)	115(7)
H(224)	5129(2)	14857(4)	6521(6)	115(7)
H(225)	4119(2)	14882(4)	5888(6)	115(7)
H(226)	3589(2)	12979(4)	5679(6)	115(7)
H(232)	4401(2)	8225(5)	6050(4)	115(7)
H(233)	4852(2)	6652(5)	7831(4)	115(7)
H(234)	4964(2)	6905(5)	10132(4)	115(7)
H(235)	4626(2)	8730(5)	10651(4)	115(7)
H(236)	4174(2)	10303(5)	8870(4)	115(7)
H(201)	3033(3)	11315(7)	5620(8)	77(11)
H(202)	3280(3)	10982(7)	7323(8)	77(11)
H(203)	3040(3)	9809(7)	6441(8)	77(11)

a Phenyl and methyl hydrogen atoms had their isotropic temperature factors tied to separate common free variables.

b Anisotropic thermal parameters.

Table 2 Anisotropic Temperature Factors *($Å^2$ x 10^3) for (XI).
E.s.d's are given in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	31.9(3)	34.0(3)	38.5(3)	-8.8(2)	12.4(2)	-3.9(2)
Ru(2)	33.9(3)	35.7(3)	34.5(3)	-8.3(2)	-0.1(2)	5.1(2)
Ru(3)	36.7(3)	26.5(3)	39.0(3)	-6.7(2)	6.4(2)	3.2(2)
Ru(4)	38.3(3)	25.6(3)	42.8(3)	-7.2(2)	11.9(3)	0.9(2)
Ru(5)	29.0(3)	37.7(3)	33.7(3)	-7.6(2)	3.9(2)	-1.4(2)
Ru(6)	37.1(3)	36.1(3)	36.8(3)	-2.6(2)	14.0(3)	3.8(2)
P(1)	34.3(10)	36.3(9)	41.7(10)	-8.2(8)	10.2(8)	-1.3(7)
P(2)	34.8(10)	39.5(10)	45.5(11)	-3.8(8)	9.1(8)	-0.8(8)

* Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\right]$$

APPENDIX 12

Fractional Atomic Coordinates and Thermal Parameters for

$[(Ph_3P)_2N]_2^+ [Ru_6H(CO)_{18}]^-$ (XII).

Table 1 Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Temperature factors ($Å^2 \times 10^3$) for (XII) {$C\bar{1}$ cell}.

atom [a,b]	x	y	z	U [c,d,e]
		Cluster (1)		
Ru(1)	3947(1)	922(1)	2787(1)	f
Ru(2)	4403(1)	1750(1)	2679(1)	f
Ru(3)	2940(1)	1527(1)	2544(1)	f
Ru(4)	4515(1)	1169(1)	1531(1)	f
Ru(5)	2997(1)	962(1)	1348(1)	f
Ru(6)	3466(1)	1754(1)	1202(1)	f
C(11)	4130(9)	433(6)	2410(10)	59(5)
O(11)	4258(7)	129(4)	2212(7)	78(4)
C(12)	3318(10)	748(5)	3388(10)	61(5)
O(12)	2966(7)	612(4)	3775(8)	82(4)
C(13)	4725(11)	898(6)	3556(12)	74(6)
O(13)	5204(9)	849(5)	4043(9)	109(5)
C(21)	4109(10)	2250(6)	2832(10)	63(5)
O(21)	3963(7)	2558(4)	3003(8)	82(4)
C(22)	4812(10)	1718(5)	3687(11)	69(6)
O(22)	5086(7)	1730(4)	4323(8)	91(4)
C(23)	5271(9)	1914(5)	2486(10)	54(5)
O(23)	5806(7)	2050(4)	2384(8)	81(4)
C(31)	2092(9)	1232(5)	2573(9)	48(4)
O(31)	1571(7)	1067(4)	2635(7)	69(4)
C(32)	3207(10)	1608(5)	3581(11)	61(5)
O(32)	3313(7)	1681(4)	4217(8)	84(4)
C(33)	2516(9)	2007(5)	2398(9)	53(5)
O(33)	2235(7)	2312(4)	2381(7)	73(4)
C(41)	4482(11)	743(6)	878(12)	76(6)
O(41)	4535(8)	473(5)	474(9)	103(5)
C(42)	4998(10)	1487(6)	969(11)	61(5)

cont...

atom	x	y	z	U
O(42)	5361(7)	1678(4)	644(7)	77(4)
C(43)	5323(10)	990(6)	2176(11)	59(6)
O(43)	5835(7)	882(4)	2516(7)	75(4)
C(51)	2991(10)	680(6)	470(11)	66(6)
O(51)	2913(8)	513(4)	-125(9)	100(5)
C(52)	2141(10)	1184(5)	935(10)	54(5)
O(52)	1584(6)	1292(3)	644(7)	63(4)
C(53)	2643(10)	520(6)	1775(11)	64(6)
O(53)	2378(7)	242(4)	1964(8)	88(4)
C(61)	4068(9)	2193(5)	1169(10)	55(5)
O(61)	4407(7)	2467(4)	1071(7)	81(4)
C(62)	3491(9)	1558(5)	253(11)	57(5)
O(62)	3468(7)	1472(4)	-384(8)	73(4)
C(63)	2658(10)	2029(5)	878(10)	60(5)
O(63)	2149(7)	2203(4)	618(8)	88(5)

Cluster (2A)

Ru(1A)	7168(1)	3965(1)	3096(1)	44.1(5)
Ru(2A)	6954(1)	3280(1)	4000(1)	40.9(5)
Ru(3C)	5813(1)	3790(1)	3498(1)	f
Ru(4C)	7874(1)	3921(1)	4614(1)	f
Ru(5A)	6707(1)	4461(1)	4190(1)	43.9(5)
Ru(6A)	6548(1)	3802(1)	5090(1)	44.7(5)
C(11A)	7777	4391	3088	98(3)
O(11C)	8156(10)	4658(5)	3100(11)	141(2)
C(12A)	6602	4063	2219	98(3)
O(12C)	6232(10)	4132(5)	1661(11)	141(2)
C(13A)	7827	3772	2575	98(3)
O(13C)	8240(10)	3645(5)	2246(11)	141(2)
C(21A)	6214	2894	3902	98(3)
O(21C)	5747(10)	2654(5)	3844(10)	141(2)
C(22A)	7100	3005	3176	98(3)

cont...

atom	x	y	z	U
O(22C)	7199(10)	2838(5)	2646(11)	141(2)
C(23A)	7630	2998	4514	98(3)
O(23C)	8056(10)	2818(5)	4836(11)	141(2)
C(31C)	5215(11)	4163(6)	3062(12)	80(7)
O(31C)	4821(9)	4379(5)	2748(9)	107(5)
C(32C)	5560(13)	3453(8)	2689(15)	108(9)
O(32C)	5340(10)	3209(6)	2200(12)	145(7)
C(33C)	5146(11)	3559(6)	3991(12)	83(7)
O(33C)	4700(8)	3420(5)	4231(9)	100(5)
C(41C)	8427(9)	4388(5)	4868(10)	56(5)
O(41C)	8808(8)	4665(5)	5007(9)	98(5)
C(42C)	8186(10)	3696(6)	5544(11)	67(6)
O(42C)	8434(7)	3548(4)	6099(8)	85(4)
C(43C)	8536(10)	3680(6)	4161(11)	64(5)
O(43C)	8982(7)	3513(4)	3973(8)	79(4)
C(51A)	7192	4856	4738	98(3)
O(51C)	7499(10)	5109(5)	5085(11)	141(2)
C(52A)	5976	4614	4527	98(3)
O(52C)	5518(10)	4703(5)	4758(11)	141(2)
C(53A)	6357	4796	3360	98(3)
O(53C)	6198(10)	5010(5)	2832(10)	141(2)
C(61A)	6530	3316	5531	98(3)
O(61C)	6518(10)	3018(5)	5802(11)	141(2)
C(62A)	7086	4117	5898	98(3)
O(62C)	7440(10)	4323(5)	6389(11)	141(2)
C(63A)	5820	3826	5508	98(3)
O(63C)	5347(10)	3848(5)	5779(11)	141(2)

Cluster (2B)

Ru(1B)	6506(2)	4042(1)	4954(2)	44.1(5)

cont...

atom	x	y	z	U
Ru(2B)	6779(2)	3277(1)	4332(2)	40.9(5)
Ru(5B)	6929(2)	4425(1)	3715(2)	43.9(5)
Ru(6B)	7138(2)	3679(1)	3063(2)	44.7(5)
C(11B)	5899	4452	4837	98(3)
C(12B)	7070	4210	5847	98(3)
C(13B)	5804	3918	5456	98(3)
C(21B)	7563	2997	4642	98(3)
C(22B)	6619	3114	5239	98(3)
C(23B)	6147	2893	4030	98(3)
C(51B)	6473	4782	3177	98(3)
C(52B)	7685	4568	3327	98(3)
C(53B)	7277	4842	4555	98(3)
C(61B)	7171	3159	2815	98(3)
C(62B)	6591	3953	2207	98(3)
C(63B)	7816	3663	2562	98(3)

Cations

P(1)	952(2)	3320(1)	3149(2)	38(1)
P(2)	2233(2)	3771(1)	2930(2)	38(1)
N(1)	1717(6)	3403(4)	2984(7)	44(3)
C(111)	989(6)	2936(3)	3828(6)	41(4)
C(112)	429(6)	2854(3)	4193(6)	59(5)
C(113)	458(6)	2537(3)	4676(6)	73(6)
C(114)	1046(6)	2302(3)	4794(6)	73(6)
C(115)	1606(6)	2385(3)	4429(6)	76(6)
C(116)	1577(6)	2702(3)	3946(6)	56(5)
C(121)	556(6)	3741(2)	3485(6)	36(4)
C(122)	804(6)	3879(2)	4229(6)	53(5)
C(123)	579(6)	4236(2)	4472(6)	71(6)
C(124)	107(6)	4455(2)	3971(6)	67(6)
C(125)	-141(6)	4316(2)	3227(6)	62(5)

cont...

atom	x	y	z	U
C(126)	84(6)	3959(2)	2984(6)	56(5)
C(131)	358(5)	3129(3)	2313(5)	45(4)
C(132)	-362(5)	3054(3)	2305(5)	56(5)
C(133)	-815(5)	2896(3)	1653(5)	74(6)
C(134)	-548(5)	2813(3)	1009(5)	80(6)
C(135)	173(5)	2887(3)	1017(5)	77(6)
C(136)	625(5)	3045(3)	1669(5)	57(5)
C(211)	1784(5)	4213(3)	2608(6)	39(4)
C(212)	1431(5)	4223(3)	1854(6)	62(5)
C(213)	1053(5)	4551(3)	1592(6)	70(6)
C(214)	1026(5)	4869(3)	2085(6)	68(6)
C(215)	1379(5)	4860(3)	2840(6)	62(5)
C(216)	1757(5)	4532(3)	3101(6)	53(5)
C(221)	2841(6)	3882(3)	3814(5)	48(4)
C(222)	3396(6)	4167(3)	3867(5)	63(5)
C(223)	3824(6)	4273(3)	4570(5)	76(6)
C(224)	3696(6)	4094(3)	5220(5)	87(7)
C(225)	3141(6)	3810(3)	5167(5)	94(7)
C(226)	2713(6)	3704(3)	4464(5)	65(6)
C(231)	2745(6)	3647(4)	2251(6)	45(4)
C(232)	3048(6)	3938(4)	1865(6)	73(6)
C(233)	3445(6)	3830(4)	1334(6)	81(6)
C(234)	3538(6)	3432(4)	1191(6)	72(6)
C(235)	3235(6)	3142(4)	1577(6)	99(8)
C(236)	2838(6)	3249(4)	2108(6)	76(6)
P(3)	8054(2)	1309(1)	393(2)	40(1)
P(4)	9314(2)	900(1)	1157(2)	39(1)
N(2)	8663(7)	1000(4)	530(7)	48(4)
C(311)	7265(5)	1051(3)	-144(6)	43(4)
C(312)	7323(5)	708(3)	-534(6)	63(5)
C(313)	6717(5)	514(3)	-971(6)	93(7)
C(314)	6054(5)	673(3)	-1018(6)	82(7)
C(315)	5996(5)	1026(3)	-628(6)	74(6)
C(316)	6601(5)	1219(3)	-191(6)	56(5)
C(321)	7843(6)	1517(3)	1234(5)	41(4)
C(322)	8173(6)	1875(3)	1545(5)	56(5)

cont...

atom	x	y	z	U
C(323)	8030(6)	2028(3)	2217(5)	75(6)
C(324)	7558(6)	1823(3)	2580(5)	73(6)
C(325)	7229(6)	1465(3)	2269(5)	75(6)
C(326)	7372(6)	1312(3)	1597(5)	53(5)
C(331)	8290(6)	1712(3)	-147(6)	39(4)
C(332)	8971(6)	1750(3)	-298(6)	68(6)
C(333)	9159(6)	2071(3)	-700(6)	96(8)
C(334)	8666(6)	2353(3)	-950(6)	92(7)
C(335)	7984(6)	2315(3)	-799(6)	112(9)
C(336)	7796(6)	1995(3)	-397(6)	85(7)
C(411)	9924(5)	662(3)	684(6)	42(4)
C(412)	10487(5)	454(3)	1077(6)	55(5)
C(413)	10950(5)	275(3)	688(6)	74(6)
C(414)	10850(5)	304(3)	-95(6)	61(5)
C(415)	10288(5)	511(3)	-489(6)	69(6)
C(416)	9825(5)	691(3)	-99(6)	47(4)
C(421)	9779(6)	1323(3)	1687(6)	47(4)
C(422)	9627(6)	1449(3)	2373(6)	61(5)
C(423)	9966(6)	1793(3)	2741(6)	83(6)
C(424)	10456(6)	2010(3)	2423(6)	80(7)
C(425)	10608(6)	1884(3)	1736(6)	85(7)
C(426)	10269(6)	1540(3)	1368(6)	61(5)
C(431)	9045(8)	570(4)	1814(7)	64(5)
C(432)	9489(8)	507(4)	2511(7)	86(7)
C(433)	9248(8)	268(4)	3034(7)	111(9)
C(434)	8563(8)	92(4)	2860(7)	109(9)
C(435)	8119(8)	155(4)	2164(7)	117(9)
C(436)	8360(8)	394(4)	1641(7)	95(7)

a Occupancies of atoms labelled (A) in the disordered sites were coupled in the least-squares refinement to a free

cont...

variable p_A which refined to 0.5840(11). The occupancy of atoms labelled (B) was set to $1-p_A$. The rest of the atoms including those labelled (C) (which are common to clusters (2A) and (2B)) are of unit occupancy.

b Disordered carbon atoms {labelled (A) and (B)} were placed in fixed positions such that d(M-C)/d(M-O) = 0.615 and M-C-O=180°. These positions were recalculated if large shifts were observed for the oxygen atoms.

c Each pair of disordered ruthenium atoms was assigned a common isotropic temperature factor which was refined as a free variable.

d All disordered carbon atoms had their isotropic temperature factors tied to the same free variable.

e Oxygen atoms attached to disordered carbon atoms had their isotropic temperature factors tied to the same free variable.

f Anisotropic thermal parameters.

variable p_A which refined to 0.5840(11). The occupancy of atoms labelled (B) was set to $1-p_A$. The rest of the atoms including those labelled (C) (which are common to clusters (2A) and (2B)) are of unit occupancy.

b Disordered carbon atoms {labelled (A) and (B)} were placed in fixed positions such that d(M-C)/d(M-O) = 0.615 and M-C-O=180°. These positions were recalculated if large shifts were observed for the oxygen atoms.

c Each pair of disordered ruthenium atoms was assigned a common isotropic temperature factor which was refined as a free variable.

d All disordered carbon atoms had their isotropic temperature factors tied to the same free variable.

e Oxygen atoms attached to disordered carbon atoms had their isotropic temperature factors tied to the same free variable.

f Anisotropic thermal parameters.

Table 2

Anisotropic Temperature Factors* ($Å^2 \times 10^3$) for (XII). E.s.d.'s in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	37.0(8)	41.1(8)	38.9(8)	9.3(7)	2.4(6)	3.0(6)
Ru(2)	33.2(8)	40.8(8)	40.0(8)	-2.4(7)	7.3(6)	-3.4(6)
Ru(3)	31.8(7)	43.0(8)	36.3(8)	2.2(7)	9.7(6)	2.6(6)
Ru(4)	34.9(8)	42.2(8)	45.8(9)	-2.8(7)	13.7(7)	3.3(6)
Ru(5)	33.5(8)	38.8(8)	39.6(8)	-0.6(7)	3.3(6)	-2.9(6)
Ru(6)	40.7(8)	37.5(8)	34.5(8)	6.1(6)	9.9(6)	3.4(6)
Ru(3C)	36.1(8)	54.7(10)	46.6(9)	-4.3(8)	2.6(7)	6.8(7)
Ru(4C)	33.4(8)	46.6(9)	40.5(9)	3.6(7)	3.0(6)	5.0(6)

*Anisotropic temperature factor defined as

$$T = \exp\left[-2\pi^2(\underline{U}_{11}h^2a^{*2}+\underline{U}_{22}k^2b^{*2}+\underline{U}_{33}l^2c^{*2}+2\underline{U}_{23}klb^*c^*+2\underline{U}_{13}hla^*c^*+2\underline{U}_{12}hka^*b^*)\right]$$

APPENDIX 13

Fractional Atomic Coordinates and Thermal Parameters for

$[Ph_4As]^+ [Ru_6H(CO)_{18}]^-$ (XIII).

Table 1 Fractional Atomic Coordinates ($\times 10^4$) and Isotopic Temperature Factors ($Å^2 \times 10^3$) for (XIII). E.s.d's are given in parentheses.

atom[a]	x	y	z	U[b]
Ru(1A)	4135(1)	100(1)	2714(1)	c
Ru(2A)	3498(1)	-1262(1)	2169(1)	c
Ru(3)	3334(1)	-188(1)	868(1)	c
Ru(4)	2743(1)	-425(1)	3376(1)	c
Ru(5A)	2537(1)	671(1)	1985(1)	c
Ru(6A)	1887(1)	-665(1)	1536(1)	c
Ru(1B)	1722(3)	-138(3)	1833(4)	c
Ru(2B)	2829(4)	-1328(2)	2006(4)	c
Ru(5B)	3115(4)	741(2)	2429(4)	c
Ru(6B)	4215(3)	-417(3)	2555(4)	c
H	2931(45)	-258(38)	2004(53)	90(27)
C(11)	4031(6)	841(4)	3506(6)	c
O(11)	4063(5)	1262(3)	4014(5)	c
C(12)	4844(6)	516(5)	2028(7)	c
O(12)	5303(4)	796(4)	1674(5)	c
C(13)	5020(5)	-299(4)	3537(6)	c
O(13)	5572(4)	-487(4)	4039(5)	c
C(21)	3250(5)	-1845(4)	1136(5)	c
O(21)	3174(4)	-2218(3)	556(4)	c
C(22)	4651(4)	-1395(4)	2292(5)	c
O(22)	5323(3)	-1541(3)	2291(4)	c
C(23)	3326(4)	-1931(4)	3013(5)	c
O(23)	3255(4)	-2362(3)	3511(4)	c
C(31)	3306(5)	641(4)	184(5)	c
O(31)	3307(4)	1107(3)	-266(4)	c
C(32)	4379(5)	-512(4)	686(6)	c
O(32)	4982(4)	-711(4)	502(5)	c

cont...

atom	x	y	z	U
C(33)	2822(6)	-696(5)	-145(6)	c
O(33)	2597(5)	-1003(4)	-795(4)	c
C(41)	2389(7)	230(5)	4160(7)	c
O(41)	2201(7)	573(4)	4703(5)	c
C(42)	1973(5)	-1097(5)	3601(6)	c
O(42)	1546(4)	-1520(3)	3782(5)	c
C(43)	3606(6)	-743(5)	4324(6)	c
O(43)	4046(5)	-946(4)	4923(5)	c
C(51)	1965(6)	1179(4)	2721(6)	c
O(51)	1573(5)	1519(4)	3106(5)	c
C(52)	1716(5)	810(4)	953(6)	c
O(52)	1249(4)	981(3)	333(5)	c
C(53)	3234(6)	1443(4)	1803(6)	c
O(53)	3592(4)	1899(3)	1658(5)	c
C(61)	1625(5)	-1611(4)	1594(6)	c
O(61)	1375(4)	-2152(3)	1627(5)	c
C(62)	1037(5)	-302(5)	2100(7)	c
O(62)	483(4)	-101(4)	2360(6)	c
C(63)	1257(6)	-583(5)	373(7)	c
O(63)	829(4)	-544(4)	-323(5)	c
As	3324(1)	3522(1)	8125(1)	c
C(111)	3093(3)	4467(3)	7865(3)	49(2)
C(112)	2456(3)	4801(3)	8194(3)	74(2)
C(113)	2281(3)	5490(3)	7979(3)	98(3)
C(114)	2742(3)	5845(3)	7434(3)	75(2)
C(115)	3379(3)	5511(3)	7105(3)	70(2)
C(116)	3555(3)	4822(3)	7321(3)	60(2)
C(121)	3709(2)	3076(2)	7153(3)	47(2)
C(122)	3216(2)	2607(2)	6588(3)	62(2)
C(123)	3518(2)	2299(2)	5875(3)	71(2)
C(124)	4311(2)	2459(2)	5727(3)	73(2)
C(125)	4804(2)	2927(2)	6292(3)	69(2)
C(126)	4503(2)	3235(2)	7005(3)	61(2)

cont...

atom	x	y	z	U
C(131)	2350(3)	3087(3)	8346(3)	55(2)
C(132)	2357(3)	2720(3)	9145(3)	68(2)
C(133)	1638(3)	2393(3)	9297(3)	81(3)
C(134)	911(3)	2433(3)	8649(3)	94(3)
C(135)	903(3)	2801(3)	7850(3)	85(3)
C(136)	1622(3)	3128(3)	7699(3)	74(2)
C(141)	4171(4)	3451(2)	9161(4)	59(2)
C(142)	4506(4)	2803(2)	9405(4)	82(3)
C(143)	5142(4)	2733(2)	10157(4)	114(4)
C(144)	5442(4)	3311(2)	10665(4)	106(4)
C(145)	5106(4)	3959(2)	10422(4)	109(4)
C(146)	4470(4)	4029(2)	9669(4)	87(3)
H(112)	2099(3)	4526(3)	8616(3)	145(8)
H(113)	1788(3)	5749(3)	8233(3)	145(8)
H(114)	2606(3)	6379(3)	7267(3)	145(8)
H(115)	3736(3)	5786(3)	6683(3)	145(8)
H(116)	4048(3)	4564(3)	7066(3)	145(8)
H(122)	2602(2)	2484(2)	6703(3)	145(8)
H(123)	3136(2)	1937(2)	5438(3)	145(8)
H(124)	4545(2)	2220(2)	5175(3)	145(8)
H(125)	5418(2)	3051(2)	6177(3)	145(8)
H(126)	4884(2)	3598(2)	7442(3)	145(8)
H(132)	2921(3)	2688(3)	9647(3)	145(8)
H(133)	1644(3)	2108(3)	9915(3)	145(8)
H(134)	353(3)	2180(3)	8766(3)	145(8)
H(135)	340(3)	2833(3)	7349(3)	145(8)
H(136)	1616(3)	3413(3)	7080(3)	145(8)
H(142)	4274(4)	2356(2)	9012(4)	145(8)
H(143)	5402(4)	2232(2)	10346(4)	145(8)
H(144)	5934(4)	3257(2)	11248(4)	145(8)
H(145)	5338(4)	4406(2)	10815(4)	145(8)
H(146)	4211(4)	4530(2)	9481(4)	145(8)

cont...

a

There is a slight disordering of the Ru_6 core in (I) (0.9:0.1) presumably of a similar nature to that observed in the $[(Ph_3P)_2N]^+$ salt of the anion (see Subsection 4.3.32).

The occupancies of Ru atoms labelled (A) in the disordered sites, and the C atoms of their associated CO ligands, were coupled in the least squares refinement to a free variable p_A which refined to 0.9015(12). The occupancy of the 'B' Ru atoms was set to $1 - p_A$. The O atoms of the CO ligands and the interstitial hydrogen, H, are not affected by the disorder so have unit occupancy.

b

Phenyl hydrogen atoms had their isotropic temperature factors tied to the same free variable.

c

Anisotropic thermal parameters.

Table 2 Anisotropic Temperature Factors * ($Å^2 \times 10^3$) for (XIII).
E.s.d's are given in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1A)	43.4(3)	42.6(3)	51.3(4)	-8.9(3)	-2.0(3)	-4.2(3)
Ru(2A)	41.6(3)	29.4(3)	44.1(3)	1.6(2)	6.0(3)	4.8(2)
Ru(3)	54.3(3)	33.8(3)	40.0(3)	0.4(2)	9.2(2)	-0.6(2)
Ru(4)	62.7(4)	46.6(3)	44.7(3)	1.3(3)	18.4(3)	6.9(3)
Ru(5A)	50.6(4)	30.6(3)	52.8(4)	-1.1(3)	12.3(3)	7.7(3)
Ru(6A)	34.1(3)	41.6(3)	52.5(4)	2.1(3)	5.3(3)	-3.3(2)
Ru(1B)	36(3)	43(3)	55(3)	1(3)	7(2)	3(2)
Ru(2B)	50(3)	29(2)	39(3)	0(2)	10(2)	-1(2)
Ru(5B)	47(3)	26(2)	41(3)	-2(2)	5(3)	-5(2)
Ru(6B)	34(3)	42(3)	49(3)	-2(3)	6(2)	4(2)
C(11)	77(6)	45(5)	58(5)	-13(4)	-14(5)	-1(4)
O(11)	147(7)	76(4)	79(5)	-27(4)	-8(5)	15(4)
C(12)	56(5)	79(6)	71(6)	-10(5)	-5(5)	-28(5)
O(12)	96(5)	153(7)	106(6)	-16(5)	25(5)	-65(5)
C(13)	47(4)	61(5)	65(5)	-16(4)	-3(4)	8(4)
O(13)	74(4)	114(6)	106(5)	1(5)	-25(4)	17(4)
C(21)	60(5)	39(4)	54(5)	-6(4)	3(4)	3(4)
O(21)	103(5)	59(4)	86(4)	-21(3)	1(4)	7(3)
C(22)	41(4)	41(4)	44(4)	6(3)	4(3)	5(3)
O(22)	56(3)	61(3)	95(4)	17(3)	18(3)	13(3)

cont...

