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PREPARATIVE AND N.M.R. STUDIES OF POLYPHOSPHORUS LIGANDS AND THEIR COMPLEXES.

A Thesis submitted to the Council for National Academic Awards in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy.

By

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Preparative and N.M.R. Studies of Polyphosphorus Ligands and Their Complexes.

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ABSTRACT.

A wide range of diphosphines and their complexes with chromium, molybdenum, and tungsten carbonyl moieties has been synthesised and characterised, and studied by proton, C-13 and P-31 n.m.r. spectroscopy. In many cases the diphosphines have one or more centres of chirality, and this leads to the formation of diastereomers that are readily distinguishable by n.m.r. The P-31 chemical shifts occur in specific ranges that are often structurally diagnostic, and are interpreted in terms of "group contributions", "coordination chemical shifts", and the effects of chelate "ring strain."

In order to obtain values of geminal and vicinal P-31 to proton coupling constants which can be used to assess conformational details, recourse was had to C-13/H-1 two-dimensional heteronuclear chemical shift correlation experiments. These use effective chemical shifts introduced by the presence of a single C-13 nucleus to reduce the extent of second-order character in the spectrum and hence give values of $\underline{N}$(PC) and $\underline{N}$(PH) together with their relative signs.

Synthetic studies have also been undertaken on the triphosphine ligand $(Ph_2P)_2CHCH_2PPhH$, which has a chiral phosphorus atom, and its complexes. When all three phosphorus atoms are coordinated to the same metal atom this leads to considerable ring strain, but nonetheless such complexes are stable, but show interesting variations in their n.m.r. properties. The presence of the P-H bond in this triphosphine and its complexes permits base-catalysed addition reactions with species such as $(Ph_2P)_2C=CH_2$ to yield derivatives of the pentaphosphine $[(Ph_2P)_2CHCH_2]_2PPh$ in a regio- and even stereo-selective manner. This behaviour has been studied, and several new complexes have been prepared and their n.m.r. properties have been determined.

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Statement of Advanced Studies.

The author has attended many national and international meetings of the Royal Society of Chemistry, in particular those associated with n.m.r. spectroscopy and various aspects of transition metal chemistry. Throughout the study constant reference was made to relevant publications such as Specialist Periodical Reports in Nuclear Magnetic Resonance, Journal of the Chemical Society and the Journal of Organometallic Chemistry. Other journals were consulted regularly in order to keep abreast of the latest advances in chemistry in general.

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CHAPTER 1

INTRODUCTION

This thesis deals with the use of a range of n.m.r. techniques to determine the factors that influence phosphorus chemical shifts and coupling constants in a range of polyphosphorus compounds that are of interest as ligands in metal complexes.

Subtle metal-ligand interactions are of importance in understanding catalytic mechanisms involving organometallic compounds. ^{31}P chemical shifts and coupling constants are very sensitive to these interactions, since a phosphorus atom may be bound directly to the metal centre in most cases. Consequently ^{31}P n.m.r. is becoming a particularly valuable analytical tool for the study of stereochemistry and bonding in phosphine complexes. Since the early 1970s there has been a dramatic increase in research on new methods for the preparation of chiral compounds. Many of the recent synthetic applications of asymmetric synthesis are linked to asymmetric catalysts. In the field of asymmetric catalysis progress has been made by using homogeneous catalysts based on transition metal complexes modified by chiral ligands. In this way chiral phosphines became important in asymmetric synthesis, many transition metal complexes have good catalytic properties when they are coordinated by a phosphine ligand. The synthetic route to the asymmetric diphosphines as adopted by M.D. Fryzuk and B. Bosnich is explained in the experimental section. However, the coordination chemistry of the ligands (i) - (iii) was never fully exploited.

Fig 1.0

(i)

$$Ph_2P \diagup \overset{\displaystyle \overset{CH_3}{(CH_2)_nCH}}{} \diagdown PPh_2 \quad \text{where } n=1,2 \text{ and } 3$$

(ii)

$$Ph_2P \diagup \overset{\displaystyle \overset{CH_3CH_3}{CH-CH}}{} \diagdown PPh_2$$

(iii)

$$Ph_2P \diagup \overset{\displaystyle \overset{CH_2CH_3}{CH-CH_2}}{} \diagdown PPh_2$$
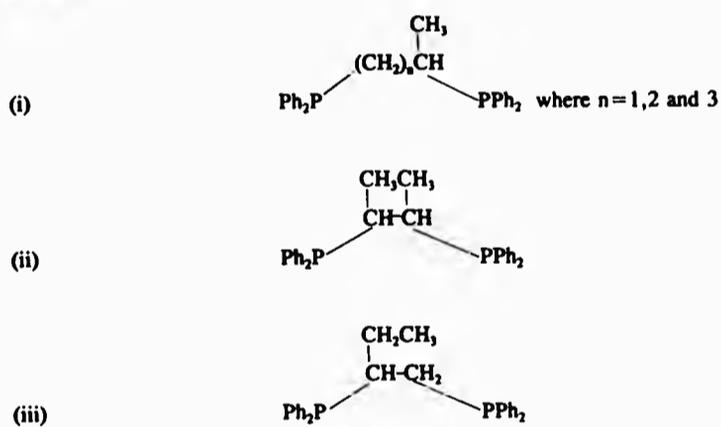
In view of this, it seemed desirable to extend the knowledge of these ligands by complexing them to the hexacarbonyls of Group VIa transition metals. Also, the sulphides and selenides of these ligands were prepared and characterised by n.m.r.. Firstly though, a comprehensive account is given of the synthesis of poly(tertiary phosphines) and of the different routes available for their formation.

The Synthesis of Poly(tertiary phosphines)

In 1967, Keiter[7] reported that lithium diphenylphosphide adds to the double bond in diphenylvinylphosphine in the following manner:

$$Ph_2PLi + Ph_2PCH=CH_2 \longrightarrow Ph_2PCHLiCH_2PPh_2 \qquad (1)$$

Hydrolysis of the above mixture produces the well-known 1,2-bis(diphenylphosphino)ethane (dppe).

$$Ph_2PCHLiCH_2PPh_2 + H_2O \longrightarrow Ph_2PCH_2CH_2PPh_2 + LiOH \qquad (2)$$

A reported variation by King and Kapoor[1] of the same reaction using instead diphenylphosphine (or phenylphosphine) and a strong base (e.g. phenyllithium) in catalytic amounts. Phenyllithium reacts with diphenylphosphine to form the lithium phosphide:

$$PhLi + Ph_2PH \longrightarrow Ph_2PLi + C_6H_6 \qquad (3)$$

$$Ph_2PLi + Ph_2PCH=CH_2 \longrightarrow Ph_2PCHLiCH_2PPh_2 \qquad (4)$$

$$Ph_2PCHLiCH_2PPh_2 + Ph_2PH \longrightarrow Ph_2PCH_2CH_2PPh_2 + Ph_2PLi \qquad (5)$$

Phenyl is more basic than diphenylphosphide (3); the lithium phosphide adds to the vinyl group exactly as in the reaction (1,4); the resulting carbon-lithium reagent thus formed reacts with more secondary phosphine to produce the product, dppe, and more lithium phosphide (5); and the cycle continues until the starting materials are exhausted. This method has been adapted to produce unsymmetrical ligands by beginning with alkyldiphenylphosphines or dialkylphenylphosphines[2]. Cleavage of these phosphines with lithium in THF removes a phenyl group with the corresponding

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alkylphenylphosphide or dialkylphosphide being formed[3]. Reaction as in the previous manner produces unsymmetrical bis(tertiary phosphines).

$$Ph_2PR + 2Li \xrightarrow{\text{THF}} PhRPLi + PhLi \qquad (6)$$

$$PhRPLi + Ph_2PCH=CH_2 \longrightarrow Ph_2PCHLiCH_2PRPh \qquad (7)$$

$$Ph_2PCHLiCH_2PPhR + H_2O \longrightarrow Ph_2PCH_2CH_2PPhR + LiOH \qquad (8)$$
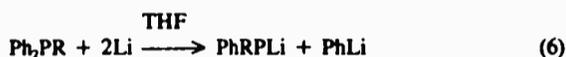
Both methods show some advantages. King's method[4] allows the preparation of poly(tertiaryphosphines) with more than two phosphorus atoms by use of primary phosphines or even phosphine, PH_3 itself. The method adopted by Grim et al eliminates the need to use the extremely unpleasant secondary and primary phosphines and is much more versatile for introduction of alkyl groups into the polyphosphines. King[5] has also adapted his method, as stated above, to permit the incorporation of methyl groups. R.B. King and P.N. Kapoor[5], have during the past few years taken a keen interest in the chemistry of cyclopentadienylmetal derivatives containing tertiary phosphine ligands. For this reason they have investigated reactions of cyclopentadienylmetal-carbon derivatives with ditertiary phosphines such as $R_2PCH_2CH_2PR_2$ ($R=CH_3$ and C_6H_5), cis- and trans- $(C_6H_5)_2PCH=CHP(C_6H_5)_2$, $(C_6H_5)_2PC \equiv CP(C_6H_5)_2$, and the tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$.

The above workers have found that one of the limiting factors in the development of the chemistry of tertiary phosphine complexes of transition metals has been the availability of appropriate tertiary phosphine ligands, especially the polytertiary phosphines. Most polytertiary phosphines are prepared by reactions of organic

polyhalides with alkali metal dialkylphosphides. For example the frequently studied 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, is readily prepared by the reaction of 1,2-dichloroethane with lithium diphenylphosphide in tetrahydrofuran solution. Similarly, the unsaturated ditertiary phosphines cis- and trans- 1,2-bis(diphenylphosphino)ethene can be prepared by stereospecific reactions of cis- and trans- 1,2-dichloroethene, respectively, with lithium diphenylphosphide. The tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ can be prepared by reaction of the trichloride $CH_3C(CH_2Cl)_3$ with sodium diphenylphosphide in liquid ammonia and tetrahydrofuran. However, attempts to extend this synthetic technique to more complex polytertiary phosphines, except for the one tetratertiary phosphine $C[CH_2P(C_6H_5)_2]_4$, have not been successful owing to the unavailability of an appropriate polyhalide or to difficulties in obtaining complete reaction of such a polyhalide with an alkali metal dialkylphosphide. Even the preparation of the tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ from $CH_3C(CH_2Cl)$ and sodium diphenylphosphide has presented some difficulties of this type. The one known potentially tetradentate tetratertiary phosphine, tris(o-diphenylphosphinophenyl)phosphine, Fig 1.01, was prepared by treatment of phosphorus trichloride with the lithium derivative from n-butyllithium and o-bromophenyldiphenylphosphine.

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Fig. 1.01. Shows structure of tetradentate tertiary phosphine
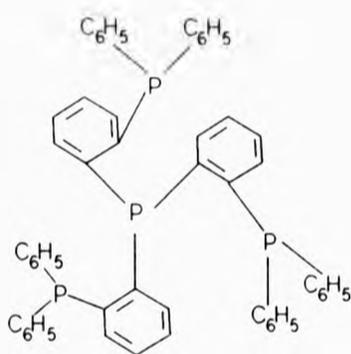
The above considerations indicate the need for a new method for the preparation of polytertiary phosphines to supplement the reactions of alkali metal dialkylphosphides with organic polyhalides. King et al interest in coordination chemistry led them to study the synthesis of polytertiary phosphines with the phosphorus atoms in suitable positions to bond to a single metal atom, i.e. to act as a multidentate chelating agent. Polytertiary phosphines which act as such chelating agents are of potential interest in coordination chemistry because of the new possibilities for the stabilisation of unusual oxidation states as well as forming new transition metal complexes with novel catalytic properties. The original preparation of the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, Fig. 1.02, gave only 14% yield from sodium diphenylphosphide and phenylbis(2-bromoethyl)phosphine.

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Fig 1.02
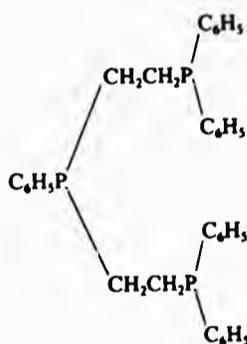
This tritertiary phosphine could be obtained in good yield ($\sim 90\%$) either by addition of 2 equiv. of diphenylphosphine (1) to the carbon-carbon double bonds of phenyldivinylphosphine or by addition of the phosphorus-hydrogen bonds of phenylphosphine (2) to the carbon-carbon double bonds in 2 equiv. of diphenylvinylphosphine according to the following equations:

$$C_6H_5P(CH=CH_2)_2 + 2(C_6H_5)_2PH \longrightarrow [(C_6H_5)_2PCH_2CH_2]_2PC_6H_5 \qquad (1)$$

$$2(C_6H_5)_2PCH=CH_2 + C_6H_5PH_2 \longrightarrow [(C_6H_5)_2PCH_2CH_2]_2PC_6H_5 \qquad (2)$$
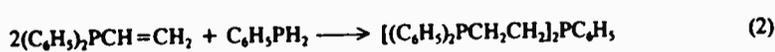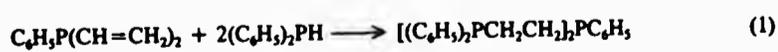
The latter method was preferred since much higher yields are obtained in the preparation of diphenylvinylphosphine from vinylmagnesium bromide and diphenylchlorophosphine than in the preparation of phenyldivinylphosphine from

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vinylmagnesium bromide and either phenyldichlorophosphine or phenyldi-n-butoxyphosphine. Either potassium tert-butoxide or phenyllithium could be employed as catalysts for this reaction, with potassium tert-butoxide giving slightly better results. The reaction between diphenylvinylphosphine and phenylphosphine in a 1:1 mole ratio gives the tritertiary phosphine, Fig. 1.02, rather than the phosphorus-hydrogen compound $(C_6H_5)_2PCH_2CH_2P(H)(C_6H_5)$, Fig. 1.03, indicating that the addition of this ligand to vinylphosphines is about as fast as or faster than the addition of diphenylphosphine to vinylphosphines.

Fig. 1.03

Fig. 1.04

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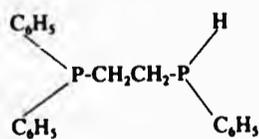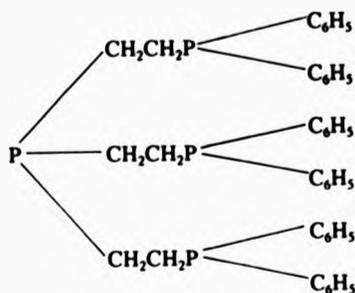
This new synthetic method was used to prepare two isomeric tetratertiary phosphines $C_{42}H_{42}P_4$ Fig. 1.04. Hence, the "tripod" tetratertiary phosphine tris(2-diphenylphosphinoethyl)phosphine, $[(C_6H_5)_2PCH_2CH_2]_3P$, Fig. 1.04, could be prepared either by addition of the phosphorus-hydrogen bonds (1) in phosphine to the carbon-carbon double bonds in 3 equiv. of diphenylvinylphosphine or by the addition of 3 equiv. of diphenylphosphine (2) to the carbon-carbon double bonds in trivinylphosphine according to the following equations:

$$3(C_6H_5)_2PCH=CH_2 + PH_3 \longrightarrow [(C_6H_5)_2PCH_2CH_2]_3P \qquad (1)$$

$$(CH_2=CH)_3P + 3(C_6H_5)_2PH \longrightarrow [(C_6H_5)_2PCH_2CH_2]_3P \qquad (2)$$
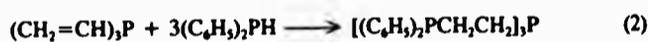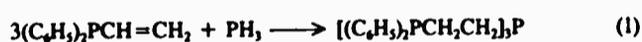
The products obtained from each of these reactions were found to be identical. Later, a large quantity of this "tripod" ligand was required for a study of its metal complexes. At that time a more convenient preparation was developed by King et al which consisted of bubbling phosphine generated by hydrolysis of aluminium phosphide into a boiling tetrahydrofuran solution of diphenylvinylphosphine containing the potassium tert-butoxide catalyst.

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Fig. 1.05

$$(C_6H_5)_2\text{PCH}_2\text{CH}_2\overset{\underset{\displaystyle |}{C_6H_5}}{\text{P}}\text{CH}_2\text{CH}_2\overset{\underset{\displaystyle |}{C_6H_5}}{\text{P}}\text{CH}_2\text{CH}_2\text{P}(C_6H_5)_2$$
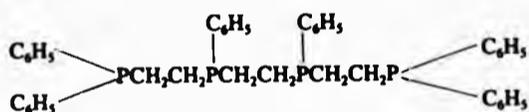
The other tertiary phosphine prepared in this work by King et al was the "linear" tetratertiary phosphine 1,1,4,7-10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, $(C_6H_5)_2\text{PCH}_2\text{CH}_2\text{P}(C_6H_5)\text{CH}_2\text{CH}_2\text{P}(C_6H_5)\text{CH}_2\text{CH}_2\text{P}(C_6H_5)_2$, Fig. 1.05, which was obtained by the addition of 1,2-bis(phenylphosphino)ethane to the carbon-carbon double bonds in 2 equiv. of diphenylvinylphosphine according to the following equation:

$$2(C_6H_5)_2\text{PCH}=\text{CH}_2 + C_6H_5\text{P(H)CH}_2\text{CH}_2\text{P(H)}C_6H_5 \longrightarrow$$
$$(C_6H_5)_2\text{PCH}_2\text{CH}_2\text{P}(C_6H_5)\text{CH}_2\text{CH}_2\text{P}(C_6H_5)\text{CH}_2\text{CH}_2\text{P}(C_6H_5)_2$$
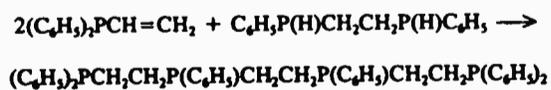
The interest shown by King in a potentially hexadentate tertiary phosphine ligand led to the preparation of the hexatertiary phosphine 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane, $[(C_6H_5)_2\text{PCH}_2\text{CH}_2]_2\text{PCH}_2\text{CH}_2\text{P}[\text{CH}_2\text{CH}_2\text{P}(C_6H_5)_2]_2$, Fig. 1.06.

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Fig. 1.06
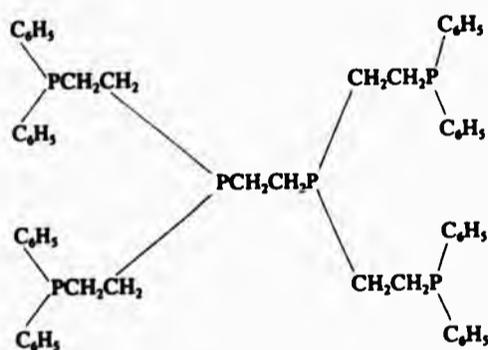
by the addition of the phosphorus-hydrogen bonds in 1,2-diphosphinoethane, $H_2PCH_2CH_2PH_2$, to the carbon-carbon double bonds in four equivalents of diphenylvinylphosphine according to the following equation:

$$4(C_6H_5)_2PCH=CH_2 + H_2PCH_2CH_2PH_2 \longrightarrow$$

$$[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$$
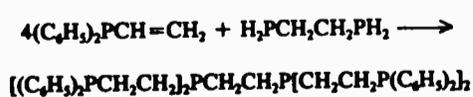
The success in the preparation of polytertiary phosphines with PCH_2CH_2P units from vinylphosphines and phosphorus-hydrogen compounds led King et al to suggest the preparation of polytertiary phosphines with $PCH=CHP$ units from ethynylphosphine and phosphorus-hydrogen compounds according to the following general scheme.

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$$P\text{-}H + PC\equiv CH \longrightarrow PCH=CHP$$

Such a reaction of this type was thought to lead to either cis- or trans- stereochemistry around the carbon-carbon double bond of the olefinic ditertiary phosphine unit in the product. This stereochemical uncertainty was clarified by an investigation of the following reaction between diphenylethynylphosphine and diphenylphosphine:

$$(C_6H_5)_2PC\equiv CH + (C_6H_5)_2PH \longrightarrow (C_6H_5)_2PCH=CHP(C_6H_5)_2$$

Both the cis- and trans- isomers of $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ are readily available and well-characterised spectroscopically by A. Aguiar and D. Daigle[5]. The product from the reaction between diphenylethynlphosphine and diphenylphosphine was identified as the trans- isomer, Fig. 1.07, from its infrared and proton n.m.r. spectra.

Fig. 1.07
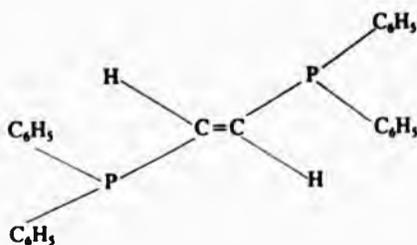
Formation of the trans- isomer, Fig. 1.07, rather than the corresponding cis- isomer from the reaction between diphenylethynylphosphine and diphenylphosphine maximises the distance between the relatively bulky diphenylphosphino substituents on the carbon-carbon double bond. King then went on to investigate the preparations of mixed tertiary phosphine-arsines by additions of diphenylarsine across the carbon-carbon double bonds of vinylphosphines. The potentially bidentate ligand $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$, Fig. 1.08.

Fig 1.08
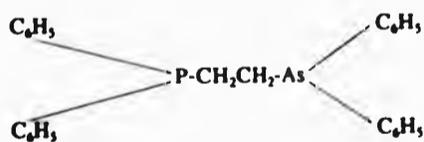
Fig. 1.09
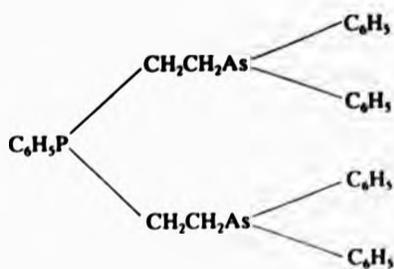
and the potentially tridentate ligand [(C₆H₅)₂AsCH₂CH₂]₂PC₆H₅, Fig. 1.09, were prepared by King[5] by the following reactions:

$$(C_6H_5)_2PCH=CH_2 + (C_6H_5)_2AsH \xrightarrow{KOBu^t} (C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$$

$$C_6H_5P(CH=CH_2)_2 + 2(C_6H_5)_2AsH \xrightarrow{KOBu^t} [(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$$

These new polytertiary phosphines and phosphine-arsines were characterised by King et al, where possible, by the infrared, proton and ^{31}P n.m.r. and mass spectra. Some interesting trends appeared, which might be expected.

One of the problems encountered in forming pentaphosphines is the tendency of the reactants to form a dimeric product; however, this problem may be circumvented by the use of sulphur as a "protecting group". In the synthesis of polyphosphines using base-catalysed addition of phosphorus-hydrogen bonds to the vinylphosphines the final product may not be the expected 1:1 adduct[6] but may be exclusively the 1:2 adduct. This problem can be overcome by the stabilisation of the carbanion by a sulphur atom. The base-catalysed addition of phosphorus-hydrogen bonds to vinylphosphorus compounds can be considered as a Michael addition[6], proceeding according to the following sequence:

$$R^1R^2PH + base \longrightarrow base\text{-}H^\oplus + R^1R^2P^\ominus \qquad (1)$$

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$$R^1R^2P^{\ominus} + CH_2{=}CHPR^3R^4 \longrightarrow R^1R^2PCH_2CH^{\ominus}PR^3R^4 \tag{2}$$

$$R^1R^2PCH_2CH^{\ominus}PR^3R^4 + \text{base-H}^{\oplus} \longrightarrow R^1R^2PCH_2CH_2PR^3R^4 + \text{base} \tag{3}$$
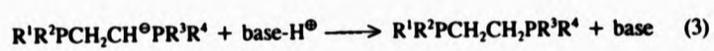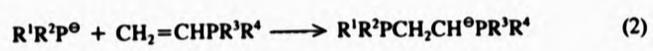
CHIRAL PHOSPHINES

Main Structures

It is worthwhile to classify the chiral phosphines according to their structures. In Fig. 1.10 are indicated some types of monophosphines (I-III), the asymmetry being on the phosphorus atom or in a side chain or both.

Fig. 1.10. Main classes of chiral phosphines

I	II	III
P* / | \ R¹ R² R³	R*PPh₂	P / | \ *R¹ R³ R²

IV	V	VI
Ph₂P-C-C-PPh₂ R*	Ph₂P-C-C-C-PPh₂ R*	Ph₂P-C-C-C-C-PPh₂ R*

VII	VIII
R¹ R¹ \ / *P-CH₂CH₂-P* / \ R² R²	P*-R*-P / | | \ R R¹ R R
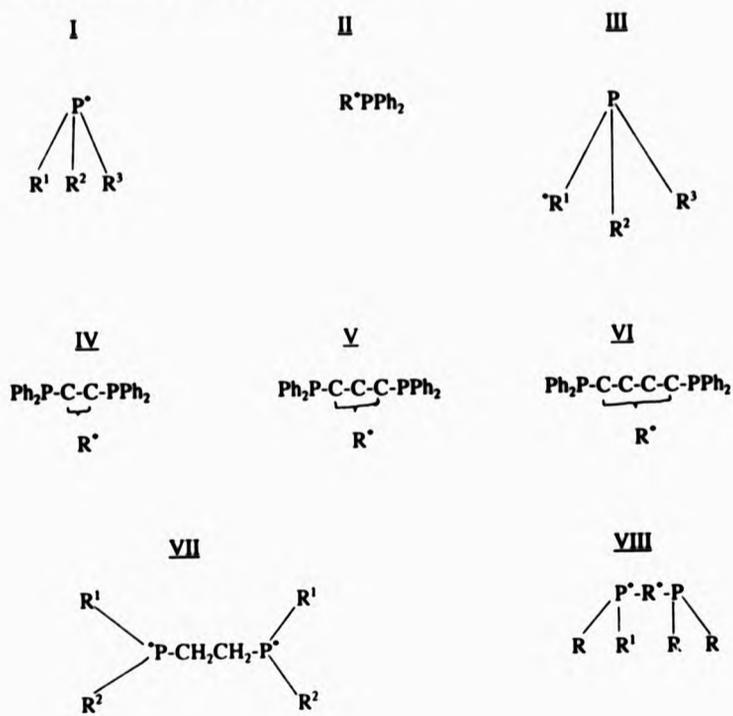
* indicates chirality

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The most often encountered chelates are classes IV-VI and are at the moment the most studied in asymmetric catalysis; the chiral diphosphines were synthesised and their coordination behaviour towards Group VIa metals were studied which forms the major part of chapter 2.

Some Selected chiral phosphines are shown below; Fig 1.11
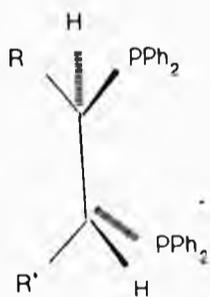
R = R' = Me; chiraphos

R = Me, R' = H; prophos

R = Ph, R' = H

norphos
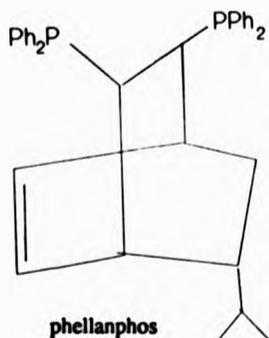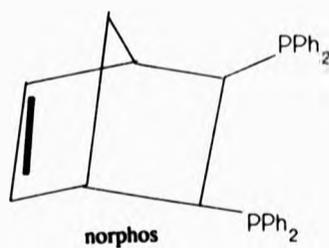
R = H; chairphos

R = Me; skewphos

phellanphos

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camphos

nopaphos
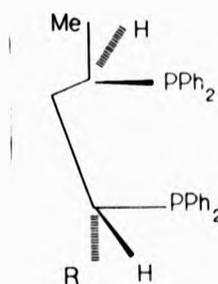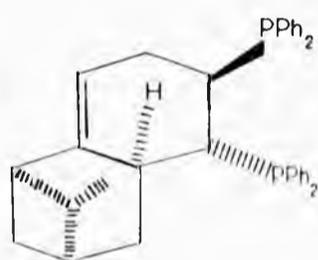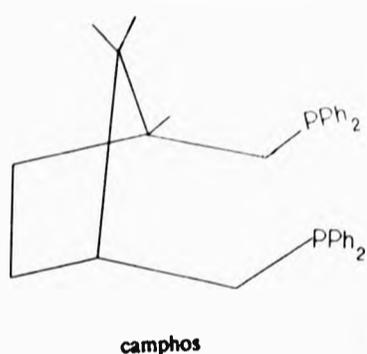
More unusual chiral diphosphines were prepared by N.C. Payne and D.W. Stephen[11] in order to study their electronic/steric properties. They observed that the order of ^{31}P chemical shifts of the bidentate alkylphosphines is found to be s,s-chiraphos > diphos > (+) - diop. The low frequency shift of the (+)-diop is thought to be due to the greater electron-donating ability of the ring. Similarly, a low frequency resonance of s,s-chiraphos with respect to diphos would most probably have been predicted, because of the additional electron-releasing methyl substituents on the C atom backbone. Such an argument is found to be not consistent with the observed order, since steric, in addition to electronic factors influence the chemical shift. In the cases of s,s-chiraphos and diphos, electronic influences are of similar magnitudes, and the differences in chemical shift can be rationalised on the basis of the size of the

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substituents on the ^{31}P atoms. This is discussed more fully in the next chapter.

The discussion so far has been centred upon ligands which have an asymmetric centre on the backbone of the ligand; this is extended below to the case where asymmetric centre is on the phosphorus atom.

Synthetic and ^{31}P n.m.r. Studies of Unsymmetrical bis-phosphorus Ligands

The synthesis of chelating phosphorus ligands with chemically and magnetically different phosphorus atoms has been successfully attempted by S.O. Grim[8] et al. These ligands have been important for investigating coordination compounds of these ligands by ^{31}P n.m.r. spectroscopy. Until 1976, most of the complexes of chelating di(tertiary phosphines), both symmetrical and unsymmetrical, have been of 1,2-bis(diphenylphosphino)ethane or have been similar derivatives, which lead to five-membered chelate rings[7,9-12]. In an attempt to study the phosphorus n.m.r. spectra of phosphorus-containing chelate rings of other sizes and compare them to the well-examined five-membered rings, Grim's group synthesised the first examples of unsymmetrical (diphenylphosphino) (diorganophosphino)methane, $Ph_2PCH_2PR^1R^2$, where $R^1 = R^2 = $ Me or i-Pr and $R^1 = $ Ph, $R^2 = $ Me, Et or i-Pr. The above ligands may be prepared by the two methods: reduction of (phosphinomethyl)phosphine sulphides with sodium (I) or hexachlorodisilane, and the reaction of (lithium methyl)-diphenylphosphine[13] with a diorganophosphinous chloride (II).

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$$Ph_2P(S)CH_2PR^1R^2 + 2Na \longrightarrow Ph_2PCH_2PR^1R^2 + Na_2S \qquad (I)$$

$$Ph_2PCH_2Li + R^1R^2PCl \longrightarrow Ph_2PCH_2PR^1R^2 + LiCl \qquad (II)$$
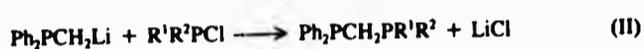
It was found that the use of Ph_2PCH_2Li is a more attractive method to form $Ph_2PCH_2PR^1R^2$ ligands, since no problems are encountered in large-scale work. It is interesting to note that in compounds which contain the isopropyl group(s), the phosphorus atom[14] appears as a prochiral centre, where the expected eight-line pattern on the ^1H n.m.r. may be present as six lines due to the accidental overlap of two pairs; this pattern shows the inequivalence of the methyl protons.[7,14] The spectra of methine protons of the isopropyl groups, as expected, were found to be generally too complex to interpret. The chemical shifts of the R_1R_2P- groups are predicted by the group contributions (GC)[15,16] and are found to be in good agreement with those determined experimentally.

Influence of Size of Chelate Ring

In a series of complexes where the ring size is varied, the observed J(PP) coupling is thought of as the algebraic combination of through-backbone and through metal contributions[17]. In dppe complexes the through-backbone coupling is expected to be intermediate between that for dppm and dppp. As a result, neither $^2J(PMP)$ nor $^3J(PCCP)$ dominates and the observed coupling is generally small or zero[7]. For the uncoordinated dppm, the through-backbone coupling $^2J(PCP)$ has been found to be large and positive[18]. This property extends to the complexed chelates, dominating the $^2J(PMP)$ coupling mechanism and producing a large positive J(PP).

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Chelate Ring Substituents Effects

Variation of substituents on the backbone or phosphorus atom will affect J(PP) and the origin of the effect may be electronic and/or steric. Substitution may influence J(PP) inductively, modifying s-orbital electron density. The steric requirements of a substituent may also influence s-orbital electron density by altering bond angles and hybridisation, this is discussed later, these effects are illustrated by the ligands $Ph_2PCH_2PR_2$[19] and $Ph_2PCH_2CH_2PPhR$[7] and their Cr, Mo and W complexes, and also for other ligands.

So far, the chelating ligands which have been discussed have shown the capacity to form complexes which give rise to a monocyclic structure. In the relevant chapters, mention is also made to structures in which the phosphorus atoms take part in forming a bicyclic structure of different ring sizes. As an example of such a case consider the following tridentate phosphorus tungsten complex (Fig. 1.12).

Fig. 1.12

21
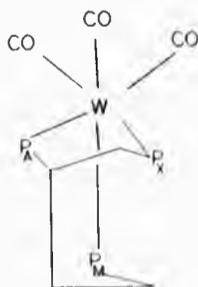
A detailed study of this tungsten carbonyl tridentate complex was carried out by I.J. Colquhoun, W. McFarlane and R.L. Keiter[20]. The complex $[Ph_2PCH(CH_2PPh_2)CH_2CH_2PPh_2]W(CO)_3$ was studied in order to determine the chelate ring size effect on the coordination chemical shift ($\Delta\delta$) and J(PP) in that the complex contains phosphorus atoms in bicyclic structures. As can be seen from Fig. 1.12 there are two five and six-membered rings associated with P_A, six and seven-membered rings associated with P_A, six and seven-membered rings with P_M and five and seven-membered rings with P_X. The structure was confirmed by its [31]P n.m.r. spectrum, showing three non-equivalent phosphorus atoms, all bonded to tungsten as shown by characteristic [183]W satellites due to $^1J(^{183}W\text{-}^{31}P)$. From this system it was determined that the phosphorus atoms in the five-membered ring (P_A,P_X) show large coordination chemical shifts expected for five-membered ring chelates (as in dppeW(CO)$_4$) and the coupling constant J(AX) is positive (+ 17.6 Hz). It appears that the constraints described by the five-membered ring that contains P_A and P_X dominate over the influence of the six- and seven-membered rings, which also contain these atoms. P_M displays a coordination chemical shift and J(PP) value for J(AM) = -18.3 Hz, J(MX) = -17.2 Hz, which are found to be the proper sign and magnitude for six and seven-membered ring structures. The finding that one of the J(PP) coupling constants is positive whilst the other two are negative lends support to the suggestion of Grim et al[21] that each of these couplings may be thought of as the algebraic sum of through-metal and backbone contributions. The positive coupling constant is due to the phosphorus atoms A and X which are linked by the shortest backbone path of the two carbon atoms.

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The two important parameters in n.m.r., namely the chemical shift and coupling constant, have been discussed in relation to ligands and their complexes. It is now pertinent to introduce a third parameter; the Ring Contribution, Δ_{RC}, which is used widely in chelate ring structures.

Ring Contribution, Δ_{RC}, to the Phosphorus-31 Chemical Shifts of Transition Metal-Phosphorus Complexes

The ^{31}P chemical shifts of a number of chelate complexes, as compiled by Garrou[22], show that of the four-, five-, and six-membered rings the five-membered analogues reveal a substantially large degree of deshielding. The data obtained for chromium, molybdenum and tungsten carbonyls offer a direct comparison[22] between four-, five- and six-membered rings (see Table 1.0).

This unusually large coordinated chemical shift (Δ) in five-membered ring systems was first observed by Meriwether and Leto[23] in nickel phosphine complexes and has been explained on the basis of ring strain[24]. Based on this reasoning, however, it would be expected that four-membered rings to show the largest shift upon coordination, which is found not to be the case. This idea has been extended by Garrou[22,25], who has defined the difference between the expected cis-disubstituted coordinated chemical shift and the observed chemical shift of an equivalent phosphorus in a chelate complex as the ring contribution, Δ_{RC}. He observed a deshielding contribution ranging from 24 to 31 ppm for five-membered rings. This concept will be extended in the following chapter but is also mentioned in this chapter

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where necessary.

METAL,M	DIPHOSPHINE	Δ	Δ_{RC}
Cr	[Ph$_2$PCH$_2$PPh$_2$]M(CO)$_4$	49.0	-12.0
	[Ph$_2$PCH$_2$CH$_2$PPh$_2$]M(CO)$_4$	91.9	+31.0
	[Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$]M(CO)$_4$	-58.7	-2.0
Mo	[Ph$_2$PCH$_2$PPh$_2$]M(CO)$_4$	23.6	-19.3
	[Ph$_2$PCH$_2$CH$_2$PPh$_2$]M(CO)$_4$	67.2	+24.3
	[Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$]M(CO)$_4$	38.3	-4.6
W	[Ph$_2$PCH$_2$PPh$_2$]M(CO)$_4$	0	-25.4
	[Ph$_2$PCH$_2$CH$_2$PPh$_2$]M(CO)$_4$	52.6	+27.3
	[Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$]M(CO)$_4$	17.3	-8.0

Data taken from reference 22.

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Evidence of Conformation from X-ray Diffraction Data

X-ray analysis has established that the chiral 1,2- or 1,4-diphosphines[26] behave as bidentate ligands on rhodium. From the X-ray analysis it is deduced that from a 1,2-diphosphine complex a five-membered ring is formed in which the ring adopts a classically twisted conformation which is chiral (δ or λ conformations) as shown below.

Fig. 1.13. Conformations adopted by a 1,2-diphosphine complex

δ $\hspace{8cm}$ λ
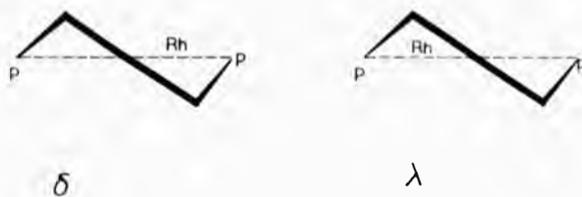
The effectiveness of chiraphos and other 1,2-diphosphines as ligands is strongly suggested to be related to the intrinsic chirality of the chelate ring. It was assumed that during catalysis the two methyl groups of chiraphos tend to be pseudo-equatorial as it appears on the X-ray structure, giving a ring of fixed absolute configuration[77]. This hypothesis was supported by reactions with phellanphos and nopaphos (see Fig. 1.10 on p.17 and p.18) which chelate onto rhodium with a rigid conformation. From this it was established that (S,S)-phellanphos and (R,R)-nopaphos (Fig. 1.11) give rise

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to δ and λ chelated rings[28]. It was determined from specific chemical reactions that a general rule of thumb is followed, that is, "a λ chelated ring induces synthesis of (S)-amino acids", which seems to be a well established rule. From this, it is clear that some correlations must exist between the ligand conformation of chiral diphosphines and the absolute configuration of the products. It is known that the twist conformation of a five-membered chelate ring tends to induce specific orientations of the P-Ph bonds and of the phenyl rings. Some correlations were made by Knowles et al concerning the orientation of phenyl groups of many types of 1,2- and 1,4-diphosphines, as shown by X-ray structures of various complexes[29]. A "face-to-edge" position of the phenyl rings is often observed; the chiral arrangement as shown in Fig. 1.14 consistently induces (S)-amino acid synthesis (the λ ring of Fig. 1.13 gives this type of phenyl arrangement).

Fig. 1.14

26
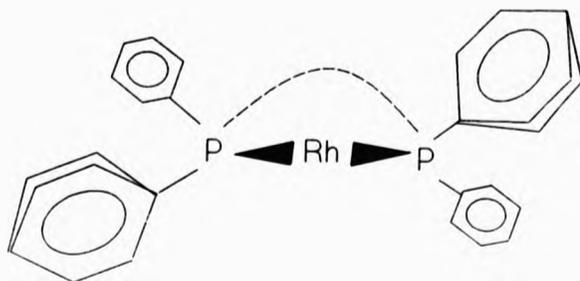
Other interpretations or correlations were proposed to correlate absolute configurations of a diphosphine and of the product[30].

Conformational Aspects of 2,4-bis(diphenylphosphino)pentane and 1,3-bis(diphenylphosphino)butane Rhodium Complexes

The rhodium complexes of skewphos and chairphos (see Fig 1.11) form two chiral chelating six-membered ring diphosphines, which are found[31] to be efficient catalysts for hydrogenation reactions. The two chiral phosphines differ in that skewphos is thought to adopt a chiral conformation whereas chairphos probably adopts an achiral conformation. The authors[31] chose to discuss the stereochemistry of the above ligands since they form six-membered chelate rings containing two- and one-chiral centres, respectively, but unlike the (S,S)-chiraphos and (R)-prophos analogues (Fig. 1.15) they give completely different results in chemical reactions. With a six-membered chelate ring, in principal, this may adopt many ring conformations, however, in this discussion only two are important: the chiral skew and the achiral chair conformations, Fig 1.16. And of these two, the chair conformation is intrinsically more stable[32,33]. When chiral centres are incorporated at the 2- and 4-carbon atoms of the ring, one or other of these two conformations may be stabilised by the requirement that the substituents be equatorially disposed[32-36].

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In Fig. 1.16 some of the ring conformations of (S,S)-skewphos two skew and two chair conformations are shown.

Fig. 1.16. A selection of possible conformations of (S,S)-skewphos
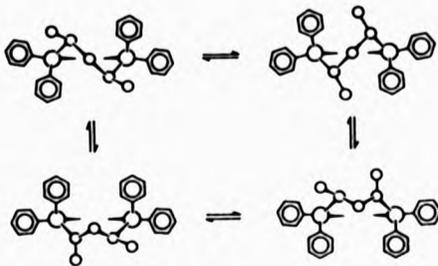
Fig. 1.17. A selection of possible conformations of (S)-chairphos
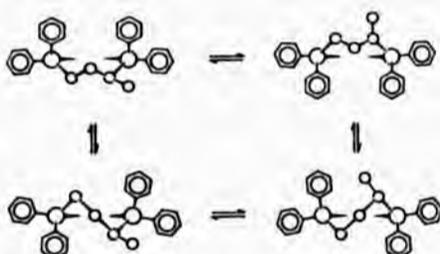
From the above conformations, it is observed that both the chair conformations have one destabilising axially disposed methyl group, one of the skew conformations has two axial methyl groups, and the remaining skew conformation has both methyl groups in the preferred[32,37] equatorial dispositions. Experiment suggests[34,36] and theory supports[32,37] the conclusion that the skew conformation having two equatorial methyl groups is preferred. P.A. MacNeil and co-workers then attempted to carry out low temperature n.m.r. to determine the conformational aspects of the rhodium complexes; this confirmed[31] the absolute configuration of the ligand and provided an insight into the stability of the ring. Other workers, N.C. Payne and D.W. Stephen, mainly[38,39] concentrated on the platinum complexes of the two chiral diphosphines; this work was carried out to give a greater understanding of the steric and electronic properties of diphosphine ligands by comparison with those of their analogous

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complexes[77,40,41] containing (+)-diop and s,s-chiraphos. However, less is known of the properties of bidentate phosphines which form four-membered rings, or those of phosphine ligands in which the chiral centre is not part of the backbone.

Steric Effects

It is convenient to distinguish between electronic and steric effects in n.m.r. parameters.

(a) Electronic - arise as a result of transmission along chemical bonds e.g. in changing from $P(p-C_6H_4OCH_3)_3$, to $P(o-C_6H_4Cl)_3$

(b) Steric - arise as a result of forces (usually non-bonding) between parts of a molecule, for example, changing from $P(p-C_6H_4CH_3)_3$, to $P(o-C_6H_4CH_3)_3$. Other examples of this are in changing n in a chelate complex $[Ph_2P(CH_2)_nPPh_2]M(CO)_4$; or from $P(p-C_6H_4CH_3)_3$, to $P(o-C_6H_4CH_3)_3$.

The above two effects cannot always be separated into two individual components. For example, increasing the angles between substituents will decrease the percentage of s-character in the phosphorus lone pair. Changing the electronegativity of atoms can also affect bond distances and angles[42]. Hence, electronic and steric effects are intimately related, and it is convenient to define two parameters, the Electronic Parameter[43],ν, and the Steric Parameter[44],φ.

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Also relevant in this connection are Mann's coordination chemical shifts[45,46] (Δ = $\Delta_{complex} - \delta_{free}$) which depend on the type of central metal atom and on the change in RPR angles on coordination. This is consistent with the usually observed high frequency (positive Δ) shift[9,25], as now found for the ligand complexes under discussion (see chapter 2). It is also found that the increase in RPR angles increases the phosphorus s-character in the P-R bonds and decreases it in the lone pair. This is reflected in the coupling constants. Conversely, a decrease in the s-character in $^1J(PP)$ shows the opposite trend.

One-bond Coupling Constants between Phosphorus and Metals

A general consensus has evolved from previous studies[47-52] that $^1J(M-P)$ in transition metal phosphine complexes[51-55] is dominated by the Fermi contact term:

$$J_{AB} = \frac{64h\beta^2}{9^3\Delta E} \ \gamma_A\gamma_B\xi^2\alpha_A^2\alpha_B^2 S_A^2(O)S_B^2(O) \qquad\qquad 1.0$$

where:
ξ =		normalising factor for the valence bond function describing the A-B bond
$S^2(O)$ =		the quantities that can vary in a series of compounds are the s-electron densities
α^2 =		the s-character of the hybrid orbitals involved in A-B bonding
ΔE =		the average triplet excitation energy

The s-character of the orbital at phosphorus used for M-P bonding and, to a lesser extent, $S^2p(O)$ are known to increase with increasing electronegativity of the alkyl groups. For a series of related compounds it is found that a good correlation between $^1J(M\text{-}P)$ and the electronegativity of the α-atoms of the substituent(s) alkyl[55] group exists. The one bond coupling will be met frequently relating to $^1J(W\text{-}P)$ coupling in order to ascertain the degree of tungsten-phosphorus overlap which gives some credence to the degree of bonding.

Ligands of the type $Ph_2P(CH_2)_nPPh_2$ and their Complexes, n=1,2,3

To go back to the earlier discussion on the evidence of ring strain on the three chelate complexes, the P-M-P bond angles of these are given below in Table 1.01. From this data it can be seen that the PMP angle approaches 90° in complexes containing a three-carbon backbone (dppp) and that the angle decreases as the ring size decreases, i.e. the ring strain increases in the order dppp complexes < dppe complexes < dppm complexes. However, it is found that the effect of increased ring strain as measured by PMP angles does not affect the n.m.r. parameters in a simple manner. The four-membered ring complexes[56] have the greatest deshielding for the Mo and W complexes, yet the shieldings in complexes with six-membered rings (with less strain) are smaller than those with the five-membered rings. The phosphorus coordination chemical shift $\Delta(\delta P)$ for cis-$(CO)_4ML_2$ complexes is found to be[17] 59, 43 and 25 ppm for Cr, Mo and W respectively.

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Table 1.01. Selected Structural Data of Biphosphine Transition Metal Complexes

COMPLEX	RING SIZE	L PMP/°	L MPC/°	Refs.
dppm Mo(CO)$_4$	4	67.3	a	57
dppe Cr(CO)$_4$	5	83.4	a	58
dppm PdCl$_2$	4	73	94.7	59
dppe PdCl$_2$	5	85	108.5	59
dppp PdCl$_2$	6	90	115.9	59
dppm Pd(SCN)$_2$	4	73.2	a	60
dppe Pd(SCN)(NCS)	5	85.1	a	60
dppp Pd(NCS)$_2$	6	89.1	a	60
dppe Ir(cod)CH$_3$	5	84.9	108.8	61
dppp Ir(cod)CH$_3$	6	93.4	114.5	61

a. Data not reported

The order of increasing $\Delta(\delta P)$ on moving up the group is probably a reflection of the metal radius which increases from chromium to tungsten. The large $\Delta(\delta P)$ for five-membered rings compared to six-membered analogues is due to ring strain[11]; from PMP angle strain it would be expected that $\Delta(\delta P)$ would be even greater for the four-membered ring systems, but this is found not to be the case. Hence, the validity of quantifying the ring strain in terms of PMP angle may be dubious. It has been suggested[60] that for the palladium thiocynate complexes the four-membered ring is the most strained structure as shown by the mode of coordination of the thiocyanate ligands. When coordinated via the sulphur atom the ligand is bent and occupies more space than when it is coordinated via nitrogen when it is linear. Steric crowding around the nucleus would tend therefore to force the thiocyanate ligand to coordinate via nitrogen and thereby reduce the crowding. In the metal carbonyls the two bond coupling constant, $^2J(P\text{-}CO)$, depends upon the metal and the stereochemistry it adopts. This can be understood only if the signs of the couplings are known. However, one of the problems of observing the carbonyls in a complex is that large accumulation times are required due to their high T_1 value (spin-lattice relaxation time) and the absence of any NOE (Nuclear Overhouse Effect). This problem can be circumvented by the introduction of a relaxating agent such as Cr(acac)$_3$ which has the effect of reducing T_1 so that a higher pulse repetition rate can be maintained. Sign determinations[56] of J(PP) in complexes of symmetrical ligands are based upon using spin-tickling experiments[67]. The complexes of the type mentioned on page 24 and elsewhere are octahedral and therefore contain two types of CO group (only if ligand is cis) - axial and equatorial.

The observed trends in phosphorus-phosphorus and the phosphorus-carbonyl couplings can be attributed to geometrical and electronic changes in the through-bond coupling pathways. This coupling pathway can be made up of two components: "through the metal" and "backbone" contributions as suggested by Grim et al[21]. For the complexes of dppb the backbone contribution is effectively zero through greater than five sigma bonds and therefore this pathway may be ignored, so that the observed coupling is predominantly via the through-metal component. The almost incremental increase in $^2J(PP)$ in the three complexes of dppb and the corresponding complexes of dppp, which are independent of the size of the metal radius, are ascribed to a backbone dependence coupling pathway giving a contribution of -6.8 Hz in the latter complexes: this value may be compared with that of the free ligand[18], ± 1.0 Hz where there is no special rigid stereochemical relationship of the two phosphorus atoms. In the complex cis-$(Me_3P)_2M(CO)_4$ which has no backbone connection, the PMP interbond closely approaches 90° and J(PP) has values of -36.0, -29.7 and -25.0, for Cr, Mo and W respectively[63].

If a comparison is made of the complexes having a five-membered chelate ring with those of dppb there is a significant dependence upon the metal atom. Thus the change in $^2J(PP)$ in going from dppb $\longrightarrow$ dppe is +16.2, +17.5 and +20.5 Hz for Cr, Mo and W respectively, while for dppb $\longrightarrow$ cis-vpp the corresponding changes are +27.0, +30.2 and +34.8 Hz. These coupling constants are found to be consistent with there being significant, but different, backbone contributions in the complexes of dppe and cis-vpp. It is seen from these results that the complexes with

a four-membered ring the differences are found to be very substantial, the chromium complex being the most obvious one, this is expected as a result of the through-metal coupling becoming more significant.

Table 1.02. Average J(PP)/Hz for [Ph$_2$P(CH$_2$)$_n$PR^{1}R^2]M(CO)$_4$

	n = 1	n = 2	n = 3
Metal[a]			
None	114	28	0
Cr	24	12	41
Mo	15	5	28
W	21	4	22

a. Data taken from reference 21

Table 1.03. Average observed and calculated values of J(PP)/Hz for [Ph$_2$P(CH$_2$)$_3$PR^{1}R^2]M(CO)$_4$

M[a]	$^1J_{pp}{}^M$	$^2J_{pp}{}^M$	J(PP) (possible values)	J(PP) (found)
Cr	30	41	71 or 11	12
Mo	30	28	58 or 2	5
W	30	22	52 or 8	4

a Data taken from reference 21

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As it can be seen from Table 1.03, the results are in fairly close agreement for Cr and Mo but poor for W: $|J(PP)|$ for Cr observed 12 Hz, calculated 11 Hz; for Mo observed 5 Hz, calculated 2 Hz; for W observed 4 Hz, calculated 8 Hz.

To summarise the discussion so far; the complexes which have been mentioned previously have been used to demonstrate that the overall phosphorus-phosphorus coupling constants can be separated into two components transmission via the σ bonds in the ligand backbone and via the σ bonds through the metal centre.

The Coordination behaviour of Hexatertiary Ligands

The only known hexatertiary phosphine (see Fig. 1.06) synthesised by King at the time of publication of his paper is of particular interest. This is due to the relative locations of its phosphorus atoms which resemble the relative locations of the donor atoms in the well-known hexadentate ligand ethylenediaminetetraacetic acid (EDTA) and hence should permit the hexatertiary phosphine, Fig. 1.06, to function as a hexadentate ligand as in Fig. 1.18.

Fig. 1.18.

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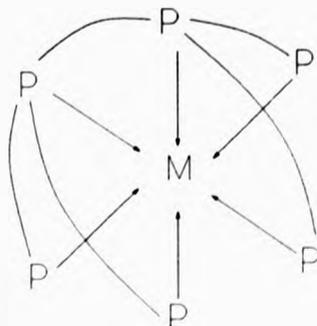
King carried out an extensive survey[44] of the reactions of this phosphine, with various transition metal compounds; however, it was found that despite the wide variety of transition metal systems investigated, no complexes, Fig. 1.06, were obtained in which it unambiguously acted as hexadentate ligand. Most often it was found that the phosphine (Fig. 1.06) acted as a tetradentate ligand in products obtained by reactions with metal halide derivatives where the chances for observing hexadentate behaviour might have been the greatest. Apparently it is difficult to bend the five CH_2CH_2 bridges in the phosphine (Fig. 1.06) around so that all six phosphorus atoms can bond to a single metal atom as in the structure described by Fig. 1.18. However there was no particular difficulty in bonding all six phosphorus atoms to a pair of metal atoms (Fig. 1.19).

The three metal hexacarbonyls $M(CO)_6$ (M=Cr, Mo and W) all react with the phosphine (Fig. 1.06) in a boiling aromatic hydrocarbon solvent (toluene or xylene) to give the light yellow compounds, [Hexatertiary phosphine] $[M(CO)_3]_2$, which were characterised by infrared spectroscopy. The above mentioned bimetallic complexes of the phosphine (Fig. 1.06) show bonding to the metal atoms see Fig. 1.19 overleaf.

Fig. 1.19. [Hexatertiary phosphine] [M(CO)₃]₂
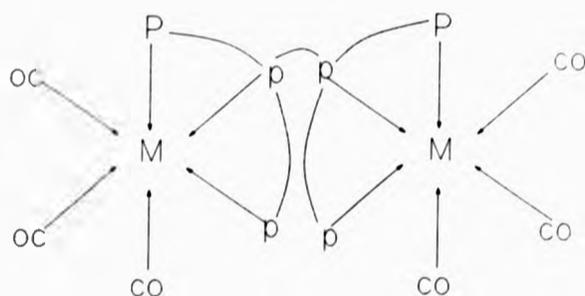
The reaction between the cycloheptatrienemolybdenum complex $C_7H_8Mo(CO)_3$ and the phosphine (Fig. 1.06) at room temperature also gave the above identifiable bimetallic product.

CHAPTER 2

Cis-substituted Octahedral Complexes of Chiral Ligands

Introduction

The measurement of the n.m.r. parameters of a number of cis-substituted metal carbonyl derivatives of the chiral bis(diphosphines) is described which provides some understanding of metal-ligand bonding in Group VIa metal carbonyl complexes which have been the subject of numerous bonding studies using ^{31}P n.m.r.[65,67], i.r.[68,69], and u.v. spectroscopies[70,71]. Explanations of the data obtained for 2D-n.m.r. concerning the carbon backbone on the ligands are also presented.

The determination of the relative signs of coupling constants was undertaken via 2D-n.m.r.; suffice it to say that a positive coupling constant refers to an interaction which minimises the spin-coupling energy when the two nuclear spins are in the antiparallel configuration, and conversely, a negative coupling corresponds to a minimum coupling energy when the nuclear-spins are in the parallel configuration.

Results and Discussion

The purpose of this work was to synthesise and study the coordination behaviour of asymmetric bidentate ligands; it is well known from studies carried out on rhodium complexes that when these type of ligands are coordinated to a central metal atom, the ring structure adopts a rigid chiral conformation. From the widely studied saturated five-membered chelate rings, it is also well known, that the ring in this type

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of complex adopts a puckered chiral conformation. However, with a straight chain carbon skeleton in the backbone and when the donor atoms are symmetrically substituted then such a ring is found to rapidly interconvert from one chiral conformation to the other, see chapter 1. In the complexes studied which have an asymmetric carbon centre, the chelate ring may be fixed into a single conformation by the requirement that the substituent, (in this case the methyl group(s)), occupy an equatorial position. Due to a lack of interest shown in these chiral ligands, it was of interest to synthesise the asymmetric ligands and to study their coordination behaviour by ^{31}P and ^{13}C n.m.r..