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(23)	47(4)	39(4)	48(4)	6(3)	15(3)	6(3)
O(23)	96(4)	56(3)	80(4)	20(3)	31(3)	11(3)
C(31)	70(5)	51(4)	62(5)	8(4)	21(4)	9(4)
O(31)	111(5)	62(4)	92(5)	34(3)	41(4)	22(3)
C(32)	74(6)	52(4)	78(6)	15(4)	34(5)	9(4)
O(32)	89(5)	110(6)	119(6)	38(5)	58(5)	33(4)
C(33)	97(7)	72(6)	55(5)	-3(5)	-11(5)	-9(5)
O(33)	154(7)	98(5)	65(4)	-21(4)	-8(4)	-27(5)
C(41)	162(11)	85(7)	63(6)	16(5)	40(7)	54(7)
O(41)	272(12)	122(7)	93(6)	-2(5)	77(7)	97(7)
C(42)	58(5)	86(6)	69(5)	19(5)	29(4)	8(4)
O(42)	80(4)	101(5)	110(5)	28(4)	42(4)	-11(4)
C(43)	75(6)	72(6)	70(6)	-7(5)	5(5)	-6(5)
O(43)	108(6)	115(6)	86(5)	23(5)	-31(4)	-4(5)
C(51)	99(7)	51(5)	53(5)	2(4)	26(5)	30(5)
O(51)	140(7)	96(5)	105(6)	-8(4)	34(5)	52(5)
C(52)	66(5)	46(4)	61(5)	-2(4)	10(5)	16(4)
O(52)	87(4)	66(4)	96(5)	24(4)	-1(4)	7(3)
C(53)	75(6)	33(4)	73(6)	-5(4)	15(5)	4(4)
O(53)	104(5)	47(3)	141(6)	0(4)	13(5)	-20(3)
C(61)	49(5)	55(5)	79(6)	-2(5)	14(4)	-19(4)
O(61)	94(5)	61(4)	115(5)	8(4)	12(4)	-30(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(62)	44(5)	77(6)	96(7)	7(6)	13(5)	20(4)
O(62)	75(5)	148(7)	157(8)	30(6)	56(5)	38(5)
C(63)	71(6)	66(6)	65(6)	8(5)	-7(5)	-14(5)
O(63)	97(5)	112(5)	84(5)	10(4)	-17(4)	-14(4)
As	46.5(4)	51.7(4)	46.8(4)	2.5(3)	8.4(3)	4.0(3)

* Anisotropic temperature factor defined as:-

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\right]$$

APPENDIX 14

Publications

$[H_3Ru_4(CO)_{12}]^-$: the *X*-Ray Crystallographic Determination of Two Structural Isomers†

By PETER F. JACKSON, BRIAN F. G. JOHNSON, and JACK LEWIS*
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Summary ***X*-Ray analysis has shown the presence of two structural isomers of the $[H_3Ru_4(CO)_{12}]^-$ anion with metal–hydrogen geometries approximating to C_s and C_{3v} symmetry; although the presence of structural isomers has been postulated for several metal carbonyl hydrides, this work presents the first confirmation of their existence in the solid state.**

THE i.r. spectrum of $[H_3Ru_4(CO)_{12}]^-$ indicates only terminal carbonyl groups, and the complexity of the pattern suggests that either a species of low symmetry or that more than one species is present. From the ^1H n.m.r. spectrum Koepke *et al.*[1] deduce that two structural isomers are present in solution, one having C_s (or C_{2v}) and the other having C_{3v} symmetry of the metal–hydrogen framework. They also interpret the broad band at 1442 cm^{-1} in the Raman spectrum to be consistent with bridging hydrogens.

In order to investigate the structure in the solid state orange-red, air stable crystals of $[(Ph_3P)_2N]$ $[H_3Ru_4(CO)_{12}]$ (I) were prepared by treating $H_4Ru_4(CO)_{12}$ with methanolic potassium hydroxide, precipitating the anion with $(Ph_3P)_2NI$, and slow recrystallization from CH_2Cl_2–MeOH. The structure was determined by single crystal *X*-ray diffraction (Figure 1).‡ Three tetrahedron edges Ru(1)–Ru(2), Ru(1)–Ru(3), and Ru(2)–Ru(4) are significantly longer [mean 2·923(1) Å], than the others [mean 2·803(1) Å] and the carbonyl ligands appear to be pushed back from these edges. This is consistent with the three hydrogens bridging these longer edges.

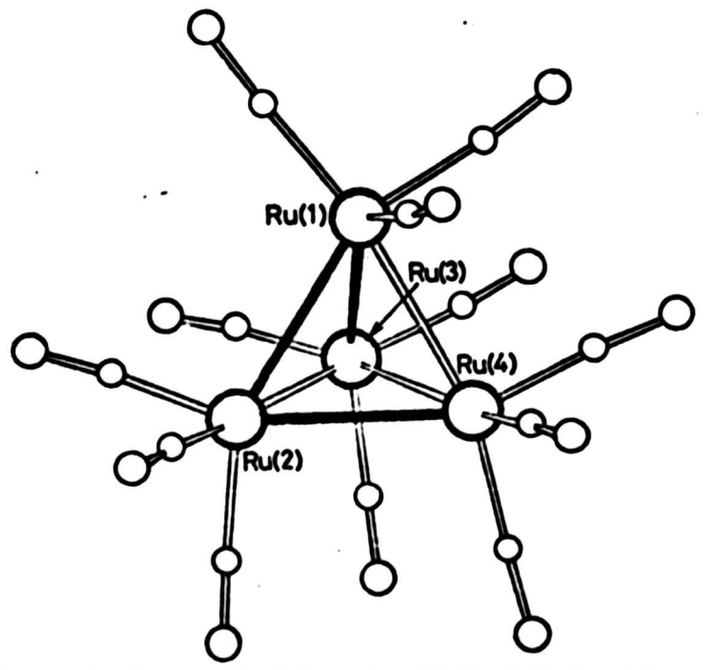

FIGURE 1. Isomer (I) of the anion $[H_3Ru_4(CO)_{12}]^-$. The solid Ru–Ru bonds are bridged by the three hydrogen atoms.

Since the original crystals diffracted rather poorly, a new crop were grown under apparently identical conditions and a crystal selected for recollection of the data. However this had a triclinic unit cell which Delaunay reduction showed was unrelated to the original, and which was *ca.* 26 $Å^3$ smaller. *X*-Ray analysis of this compound (II) has shown it to be a structural isomer of (I) (Figure 2).‡

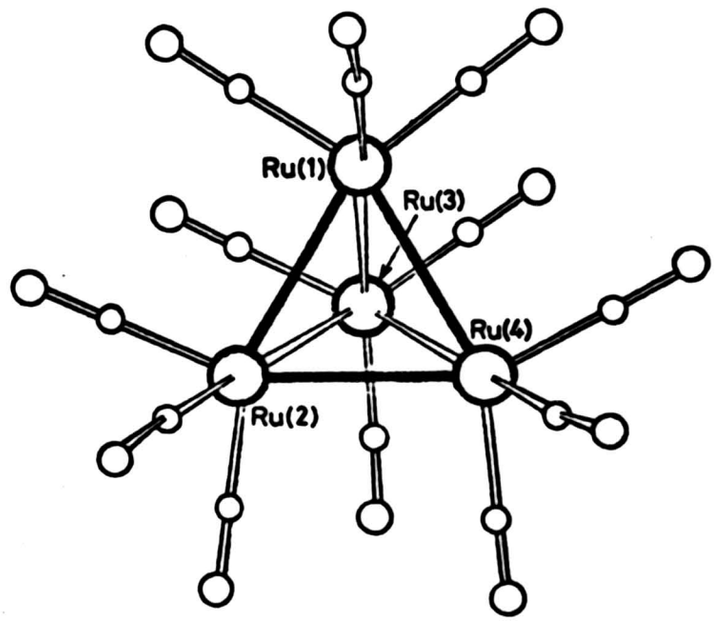

FIGURE 2. Isomer (II) of the anion $[H_3Ru_4(CO)_{12}]^-$. The three hydrogen atoms bridge the edges of the triangular face Ru(1), Ru(2), Ru(4).

The anion in (II) has three Ru–Ru bonds, in this case forming the triangular face Ru(1), Ru(2), Ru(4), which are significantly longer [mean 2·937(1) Å] than the others [mean 2·787(1) Å]. The carbonyl ligands appear to be pushed back from these edges indicating that they are bridged by the three hydrogens. Thus the metal–hydrogen geometry in the two isomeric forms of the $[H_3Ru_4(CO)_{12}]^-$ anion has symmetry approximating to C_s in (I) and C_{3v} in (II). Although evidence in favour of such isomers has appeared for several metal carbonyl hydrides,[1,2] this work apparently presents the first confirmation of their existence

† No reprints available.

‡ *Crystal data:* (I), triclinic, space group $P\bar{1}$, a = 17·361, b = 11·735, c = 12·321 Å, α = 94·61°, β = 98·44°, γ = 88·52°, Z = 2, $I/\sigma(I) > 3·0$, 2θ = 3–30°, present R-value = 0·0545 for 6050 reflections; (II), triclinic, space group $P\bar{1}$, a = 15·608, b = 15·370, c = 11·219 Å, α = 99·26°, β = 103·27°, γ = 105·72°, Z = 2, $I/\sigma(I) > 3·0$, 2θ = 3–32°, present R-value = 0·0432 for 10945 reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

in the solid state. In both isomers, the lengths of the hydrogen bridged Ru–Ru bonds are in good agreement with those determined for α-$H_2Ru_4(CO)_{13}$[3] [mean 2·930(12) Å] which has two μ_2 hydrogen ligands.

A better crystal of (I) was obtained from a later recrystallisation and the recollected data used in the final refinement. Koepke *et al.* found that the equilibrium in solution, $C_s \rightleftharpoons C_{3v}$, is influenced by the polarity of the solvent system, the more polar C_{3v} isomer being favoured in solvents of increasing polarity. This suggests that the crystals of the two isomers separated from solution under differing conditions of solvent polarity. Further, their occurrence in solution and in the solid state indicates relatively little energy difference between the possible hydrogen bridging positions, as shown by Hoffmann *et al.*[4] using extended Hückel calculations on $H_4Fe_4(CO)_{13}$.

This work draws attention to the fact that the determination of structure by single crystal analysis does not necessarily give the unique solid state geometry. Where there is the possibility of more than one isomer existing, it may be necessary not only to examine several crystals, but to repeat the recrystallization under different conditions.

In this connection it is interesting to note the work of Bau[5] and Churchill[6] who have shown that in the structures of $H_4Ru_4(CO)_{10}(PPh_3)_2$ and $H_4Ru_4(CO)_{10}Ph_2PCH_2CH_2PPh_2$ the bridging H-atoms adopt different bridging arrangements.

We thank the S.R.C. for the award of research studentships (to P.F.J. and W.J.H.N.).

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Copper(I) Ethylenediamine Carbonyl Complexes: 'Models' for Carbon Monoxide Activation. *X*-Ray Structure of the Ion-pair Carbonylethylenediaminetetraphenylboratocopper

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Summary Copper (I) iodide absorbs carbon monoxide in methanol in the presence of ethylenediamine (en), giving solutions from which $[Cu_2(en)_3(CO)_2]I_2$, $[Cu_2)en)_3(CO)_2](BPh_4)_2$, and $[Cu(en)_2CO]I$ have been obtained as thermally stable compounds; the reaction of CuCOCl with en allowed the isolation of $[Cu(en)(CO)PhBPh_3]$, an *X*-ray structure determination of which shows the presence of a three-co-ordinate copper(I) interacting with the BPh_4^- anion.

DESPITE their interesting properties,[1,2] copper carbonyls have hitherto hardly been investigated. Their extreme lability and ready disproportionation have frustrated attempts to explore reactions of copper(I) with carbon monoxide in the presence of suitable nitrogen ligands.[1,2] Ethylenediamine (en), while it seems to stabilize Cu–CO bonds,[3] provides a potentially unsaturated copper(I) atom able to co-ordinate two additional molecules. This system could be an interesting model for copper(I)-promoted transfer of carbon-monoxide to organic substrates.[4] A preliminary study on the reaction of CuCOCl with ethylenediamine[3] failed to establish the various species which could be generated by the copper(I)–en–carbon monoxide system and to isolate thermally stable carbonyl complexes.

Herein we report the synthesis of the following thermally stable copper(I) carbonyls: $[Cu_2(en)_3(CO)_2]I_2$ (I), $[Cu_2(en)_3(CO)_2](BPh_4)_2$ (II), $[Cu(en)_2(CO)]I$ (III), and $[Cu(en)CO(BPh_4)]$ (IV), along with results of an *X*-ray analysis of complex (IV).†

CuI suspended in methanolic solutions of en (en : Cu molar ratio 4 : 1) reversibly absorbs carbon monoxide (1 mol of CO per Cu) at room temperature and atmospheric pressure, giving a solution from which either $[Cu_2(en)_3(CO)_2]I_2$ (I) [ν_{CO}(Nujol) 2062 cm^{-1}] or, by addition of $NaBPh_4$, $[Cu_2(en)_3(CO)_2](BPh_4)_2$ (II)‡ [ν_{CO}(Nujol) 2078 cm^{-1}] can be obtained as white crystalline solids. A much larger excess of en over CuI allows the isolation of $[Cu(en)_2CO]I$ (III) [ν_{CO}(Nujol) 2060 cm^{-1}].

As previously described, CuCOCl (1 mol) reacts in methanol at −30 °C with en (1 mol) producing a solution from which the rather unstable [Cu(en)COCl] was recovered.[3] The addition of $NaBPh_4$ to the same solution allowed the isolation of the thermally stable $[Cu(en)CO(BPh_4)]$ (IV) [ν_{CO}(Nujol) 2117 cm^{-1}]. On reaction with en, (IV) gives

† Satisfactory elemental analytical data were obtained for all the compounds reported.

‡ The molecular complexity of (II) is deduced from on *X*-ray analysis which is in progress.

is assigned to P_β of (4). It seems clear that the magnitude of the isotope shift is a parameter which will enhance the range of applications of this technique.

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$H_2Ru_6(CO)_{18}$, $[HRu_6(CO)_{18}]^-$, and $[Ru_6(CO)_{18}]^{2-}$: a Simple High Yield Route to these Clusters and the *X*-Ray Structure of $[Ph_3MeP]_2$ $[Ru_6(CO)_{18}]$†

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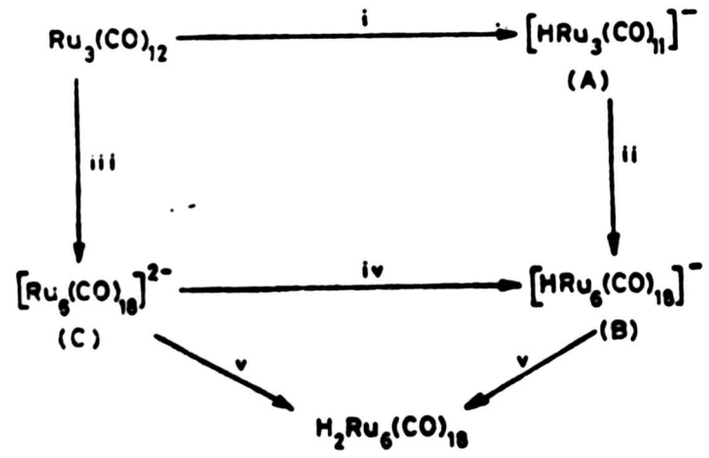
Summary Reaction of $Ru_3(CO)_{12}$ with base gives $[HRu_3(CO)_{11}]^-$ or $[Ru_6(CO)_{18}]^{2-}$ depending upon reaction conditions, and acidification of either produces $[HRu_6(CO)_{18}]^-$ then $H_2Ru_6(CO)_{18}$; *X*-ray analysis has shown the $[Ru_6(CO)_{18}]^{2-}$ dianion to possess octahedral metal geometry with bridging as well as terminal carbonyl ligands.

THE hexanuclear clusters $H_2Ru_6(CO)_{18}$, $[HRu_6(CO)_{18}]^-$, and $[Ru_6(CO)_{18}]^{2-}$ have previously been synthesized in low yield[1] by the reduction of $Ru_3(CO)_{12}$ by $[Mn(CO)_5]^-$ or $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$. We now report a simplified high yield route to these clusters (Scheme).



SCHEME. i, KOH–MeOH; ii, conc. H_2SO_4; iii, $Ru_3(CO)_{12}$–THF added to saturated KOH–H_2O solution; iv, acidification in THF by conc. H_2SO_4; v, acidification in CH_2Cl_2 by conc. H_2SO_4.

Treatment of $Ru_3(CO)_{12}$ with base gives $[HRu_3(CO)_{11}]^-$ (A), which was postulated as an intermediate[2] in the reduction of $Ru_3(CO)_{12}$ by $[Mn(CO)_5]^-$, but it has only recently been fully characterized as one of the products from the reaction of $Ru_3(CO)_{12}$ with $NaBH_4$.[3] Careful acidification of (A) with concentrated sulphuric acid surprisingly produces moderate yields of $[HRu_6(CO)_{18}]^-$ (B) rather than the neutral trinuclear dihydride $H_2Ru_3(CO)_{11}$.‡ However, addition of $Ru_3(CO)_{12}$ in tetrahydrofuran (THF) to a saturated solution of KOH in water gives high yields of the $[Ru_6(CO)_{18}]^{2-}$ dianion (C). Acidification in basic solvents such as THF gives (B) quantitatively, but in CH_2Cl_2 quantitative yields of $H_2Ru_6(CO)_{18}$ (D) are obtained. (A), (B), (C), and (D) were characterized by microanalysis and i.r. (ν_{CO}) and ^1H n.m.r. spectroscopy.

The dihydride $H_2Ru_6(CO)_{18}$ was one of the first 86-electron clusters prepared and *X*-ray structural analysis[4] showed octahedral metal geometry with three terminal carbonyls per metal and the H-ligand bridging two opposite triangular faces of the metal polyhedron. The structure of the dianion $[Ru_6(CO)_{18}]^{2-}$ was assumed to be derived from that of $H_2Ru_6(CO)_{18}$, and this model has been widely used to illustrate the fundamentals of skeletal electron counting.[5] Recently this geometry with only terminal carbonyl ligands has been found[1b,6] in the anions $[Os_6(CO)_{18}]^{2-}$, $[HOs_6(CO)_{18}]^-$, and $[HRu_6(CO)_{18}]^-$. However, the i.r. (ν_{CO}) spectrum of $[Ru_6(CO)_{18}]^{2-}$ is quite unlike that of its osmium analogue suggesting that they are not isostructural; this has been confirmed by an *X*-ray structural analysis.

Suitable crystals of $[Ph_3MeP]_2[Ru_6(CO)_{18}]$ were grown by slow recrystallization from CH_2Cl_2–MeOH and the structure was determined by single crystal *X*-ray diffraction.

† No reprints available.

‡ The corresponding Fe and Os dihydrides are known although $H_2Fe_3(CO)_{11}$ is rather unstable.

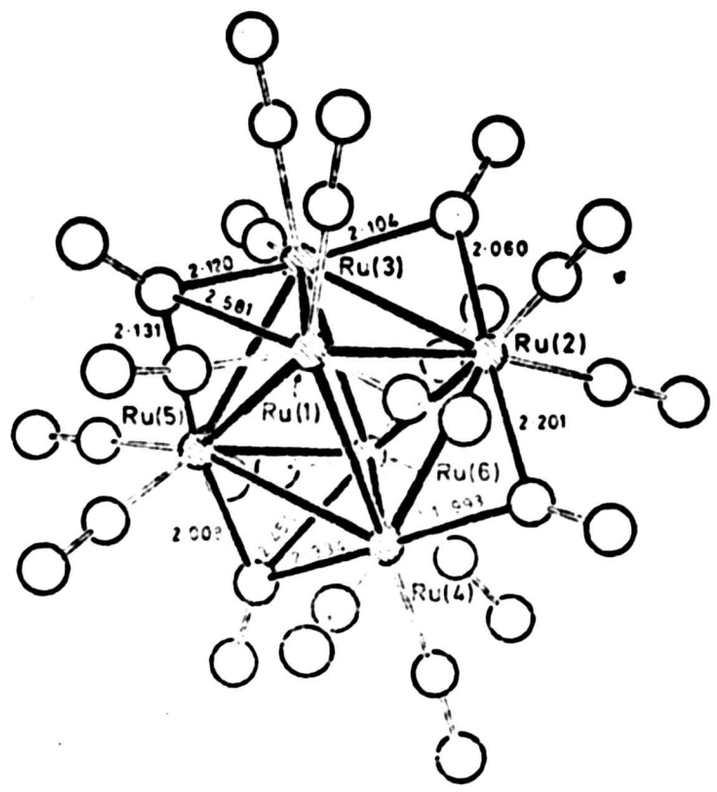


FIGURE. The geometry of the $[Ru_6(CO)_{18}]^{2-}$ dianion in $[Ph_3MeP^+]_2[Ru_6(CO)_{18}]$. The metal atoms form a slightly distorted octahedron with Ru–Ru distances in the range 2·80—2·89 Å. The two μ_3-CO ligands are symmetrically bonded to the cluster but the two μ_3-carbonyl groups are strongly asymmetric with some long Ru–C contacts. This bonding mode has previously been observed for CO ligands and it is thought to provide a means by which charge is delocalized in metal carbonyl clusters (see *e.g.*, V. G. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1969, **16**, 461, 471). Maximum e.s.d. on Ru–C distances indicated is 0·009 Å.

Crystal data: $C_{20}H_{30}O_{18}PRu_6$, triclinic, space group $P\bar{1}$, $a = 25·084$, $b = 11·296$, $c = 10·663$ Å, $\alpha = 79·44$, $\beta = 102·57$, $\gamma = 93·61°$, $Z = 2$, $I/\sigma(I) > 3·0$, θ range 3—25°, present R-value = 0·0478 for 7800 reflections.§ The geometry of the dianion is shown in the Figure; although the Ru_6 core is approximately octahedral, similar to that found in $[Os_6(CO)_{18}]^{2-}$, the carbonyl distribution is quite unlike that of the osmium dianion. In particular doubly and triply bridging carbonyl ligands are present as well as terminal. Although it is valid for electron counting procedures to consider all carbonyls as terminal, their precise disposition is of interest in the light of recent arguments presented to rationalize the geometry of simple binary carbonyls.[7] Thus it would appear that there is a simple relationship between the anions $[Ru_6(CO)_{18}]^{2-}$ and $[Os_6(CO)_{18}]^{2-}$; the CO polyhedra appear to be similar in each case and the differences in structure are the result of a small rotation of the octahedron of metal atoms within this polyhedron.

This work emphasizes the fact that although skeletal electron counting rules may be used to predict the metal geometry in many clusters, no account is taken of the associated requirements of the ligands attached to the metal unit. The ruthenium dianion (C) is the last member of the series $[M_6(CO)_{18}]^{2-}$, $[HM_6(CO)_{18}]^-$, and $H_2M_6(CO)_{18}$ (M = Ru, Os) to be studied by *X*-ray diffraction. Significantly, now that this cluster has been shown to possess a different structure to $[Os_6(CO)_{18}]^{2-}$, no two analogous clusters of this series have the same overall geometry although formally they have identical numbers of electrons available for bonding.

We thank the S.R.C. for the award of research studentships (to P. F. J. and W. J. H. N.).

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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Working Haem Analogues; Reversible Oxygenation of the Manganese–Tertiary Phosphine Complexes $MnLX_2$

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Summary The reversible oxygenation of the complexes $MnLX_2$ (L = tertiary phosphine, but not PPh_3, X = anion) has been investigated; these complexes resemble haemoglobin and myoglobin to a remarkable degree as reversible dioxygen carriers.

THERE is considerable current interest in mimicking the action of natural dioxygen carriers such as haemoglobin and myoglobin, and as well as several elegant steric approaches to the development of iron(II) porphyrins[1,2] there have been studies on cobalt(II) porphyrins.[3] Whilst these systems have significantly advanced our understanding of some of

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Preliminary communication

The Reaction of $H_2Os_5(CO)_{15}$ with Nucleophilic Reagents

by Glyn R John, Brian F G Johnson and Jack Lewis (University Chemical Laboratory, Lensfield Road, Cambridge) and William J Nelson and Mary McPartlin (North London Polytechnic, London)

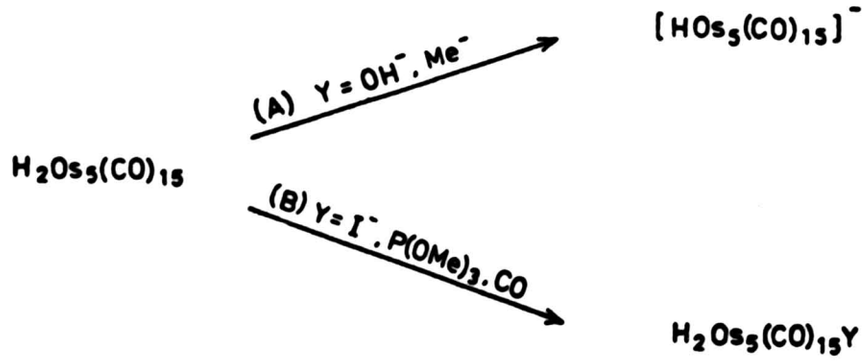
(Received February 26th, 1979)

SUMMARY

The reaction of $H_2Os_5(CO)_{15}$ with nucleophiles Y leads either to deprotonation (Y = OH^- or Me^-) or addition (Y = I^-, $P(OMe)_3$, or CO). The geometrical consequences of these reactions are discussed.

As part of our investigation into the chemistry of the higher osmium carbonyl clusters, we wish to report on the nature of nucleophilic attack on the dihydrocluster $H_2Os_5(CO)_{15}$. On reaction with nucleophiles such as OH^- and Me^-, deprotonation occurs to give either $[HOs_5(CO)_{15}]^-$ or $[Os_5(CO)_{15}]^{2-}$; the degree of deprotonation depending on the solvent employed. (Scheme 1, route A). In contrast, nucleophiles such as I^-,

$P(OMe)_3$ or CO react according to route B, Scheme 1, to give the adducts $[H_2Os_5(CO)_{15}I]^-$, $H_2Os_5(CO)_{15}[P(OMe)_3]$ or $H_2Os_5(CO)_{16}$. In these reactions a major structural transformation of the Os_5 unit occurs; changing from a trigonal bipyramidal geometry to an edge-bridged tetrahedral arrangement.



Scheme 1

$H_2Os_5(CO)_{15}$ is almost totally insoluble in methanol but on treatment with a 50-fold excess of methanolic KOH a deep red-brown solution is formed. On addition of excess $[PPN]^+Cl^-$ to this solution purple-brown crystals of $[PPN]_2^+[Os_5(CO)_{15}]^{2-}$ separate quantitatively. When KOH or MeLi in ether (4%) is added to a stirred solution of $H_2Os_5(CO)_{15}$ in warm dichloromethane, conversion to $[HOs_5(CO)_{15}]^-$ takes place, which again may be quantitatively precipitated as the $[PPN]^+$ salt.
When a 10-fold excess of $n\text{-}Bu_4NI$ is added to $H_2Os_5(CO)_{15}$ in refluxing dichloromethane a deep red solution is slowly formed. Thin layer chromatography (90% dichloromethane/10% hexane) of the reaction mixture after ca. 2 hours leads to a high yield (80%) of the pure red-brown product $[Bu_4N]^+[H_2Os_5(CO)_{15}I]^-$ (I) characterised by microanalysis, ^1H n.m.r. [τ28.56(s) and 30.05(s), CD_2Cl_2, 35°C] and i.r. spectroscopy [ν_{CO} (CH_2Cl_2) 2089w, 2061vs, 2037s, 2026s, 2011w(sh) and 1985m(br) cm^{-1}]. Interestingly this anionic cluster reverts back to $H_2Os_5(CO)_{15}$ upon treatment with excess acid (H_2SO_4 in acetonitrile).

In a similar manner treatment of $H_2Os_5(CO)_{15}$ with a 50-fold excess of $P(OMe)_3$ in refluxing dichloromethane for approximately 20 hours and t.l.c. (as above) of the reaction mixture leads to the neutral orange-red cluster $H_2Os_5(CO)_{15}P(OMe)_3$ (II) also in good yield (67%). This was fully characterised by microanalysis, ^1H n.m.r. [τ30.72(s) and 31.02(s), CD_2Cl_2, 35°C], i.r. spectroscopy [ν_{CO} (CH_2Cl_2) 2116w, 2070s, 2048vs, 2036s, 2014m(sh) and 1997w cm^{-1}] and mass spectrometry [$^m/_e$ 1497(M^+), (M^+-n CO), n = 1-15].

CO can also be added to $H_2Os_5(CO)_{15}$ but requires the more severe conditions of an autoclave. When $H_2Os_5(CO)_{15}$ in deoxygenated hexane is heated to 150°C for <u>ca</u>. 16 hours under a working pressure of 6 atmospheres of CO, a reasonable yield (40%) of the anticipated $H_2Os_5(CO)_{16}$ is obtained. An appreciable amount of decomposition also takes place, although the yield of product has yet to be optimised. Certainly this route to $H_2Os_5(CO)_{16}$ is an improvement on the pyrolysis of $Os_3(CO)_{12}$ in the presence of traces of water[1], where yields do not exceed 2%.