The plan of work was as follows:

(i) Synthesise unsymmetrical diphosphines which could serve as potential bidentate chelators

(ii) Complex the chiral ligands (Fig 1.0) with $M(CO)_6$ where $M = Cr$, Mo, W

(iii) To form the diselenides and disulphides (see chapter 4).

(iv) To attempt the preparation of new di- and tri- complexes which are discussed in detail in Chapter 3.

(v) Attempt the preparation of pentaphosphines from the triphosphines, shown in Fig. 3.0 (Chapter 3)

(vi) To study the ^{31}P and ^{13}C nuclear magnetic resonance properties.

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Each of the five chiral ligands (Fig. 1.0) was complexed with Cr, Mo and W hexacarbonyl and the series for each ligand studied. In those species where the two phosphorus atoms are magnetically and chemically inequivalent two phosphorus signals were observed which showed J(PP) coupling in most cases. In those species where the two phosphorus atoms are magnetically equivalent with respect to the ^{13}C atom, the condition found when ^{13}C is in position C_4 as shown in Fig. 2.0 for dppmM(CO)$_4$, a first order triplet ^{31}P spectrum will arise. However, if ^{13}C is situated such that the two phosphorus nuclei are magnetically inequivalent, as depicted by C''', C_2 and C_3 in s,s-chiraphos M(CO)$_4$, the ^{31}P spectra of the species form the AA' part of an AA'X spin system (Fig. 2.0).

Spectral Analysis of the AA'X spin-system

Taking the symmetrical ligand complexes, bis(diphenylphosphino) alkane metal carbonyl complexes, for the explanation of an AA'X spin system, it is apparent that the ^{13}C spectrum of the axial carbonyl atoms (C_1, dppmM(CO)$_4$, Fig. 2.0) is part of a A_2X spin system, where X = C_1, AA = ^{31}P. Since the two phosphorus atoms are magnetically and chemically equivalent (AA = ^{31}P) the ^{13}C$_1$O spectrum will therefore consist of a triplet with spacings of cis-^{2}J(^{31}P-^{13}C$_1$O). In contrast, the ^{13}C spectra of dppbM(CO)$_4$ for the equatorial carbon atoms (^{13}C$_2$O$_{eq}$ and ^{13}C$_3$O$_{eq}$ at high frequency, Fig. 2.0) are the X part of an AA'X spin system, where X=C_2 or C_3 and AA'=^{31}P. For the C_2 atom the trans phosphorus (P_A in Fig. 2.0 for dppbM(CO)$_4$), is magnetically inequivalent to the cis phosphorus (P_A') and so it follows that the coupling trans ^{2}J(^{31}P$_A$ - ^{13}C$_2$O) $\neq$ cis ^{2}J(^{31}P$_{A'}$ - ^{13}C$_2$O). This also applies to C_3, which

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Fig. 2.0. Numbering scheme adopted for chiral diphosphine complexes

which give AA'X spectra.

(prophos) M(CO)₄

M = Cr, Mo, W

dppbM(CO)₄

dppmM(CO)₄

s,s-chiraphos M(CO)₄

43
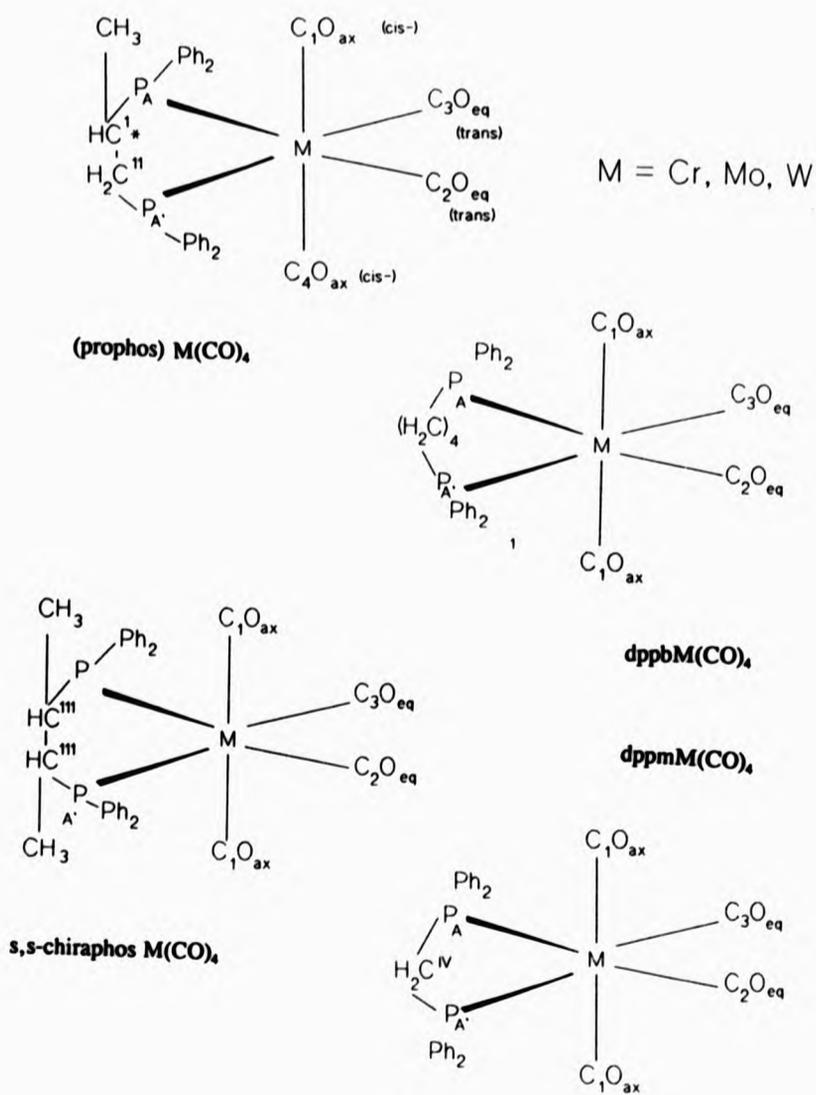
Fig. 2.01. Numbering Scheme adopted for chiral diphosphine complexes towards the phenyl region for the tetracarbonyl complexes.
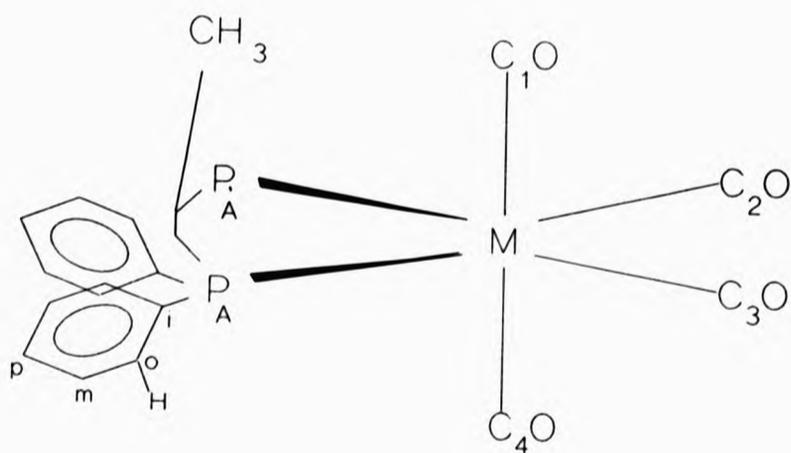
$$M = Cr, Mo, W$$

gives an identical pattern to C_2. It is generally found that the trans-carbonyls appear at a higher frequency chemical shift with respect to a cis-CO; however it is not possible to distinguish between the cis $^2J(^{31}P-^{13}CO)$ and trans $^2J(^{31}P-^{13}CO)$ couplings solely from the spectral analysis. These couplings may be reliably identified by analogy with the magnitude of the cis $^2J(^{31}P-^{13}CO)$ coupling for the axial carbonyl groups, which are normally readily measured directly from the ^{13}C spectrum.

When A and X are different nuclear species three coupling constants determine[70] the spectra given by the AA'X spin-system, but it is generally more convenient to work in terms of the parameters N,L and J defined as:

$$N = J_{AX} + J_{AX'} \qquad 2.0$$

$$L = J_{AX} - J_{AX'} \qquad 2.1$$

$$J = J_{XX'} \qquad 2.2$$

Hence, three pieces of information are involved for the spectral analysis. The X part of an AA'X spectrum consists of six lines, of which two (the N lines) are strong and of equal intensity separated by N and have a combined intensity equal to half of the total intensity of the X spectrum. Centrally positioned between the N lines are two degenerate transitions. The remaining two lines are of equal intensity and symmetrically placed about the central degenerate pair of lines, as exhibited by the CO_{eq}(trans), C_i and C_e in Fig. 2.02.

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Fig 2.02 Carbonyl and phenyl region of the ^{13}C n.m.r spectrum of dppbMo(CO)$_4$ showing the ipso (C$_i$) ortho (C$_o$), meta (C$_m$) and para (C$_p$) carbon atoms.
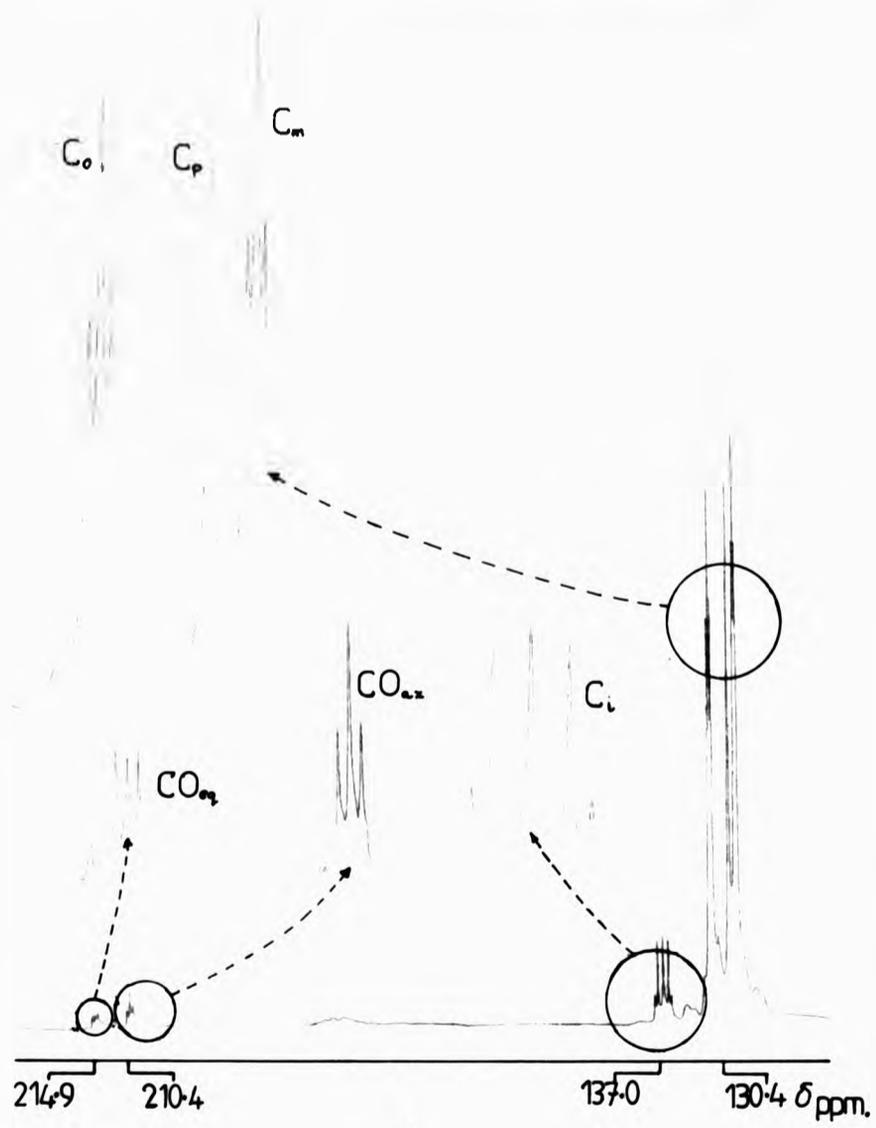
They may occur within or outside (as is the case here) of the N lines and their separation[71] is given by s, where:

$$s = (L^2 + 4J^2)^{1/2} \qquad 2.3$$

This is shown in Fig. 2.02, where the X part of an AA'X spectrum of the complex dppbMo(CO)$_4$ shows all five lines fully resolved for carbons CO$_{eq}$(trans), C$_i$ and C$_o$. The long range coupling through the metal centre of the complex to C$_m$, $^5J(^{31}P_{A'}-^{13}C_m)$, can be taken to be zero. From equations 2.0 and 2.1 it therefore follows that N=L. As N is readily inferred directly from the spectrum, a value of L can be substituted into equation 2.3 and a value of |J| determined.

Once J is known, the AA'X pattern given by C$_o$ can be analysed fully and hence $^4J(^{31}P_{A'}-^{13}C_o)$ may be determined using equation 2.3, such values are found[56] to be small <1.5 Hz and serve to justify the assumption that $^5J(^{31}P_{A'}-^{13}C_m) = 0$. In subsequent calculations the value of |J| derived from the $^{13}C_o$ spectrum can be used.

Previous studies of transition metal complexes with unsymmetrical bis(diphenylphosphino) ligands of the type $Ph_2PCH(CH_3)CH_2PPh_2$, $Ph_2PCH(CH_3)CH(CH_3)PPh_2$, $Ph_2PCH(CH_2CH_3)CH_2PPh_2$, $Ph_2P(CH_2)_2CH(CH_3)PPh_2$, $Ph_2P(CH_2)_3CH(CH_3)PPh_2$ have been as rhodium complexes[56], and were then limited to the ligands $Ph_2PCH(CH_3)CH_2PPh_2$ (prophos) and $Ph_2PCH(CH_3)CH(CH_3)PPh_2$ (s,s-chiraphos).

In this work more ligands and their complexes with Cr, Mo and W have been studied. Since these new complexes have chemically and magnetically different phosphorus atoms, the ^{31}P n.m.r. spectra show simple AX type spectra with the expected pairs of doublets except for the complexes of (s,s)-chiraphos. It is observed from the ^{31}P n.m.r., Table 2.01, that the magnitude of $|J(PP)|$ for the complexes increase in the same order $W < Mo < Cr$ found for the cis-$L_2M(CO)_4$ complexes; this trend is found to be in agreement with that for similar diphosphines[9,17,21].

As shown by Table 2.0 the phosphorus chemical shifts for the chiral ligands can be compared with those of the biphosphine symmetrical ligands dppe, dppp and dppb which give phosphorus chemical shifts of -13.2, -17.2 and -17.0 ppm, respectively. It is observed that only the ligands dppp and dppb are in favourable agreement to those of $Ph_2P(CH_2)_2CH(CH_3)PPh_2$ and $Ph_2P(CH_2)_3CH(CH_3)PPh_2$, respectively; therefore, it can be stated unequivocally that $\delta^{31}P_a$ for the three carbon backbone ligand $Ph_2P(CH_2)_2CH(CH)_3PPh_2$ corresponds very well with that of $\delta^{31}P$ for dppp; as shown by Fig. 2.03.

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$$\begin{array}{c} CH_3 \\ | \\ CH_2CH_2CH \end{array}$$

Ph₂P ∕   ∖ PPh₂

$\delta^{31}P_A = -3.7$ ppm

$$\begin{array}{c} CH_3 \\ | \\ CH_2CH_2CH_2CH \end{array}$$

Ph₂P ∕   ∖ PPh₂

$\delta^{31}P_A = -1.30$ ppm
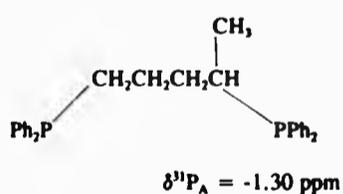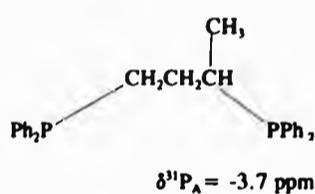
Since it is now known which phosphorus atom (in this case, $\delta^{31}P_B$) gives a chemical shift at low frequency, this method can be used as a diagnostic aid for decoupling experiments such as double resonance for determination of sign in the ligand or their respective complexes since the chemical shifts are found to be in fairly close agreement, differing by 2-3 ppm. when compared with dppp and dppb complexes, respectively (signs determined by 2D-n.m.r. are reported in this work). From Table 2.0, it is interesting to note that the phosphorus chemical shifts for the ligands and complexes of dppe type chiral ligands are not in agreement with those determined previously[56] for a five membered ring complex. It may have been predicted that the larger electron releasing effect (positive inductive effect) of the methyl groups on the

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Table 2.0. ^{31}P n.m.r. data for chiral ligands and their complexes

COMPOUND	$^c\delta(^{31}P_A)$/ppm	$\delta(^{31}P_B)$/ppm
Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$	-9.2	
[Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$]Cr(CO)$_4$ [b]	84.0	
[Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$]Mo(CO)$_4$ [b]	62.3	
[Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$]W(CO)$_4$ [b]	46.9	
Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$	1.0	-21.3
[Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$]Cr(CO)$_4$	88.5	71.8
[Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$]Mo(CO)$_4$	66.4	49.3
[Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$]W(CO)$_4$	52.0	34.0
Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$	-6.1	-31.0
[Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$]Cr(CO)$_4$	85.5	67.7
[Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$]Mo(CO)$_4$	66.2	48.1
[Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$]W(CO)$_4$	51.0	32.2
Ph$_2$PCH(CH$_3$)(CH$_2$)$_2$PPh$_2$	-3.7	-17.7
[Ph$_2$PCH(CH$_3$)(CH$_2$)$_2$PPh$_2$]Cr(CO)$_4$	54.7	43.5
[Ph$_2$PCH(CH$_3$)(CH$_2$)$_2$PPh$_2$]Mo(CO)$_4$	33.6	22.5
[Ph$_2$PCH(CH$_3$)(CH$_2$)$_2$PPh$_2$]W(CO)$_4$	13.4	2.6
Ph$_2$PCH(CH$_3$)(CH$_2$)$_3$PPh$_2$	-1.3	-16.2
[Ph$_2$PCH(CH$_3$)(CH$_2$)$_3$PPh$_2$]Cr(CO)$_4$	64.4	43.5
[Ph$_2$PCH(CH$_3$)(CH$_2$)$_3$PPh$_2$]Mo(CO)$_4$	46.0	26.3
[Ph$_2$PCH(CH$_3$)(CH$_2$)$_3$PPh$_2$]W(CO)$_4$	30.3	8.3
Ph$_2$P(CH$_2$)$_2$PPh$_2$	-13.2	
Ph$_2$P(CH$_2$)$_3$PPh$_2$	-17.2	
Ph$_2$P(CH$_2$)$_4$PPh$_2$	-17.0	

a.   All ^{31}P chemical shifts observed in deuterated CDCl$_3$.
b.   No diastereomers observed.
c.   All chemical shifts relative to external 85% H$_3$PO$_4$ = 0.0 ppm.

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C-atom backbone of s,s-chiraphos would have tended to shield the phosphorus nuclei even more thereby causing a low frequency resonance of the phosphorus nuclei compared to dppe. However, such an argument is found not to be consistent with the observed order, since steric, in addition to the electronic factors, influence the chemical shift, as mentioned in Chapter 1. In the observation of s,s-chiraphos (-9.2 ppm) and dppe(-13.2 ppm) phosphorus chemical shifts, the electronic influences are generally of a similar magnitude, and therefore, the differences in the phosphorus chemical shifts of the chiral ligands can be rationalised on the basis of the size of the substituent group(s) attached to the phosphorus atom. On this basis, in the case of s,s-chiraphos, the larger methyl groups have a steric effect which most probably cause a greater distortion of the secondary carbon atoms in the carbon backbone from a sp^3 hybridised carbon atom which leads to a decrease in the s-character of the lone pair electrons; this produces a greater deshielding of the phosphorus atoms which results in a small high frequency phosphorus resonance. A similar argument to the one presented here has been used to explain orders of chemical shifts for monophosphines[46] when the electronic differences between the substituents are small. Similarly, the above argument as explained for s,s-chiraphos was also applied to 1,2-bis(diphenylphosphino)propane and 1,2-bis(diphenylphosphino)butane; the rationale is that the chemical shift values for the high frequency resonance of 1,2-bis(diphenylphosphino)propane allows for the assignment of the high frequency resonance to the phosphorus atom adjacent to the secondary carbon atom, as shown previously in Fig. 2.03. It appears from the phosphorus chemical shift, $\delta^{31}P_A$, that as a stronger electron donating group is substituted onto the carbon backbone, in this

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case an ethyl group, the phosphorus atom becomes even more deshielded than dppe, hence a high frequency shift occurs for $\delta^{31}P_A$, when compared with the free ligand of 1,2-bis(diphenylphosphino)ethane. However, overall the chemical shift for these ligands does not exceed that of dppe(-13.2 ppm), as steric/electronic factors play a major part in the determination of the ^{31}P chemical shift. In this case, the steric factor slightly overrides the electronic parameter.

The ^{31}P chemical shifts for the five diphosphines and diphosphine complexes are presented in Table 2.0. It is observed that complex formation always causes a shift in the position of the phosphorus resonance, $\delta_{free\ ligand}$, to a new value, which is called $\delta_{complex}$. It has been found useful to consider the coordination chemical shift, Δ, (where $\Delta = \delta_{complex} - \delta_{free\ ligand}$) for each complex i.e. the magnitude of the coordination chemical shift on complex formation. In the complexes studied here, it is found that Δ is always positive, agreeing with the well known assumption that the formation of a donor bond from phosphorus to the metal results in a decrease of electron density on the phosphorus atom and thus a decrease in the shielding and the increase in the chemical shift. See Table 2.01.

Before the data reported for the asymmetric diphosphine complexes can be analysed, a general consideration of the factors[23] influencing the absolute value of the ^{31}P resonance in the complexes is warranted. It may be possible to use these results to obtain a better understanding of the structural and bonding features of the diphosphine and their complexes. The following factors have been considered:

(i)   the formation of a donor σ-bond from phosphorus to the metal

(ii)   the contribution from dπ-dπ back donation from the metal to phosphorus

(iii)   inductive effects of the diphosphine substituents

(iv)   bond rehybridisation effects due to changes in phosphorus bond angles on complex formation

(v)   electronegativities of the atoms joined to the phosphorus and

(vi)   steric effects, including chelation leading to ring strain

From Table 2.01, the coordination chemical shifts are in the order Cr > Mo > W for five, six and seven membered ring complexes with increase in metal radii. It is interesting to note that the coordination chemical shift, $\Delta(^{31}P_a)$, for the 5, 6 and 7 membered rings closely parallels that for the complexes[56] of dppe, dppp and dppb. Similarly, for the chiral complexes[21] of 1,3-bis(diphenylphosphino)butane the $\Delta(\delta^{31}P_a)$ chemical shifts are in very good agreement to that of the alkylphenylphosphino $[Ph_2P(CH_2)_3PPhR]M(CO)_4$ where R = Me, Et or i-Pr and M = Cr, Mo and W. This shows that the alkyl substituents on the phosphorus or the carbon backbone have a negligible effect on the coordination chemical shift on both types of chiral complexes.

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The much larger coordination chemical shift shown by five-membered chelate rings over the six-membered rings can be attributed principally to the decrease in the bond angle at the phosphorus atom in the complexes so far discussed. It is interesting to note, based on the above discussion, that the expected behaviour for the four-membered rings[65] would show the largest coordination chemical shift. However, contrary to this expectation[56] this is not the case and the large high frequency shift shown by the five-membered ring is anomalous. However, for a series of related complexes, such as those described in Table 2.01 the coordination chemical shift, $\Delta(^{31}P_{b})$, is fairly constant for a range of phosphorus ligands, and therefore for known structures it is often possible to predict closely the ^{31}P chemical shifts of coordinated ligands (see also Fig. 2.04). A knowledge of the factors which influence ^{31}P chemical shifts in phosphine complexes, as also outlined in Chapter 1, made the analysis of the ^{31}P n.m.r. spectra for the chiral ligand complexes fairly straightforward, as shown in Table 2.01. As shown by Fig. 2.04 a distinct pattern develops governing the chemical coordination shifts [72] of five-membered ring complexes compared with six- and seven-membered ring complexes, which demonstrates nicely two important features:

(i)   A monotonic decrease in Δ as the group Cr, Mo and W is descended.

(ii)   For any particular metal atom the ranges of Δ for a given ring size do not overlap.

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Table 2.01. ³¹P n.m.r. data for coordination chemical shift and coupling constants

COMPOUND	Δ(δ³¹P_A)/ppm	Δ(δ³¹P_B)/ppm	J(P_A,P_B)/Hz
Ph₂PCH(CH₃)CH(CH₃)PPh₂			
[Ph₂PCH(CH₃)CH(CH₃)PPh₂]Cr(CO)₄ [b]	93.2		
[Ph₂PCH(CH₃)CH(CH₃)PPh₂]Mo(CO)₄ [b]	71.5		
[Ph₂PCH(CH₃)CH(CH₃)PPh₂]W(CO)₄ [b]	56.1		
Ph₂PCH(CH₃)CH₂PPh₂			22.0
[Ph₂PCH(CH₃)CH₂PPh₂]Cr(CO)₄	87.5	93.4	14.7
[Ph₂PCH(CH₃)CH₂PPh₂]Mo(CO)₄	65.4	70.6	4.3
[Ph₂PCH(CH₃)CH₂PPh₂]W(CO)₄	51.0	55.3	5.5
Ph₂PCH(CH₂CH₃)CH₂PPh₂			19.8
[Ph₂PCH(CH₂CH₃)CH₂PPh₂]Cr(CO)₄	91.6	98.7	14.6
[Ph₂PCH(CH₂CH₃)CH₂PPh₂]Mo(CO)₄	72.3	79.1	4.9
[Ph₂PCH(CH₂CH₃)CH₂PPh₂]W(CO)₄	57.1	63.2	4.9
Ph₂PCH₂(CH₃)₂PPh₂			no coupling observed
[Ph₂PCH₂(CH₃)₂PPh₂]Cr(CO)₄	58.3	61.1	39.1
[Ph₂PCH₂(CH₃)₂PPh₂]Mo(CO)₄	37.2	40.2	28.1
[Ph₂PCH₂(CH₃)₂PPh₂]W(CO)₄	17.1	20.3	20.8
Ph₂PCH(CH₃)(CH₃)₂PPh₂			no coupling observed
[Ph₂PCH(CH₃)(CH₃)₂PPh₂]Cr(CO)₄	65.7	59.7	26.9
[Ph₂PCH(CH₃)(CH₃)₂PPh₂]Mo(CO)₄	47.3	42.5	22.0
[Ph₂PCH(CH₃)(CH₃)₂PPh₂]W(CO)₄	31.6	24.5	17.1

a.   All positive values are downfield from 85% H_3PO_4.
b.   No diastereomers observed.
c.   Coordinated chemical shift, $\Delta = \delta_{complex} - \delta_{free\ ligand}$.

It is useful to consider[20]the tridentate phosphorus tungsten complex (Fig. 1.12) in conjunction with the above work where the complex contains phosphorus atoms in bicyclic structures.

Since it has been established in this work and elsewhere[20,22] that when phosphorus is coordinated to a metal as part of a five-membered chelate ring there is an unusually high frequency change in the phosphorus chemical shift; it is therefore interesting to observe that the phosphorus atom, P_A, (Fig. 1.12) which is incorporated in both five- and six-membered rings should exhibit a Δ value in the region associated with six-membered rings. Since these new complexes have chemically and magnetically different phosphorus atoms, their [31]P n.m.r. spectra show a pair of doublets from which J(PP) can be read directly. Previously numerous J(PP) coupling constants for cis-$L_2M(CO)_4$ compounds, where L is a phosphorus donor and M is Cr, Mo or W, have been tabulated[23], but very few have been measured for the two donor atoms being tertiary diphosphines. It is generally found, in line with other diphosphines discussed, that the magnitude of |J(PP)| for the compounds reported here increases in the same order (W < Mo < Cr).

In the six-membered ring complexes of alkyldiphenyldiphosphines[21] it was observed that the coordination chemical shifts for the alkylphenylphosphino groups are slightly smaller than that of the diphenylphosphino group; a similar trend is also found for the six-membered complexes of 1,3-bis(diphenylphosphino)pentane where the phosphorus atom nearest to the substituted secondary carbon atom shows a slightly lower coordination shift, $\Delta(\delta^{31}P_A)$, (ca. 3 ppm) than the diphenylphosphino end, $\Delta(\delta^{31}P_B)$.

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Fig. 2.04. Dependence of ^{31}P coordination chemical shift on the ring size
and metal atom for Group VIa metal carbonyl complexes of chiral ligands.

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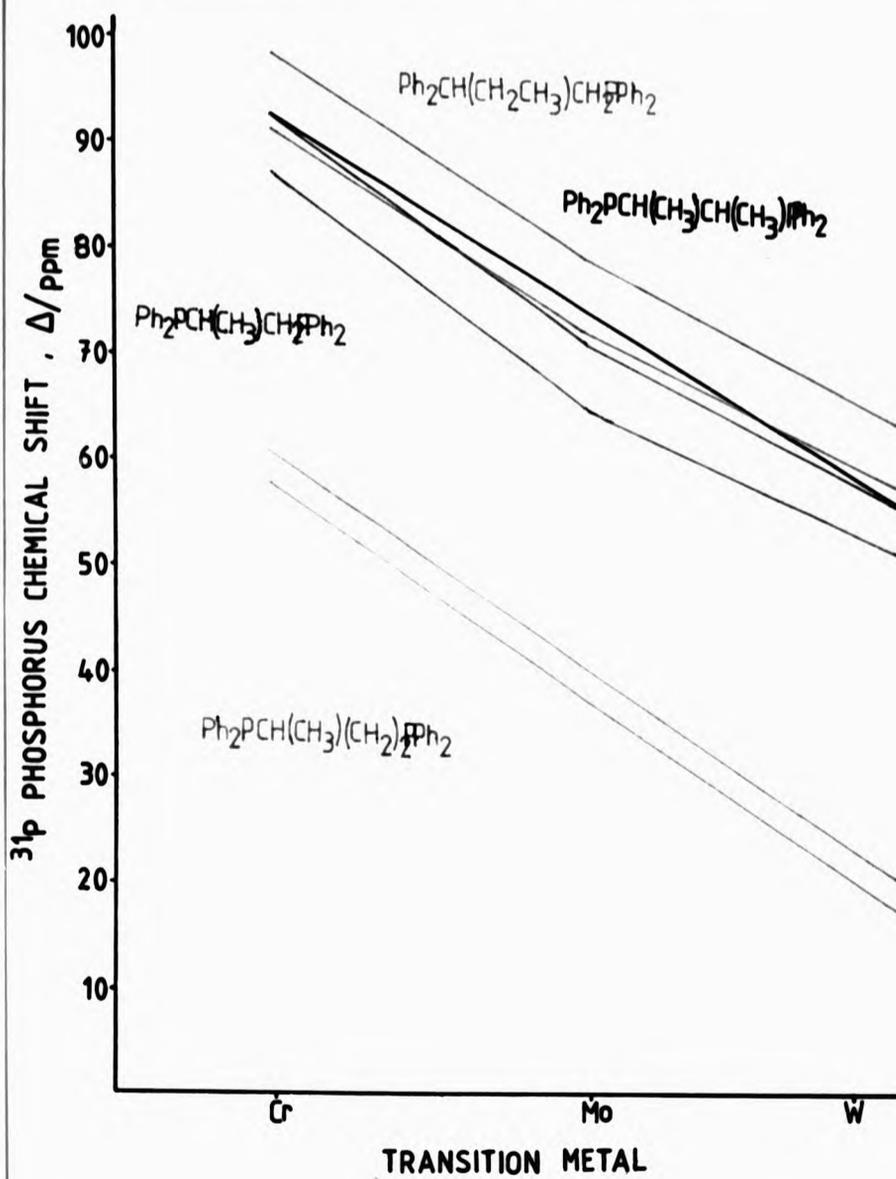
A similar trend is also found for five-membered ligand complexes, as shown in Table 2.01. This observation is contrary to that determined for the five-membered alkylphenylphosphines by Grim[7] and co-workers where the coordination chemical shift for the diphenylphosphide shows a lower value than that observed for the phosphorus attached to a secondary substituted carbon atom in the same compound. The large coordination shifts shown by five-membered ring complexes may be attributed to the distortion of the P-M-P and M-P-C angles; the ideal bond angles in octahedral complexes should be 90° (P-M-P) and 109° (at the P atom, M-P-C), however, no data are at present available for the complexes under study. The resulting changes in hybridisation might be expected to have a marked effect on the position of the phosphorus resonance, as discussed earlier, the unexpected high frequency shift of the phosphorus atom $\delta^{31}P_A$ (Fig. 2.03) closest to the substituted secondary carbon atom causes a steric effect leading to a much lower coordination shift, $\Delta(\delta^{31}P_A)$, than that further removed, $\Delta(\delta^{31}P_B)$.

From Table 2.01 a gradual decrease of $J(P_AP_B)$ is observed as the transition metal radius increases for the six- and seven-membered ring complexes, the seven-membered chelates showing a gradual average decrease of 4.9 Hz; this decrease in magnitude of $J(P_AP_B)$ down the group must therefore, if conformational effects are the same for each complex, arise from differences in the through-the-metal couplings. As mentioned earlier in Chapter 1 and also in the discussion on symmetrical ligands by Grim[21] and co-workers suggest that values of $^nJ(^{31}P-^{31}P)$ within a chelate-ring structure can be considered as a sum of the "through-the-metal" and "through-the-backbone" contributions as shown by the equation below,

$$^2J(^{31}P-^{31}P)=^3J(^{31}P-^{31}P) + ^MJ(^{31}P-^{31}P) \qquad 2.4$$

Values which are typical of $^MJ(^{31}P-^{31}P)$ in such complexes are -41.0 Hz, -28.0 Hz and -22.0 Hz for chromium, molybdenum and tungsten respectively[21]. From the results of Table 2.01 for prophos complexes, therefore, it is possible to make approximate calculations of $^3J(^{31}P-^{31}P)$, although in applying this equation it is essential to take into account signs of coupling constants. Since the signs of $J(^{31}P_A^{31}P_B)$ are not known, two sets of values for $^3J(^{31}P_A-^{31}P_B)$ are possible for the chiral ligand complexes:

i) if $J(^{31}P_A^{31}P_B)$ is positive, $^3J(^{31}P_A-^{31}P_B) = +55.70$ Hz, +32.3 Hz and +27.5 Hz for Cr, Mo and W respectively;

ii) if $J(^{31}P_A^{31}P_B)$ is negative, $^3J(^{31}P_A-^{31}P) = +26.4$ Hz, +23.7 Hz and +16.5 Hz for Cr, Mo and W respectively.

Since the conformational differences do not differ greatly it is reasonable to assume that $^3J(^{31}P_A-^{31}P_B)$ contributions within the chiral ligand complexes are comparable for different metals. This is found clearly to be the result if values of $J(^{31}P_A-^{31}P_B)$ are negative for these complexes and leads to the prediction that $^3J(^{31}P_A-^{31}P_B)$ is of the order of +22 Hz compared to the free ligand 1,2-bis(diphenylphosphino)propane, which also gives a value of 22.0 Hz. This treatment was undertaken for the ligands

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1,2-bis(diphenylphosphino)propane and 1,2-bis(diphenylphosphino)butane and a summary of such calculations is given in Table 2.02.

It is clear from the results that the values determined experimentally are not in close agreement to those calculated; as before, the explanation for this was earlier rationalised in terms of the steric/electronic effects.

Table 2.02. Comparison of $J(^{31}P_A,^{31}P_B)$ which is found experimentally to that calculated

COMPLEX TYPE	$^3J(^{31}P_A,^{31}P_B)$/Hz	$^2J(^{31}P_A,^{31}P_B)$/Hz	$J(^{31}P_A,^{31}P_B)$/Hzcalc.	$J(^{31}P_A,^{31}P_B)$/Hz expt.
[Ph₂PCH(CH₃)CH₂PPh₂]Cr(CO)₄	-41	+22	-19	±14.7
[Ph₂PCH(CH₃)CH₂PPh₂]Mo(CO)₄	-28	+22	-6	±4.3
[Ph₂PCH(CH₃)CH₂PPh₂]W(CO)₄	-22	+22	0	±5.5
[Ph₂PCH(CH₃CH₂)CH₂PPh₂]Cr(CO)₄	-41	+22	-19	±14.7
[Ph₂PCH(CH₃CH₂)CH₂PPh₂]Mo(CO)₄	-28	+22	-6	±4.9
[Ph₂PCH(CH₃CH₂)CH₂PPh₂]W(CO)₄	-22	+22	0	±4.9
Ph₂PCH(CH₃)CH₂PPh₂	0	+22.0	22.0	.
Ph₂PCH(CH₃CH₂)CH₂PPh₂	0	+19.8	19.8	.

a.   Free Ligand

Analysis of ^{13}C n.m.r. Spectra

A summary of the ^{13}C n.m.r. data obtained in this study is tabulated. Discussion of the data can be simplified by taking advantage of the natural division of the ^{13}C spectra into aliphatic, aromatic and carbonyl regions.

^{13}C-Aliphatic Region

The most complicated of the ^{13}C spectra among those of the ligands studied here is that of 1,4-bis(diphenylphosphino)pentane which was obtained by a DEPT (distortionless enhancement by polarisation transfer) experiment[73,74]. The DEPT experiment gives definite chemical shifts for the three different types of carbon atoms present. With this information the two quartets for the methylene protons are identifiable and both show $|^3J + ^2J|$ coupling. The quartet at a higher chemical shift is attributed to the γ-carbon atom which is two bonds away from the substituted secondary carbon atom, since this γ-carbon is in close proximity to a phosphorus atom (two bonds away) and is more greatly deshielded than that which is directly attached to the secondary carbon atom which has a methyl group showing a positive inductive effect. The third methylene group shows a doublet of $^1J(PC) = 12.2$ Hz and a chemical shift of δ28.1 ppm. The secondary carbon atom shows a chemical shift of δ29.8 ppm with $^1J(PC) = 9.8$ Hz, the methyl group, as would be expected is found at δ16.1 ppm with $^2J(PC) = 16.0$ Hz.

The following ^{13}C chemical shift and coupling constant parameters for the carbon backbone are tabulated in Table 2.03 and Table 2.04. In general, except for the complexes of 1,2-bis(diphenylphosphino)propane, the carbon atoms in the carbon

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backbone all show small high frequency shifts with respect to the free ligand. This trend could reflect an inductive effect accompanying the donation of charge to the metal by the phosphorus atom. Mann has suggested, however, that ^{13}C- chemical shifts in tertiary phosphines increase with the C-P-C bond angle when changes in electronegativity are small[46].

^{13}C-Aromatic Region

Due to the ligands being chiral this information is transmitted down to the phenyl groups which show the inequivalency of the phenyl carbons; when the ligand is complexed with a transition Group VIa metal atom the rigid five-membered ring complexes are then "locked" in a particular conformation such that any excess ring strain is reduced. When such a condition is fulfilled, it is found that the methyl group(s) are in the axial position(s), as found for the complexes of 2,3-bis(diphenylphosphino)butane from the carbonyl region studied in the ^{13}C n.m.r. spectrum.

Except for the complexes of 2,3-bis(diphenylphosphino)butane it is generally observed (Table 2.05) that there is a high frequency shift for the ipso-carbon atom (C_1) on complexation. In complexes the ipso-carbon (C_1) of this ligand shows a small frequency shift.

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Table 2.03. ¹³C chemical shifts for the carbon backbone
of chiral ligands and complexes

COMPOUND	δ(¹³CH)	CHEMICAL SHIFT/ppm δ(¹³CH₂)	δ(¹³CH₃)
Ph₂PCH(CH₃)CH(CH₃)PPh₂ = L	31.7		12.4
LCr(CO)₄ [b]	38.4		16.1
LMo(CO)₄ [b]	37.0		15.5
LW(CO)₄ [b]	39.1		16.2
Ph₂PCH(CH₃)CH₂PPh₂ = L	55.6	52.8	47.9
LCr(CO)₄	36.2	34.7	17.1
LMo(CO)₄	36.3	33.8	17.1
LW(CO)₄	37.4	35.4	17.0
Ph₂PCH(CH₂CH₃)CH₂PPh₂ = L	34.0	30.0, 23.7	11.6
LCr(CO)₄	42.4	32.0, 24.2	14.5
LMo(CO)₄	41.4	31.8, 23.7	14.3
LW(CO)₄	43.0	33.0, 23.5	14.4
Ph₂P(CH₃)₂CH(CH₃)PPh₂ = L	31.9	30.2, 26.5	16.7
LCr(CO)₄	32.8	31.2, 29 1	18.8
LMo(CO)₄	33.0	30.1	29.0
LW(CO)₄	33.0	30.4, 29.4	18.4
Ph₂P(CH₃)₃CH(CH₃)PPh₂ = L	29.8	35.0, 28.0, 24.0	16.1
LCr(CO)₄	32.6	36.0, 32.8, 25.2	20.7
LMo(CO)₄	31.2	34.0, 34.0, 24.4	19.3
LW(CO)₄	31.3	34.8, 32.7 24.1	19.3

a.   Chemical shift observed in saturated CDCl₃.
b.   No diastereomers observed.

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Table 2.04. $J(^{31}P-^{13}C)$ coupling constants for the carbon backbone of the chiral ligands and their complexes

COMPOUND	$J(^{31}P-^{13}CH)$	COUPLING CONSTANT/Hz $J(^{31}P-^{13}CH_2)$	$J(^{31}P-^{13}CH_3)$	J(PW)
$Ph_2PCH(CH_3)CH(CH_3)PPh_2$ = L	30.0	-	30.0	
$LCr(CO)_4$	43.0	-	10.7	
$LMo(CO)_4$	12.7	-	21.5	
$LW(CO)_4$	25.4	-	14.7	227.0
$Ph_2PCH(CH_3)CH_2PPh_2$ = L	16.5	6.1	6.1	
$LCr(CO)_4$	43.0	20.5	10.7	
$LMo(CO)_4$	42.0	21.5	9.8	
$LW(CO)_4$	26.4	25.4	9.8	230.1
$Ph_2PCH(CH_2CH_2CH_3)CH_2PPh_2$ = L	14.7	14.7, 10.7	10.7	
$LCr(CO)_4$	20.5	44.0, 10.7	6.8	
$LMo(CO)_4$	21.5	43.0, 10.7	8.8	
$LW(CO)_4$	25.4	27.3, 10.7	8.8	229.0

cont. Table 2.04. $J(^{31}P^{13}C)$ coupling constants for the carbon backbone of the chiral ligands and their complexes

COMPOUND	$J(^{31}P-^{13}CH)$	COUPLING CONSTANT/Hz $J(^{31}P-^{13}CH_2)$	$J(^{31}P-^{13}CH_3)$	$J(PW)$
$Ph_2P(CH_2)_2CH(CH_3)PPh_2$ = L	10.4	34.8, 23.8	16.0	
$LCr(CO)_4$	16.6	19.5, 6.0	4.0	
$LMo(CO)_4$	16.6	20.5, 6.8	no coupling	
$LW(CO)_4$	20.4	24.4, 6.0	no coupling	227.0
$Ph_2P(CH_2)_3CH(CH_3)PPh_2$ = L	9.8	12.8, 12.2	16.0	
$LCr(CO)_4$	17.6	10.7, 12.7, a	6.8	
$LMo(CO)_4$	17.6	13.7, a, 7.8	6.0	
$LW(CO)_4$	21.4	17.2, a, 2.0	5.6	232.0

a.   no coupling observed.

This has been rationalised[75] as reflecting an increase in P-C π-bond order but this seems inconsistent with the high frequency shifts observed for C_1 carbons in aliphatic tertiary phosphines on complexation. However, a steric effect due to the two methyl groups being in close proximity could account for the low frequency shift. Although the ^{13}C resonance signals of aryl phosphorus donor ligands have been frequently neglected, some reports including total analysis have been given[76]. Analysis for the aromatic ^{13}C region of the complexes reported here is summarised in Table 2.05 and Table 2.06.

A special comment regarding the shape of the ^{13}C aromatic resonance signals is necessary. The spin-set comprising any one ^{13}C atom and the two ^{31}P nuclei is described as AA'X (A=A'=^{31}P, X=^{13}C) only when the two phosphorus nuclei are equivalent, and the line width ($W_{\frac{1}{2}}$) is very dependent upon the relative values of the three coupling constants $^2J(AA')$, $^nJ(AX)$ and $^{n+2}J(A'X)$. The form of the signal is an apparent sharp triplet with the separation of the outer lines equal to $|^nJ(AX)+^{n+2}J(A'X)|$ when $^2J(AA')$ is large, this is shown by the meta-carbon in Fig. 2.02. For $^2J(AA')=0$, the system degenerates to a real doublet with a separation of $^nJ(AX)$. For intermediate $^2J(AA')$ values, the spectrum may consist of five lines with the separation of the second and fourth lines[77] equal to $N=|^nJ(AX)+^{n+2}J(A'X)|$, however, other lines may appear inside or outside the N lines, this is nicely demonstrated for the equatorial carbonyl, the ipso-carbon and for the ortho-carbon in dppbMo(CO)$_4$ complex, Fig. 2.02.

Table 2.05. ^{13}C chemical shifts for the phenyl carbon atoms of the chiral ligands and their complexes

PHENYL CARBON CHEMICAL SHIFT / ppm

COMPOUND	C_1	C_2	C_3	C_4
Ph$_2$PCH(CH$_2$)CH(CH$_3$)PPh$_2$ = L	137.4	134.7	129.0	a
LCr(CO)$_5$	136.1	134.3, 132.1	129.3, 128.7	130.7, 130.2
LMo(CO)$_5$	135.7	133.8, 131.4	128.5, 128.0	130.0, 129.4
LW(CO)$_5$	136.1	134.6, 132.1	130.6, 129.1	129.1, 128.6
Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$ = L	108.8, 107.7	106.0, 105.6	103.5, 103.4	103.5, 103.2
LCr(CO)$_5$	139.6, 137.2	134.4, 132.6	129.3, a	129.9, 128.7
LMo(CO)$_5$	138.5, 137.0	134.5, 132.8	131.6, a	128.8, a
LW(CO)$_5$	138.3, 136.7	134.6, 133.0	131.2, a	131.8, a
Ph$_2$PCH(CH$_2$CH$_2$)CH$_2$PPh$_2$ = L		134.7, a	128.80, a	133.9, a
LCr(CO)$_5$	139.0, 137.5	134.1, 132.7	131.6, 131.0	129.00, a
LMo(CO)$_5$	138.6, 136.1	134.6, 133.0	131.7, a	131.8, a
LW(CO)$_5$	138.3, 135.0	134.5, 133.10	129.3, 131.2	131.80, a

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cont. Table 2.05. ^{13}C chemical shifts for the phenyl carbon atoms of the chiral ligands and their complexes

COMPOUND	PHENYL CARBON CHEMICAL SHIFT / ppm			
	C_1	C_2	C_3	C_4
$Ph_2P(CH_2)_2CH(CH_3)PPh_2$ = L	137.7	134.6	129.0	134.0, 133.0
$LCr(CO)_4$	139.7, 138.5	135.77, 131.8	131.4, 128.0	131.2
$LMo(CO)_4$	139.0, 137.6	135.4, 132.5	131.6, 128.3	130.4
$LW(CO)_4$	138.7, 137.4	137.0, 135.6	133.2, 128.4	129.2, 128.8
$Ph_2P(CH_2)_3CH(CH_3)PPh_2$ = L	138.8, 137.2	132.6, 132.8	134.0, 133.1	128.3, a
$LCr(CO)_4$	142.7, 139.7	135.3, 133.8	132.1, a	129.2, 128.6
$LMo(CO)_4$	142.5, 139.2	135.3, 133.0	130.5, a	130.5, a
$LW(CO)_4$	139.6, 139.0	135.0, 132.7	131.6, 131.4	128.6, 128.2

a. Overlap of resonance, therefore, definite chemical shift cannot be determined.

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Table 2.06. J(^{31}P-^{13}C) coupling constants for the phenyl carbons and their Group VIa transition metal complexes

COMPOUND		J(^{31}P-^{13}C) COUPLING CONSTANT / Hz		
	C_1	C_2	C_3	C_4
Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$ = L	28.7	10.4	7.9	2.1
LCr(CO)$_4$	19.5	11.8, 9.76	9.26, 9.26	2.0
LMo(CO)$_4$	38.00	12.7, 9.8	8.8, 9.7	1.6
LW(CO)$_4$	43.9	12.7, 9.8	13.70, 9.8	1.9
Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$ = L	16.5, 14.7	10.2, 10.8	8.8, 9.2	21., 2.4
LCr(CO)$_4$	33.4, 34.2	10.7, 11.7	7.8, a	3.9, 3.9
LMo(CO)$_4$	33.2, 33.4	12.7, 13.7	10.8, a	2.2, a
LW(CO)$_4$	34.2, 35.2	12.7, 12.7	6.8, a	3.9, a
Ph$_2$PCH(CH$_3$)CH$_2$CH$_2$PPh$_2$ = L	a	4.9, a	-	-
LCr(CO)$_4$	35.2, 34.2	11.7, 11.7	9.8, a	3.9, a
LMo(CO)$_4$	33.20, 33.2	12.7, 13.7	12.7, 9.8	3.9, a
LW(CO)$_4$	30.3, 31.2	11.7, 12.7	8.8, 7.8	2.9, a

cont. Table 2.06. $J(^{31}P^{-13}C)$ coupling constants for the phenyl carbons and their Group VIa transition metal complexes

| COMPOUND | C_1 | $J(^{31}P^{-13}C)$ COUPLING CONSTANT / Hz | | |
		C_2	C_3	C_4
$Ph_2P(CH_2)_2CH(CH_3)PPh_2 = L$	14.0	9.2	6.1	3.7, 3.0
$LCr(CO)_4$	26.4, 27.4	11.7, 9.8	7.8, 8.8	2.2, a
$LMo(CO)_4$	31.3, 30.6	12.7, 12.7	9.8, 9.8	4.9, a
$LW(CO)_4$	35.2, 34.8	11.7, 11.7	9.8, 8.8	3.9, a
$Ph_2P(CH_2)_3CH(CH_3)PPh_2 = L$	13.4, 10.0	7.3, 8.2	4.6, 5.2	1.5, a
$LCr(CO)_4$	35.0, 31.2	9.8, 10.7	8.8, a	9.8, a
$LMo(CO)_4$	29.6, 31.2	11.7, 11.7	9.7, a	6.8, a
$LW(CO)_4$	38.1, 37.5	11.2, 11.6	10.7, 10.8	2.3, 2.1

a. Overlap of resonance, therefore, coupling constants cannot be determined correctly.

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For the chromium complex of the 2,3-bis(diphenylphosphino)butane ligand, shows an apparent sharp triplet for the equivalent methyl and methylene groups. This is also true of the inequivalent phenyls which show two separate ortho-carbons each producing an apparent triplet. Similarly, the meta-carbons show two sets of apparent triplets which also indicates inequivalency amongst the phenyl carbons. The shape of the signals produced, which show an apparent triplet, is a reflection of the strong $^2J(AA')$ coupling. For an example an intermediate $^2J(AA')$, the molybdenum complex of the above ligand serves. It is immediately apparent from the ^{13}C n.m.r. spectrum that the methyl carbons, ortho-carbon atoms and the equatorial carbonyl at high chemical shift each give a five line resonance from which the parameter, N, can be determined. For the tungsten complex of the same ligand, the ^{13}C spectrum degenerates to sets of doublets which is probably due to $^2J(AA')$ being close to zero.

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[13]C-Carbonyl Region

There are three obvious trends in δCO:

i) δCO increases, i.e. there is a high frequency shift, if CO is replaced by any ligand

ii) δCO(trans to ligand) > δCO (cis to ligand), and

iii)   there is an essentially constant difference in δCO with change of metal for any particular type of complex

These empirical trends are discussed in the light of current theory[76]. Carbon chemical shifts are dominated by the paramagnetic term of the screening constant which arises from mixing of ground and excited states of carbon in the magnetic field according, in the Pople MO treatment[78], to the equation.

$$\delta_p = -\frac{K}{\Delta E} <r^3>_{2p} \{Q_{AA} + Q_{AB}\} \qquad 2.5$$

where ΔE is an average excitation energy, $<r^3>_{2p}$ is the inverse cubed radius of the 2p-orbitals, and the Q-terms contain elements of the charge density, bond order matrix. Both $<r^3>_{2p}$ and Q_{AA} depend on the local charge density with Q_{AA} remaining essentially constant for most carbon nuclei[78,79].

δCO for organic carbonyls[80,81] and coordinated carbon monoxide in octahedral monosubstituted tungsten carbonyls[82] has been correlated with C-O stretching frequencies in order to gain a greater understanding of the metal-carbonyl bonding.

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A similar correlation holds for the Mo and W complexes. Equation 2.5 has been applied to the case of substituted organic carbonyls[20] and the results interpreted in terms of changes in the C-O π-bond polarity (affecting $<r^3>_{2p}$ and Q_{AB} in equation 2.5, with the r term dominant) as a function of the electronegativity of the substituent such that electronegative groups decrease the π-bond polarity, increase r, and give low frequency shifts. This essentially inductive argument is adapted to the case of metal carbonyls by postulating that the ligands L are better charge donors than the CO groups being replaced. Such inductive effects are however thought to be small for carbon monoxide complexes compared with the effects produced by dative (p-d) π-bonding as found from i.r. evidence[66]. It is found that π-donation to organic carbonyls causes a low frequency shift[81] and a similar result would be predicted for coordinated CO. However, the order of δCO for different metals (Cr > Mo > W) cannot readily be attributed to differences in π-bonding since their carbonyl i.r. stretching frequencies[66], metal-ligand charge transfer bands[70,83] and orbital electronegativities are all essentially the same. Also, the change in δCO with metal is independent of the nature of the other ligands and the overall symmetry of the complex. The same order Cr > Mo > W is seen in ^{13}C n.m.r. for these compounds, see Tables 2.07 and 2.08.

It is suggested by P.S. Braterman et al that[76] paramagnetic currents which are dependent on the d-d transition energies on the metal have a direct field effect on δCO and δ^{31}P.

As mentioned earlier the chirality of the backbone makes all four carbonyls chemically inequivalent. However, it is generally seen that two carbonyl resonances

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Table 2.07. ^{13}C chemical shifts for the chiral carbonyl complexes

COMPOUND	CO_{eq} (trans)	CO_{ax} (cis)
Cr(CO)$_6$	212.1[a]	
Mo(CO)$_6$	214.6[a]	
W(CO)$_6$	202.0[a]	
Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$ = L		
LCr(CO)$_4$	228.8	222.5
LMo(CO)$_4$	217.6, 217.0	210.9
LW(CO)$_4$	209.11	203.9
Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$ = L		
LCr(CO)$_4$	229.3	223.3, 220.0
LMo(CO)$_4$	218.0	212.3, 209.0
LW(CO)$_4$	209.4, 208.3	204.1, 201.0
Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$ = L		
LCr(CO)$_4$	229.3	223.4, 220.0
LMo(CO)$_4$	218.0	212.5, 209.0
LW(CO)$_4$	209.4, 208.4	204.2, 201.0
Ph$_2$P(CH$_2$)$_2$CH(CH$_3$)PPh$_2$ = L		
LCr(CO)$_4$	227.5	222.3
LMo(CO)$_4$	215.6	211.2
LW(CO)$_4$	206.3	204.2, 203.4
Ph$_2$P(CH$_2$)$_3$CH(CH$_3$)PPh$_2$ = L		
LCr(CO)$_4$	226.5, 224.4	221.0
LMo(CO)$_4$	216.2, 215.0	212.7, 209.6
LW(CO)$_4$	206.0, 205.2	205.0, 202.1

a. See reference 76.

Table 2.08. Coupling constants $J(^{31}P-^{13}CO)$ for the chiral carbonyl complexes

COMPOUND	CO_{eq} (trans)	CO_{ax} (cis)
$Ph_2PCH(CH_3)CH(CH_3)PPh_2 = L$		
$LCr(CO)_4$	17.6	23.4
$LMo(CO)_4$	8.3	16.6
$LW(CO)_4$	22.5	11.7
$Ph_2PCH(CH_3)CH_2PPh_2 = L$		
$LCr(CO)_4$	25.4	26.4, 25.4
$LMo(CO)_4$	24.4	18.6, 15.6
$LW(CO)_4$	9.8, 10.7	14.6, 11.7
$Ph_2PCH(CH_2CH_3)CH_2PPh_2 = L$		
$LCr(CO)_4$	26.4	26.4, 25.4
$LMo(CO)_4$	19.5	17.6, 15.6
$LW(CO)_4$	14.6, 9.8	15.6, 13.7
$Ph_2P(CH_3)_2CH(CH_3)PPh_2 = L$		
$LCr(CO)_4$	a	13.0
$LMo(CO)_4$	24.4	16.6
$LW(CO)_4$	20.5	14.6, 15.1
$Ph_2P(CH_3)_3CH(CH_3)PPh_2 = L$		
$LCr(CO)_4$	14.6, 27.3	25.4
$LMo(CO)_4$	15.6, 15.6	17.6, 15.6
$LW(CO)_4$	24.2, 24.4	12.7, 12.0

a. due to overlap J not measurable.

overlap to give a five line spectrum see Fig. 2.05 diag. c, which is normally found for the equatorial carbonyls, this of course depends upon to a large degree to the value of $^2J(PP')$. The axial carbonyls quite frequently give an apparent sharp triplet and are normally found at low frequency from the equatorial carbonyls, these values are readily measured directly from the ^{13}C spectrum which yield $^2J(^{31}P-^{13}CO_{ax})$.