Infrared Spectra in the CO Stretching Region for
(a) $[H_2Os_5(CO)_{15}I]^-$, (b) $[H_2Os_5(CO)_{15}P(OMe)_3]$ and (c) $[H_2Os_5(CO)_{16}]$

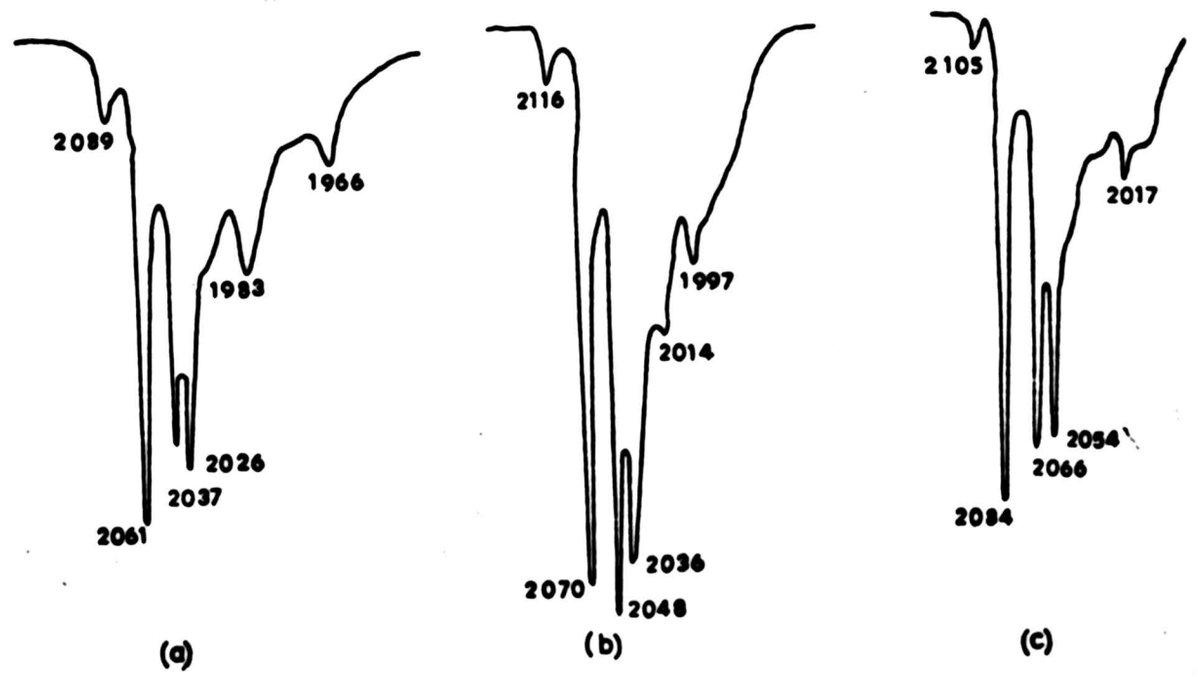
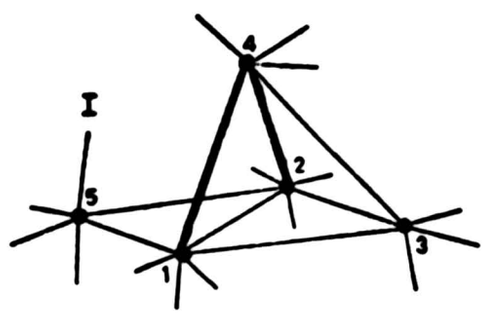


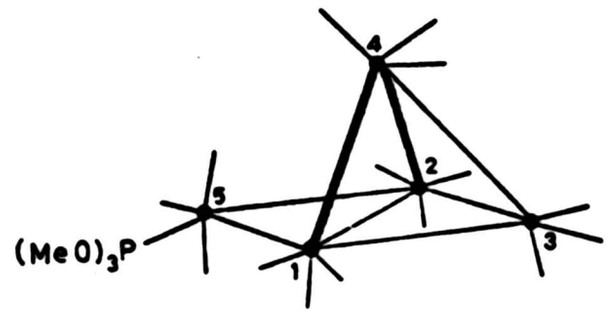
Figure 1

These dihydrides each have seven electron pairs available for cluster bonding and a square pyramidal metal geometry, similar to that found in $Fe_5(CO)_{15}C$ [2] and $Os_5(CO)_{15}P(OMe)$ [3], is predicted on the basis of the Wade Theory. In order to investigate the solid-state structures, crystals of $[Bu_4N]^+[H_2Os_5(CO)_{15}I]^-$ (I) and $H_2Os_5(CO)_{15}P(OMe)_3$ (II) suitable for X-ray analysis were grown by slow evaporation from dichloromethane. Their molecular structures are shown in Figures 2 and 3. A full report of these analyses will be given elsewhere.



(I)

Figure 2



(II)

Figure 3

The geometry of the metal atoms is not square pyramidal but is related to that found in $H_2Os_5(CO)_{16}$ [4] which consists of a tetrahedron of osmium atoms with one edge bridged by the fifth osmium atom. This alternative geometry may still be rationalised by skeletal electron counting procedures. It is fundamental to Wade's Theory that closo-, nido- and arachno-variants of the same polygon require the same number of skeletal electron pairs. It has been shown that a nido-capped octahedron is a suitable metal geometry for a six metal atom cluster having seven skeletal

electron pairs. Thus, by analogy, the structure of the dihydrides (I) and (II) and $H_2Os_5(CO)_{16}$ may be looked upon as an arachno-capped octahedron which is a valid alternative geometry for five metal atoms and seven skeletal electron pairs (Figure 4). It is consistent with this description that the structure forms part of a close-packed array and the four osmium atoms Os(1), Os(2), Os(3) and Os(5) are roughly coplanar.

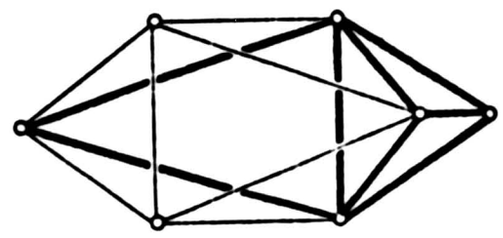
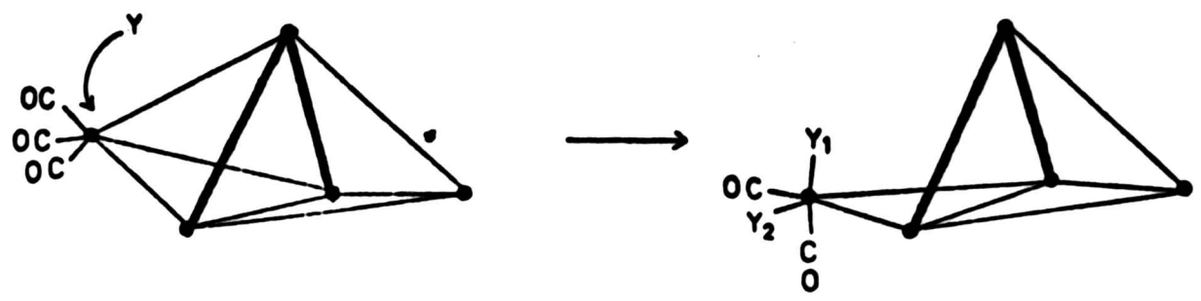


Figure 4

The only other cluster known[5] with a similar geometry is $Co_5(CO)_{11}[P(CH_3)_2]_3$ which has eight skeletal electron pairs. This structure cannot be explained by Wade's Theory, nor by the 18-electron rule; only a valence bond notation invoking canonical forms provides an acceptable picture of the bonding in this compound.

The difference in site preference for the I^- (axial on Os_5) and $P(OMe)_3$ (equatorial on Os_5) moietes is rationalised simply in terms of the much greater steric demands of the phosphite ligand. In both (I) and (II) the hydrogen atoms appear to bridge the long Os-Os bonds, Os(1)-Os(4) and Os(2)-Os(4). Significantly in $H_2Os_5(CO)_{16}$ these same edges appear to be bridged by the hydrogen atoms which suggests that the parent $H_2Os_5(CO)_{15}$ contains the two hydride ligands in the equatorial edge-bridging sites indicated (Figure 5).



$H_2Os_5(CO)_{15}$ $H_2Os_5(CO)_{15}Y$

$Y_1 = Y_2 = CO$;
$Y_1 = I^-$, $Y_2 = CO$;
$Y_1 = CO$, $Y_2 = P(OMe)_3$.

Figure 5

It is apparent from the above studies that while strongly basic nucleophiles tend to deprotonate $H_2Os_5(CO)_{15}$, those with much less basic character undergo addition to the cluster. $H_2Os_5(CO)_{15}$ is isoelectronic with $Os_5(CO)_{16}$ for which a trigonal bipyramidal structure has been determined[6] and a similar structure for $H_2Os_5(CO)_{15}$ is predicted both by the Wade Theory and the skeletal electron counting scheme. Thus, it is seen that the addition of nucleophiles such as I^-, $P(OMe)_3$ and even CO to $H_2Os_5(CO)_{15}$ results in cleavage of an Os-Os bond, followed by an opening out of the structure to yield the edge-bridged tetrahedral arrangement.

This provides a further example of the fascinating changes in structure that my be effected chemically in the reactions of the higher osmium carbonyl clusters, in sharp contrast to the widely varied chemistry of, for example, Os_3 derivatives where the basic Os_3 triangle usually remains intact. Indeed, the reversibility of (at least) $[H_2Os_5(CO)_{15}I]^-$ to $H_2Os_5(CO)_{15}$ upon treatment with acid demonstrates the exciting potential of facile structural transformations that may one day lead to catalysis by metal clusters.

ACKNOWLEDGMENTS

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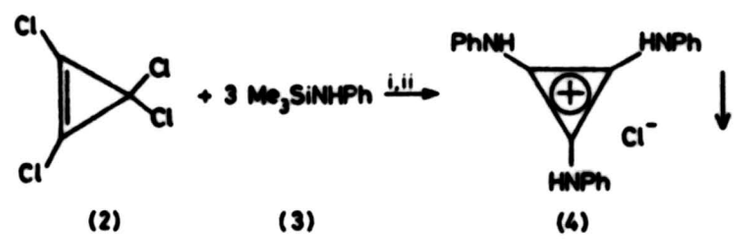

(2) (3) (4)

SCHEME i, CH_2Cl_2, room temperature, 6 h; ii, $-3\ Me_3SiCl$.

under these conditions as a stable, CH_2Cl_2-insoluble salt of m.p. 207 °C (decomp.); i.r. (KBr) 1540 br vs cm^{-1} [characteristic ring vibration (*E'*)[3]]; u.v. (MeCN) λ_{max} 270 nm (log ϵ 4·41); ^{1}H-n.m.r. δ (CD_3CN/Me_4Si standard) 10·1 (brs, 3H, N–H) and 7·3 (s, 15H).

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$$(4) + NaN(SiMe_3)_2 \xrightarrow[-78\ °C,\ 12\ h]{\text{tetrahydrofuran}} (1b) + NaCl + HN(SiMe_3)_2 \quad (1)$$

Low-temperature work-up yields the colourless imine (**1b**) in 72% yield, with m.p. 130 °C (decomp.); i.r. (KBr) 1910 and 1510 br vs cm^{-1}; u.v. ($CHCl_3$) λ_{max} 271 nm (log ϵ 4·39); m.s. (70 eV) *m/e* (rel. intensity) 622 (M_2^+, 87%), 529 (M_2^+ – Ph – NH_2, 100), 311 (M^+, 4), and 208 (M^+ – PhNC, 10). The ^{13}C-n.m.r. spectrum of (**1b**) indicates rapid intra- or inter-molecular proton exchange: apart from the sub-spectrum of the equivalent anilino groups it shows only one singlet for the cyclopropenium C-atoms at δ 115·0 p.p.m. (CD_3CN/Me_4Si standard).

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Synthesis of the Carbido Cluster $[Os_{10}(CO)_{24}C]^{2-}$ and the *X*-Ray Structure of $[Os_{10}(CO)_{24}C][(Ph_3P)_2N]_2$

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(*University Chemical Laboratories, Lensfield Road, Cambridge* CB2 1EW)

and MARY MCPARTLIN and WILLIAM J. H. NELSON
(*Department of Chemistry, The Polytechnic of North London, London* N7 8DB)

Summary The carbido dianion $[Os_{10}(CO)_{24}C]^{2-}$ has been isolated from the pyrolysis of $Os_3(CO)_{11}(py)$ (py = pyridine), and the pyrolysis of $Os_3(CO)_{12}$; an *X*-ray structural analysis of the $[(Ph_3P)_2N]^+$ salt has shown a tetrahedral arrangement of ten metal atoms that is a fragment of a cubic close packed array.

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Pyrolysis of $Os_3(CO)_{11}(py)$ (py = pyridine) *in vacuo* at 250 °C for 24 h gives a red-brown crystalline solid which may be extracted with ethyl acetate. Addition of diethyl ether causes precipitation of the major product of the reaction (*ca.* 80%), a pink-red solid (**2**), leaving in solution mainly $[HOs_3(CO)_{15}]^-$ but small amounts of $H_4Os_4(CO)_{12}$ and Os_3 clusters have also been identified by i.r. [ν(CO)] and mass spectroscopy. The new compound (**2**) exhibits i.r. vibrational frequencies at 2033 and 1986 cm^{-1} of approximately equal intensity indicative of an anionic species of very high symmetry. Although the cation in (**2**) has yet to be identified, the $[Bu_4N]^+$ salt was prepared by metathesis. The dianion (**1**) has also been isolated from the metallic residues left from the pyrolysis of $Os_3(CO)_{12}$ by the use of acetone rather than ethyl acetate for extraction. The $[(Ph_3P)_2N]^+$ and $[Ph_4As]^+$ salts are formed on addition of $(Ph_3P)_2NCl$ or Ph_4AsCl to this solution and these may be purified by fractional recrystallization. No resonance

characteristic of an M H linkage was detected in the ^1H n.m.r. spectrum of (**1**) (τ −40 to +100) and no reaction was observed with $[OH]^-$, indicating that (**1**) was not protonated and therefore probably dianionic. Since ionic species are not usually the product of these pyrolysis reactions it is likely that a neutral hydrido carbonyl is originally formed, which then dissociates in the polar solvents used for extraction to give the charged cluster (**1**). This idea is supported by the fact that much higher yields are obtained from the pyrolysis of $Os_3(CO)_{11}(py)$, where the pyridine ligand can function as a hydrogen source, than that of $Os_3(CO)_{12}$ where the H must come from minute quantities of water present on the glass of the Carius tube itself.

Crystals of the $[(Ph_3P)_2N]^+$ salt suitable for *X*-ray diffraction were grown from Me_2CO–MeOH and the data were recorded on a Philips PW1100 four-circle diffractometer using the $\omega/2\theta$ technique and graphite-monochromated Mo-K_α radiation. The positions of six osmium atoms (defining an octahedron) were obtained from a Patterson map, and four more Os atoms and the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses establishing the molecular formula to be $[Os_{10}(CO)_{24}C]^{2-}[(Ph_3P)_2N]_2^+$.† The dianion (**1**) has approximate overall T_d symmetry (Figure) and the structure may be described as a carbido-centred Os_6 octahedron, with two terminal carbonyls per osmium, capped on four tetrahedrally related faces by $Os(CO)_3$ groups. There are thus only two different environments for the 24 carbonyl ligands (12 of each type) which is completely consistent with the i.r. pattern of this species.

Although many carbido-centred octahedral Ru_6 clusters are known,[4] this is the first osmium cluster to be shown by *X*-ray analysis to have a completely encapsulated carbon atom. There is a striking difference between the Os–Os bond lengths of the octahedron [2·88(1) Å, mean] and those from the capping groups [2·79(1) Å, mean]. In the $[Os_8(CO)_{22}]^{2-}$ dianion[5] this trend is not observed and the mean Os–Os bond length is 2·816 Å so therefore the expansion of the octahedron in (**1**) must be attributed to the presence of the central carbon atom.

The metal skeleton in (**1**) is a fragment of a cubic close packed (c.c.p) array and corresponds to a face-centred cubic unit cell with four tetrahedrally related corners removed. Although large Rh[6a] and Ni[6b] clusters are known with a hexagonal close packed (h.c.p.) arrangement of metals, a c.c.p. array has not previously been observed in a metal carbonyl cluster. Several examples have been reported which indicate that cluster geometries differ from those of the bulk metal,[7] and indeed osmium metal has an h.c.p. rather than a c.c.p. lattice. Interestingly, rhodium metal has a c.c.p. lattice rather than the h.c.p. geometry that some of the large clusters display. The metal core in the dianion (**1**) has the largest planar surfaces observed to date in a carbonyl cluster and the arrangement of CO ligands perpendicular to each face (Figure) may provide the best analogy so far of a monolayer of carbon monoxide chemisorbed on a metal surface.

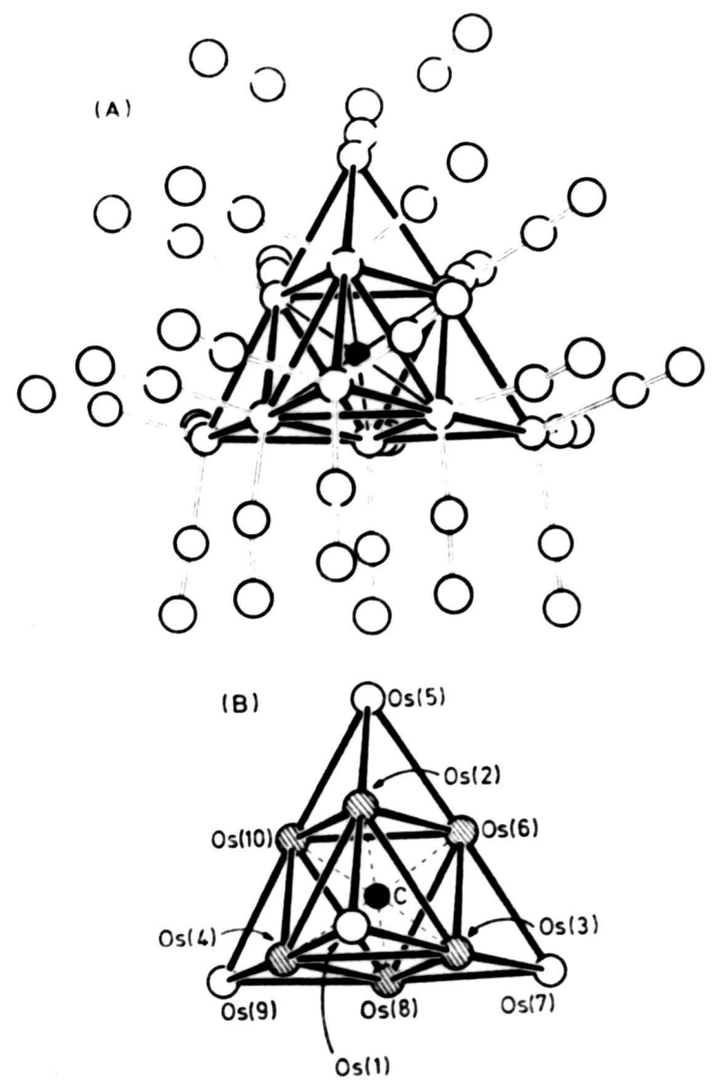
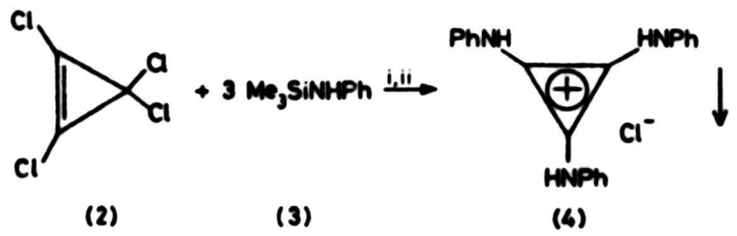


FIGURE. The structure of (**1**). (A) The $[Os_{10}C(CO)_{24}]^{2-}$ dianion. (B) The $Os_{10}C$ unit without the carbonyl ligands. Important bond lengths are Os–Os: (1)–(2) 2·782, (1)–(3) 2·801, (1)–(4) 2·779, (2)–(3) 2·874, (2)–(4) 2·866, (2)–(5) 2·788, (2)–(6) 2·875, (2)–(10) 2·857, (3)–(4) 2·865, (3)–(6) 2·902, (3)–(7) 2·782, (3)–(8) 2·882, (4)–(8) 2·889, (4)–(9) 2·786, (4)–(10) 2·904, (5)–(6) 2·796, (5)–(10) 2·775, (6)–(7) 2·782, (6)–(8) 2·887, (6)–(10) 2·885, (7)–(8) 2·787, (8)–(9) 2·809, (8)–(10) 2·903, and (9)–(10) 2·759 Å; maximum Os–Os e.s.d. 0·004 Å; mean Os–C (carbido) 2·04(3) Å.

The dianion (**1**) has 134 valence electrons, so using Wade's electron counting scheme[8] (12 electrons allocated to each Os for M–C bonds and essentially non-bonding orbitals, the remainder are used for cluster bonding), seven electron pairs are available for cluster bonding indicating that the fundamental polyhedron should be an octahedron. Since capped and uncapped versions of the same polyhedron require the same number of skeletal electron pairs the remaining four osmium atoms may be accommodated in face-capping positions, thus giving the observed structure. Other approaches are less successful in rationalizing the structure. For example, although Lauher[9] envisaged a

† *Crystal data*: triclinic, space group $P\bar{1}$, $a = 27·157$, $b = 17·535$, $c = 10·470$ Å, $\alpha = 96·37$, $\beta = 100·71$, $\gamma = 85·92°$, $Z = 2$, $I/\sigma(I) \geqslant 3·0$, θ-range 3—25°, present R value = 0·1113 for 9069 reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



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Summary The carbido dianion $[Os_{10}(CO)_{24}C]^{2-}$ has been isolated from the pyrolysis of $Os_3(CO)_{11}$(py) (py = pyridine), and the pyrolysis of $Os_3(CO)_{12}$; an *X*-ray structural analysis of the $[(Ph_3P)_2N]^+$ salt has shown a tetrahedral arrangement of ten metal atoms that is a fragment of a cubic close packed array.

THE pyrolysis of dodecacarbonyl triosmium and its substituted derivatives provides the only means at present of synthesizing high-nuclearity clusters of osmium. Thus $Os_3(CO)_{12}$ itself is known to undergo pyrolysis to form a mixture of cluster carbonyls based on Os_5, Os_6, Os_7, and Os_8 units[1] but pyrolyses of $Os_3(CO)_{11}P(OMe)_3$[2] and $Os_3(CO)_{12-n}(CNR)_n$[3] lead exclusively to the formation of Os_5 and Os_6 clusters respectively. High-temperature pyrolysis of $Os_3(CO)_{12}$ was thought to produce clusters of increased nuclearity since solid state i.r. spectra of the ethyl acetate-insoluble residues revealed carbonyl bands. We now report the synthesis, characterization, and *X*-ray structure of the dianion $[Os_{10}(CO)_{24}C]^{2-}$ (**1**) which is the largest osmium cluster prepared to date and the first polynuclear carbonyl to have ten metal atoms.

Pyrolysis of $Os_3(CO)_{11}$(py) (py = pyridine) *in vacuo* at 250 °C for 24 h gives a red-brown crystalline solid which may be extracted with ethyl acetate. Addition of diethyl ether causes precipitation of the major product of the reaction (*ca.* 80%), a pink-red solid (**2**), leaving in solution mainly $[HOs_3(CO)_{15}]^-$ but small amounts of $H_4Os_4(CO)_{12}$ and Os_3 clusters have also been identified by i.r. [ν(CO)] and mass spectroscopy. The new compound (**2**) exhibits i.r. vibrational frequencies at 2033 and 1986 cm^{-1} of approximately equal intensity indicative of an anionic species of very high symmetry. Although the cation in (**2**) has yet to be identified, the $[Bu_4N]^+$ salt was prepared by metathesis. The dianion (**1**) has also been isolated from the metallic residues left from the pyrolysis of $Os_3(CO)_{12}$ by the use of acetone rather than ethyl acetate for extraction. The $[(Ph_3P)_2N]^+$ and $[Ph_4As]^+$ salts are formed on addition of $(Ph_3P)_2NCl$ or Ph_4AsCl to this solution and these may be purified by fractional recrystallization. No resonance

characteristic of an M–H linkage was detected in the ^1H n.m.r. spectrum of (**1**) (τ −40 to +100) and no reaction was observed with $[OH]^-$, indicating that (**1**) was not protonated and therefore probably dianionic. Since ionic species are not usually the product of these pyrolysis reactions it is likely that a neutral hydrido carbonyl is originally formed, which then dissociates in the polar solvents used for extraction to give the charged cluster (**1**). This idea is supported by the fact that much higher yields are obtained from the pyrolysis of $Os_3(CO)_{11}(py)$, where the pyridine ligand can function as a hydrogen source, than that of $Os_3(CO)_{12}$ where the H must come from minute quantities of water present on the glass of the Carius tube itself.

Crystals of the $[(Ph_3P)_2N]^+$ salt suitable for *X*-ray diffraction were grown from Me_2CO–MeOH and the data were recorded on a Philips PW1100 four-circle diffractometer using the $\omega/2\theta$ technique and graphite-monochromated Mo-K_α radiation. The positions of six osmium atoms (defining an octahedron) were obtained from a Patterson map, and four more Os atoms and the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses establishing the molecular formula to be $[Os_{10}(CO)_{24}C]^{2-}[(Ph_3P)_2N]_2^+$.† The dianion (**1**) has approximate overall T_d symmetry (Figure) and the structure may be described as a carbido-centred Os_6 octahedron, with two terminal carbonyls per osmium, capped on four tetrahedrally related faces by $Os(CO)_3$ groups. There are thus only two different environments for the 24 carbonyl ligands (12 of each type) which is completely consistent with the i.r. pattern of this species.

Although many carbido-centred octahedral Ru_6 clusters are known,[4] this is the first osmium cluster to be shown by *X*-ray analysis to have a completely encapsulated carbon atom. There is a striking difference between the Os–Os bond lengths of the octahedron [2·88(1) Å, mean] and those from the capping groups [2·79(1) Å, mean]. In the $[Os_8(CO)_{22}]^{2-}$ dianion[5] this trend is not observed and the mean Os–Os bond length is 2·816 Å so therefore the expansion of the octahedron in (**1**) must be attributed to the presence of the central carbon atom.

The metal skeleton in (**1**) is a fragment of a cubic close packed (c.c.p) array and corresponds to a face-centred cubic unit cell with four tetrahedrally related corners removed. Although large Rh[6a] and Ni[6b] clusters are known with a hexagonal close packed (h.c.p.) arrangement of metals, a c.c.p. array has not previously been observed in a metal carbonyl cluster. Several examples have been reported which indicate that cluster geometries differ from those of the bulk metal,[7] and indeed osmium metal has an h.c.p. rather than a c.c.p. lattice. Interestingly, rhodium metal has a c.c.p. lattice rather than the h.c.p. geometry that some of the large clusters display. The metal core in the dianion (**1**) has the largest planar surfaces observed to date in a carbonyl cluster and the arrangement of CO ligands perpendicular to each face (Figure) may provide the best analogy so far of a monolayer of carbon monoxide chemisorbed on a metal surface.

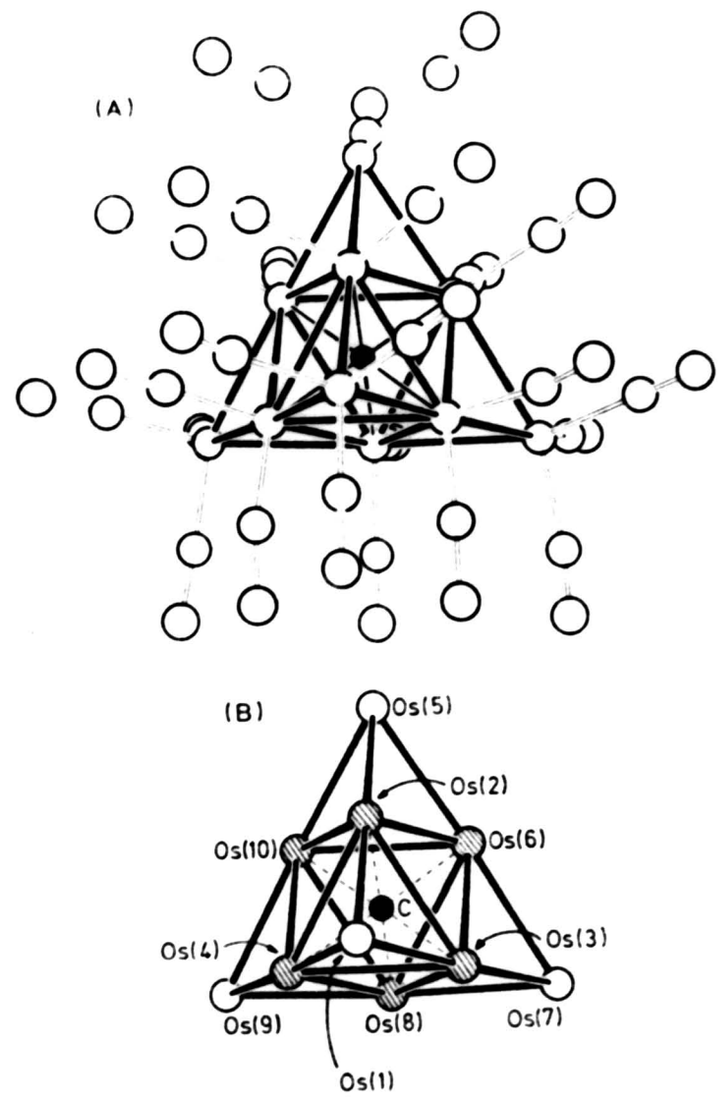

FIGURE. The structure of (**1**). (A) The $[Os_{10}C(CO)_{24}]^{2-}$ dianion. (B) The $Os_{10}C$ unit without the carbonyl ligands. Important bond lengths are Os–Os: (1)–(2) 2·782, (1)–(3) 2·801, (1)–(4) 2·779, (2)–(3) 2·874, (2)–(4) 2·866, (2)–(5) 2·788, (2)–(6) 2·875, (2)–(10) 2·857, (3)–(4) 2·865, (3)–(6) 2·902, (3)–(7) 2·782, (3)–(8) 2·882, (4)–(8) 2·889, (4)–(9) 2·786, (4)–(10) 2·904, (5)–(6) 2·796, (5)–(10) 2·775, (6)–(7) 2·782, (6)–(8) 2·887, (6)–(10) 2·885, (7)–(8) 2·787, (8)–(9) 2·809, (8)–(10) 2·903, and (9)–(10) 2·759 Å; maximum Os–Os e.s.d. 0·004 Å; mean Os–C (carbido) 2·04(3) Å.

The dianion (**1**) has 134 valence electrons, so using Wade's electron counting scheme[8] (12 electrons allocated to each Os for M–C bonds and essentially non-bonding orbitals, the remainder are used for cluster bonding), seven electron pairs are available for cluster bonding indicating that the fundamental polyhedron should be an octahedron. Since capped and uncapped versions of the same polyhedron require the same number of skeletal electron pairs the remaining four osmium atoms may be accommodated in face-capping positions, thus giving the observed structure. Other approaches are less successful in rationalizing the structure. For example, although Lauher[9] envisaged a

† *Crystal data*: triclinic, space group $P\bar{1}$, $a = 27·157$, $b = 17·535$, $c = 10·470$ Å, $\alpha = 96·37$, $\beta = 100·71$, $\gamma = 85·92°$, $Z = 2$, $I/\sigma(I) \geqslant 3·0$, θ-range 3—25°, present R value = 0·1113 for 9069 reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

tetrahedral arrangement for 10 metal atoms his calculations indicate that it would require 140 valence electrons, which would correspond to the incorrect formulation $[Os_{10}(CO)_{27}C]^{2-}$ for (1).

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Michaelis–Arbuzov Intermediates: *X*-Ray Crystal Structures of the Methyl Bromide Adducts of Neopentyl Diphenylphosphinite and Dineopentyl Phenylphosphonite

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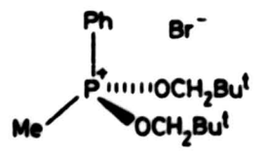
Summary Single crystal *X*-ray structure determinations of the Michaelis–Arbuzov intermediates $Ph_2Me(Bu^tCH_2O)P^+Br^-$ and $PhMe(Bu^tCH_2O)_2P^+Br^-$ clearly demonstrate that these species are four-co-ordinate phosphonium salts.

INTERMEDIATES of the Michaelis–Arbuzov reaction (Scheme) have either a tetraco-ordinate (phosphonium) or pentaco-ordinate (phosphorane) structure in solution, depending on the nature of XY and the reaction conditions.[1–4] For

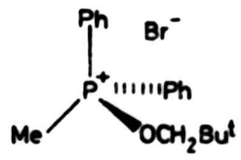
$$R\text{–}O\text{–}\underset{|}{\overset{|}{P}}\text{:} + XY \rightarrow [R\text{–}O\text{–}\underset{|}{\overset{|}{P}}XY] \rightarrow RY + O{=}\underset{|}{\overset{|}{P}}\text{–}X$$

SCHEME

reactions in which XY is an alkyl halide, only the phosphonium species has been detected by ^{31}P n.m.r. spectroscopy,[1,3,4] although it was previously suggested that the pentacovalent form might exist in the solid state or in non-polar media.[5] Stereochemical evidence for the initial formation of a pentaco-ordinate intermediate in the reaction of a cyclic phosphite with methyl iodide[6] has been questioned.[7]



(1)



(2)

The absence of crystallographic data for Michaelis–Arbuzov intermediates is due in part to the difficulties associated with the handling of these moisture-sensitive and thermally unstable compounds. We have found that the attachment of phenyl groups to phosphorus considerably enhances their stability,[8] both to hydrolysis and to thermal decomposition [relative k ($CDCl_3$; 33 °C; R = neopentyl: $(RO)_3PMeBr$ 1·00, $(RO)_2PPhMeBr$ 0·21, $(RO)PPh_2MeBr$ 0·0023]. Compounds (1) and (2) were prepared by the reaction of bromomethane with the corresponding phosphorus esters in sealed tubes at room temperature. The crystals which separated were washed with anhydrous ether and dried *in vacuo* and could be handled in the open laboratory without difficulty.

The *X*-ray structures of (1) and (2) clearly show that these compounds are phosphonium salts composed of tetrahedral cations with minimum $P^+ \ldots Br^-$ distances of 4·43 and 4·61 Å for (1) and (2) respectively (see Figures 1 and 2 respectively).

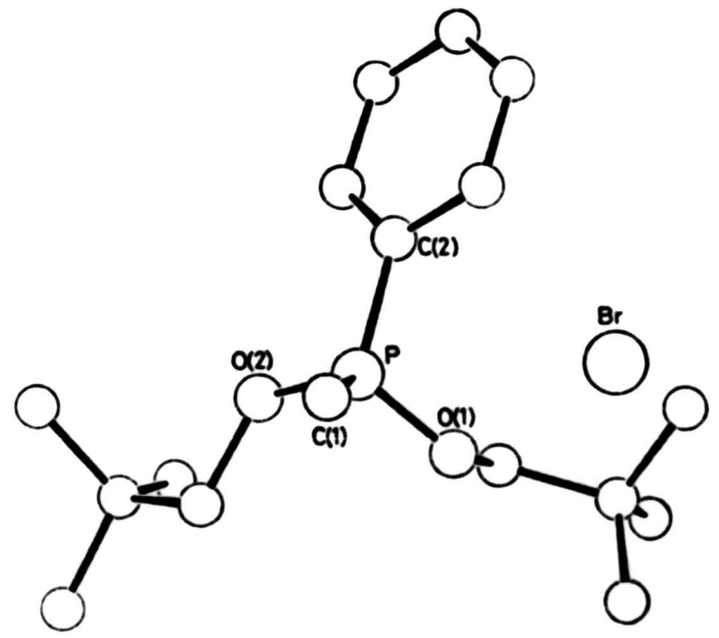


FIGURE 1. The structure of the dialkoxyphosphonium bromide (1). Bond lengths to the P atom (Å) are C(1) 1·756(7), C(2) 1·771(8), O(1) 1·545(5), O(2) 1·553(5). Bond angles at the P atom (°) are, O(1)–P–O(2) 111·4(3); O(1)–P–C(1) 103·4(4); O(1)–P–C(2) 111·0(3); O(2)–P–C(1) 113·5(4); O(2)–P–C(2) 103·8(4); C(1)–P–C(2) 114·0(4); mean 109·5(1).

Direct Location of the Interstitial Hydride Ligand in $[HRu_6(CO)_{18}]^-$ by both *X*-Ray and Neutron Analyses of $[Ph_4As][HRu_6(CO)_{18}]$

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Summary The proposed interstitial location of the hydride ligand in $[HRu_6(CO)_{18}]^-$ has been established by *X*-ray and neutron analyses of $[Ph_4As][HRu_6(CO)_{18}]$.

Although the interstitial nature of hydrogen in binary metal hydrides is well established,[1] the anion $[HRu_6(CO)_{18}]^-$ (1) was the first polynuclear carbonyl in which an interstitial hydrogen atom was detected.[2] For this compound

...and in $[HRu_6(CO)_{18}]^-$ by
$[Ph_4As][HRu_6(CO)_{18}]$

...s,* and PAUL R. RAITHBY
...mbridge CB2 1EW)
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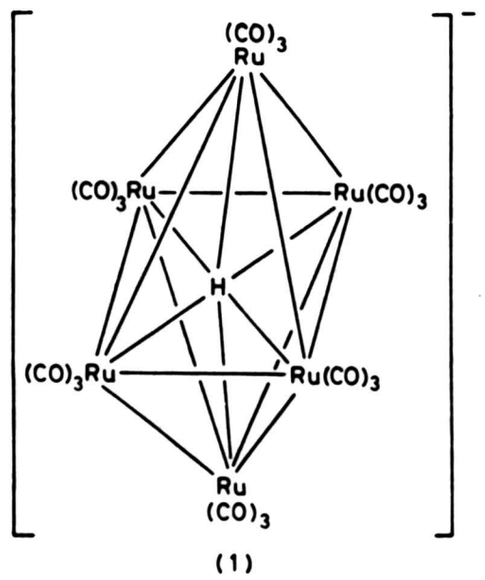

(1)

the possibility of the hydrogen ligand being on the exterior of the cluster was ruled out by the highly symmetrical overall structure, which was shown by *X*-ray analysis[2] to be almost identical to that in the dianion $[Os_6(CO)_{18}]^{2-}$ which has crystallographic D_3 symmetry.[3] Thus, no sign of the characteristic displacement of the close packed carbonyls necessary to accommodate an external hydrogen atom was observed and furthermore no ^{13}C–^1H n.m.r. coupling could be detected. The unusual low field signal (τ −6·41) in the ^1H n.m.r. spectrum was attributed to this novel hydrogen environment, but this assignment proved to be controversial. For example, recent neutron diffraction studies of the extended polynuclear carbonyls $[H_nNi_{12}(CO)_{21}]^{(4-n)-}$ [(**2**) $n = 1$, (**3**) $n = 2$] have shown that the

$[HNi_{12}(CO)_{21}]^{3-}$ (**2**) $[H_2Ni_{12}(CO)_{21}]^{2-}$ (**3**)

hydrogen ligands are also interstitial, being located in distorted octahedral cavities, but the ^1H n.m.r. spectra show the normal high field shifts (τ 34·0 and 28·0)[4] characteristic of transition metal hydrides. This prompted the conclusion, in a review published at the same time, that the hydrogen atom in (**1**) was not interstitial but that the large downfield shift exhibited in the ^1H n.m.r. spectrum was due to a hydrogen atom associated with a carbonyl ligand.[5] The authors made a similar assignment for $[HCo_6(CO)_{15}]^-$ (τ − 13·2) and proposed that a particularly low field ^1H n.m.r. shift in polynuclear carbonyls is diagnostic of a new class of cluster hydrides with direct carbonyl–hydrogen linkages. (A recent neutron analysis has shown that this cluster contains an interstitial hydrogen atom[6]). In addition, from consideration of the weakening effect of hydrogen ligands on M–M bonds, they concluded that interstitial hydrides would not occur in M_6 clusters except in the presence of μ_2- or μ_3-carbonyl ligands.

Recently with accurate *X*-ray data hydrogen atoms have been occasionally located directly in carbonyl clusters with up to four metal atoms.[7] Prompted by this, crystals of the anion (**1**) with a range of counter ions were prepared with the purpose of directly locating the H atom and confirming the original interstitial assignment. The $[Ph_4As]^+$ salt of (**1**) gave very good *X*-ray data which afforded ready location of the hydrogen atom at the centre of the Ru_6 octahedron; the positional and isotropic thermal parameters were successfully refined giving a mean Ru–H distance of 2·04 Å. Thus the interstitial site of the hydrogen ligand is confirmed beyond further question. This cluster is the first hexanuclear ruthenium species to be obtained with no external bridging ligand, so clearly octahedral clusters with interstitial hydride atoms are not too unstable to exist without the presence of bridging carbonyl ligands.

TABLE. The M–H distances in $[HRu_6(CO)_{18}]^-$ (from *X*-ray/neutron refinement) together with those reported for the other interstitial hydrides.

Interstitial hydride	*d* (M–H)/Å	^1H n.m.r. shift (τ)
$[HCo_6(CO)_{15}]^-$	1·80—1·87(2)[a]	−13·2[a]
$[HRu_6(CO)_{18}]^-$	2·03—2·06(1)	−6·4
(**3**)	long 2·00(av.)[b] short 1·84(av.)	28·0[b]
(**2**)	long 2·22(av.)[b] short 1·72(av.)	34·0[b]
$[H_2Rh_{12}(CO)_{24}]^{3-}$	[c]	36·7[d]
$[H_3Rh_{12}(CO)_{24}]^{2-}$	[c]	39·3[d]

[a] Ref. 6. [b] Ref. 4. [c] These hydrides are not truly interstitial; the position of the H-atoms, in square pyramidal sites on the surface, has been deduced from *X*-ray analyses (ref. 10). [d] Ref. 10.

In view of the very large difference in the ^1H n.m.r. shift observed for the intersitial hydride in this octahedral cluster compared to those for the hydrogen atoms in the extended clusters (**2**) and (**3**) it was important to obtain a more accurate location of the hydrogen atom within the Ru_6 octahedron of (**1**). Neutron data† were collected with a larger crystal of the $[Ph_4As]^+$ salt and a combined refinement of single set of positional and thermal parameters using the *X*-ray and neutron data was carried out by the method described by Sheldrick.[8] The results together with data reported for other interstitial hydrides are shown in the Table, and the overall structure of (**1**) is shown in the Figure.

The range of ^1H n.m.r. shifts for the four interstitial polynuclear carbonyl cluster hydrides that are known (Table) varies from τ − 13·2 to 34, a wide range compared to that of the hundreds of other reported compounds of the later

† *Crystal data*: $C_{42}H_{21}AsO_{18}Ru_6$, *M* 1495·1, monoclinic, space group $P2_1/n$, $a = 16·393(5)$, $b = 19·426(7)$, $c = 15·023(5)$ Å, $\beta = 100·64(2)°$, $U = 4,701·8$ Å^3, $D_c = 2·11$ g cm^{-3}, $Z = 4$; Mo-K_α radiation, $\lambda = 0·71069$ Å, μ(Mo-K_α) = 24·45 cm^{-1}; neutrons, $\lambda = 1·2641$ Å, $\mu = 0·65$ cm^{-1}. The structure was initially solved from the *X*-ray data alone, and then refined to current residuals of $R = 0·073$, $R_w = 0·079$ (*X*-ray), and $R = 0·091$, $R_w = 0·087$ (neutron) for 4480 *X*-ray ($\sin\theta/\lambda > 0·45$) and 2261 observed neutron data [$F > 5\sigma(F)$].

There is a slight disorder (0·906 : 0·094) of the $[HRu_6(CO)_{18}]^-$ anion similar in nature to that present for one of the two independent anions of the $[Ph_3P)_2N]^+$ salt (C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, accepted for publication). The two orientations of the cluster are related by rotation about an axis through the centre of the cluster so that the H atom is unaffected by the disorder.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

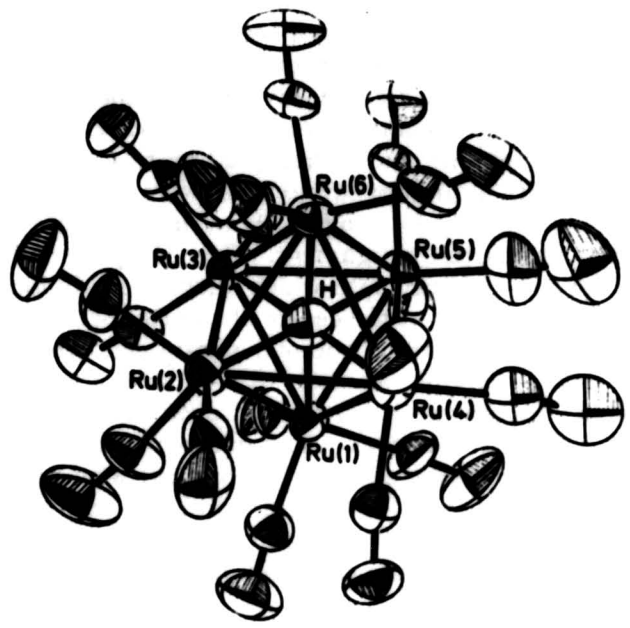

FIGURE. The structure of the dianion $[HRu_6(CO)_{18}]^-$ from the neutron analysis of the $[Ph_4As]^+$ salt. Ruthenium hydride bond lengths are: Ru(1)–H, 2·033(11); Ru(2)–H, 2·034(11); Ru(3)–H. 2·039(12); Ru(4)–H, 2·055(12); Ru(5)–H, 2·028(11); Ru(6)–H 2·034(11)Å.

transition elements where, in spite of a variety of modes of hydride bonding, this shift lies in the range τ 10—69 with very few exceptions.[9] Clearly ^{1}H n.m.r. spectroscopy alone cannot be used as a diagnostic test for the position of an H-atom in a polynuclear cluster as interstitial hydrides are very sensitive to the exact symmetry of the surrounding metals. In (**1**) and in $[HCo_6(CO)_{15}]^-$ a nearly O_h symmetry is observed for the metals together with almost equal M–H distances; this environment is associated with large downfield shifts of the ^{1}H n.m.r. resonance. However, the hydride ligands in the D_{3d} cavities of the extended clusters (**2**) and (**3**) are in less symmetrical positions being much closer in each case to the central hexa-metal plane than to the outer triangular metal set (Table), so that in (**2**) the hydride may be considered as triply bridging three nickel atoms and only very weakly bonded to the other three.[4] The unsymmetrical bonding of the H-atoms in (**2**) and (**3**) is accompanied by ^{1}H n.m.r. signals in the normal upfield region (Table). It seems consistent with this trend that the 'interstitial' H-atoms in the extended cluster $[H_nRh_{13}(CO)_{24}]^{(5-n)-}$ (n = 2, and 3), which are in incomplete octahedral (*i.e.* square pyramidal) sites on the surface of the clusters have ^{1}H n.m.r. shifts at the even higher τ values of 36·7 and 39·3.[10]

Many transition metals absorb hydrogen to produce non-stoicheiometric hydrides in which the hydrogen atoms occupy octahedral sites within the close-packed metal array. This is always accompanied by an expansion of the metal lattice; for example, an octahedral site in the cubic close-packed structure of palladium metal has a radius of 1·94 Å, but the radius of this site increases to 2·04 Å in $PdH_{0.7}$.[11] Of the three polynuclear carbonyl species $[H_nRu_6(CO)_{18}]^{n-2}$ (n = 0, 1, 2) the dianion, with no hydride ligands, has an octahedral site radius of 2·02 Å. The introduction of an interstitial hydride ligand increases this to 2·04 Å in (**1**), and in the neutral $H_2Ru_6(CO)_{18}$ molecule,[12] where the two hydrogens are on the outside of the cluster, there is a further expansion of the octahedral hole giving a mean radius of 2·05 Å. This casts doubt on any assumption that increase in the metal–metal distances is merely a reflection of the 'size' of the interstitial hydrogen atom. Significantly the mean Ru–C distance in $[Ru_6(CO)_{16}C]^{2-}$ is 2·05 Å,[13] very similar to the mean Ru–H bond length observed in $[HRu_6(CO)_{18}]^-$. From the limited data available for external Ru–H bridging bond lengths it seems that a value of *ca.* 1·8 Å is typical; for example the eight μ_2-H–Ru lengths in $H_4Ru_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$ average 1·76(5) Å.[7] This supports the conclusion that the space available in an 'unexpanded' Ru_6 octahedral hole of radius 2·02 Å would be more than adequate to accommodate an interstitial hydride. Thus it seems probable that the expansion in M–M bond lengths produced by external μ-H ligands and those produced by interstitial H-atoms are related and are electronic in origin.

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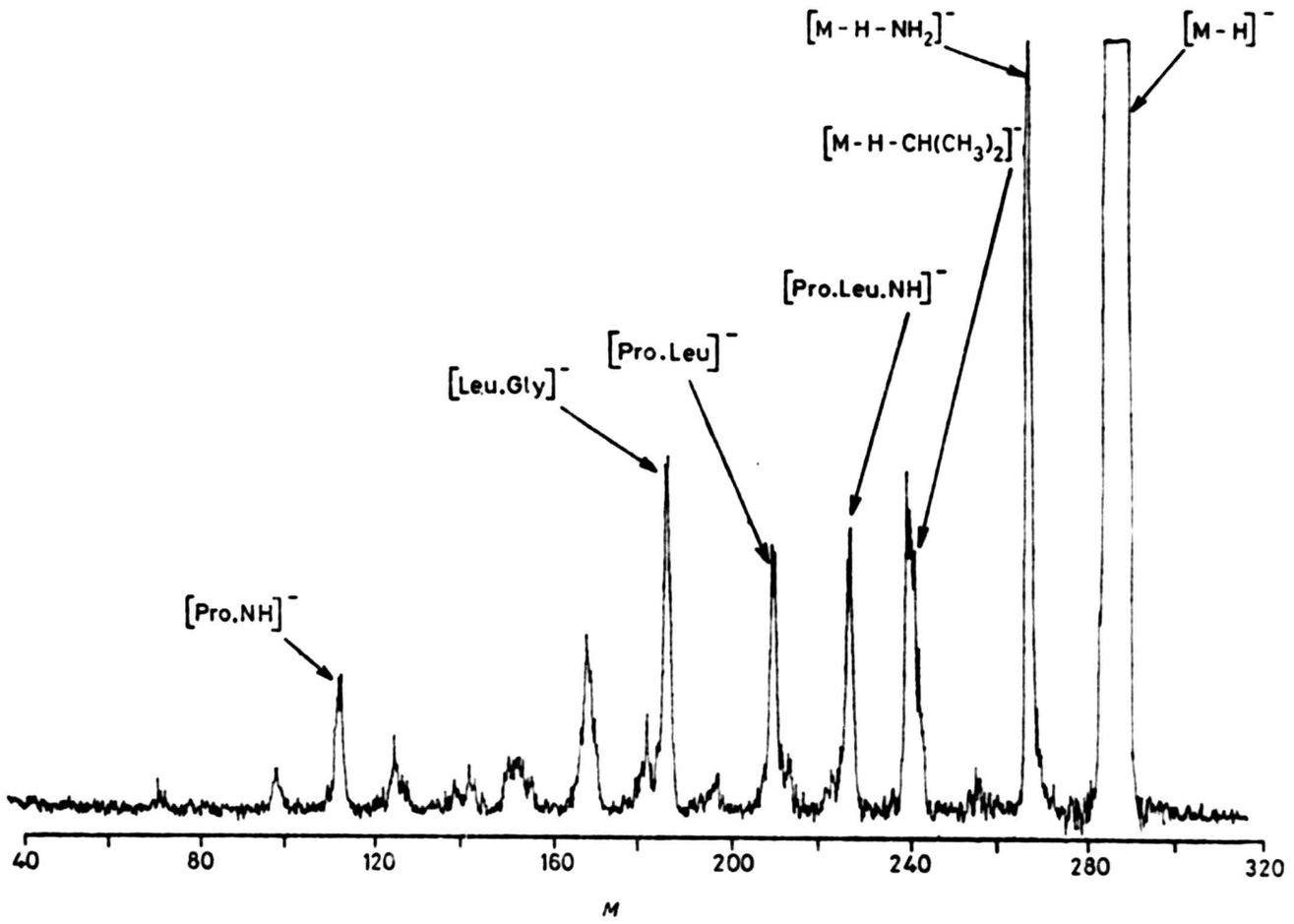

FIGURE 3. CID–MIKE spectrum of Pro–Leu-Gly-Amide. (CID = collision-induced dissociation, MIKE = mass-analysed-ion-kinetic-energy.)

tripeptide may then be unambiguously identified (see, for example in Figure 3 the CID–MIKE spectrum of the m/z 283 negative ion from this mixture). Sequence ions are formed according to the scheme shown in Figure 1 and are indicated on the MIKE spectrum. The ion formed by $CH(Me)_2$ loss is indicative of a leucine component.

The method discussed in this paper illustrates that concrete molecular weight and sequence information may be obtained on all components of an underivatised peptide mixture without prior physical separation. It is proposed to investigate the applicability of the technique to a wider range of peptides and to utilise laser radiation as an alternative to collision-induced dissociation.

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Synthesis of the Carbido Anion $[Os_5C(CO)_{15}I]^-$ and the *X*-Ray Crystal Structures of $Os_5C(CO)_{15}$ and $[(Ph_3P)_2N][Os_5C(CO)_{15}I]$

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Summary $Os_5C(CO)_{15}$ has been shown to be isostructural (but not isomorphous) with its iron analogue $Fe_5C(CO)_{15}$ which has a square pyramidal metal geometry and its reaction with iodide gives the anion $[Os_5C(CO)_{15}I]^-$ in

which the osmium atoms have opened out to a bridged butterfly arrangement; the flexibility of the cluster units in reversibility towards electron donation is illustrated.

MUCH interest has recently been shown in polynuclear carbonyl clusters that contain interstitial atoms. To date H,[1a] C,[1b] N,[1c] P,[1d] and S[1e] have been found embedded in the interstices of metal polyhedra but little is known about their chemistry in these sites since they are usually completely surrounded by the metal atoms and therefore shielded from attack.

We have previously reported the synthesis and characterisation of both $Os_5C(CO)_{15}$[2a,2b] (**1**) and $Ru_5C(CO)_{15}$,[2a] and the similarity of their i.r. spectra to that of their iron analogue $Fe_5C(CO)_{15}$[3] suggested that these three clusters were isostructural [ν(CO)(CH_2Cl_2) 2070s and 2030s cm^{-1} for $Os_5C(CO)_{15}$]. A single crystal *X*-ray analysis has now verified this for the osmium cluster.† Orange air-stable crystals of (**1**),‡ which were characterised by i.r. and mass spectrometry, were fractionally crystallised from an ethyl acetate solution containing several polynuclear species formed by the pyrolysis of $Os_3(CO)_{12}$.[2b] The structure of (**1**) is shown in Figure 1; the osmium atoms define the vertices of a square pyramid, with three terminal carbonyls per metal, and the carbido atom sits slightly below the square face (0·12 Å) as it does in the iron species.[4] Thus $Os_5C(CO)_{15}$ is isostructural with $Fe_5C(CO)_{15}$.