Fig. 2.05. Shows the Carbonyl Region for the Chiral Complexes

Fig A, C at 22.5 MHz and B at 75.5 MHz

A

[Ph₂PCH(CH₃)CH₂PPh₂]Cr(CO)₄

229.3   223.3   220.0 δ ppm.

C

217.3   211.0 δ ppm.

B

[Ph₂PCH(CH₃)CH(CH₃)PPh₂]Mo(CO)₄

[Ph₂PCH(CH₃)(CH₃)PPh₂]W(CO)₄
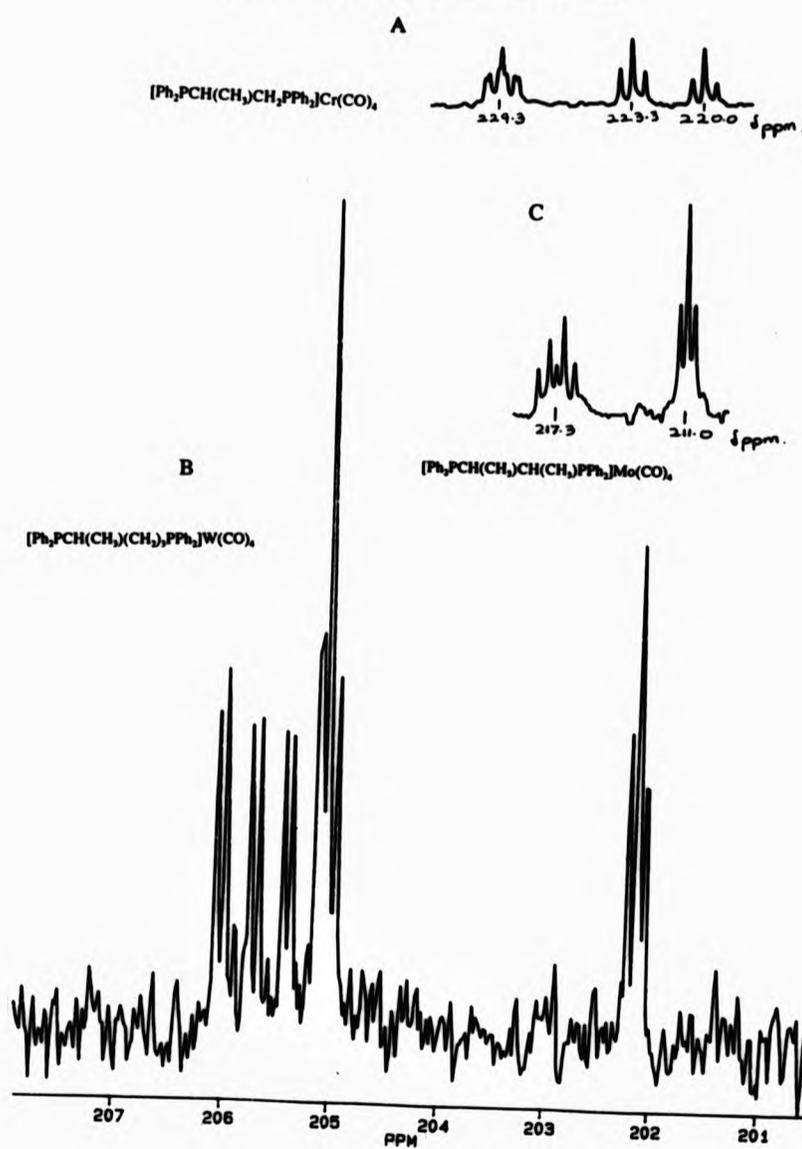
Ring Contributions to Transition-Metal-Phosphorus Chelate Complexes

As mentioned towards the end of Chapter 1 the "ring contribution" Δ_{RC}, is assumed in some way responsible for unusual chemical shifts[22,25]. This is demonstrated by the complex dppmW(CO)$_4$ where the $\delta^{31}P = -23.5$ ppm would be assumed to represent the free ligand (where $\delta^{31}P = -23.6$ ppm) without offering a possible explanation to why no Δ is observed. It is now known that coordination deshields the $\delta^{31}P$ resonance and the Δ_{RC} value, for the four-membered ring, has an anomalous shielding effect of the same magnitude.

From the definition of Δ_{RC}, a comparison of the chiral complexes may be made with the bridging ligand, L(M(CO)$_5$)$_2$, shown below:

Fig. 2.06

M(CO)$_5$
|
Ph$_2$P——CH$_2$CH$_2$——PPh$_2$
|
M(CO)$_5$
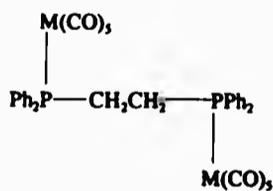
where M = Cr, Mo and W.

Since at present no data are available for the analogous chiral bridging ligands a direct comparison of the chiral complexes may be made with the above bridging ligands only if the $\delta^{31}P_B$ of the chemical shift is taken into account. Since these values, as stated earlier, correlate well in symmetrical diphosphines, the coordinated (dppe) complexes[34] of L(M(CO)$_5$)$_2$, where M = Cr, Mo and W $\delta^{31}P$ 51.1 ($\Delta^{31}P$ 63.6), $\delta^{31}P$ 31.7 ($\Delta^{31}P$ 44.2), and $\delta^{31}P$ 12.7 ppm ($\Delta^{31}P$ 25.2), respectively.

As shown by Table 2.09, when compared with other data from four and six-membered rings[22], it is seen that there is a large shielding effect for the highly-strained four-membered rings and to a lesser extent for the six-membered rings. However a deshielding effect for the relatively unstrained five-membered rings is observed.

Problems Encountered in the Preparation of the Chiral Ligands

Initially, it was thought that a commercially available mixture of diols (2R, 3R) and (2S, 3S)-butanediol (Aldrich Chem. Co) would yield a mixture of the corresponding ligands: (2S, 3S) and (2R, 3R) chiraphos, respectively. However, this was not found to be the case. The method of synthesis for the aforementioned ligand as described by Fryzuk and Bosnich[27] (for a more detailed account see experimental section) is represented schematically, Fig. 2.07.

Contrary to the method adopted by Fryzuk et al, the ligand was isolated when left to stand in industrial methylated spirits (I.M.S.) for ca. 4 weeks. The latter procedure was applied to the following ligands described in the experimental section, which on standing at room temperature in I.M.S., deposited lustrous colourless plates of the diphosphine. As mentioned earlier, the attempt to produce a diastereomeric product of chiraphos containing both the (2S, 3S) and (2R, 3R) isomers did not lead to the expected products due to the reaction of only one form of the diol with tosyl chloride which is thought to be the trans-form.

Table 2.09. ^{31}P n.m.r. Parameters for chiral LM(CO)$_4$ complexes
containing a five-membered ring.

COMPOUND	$\delta^{31}P_a$/ppm	$\Delta(\delta^{31}P_a)$/ppm	Δ_{ac}/ppm
L = Ph$_2$PCH(CH)$_3$CH(CH$_3$)PPh$_2$	-9.2		
LCr(CO)$_4$	84.0	93.2	29.9
LMo(CO)$_4$	62.3	71.5	27.3
LW(CO)$_4$	46.9	56.0	30.9
L = Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$	-21.3		
LCr(CO)$_4$	71.8	93.4	29.8
LMo(CO)$_4$	49.3	70.6	26.4
LW(CO)$_4$	34.0	55.3	30.1
L = Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$	-31.0		
LCr(CO)$_4$	67.7	98.7	35.1
LMo(CO)$_4$	48.1	79.1	34.9
LW(CO)$_4$	32.2	63.2	38.0

Fig. 2.07. An outline of the preparation of (s,s)-chiraphos.
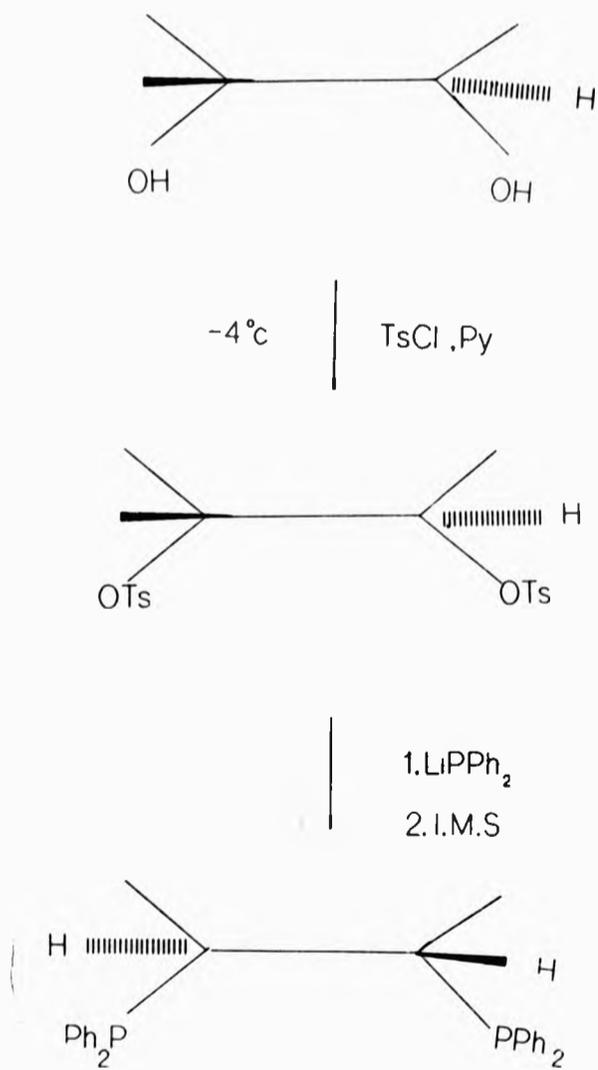
This suggestion achieves greater cogency when the ligand is in a complex form and the ^{13}C n.m.r. of the carbonyl region is compared to the known conformation of the complex[85] for the ligand (2S, 3S)-bis(diphenylphosphino)-1,2-diphenylethane shown below.

$$Ph_2P \text{---} \underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{CHCH}} \text{---} PPh_2$$
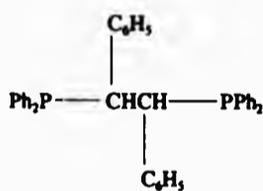
Fig. 2.08 shows the structure of trans-diphenyl bis(diphenylphosphino)ethane. The above ligand when complexed shows a very similar pattern in the carbonyl region to that of the complex with the unknown conformation such that, when working backwards to identify the unknown conformation of (2S,3S)-bis(diphenylphosphino)butane, this is achieved by knowing the structure of the starting material with known conformation, in this case, trans-1,2-dichloro, 1,2-diphenylethane to which the lithium diphenyl phosphide is added. A possible explanation is also put forward for the observation that only one isomer is formed as the major product. This is probably due to the strong hydrogen bonding experienced by the diol in the cis-position which inhibits the reaction between the tosyl chloride and one of the two hydroxy groups thereby making the trans- form as the major product in this reaction.

Another ligand of interest for n.m.r. studies was 2,2-dimethyl-1,3-bis(diphenylphosphino)propane and its Group VIa complexes. However, the starting material 2,2-dimethyl-1,3-dibromopropane could not be purchased and therefore the known synthetic route for this ligand was abandoned; a similar method to the synthesis of asymmetric ligands was then carried out with 1,3-dihydroxy-2,2-dimethyl propane as the available starting diol. It was found that even after prolonged stirring only one mole of diphenyl phosphide, $Ph_2P^\ominus$, had reacted with the tosyl derivative to yield $Ph_2PCH_2C(CH_3)_2CH_2$-OTs, which was characterised by ^{13}C and ^{31}P n.m.r.. The ^{13}C n.m.r. spectrum of the tungsten complex of the monophosphine tosyl derivative, $LM(CO)_5$ where $M=W$, is characterised by two sharp resonances at high frequency of relative intensity 1:4·5. This is split by $^2J(^{31}P-^{13}CO)$ nuclear spin-spin coupling, corresponding to the trans- and cis- carbonyl groups in these octahedral complexes and a pattern of resonances at low frequency which is analogous to those observed for the free ligand, L. $^2J(^{31}P-^{13}CO)$ for the trans- carbonyl at high frequency and the cis-carbonyl at low frequency are found to be 22.50 Hz and 6.80 Hz, respectively, hence, it is seen that the trans-coupling constant is significantly larger than the cis- coupling constant to their chemical shifts at 205.0 ppm and 197.8 ppm respectively.

As a satisfactory route to the ligand 2,2-dimethyl-1,3-bis(diphenylphosphino)propane could not be found, its further study was abandoned; the original interest in this ligand arose because of the formation of a six-membered ring structure when the ligand is complexed with a Group VIa transition metal thereby making the chelate ring system amenable to study by applying the concepts used in analysing spectra of

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substituted cyclohexanes. This would have involved an interesting study on the two methyl groups contained in the ring structure, probably carrying out a dynamic n.m.r. study of the equivalence or non-equivalence of the methyl groups (which undergo a rapid chair-chair interconversion at room temperature) at reduced temperatures[56-57].

Mass Spectra and Microanalytical Results

It is found, as would be expected, that the diphosphines in the coordinated mode show a molecular ion in its mass spectrum, $LM(CO)_4^+$. See Table 2.10. For the complexes of smaller molecular mass the detection of the parent molecular ion was possible but for the larger ligands only breakdown products were identified. These results confirm the data which was obtained from ^{31}P and ^{13}C n.m.r.; a typical schematic fragmentation pattern is shown in Fig. 2.09 for the complex $[Ph_2PCH(CH_3)CH_2PPh_2]M(CO)_4$. The breakdown of these complexes follows a consistent pattern in that generally the most intense signal was found to be $m/e = 185$ which corresponds to a Ph_2P- fragment. Characteristic isotope patterns for Cr, Mo and W also help to confirm the proposed structure.

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Table 2.10. Mass spectra data for chiral complexes

COMPOUND	$LM(CO)_4^+$	$(M-CO)^+$	$(M-2CO)^+$	$(M-3CO)^+$	$(M-4CO)^+$	Major ions detected, m/e
$[Ph_2PCH(CH_3)CH_2PPh_2]Cr(CO)_4$	576	-	-	492	464	422, 236, 184
$[Ph_2PCH(CH_3)CH_2PPh_2]Mo(CO)_4$	620	592	564	536	508	454, 388, 310, 280, 184
$[Ph_2PCH(CH_3)CH_2PPh_2]W(CO)_4$	708	680	652	624	596	554, 474, 398, 368, 184
$[Ph_2PCH(CH_3)CH(CH_3)PPh_2]Cr(CO)_4$	590	562	-	506	478	412, 344, 266, 236, 184
$[Ph_2PCH(CH_3)CH(CH_3)PPh_2]Mo(CO)_4$	634	606	578	550	522	464, 384, 310, 280, 184
$[Ph_2PCH(CH_3)CH(CH_3)PPh_2]W(CO)_4$	722	694	666	638	610	552, 474, 398, 368, 184
$[Ph_2PCH(CH_2CH_3)CH_2PPh_2]Cr(CO)_4$	590	-	-	506	478	422, 397, 312, 262, 184
$[Ph_2PCH(CH_2CH_3)CH_2PPh_2]Mo(CO)_4$	634	-	-	.	.	426, 397, 320, 184
$[Ph_2PCH(CH_2CH_3)CH_2PPh_2]W(CO)_4$	722	-	-	638	610	610, 397, 184

cont. Table 2.10. Mass spectra data for chiral complexes

COMPOUND	$LM(CO)_4^+$	$(M-CO)^+$	$(M-2CO)^+$	$(M-3CO)^+$	$(M-4CO)^+$	Major ions detected, m/e
$[Ph_2P(CH_2)_2CH(CH_3)PPh_2]Cr(CO)_4$	590	-	-	506	478	426, 349, 238, 184
$[Ph_2P(CH_2)_2CH(CH_3)PPh_2]Mo(CO)_4$	634	606	578	550	520	426, 349, 184
$[Ph_2P(CH_2)_2CH(CH_3)PPh_2]W(CO)_4$	722	694	666	638	610	554, 475, 398, 184
$[Ph_2P(CH_2)CH(CH_3)PPh_2]Cr(CO)_4$	604	-	-	520	492	440, 363, 254, 184
$[Ph_2P(CH_2)CH(CH_3)PPh_2]Mo(CO)_4$	648	620	592	564	536	440, 363, 254, 184
$[Ph_2P(CH_2)CH(CH_3)PPh_2]W(CO)_4$	736	708	680	652	624	434, 364, 256, 184

$$CH_3$$
$$|$$
$$CH\text{-}CH_2$$
$$Ph_2P \quad \overset{+}{} \quad PPh_2 \qquad RMM = 620$$
$$Mo$$
$$(CO)_4$$

$$\downarrow \; -4CO$$

$$CH_3$$
$$|$$
$$CH\text{-}CH_2$$
$$Ph_2P \quad \overset{+}{} \quad PPh_2 \qquad {}^m/_e \; 508$$
$$Mo$$

$$\downarrow \begin{array}{l} -CH_3 \\ -PPh_2 \end{array}$$

$$CH\text{-}CH_2 \qquad {}^m/_e \; 308$$
$$Ph_2P \; +$$
$$Mo$$

$$\downarrow \; -CH\text{-}CH_2$$

$$Ph_2P^+ \qquad {}^m/_e \; 281$$
$$Mo$$

$$\downarrow \; -Mo$$

$$Ph_2P^+ \qquad {}^m/_e \; 185$$
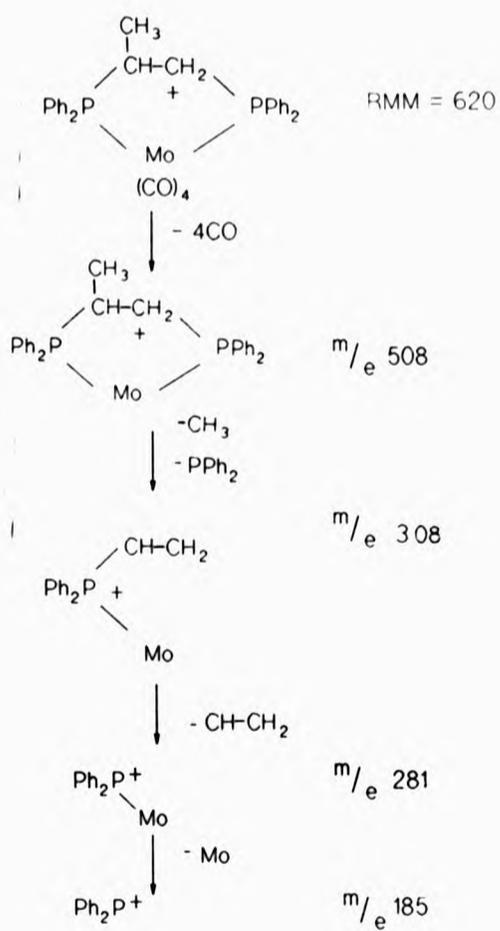
Fig 2.09 A schematic representation of a typical fragmentation pattern for the complex [Ph₂P CH(CH₃) CH₂PPh₂]Mo(CO)₄

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Table 2.11. Microanalytical Results

COMPOUND	FOUND % C	H	CALCULATED % C	H
[Ph₂PCH(CH₃)CH₂PPh₂]Cr(CO)₄	63.8	4.3	64.6	4.5
[Ph₂PCH(CH₃)CH₂PPh₂]Mo(CO)₄	60.3	4.2	60.0	4.2
[Ph₂PCH(CH₃)CH₂PPh₂]W(CO)₄	52.3	3.7	52.5	3.7
[Ph₂PCH(CH₃)CH(CH₃)PPh₂]Cr(CO)₄	64.6	4.6	65.1	3.9
[Ph₂PCH(CH₃)CH(CH₃)PPh₂]Mo(CO)₄	59.5	4.3	60.6	4.4
[Ph₂PCH(CH₃)CH(CH₃)PPh₂]W(CO)₄	53.0	3.8	53.2	3.9
[Ph₂PCH(CH₂CH₃)CH₂PPh₂]Cr(CO)₄	64.2	4.7	65.1	4.7
[Ph₂PCH(CH₂CH₃)CH₂PPh₂]Mo(CO)₄	59.4	4.0	60.6	4.4
[Ph₂PCH(CH₂CH₃)CH₂PPh₂]W(CO)₄	52.0	3.6	53.2	3.9
[Ph₂P(CH₂)₂CH(CH₃)PPh₂]Cr(CO)₄	64.0	4.8	65.1	4.7
[Ph₂P(CH₂)₂CH(CH₃)PPh₂]Mo(CO)₄	60.4	4.4	60.6	4.4
[Ph₂P(CH₂)₂CH(CH₃)PPh₂]W(CO)₄	51.8	3.9	52.9	4.1
[Ph₂P(CH₂)₃CH(CH₃)PPh₂]Cr(CO)₄	65.4	5.0	65.6	5.0
[Ph₂P(CH₂)₃CH(CH₃)PPh₂]Mo(CO)₄	59.0	4.0	61.1	4.6
[Ph₂P(CH₂)₃CH(CH₃)PPh₂]W(CO)₄	52.1	3.8	53.8	4.1

2D-Heteronuclear Chemical Shift Correlation N.M.R. Spectroscopy

The complexity of the ^{1}H spectra of several of the ligands and their complexes precluded direct analysis. However, this was possible via ^{13}C/^{1}H 2D-n.m.r. experiments and an outline of the method is given here. The initial idea of two-dimensional Fourier Transformation (F.T.) was proposed by Jeener[94], but the significance of his proposals was not realised and lay dormant for several years. In 1976 applications of two dimensional Fourier were described by Ernst[95].

In the experiments carried out on 1,1,2-trichloroethane, Ernst describes how pulses applied successively can lead to a response which is a function of two frequencies and so can lead to a 2D-n.m.r. spectrum[96-107]. At the present time there are various 2D-experiments which can be applied to solve chemical problems. This discussion will concentrate on ^{13}C/^{1}H heteronuclear chemical shift[102] correlation spectroscopy. This method is distinguished from J-resolved 2D-spectroscopy in that both frequency axes, F_1 and F_2, now contain chemical shifts related to ^{1}H and ^{13}C respectively. In addition, an extra time interval is included between the evolution and detection period, the so-called mixing time.

The pulse sequence for the generation of heteronuclear correlated 2D-n.m.r. spectra is shown in Fig. 2.10.

Fig. 2.10. Pulse sequence and vector representation of a heteroscalar-correlated 2D-n.m.r. experiment using the example of a CH fragment (A=¹H, X=¹³C)
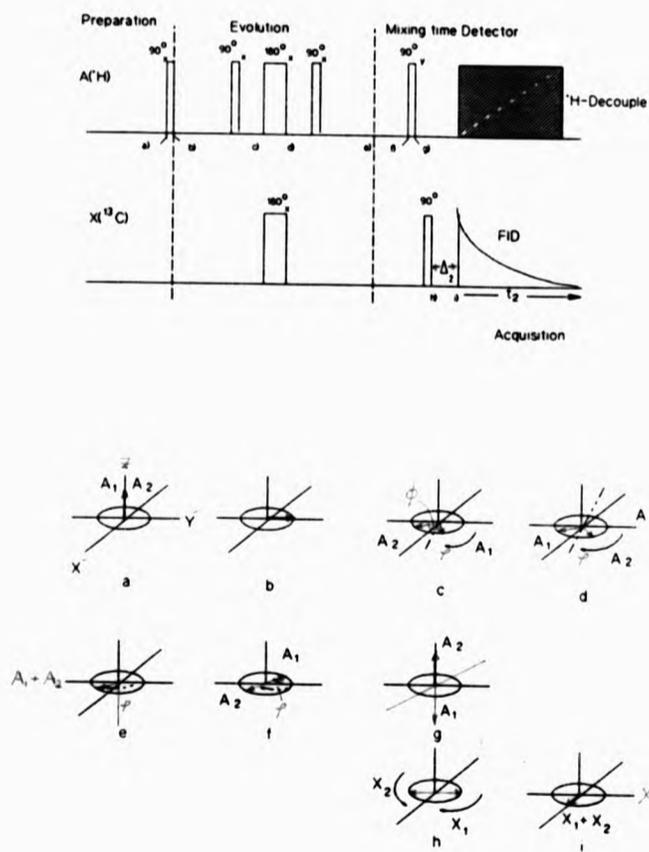
After a $90_x°^1$H-pulse both components of the ^{1}H doublet rotate in the X,Y-plane according to the difference of their frequencies from that of the carrier (a-c). A $180_x°$ ^{13}C pulse (d) allows for refocusing at (e); $\delta(^1$H) is retained in form of the angle θ. This information is transferred to the ^{13}C nuclei through ^{13}C-^{1}H spin-spin coupling during the mixing time. Polarisation of the ^{1}H-magnetisation with a $90_y°$ pulse (g) results in a corresponding polarisation of ^{13}C-magnetisation which is transformed into transverse magnetisation by the $90_x°$ pulse (h).

In the remaining mixing time the ^{13}C vectors precess around their corresponding ^{1}H vectors. They are refocused after Δ_2 sec and can be detected with simultaneous ^{1}H decoupling if desired. The phase modulation obtained depends on the angle θ.

The transfer of magnetisation from a nuclear species of low gyromagnetic ratio (the X-spins) to a nuclear species of high gyromagnetic ratio the (A-spins) was shown by Maudsley and Ernst which afforded an improvement in sensitivity when plotting out the spectrum of the X-spins. A reversal of Maudsley and Ernst's[108] experiment was carried out when 2D-experiments were run. This involved changing the roles of protons and carbon. The spectrometer is tuned to observe ^{13}C such that information concerning the protons was transferred to ^{13}C nuclei, this also gives considerable improvements in sensitivity and the detected ^{13}C signal strength then depends on proton spin-populations.

When a normal ^{1}H n.m.r. spectra for the chiral complexes is observed the region of interest, in this case it is the alkyl backbone region, always shows gross overlap of similar degenerate spins.

However, by 2D-n.m.r. experiment various couplings relating to $J(^{31}P-^1H)$ can be identified; also, the relative sign of N(PC) and N(PH) (see Fig. 2.11) are obtained by inspection of the 2D-n.m.r. ^1H slices. A full explanation of this is given below. The experiments performed on the methylene alkyl backbone of some of the ligands and their complexes involve the correlation of the ^{13}C resonances with those of the directly-bound proton and resulted in C-H correlated 2D-spectra. Fig. 2.11 shows cross-sections from the $^{13}C/^1H$ chemical shift correlation spectrum of $[Ph_2P(CH_2)_3PPh_2]Mo(CO)_4$, where the equivalent proton signals in the methylene backbone become part of an A_2X-pattern resulting in triplets.

Inspection of Fig. 2.11 shows that the ^{13}C resonance at high frequency has a corresponding ^1H triplet signal; the same also applies to the ^{13}C at low frequency but with half the intensity corresponding to the central methylene group. However, the ^1H transitions seen at high frequency (a, b and c) show the opposite sign N(PH) to that of ^{13}C N(PC) when the frequency of the proton transitions are correlated to that of the ^{13}C n.m.r. signal, i.e. there is an increase of ^1H n.m.r. frequency (a, b and c) when compared to that with ^{13}C (1,2 and 3) transitions.

For the central methylene group the ^{13}C triplet shows the corresponding decrease for each ^1H transition (d, e and f), thereby resulting in both J(PC) and J(PH) having the same sign, see Table 2.12. Hence:

$$J(^{31}P-^1H)=7 \text{ Hz} \qquad \text{of opposite sign to } J(^{31}P-^{13}C)$$

Fig. 2.11 Shows slices from $^{13}C-^1H$ 2D-chemical shift correlated spectrum of the complex [Ph$_2$P(CH$_2$)$_2$PPh$_2$]Mo(CO)$_4$.