Reaction of $Os_5C(CO)_{15}$ in tetrahydrofuran with iodide, followed by addition of $(Ph_3P)_2NCl$ in methanol, leads to the precipitation of $[(Ph_3P)_2N][Os_5C(CO)_{15}I]$ (**2**) [ν(CO)-(CH_2Cl_2) 2091w, 2059s, 2045vs, 2010br s, 1981w, 1959w, and 1938w cm^{-1}]. In order to investigate the solid state geometry, orange air-stable crystals of (**2**) suitable for *X*-ray diffraction were grown from CH_2Cl_2–MeOH.‡ The structure of the anion is shown in Figure 2. As the iodide behaves as a two electron donor group, the anion has two more skeletal electron pairs (*S*) than the six required for the appropriate closed polyhedron[5] (a trigonal bipyramid), so an open structure is expected in which the carbido atom occupies a more exposed position. The metal atoms define five of the seven vertices of a pentagonal bipyramid which has an *arachno*-geometry predicted by Wade theory[5] for a cluster having eight skeletal electron pairs and five skeletal atoms. The carbido atom lies approximately at the centre of this polyhedron but is not equidistant from the five Os atoms (Figure 2).

A similar Os_5C geometry has been observed in $HOs_5C(CO)_{13}[OP(OMe)OP(OMe)_2]$[6a] and $HOs_5C(CO)_{14}[OP(OMe)_2]$[6b] which were isolated in low yield from the pyrolysis of $Os_3(CO)_{11}P(OMe)_3$. Since the central carbon atom in clusters of this geometry is contained in a metal polyhedron that has two vertices missing it is open to attack by incoming

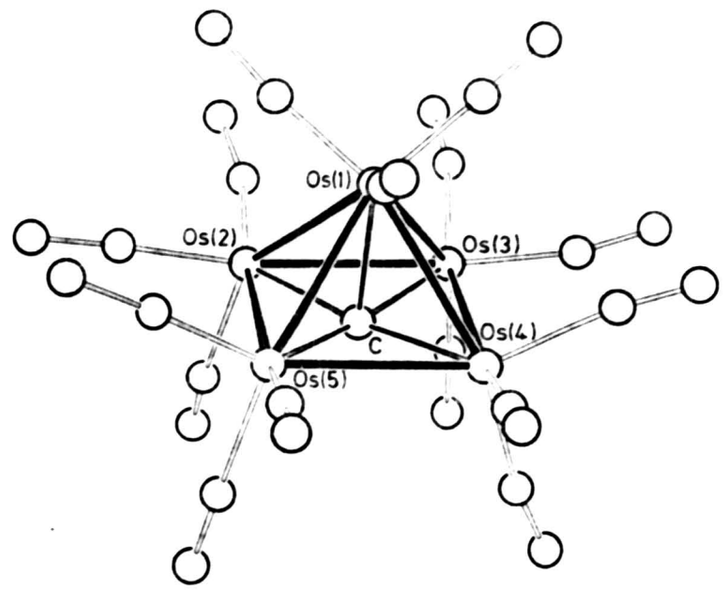

FIGURE 1. The structure of $Os_5C(CO)_{15}$ (**1**). There are 2 independent molecules in the asymmetric unit for (**1**) but the overall geometry is the same for the two molecules. Important mean bond lengths are Os(basal)–Os(basal) 2·88(2), Os(apical)–Os(basal) 2·85(3), and Os–C 2·06(4) Å. The carbido atom lies 0·12 Å below the basal osmium plane.

molecules. The anion in (**2**) has only simple ligands present so the chemistry of a 'semi-interstitial' carbon atom in such an environment may now be conveniently investigated for the first time. The exciting potential of these clusters as catalysts has recently been demonstrated by Bradley *et al.*[7] who showed that a partially encapsulated carbon atom exhibits a chemistry conducive to C–C bond formation and succeeded in synthesizing methyl acetate from CO and H_2 only.

It is interesting to compare the differing modes of reaction of clusters with iodide. The neutral compound $Os_6(CO)_{18}$ is reduced by I^- to the dianion $[Os_6(CO)_{18}]^{2-}$;[8] this is accompanied by a structural change of the metal skeleton from a bicapped tetrahedron ($S = 6$) to an octahedron ($S = 7$). This reaction is reversible; treatment of $[Os_6(CO)_{18}]^{2-}$ with I_2 regenerates the neutral species and the iodine is reduced to I^-. In contrast, the dihydride $H_2Os_5(CO)_{15}$ adds I^- and the metal core changes from a trigonal bipyramid ($S = 6$) to an edge-bridged tetrahedron which is an *arachno* capped-octahedron ($S = 7$).[9] In this case addition of H^+ regenerates the neutral species.

Similarly when iodide reacts with $Os_5C(CO)_{15}$ it also functions as a Lewis base and co-ordinates to an osmium atom. Again, an appropriate change in metal polyhedron occurs, but in this system the reaction is irreversible.

† A new high yield synthesis of $Ru_5C(CO)_{15}$ has given crystals which are isomorphous with those of $OsC(CO)_{15}$ and this therefore confirms that all three carbides are isostructural.

‡ *Crystal data*: (**1**) monoclinic, space group $P2_1/c$, $a = 16{\cdot}404$, $b = 14{\cdot}170$, $c = 20{\cdot}798$ Å, $\beta = 91{\cdot}71°$, $Z = 8$, $I/\sigma(I) \geqslant 3{\cdot}0$, θ-range 3—30°, present *R*-value = 0·0499 for 5946 reflections; (**2**) monoclinic, space group $P2_1/n$, $a = 34{\cdot}337$, $b = 10{\cdot}042$, $c = 16{\cdot}382$ Å, $\beta = 101{\cdot}77°$, $Z = 4$, $I/\sigma(I) \geqslant 3{\cdot}0$, θ-range 3—25°, present *R*-value = 0·0399 for 6134 reflections. Empirical absorption corrections were applied to both data sets [(**1**) $\mu = 252{\cdot}5$ cm^{-1}, (**2**) $\mu = 116{\cdot}3$ cm^{-1}]. The atomic co-ordinates for $[(Ph_3P)_2N][Os_5C(CO)_{15}I]$ are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. The atomic co-ordinates for $OsC(CO)_{15}$, and also for $[(Ph_3P)_2N][Os_5C(CO)_{15}]$, are available on request from Prof. Dr. G. Bergerhoff, Institut für Anogonische Chemie, Universität, Gerhard Domagk-Str. 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

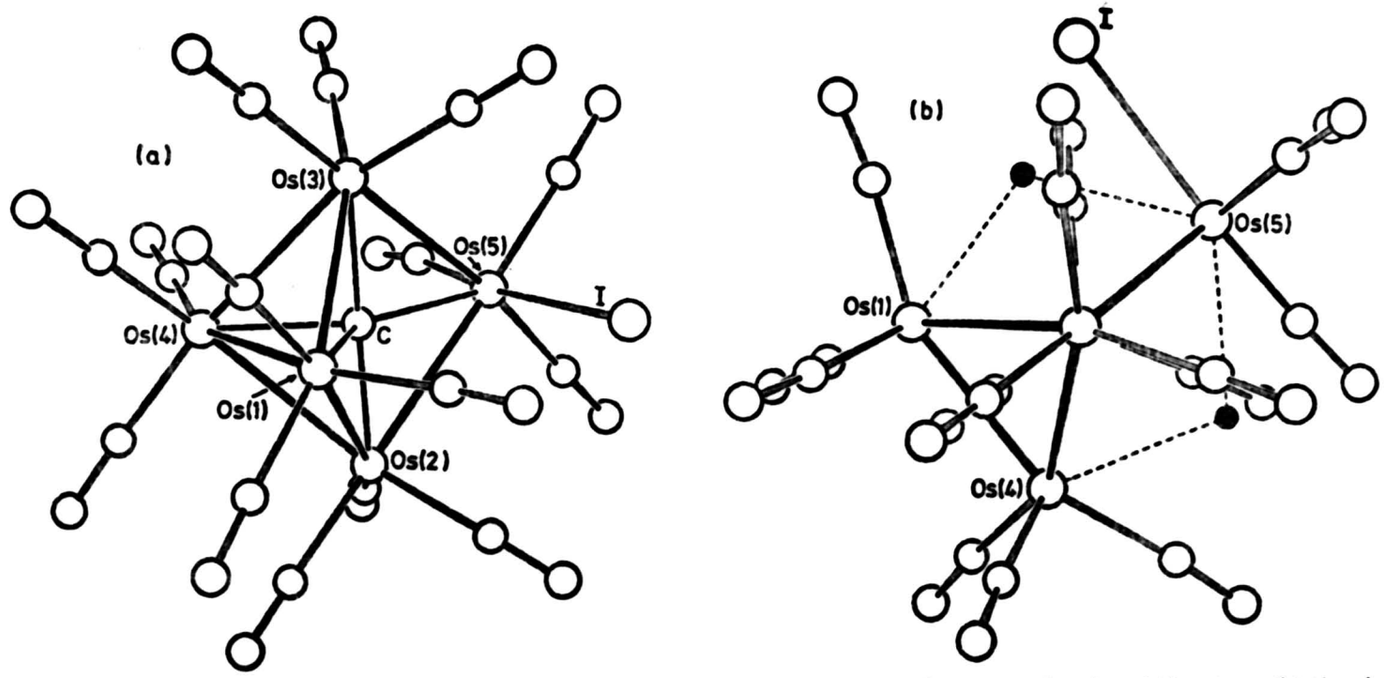

FIGURE 2. The structure of the $[Os_5C(CO)_{15}I]^-$ anion (**1**): (a) a view showing the partially encapsulated carbido atom, (b) the cluster viewed down Os_2 and Os_3 to illustrate the *arachno*-pentagonal bipyramidal metal geometry. Important bond lengths are Os(1)–Os(2) 2·903, Os(1)–Os(3) 2·921, Os(1)–Os(4) 2·748, Os(2)–Os(4) 2·899, Os(2)–Os(5) 2·933, Os(3)–Os(4) 2·896, Os(3)–Os(5) 2·934, Os(1)–C 2·108, Os(2)–C 1·978, Os(3)–C 1·995, Os(4)–C 2·108, and Os(5)–C 2·174 Å. Max. e.s.d's are Os–Os 0·001, Os–C 0·012 Å.

However, protonation of $[Os_5C(CO)_{15}I]^-$ in acetonitrile yields the neutral complex $HOs_5C(CO)_{15}I$. Reaction of this with silver nitrate and subsequent protonation produces a nitrate complex which dissociates in decane at 150 °C to yield the parent carbonyl carbide $Os_5(CO)_{15}C$. Thus, in these series of complexes, owing to the flexibility in the metal framework, it is possible to generate a new co-ordination site within the metal polyhedra *via* the breaking of metal–metal bonds. The reversibility of this process also adds to the potential use of complexes of this type as catalytic intermediates.

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Biaryl Formation in the Photochemical Reaction of Halogenated Aromatic Nitriles with Methoxybenzenes

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Summary Irradiation of tetrachloro- and tetrafluorophthalonitriles in the presence of anisole, 1,3-dimethoxybenzene, or 1,4-dimethoxybenzene, led to formation of biaryls; a similar process occurred with mixtures of 1,4-dimethoxybenzene and 2- or 4-chlorobenzonitrile, but not 3-chlorobenzonitrile.

IRRADIATION of tetrachlorophthalonitrile (TCPN, **1**; R=Cl) and tetrafluorophthalonitrile (TFPN, **2**; R = F) in the presence of aliphatic ethers leads to replacement of the 4-halogeno substituent by an α-alkoxyalkyl group derived from the ether.[1] We now report that reaction with aromatic ethers leads to formation of biaryls, a process that

Improved Syntheses of the Hexanuclear Clusters $[Ru_6(CO)_{18}]^{2-}$, $[HRu_6(CO)_{18}]^{-}$, and $H_2Ru_6(CO)_{18}$. The *X*-Ray Analysis of $[HRu_6(CO)_{18}]^{-}$,† a Polynuclear Carbonyl containing an Interstitial Hydrogen Ligand

By Colin R. Eady, Peter F. Jackson, Brian F. G. Johnson, Jack Lewis,* and Maria Carlotta Malatesta, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
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Improved Syntheses of the Hexanuclear Clusters $[Ru_6(CO)_{18}]^{2-}$, $[HRu_6(CO)_{18}]^-$, and $H_2Ru_6(CO)_{18}$. The *X*-Ray Analysis of $[HRu_6(CO)_{18}]^-$,† a Polynuclear Carbonyl containing an Interstitial Hydrogen Ligand

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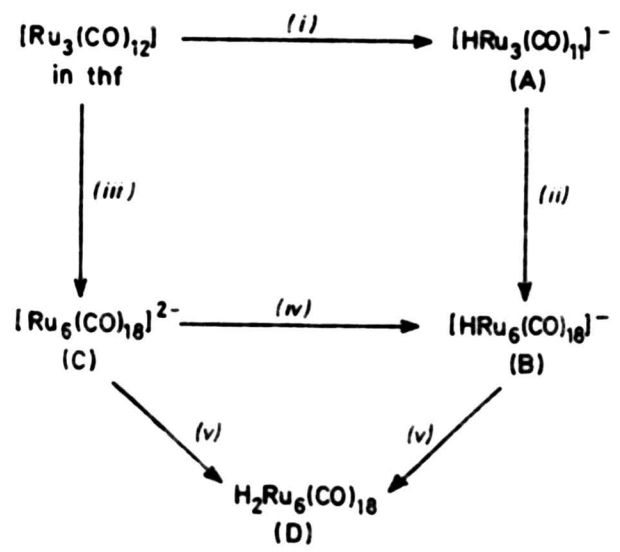
The *X*-ray analyses of two crystalline modifications, (I) and (II), of $[N(PPh_3)_2][HRu_6(CO)_{18}]$ are reported, together with improved synthetic routes to this and the related clusters $[Ru_6(CO)_{18}]^{2-}$ and $H_2Ru_6(CO)_{18}$. Crystals of (I) are triclinic, space group $P\bar{1}$, with $a = 18.083(4)$, $b = 19.101(4)$, $c = 19.238(5)$ Å, $\alpha = 117.70(4)$, $\beta = 78.13(2)$, $\gamma = 97.05(2)°$, and $Z = 4$. Crystals of (II) are monoclinic, space group $P2_1/n$, with $a = 33.82(8)$, $b = 52.55(10)$, $c = 9.832(2)$ Å, $\beta = 92.66(2)°$, and $Z = 12$. Least-squares refinement using diffractometer data (Mo-K_α) has given an R of 0.068 1 for 9 165 reflections for (I) and an R of 0.23 (Ru only) for 1 485 reflections for (II). The unit cell in (I) contains two independent molecules of $[HRu_6(CO)_{18}]^-$, cluster (1) which is ordered and cluster (2) which is disordered between two sites (2A) and (2B) that are related by a non-crystallographic two-fold axis. The combined evidence of the *X*-ray analyses, ^{1}H n.m.r. studies, i.r. [ν(CO)] spectra, and variable-temperature ^{13}C n.m.r. is only consistent with the hydrogen ligand lying inside the Ru_6 octahedron.

THE monoanion $[HRu_6(CO)_{18}]^-$, which was the first authenticated example of a polynuclear carbonyl compound containing an H atom within the metal polyhedron,[1] is obtained on acidification of $[Ru_6(CO)_{18}]^{2-}$ or $[HRu_3(CO)_{11}]^-$. The dianion was originally prepared in low yield from the reaction of $[Ru_3(CO)_{12}]$ with $[Mn(CO)_5]^-$, but we have since developed more convenient syntheses of this and related compounds [2] which are now reported in detail.

For many years $[HNb_6I_{11}]$ provided the only confirmed example [3] of an H ligand occupying an interstice within a metal polyhedron, although many clusters containing interstitial carbon atoms were known. Recently $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 2$ or 3),[4] $[HCo_6(CO)_{15}]^-$,[5] $[HNi_{12}(CO)_{21}]^{3-}$,[6] and $[H_2Ni_{12}(CO)_{21}]^{2-}$ (ref. 6) have also been shown to contain interstitial H atoms; evidence presented for such an H environment in $[HFe_4(CO)_{13}]^-$ (ref. 7) and $[HFeCo_3(CO)_{12}]$ [8] appears to be contradicted by subsequent *X*-ray and neutron-diffraction analyses.[9,10] Therefore, in addition to the three well documented types of bonding for hydrogen attached to polynuclear metal clusters (terminal, edge-bridging, and face-bridging) a fourth class has now been firmly established in which the hydrogen atom is embedded inside the metal polyhedron.

RESULTS AND DISCUSSION

Dodecacarbonyltriruthenium, $[Ru_3(CO)_{12}]$, reacts with $Na[Mn(CO)_5]$ in tetrahydrofuran(thf) at elevated temperatures over a period of 4 h to produce a brown solution. Treatment with concentrated sulphuric acid (slight excess) yields the anions $[HRu_6(CO)_{18}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ as the major products which were separated as their bis(triphenylphosphine)iminium salts. The trihydride $[H_3Ru_4(CO)_{12}]^-$ was not named previously as a product of this reaction, the neutral dihydrides $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ being reported as the major acidification products.[1] Similarly the reaction of $[Ru_3(CO)_{12}]$ with base (K[OH] in methanol,[11] sodium amalgam,[11] or tetrahydroborate),[11,12] which has been extensively studied, was also thought to give $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ as the only hydrido-species. We now find that under slight variation of the conditions, $[Ru_3(CO)_{12}]$ reacts with methanol–K[OH] in thf to produce $[HRu_3(CO)_{11}]^-$ (A) in almost quantitative yield (Scheme). Knight and Mays [13] suggested that the reaction of $[Ru_3(CO)_{12}]$ with $[Mn(CO)_5]^-$ to produce hexaruthenium species involved the intermediate formation of (A), but this anion has only recently been fully characterized.[14]



SCHEME (*i*) K[OH]–MeOH; (*ii*) 10% H_2SO_4–thf; (*iii*) $[Ru_3(CO)_{12}]$–thf added to saturated solution of K[OH] in water; (*iv*) acidification in thf by concentrated H_2SO_4; (*v*) acidification in CH_2Cl_2 by concentrated H_2SO_4

This route appears to be confirmed by our observation that careful acidification of (A) with 10% H_2SO_4–thf produces moderate yields of $[HRu_6(CO)_{18}]^-$ (B); rapid addition of acid results in the formation of equal amounts of (B) and $[Ru_3(CO)_{12}]$. The trinuclear dihydride $H_2Ru_3(CO)_{11}$ was not observed under these conditions although the iron and osmium analogues are known to exist.[15,16]

† Octadecacarbonylhydrogen-*octahedro*-hexaruthenate(1−).

rs $[Ru_6(CO)_{18}]^{2-}$, $[HRu_6$-
s of $[HRu_6(CO)_{18}]^-$,† a
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$h_3)_2][HRu_6(CO)_{18}]$ are reported, to-
$CO)_{18}]^{2-}$ and $H_2Ru_6(CO)_{18}$. Crystals
= 19.238(5) Å, α = 117.70(4), β =
group $P2_1/n$, with a = 33.82(8), b =
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$_{18}]^-$, cluster (1) which is ordered and
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O)] spectra, and variable-temperature
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H] in methanol,[11] sodium amal-
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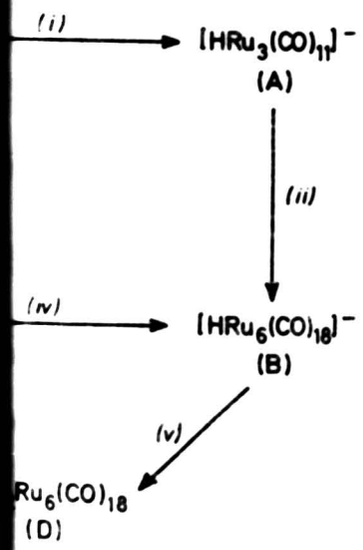

; (ii) 10% H_2SO_4–thf; (iii) [Ru_3-
rated solution of K[OH] in water;
concentrated H_2SO_4; (v) acidific-
rated H_2SO_4

e confirmed by our observation
n of (A) with 10% H_2SO_4–thf
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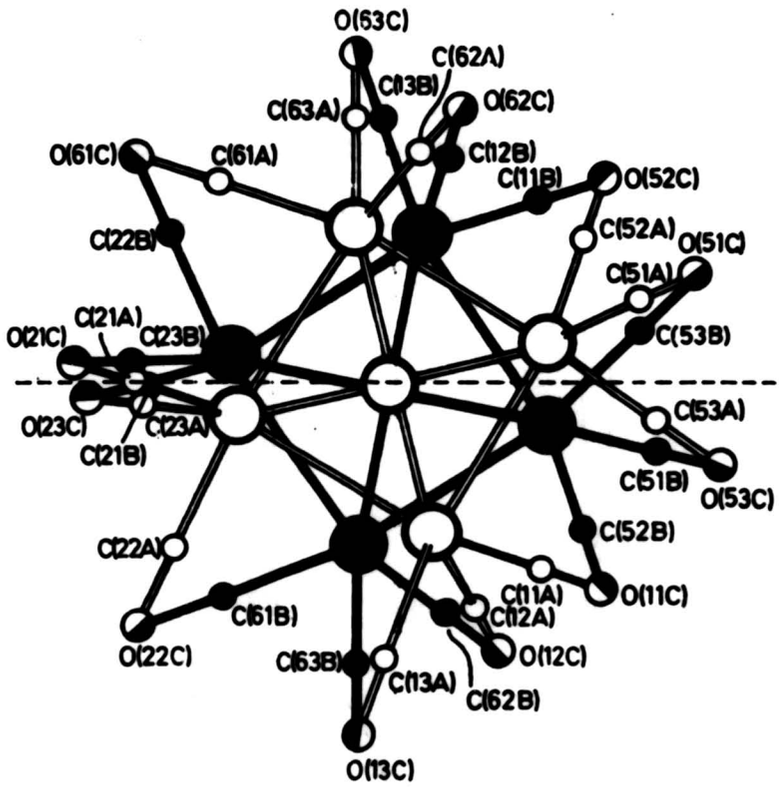


FIGURE 1 (*a*) The disordered cluster (2) of $[HRu_6(CO)_{18}]^-$ (I) viewed down the ordered ruthenium atoms Ru(4C), Ru(3C). The components (2A) and (2B) are related by a pseudo two-fold axis passing through the midpoints of Ru(2A) ··· Ru(2B) and Ru(5A) ··· Ru(5B). All of the oxygen atoms are common to clusters (2A) and (2B) so they have been labelled (C) and numbered to correspond to the carbon atoms of the major component (2A). For clarity the six ordered CO ligands attached to Ru(3C) and Ru(4C) have been omitted. (*b*) The orientation of the six ordered carbonyls in cluster (2) with respect to the metal atoms

The reaction of $[Ru_3(CO)_{12}]$ with K[OH] in aqueous thf is more complex giving a new high yield route to $[Ru_6(CO)_{18}]^{2-}$ (C) together with (A) and (B). The actual product distribution is dependent on the reaction conditions (see Experimental section). Acidification of (C) gives (B) or $H_2Ru_6(CO)_{18}$ (D) depending on the solvent employed, so these ruthenium clusters behave similarly to the $[Os_6(CO)_{18}]^{2-}$, $[HOs_6(CO)_{18}]^-$, $H_2Os_6(CO)_{18}$ series with respect to protonation.[17]

Despite disordering of one of the independent clusters of one crystal modification [(I), see Experimental section] the structure of $[HRu_6(CO)_{18}]^-$ is clearly established and is shown in Figures 1—3. The anion has approximate non-crystallographic D_3 symmetry with three terminal carbonyl ligands per metal atom, and thus the carbonyl distribution has a marked

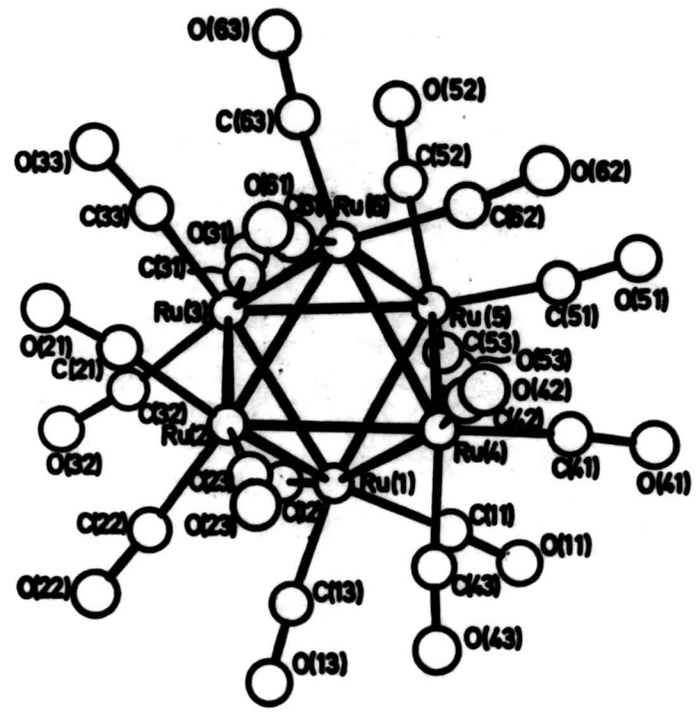
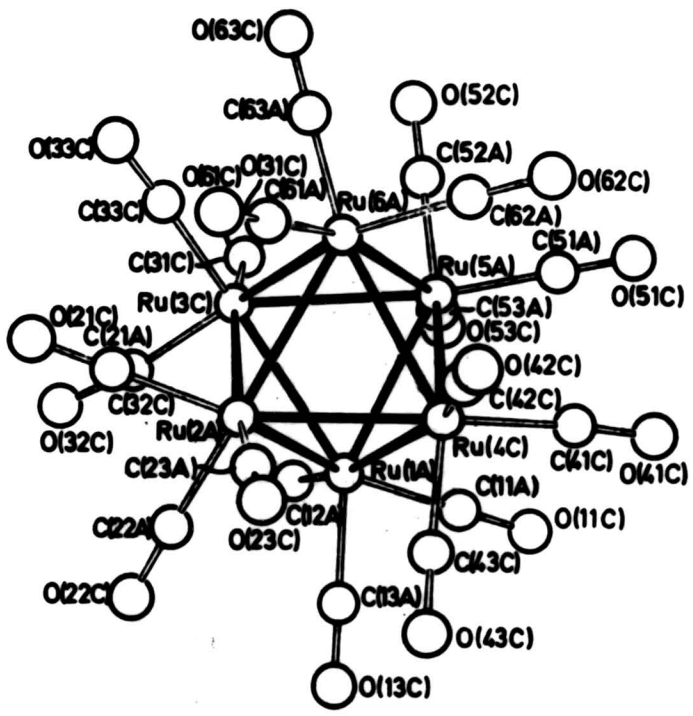


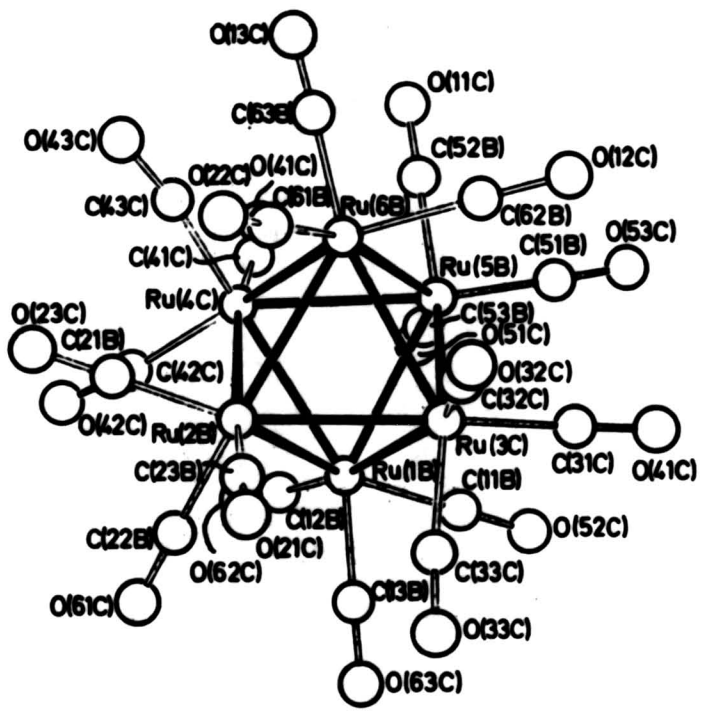
FIGURE 2 Comparison of the geometries of (*a*) $[HRu_6(CO)_{18}]^-$ and (*b*) $[Os_6(CO)_{18}]^{2-}$

resemblance to that in $[Os_6(CO)_{18}]^{2-}$ [Figure 2(*b*)] which has an overall structure of exact D_3 symmetry.[18] The Ru_6 core has two equivalent parallel faces that are approximately equilateral [mean Ru–Ru, 2.877(13) Å]; these are slightly twisted from O_h symmetry so that the

remaining bond lengths * are alternately long [mean 2.924(3) Å] and short [mean 2.839(6) Å]. However, the ruthenium octahedron is expanded compared to the metal octahedron in $[Os_6(CO)_{18}]^{2-}$ {and [2] $[Ru_6(CO)_{18}]^{2-}$} in



(a) Cluster (2A)



(b) Cluster (2B)

FIGURE 3 The two components (2A) and (2B) of the disordered cluster in $[HRu_6(CO)_{18}]^-$ (I). See Figure 1 (*a*) for explanation of the labelling scheme

which the medium, long, and short bond lengths are 2.876(2), 2.884(3), and 2.816(3) Å respectively. The insertion of the H atom into $[Co_6(CO)_{18}]^{2-}$ has also been observed to cause a small but appreciable swelling of the Co_6 octahedron.[5] The structure of $[HRu_6(CO)_{18}]^-$ is quite unlike that of $[HOs_6(CO)_{18}]^-$ where the carbonyl ligands on one face are markedly pushed back to accommodate the external H ligand;[18] this confirms the evidence of the solution i.r. spectrum [ν(CO)] which shows just one broad band [Figure 4(*c*)] consistent with the presence of six equivalent $Ru(CO)_3$ groups. The solid-state i.r. spectrum [ν(CO), KBr] shows one main band with shoulders [Figure 4(*d*)] which is again consistent with equivalent $Ru(CO)_3$ groups, the slight asymmetry probably arising from intermolecular interactions in the crystal lattice. These spectra are significantly different from that of $[HOs_6(CO)_{18}]^-$, but closely resemble (in pattern) that of the highly symmetrical $[Os_6(CO)_{18}]^{2-}$ dianion [Figure 4(*b*)]. Thus there is no crystallographic or spectroscopic evidence for an external H atom in $[HRu_6(CO)_{18}]^-$. For comparison, Ru–Ru bond lengths in other octahedral ruthenium clusters are 2.840—3.034 Å for $[Ru_6(CO)_{17}C]$,[19] 2.853—2.956 Å for $[Ru_6(CO)_{14}C(mesitylene)]$,[20] and 2.954(3) and 2.867(5) Å (mean values) for the hydrogen-bridged and normal Ru–Ru bonds in $H_2Ru_6(CO)_{18}$ respectively.[21]

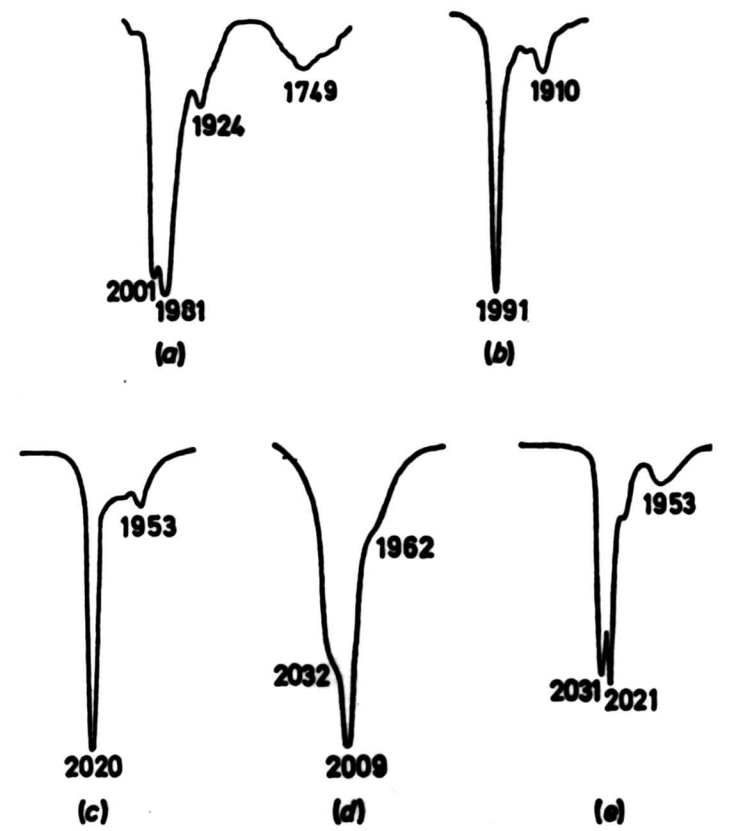


FIGURE 4 Infrared spectra [ν(CO), cm^{-1}] of (*a*) $[Ru_6(CO)_{18}]^{2-}$, (*b*) $[Os_6(CO)_{18}]^{2-}$, (*c*) $[HRu_6(CO)_{18}]^-$, (*d*) $[NMe_4][HRu_6(CO)_{18}]$ solid in KBr, and (*e*) $[HOs_6(CO)_{18}]^-$ $\{[N(PPh_3)_2]^+$ salts in CH_2Cl_2 unless otherwise stated, calibrant CO}

TABLE 1

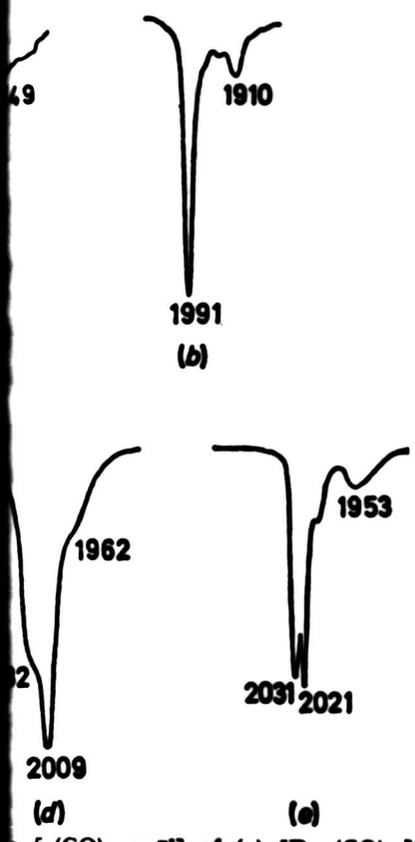
Infrared absorptions in the carbonyl region

Compound [a]	Maxima (cm^{-1}) [b]
$[H_2Ru_4(CO)_{13}]^-$	2 034s, 2 029s, 2 014s, 1 994 (s+), 1 969m, br
(A) $[HRu_3(CO)_{11}]^-$	2 070vw, 2 012s, 1 984s, 1 947m, 1 798vw, 1 725w
(B) $[HRu_6(CO)_{18}]^-$	2 020s, 1 953vw
(C) $[Ru_6(CO)_{18}]^{2-}$	2 001s, 1 981 (s+), 1 924w, 1 749w, br
(D) $H_2Ru_6(CO)_{18}$	2 058s, 2 052s, 2 003w

[a] CH_2Cl_2 as solvent with exception of $[HRu_3(CO)_{11}]^-$ which was run in thf. [b] CO calibrant, central position 2 143 cm^{-1}.

* These bond lengths refer to the ordered cluster (1), but the same pattern is observed in the disordered cluster (2).

markedly pushed back to accom-
H ligand;[18] this confirms the
on i.r. spectrum [ν(CO)] which
and [Figure 4(*c*)] consistent with
uivalent $Ru(CO)_3$ groups. The
[ν(CO), KBr] shows one main
igure 4(*d*)] which is again con-



[ν(CO), cm^{-1}] of (*a*) $[Ru_6(CO)_{18}]^{2-}$, $Ru_6(CO)_{18}]^-$, (*d*) $[NMe_4][HRu_6(CO)_{18}]$ $[HOs_6(CO)_{18}]^-$ {$[N(PPh_3)_2]^+$ salts in tated, calibrant CO}

t $Ru(CO)_3$ groups, the slight ising from intermolecular inter- ttice. These spectra are signi- hat of $[HOs_6(CO)_{18}]^-$, but closely hat of the highly symmetrical Figure 4(*b*)]. Thus there is no

TABLE 1

ons in the carbonyl region

	Maxima (cm^{-1}) [b]
	034s, 2 029s, 2 014s, 1 994 (s+), 969m, br
	070vw, 2 012s, 1 984s, 1 947m, 798vw, 1 725w
	020s, 1 953vw
	001s, 1 981 (s+), 1 924w, 1 749w, br
	058s, 2 052s, 2 003w

h exception of $[HRu_3(CO)_{11}]^-$ which ibrant, central position 2 143 cm^{-1}.

roscopic evidence for an external $_{18}]^-$. For comparison, Ru–Ru tahedral ruthenium clusters are $_6(CO)_{17}C]$,[19] 2.853—2.956 Å for],[20] and 2.954(3) and 2.867(5) Å hydrogen-bridged and normal $(CO)_{18}$ respectively.[21]

Fourier-transform (F.t.) ^1H spectroscopy {$[N(PPh_3)_2]^+$ salt} over the usual range [22] τ 0—40 failed to show any metal-hydrogen resonances, but an extension of the range to between τ −40 and +100 revealed a singlet at τ −6.43 (CD_2Cl_2, 40 °C, 30-s pulse delay) (Figure 5)

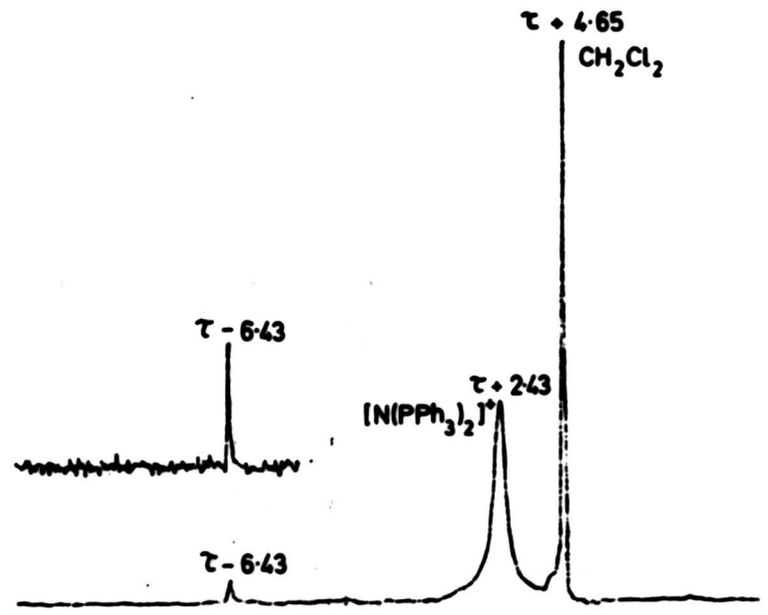


FIGURE 5 F.t. ^1H n.m.r. spectrum of $[N(PPh_3)_2][HRu_6(CO)_{18}]$ in CD_2Cl_2 at 40 °C (CH_2Cl_2 as internal calibrant)

together with the expected cation multiplet at τ 2.43; the occurrence of the hydride resonance at such a low-field position indicates a highly unusual environment for the H ligand. The anion $[HCo_6(CO)_{15}]^-$, which has also recently been shown to contain an interstitial H atom,[5] shows a ^1H n.m.r. signal with a similar downfield shift (τ −13.2), whereas the signals of the larger interstitial clusters $[HNi_{12}(CO)_{21}]^{3-}$ (τ 34.0),[6] $[H_2Ni_{12}(CO)_{21}]^{2-}$ (τ 28.0),[6] $[H_2Rh_{12}(CO)_{24}]^{3-}$ (τ 36.7),[4] and $[H_2Rh_{13}(CO)_{25}]^{2-}$ (τ 39.3) [4] are all found at the expected high-field position. The $[NMe_4]^+$ salt of $[HRu_6(CO)_{18}]^-$ shows a similar singlet at τ −6.49 ([$^2H_8$]thf, 40 °C, 30-s pulse delay), so the possibility that the H atom is associated with the $[N(PPh_3)_2]^+$ cation in (I) may be rejected. Furthermore, a variable-temperature ^{13}C (CO) n.m.r. study on $[HRu_6(CO)_{18}]^-$ (^{13}CO, *ca.* 40%) reveals a sharp singlet which remains unchanged over the temperature range 0 to −104 °C, but significantly no ^1H–^{13}C coupling could be detected. This rules out the possibility that the H ligand is located in the vicinity of the carbonyl ligands, as in $H_2Fe_2(CO)_{11}$,[15] which also shows a ^1H n.m.r. signal with a downfield shift. This location for the hydrogen had been suggested for $[HCo_6(CO)_{15}]^-$ before neutron-diffraction analysis showed [5] that, as in $[HRu_6(CO)_{18}]^-$, it was located at the centre of the metal octahedron. In contrast, the related $[HOs_6(CO)_{18}]^-$ shows a characteristic high-field resonance in its ^1H n.m.r. spectrum at τ 21.26 (CD_2Cl_2, 40 °C);[17] ^{13}C n.m.r. studies [17] and single-crystal *X*-ray analysis [18] are consistent with an external face-bridging hydride in this cluster.

Thus the H ligand in $[HRu_6(CO)_{18}]^-$ occupies a very unusual position as revealed by the ^1H n.m.r. studies, together with the combined evidence of the i.r. [ν(CO)] spectrum, variable-temperature ^{13}C n.m.r., and the *X*-ray analysis that shows it is not outside the metal polyhedron. The only explanation consistent with these facts is that the H atom occupies the centre of the Ru_6 octahedron.* This interstitial position for the hydride ligand explains the stability of $[HRu_6(CO)_{18}]^-$ towards base. Infrared spectroscopy revealed that neither excess of K[OH] in methanol nor excess of KH in thf could deprotonate the cluster, a large excess of base causing decomposition with loss of the carbonyl i.r. spectrum. In contrast, the H atom in $[HCo_6(CO)_{15}]^-$ may quite easily enter and leave the Co_6 octahedron as shown by the protonation of $[Co_6(CO)_{15}]^{2-}$, and the converse reaction of $[HCo_6(CO)_{15}]^-$ observed on simple dissolution in solvents such as water, methanol, or thf.[5] However, the H atom in $[HRu_6(CO)_{18}]^-$ can be made to leave the metal polyhedron by protonation to give $H_2Ru_6(CO)_{18}$ which has two external face-bridging hydride ligands. Although $[HOs_6(CO)_{18}]^-$ may be obtained by the dissociation of $H_2Os_6(CO)_{18}$ in basic solvents,[17] $H_2Ru_6(CO)_{18}$ does not deprotonate to give $[HRu_6(CO)_{18}]^-$, but reacts with K[OH] in methanol under mild conditions to give an unidentified species.

As the six $M(CO)_3$ groups are all equivalent, there is no apparent reason why the metal core in $[Os_6(CO)_{18}]^{2-}$ and $[HRu_6(CO)_{18}]^-$ should distort from regular O_h symmetry. However, exact O_h symmetry for the metal atoms in octahedral clusters is extremely rare; factors such as strongly asymmetric carbonyl bridges, as in $[Co_6(CO)_{14}]^{4-}$,[23] or the presence of an unpaired electron, as in $[Co_6(CO)_{14}C]^-$,[24] are thought to be responsible for the distortion in some clusters although $[Co_6(CO)_{14}]^{4-}$ is geometrically capable of exact overall O_h symmetry.

The structure of the dianion $[Ru_6(CO)_{18}]^{2-}$ is of interest. Since there are no H ligands present it might be expected to have the same metal geometry and carbonyl distribution as $[HRu_6(CO)_{18}]^-$ where the H atom is in the centre of the octahedron. However, the i.r. [ν(CO)] of $[Ru_6(CO)_{18}]^{2-}$ differs considerably from that of $[HRu_6(CO)_{18}]^-$ and $[Os_6(CO)_{18}]^{2-}$; in particular, bridging CO ligands are indicated, implying that it is not isostructural with these anions. This has been confirmed by an *X*-ray analysis of the $[PMePh_3]^+$ salt. Preliminary results show [2] that the metal core is a slightly distorted octahedron with Ru–Ru bond lengths in the range 2.80—2.89 Å, but as well as terminal there are two doubly bridging and two strongly asymmetric triply bridging carbonyl ligands bonded to the cluster.

This work establishes that the complexes $[H_2M_6(CO)_{18}]$, $[HM_6(CO)_{18}]^-$, and $[M_6(CO)_{18}]^{2-}$ (M = Ru or Os) are not isostructural. The preferred structure clearly depends on subtle quantitative factors, and simple electronic arguments [25] cannot be used to predict the structures of metal carbonyl clusters with certainty, especially if one or more hydride ligands are present.[18,26,27]

The versatility of some transition metals in giving

* *Note added in proof:* We have now confirmed this both by *X*-ray and neutron analyses of the $[AsPh_4]^+$ salt.

polynuclear carbonyl compounds seems to be enhanced if C atoms are inserted into the interstices of the metal polyhedron;[28] the unusual stability of such clusters has been attributed to the presence of additional bonds with the central atom.[24] Significantly, all of the known octahedral ruthenium complexes possess external bridging ligands except for $[HRu_6(CO)_{18}]^-$. The presence of an interstitial atom in this and other octahedral ruthenium complexes [19,20,29] suggests that the role of this atom may be to stabilize an otherwise unfavourable geometry for this metal. In contrast, no octahedral osmium carbonyls have been reported containing interstitial atoms. Recent work has also shown that atoms other than carbon and hydrogen may be successfully incorporated into the interstices of metal polyhedra, for example clusters containing interstitial S and P atoms have been synthesized.[30]

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen. However, the products were stable in air in the solid state although warming to even moderate temperatures (50—60 °C) sometimes initiated decomposition. Solvents were either AnalaR or redistilled, but the exclusion of all water was found to be unnecessary.

Infrared spectra were recorded on a Perkin-Elmer 257 instrument using carbon monoxide gas as calibrant (central position 2 143 cm^{-1}). N.m.r. spectra were obtained on a Varian XL-100 spectrometer.

Preparation of $[Ru_3(CO)_{12}]$.—The salt $RuCl_3 \cdot 3H_2O$ (5 g) in dry methanol (200 cm^3) was pressurised to 50 atm * with CO and heated at 125 °C for 8 h.[31] Orange-red crystals of the required product were filtered from the mother liquor and recrystallized from toluene. Yields were variable but normally between 85 and 95%. It was found to be beneficial to reuse the mother liquor several times, adding a weight of $RuCl_3 \cdot 3H_2O$ equivalent to the weight of $[Ru_3(CO)_{12}]$ removed.

Reaction of $[Ru_3(CO)_{12}]$ *with* $[Mn(CO)_5]^-$.—The compound $[Mn_2(CO)_{10}]$ (195 mg, 0.5 mmol) was reduced to the anion by sodium amalgam in dry thf (30 cm^3) (1 h) and the pale yellow solution added to $[Ru_3(CO)_{12}]$ (639 mg, 1.0 mmol) in dry thf (100 cm^3). The resulting deep red solution was refluxed for 4 h and the then dark brown solution acidified with a small excess of concentrated sulphuric acid (0.25 cm^3) (colour change brown to red). The salt $[N(PPh_3)_2]Cl$ (430 mg, 0.75 mmol) was added to the filtered solution in pure methanol (20 cm^3), and the product obtained by fractional crystallization. Evaporation by nitrogen flow gave first small amounts of a mixture of $H_4Ru_4(CO)_{12}$ and $[Ru_3(CO)_{12}]$. Continued evaporation to remove most of the thf and crystallization from CH_2Cl_2–MeOH then yielded the two major products: $[N(PPh_3)_2][H_3Ru_4(CO)_{12}]$, crystallized first, followed by $[N(PPh_3)_2][HRu_6(CO)_{18}]$. Further smaller amounts of the two anions were recovered and overall yields were $[N(PPh_3)_2][H_3Ru_4(CO)_{12}]$ (394 mg, 41%) and $[N(PPh_3)_2][HRu_6(CO)_{18}]$ (305 mg, 37%). All products were characterized by i.r. spectroscopy, and the two anions crystallized from CH_2Cl_2–MeOH.

Preparation of $[HRu_3(CO)_{11}]^-$.—Potassium hydroxide (11.2 mg, 0.2 mmol) in pure methanol (1 cm^3) was added to a magnetically stirred solution of $[Ru_3(CO)_{12}]$ (63.9 mg, 0.1 mmol) in thf (20 cm^3). The orange-red solution rapidly darkened to deep red and the reaction was complete in 6 h. The anion was characterized by i.r. spectroscopy.

Preparation of $[Ru_6(CO)_{18}]^{2-}$.—The compound $[Ru_3(CO)_{12}]$ (96 mg, 0.15 mmol) in thf (20 cm^3) was added dropwise over 30 min to excess of K[OH] (255 mg, 4.5 mmol) in water (0.1 cm^3) which was stirred under thf (2 cm^3). The resulting deep red-brown solution was stirred for 1.5 h to complete reaction prior to evaporation of the thf by nitrogen flow. The brown residue was taken up in pure methanol, the solution was filtered, and the dianion crystallized by the addition of $[N(PPh_3)_2]Cl$ (103 mg, 0.18 mmol). The product was characterized by microanalysis and i.r. spectroscopy. Yield 80% (Found: C, 49.5; H, 3.05; N, 1.25. Calc. for $C_{90}H_{60}N_2O_{18}P_4Ru_6$: C, 49.4; H, 2.75; N, 1.30%).

Preparation of $[HRu_6(CO)_{18}]^-$.—(*a*) *Acidification of* $[HRu_3(CO)_{11}]^-$. The anion $[HRu_3(CO)_{11}]^-$ was prepared as described above and to the reaction solution was added excess of concentrated H_2SO_4 (0.2 cm^3) in thf (2 cm^3). The salt $[NMe_4]Cl$ (7 mg, 0.06 mmol) in methanol was added. Careful evaporation produced $[Ru_3(CO)_{12}]$ (26 mg, 40% yield) and following complete evaporation and recrystallization from CH_2Cl_2–MeOH, $[NMe_4][HRu_6(CO)_{18}]$ in 50% yield. The monoanion was characterized by microanalysis and i.r. and ^1H n.m.r. spectroscopy (Found: C, 22.05; H, 1.45; N, 0.95. Calc. for $C_{22}H_{13}NO_{18}Ru_6$: C, 22.3; H, 1.10; N, 1.20%).

(*b*) *Acidification of* $[Ru_6(CO)_{18}]^{2-}$. The anion $[Ru_6(CO)_{18}]^{2-}$ was prepared as described above, but prior to isolation a slight excess of concentrated H_2SO_4 was added to the reaction solution until i.r. spectroscopy [ν(CO)] revealed the single-band spectrum of the monoanion. The salt $[N(PPh_3)_2]Cl$ (52 mg, 0.09 mmol) was added in MeOH and, following complete evaporation by nitrogen flow, the product was recrystallized from CH_2Cl_2–MeOH by slow evaporation techniques. The monoanion was characterized as described above, yield 80%.

Preparation of $H_2Ru_6(CO)_{18}$.—Protonation of both $[Ru_6(CO)_{18}]^{2-}$ and $[HRu_6(CO)_{18}]^-$ in non-polar solvents such as CH_2Cl_2 yields $H_2Ru_6(CO)_{18}$. In the case of the dianion the reaction is distinctly two-stage, $[HRu_6(CO)_{18}]^-$ being the product of the first stage. Thus $[N(PPh_3)_2]_2[Ru_6(CO)_{18}]$ (109 mg, 0.05 mmol) was stirred in CH_2Cl_2 (25 cm^3) to give a deep brown solution. Slow addition of excess of concentrated H_2SO_4 (0.5 cm^3) caused the colour to change first to deep red (the monoanion) and finally to purple. The solution was extracted with water, the organic portion dried over $Mg[SO_4]$, and evaporated by nitrogen flow to give $H_2Ru_6(CO)_{18}$, which was recrystallized from CH_2Cl_2 and characterized by i.r. spectroscopy, yield 90%.

Reaction of $[HRu_6(CO)_{18}]^-$ *with Base*.—(*a*) K[OH]. The salt $[N(PPh_3)_2][HRu_6(CO)_{18}]$ was treated with K[OH] in a solution i.r. cell which incorporated a reaction vessel. No reaction was observed in 24 h in either methanol or thf–water solvent systems even though large molar excesses of K[OH] were employed (>10 mol K[OH] per mol of cluster). The anion eventually decomposed when in vast excess of base, with complete loss of the carbonyl i.r. spectrum.

(*b*) KH *in* thf. The salt $[NMe_4][HRu_6(CO)_{18}]$ (47 mg, 0.04 mmol) was dissolved in redistilled dry thf and added to a reaction vessel which was attached to a solution i.r. cell. A thf dispersion of KH suspended in mineral oil [32] (22.7 mg in 0.1 cm^3 oil diluted in 10 cm^3 of thf) was added in small portions *via* a syringe and any reaction followed

* Throughout this paper: 1 atm = 101 325 Pa.

The orange-red solution rapidly
d the reaction was complete in
acterized by i.r. spectroscopy.
$CO)_{18}]^{2-}$.—The compound $[Ru_3$-
) in thf (20 cm^3) was added drop-
s of K[OH] (255 mg, 4.5 mmol) in
s stirred under thf (2 cm^3). The
solution was stirred for 1.5 h to
evaporation of the thf by nitrogen
was taken up in pure methanol,
and the dianion crystallized by
$_2]Cl$ (103 mg, 0.18 mmol). The
by microanalysis and i.r. spectros-
d: C, 49.5; H, 3.05; N, 1.25.
u_6: C, 49.4; H, 2.75; N, 1.30%).
$u_6(CO)_{18}]^-$.—(*a*) *Acidification of*
n $[HRu_3(CO)_{11}]^-$ was prepared as
the reaction solution was added
SO_4 (0.2 cm^3) in thf (2 cm^3). The
3 mmol) in methanol was added.
duced $[Ru_3(CO)_{12}]$ (26 mg, 40%
plete evaporation and recrystal-
OH, $[NMe_4][HRu_6(CO)_{18}]$ in 50%
as characterized by microanalysis
ectroscopy (Found: C, 22.05; H,
r $C_{22}H_{13}NO_{18}Ru_6$: C, 22.3; H,

$Ru_6(CO)_{18}]^{2-}$. The anion $[Ru_6$-
s described above, but prior to
f concentrated H_2SO_4 was added
until i.r. spectroscopy [ν(CO)]
pectrum of the monoanion. The
0.09 mmol) was added in MeOH
evaporation by nitrogen flow, the
ed from CH_2Cl_2–MeOH by slow
The monoanion was characterized
80%.
$CO)_{18}$.—Protonation of both $[Ru_6$-
$_{18}]^{2-}$ in non-polar solvents such as
$_{18}$. In the case of the dianion the
o-stage, $[HRu_6(CO)_{18}]^-$ being the
ge. Thus $[N(PPh_3)_2]_2[Ru_6(CO)_{18}]$
stirred in CH_2Cl_2 (25 cm^3) to give
Slow addition of excess of concen-
used the colour to change first to
n) and finally to purple. The
with water, the organic portion
evaporated by nitrogen flow to
was recrystallized from CH_2Cl_2
spectroscopy, yield 90%.
$O)_{18}]^-$ *with Base.*—(*a*) K[OH].
$(CO)_{18}]$ was treated with K[OH] in
incorporated a reaction vessel.
d in 24 h in either methanol or
even though large molar excesses
d (>10 mol K[OH] per mol of
tually decomposed when in vast
mplete loss of the carbonyl i.r.

alt $[NMe_4][HRu_6(CO)_{18}]$ (47 mg,
in redistilled dry thf and added
h was attached to a solution i.r.
KH suspended in mineral oil [33]
luted in 10 cm^3 of thf) was added
yringe and any reaction followed

by i.r. spectroscopy. After 18 h and the addition of KH (0.1 mmol), no reaction had occurred. Subsequent addition of neat KH (0.2 mmol) in mineral oil eventually caused decomposition of the cluster and loss of the carbonyl i.r. spectrum.