^1H-slices

c 156.7 Hz

b 133.2 Hz

a 129.7 Hz from R.H.S.

f 91.0 Hz

e 112.5 Hz

d

N(PC) opposite in sign to N(PH)

N= 22.0 Hz

1 2 3

$^2J = 3.9$ Hz ^{13}C

500 Hz

4 5 6

94
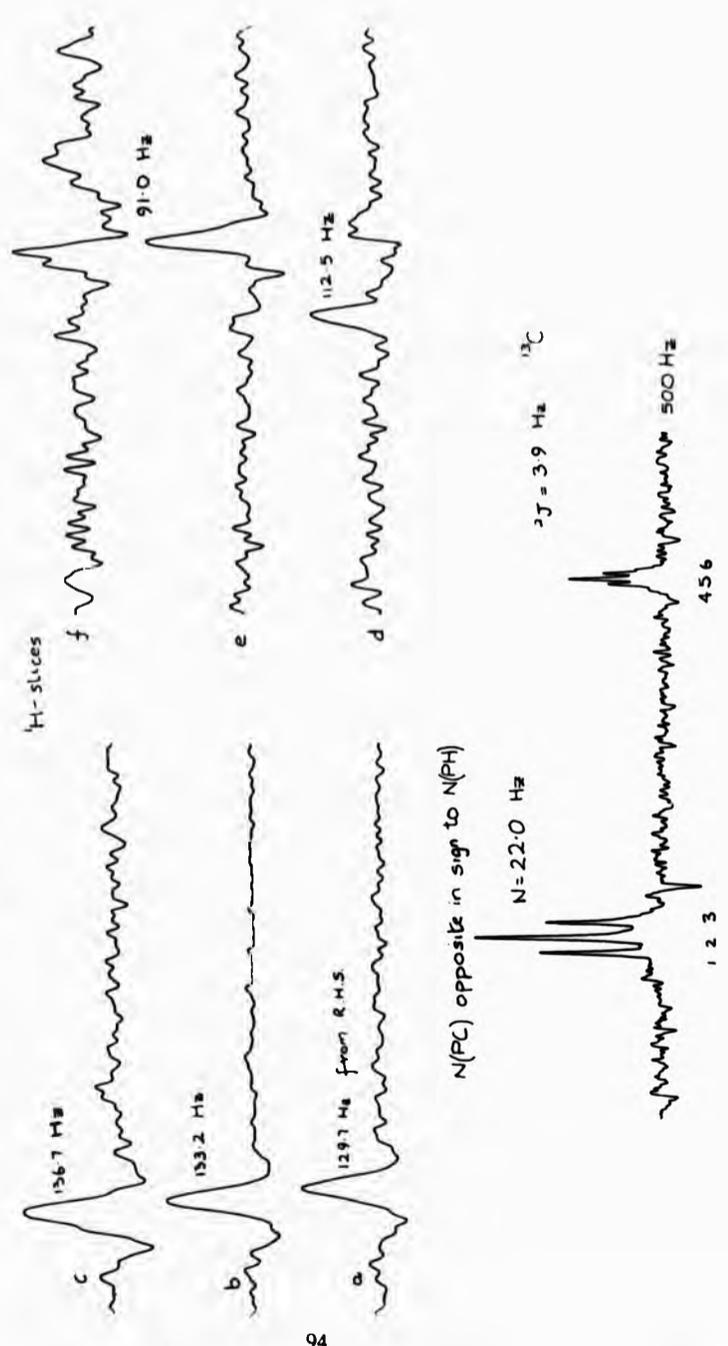
Similarly the central carbon in the methylene group in the $[Ph_2P(CH_2)_3PPh_2]Mo(CO)_4$ complex shows transitions (4), (5) and (6) which are correlated with the proton transitions (d), (e) and (f) which are separated by 43 Hz. Similarly, as for the previous case it is found that

$$J(^{31}P\text{-}^1H) = 43 \text{ Hz same sign as } J(^{31}P\text{-}^{13}C)$$

In order to determine the absolute sign of any single coupling constant it is necessary to compare the unknown with a coupling of known sign such as $^1J(^{13}C\text{-}^1H)$ which is known to be positive in all cases[109]; this could be determined by a selective decoupling experiment of the type $^{13}C \cdots \{^{31}P\}$. Table 2.12 and 2.13 show parameters determined from 2D-n.m.r. experiments for ligands and complexes.

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Table 2.12. Data taken from 2D-n.m.r. ^{13}C/^{1}H heteronuclear chemical shift
correlation for bridging alkyl backbone of free ligands

COMPOUND[a]	J(^{31}P-^{1}H) and J(^{31}P-^{13}C) coupling constants / Hz Free ligand
Ph$_2$P(CH$_2$)$_5$PPh$_2$	[b]J(2.9) same sign as [c]J(11.5) J(7.8) same sign as J(16.1)
Ph$_2$P(CH$_2$)$_6$PPh$_2$	J(0.0) and J(12.8) J(0.78) same sign as J(11.6) J(9.0) same sign as J(15.9)
Ph$_2$P(CH$_2$)$_4$PPh$_2$	J(0.59) same sign as J(12.1) J(39.6) same sign as J(29.3)
Ph$_2$P(CH$_2$)$_3$CH(CH$_3$)PPh$_2$	For CH$_3$: J(14.5) same sign as J(15.9) For CH$_2$: J(1.5) opposite sign to J(12.2) For CH: J(6.5) same sign as J(9.8) No results for two methylene quartets.
Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$	For CH$_3$: J(13.3) same sign as J(30.0) For CH: J(14.0) same sign as J(30.0)

a.   All 2D-n.m.r. expts. carried out in saturated CDCl$_3$ solution and
        locked to internal ^{2}D.
b.   Gives J(^{31}P-^{1}H) in all cases.
c.   Gives J(^{31}P-^{13}C) in all cases.

Table 2.13. 2D-n.m.r. data for the alkyl backbone of complexes

COMPOUND	$J(^{31}P-^1H)$ and $J(^{31}P-^{13}C)$ coupling constants / Hz Complex
[Ph$_2$P(CH$_2$)$_3$PPh$_2$]Mo(CO)$_4$	For CH$_2$: $^3J(7.0)$ opposite sign to $^4J(22.0)$ For central CH$_2$: $J(21.5)$ same sign as $J(3.9)$
[Ph$_2$P(CH$_2$)$_4$PPh$_2$]Mo(CO)$_4$	$J(5.1)$ opposite sign to $J(22.0)$ $J(22.3)$ opposite sign to $J(9.5)$

a.   All 2D-n.m.r. expts. carried out in saturated CDCl$_3$ solution and locked to internal ^{2}D.
b.   Gives $J(^{31}P-^1H)$ in all cases.
c.   Gives $J(^{31}P-^{13}C)$ in all cases.

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CHAPTER 3

The New Polyphosphorus Ligands

Introduction

The Preparation of the ligand [2,2-bis(diphenylphosphino)ethyl]phenylphosphine, $(Ph_2P)_2CHCH_2PPhH$, and its reactions with $M(CO)_6$ where $M=Cr,Mo$ and W are described along with the different modes of reaction with $W(CO)_5$.[THF]. As this ligand can co-ordinate in many different ways, resembling dppm and dppe in that it shows the potential to form complexes with four- and five-membered chelate rings in a reaction mixture, a more selective synthetic approach was adopted. In practice, direct reaction between the ligand and the metal tends to give complexes in which five-membered rings are favoured, this is presumably due to the inherently less strain offered by such a structure.

As part of the synthetic studies of the co-ordinative behaviour of this ligand, its ability to form complexes with chromium, molybdenum and tungsten carbonyl moieties, and its n.m.r. spectral characteristics are reported along with a total of four different coordination modes displayed by this ligand.

Other ligands have been reported[20,110,111] which show the potential to coordinate through three phosphorus atoms but few are so suitable for the study of competition between the formation of four- and five-membered rings.

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Results and Discussion

The ligand $(Ph_2P)_2CHCH_2PPhH$ was prepared by the base-catalysed $(K^+O^-Bu^t)$ addition of phenylphosphine to the double bond of 1,1-bis(diphenylphosphino)ethene[8], which was described earlier as a method developed by King et al in polytertiary ligand synthesis. Its ^{31}P n.m.r. spectrum consists of a doublet of doublets (δ-3.7 ppm 111.3 Hz and -5.5 ppm 16.3Hz) and a triplet (δ-54.5 ppm 17.5 Hz) which are consistent with the ligand possessing a prochiral phosphorus atom so that all three phosphorus atoms are intrinsically inequivalent.

Some New Transition Metal Complexes of the Triphosphine Ligand

In the previous chapter the preparation and characterisation of the new diphosphine complexes was described and their modes of coordination were described. The present chapter extends this work to triphosphines and discusses the greater range of coordination behaviour shown by the complexes of the triphosphine ligand.

It is found from the synthetic studies of the ligand, $(Ph_2P)_2CHCH_2PPhH$, that in principle the triphosphine can coordinate to a single metal in any of the modes shown below (I) - (IV), in Fig 3.0

Where, for simplicity, $M(CO)_n$, is a Group VIa metal carbonyl moiety and $n = 3$, 4 or 5. It should be expected that there is free rotation about the $-CH-CH_2-$ bond in the free ligand and also in structures (I) and (II), this will not lead to equivalence of the geminally related phosphorus atoms in the above mentioned structures due to the presence of a prochiral phosphorus atom, P_a.

$M(CO)_n$

$Ph_2 P_A$
$Ph_2 P_B$
CH——CH$_2$
P_XPh H

(I)

Ph_2
P
$(CO)_n M$
P_B
Ph_2
CH—CH$_2$
P_XPh H

(II)

$(CO)_n$
M
Ph_2
P_A
P_BPh H
CH–CH$_2$
P_C
Ph_2

(III)

HPhP$_X$——CH$_2$
Ph_2
P_A
M
$(CO)_n$
CH
P_BPh$_2$

(IV)

M=Cr,Mo and W
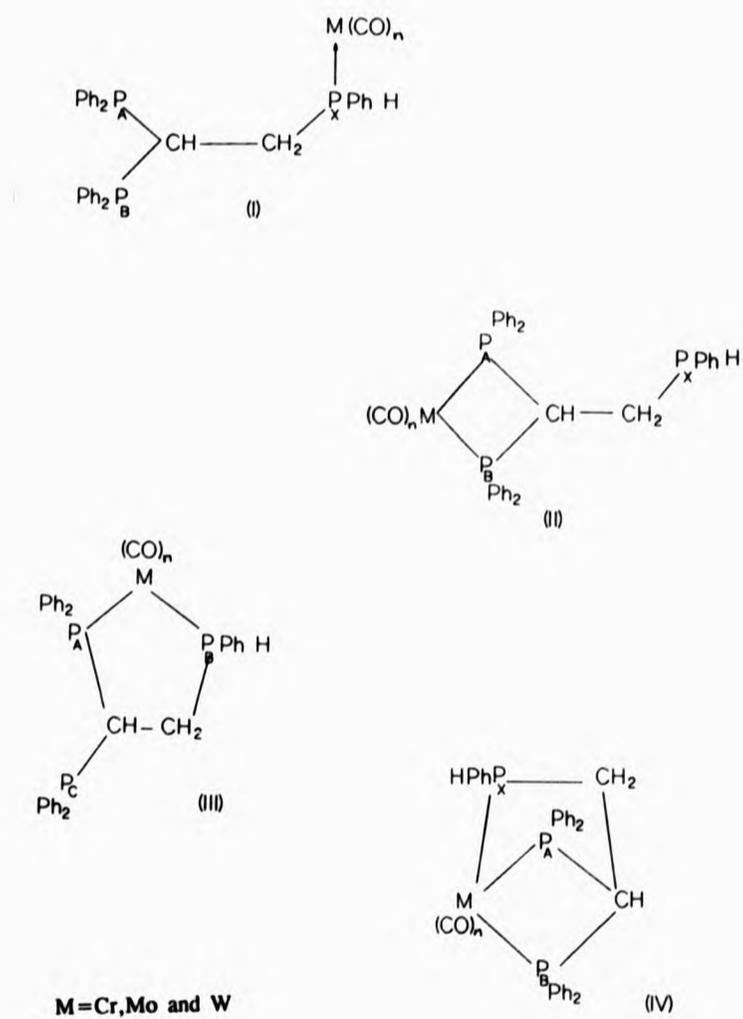
Fig 3.0 Shows the new polyphosphines under investigation

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Consideration of the ring structures for the above metal complexes would therefore show that ring strain effects would be at a minimal for (III) in view of the presence of a five-membered ring, but of increasing significance in for (II), and would be expected to be fairly substantial in (IV). In fact, it is found from transition metal studies with the free ligand that when $Mo(CO)_4(pip)_2$ is reacted with the triphosphine as well as forming the predominantly five-membered ring structure (III), the four-membered ring complex is formed also in the reaction mixture (II), but the diastereomeric complex (III) is formed as the major product when analysing the [31]P n.m.r. spectrum. The existence of many chelate complexes of bidentate dppm suggests that mode (II) should readily occur.

In many of the reactions leading to these complexes more than one product can be formed, and [31]P n.m.r. spectroscopy was found to be a very useful probe in identifying the components of unseparated reaction mixtures. In general, the direct reaction between the free ligand and a Group VIa transition metal hexacarbonyl results in a mixture of complexes exhibiting the above and other modes, and therefore a more selective synthetic approach was adopted. As a typical example take the reaction between the free ligand and $Cr(CO)_6$, this gave the derivative (III) as the major product; similar results were obtained using $Mo(CO)_6$ and $W(CO)_6$, when refluxed in diglyme. However, it was found that prolonged refluxing of the last two metal hexacarbonyls led to the formation of complexes showing mode (IV) in ca. 1:1 yield, with possible additional formation of di- and -pentaphosphine as additional components.

Transition-Metal Complexes of [2.2-bis(diphenylphosphino)ethyl]phenylphosphine.

The inequivalence shown by the two geminally related phosphorus atoms induced by the chiral secondary phosphine atom leads to the formation of isomeric species. This is demonstrated by the reaction between $Mo(CO)_4(pip)_2$

trans-for···   cis-form
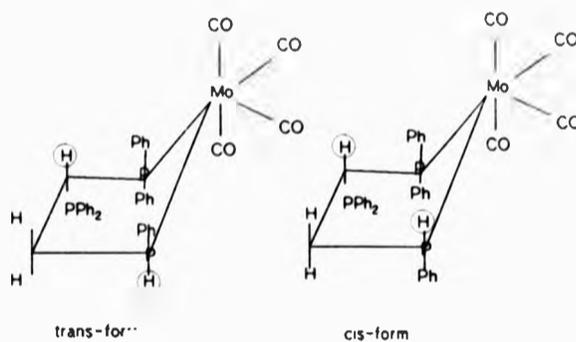
Fig 3.01 Formation of isomeric five-membered ring complexes

and the free ligand which led to the formation of both the cis and trans isomers and also the corresponding four-membered ring structure (II) in approximately equal proportions. After prolonged reflux of the solution the four-membered ring structure was still present, this demonstrates again the apparently equal preferences of molybdenum to form four- and five-membered chelate rings. For the synthesis of the four-membered ring complex a different synthetic strategy had to be adopted in order to obtain the product in its pure isolatable form. To this end the species $PhPH_2/[THF]$ was generated by u.v. irradiation to which was then added the appropriate amount of the catalyst, $K^+O^-Bu^t$, the reaction was then completed by the

addition of the four-membered ring vinyl complex. The reaction mixture was then refluxed overnight after which time the product was isolated in a pure form; it should be noted that the preparation of this particular complex required a very large excess of $PhPH_2$/[THF] species in order for the reaction to take place.

Once the triphosphine complex had been isolated in a pure form it was refluxed in diglyme so that the uncoordinated phosphorus atom would undergo coordination at the metal site via a loss of one CO producing a complex containing both a five- and four-membered rings, giving a fully coordinated complex, shown below schematically, Fig. 3.02.

However, ^{31}P n.m.r. analysis of the reaction mixture showed an extensive amount of the adduct pentaphosphine to be present as well as other bimetallic products. Use of a low boiling point solvent did not produce the desired product, in fact the ^{31}P n.m.r. confirmed the presence of the starting material.

The problem was solved by adopting the method developed by Kubas[112]. It is found much simpler to use the free triphosphine ligand to displace EtCN from fac-$[M(CO)_3(EtCN)_3]$ where M=Cr,Mo and W (see Fig 3.03); the reaction proceeds rapidly in refluxing dichloromethane, but at room temperature was found to be slower. It was initially thought that this reaction may produce significant amount of the monodentate species (1), but this was not found to be true; the ^{31}P n.m.r. spectra of these complexes are fairly straightforward and can be analysed as ABX or AMX spin-systems. The interest in species (1) originally arose due to the potential it showed in forming the five-membered ring complex in >90% yield.

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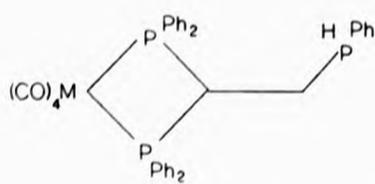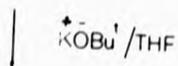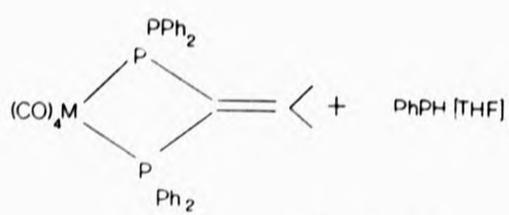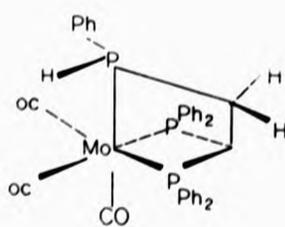
Fig 3.02. Complex containing both four - and - five membered rings

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Fig 3.03 ^{31}P n.m.r spectrum of W(CO)$_3${(Ph$_2$P)$_2$CHCH$_2$CH$_2$PPhH}

δ ppm.

-14.9

5.6
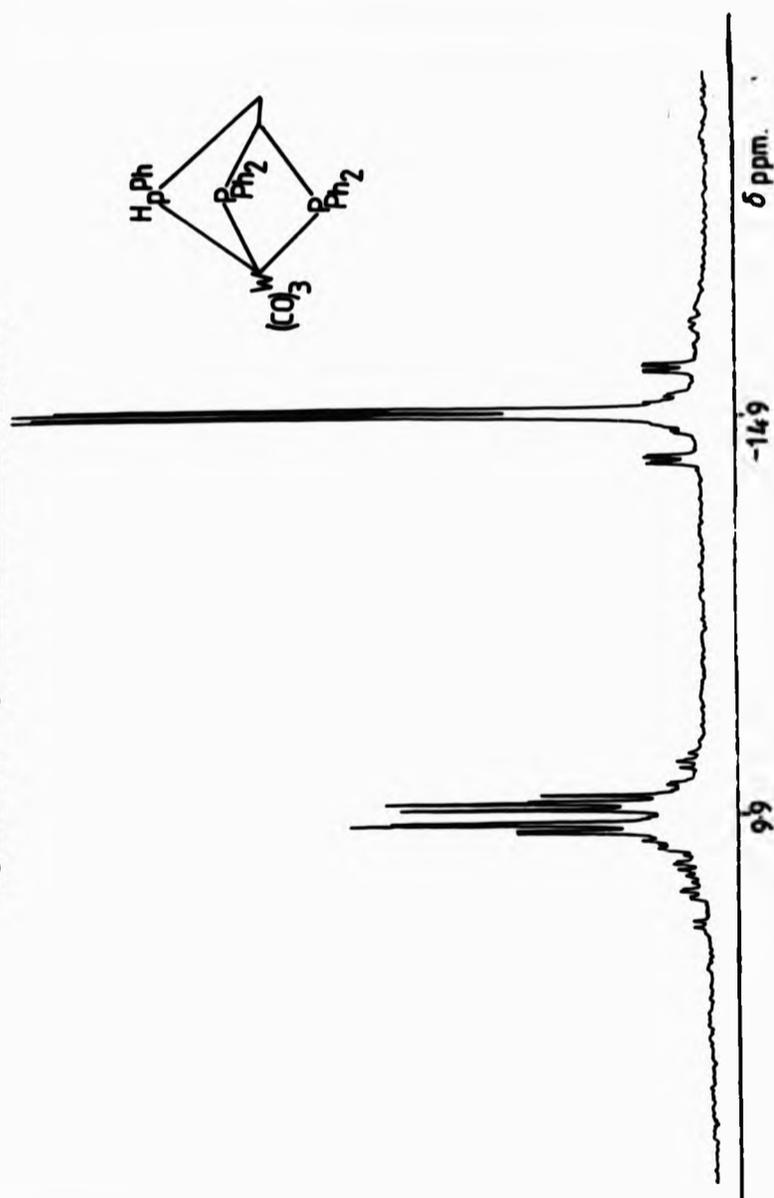
After generation and isolation of the species $Mo(CO)_5PPhH_2$ (see experimental for detail) as a pure product the appropriate amount of $K^+O^-Bu^t$ was added to the phosphine metal complex in THF solution and the vinyl diphosphine added dropwise. From ^{31}P n.m.r. spectroscopy the characteristic ABX spin-system characteristic of the monodentate triphosphine (1) was identified, Fig 3.04.

The isolated product was then refluxed in 2-Methoxyethanol for ca. 17 hours after which time one CO would be lost to enable the metal to coordinate at one of the geminal phosphorus atoms, thereby yielding the desired isomeric product. However, after analysis of the reaction mixture in $CDCl_3$ it seems that the expected product was not formed as hoped; chelation at one of the geminal phosphorus atoms does occur but it is tentatively suggested that a rearrangement has occurred to the phenylphosphine end, on consideration of the ^{31}P n.m.r. chemical shifts, such that the metal coordinates through two diphenylphosphino groups with the five-membered ring format still existing, as shown by the reaction scheme in Fig 3.05.

Fig. 3.05.
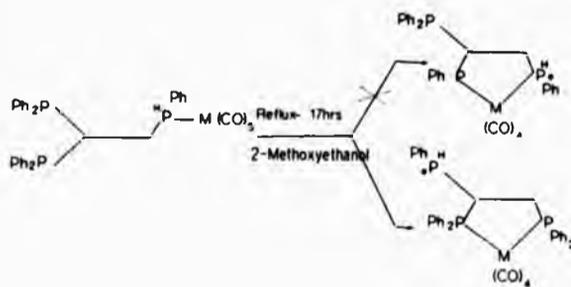
Fig 3.04 ^{31}P n.m.r. spectrum of (Ph₂PCH₂CHCH₂P(H)Ph)W(CO)₅

112.9 Hz

$P_A = -1.7$ $P_B = -7.8$ $P_X = -28.0$ δ ppm.
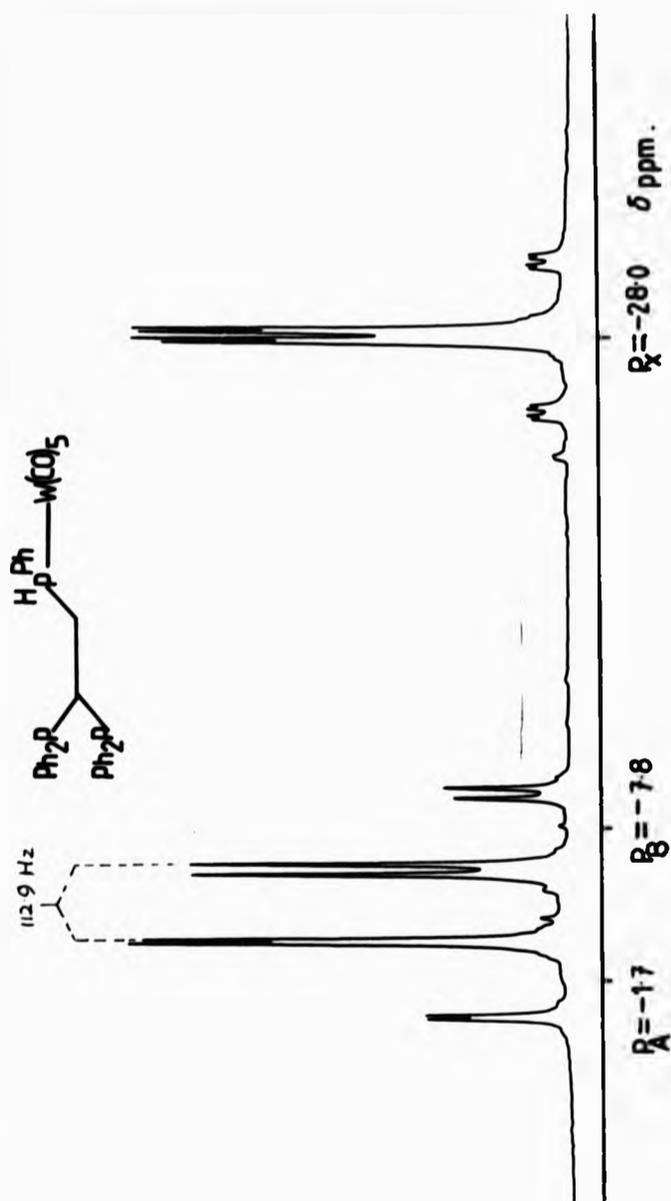
To attain a better understanding of the unexpected structure of the complex, an attempt was made to obtain the complex in a pure form, but this was found to be fruitless as the product tended to break down under crystallisation. This prevented any further study via ^1H n.m.r. which would elucidate its correct structure unequivocally, its ^{31}P n.m.r. spectrum in the reaction mixture is given in Fig. 3.06, analysed as an AMX spin-system, see Table 3.02

Although the different modes of coordination can, in some cases, be distinguished by ^{31}P n.m.r. such as for the molybdenum complex for mode (III); consideration of the parameters for the two isomeric complexes does not identify the particular structure to which they relate see Table 3.0 and Table 3.01. Since the values of $^2J(P_AP_B)$ are similar in the two isomers it can be deduced that the constraint provided by the transition metal in the four-membered ring, for the phosphorus atoms P_A and P_B, is constant and therefore the difference in coupling constant values of $^2J(P_AP_C)$ and to a lesser degree the value of $^3J(P_BP_C)$ between the isomers results from the geometrical disposition of P_C. Table 3.01 shows a very large discrepancy in the values of $^2J(P_AP_C)$ (35.4 Hz and 109 Hz) which is unexpected since there is relatively small differences in the configuration of the two isomers. It would also appear that the geometrical relationship between P_A and P_C with respect to each other is virtually identical.

Table 3.0. ^{31}P n.m.r. chemical shift data for the metal carbonyl complexes of the mode (I), (II), (III) and (IV)

COMPLEX	$\delta(^{31}P_a)$/ppm[a]	$\Delta\delta$/ppm[b]	$\delta(^{31}P_b)$/ppm	$\Delta\delta$/ppm	$\delta(^{31}P_c)$/ppm	$\Delta\delta$/ppm
(I) Cr(CO)$_5$[c]	-1.42	2.28	-6.2	.	19.6	.
(I) W(CO)$_5$	-1.7	2.0	-7.8	.	-28.04	.
(II) Cr(CO)$_4$[c]	50.1	53.8	50.1	53.8	-53.8	.
(II) W(CO)$_4$	2.05	5.75	2.05	5.75	-53.7	.
(III) Mo(CO)$_4$[d]	66.9	72.1	13.4	67.7	-15.9	.
(III) Mo(CO)$_4$[d]	69.7	73.4	10.6	64.9	-20.7	.
(IV) Cr(CO)$_4$	51.2	54.9	50.01	55.2	-3.9	50.4
(IV) Mo(CO)$_4$	31.80	35.5	30.5	35.7	1.9	56.2
(IV) W(CO)$_4$	10.6	14.3	9.0	14.2	-14.0	39.4
Free ligand[e]	-3.7	.	-5.2	.	-54.3	.

a. Relative to external 85% H$_3$PO$_4$
b. Δ = coordination chemical shift
c. See page 100 for labelling scheme
d. Analysed as ABC spin-system
e. [2,2-bis(diphenylphosphino)ethyl]diphenylphosphine
f. Really $\delta^{31}P_c$

Table 3.01. ^{31}P n.m.r. coupling constants for the metal carbonyl complexes of the mode (I), (II), (III) and (IV)

COMPLEX	$J(P_AP_B)$/Hz	$J(P_AP_2)$/Hz	$J(P_BP_2)$/Hz	$^1J(WP)$/Hz
(I) Cr(CO)$_5$	90.6	4.9	16.1	
(I) W(CO)$_5$	112.9	6.10	14.6	224.6
(II) Cr(CO)$_4$	c	7.3	7.3	
(II) W(CO)$_4$	c	7.9	7.9	174.5
(III) Mo(CO)$_4$	9.1	35.04[a]	0.0[b]	
(III) Mo(CO)$_4$	7.3	109[a]	17.1[b]	
(IV) Cr(CO)$_5$	8.8	18.3	19.5	
(IV) Mo(CO)$_5$	14.04	10.9	19.5	
(IV) W(CO)$_5$	9.5	18.3	13.9	204.7
Free ligand	111.3	16.3	17.5	

a. Really, $^2J(P_AP_C)$
b. Really, $^2J(P_BP_C)$
c. Due to overlap of ^{31}P resonances, parameter not available.

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Table 3.02. ^{31}P n.m.r. parameters for the diastereomer of the complex shown in Fig 3.05.

COMPLEX	$\delta(^{31}P_A)$/ppm[a]	$\Delta^{31}P_A$/ppm	$\delta(^{31}P_M)$/ppm[a]	$\Delta^{31}P_M$/ppm	$\delta(^{31}P_X)$/ppm[a]	$\Delta^{31}P_X$/ppm	$J(P_A,P_M)$/Hz	$J(P_A,P_X)$/Hz	$J(P_M,P_X)$/Hz	$^1J(WP)$/Hz
(I) W(CO)$_5$	74.9	78.6	58.2	63.4	-54.2	-	13.4	34.2	34.2	229.4[b] 234.4[c]
(II) W(CO)$_5$	68.3	71.2	51.7	56.9	-31.5	-	17.1	17.1	11.0	229.4[b] 234.4[c]
Free Ligand[a]	-3.7		-5.2		-54.3	-	111.3	16.3	17.5	

a. Analysed as ABX spin-system.
b. Coupling constant refers to A and A´ for AA´MM´XX´ spin-system, respectively
c. Coupling constant refers to M and M´ for AA´MM´XX´ spin-system, respectively
d. All phosphorus chemical shifts taken relative to 85% H_3PO_4

Fig 3.06 31P n.m.r. of reaction mixture for the isomeric complex shown below

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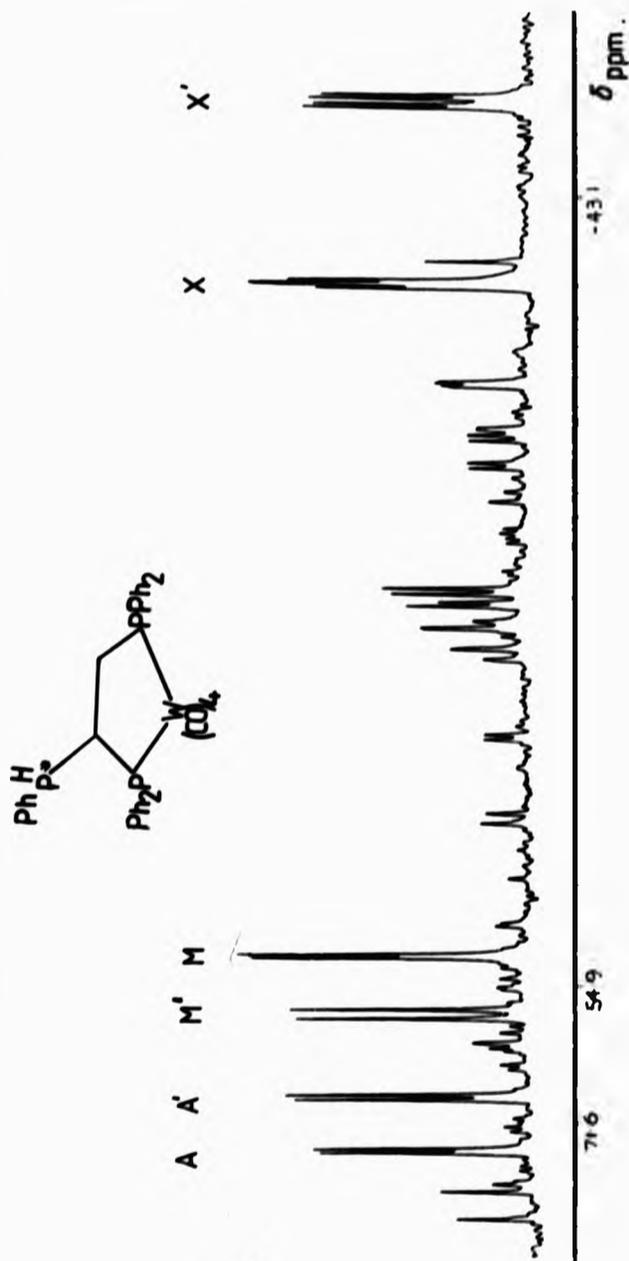
It is now well established that when phosphorus is coordinated to a metal there is a large high-frequency change in the phosphorus chemical shift[7] which is termed the coordination chemical shift, Δ. The pair of ΔP_A and ΔP_B values for the isomeric complexes of mode (III) show very close similarity when compared to that of dppeMo(CO)$_4$, as would be expected for a five-membered ring. However, more interesting features are shown by the complex (IV) which exhibits two rings within the single molecule; the phosphorus atom P_A which is simultaneously part of a four- and five-membered rings shows ΔP_A for one four-membered ring only. As for ΔP_X, which is incorporated in two five-membered rings, this does not show good agreement with a diphosphine in a single five-membered ring. This latter result can be attributed to the fact that phosphorus chemical shifts are sensitive to hybridisation and electronic effects and also bond-angle distortions which these terminal phosphorus atoms, P_X, may experience; this seems to be the case when the Δ values are correlated[113] to similar complexes to mode (IV), containing a -PPh$_2$ terminal group at P_X, where these latter complexes show fairly good correlation for ΔP_A and ΔP_X for single four- and five-membered ring complexes, respectively.

The geminally related phosphine atoms in these species generally show good agreement with those for similar complexes[113], discussed above, however, the phosphorus atoms bearing the proton tend to show lower Δ values. The reasoning for this was as explained earlier.

Small variations in the vicinal, $^3J(PP)$, parameters for complexes of mode(I) and (II) when the metal atom changes, are probably a reflection of changes in the hybridisation and effective nuclear charge of the coordinated phosphorus atom since

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conformational differences are not likely to be of great significance.

Transition–Metal Complexes of some Pentatertiary Phosphine Ligands

In the previous section the preparation of the various triphosphine ligand complexes was described and coordination modes for these ligands were shown. This work is now extended to new pentatertiary phosphine complexes for which a greater number of coordination modes are available: this does not mean that a complete series of preparations is given but an insight is given into the available routes.

The possible formation of the singly coordinated mode is shown in Fig 3.07.
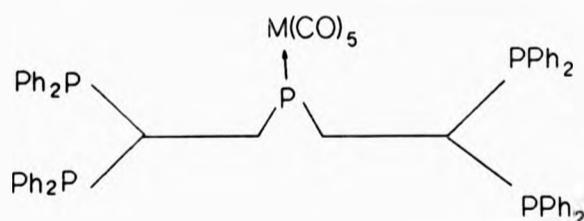
Fig 3.07 Attempted formation of the pentaphosphine

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It was observed that, as initially expected, the direct reaction between the free ligand and the metal pentacarbonyl species, $M(CO)_5.[THF]$, resulted in the formation of a mixture of complexes with the metal species coordinated to any of the five phosphorus sites; this inevitably made characterisation via ^{31}P n.m.r. impossible. However, a more selective procedure was attempted whereby the chelate complex of mode (I) and the vinyl diphosphine were made to undergo reaction in order to give the expected product as shown in Fig 3.08.
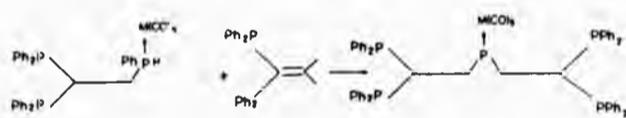
Fig 3.08 A selective procedure adopted for the formation of the pentaphosphine.

From the analysis of the reaction mixture via ^{31}P n.m.r. it was found that the reaction to form the pentaphosphine did not proceed as expected; this is thought to be due to the large volume occupied by the pentacarbonyl groups which hinder the attack by $K^+O^-Bu^t$ catalyst which also has large bulky groups. However, the formation[114] of the pentaphosphine shown in Fig 3.09 proceeds with no apparent difficulty, approximately equal proportions of only the diastereomeric complexes exhibiting the above mode being formed. This shows the presence of two chiral centers, (marked *).

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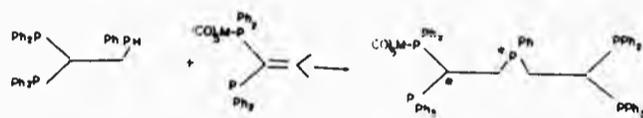
Fig 3.09 Diastereomeric complexes shown by the pentaphosphine

An attempt was also made to synthesise a bimetallic pentaphosphine which contained two four-membered rings showing exactly the same metal atoms, as shown by the reaction in Fig 3.10, which is similar to the preceding one.

where M=M
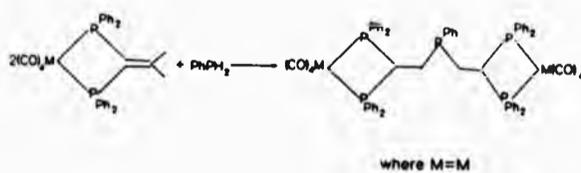
Fig 3.10 Formation of a bimetallic pentaphosphine

These bimetallic pentaphosphines were synthesised in good yield as they formed the major product, in contrast to another method employed to obtain the bimetallic molybdenum complex in greater yield. Another method as described below, gave equally good yield although this was rather surprising in the view of the many

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coordination sites available on the free pentaphosphine ligand. The reaction between two moles of $Mo(CO)_4(pip)_2$ and one mole of the free ligand resulted in complete formation of the bimetallic complex with two independent four-membered rings rather than the more stable five-membered rings. In complete contrast to the above two reactions, a small-scale reaction was carried out where the reactants were present in equimolar amounts; this resulted in a mixture of bi- and mono-metallic complexes along with some unreacted ligand. The desired product containing only one metal atom had to be prepared by a more selective procedure as shown below (Fig 3.11).
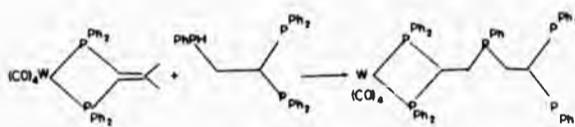
Fig 3.11 Formation of monometallic pentaphosphine.

Initially it was found by ^{31}P n.m.r. that the addition reaction between the triphosphine complex (mode II) and the free vinyl diphosphine ligand did not take place. This could be explained by the drift of charge onto the phosphorus bearing a proton in the triphosphine, to leave a net positive charge on the metal atom; the nucleophile ($^tBuO^-$) then attacks the centre with a low charge density, which in this case is the tungsten atom, thereby leaving the phosphorus bearing a proton unchanged. In effect, what has really occurred is a shift in charge density from the transition metal to the -PhPH group in the complex of mode (II) thereby activating this site for nucleophilic attack.

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An extension of the work in the formation of the bimetallic pentaphosphines was to coordinate the central phosphorus atom P_M with a sulphur or Group VIa transition metal. The pentasulphide was easily formed by refluxing an equimolar amount of the bimetallic pentaphosphine with sulphur in refluxing toluene whereby coordination resulted at the P_M site. The introduction of $W(CO)_5.[THF]$ was also attempted at the P_M position but was found to be fruitless. This was probably due to the large bulk of the pentacarbonyls which inhibits the binding of the tungsten atom at this position.

The spin-system used to designate the pentaphosphines for ^{31}P n.m.r. analysis is shown in Fig. 3.12; data for these complexes is given in Table 3.03 and 3.04.
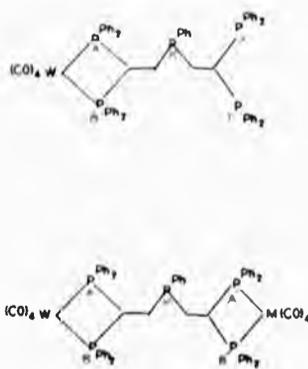
Fig 3.12 The spin-system adopted for the ^{31}P n.m.r. analysis

for the pentaphosphine

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Table 3.03. ^{31}P chemical shifts for mono- and bimetallic pentaphosphines

Metal[a]	$\delta(^{31}P_A)$/ppm[b]	ΔP_A/ppm[d]	$\delta(^{31}P_B)$/ppm	ΔP_B/ppm	$\delta(^{31}P_M)$/ppm	$\delta(^{31}P_X)$/ppm	$\delta(^{31}P_Y)$/ppm
Cr	47.6	50.3	47.3	51.4	-31.8	-	-
Mo	27.9	30.6	26.8	31.0	-28.6	-	-
W	3.3	6.0	2.9	6.9	-28.8	-	-
W[c]	2.9	5.7	1.02	5.1	-28.3	-2.2	-4.9
Free Ligand	-2.7		-4.03		-28.0		

a. For labelling scheme of these complexes see Fig. 3.12.
b. All phosphorus chemical shifts shown are relative to 85% H_3PO_4
c. Monometallic complex
d. Coordination chemical shift, $\Delta = \delta_{complex} - \delta_{free\ ligand}$

Table 3.04. Coupling constant for the series of bimetallic pentaphosphines

Metal	$J(P_A-P_B)$/Hz	$J(P_A-P_M)$/Hz	$J(P_B-P_M)$/Hz	$J(P_M-P_X)$/Hz	$J(P_M-P_Y)$/Hz	$J(P_X-P_Y)$/Hz
Cr	11.3	4.9	6.7	-	-	-
Mo	32.3	4.6	6.1	-	-	-
W[c]	40.3	4.9	5.9	-	-	-
W[d]	41.5	3.67	9.3	36.7	16.6	83.7
Free Ligand	100.7	28.6[a]	17.0[b]			

a. Really, value represents $^3J(AX) = ^3J(A'X)$ for a AA'BB'X spin-system
b. Really, value represents $^3J(BX) = ^3J(B'X)$ for a AA'BB'X spin-system
c. $^2J(WP) = 211.3$ Hz
d. Monometallic complex, $J(^{183}W^{-31}P) = 205$ Hz

On consideration of the coordination chemical shift values in the pentaphosphine complexes the results are clearly indicative of four-membered chelate-type structures and are therefore consistant with the configuration shown in Fig.3.12. The coupling constant values are all in fairly close agreement, except that for $J(P_A P_B)$ values, in the bimetallic series which suggests a consistant configuration throughout, and the variation in the parameter $J(P_A P_B)$ is most probably due to the different "through- the- metal" contributions as discussed previously in chapter 2.

The ^{13}C n.m.r. data for the bimetallic pentaphosphines are shown in Table 3.05, and Table 3.06.

As previously discussed (see pages 73) the carbonyl chemical shifts for the pentaphosphines are found to be in accordance with those determined earlier; with the highest chemical shift given by the chromium complex and the lowest given by tungsten. The theory relating to carbonyl shift is explained in the light of current[76] theory and that by the MO treatment[75] as explained by Pople of which a brief mention is made on page 73.

The sulphides were formed for these bimetallic pentaphosphines, and as expected, the P_M position showed a general high frequency chemical shift for the dichromium and ditungsten metals of 52.8 ppm and 33.0 ppm respectively. Attempts were also made to synthesise the "mixed metal" bimetallic complexes where $M \neq M$, see Fig 3.12 however, this was found to be unsuccessful when the reaction scheme outlined in Fig 3.10 was attempted (when $M \neq M$) along with another method which involved the reaction of the four-membered ring complex, mode (II), with a vinyl complex.

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Table 3.05. ^{13}C chemical shifts for the bimetallic pentaphosphines

METAL	Alkyl backbone/ppm		Carbonyl Groups/ppm	
	>CH$_2$	>CH	Trans	Cis
Cr	29.3	55.9	228.3	224.6,221.3
Mo	26.5	60.5	219.7	213.6,210.7
W	31.1	59.4	210.1	205.7,202.1

Table 3.06. $^{31}P-^{13}C$ coupling constant for the bimetallic pentaphosphines

METAL	J(PC)/Hz Alkyl backbone		J(PC)/Hz Carbonyl Groups	
	>CH$_2$	>CH	Trans	Cis
Cr	28.5	32.2, 18.3	25.4, 12.7	24.4, 24.4
Mo	26.3	33.5, 17.4	a	7.8, 7.8
W	28.5	35.8, 13.9	15.4	13.9, 12.5

a   Overlap of resonances therefor coupling constant not observable.

The latter synthetic route was not successful, as shown by ^{31}P n.m.r., and similarly, the former route only gave mixtures of bimetallic pentaphosphine complexes where the two metals in the structure are the same.

In order to avoid problems with isomers an alternative route was sought to a pentaphosphine complex. This was more selective, and involved the reaction of $Mo(CO)_3$(triphos) and the vinyl complex; the reaction mixture was analysed via ^{31}P n.m.r. which confirmed the formation of a fully-coordinated complex having no isomers and gave an ABMXY spin-system as shown below, for which the parameters are tabulated in Table 3.07.
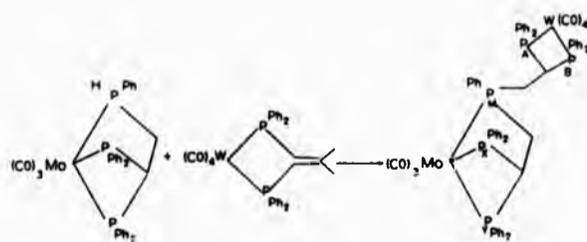
Fig. 3.13. Formation of a pentaphosphine which shows an ABMXY spin-system.

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This particular reaction gives greater scope for the synthesis of bimetallic pentaphosphines which have three rings with two four-membered and one five-membered structures; an extension of this work could involve the reaction of the triphosphine complex with ligands containing double and/or triple bonds.

Table 3.07. ^{31}P n.m.r. data for the reaction mixture of [(CO)$_3$Mo(triphos)] gem-pp W(CO)$_4$

^{31}P atom	$\delta(^{31}P)$/ppm [b]	$\Delta^{31}P$/ppm	J(P$_A$-^{31}P)/Hz	J(P$_B$-^{31}P)/Hz	J(P$_M$-^{31}P)/Hz	J(P$_X$-^{31}P)/Hz	J(P$_Y$-^{31}P)/Hz	J(^{183}W-^{31}P)/Hz
P$_A$	8.6	+11.8	-	32.6	6.4	0.0	0.0	207.0
P$_B$	6.6	+11.3	32.4	-	0.4	0.0	0.0	205.0
P$_M$	41.8	+71.6	6.4	0.4	-	12.5	12.5	0.0
P$_X$	31.2	+33.5	0.0	0.0	12.5	-	-	0.0
P$_Y$	31.2	+35.6	0.0	0.0	12.5	-	-	0.0

a. All ^{31}P n.m.r. chemical shifts are relative to 85% H$_3$PO$_4$
b. See Fig. 3.13 for labelling scheme

Transition-Metal Complexes of 1,2-bis(diphenylphosphino)benzene

Previous work has been carried out on 1,2-bis(phosphino)benzene and related alkylated species[115,116] and its macrocycles[117]; complexes of these ligands have also been extensively studied[116,118].

However, very little has been reported on transition–metal complexes of 1,2-bis(diphenylphosphino)benzene. Suffice it to say that the previously reported synthetic route has been simplified by a convenient one-pot synthesis[119]. Due to the lack of data available it was of interest to synthesise the transition Group VIa metal carbonyls in order to compare and contrast their phosphorus chemical shifts with those complexes containing a similar carbon backbone.

As with other complexes studied and highlighted in this and the previous chapter, direct reaction of the ligand with the metal carbonyl leads to a range of species. This observation was found to be typical of the ligand under investigation. For example, in addition to maximise the required species, the dimeric species shown in Fig.3.14 was also formed.
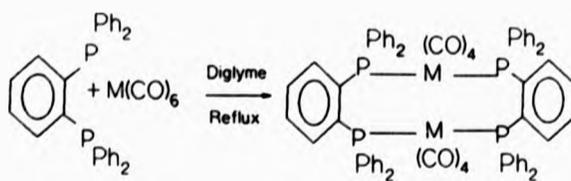
where M= Cr. W

Fig 3.14. Shows formation of the adduct-form when the diphosphine is refluxed directly with the metal hexacarbonyl.

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This fact required a more selective approach to the synthesis of the complex; to this end the species $M(CO)_5.[THF]$ was generated under a u.v. lamp and then reacted with diglyme Fig 3.15, to give the required product. However, characterisation by ^{31}P n.m.r. was only possible if the complex was analysed in hot diglyme and further proof of the structure was gleaned from mass spectra.
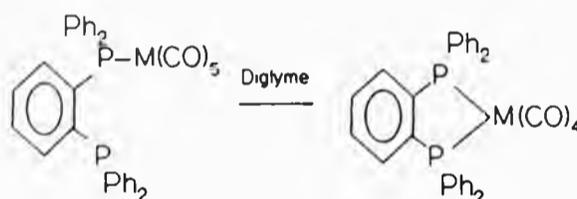
Fig 3.15 A more selective procedure adopted for the formation
of the required diphosphine.

The ^{31}P n.m.r. chemical shifts are tabulated in Table 3.08 along with those of dppe and cis-vpp which are taken from reference 56.

From the above table it can be seen that there is a consistent decrease in coordination chemical shift in going from chromium to tungsten, the Δ values for the monomeric species shown in Fig 3.15 for Mo and W show consistent Δ values as observed for five-membered rings. It would have been expected that the presence of two sp^2 hybridised carbon atoms in the aromatic framework would probably have given a greater distortion from the normal P-M-P bond angle of $90°$ compared with the saturated sp^3 and the cis-vpp complexes.

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Table 3.08. ^{31}P Chemical shifts for Transition Group VIa metal carbonyls.

COMPLEX	δ^{31}P/ppm	Δ^{31}P/ppm [b]
C$_6$H$_4$-1,2-(PPh$_2$)$_2$=L	-13.8	
Mo(CO)$_4$L	61.3	75.1
W(CO)$_4$L	30.6	44.4
(dimeric)Mo[a]	29.5	43.3
(dimeric)W[a]	28.8	42.6
dppe Cr(CO)$_4$[c]	79.4	91.9
Mo(CO)$_4$	54.7	67.2
W(CO)$_4$	40.1	52.6
cis-vpp Cr(CO)$_4$[c]	88.0	111.1
Mo(CO)$_4$[c]	63.9	87.0
W(CO)$_4$[c]	49.8	72.9

a. ^{31}P n.m.r. observed in hot diglyme in these complexes

b.   coordination chemical shift, see page 52

c.   data taken from reference 56

The presence of two sp^2 hybridised carbon atoms in the aromatic system to which phosphorus atoms are coordinated to transition metals does not appear to have made any great difference to the Δ values. However, it seems that the opposite is true whereby the sp^2 hybridised atoms in cis-vpp complex are deshielded more than that found in the aromatic system which could be said to be due to the greater degree of freedom of the carbon framework imparted by the sp^2 carbon atoms in the alkene-type complexes.

Mass Spectroscopy and Microanalytical Results.

Mass spectroscopy shows the fragmentation pattern of the complexes which give information concerning the identification of the known structure; the breakdown of the complexes follows a general pattern with an intense signal at m/e 185 which corresponds to Ph_2P-. The metal carbonyl complexes also give a constant fragmentation pattern with a sequential loss of m/e 28 for a carbonyl group; the characteristic grouping of the isotope peaks, for example, tungsten, also help to confirm the proposed structure.

Table 3.09. Mass Spectroscopy Data.

COMPLEX	Molecular Ion, m/e	Major ion detected, m/e
C_6H_4-1,2-(PPh_2) = L		
$LCr(CO)_4$	610	500,448,370,185
$LMo(CO)_4$	654	622,570,542,448,370,185
$LW(CO)_4$	742	714,654,630,550,474,444,364,185
mode (I)	670	642,558,420,185

Table 3.10. Microanalytical Results

COMPOUND	FOUND		CALCULATED	
	%C	%H	%C	%H
Cr mode (II)	64.0	4.5	64.5	4.3
W mode (II)	53.1	3.7	53.8	3.6

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CHAPTER 4

Sulphur and Selenium Derivatives of the Chiral Ligands

Introduction

When a phosphorus atom coordinates to a metal there is an accompanying increase in $\delta(^{31}P)$, and a similar but larger shift is also obtained when the oxidation number of phosphorus is increased by reaction with sulphur or selenium. This sulphurisation or selenisation reaction can provide a possible model for complex formation and its effect upon $\delta(^{31}P)$.

The first tertiary phosphine sulphides were prepared by the direct reaction of a trialkylphosphine with elemental sulphur[120, 121], and today this is still the most generally used method available. It is found that the rates of these reactions are generally fast for octatomic sulphur[122] and therefore the use of the other forms of sulphur, which results in even faster reaction rates, is seldom required. In addition, the reaction rates are strongly solvent-dependent, anion-solvating solvents generally inducing faster reactions[123]. The sulphurisation reactions of diphosphine species have been less extensively studied, but reactions analogous to those of monophosphines have been reported previously[124-126].

It has been found previously[127, 128] to this study of sulphur that the addition of selenium to tertiary phosphines proceeds less vigorously than the analogous addition of sulphur. In general, it is found that where as the lower aliphatic-substituted tertiary phosphines react with elemental selenium at room temperature, the higher

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homologues may require reflux in high boiling solvents or other stronger inducing methods to undergo reaction[129-131]. It has also been found recently by other workers[132] that when elemental selenium is reacted with the triphosphine ligand 1,1,2-tris(diphenylphosphino)ethane, the reaction leads to a mixture of mono-, di- and triselenium derivatives. By the use of homonuclear [31]P 2D-J resolved n.m.r. spectroscopy it was found possible to identify all the individual species in the reaction mixture. This chapter discusses work concerning the reactions of sulphur and selenium with chiral ditertiary phosphines.

Results and Discussion

Octatomic sulphur has been used extensively in poly(tertiaryphosphine) synthesis, in these reactions it serves two purposes.

Firstly, the extension of the preparative route to the synthesis of poly(tertiaryphosphines) with methyl groups rather than phenyl groups bonded to the phosphorus atoms[4] has been discouraged by the inconvenience of preparing and handling the highly volatile and air-sensitive dimethylvinylphosphine and/or methyldivinylphosphine which would be required as starting materials. This problem is circumvented by the protection of the corresponding phosphorus atom(s) with sulphur, the methyl groups are bonded to the phosphorus atom in the ultimate product. For this reason dimethylvinylphosphine sulphide and the other vinylphosphine sulphides are always protected by storage under nitrogen in the dark. The dimethylvinylphosphine sulphide are usually liquids and therefore easier to handle.

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Secondly, it is also found that when a primary phosphine undergoes a base-catalysed addition reaction in a 1:1 mole ratio with a vinylphosphine the products tend to be of the adduct-form. An example of this is the base-catalysed addition of $C_6H_5PH_2$ to $CH_2=CHP(C_6H_5)_2$ which gives almost exclusively the 1:2 adduct $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ even when the reactants are used in a 1:1 ratio. Therefore the nature of the vinylphosphorus compound is thus critical in determining the ease of stopping the reaction with primary phosphines at the 1:1 adduct[8,133] stage.

In all cases the sulphur atoms which are used as "protection" can be removed from the final phosphine sulphide phosphorus atom(s) by treatment with lithium aluminium hydride in boiling dioxane to give the corresponding methyl poly(tertiaryphosphine). The base-catalysed addition of phosphorus-hydrogen bonds to vinylphosphorus compounds can be considered to be of the Michael additon type which proceeds according to the sequence given at the end of chapter 1.

Grim has noted the ability of various derivatives of (phosphinomethyl)phosphine sulphides to form potentially five-membered chelate rings when the phosphine sulphide is refluxed with a Group VIa metal carbonyl in diglyme or via an exchange[134] reaction in hexane. Another interesting reaction of the phosphine sulphides is brought about by the close proximity of the phosphino and thiophosphoryl groups in the same molecule which provides for an additional unique reaction[135]. It is a well-known synthetic procedure in which sulphur is transferred to tributylphosphine from sulphides of tertiary phosphines of lesser basicity, especially triarylphosphines[19], as shown below.

Figure 4.0

$$Ph_2P(S)CH_2PR^1R^2 \longrightarrow Ph_2PCH_2P(S)R^1R^2$$
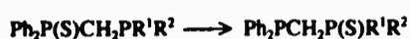
The above system permits this transfer in the same molecule when dimethylphosphino(diphenylthiophosphoryl)methane is heated at ca. 160°C in an inert solvent such as diglyme.

N.M.R. Characterisation

For the sulphur derivatives of asymmetric diphosphines containing the mono- and di-sulphides synthesised by Grim, data[136] are presented for which the parameter Δ_s (similar to the coordination chemical shift $\Delta(\delta^{31}P)$) can be defined[136] as the change in chemical shift upon sulphurisation.

$$\Delta_s = \delta^{31}P^V_{(s\text{-derivative})} - \delta^{31}P^{III}_{(free\ ligand)} \qquad 4.0$$

It is found from these series of derivatives that the ^{31}P chemical shifts of the P^V atoms lie within narrow ranges for each different environment (Fig 4.01).