X-Ray Crystallographic Determination of $[HRu_6(CO)_{18}]^-$.—Recrystallization by slow diffusion techniques from CH_2Cl_2–cyclohexane gave two crystalline modifications, (I) and (II), of $[N(PPh_3)_2][HRu_6(CO)_{18}]$ which from i.r. spectroscopy appeared to be chemically identical. They pose an unusual crystallographic problem, having different space groups with two and three formula units respectively per equivalent position.

Crystal data. (I). Triclinic, space group $P\bar{1}$, a = 18.083(4), b = 19.101(4), c = 19.238(5) Å, α = 117.70(4), β = 78.13(2), γ = 97.05(2)°, U = 5 767 Å^3, Z = 4, D_c = 1.90 g cm^{-3}, $F(000)$ = 3 196, θ range 3—25° in one hemisphere, $I/\sigma(I) \geqslant 3.0$, R = 0.068 1 for 9 165 reflections. The primitive cell had a large α angle, so it was converted into a centred cell to avoid correlations during refinement [$C\bar{1}$ cell: a = 19.248(4), b = 33.912(8), c = 18.081(4) Å, α = 91.23(2), β = 101.86(3), γ = 92.53(2)°].

(II). Monoclinic, space group $P2_1/n$, a = 33.82(8), b = 52.55(10), c = 9.832(2) Å, β = 92.66(2)°, U = 17 452 Å^3, Z = 12, D_c = 1.88 g cm^{-3}, $F(000)$ = 9 588, θ range 3—

TABLE 2

Fractional atomic co-ordinates (× 10^4) for (I) ($C\bar{1}$ cell)

Atom *	x	y	z
(*a*) Cluster (1)			
Ru(1)	3 947(1)	922(1)	2 787(1)
Ru(2)	4 403(1)	1 750(1)	2 679(1)
Ru(3)	2 940(1)	1 527(1)	2 544(1)
Ru(4)	4 515(1)	1 169(1)	1 531(1)
Ru(5)	2 997(1)	962(1)	1 348(1)
Ru(6)	3 466(1)	1 754(1)	1 202(1)
C(11)	4 130(9)	433(6)	2 410(10)
O(11)	4 258(7)	129(4)	2 212(7)
C(12)	3 318(10)	748(5)	3 388(10)
O(12)	2 966(7)	612(4)	3 775(8)
C(13)	4 725(11)	898(6)	3 556(12)
O(13)	5 204(9)	849(5)	4 043(9)
C(21)	4 109(10)	2 250(6)	2 832(10)
O(21)	3 963(7)	2 558(4)	3 003(8)
C(22)	4 812(10)	1 718(5)	3 687(11)
O(22)	5 086(7)	1 730(4)	4 323(8)
C(23)	5 271(9)	1 914(5)	2 486(10)
O(23)	5 806(7)	2 050(4)	2 384(8)
C(31)	2 092(9)	1 232(5)	2 573(9)
O(31)	1 571(7)	1 067(4)	2 635(7)
C(32)	3 207(10)	1 608(5)	3 581(11)
O(32)	3 313(7)	1 681(4)	4 217(8)
C(33)	2 516(9)	2 007(5)	2 398(9)
O(33)	2 235(7)	2 312(4)	2 381(7)
C(41)	4 482(11)	743(6)	878(12)
O(41)	4 535(8)	473(5)	474(9)
C(42)	4 998(10)	1 487(6)	969(11)
O(42)	5 361(7)	1 678(4)	644(7)
C(43)	5 323(10)	990(6)	2 176(11)
O(43)	5 835(7)	882(4)	2 516(7)
C(51)	2 991(10)	680(6)	470(11)
O(51)	2 913(8)	513(4)	−125(9)
C(52)	2 141(10)	1 184(5)	935(10)
O(52)	1 584(6)	1 292(3)	644(7)
C(53)	2 643(10)	520(6)	1 775(11)
O(53)	2 378(7)	242(4)	1 964(8)
C(61)	4 068(9)	2 193(5)	1 169(10)
O(61)	4 407(7)	2 467(4)	1 071(7)
C(62)	3 491(9)	1 558(5)	253(11)
O(62)	3 468(7)	1 472(4)	−384(8)
C(63)	2 658(10)	2 029(5)	878(10)
O(63)	2 149(7)	2 203(4)	618(8)

TABLE 2 (*Continued*)

Atom *	x	y	z
(*b*) Cluster (2A)			
Ru(1A)	7 168(1)	3 965(1)	3 096(1)
Ru(2A)	6 954(1)	3 280(1)	4 000(1)
Ru(3C)	5 813(1)	3 790(1)	3 498(1)
Ru(4C)	7 874(1)	3 921(1)	4 614(1)
Ru(5A)	6 707(1)	4 461(1)	4 190(1)
Ru(6A)	6 548(1)	3 802(1)	5 090(1)
C(11A)	7 777	4 391	3 088
O(11C)	8 156(10)	4 658(5)	3 100(11)
C(12A)	6 602	4 063	2 219
O(12C)	6 232(10)	4 132(5)	1 661(11)
C(13A)	7 827	3 772	2 575
O(13C)	8 240(10)	3 645(5)	2 246(11)
C(21A)	6 214	2 894	3 902
O(21C)	5 747(10)	2 654(5)	3 844(10)
C(22A)	7 100	3 005	3 176
O(22C)	7 199(10)	2 838(5)	2 646(11)
C(23A)	7 630	2 998	4 514
O(23C)	8 056(10)	2 818(5)	4 836(11)
C(31C)	5 215(11)	4 163(6)	3 062(12)
O(31C)	4 821(9)	4 379(5)	2 748(9)
O(32C)	5 560(13)	3 453(8)	2 689(15)
O(32C)	5 340(10)	3 209(6)	2 200(12)
C(33C)	5 146(11)	3 559(6)	3 991(12)
O(33C)	4 700(8)	3 420(5)	4 231(9)
C(41C)	8 427(9)	4 388(5)	4 868(10)
O(41C)	8 808(8)	4 665(5)	5 007(9)
C(42C)	8 186(10)	3 696(6)	5 544(11)
O(42C)	8 434(7)	3 548(4)	6 099(8)
C(43C)	8 536(10)	3 680(6)	4 161(11)
O(43C)	8 982(7)	3 513(4)	3 973(8)
C(51A)	7 192	4 856	4 738
O(51C)	7 499(10)	5 109(5)	5 085(11)
C(52A)	5 976	4 614	4 527
O(52C)	5 518(10)	4 703(5)	4 758(11)
C(53A)	6 357	4 796	3 360
O(53C)	6 198(10)	5 010(5)	2 832(10)
C(61A)	6 530	3 316	5 531
O(61C)	6 518(10)	3 018(5)	5 802(11)
C(62A)	7 086	4 117	5 898
O(62C)	7 440(10)	4 323(5)	6 389(11)
C(63A)	5 820	3 826	5 508
O(63C)	5 347(10)	3 848(5)	5 779(11)
(*c*) Cluster (2B)			
Ru(1B)	6 506(2)	4 042(1)	4 954(2)
Ru(2B)	6 779(2)	3 277(1)	4 332(2)
Ru(5B)	6 929(2)	4 425(1)	3 715(2)
Ru(6B)	7 138(2)	3 679(1)	3 063(2)
C(11B)	5 899	4 452	4 837
C(12B)	7 070	4 210	5 847
C(13B)	5 804	3 918	5 456
C(21B)	7 563	2 997	4 642
C(22B)	6 619	3 114	5 239
C(23B)	6 147	2 893	4 030
C(51B)	6 473	4 782	3 177
C(52B)	7 685	4 568	3 327
C(53B)	7 277	4 842	4 555
C(61B)	7 171	3 159	2 815
C(62B)	6 591	3 953	2 207
C(63B)	7 816	3 663	2 562
(*d*) Cations			
P(1)	952(2)	3 320(1)	3 149(2)
P(2)	2 233(2)	3 771(1)	2 930(2)
N(1)	1 717(6)	3 403(4)	2 984(7)
C(111)	989(6)	2 936(3)	3 828(6)
C(112)	429(6)	2 854(3)	4 193(6)
C(113)	458(6)	2 537(3)	4 676(6)
C(114)	1 046(6)	2 302(3)	4 794(6)
C(115)	1 606(6)	2 385(3)	4 429(6)
C(116)	1 577(6)	2 702(3)	3 946(6)
C(121)	556(6)	3 741(2)	3 485(6)
C(122)	804(6)	3 879(2)	4 229(6)
C(123)	579(6)	4 236(2)	4 472(6)
C(124)	107(6)	4 455(2)	3 971(6)
C(125)	−141(6)	4 316(2)	3 227(6)

TABLE 2 (*Continued*)

Atom *	*x*	*y*	*z*
C(126)	84(6)	3 959(2)	2 984(6)
C(131)	358(5)	3 129(3)	2 313(5)
C(132)	−362(5)	3 054(3)	2 305(5)
C(133)	−815(5)	2 896(3)	1 653(5)
C(134)	−548(5)	2 813(3)	1 009(5)
C(135)	173(5)	2 887(3)	1 017(5)
C(136)	625(5)	3 045(3)	1 669(5)
C(211)	1 784(5)	4 213(3)	2 608(6)
C(212)	1 431(5)	4 223(3)	1 854(6)
C(213)	1 053(5)	4 551(3)	1 592(6)
C(214)	1 026(5)	4 869(3)	2 085(6)
C(215)	1 379(5)	4 860(3)	2 840(6)
C(216)	1 757(5)	4 532(3)	3 101(6)
C(221)	2 841(6)	3 882(3)	3 814(5)
C(222)	3 396(6)	4 167(3)	3 867(5)
C(223)	3 824(6)	4 273(3)	4 570(5)
C(224)	3 696(6)	4 094(3)	5 220(5)
C(225)	3 141(6)	3 810(3)	5 167(5)
C(226)	2 713(6)	3 704(3)	4 464(5)
C(231)	2 745(6)	3 647(4)	2 251(6)
C(232)	3 048(6)	3 938(4)	1 865(6)
C(233)	3 445(6)	3 830(4)	1 334(6)
C(234)	3 538(6)	3 432(4)	1 191(6)
C(235)	3 235(6)	3 142(4)	1 577(6)
C(236)	2 838(6)	3 249(4)	2 108(6)
P(3)	8 054(2)	1 309(1)	393(2)
P(4)	9 314(2)	900(1)	1 157(2)
N(2)	8 663(7)	1 000(4)	530(7)
C(311)	7 265(5)	1 061(3)	−144(6)
C(312)	7 323(5)	708(3)	−534(6)
C(313)	6 717(5)	514(3)	−971(6)
C(314)	6 054(5)	673(3)	−1 018(6)
C(315)	5 996(5)	1 026(3)	−628(6)
C(316)	6 601(5)	1 219(3)	−191(6)
C(321)	7 843(6)	1 517(3)	1 234(5)
C(322)	8 173(6)	1 875(3)	1 545(5)
C(323)	8 030(6)	2 028(3)	2 217(5)
C(324)	7 558(6)	1 823(3)	2 580(5)
C(325)	7 229(6)	1 465(3)	2 269(5)
C(326)	7 372(6)	1 312(3)	1 597(5)
C(331)	8 290(6)	1 712(3)	−147(6)
C(332)	8 971(6)	1 750(3)	−298(6)
C(333)	9 159(6)	2 071(3)	−700(6)
C(334)	8 666(6)	2 353(3)	−950(6)
C(335)	7 984(6)	2 315(3)	−799(6)
C(336)	7 796(6)	1 995(3)	−397(6)
C(411)	9 924(5)	662(3)	684(6)
C(412)	10 487(5)	454(3)	1 077(6)
C(413)	10 950(5)	275(3)	688(6)
C(414)	10 850(5)	304(3)	−95(6)
C(415)	10 288(5)	511(3)	−489(6)
C(416)	9 825(5)	691(3)	−99(6)
C(421)	9 779(6)	1 323(3)	1 687(6)
C(422)	9 627(6)	1 449(3)	2 373(6)
C(423)	9 966(6)	1 793(3)	2 741(6)
C(424)	10 456(6)	2 010(3)	2 423(6)
C(425)	10 608(6)	1 884(3)	1 736(6)
C(426)	10 269(6)	1 540(3)	1 368(6)
C(431)	9 045(8)	570(4)	1 814(7)
C(432)	9 489(8)	507(4)	2 511(7)
C(433)	9 248(8)	268(4)	3 034(7)
C(434)	8 563(8)	92(4)	2 860(7)
C(435)	8 119(8)	155(4)	2 164(7)
C(436)	8 360(8)	394(4)	1 641(7)

* Occupancies of atoms labelled (A) in the disordered sites were coupled in the least-squares refinement to a free variable p_A which refined to 0.584 0(11). The occupancy of atoms labelled (B) was set to $1 - p_A$. The rest of the atoms including those labelled (C) [which are common to clusters (2A) and (2B)] are of unit occupancy. Disordered carbon atoms [labelled (A) and (B)] were placed in fixed positions such that d(M–C)/d(M–O) = 0.615 and M–C–O 180°. These positions were recalculated if large shifts were observed for the oxygen atoms.

15° in one quadrant only, $I/\sigma(I) \geqslant 3.0$, $R = 0.23$ (Ru only) for 1 485 reflections.

Data were collected using a Philips PW1100 four-circle diffractometer and graphite-monochromatized Mo-K_α radiation [λ(Mo-K_α) = 0.710 69 Å]. A θ—2θ scan mode was used and weak reflections which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on the first scan were not further examined. (I_t = the count rate at the top of the reflection peak and I_b = the mean count rate of two preliminary 5-s background measurements on either side of the peak.) Of the remaining reflections, those for which the total intensity recorded in the first scan of the peak (I_1) was <100 were scanned twice to increase their accuracy. A constant scan speed of 0.05° s^{-1} and scan widths of 0.7° (I) and 0.54° (II) were used, with a background measuring time proportional to I_b/I_1. Three standard reflections were measured every 5 h during data collection and showed no significant variations in intensity.

The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer.[33] The variance of the intensity, I, was calculated as the sum of the variance due to counting statistics and $(0.04I)^2$, where the term in I^2 was introduced to allow for other sources of error.[34] I and $\sigma(I)$ were corrected for Lorentz and polarization factors; no absorption corrections were applied (μ = 14.95 cm^{-1}).

TABLE 3

Selected interatomic distances (Å) for (I) [a] with estimated standard deviations in parentheses

(*a*) Metal–metal bonds

	[$HRu_3(CO)_{13}$] Cluster (1)	Cluster (2A)	Cluster (2B)	[$Os_3(CO)_{12}$]$^{2-}$
M(1)–M(2)	2.927(2)	2.931(4)	2.917(5)	2.884(3)
M(3)–M(6)	2.921(2)	2.934(3)	2.951(3)	
M(4)–M(5)	2.924(2)	2.950(3)	2.936(4)	
M(1)–M(4)	2.841(2)	2.812(3)	2.793(3)	2.816(3)
M(2)–M(3)	2.843(2)	2.867(3)	2.928(4)	
M(5)–M(6)	2.832(2)	2.835(4)	2.847(5)	
M(1)–M(3)	2.863(2)	2.890(3)	2.869(4)	2.876(2)
M(1)–M(5)	2.865(2)	2.872(4)	2.856(5)	
M(2)–M(4)	2.878(2)	2.800(3)	2.829(4)	
M(2)–M(6)	2.900(2)	2.870(4)	2.883(5)	
M(3)–M(5)	2.881(2)	2.890(3)	2.838(3)	
M(4)–M(6)	2.876(2)	2.871(3)	2.858(4)	

(*b*) Metal–carbon distances [b]

	Cluster (1)	Cluster (2)
Ru(1)–C(11)	1.856(19)	
Ru(1)–C(12)	1.872(20)	
Ru(1)–C(13)	1.828(19)	
Ru(2)–C(21)	1.843(19)	
Ru(2)–C(22)	1.838(18)	
Ru(2)–C(23)	1.841(19)	
Ru(3)–C(31)	1.886(17)	1.830(21)
Ru(3)–C(32)	1.850(19)	1.808(26)
Ru(3)–C(33)	1.852(17)	1.861(23)
Ru(4)–C(41)	1.838(21)	1.863(17)
Ru(4)–C(42)	1.846(20)	1.858(20)
Ru(4)–C(43)	1.875(18)	1.859(21)
Ru(5)–C(51)	1.833(21)	
Ru(5)–C(52)	1.863(18)	
Ru(5)–C(53)	1.865(20)	
Ru(6)–C(61)	1.853(17)	
Ru(6)–C(62)	1.838(19)	
Ru(6)–C(63)	1.846(18)	
Mean Ru–C	1.850(17) [c]	

, $I/\sigma(I) \geqslant 3.0$, $R = 0.23$ (Ru only)

sing a Philips PW1100 four-circle
ite-monochromatized Mo-K_α radi-
) 69 Å]. A θ—2θ scan mode was
s which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on
rther examined. (I_t = the count
eflection peak and I_b = the mean
nary 5-s background measurements
k.) Of the remaining reflections,
intensity recorded in the first scan
00 were scanned twice to increase
ant scan speed of 0.05° s^{-1} and scan
.54° (II) were used, with a back-
proportional to I_b/I_t. Three stan-
neasured every 5 h during data
significant variations in intensity.
ies were calculated from the peak
ements using a program written
ctometer.[33] The variance of the
ed as the sum of the variance due
$(0.04I)^2$, where the term in I^2 was
other sources of error.[34] I and
Lorentz and polarization factors;
were applied ($\mu = 14.95$ cm^{-1}).

TABLE 3

tances (Å) for (I) [a] with estimated
viations in parentheses

$[HRu_6(CO)_{18}]$		
Cluster (2A)	Cluster (2B)	$[Os_6(CO)_{18}]^{2-}$
2.931(4)	2.917(5)	2.884(3)
2.934(3)	2.951(3)	
2.950(3)	2.936(4)	
2.812(3)	2.793(3)	2.816(3)
2.867(3)	2.928(4)	
2.835(4)	2.847(5)	
2.890(3)	2.869(4)	2.876(2)
2.872(4)	2.856(5)	
2.800(3)	2.829(4)	
2.870(4)	2.883(5)	
2.890(3)	2.838(3)	
2.871(3)	2.858(4)	

es [b]

Cluster (1)	Cluster (2)
1.856(19)	
1.872(20)	
1.828(19)	
1.843(19)	
1.838(18)	
1.841(19)	
1.886(17)	1.830(21)
1.850(19)	1.808(26)
1.852(17)	1.861(23)
1.838(21)	1.863(17)
1.846(20)	1.858(20)
1.875(18)	1.858(21)
1.833(21)	
1.863(18)	
1.865(20)	
1.853(17)	
1.838(19)	
1.846(18)	
1.850(17) [c]	

TABLE 3 (*Continued*)

(*c*) Carbon–oxygen distances [b]

	Cluster (1)	Cluster (2)
C(11)–O(11)	1.136(24)	
C(12)–O(12)	1.158(25)	
C(13)–O(13)	1.157(24)	
C(21)–O(21)	1.146(24)	
C(22)–O(22)	1.162(22)	
C(23)–O(23)	1.161(23)	
C(31)–O(31)	1.154(21)	1.149(26)
C(32)–O(32)	1.145(24)	1.195(32)
C(33)–O(33)	1.188(22)	1.129(28)
C(41)–O(41)	1.180(27)	1.156(23)
C(42)–O(42)	1.181(25)	1.155(24)
C(43)–O(43)	1.129(22)	1.154(25)
C(51)–O(51)	1.183(26)	
C(52)–O(52)	1.170(21)	
C(53)–O(53)	1.144(25)	
C(61)–O(61)	1.151(21)	
C(62)–O(62)	1.173(24)	
C(63)–O(63)	1.184(23)	
Mean C–O	1.160(18) [c]	

[a] In Figure 3(*b*) cluster (2B) has been rotated about the pseudo-two-fold axis to obtain a view that corresponds to those of clusters (1) and (2A) in Figures 2(*a*) and 3(*a*) respectively. Under this operation Ru(3C) and its associated carbonyl ligands exchange position with Ru(4C) and its carbonyl groups, but in order to allow ease of comparison of their geometries the bond lengths and angles for cluster (2B) have been listed next to those in clusters (1) and (2A) to which they are equivalent. The correct labels for cluster (2B) may be obtained by simply interchanging those involving M(3) and M(4). For the other clusters, the labels given are correct. [b] See footnote to Table 2. [c] Estimated standard deviations of mean bond lengths are calculated from the equation $\sigma = \{[\sum_i^n (x_i - \bar{x})^2]/(n-1)\}^{\frac{1}{2}}$ where x_i is the ith bond length and $\bar{x}$ is the mean of n equivalent bond lengths.

Structure solution and refinement. (*a*) *Triclinic modification* (I). The 12 ruthenium atoms of the asymmetric unit were located by multisolution Σ_2 sign expansion as discrete Ru_6 octahedra. Least-squares refinement of their positional and isotropic thermal parameters gave R 0.28. Four of these Ru atoms within one octahedron showed relatively large isotropic thermal parameters, indicative of disorder. Subsequent difference-Fourier syntheses revealed the positions of the two independent $[N(PPh_3)_2]^+$ cations and all the carbonyl ligands associated with cluster 1, but only six carbonyl groups of cluster 2 could be conclusively identified, although all the oxygen atoms appeared to be present.

At this stage a difference-Fourier map in the region of the apparently disordered Ru atoms was computed, these atoms being omitted from the structure-factor calculations. This revealed that each peak, originally assigned as ruthenium sites of full occupancy, could be resolved into two components *ca.* 1 Å apart. Thus the four most intense independent maxima were assigned as Ru(1A), Ru(2A), Ru(5A), and Ru(6A), the remaining four high peaks as Ru(1B), Ru(2B), Ru(5B), and Ru(6B). The isotropic thermal parameter for each of these disordered atoms was initially constrained to be equal to the same free variable; refinement of their population parameters yielded values in the range 0.58—0.60 for the ' A ' set and 0.40—0.42 for the ' B ' set of atoms. Subsequent difference-Fourier syntheses utilizing this model revealed suitable maxima for the missing disordered carbon atoms of the second cluster. The component pairs of these carbon atoms were too close to one another to be refined independently, so they were placed in calculated positions, but their atomic co-ordinates were recalculated after each cycle of refinement if large shifts were observed for the attached oxygen atoms.

Apparently the disorder of the second cluster arises from two different orientations, (2A) and (2B) in the lattice, having occupancies of *ca.* 0.6 and 0.4 respectively. The alternative orientations (2A) and (2B) are approximately

TABLE 4

Selected intramolecular angles (°) for (I) [a] with estimated standard deviations in parentheses

(*a*) Ru–C–O Angles

	Cluster (1)	Cluster (2)
Ru(1)–C(11)–O(11)	176.8(16)	
Ru(1)–C(12)–O(12)	174.0(16)	
Ru(1)–C(13)–O(13)	174.3(18)	
Ru(2)–C(21)–O(21)	173.0(16)	
Ru(2)–C(22)–O(22)	174.4(17)	
Ru(2)–C(23)–O(23)	174.0(16)	
Ru(3)–C(31)–O(31)	175.2(15)	175.2(17)
Ru(3)–C(32)–O(32)	172.9(17)	172.4(24)
Ru(3)–C(33)–O(33)	173.1(15)	173.9(17)
Ru(4)–C(41)–O(41)	173.1(18)	175.3(17)
Ru(4)–C(42)–O(42)	174.1(15)	173.9(18)
Ru(4)–C(43)–O(43)	174.5(19)	171.0(16)
Ru(5)–C(51)–O(51)	172.5(17)	
Ru(5)–C(52)–O(52)	174.1(14)	
Ru(5)–C(53)–O(53)	172.7(15)	
Ru(6)–C(61)–O(61)	172.8(14)	
Ru(6)–C(62)–O(62)	172.2(15)	
Ru(6)–C(63)–O(63)	175.2(17)	
Mean Ru–C–O	173.8(13) [b]	

(*b*) Angles between metal atoms

	Cluster (1)	Cluster (2A)	Cluster (2B)
Ru(2)–Ru(1)–Ru(3)	58.8(1)	59.0(1)	60.8(1)
Ru(2)–Ru(1)–Ru(4)	59.8(1)	58.3(1)	59.3(1)
Ru(2)–Ru(1)–Ru(5)	89.6(1)	89.1(1)	90.2(1)
Ru(3)–Ru(1)–Ru(4)	90.9(1)	90.9(1)	91.7(1)
Ru(3)–Ru(1)–Ru(5)	60.4(1)	60.2(1)	59.4(1)
Ru(4)–Ru(1)–Ru(5)	61.7(1)	62.5(1)	62.6(1)
Ru(1)–Ru(2)–Ru(3)	59.5(1)	59.8(1)	58.8(1)
Ru(1)–Ru(2)–Ru(4)	58.6(1)	58.7(1)	58.2(1)
Ru(1)–Ru(2)–Ru(6)	88.4(1)	89.0(1)	88.4(1)
Ru(3)–Ru(2)–Ru(4)	90.6(1)	91.6(1)	89.8(1)
Ru(3)–Ru(2)–Ru(6)	61.1(1)	61.5(1)	61.0(1)
Ru(4)–Ru(2)–Ru(6)	59.7(1)	60.8(1)	60.0(1)
Ru(1)–Ru(3)–Ru(2)	61.7(1)	61.2(1)	60.4(1)
Ru(1)–Ru(3)–Ru(5)	59.8(1)	59.6(1)	60.1(1)
Ru(1)–Ru(3)–Ru(6)	89.3(1)	88.6(1)	88.0(1)
Ru(2)–Ru(3)–Ru(5)	91.0(1)	90.0(1)	90.3(1)
Ru(2)–Ru(3)–Ru(6)	60.4(1)	59.3(1)	58.7(1)
Ru(5)–Ru(3)–Ru(6)	58.4(1)	58.3(1)	58.9(1)
Ru(1)–Ru(4)–Ru(2)	61.6(1)	63.0(1)	62.5(1)
Ru(1)–Ru(4)–Ru(5)	59.6(1)	59.7(1)	59.7(1)
Ru(1)–Ru(4)–Ru(6)	90.6(1)	91.4(1)	91.4(1)
Ru(2)–Ru(4)–Ru(5)	89.4(1)	90.1(1)	90.3(1)
Ru(2)–Ru(4)–Ru(6)	60.5(1)	60.8(1)	60.9(1)
Ru(5)–Ru(4)–Ru(6)	58.4(1)	58.3(1)	58.9(1)
Ru(1)–Ru(5)–Ru(3)	59.8(1)	60.2(1)	60.5(1)
Ru(1)–Ru(5)–Ru(4)	58.8(1)	57.7(1)	57.6(1)
Ru(1)–Ru(5)–Ru(6)	91.0(1)	90.9(1)	90.3(1)
Ru(3)–Ru(5)–Ru(4)	88.9(1)	88.2(1)	89.5(1)
Ru(3)–Ru(5)–Ru(6)	61.5(1)	61.6(1)	62.5(1)
Ru(4)–Ru(5)–Ru(6)	59.9(1)	59.5(1)	59.2(1)
Ru(2)–Ru(6)–Ru(3)	58.5(1)	59.2(1)	60.2(1)
Ru(2)–Ru(6)–Ru(4)	59.8(1)	58.4(1)	59.0(1)
Ru(2)–Ru(6)–Ru(5)	90.8(1)	91.0(1)	91.0(1)
Ru(3)–Ru(6)–Ru(4)	89.1(1)	88.9(1)	88.8(1)
Ru(3)–Ru(6)–Ru(5)	60.1(1)	60.1(1)	58.6(1)
Ru(4)–Ru(6)–Ru(5)	61.6(1)	62.2(1)	61.9(1)

TABLE 4 (*Continued*)

(*c*) Carbon–metal–metal angles

	Cluster (1)	$[Os_6(CO)_{18}]^{2-}$
C(11)–M(1)–M(2)	137.8(6)	147.5
C(11)–M(1)–M(3)	142.0(5)	141.8
C(11)–M(1)–M(4)	80.6(6)	90.1
C(11)–M(1)–M(5)	83.4(5)	87.5
C(12)–M(1)–M(2)	124.2(6)	122.4
C(12)–M(1)–M(3)	79.4(6)	83.5
C(12)–M(1)–M(4)	162.5(5)	169.3
C(12)–M(1)–M(5)	100.8(5)	108.4
C(13)–M(1)–M(2)	86.2(6)	81.2
C(13)–M(1)–M(3)	127.7(7)	126.3
C(13)–M(1)–M(4)	104.3(7)	99.4
C(13)–M(1)–M(5)	165.3(7)	160.2
C(21)–M(2)–M(1)	140.0(6)	147.5
C(21)–M(2)–M(3)	83.7(6)	90.1
C(21)–M(2)–M(4)	143.5(6)	141.8
C(21)–M(2)–M(6)	86.5(5)	87.5
C(22)–M(2)–M(1)	85.0(6)	81.2
C(22)–M(2)–M(3)	106.0(6)	99.4
C(22)–M(2)–M(4)	124.5(6)	126.3
C(22)–M(2)–M(6)	167.2(6)	160.2
C(23)–M(2)–M(1)	124.1(5)	122.4
C(23)–M(2)–M(3)	164.2(5)	169.3
C(23)–M(2)–M(4)	80.5(5)	83.5
C(23)–M(2)–M(6)	103.1(5)	108.4
C(31)–M(3)–M(1)	100.8(5)	108.4
C(31)–M(3)–M(2)	162.1(5)	169.3
C(31)–M(3)–M(5)	82.4(5)	83.5
C(31)–M(3)–M(6)	127.1(5)	122.4
C(32)–M(3)–M(1)	83.8(6)	87.5
C(32)–M(3)–M(2)	79.9(6)	90.1
C(32)–M(3)–M(5)	142.0(6)	141.8
C(32)–M(3)–M(6)	137.7(6)	147.5
C(33)–M(3)–M(1)	164.0(5)	160.2
C(33)–M(3)–M(2)	102.3(5)	99.4
C(33)–M(3)–M(5)	124.3(5)	126.3
C(33)–M(3)–M(6)	81.9(6)	81.2
C(41)–M(4)–M(1)	108.5(7)	99.4
C(41)–M(4)–M(2)	169.8(7)	160.2
C(41)–M(4)–M(5)	82.9(6)	81.2
C(41)–M(4)–M(6)	119.8(6)	126.3
C(42)–M(4)–M(1)	158.3(6)	169.3
C(42)–M(4)–M(2)	97.6(6)	108.4
C(42)–M(4)–M(5)	130.8(5)	122.4
C(42)–M(4)–M(6)	83.2(6)	83.5
C(43)–M(4)–M(1)	78.4(7)	90.1
C(43)–M(4)–M(2)	88.8(6)	87.5
C(43)–M(4)–M(5)	132.6(6)	147.5
C(43)–M(4)–M(6)	148.8(6)	141.8
C(51)–M(5)–M(1)	128.9(6)	126.3
C(51)–M(5)–M(3)	169.2(6)	160.2
C(51)–M(5)–M(4)	91.3(6)	81.2
C(51)–M(5)–M(6)	109.5(6)	99.4
C(52)–M(5)–M(1)	138.7(6)	141.8
C(52)–M(5)–M(3)	80.7(5)	87.5
C(52)–M(5)–M(4)	137.5(6)	147.5
C(52)–M(5)–M(6)	79.2(5)	90.1
C(53)–M(5)–M(1)	76.6(5)	83.5
C(53)–M(5)–M(3)	97.7(6)	108.4
C(53)–M(5)–M(4)	123.3(6)	122.4
C(53)–M(5)–M(6)	159.2(6)	169.3
C(61)–M(6)–M(2)	78.3(5)	83.5
C(61)–M(6)–M(3)	124.0(5)	122.4
C(61)–M(6)–M(4)	98.8(5)	108.4
C(61)–M(6)–M(5)	160.4(5)	169.3
C(62)–M(6)–M(2)	135.3(5)	141.8
C(62)–M(6)–M(3)	139.9(6)	147.5
C(62)–M(6)–M(4)	78.0(5)	87.5
C(62)–M(6)–M(5)	80.6(6)	90.1
C(63)–M(6)–M(2)	130.0(6)	126.3
C(63)–M(6)–M(3)	89.8(6)	81.2
C(63)–M(6)–M(4)	166.3(5)	160.2
C(63)–M(6)–M(5)	106.2(6)	99.4

TABLE 4 (*Continued*)

(*d*) OC–M–CO Angles

	Cluster (1)	$[Os_6(CO)_{18}]^{2-}$
C(11)–M(1)–C(12)	98.0(8)	89.1
C(11)–M(1)–C(13)	90.2(8)	91.2
C(12)–M(1)–C(13)	93.1(9)	91.3
C(21)–M(2)–C(22)	91.5(8)	91.2
C(21)–M(2)–C(23)	95.7(8)	89.1
C(22)–M(2)–C(23)	89.7(8)	91.3
C(31)–M(3)–C(32)	95.1(8)	89.1
C(31)–M(3)–C(33)	95.2(7)	91.3
C(32)–M(3)–C(33)	93.7(8)	91.2
C(41)–M(4)–C(42)	92.5(9)	91.3
C(41)–M(4)–C(43)	91.4(8)	91.2
C(42)–M(4)–C(43)	96.3(8)	89.1
C(51)–M(5)–C(52)	91.9(8)	91.2
C(51)–M(5)–C(53)	91.2(9)	91.3
C(52)–M(5)–C(53)	99.0(8)	89.1
C(61)–M(6)–C(62)	95.7(8)	89.1
C(61)–M(6)–C(63)	93.2(8)	91.3
C(62)–M(6)–C(63)	94.3(8)	91.2

[a,b] See footnotes *a* and *c* in Table 3.

related by a non-crystallographic two-fold axis which lies in the plane of the disordered atoms, and passes through the midpoints of Ru(2A) · · · Ru(2B) and Ru(5A) · · · Ru(5B) (Figure 1). Under this operation Ru(3C) and its associated carbonyl ligands would exchange position with Ru(4C) and its carbonyl groups, therefore the sites of these atoms are of full occupancy. Significantly, the remaining oxygen atoms also coincide in position for the two orientations, indicating that the packing is effectively determined by these peripheral oxygen atoms and is independent of the arrangement of the internal atoms of the cluster. A similar type of disorder has previously been observed for several other polynuclear carbonyl clusters.[35] Crucially, clusters (1), (2A), and (2B) appear to be stereochemically equivalent [Figures 2(*a*) and 3] within the limits imposed by the crystal disorder.

The structure was further refined with the occupancy (p_A) of orientation (2A) allowed to vary between 0 and 1, and the occupancy of (2B) set to $1 - p_A$. The isotropic temperature factors of the oxygen and carbon atoms of the disordered part of the second cluster were constrained to be equal to two independent free variables. Similarly, the isotropic temperature factors of each pair of disordered Ru atoms were constrained to be equal to a separate free variable. In the final cycles of blocked full-matrix least-squares refinement, the ordered Ru atoms were assigned anisotropic thermal parameters. The phenyl rings of the $[N(PPh_3)_2]^+$ cations were treated as rigid groups (C–C 1.395 Å), no allowance being made for the H atoms in the structure-factor calculations. This resulted in R 0.068 1 and R' 0.068 7 ($= \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$) and weights ($w$) were assigned to reflections as $w = 1/\sigma^2(F_o)$. The final difference-Fourier map showed no maxima greater than 1.7 e Å^{-3} which were in the region of the disordered Ru atoms.

(*b*) *Monoclinic modification* (II). It proved possible to resolve the diffraction data using Mo-K_α radiation in spite of the very long b axis of 52.55 Å. This would probably not have been attempted if a preliminary photographic examination of the crystal had been carried out. However, the initial unit-cell dimensions were determined using the PW1100 peak-search routine and a preliminary scan of the $h0l$ and $0k0$ data unambiguously indicated the space group $P2_1/n$. Since resolution appeared to be satisfactory, due

4 (*Continued*)

Cluster (1)	$[Os_6(CO)_{18}]^{2-}$
98.0(8)	89.1
90.2(8)	91.2
93.1(9)	91.3
91.5(8)	91.2
95.7(8)	89.1
89.7(8)	91.3
95.1(8)	89.1
95.2(7)	91.3
93.7(8)	91.2
92.5(9)	91.3
91.4(8)	91.2
96.3(8)	89.1
91.9(8)	91.2
91.2(9)	91.3
99.0(8)	89.1
95.7(8)	89.1
93.2(8)	91.3
94.3(8)	91.2

otes *a* and *c* in Table 3.

llographic two-fold axis which lies rdered atoms, and passes through (2A) · · · Ru(2B) and Ru(5A) · · · nder this operation Ru(3C) and its nds would exchange position with groups, therefore the sites of these ancy. Significantly, the remaining cide in position for the two orient- he packing is effectively determined gen atoms and is independent of the nal atoms of the cluster. A similar eviously been observed for several onyl clusters.[35] Crucially, clusters ar to be stereochemically equivalent hin the limits imposed by the crystal

urther refined with the occupancy allowed to vary between 0 and 1, (2B) set to $1 - p_A$. The isotropic he oxygen and carbon atoms of the econd cluster were constrained to be ent free variables. Similarly, the actors of each pair of disordered Ru d to be equal to a separate free cycles of blocked full-matrix least- ordered Ru atoms were assigned rameters. The phenyl rings of the e treated as rigid groups (C–C 1.395 made for the H atoms in the struc- . This resulted in R 0.068 1 and $|F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$) and weights ($w$) ctions as $w = 1/\sigma^2(F_o)$. The final showed no maxima greater than n the region of the disordered Ru

cation (II). It proved possible to lata using Mo-K_α radiation in spite of 52.55 Å. This would probably ted if a preliminary photographic tal had been carried out. However, ensions were determined using the utine and a preliminary scan of the biguously indicated the space group appeared to be satisfactory, due

mainly to the weak diffraction and to the absence of data of the type $0k0$ with $k = 2n + 1$, it was decided to collect a small proportion of low-angle data in order to locate the metal atoms. Multisolution Σ_2 sign expansion showed three separate Ru_6 octahedra in the asymmetric unit, which is

TABLE 5

Selected bond lengths (Å) and angles (°) in the two $[N(PPh_3)_2]^+$ cations * in (I), with estimated standard deviations in parentheses

P(1)–N(1)	1.577(14)	P(1)–N(1)–P(2)	138.1(9)
P(2)–N(1)	1.577(13)	P(3)–N(2)–P(4)	138.8(9)
P(3)–N(2)	1.591(14)		
P(4)–N(2)	1.561(13)		
		N(1)–P(1)–C(111)	109.1(6)
		N(1)–P(1)–C(121)	115.2(6)
		N(1)–P(1)–C(131)	110.1(6)
		N(1)–P(2)–C(211)	114.2(6)
P(1)–C(111)	1.802(11)	N(1)–P(2)–C(221)	111.8(6)
P(1)–C(121)	1.799(11)	N(1)–P(2)–C(231)	107.5(7)
P(1)–C(131)	1.788(10)	N(2)–P(3)–C(311)	107.9(6)
P(2)–C(211)	1.812(10)	N(2)–P(3)–C(321)	115.1(6)
P(2)–C(221)	1.799(10)	N(2)–P(3)–C(331)	110.7(7)
P(2)–C(231)	1.777(13)	N(2)–P(4)–C(411)	106.5(6)
P(3)–C(311)	1.790(10)	N(2)–P(4)–C(421)	114.6(6)
P(3)–C(321)	1.792(11)	N(2)–P(4)–C(431)	110.6(7)
P(3)–C(331)	1.794(12)		
P(4)–C(411)	1.798(12)		
P(4)–C(421)	1.803(10)		
P(4)–C(431)	1.787(14)		
		C(111)–P(1)–C(121)	108.9(5)
		C(111)–P(1)–C(131)	105.7(5)
		C(121)–P(1)–C(131)	107.4(5)
		C(211)–P(2)–C(221)	108.9(5)
		C(211)–P(2)–C(231)	106.5(6)
		C(221)–P(2)–C(231)	107.6(5)
		C(311)–P(3)–C(321)	107.9(5)
		C(311)–P(3)–C(331)	107.9(5)
		C(321)–P(3)–C(331)	107.0(5)
		C(411)–P(4)–C(421)	108.0(5)
		C(411)–P(4)–C(431)	109.2(6)
		C(421)–P(4)–C(431)	107.7(6)

* The cations are in the usual bent form (R. D. Wilson and R. Bau, *J. Amer. Chem. Soc.*, 1974, **96**, 7601 and refs. therein).

consistent with the spectroscopic evidence that the two modifications, (I) and (II), are of the same compound. Least-squares refinement of the Ru atom positions with isotropic thermal parameters gave R 0.23 indicating that the solution for the metal-atom positions was probably correct. No further work was carried out on this modification because of the poor quality of the crystals.

Major computations were made using the 'SHELX' system of programs.[36] Scattering factors were taken from ref. 37 and included both real and imaginary contributions to anomalous scattering.[38] The final atomic co-ordinates for (I) are given in Table 2, selected bond lengths and angles in Tables 3—5. Supplementary Publication No. SUP 22685 (64 pp.) * contains thermal parameters and the observed and calculated structure factors for (I).

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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Preliminary communication

AN IMPROVED SYNTHESIS OF THE HEXARUTHENIUM CARBIDO CLUSTER $Ru_6C(CO)_{17}$; X-RAY STRUCTURE OF THE SALT $[Ph_4As]_2[Ru_6C(CO)_{16}]$

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Summary

Reaction of ethylene with $Ru_3(CO)_{12}$ under conditions of moderate pressure and temperature gives $Ru_6C(CO)_{17}$ (I) in ca. 70% yield. Reaction of this carbonyl carbido species with base gives the dianion $[Ru_6C(CO)_{16}]^{2-}$; X-ray analysis of the $[Ph_4As]^+$ salt indicates an octahedral array of metal atoms with the carbon at the centre of the octahedron and twelve terminal and four edge bridging carbonyl ligands giving an approximate overall C_{2v} symmetry.

In contrast to dodecarbonyltriosmium, which undergoes pyrolysis to form a series of cluster carbonyl compounds based on Os_5, Os_6, Os_7 and Os_8 units, dodecacarbonyltriruthenium undergoes thermal decomposition in vacuo to produce low yields of the hexaruthenium carbido cluster $Ru_6C(CO)_{17}$ (I) [1]; the source of the carbido atom is carbon monoxide and CO_2 is produced during pyrolysis. We report an improved synthesis of this cluster from $Ru_3(CO)_{12}$ by reaction with ethylene under conditions of moderate pressure (~ 30 atm) and temperature (150°C); I is the major product of this reaction in yields approaching 70%, a significant improvement on previously reported methods [1]. Mass spectrometry indicates that the products obtained in low yield are mainly Ru_6 species but an Ru_4 cluster has also been isolated; X-ray analyses of these compounds are currently being undertaken.

The hexaruthenium carbide(I) reacts with OMe^- (Na_2CO_3/MeOH) via attack at a coordinated carbonyl group, to yield the anion $[Ru_6C(CO)_{16}(CO_2Me)]^-$ which may be isolated as the $[(Ph_3P)_2N]^+$ salt. Subsequent reaction of this anion with aqueous base yields the dianion $[Ru_6C(CO)_{16}]^{2-}$ which was separated as the

$[(Ph_3P)_2N]^+$ and $[Ph_4As]^+$ salts. The structure of the dianion is of interest in that it has the same number of CO ligands and an electronic equivalence to the clusters $[Fe_6C(CO)_{16}]^{2-}$ [2] and $Rh_6(CO)_{16}$ [3]. Protonation of $[Ru_6C(CO)_{16}]^{2-}$ by H_2SO_4 at −30°C in acetonitrile leads to the formation of a red crystalline material which on the basis of analytical and spectroscopic data (^1H, NMR, τ 25.71) may be formulated as the dihydride $H_2Ru_6C(CO)_{16}$.

X-ray analysis of $[Ph_4As]_2[Ru_6C(CO)_{16}]$ (II) shows the dianion to have the structure illustrated in Figure 1. The carbido atom is situated at the centre of an octahedral array of Ru atoms and of the sixteen carbonyl groups twelve are terminal and four are asymmetrically edge bridging. This arrangement contrasts with that in $Rh_6(CO)_{16}$ where four carbonyl ligands are face rather than edge bridging. Surprisingly this carbonyl distribution is different from that in the tetramethyl ammonium salt of $[Ru_6C(CO)_{16}]^{2-}$ (III) in which the dianion is isostructural with its Fe analogue and has only *three* edge-bridging carbonyl ligands, the remaining thirteen being terminal [4].

The $[Ru_6C(CO)_{16}]^{2-}$ salts of $[Ph_4As]^+$ and $[Me_4N]^+$ therefore appear to be the first example of two different isomeric forms of a metal carbonyl cluster anion, differing only in their carbonyl distribution, to be characterised by X-ray analysis. No details of the Ru—CO bond lengths in III have been published.

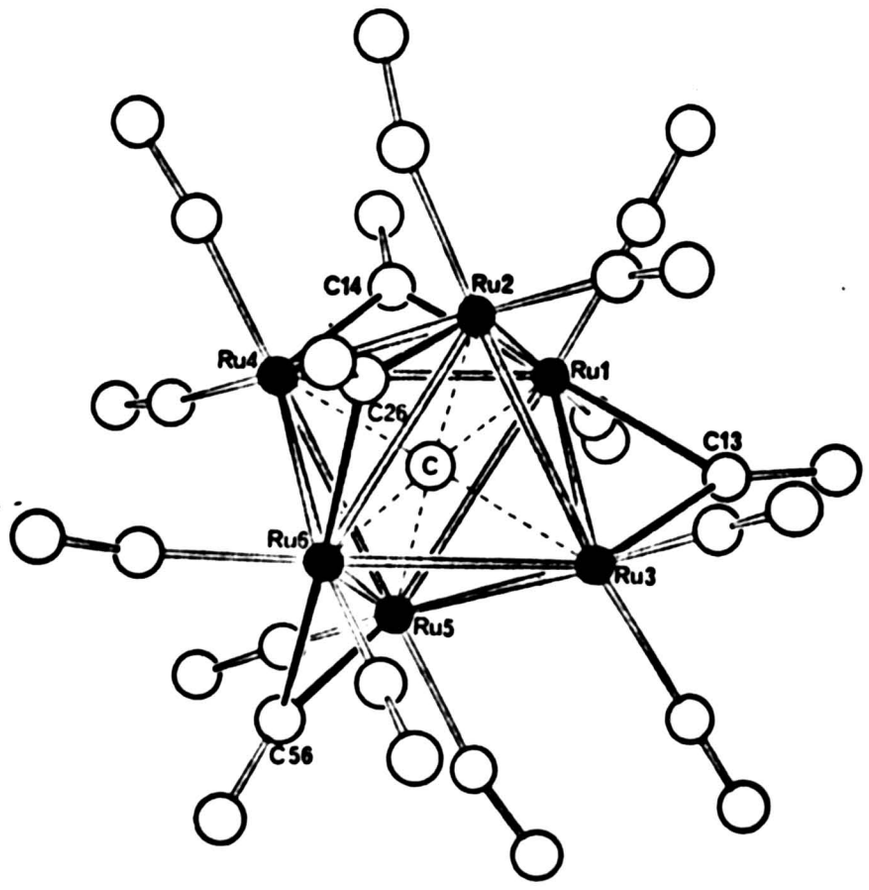

Fig. 1. The structure of the carbido dianion $[Ru_6C(CO)_{16}]^{2-}$ which has approximate C_{2v} symmetry. Important bond lengths are: Ru—Ru (mean) 2.89, Ru—C (mean) 2.05, Ru—CO (terminal, mean) 1.895, Ru(1)—C(13) 2.327, Ru(3)—C(13) 2.015, Ru(1)—C(14) 2.009, Ru(4)—C(14) 2.187, Ru(2)—C(26) 2.104, Ru(6)—C(26) 2.273, Ru(5)—C(56) 1.996 and Ru(6)—C(56) 2.070 Å.

However, comparison of its isostructural $[Fe_6C(CO)_{16}]^{2-}$ analogue (IV), Figure 2, with that of the $[Ru_6C(CO)_{16}]^{2-}$ dianion in II, Figure 1, shows that the only gross difference is the overall arrangement of the carbonyls in these two $[M_6C(CO)_{16}]^{2-}$ clusters is that the bridging carbonyl CO(13) in the Ru dianion in II corresponds to the terminal carbonyl CO(7) in the Fe structure. The mean Fe(4)—C(7) bond length in the two independent Fe clusters is 1.55(7) Å and significantly this "terminal" carbonyl is very close to a second iron atom so that the mean Fe(3) ...C(7) contact {2.65(7) Å} is considerably shorter than any other non-bonded contact within the dianion. The X-ray analysis of the tetramethylammonium salt of IV was very problematic due to poor diffraction and decomposition [2]. A more accurate location of the C in this CO ligand would be expected to show a longer, more normal, Fe(4)—C(7) bond length close to the mean value of 1.72 Å observed for the other terminal Fe—C distances, and this would correspondingly produce an even shorter Fe(3) ... C(7) contact if a normal C—O bond length is retained. As the three bridging carbonyls are very asymmetric in IV with the Fe—C bond lengths ranging from 1.78 to 2.33 Å it is possible that CO(7) should be regarded as a fourth asymmetric edge bridge. The

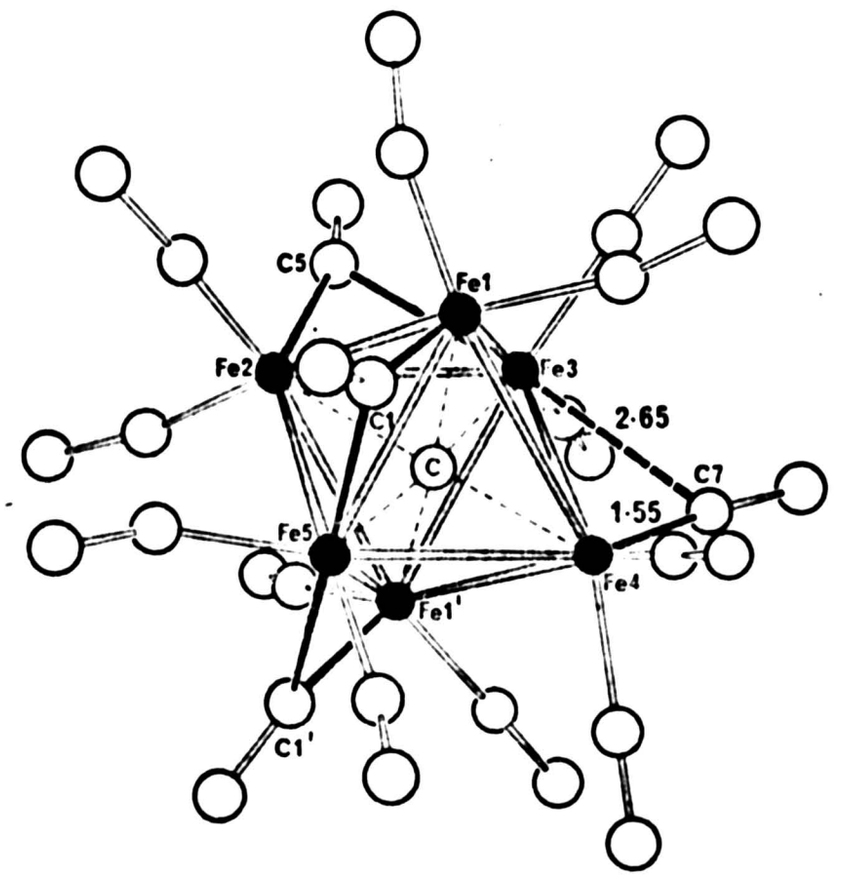

Fig. 2. The reported structure [2] of the carbido dianion $[Fe_6C(CO)_{16}]^{2-}$ drawn in a comparable manner to Figure 1 to emphasize the similarity between the two structures. The Fe—C bond lengths (mean value from two independent clusters) in the bridging carbonyls are Fe(5)—C(1) 2.188, Fe(1)—C(1) 1.785, Fe(5)—C(1′) 2.188, Fe(1′)—C(1′) 1.785, Fe(4)—C(7) 1.554, Fe(3)—C(7) 2.650, Fe(2)—C(5) 1.937 and Fe(3)—C(5) 2.165. For ease of comparison with II symmetry related bond lengths have been quoted separately.

marked similarity in distribution of the rest of the CO ligands in IV to those in II supports this conclusion.

Further details of the $[Me_4N]_2[Ru_6C(CO)_{16}]$ structure should confirm whether the dianion in this salt is a different isomer from that in $[Ph_4As]_2$-$[Ru_6C(CO)_{16}]$ or whether the two differ only in the degree of asymmetry of the bridging carbonyls.

The metal atoms surrounding the carbon in carbido carbonyl clusters are usually observed in one of two alternative arrangements. For the species $[Co_6C(CO)_{15}]^{2-}$ [5], $[Rh_6C(CO)_{15}]^{2-}$ [6], $Co_6C(CO)_{12}S_2$ [7] and $Rh_8C(CO)_{19}$ [8], a prismatic arrangement of metal atoms occurs whilst for $Ru_6C(CO)_{17}$ [9], $Ru_6C(CO)_{14}$-(arene) [10], $[Ru_6C(CO)_{16}]^{2-}$, $[Fe_6C(CO)_{16}]^{2-}$ [2], $[Co_6C(CO)_{14}]^{4-}$ [11] and $[Co_8C(CO)_{18}]^{2-}$ [12] an antiprismatic geometry is found. In $[Rh_{15}C_2(CO)_{28}]^-$ [13] the two carbon atoms also reside in antiprismatic cavities. For the second row elements, as may be anticipated, the M—C distance varies between these two alternative environments having a value of 2.13 Å in the prismatic cavity of $[Rh_6C(CO)_{15}]^{2-}$ and $Rh_8C(CO)_{19}$ whilst in the octahedral cavities of $[Rh_{15}C_2(CO)_{28}]^-$ a value of 2.04 Å is observed. In the ruthenium carbido species the octahedral hole has a radius of 2.05 Å, similar to that observed in the Rh_{15} cluster. Interestingly, the Ru—C distance of 2.05 Å in $[Ru_6C(CO)_{16}]^{2-}$ is close to the Ru—H distance (2.04 Å) observed [14] in the interstitial hydride $[Ru_6H(CO)_{18}]^-$. Thus since there is plenty of room within an Ru_6 octahedron to accommodate a neutral H atom without distortion the expansion of the polyhedron in these species appears to be caused by electronic rather than steric factors.

Crystal data

II, monoclinic space group *Pn*, a = 19.329, b = 14.958, c = 11.498 Å, β = 101.33°, Z = 2, $I/\sigma(I) \geq 3.0$, θ range 3—25°, present R-value 0.0805 for 4520 reflections. The positions of the Ru, As, and half the phenyl carbon atoms and eight CO ligands are nearly centrosymmetrically related. This posed some difficulty in refinement in the non-centric spacegroup *Pn*. However, refinement in the centric spacegroup $P2_1/n$ would require that most of the atoms in both the anion and cation be treated as disordered. The two atoms of each of the pairs related by the approximate centre of symmetry were refined in separate cycles with equivalent bond lengths constrained to be equal. Refinement converged satisfactorily giving an R-value of 0.0805 and a final difference Fourier revealed no electron density $> 1\ e\ Å^{-3}$ except in the region of the metal atoms.

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