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Fig 4.01
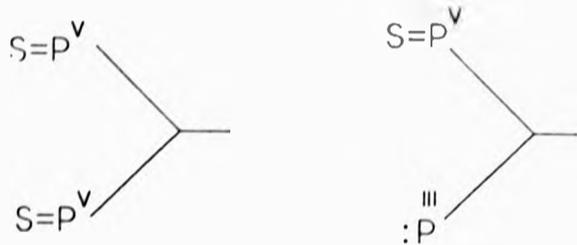
For the species containing two geminally related P^V atoms the mean, Δ_s, for the unsymmetrical diphosphines is 54.9 ppm, whilst for the P^V atoms that are geminally related to P^{III} atoms (i.e. the monosulphide), $\Delta_s = 62.0$ ppm. From this it can be concluded that the two types of P^V atoms (Fig 4.01) which have inherently different environment show characteristic and mutually exclusive Δ_s ranges (see Table 4.0). This is ca. 7 ppm difference, which is sufficient to distinguish the two resonances due to the two different types of P^V atoms when present in a mixture.

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Table 4.0. Sulphurisation chemical shift, Δ,

data for unsymmetrical phosphine sulphides

a COMPOUND	b Δ/ppm Δ(δPPh$_2$)	Δ(δPR^{1}R^2)	|Jpp|/Hz
Ph$_2$P(S)CH$_2$PMe$_2$	61.8	-1.7	56.0
Ph$_2$P(S)CH$_2$PPhMe	61.6	-4.2	66.0
Ph$_2$P(S)CH$_2$PPhEt	62.3	-5.5	68.0
Ph$_2$P(S)CH$_2$PPh(i-Pr)	62.9	-5.8	71.0
Ph$_2$P(S)CH$_2$P(i-Pr)$_2$	61.5	-5.0	77.0
Ph$_2$P(S)CH$_2$P(S)Me$_2$	55.2	87.3	17.0
Ph$_2$P(S)CH$_2$(S)PPhMe	55.8	73.7	16.0
Ph$_2$P(S)CH$_2$(S)PPhEt	56.0	69.8	15.0
Ph$_2$P(S)CH$_2$P(S)Ph(i-Pr)	55.5	66.8	18.0
Ph$_2$P(S)CH$_2$P(S)(i-Pr)$_2$	51.8	73.8	16.0

a.   For chemical shift data see reference 134.

b.   Since both Δ(δPPh$_2$) and Δ(δPR^{1}R^2) are shown, the discussion
is centred only upon the Δ(δPPh$_2$) shift.

From inspection of Table 4.01 it becomes evident that there is a wide variation of the sulphur coordination chemical shift, Δ_s, and that there is no consistency in the data; this may be a reflection of the large steric bulk around the phosphorus atom of the large diphenyl groups being in close proximity to the coordinated sulphur atom; furthermore, the phosphorus atom is attached to a secondary carbon atom bearing a methyl or ethyl group, which (as discussed in chapter 2) is known to have a steric effect on the ^{31}P chemical shifts.

The chemical shift of the disulphide for $dppeS_2 = 44$ ppm, that is, to low frequency when compared with the disulphide of 2,3-bis(diphenylphosphino)butane, (Table 4.01). As previously stated, this would suggest an influence of steric/electronic factors for the high frequency shift of the chiral disulphide ligand although the steric factor would be expected to be dominant.

Table 4.01. ^{31}P n.m.r. chemical shift data for the chiral ligands of Sulphur and Selenium derivatives and their coordination chemical shift, Δ.

COMPOUND[a]	CHEMICAL SHIFT/ppm		Δ/ppm	
	$\delta^{31}P_A$	$\delta^{31}P_B$	$\Delta_c(\delta^{31}P_A)$	$\Delta_c(\delta^{31}P_B)$
Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$	-9.2			
Ph$_2$P(S)CH(CH$_3$)CH(CH$_3$)(S)PPh$_2$	52.8		62.0	
Ph$_2$P(Se)CH(CH$_3$)CH(CH$_3$)(Se)PPh$_2$	46.6		55.8	
Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$	1.0	-21.3		
Ph$_2$P(S)CH(CH$_3$)CH$_2$(S)PPh$_2$	20.4	11.4	19.4	32.7
Ph$_2$P(Se)CH(CH$_3$)CH$_2$(Se)PPh$_2$	29.8	13.6	28.8	34.9
Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$	-6.1	-31.0		
Ph$_2$P(S)CH(CH$_2$CH$_3$)CH$_2$(S)PPh$_2$	50.1	37.0	56.2	68.0
Ph$_2$P(Se)CH(CH$_2$CH$_3$)CH$_2$(Se)PPh$_2$	48.7	35.6	54.8	66.6
Ph$_2$P(CH$_2$)$_2$CH(CH$_3$)PPh$_2$	-3.7	-17.7		
Ph$_2$P(S)(CH$_2$)$_2$CH(CH$_3$)(S)PPh$_2$	51.8	42.1	55.5	59.8
Ph$_2$P(Se)(CH$_2$)$_2$CH(CH$_3$)(Se)PPh$_2$	33.3	17.8	37.0	35.5
Ph$_2$P(CH$_2$)$_3$CH(CH$_3$)PPh$_2$	-1.3	-16.2		
Ph$_2$P(S)(CH$_2$)$_3$CH(CH$_3$)(S)PPh$_2$	53.0	42.5	54.3	58.7

a. Dissolved in CDCl$_3$ solution.

b. In ppm to high frequency of external 85% H$_3$PO$_4$.

It is observed that the $^3J(^{31}P-^{31}P)$ couplings (Table 4.02) in these derivatives are generally larger when the phosphorus atoms are pentavalent. This could possibly be attributed to two factors (i) the increase in s- character of the phosphorus bonds as the quadruply connected phosphorus approaches sp^3-hybridisation, with a concomitant increase in the effective nuclear charge and (ii) the generally large values of $^3J(^{31}P^V-^{31}P^V)$ may reflect conformational differences within the molecule arising from the increased bulk of the phosphorus moiety upon sulphurisation.

The disulphides synthesised by Grim[134] of the type $Ph_2P(S)CH_2PR^1R^2$ show that $^2J(PP)$ increase in magnitude as the bulk of R^1 and R^2 groups increases. The argument above can also be applied in the case of these different chiral phosphines where the chiral centre resides on the phosphorus atom rather than the backbone.

Sulphide-Metal Carbonyl Complexes

When a (phosphinomethyl)phosphine sulphide is reacted with $Cr(CO)_6$ or $Mo(CO)_6$ in diglyme, a chelate complex is produced in which the phosphino phosphorus and the sulphur are donor atoms, thus producing a five-membered chelate ring. A short discussion for these chelate rings is given.

The $|J_{pp}|$ values for the $[Ph_2P(S)CH_2PR^1R^2]M(CO)_4$ complexes[134] vary from slightly larger than in the free ligand (most of the compounds) to slightly less than in the free ligand $Ph_2P(S)CH_2P(i-Pr)_2$.

$|J_{pp}|$ can be regarded as the sum of the contributions of phosphorus-phosphorus coupling through the P-C-P backbone, $^2J^B(PP)$, and through the metal center, $^2J^M(PP)$. It is found difficult to separate these terms. However, other results indicate that the

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model has validity[17,21]. It is found that $|Jpp|$ is consistently 5-7 Hz larger for the chromium complexes than for the corresponding molybdenum and tungsten complexes, in which $|Jpp|$ is nearly identical. Also, $|Jpp|$ is found to be larger for the diphenyl complexes, i.e. $[Ph_2P(S)CH_2PPh_2]M(CO)_4$, and smallest for the dialkyl complexes, $[Ph_2P(S)CH_2PR_2]M(CO)_4$.

From the data collected[21] in the studies of the disulphide derivatives of the ligands 1-(diphenylphosphino)-3-(alkylphenylphosphino)propane, $Ph_2P(CH_2)_3PPhR$, it is found that the ligand backbone contribution $^4J^BPP$ is nil, from which it is assumed also that $^4J^BPP$ is also zero in the chelate such that (from equation 2.4 page 59) $Jpp = {}^2J^MPP$; which is in agreement to the disulphide of 1,3-bis(diphenylphosphino)butane.

Chemical Exchange

A temperature-dependent phenomenon are observed in the case of a nucleus exchanging between two equally populated sites. For example in the ^{31}P n.m.r. spectra for the tripodal ligand shown:

Fig 4.02
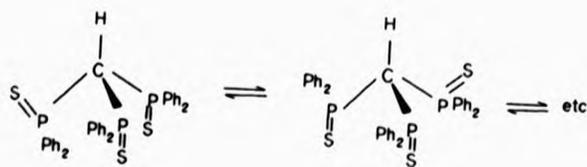
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COMPOUND	$J(P_A P_B)$/Hz	$^1J(SeP)$/Hz
Ph₂PCH(CH₃)CH(CH₃)PPh₂	a	-
Ph₂P(S)CH(CH₃)CH(CH₃)(S)PPh₂	a	-
Ph₂P(Se)CH(CH₃)CH(CH₃)(Se)PPh₂	a	734.9
Ph₂PCH(CH₃)CH₂PPh₂	22.0	-
Ph₂P(S)CH(CH₃)CH₂(S)PPh₂	58.6	-
Ph₂P(Se)CH(CH₃)CH₂(Se)PPh₂	61.0	731.2, 727.5
Ph₂PCH(CH₂CH₃)CH₂PPh₂	19.8	-
Ph₂P(S)CH(CH₂CH₃)CH₂(S)PPh₂	59.8	-
Ph₂P(Se)CH(CH₂CH₃)CH₂(Se)PPh₂	59.8	740.4, 709.2
Ph₂P(CH₂)₂CH(CH₃)PPh₂	b	-
Ph₂P(S)(CH₂)₂CH(CH₃)(S)PPh₂	b	-
Ph₂P(Se)(CH₂)₂CH(CH₃)(Se)PPh₂	b	732.4, 723.9
Ph₂P(CH₂)₃CH(CH₃)PPh₂	b	-
Ph₂P(S)(CH₂)₃CH(CH₃)(S)PPh₂	b	-

a. Symmetrical ligand therefore no observable coupling.
b. No observable coupling.

the spectra range from two sharp lines at the frequencies corresponding to the chemical shifts of the two sites when the exchange rate is slow on the n.m.r. time scale, as the temperature is slowly increased a gradually broadening and converging signals is seen[137] as the exchange rate increases. Finally, at high temperatures a single sharp line at the mean chemical shift position is seen when the exchange is rapid.

This type of variable temperature n.m.r. spectroscopy has been used extensively to study many dynamic processes. The rates of exchange involved and line-separations vary considerably, so that some samples require cooling rather than heating to reach the temperature where the exchange rate affects the form of the n.m.r. spectra. Studies have for instance been made on the hindered rotation which occurs in the complex $[MeS_2PCH_2PMeS_2]Mo(CO)_4$, (where MeS = 2,4,6 - trimethylphenyl) under low temperature ^{13}C n.m.r., it is found that rotation about the aromatic ipso-carbon-phosphorus bond is stopped. From the coalescence temperature, T, the free energy barrier to rotation ΔG^+ was evaluated[138]. Other areas where variable temperature n.m.r. has been used is in the study of the flexing of saturated rings and of the exchange of ligands on transition metal complexes.

Other types of disulphide derivatives which have been of interest to structural chemists are the dithioxodi-λ^5-phosphanes, $[R^1R^2(S)P]_2$ shown overleaf.

Fig 4.03
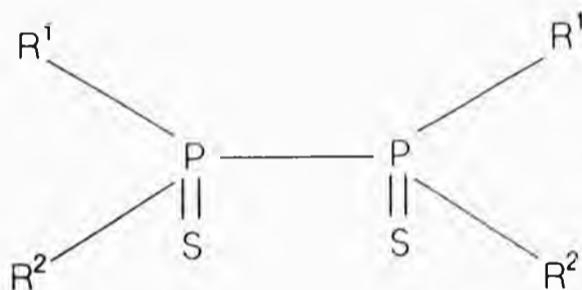
Such compounds have been of interest (a) to n.m.r. spectroscopists because of the problems of spectral analysis for symmetrical spin-systems[140,141] and because of the wide, and so far unexplained, variation in the values of $^1J(PP)$, and (b) to structural chemists because of the problem of internal rotation about the P-P bond[143].

It appears that in these disulphides the predominant influence on chemical shifts and coupling constants is the size of the substituent and the effect this has on the bond angles at phosphorus and therefore on hybridisation.

The large increase in ^{31}P chemical shift caused by the substituent replacement Me —> Et —> Pr^i —> Bu^t for both series of compounds is presumably due to an increase in CPC bond angle leading to a change in hybridisation at phosphorus. This, as explained in Chapter 1, leads to an increase in s-orbital character in the phosphorus bonds, but a decrease in s-character of the lone-pair electrons, and hence a decrease in shielding of the phosphorus nucleus[16].

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The values of J(PP) for the disulphide ligands are found[144] to be consistently lower than the corresponding free ligands and the variation with the substituent bulk is found to be smaller. That the effect is primarily one of substituent bulk is shown by the fact that J(PP) for $[R_2P(S)]_2$ with $R = Pr^n$ is close to that for $R = Et$, but very different from that for $R = Pr^i$. It is seen that with an increase in steric bulk in $MeBu^tP(S)P(S)BU^tMe$ the CPC interbond angle will be increased by t-butyl groups. Hence, the s-character of hybrid orbitals used to form the P-P bond will be reduced thereby resulting in a change of phosphorus hybridisation arising from the bulk of the t-butyl groups. This invariably will result in a hindered internal rotation about the P-P bond.

From heteronuclear magnetic triple resonance studies of similar disulphides[145], signs of some of these diphosphines have been determined and are found to be negative, it also appears from these results that increasing the bulk of the groups attached to phosphorus makes the coupling constant more negative; this is attributed to increasing s-character in the P-C bonds and correspondingly reduced s-character in the P-P bonds, a similar situation to that found for $^1J(^{31}P-^{31}P)$ in species containing $P^{III}-P^{III}$ bonds.

Overlap of the signals from phenyl groups in the ^{13}C n.m.r. spectra makes it difficult to carry out a full analysis of the ipso, ortho, meta and para-carbon resonances.

From Table 4.03, the backbone bridging groups do not appear to show a significant high frequency chemical shift on sulphurisation or selenisation when compared to the corresponding free ligand, however, the exception to this generalisation is shown by

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the ligand 1,2-bis(diphenylphosphino)propane and its sulphur and selenium derivatives. It would have been expected that on coordination of the phosphorus to the sulphur (or selenium) atom the σP-C____ bond would be deshielded resulting in a high frequency chemical shift. However, contrary to this expectation, it is shown by the ^{13}C n.m.r. data in Table 4.03, that the bridging carbon atoms in the backbone are found considerably at a low frequency from the corresponding carbon atoms in the free ligand.

This observation could be attributed to the electron donating ability of the methyl group which has a positive inductive effect by releasing electrons to the carbon backbone thereby resulting in greater shielding. A steric constraint which could contribute to the unexpected ^{13}C chemical shifts is not thought to be of any great significance. However, this factor was found to be of importance in the understanding of ^{31}P chemical shifts, page 51. Table 4.04 shows the J(P-C) coupling constant values when the ligands undergo sulphurisation or selenisation.

Probably the most striking feature of the results presented in Table 4.02 is the large $^1J(^{77}Se-^{31}P)$ coupling shown when the ligand undergoes selenisation or sulphurisation. All these couplings fall within the range of 709-740 Hz, with the unsubstituted diphenylphosphino end having a slightly larger value than the diphenylphosphino end closest to the substituted carbon.

Table 4.03. ^{13}C n.m.r. chemical shift data for bridging carbon atoms in the chiral sulphur and selenium ligands

COMPOUND	$\delta^{13}CH^a$	$\delta^{13}CH_2^a$	$\delta^{13}CH_3^a$
Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$	31.7	-	12.4
Ph$_2$P(S)CH(CH$_3$)CH(CH$_3$)(S)PPh$_2$	32.2	-	10.5
Ph$_2$P(Se)CH(CH$_3$)CH(CH$_3$)(Se)PPh$_2$	32.2	-	11.2
Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$	55.6	52.8	47.9
Ph$_2$P(S)CH(CH$_3$)CH$_2$(S)PPh$_2$	32.9	29.2	13.9
Ph$_2$P(Se)CH(CH$_3$)CH$_2$(Se)PPh$_2$	32.9	29.6	14.3
Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$	34.0	29.9, 23.7	11.6
Ph$_2$P(S)CH(CH$_2$CH$_3$)CH$_2$(S)PPh$_2$	33.8	29.3, 23.3	12.7
Ph$_2$P(Se)CH(CH$_2$CH$_3$)CH$_2$(Se)PPh$_2$	35.5	31.3, 23.5	12.9
Ph$_2$P(CH$_2$)$_2$CH(CH$_3$)PPh$_2$	31.9	30.2, 26.5	16.7
Ph$_2$P(S)(CH$_2$)$_2$CH(CH$_3$)(S)PPh$_2$	34.4	31.6, 28.8	13.3
Ph$_2$P(Se)(CH$_2$)$_2$CH(CH$_3$)(Se)PPh$_2$	33.6	31.2, 28.7	14.1
Ph$_2$P(CH$_2$)$_3$CH(CH$_3$)PPh$_2$	29.8	34.9, 28.0, 24.0	16.1
Ph$_2$P(S)(CH$_2$)$_3$CH(CH$_3$)(S)PPh$_2$	34.6	31.7, 21.0	13.2

a.   In ppm to high frequency of Me$_4$Si(in CDCl$_3$ solut^n).

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Table 4.04. ^{13}C n.m.r. data show J(P-C) coupling constants for the sulphur and selenium chiral ligands

COMPOUND	J(^{31}P-^{13}CH)	$J(^{31}P-^{13}C)$/Hz J(^{31}P-^{13}CH$_2$)[a]	J(^{31}P-^{13}CH$_3$)
Ph$_2$PCH(CH$_3$)CH(CH$_3$)PPh$_2$	30.0	-	30.0
Ph$_2$P(S)CH(CH$_3$)CH(CH$_3$)(S)PPh$_2$	52.0	-	-
Ph$_2$P(Se)CH(CH$_3$)CH(CH$_3$)(Se)PPh$_2$	44.7	-	-
Ph$_2$PCH(CH$_3$)CH$_2$PPh$_2$	16.5	6.1	6.1
Ph$_2$P(S)CH(CH$_3$)CH$_2$(S)PPh$_2$	52.8	54.2	-
Ph$_2$P(Se)CH(CH$_3$)CH$_2$(Se)PPh$_2$	48.4	-	-
Ph$_2$PCH(CH$_2$CH$_3$)CH$_2$PPh$_2$	14.7	14.7, 10.7	10.7
Ph$_2$P(S)CH(CH$_2$CH$_3$)CH$_2$(S)PPh$_2$	56.7	45.0	4.9
Ph$_2$P(Se)CH(CH$_2$CH$_3$)CH$_2$(Se)PPh$_2$	45.8	39.7	4.9
Ph$_2$P(CH$_2$)$_2$CH(CH$_3$)PPh$_2$	10.4	34.8, 23.8	15.9
Ph$_2$P(S)(CH$_2$)$_2$CH(CH$_3$)(S)PPh$_2$	11.6	15.9, 9.8	b
Ph$_2$P(Se)(CH$_2$)$_2$CH(CH$_3$)(Se)PPh$_2$	12.5	24.2, 10.3	< 1.0
Ph$_2$P(CH$_2$)$_3$CH(CH$_3$)PPh$_2$	9.8	12.8, 12.2	15.9
Ph$_2$P(S)(CH$_2$)$_3$CH(CH$_3$)(S)PPh$_2$	12.2	18.3, 15.3	< 1.0

a. Really, shows N = |J(AX) + J(A'X)
b. No coupling.

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$^1J(SeP)$ is usually found to occur in the range 700-1000 Hz; with Selenium satellites ($I = \frac{1}{2}$ natural abundance 7.1 %) symmetrically displaced from the central phosphorus resonance. The monoselenide derivative[146] $MeS_2P(Se)CH_2PMeS_2$ shows two chemically inequivalent phosphorus nuclei with $^1J(SeP) = 708$ Hz and on close inspection the P^{III} resonance also reveals a set of ^{77}Se satellites due to long range coupling $^3J(SeP)$ of 13.7 Hz.

It is interesting to note that the ^{31}P chemical shift of $Ph_2P(Se)CH(CH_3)CH(CH_3)(Se)PPh_2$ of 46.6 ppm is at a slightly higher frequency than that of its analogue derivative[147] $Ph_2P(Se)CH_2CH_2P(Se)PPh_2$ 35.9 ppm. This is most probably a reflection of the presence of two bulky methyl groups causing a distortion of the normal sp^3-hybridisation of phosphorus.

Table 4.05. Mass spectral fragmentation results for the disulphides and diselenides of the chiral ligands

COMPOUND	MAJOR IONS DETECTED, m/e
$Ph_2P(Se)CH(CH_3)CH_2(Se)PPh_2$	570, 304, 264, 185
$Ph_2P(Se)CH(CH_2CH_3)CH_2(Se)PPh_2$	584, 320, 264, 184
$Ph_2P(S)CH(CH_3)CH(CH_3)(S)PPh_2$	490, 274, 218, 184
$Ph_2P(Se)CH(CH_3)CH(CH_3)(Se)PPh_2$	584, 320, 264, 184
$Ph_2P(S)(CH_2)_2CH(CH_3)(S)PPh_2$	490, 274, 256, 218, 184
$Ph_2P(Se)(CH_2)_2CH(CH_3)(Se)PPh_2$	584, 320, 264, 184
$Ph_2P(S)(CH_2)_3CH(CH_3)(S)PPh_2$	504, 288, 218, 184

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From the mass spectra the detection of the parent molecular ion M^+ was possible for these small ligands of low molecular weight. The fragmentation pattern of these ligands followed a generally consistent pattern in that the most intense signal shown by the mass spectra was found to be $m/e = 184$, as shown above in the table, this corresponds to the Ph_2P- fragment. The parent molecular ion M^+ was always present in these ligands which confirms the expected structure.

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CHAPTER 5

EXPERIMENTAL

Instrumentation

^{1}H, ^{13}C and ^{31}P n.m.r. spectra were recorded on a JEOL FX90Q Fourier transform spectrometer. Samples were examined as solutions in 10 mm o.d. spinning n.m.r. tube and at ambient temperature (21°C) unless otherwise stated. The field/frequency lock was provided by means of the ^{2}D signal from either a permanent external (D_2O) sample or in cases where higher resolution was required, an internal deuterated solvent was added to the sample.

The transition metal complexes were examined in deutero chloroform ($CDCl_3$) to which was also added $Cr(acac)_3$ (0.07 molar), this effectively reduces the relaxation time (T_1) of the ^{13}C nuclei in the carbonyl region, hence, this allowed for a faster rate of accumulation. Typically for ^{13}C spectra of carbonyl groups a pulse interval of 2 sec. and pulse angle of 60° were maintained. Chemical shifts are expressed relative to the standard references using the δ convention i.e. shifts to high frequency are positive. All ^{13}C chemical shifts are from the reference compound TMS (0.0 ppm) in $CDCl_3$.

PREPARATIONS

General

Synthetic reactions were carried out under an atmosphere of dry dinitrogen. Solvents used in the reactions were de-aerated with dinitrogen prior to use and in cases where dry solvents were required, these were distilled over calcium hydride and stored over sodium wire. Some complexes were prepared using the u.v. irradiation methods of Strohmeier[148-152] via the reactive intermediate[153] $W(CO)_5.[THF]$. A diagram of the apparatus is given.

Preparation of 1,4-bis(diphenylphosphino)butane[154]

$$2Na + PPh_3 \longrightarrow NaPh + NaPPh_2$$

$$\downarrow NH_4Cl$$

$$NaCl + NaPPh_2 + PhH + NH_3$$

$$\downarrow \tfrac{1}{2}Br(CH_2)_4Br$$

$$\tfrac{1}{2}Ph_2P(CH_2)_4PPh_2 + NaBr\downarrow$$

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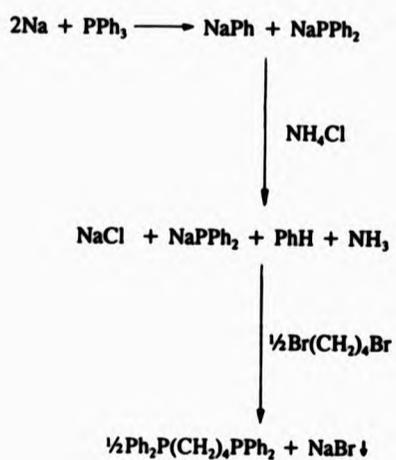
Apparatus used for u.v. irradiation.

WATER
OUT

WATER
IN

NITROGEN
BUBBLER

ADDITION OF
REACTANT

PYREX
VESSEL

MEDIUM PRESSURE
MERCURY LAMP

QUARTZ
INSERT

MAGNETIC
STIRRER

153
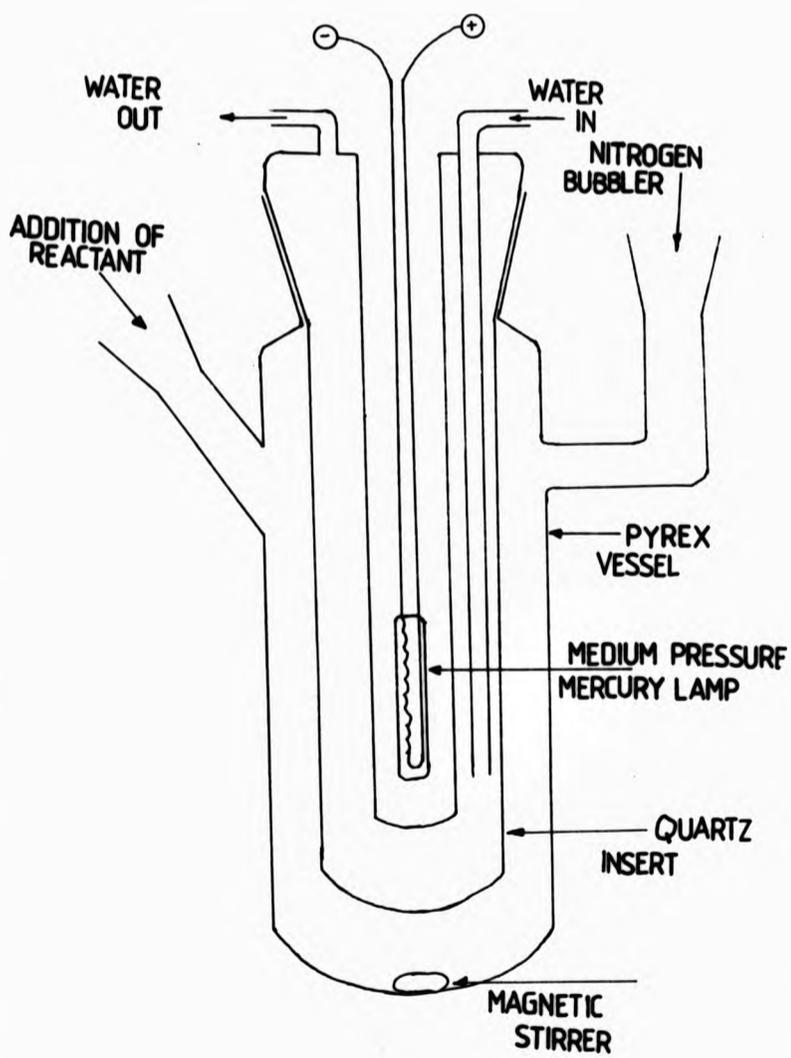
In a 1 litre three neck flask equipped with a mechanical stirrer and reflux condenser, sodium metal (6.75g, 0.29 moles) was added to the flask containing liquid NH_3 which was filled to 60% capacity. The addition of sodium was in small pieces such that complete dissolution of the metal took place and the solution finally turning dark blue. This was then left to stir for ca. 15 mins. after complete addition.

A solution of triphenylphosphine (38.4g, 0.14 moles) in THF(100 cm³) was dissolved; the solution was then added dropwise over a period of 1 hour, this formed the required product, $NaPPh_2$, and left to stir for ca. 15 mins. after which time dried NH_4Cl (7.85g 0.14 moles), was added via a small condenser.

Addition of NH_4Cl (reaction mixture turns orange) is carried out so that NaPh is eliminated to give NaCl and C_6H_6 leaving behind $NaPPh_2$ which when reacted with 1,4-dibromobutane (15.84g 0.073 moles) in 65 cm³ deoxygenated THF (added dropwise) gave the expected diphosphine.

The reaction mixture was then left overnight for the liquid NH_3 to evaporate after which time 40 cm³ methanol was added to the crude product and refluxed for ca. 30 mins. under N_2 such that any unreacted Na was destroyed.

To the reaction mixture was added ca. 80 cm³ deoxygenated water whilst stirring, such that a seperate layer formed, the bottom aqueous layer contained the inorganic salts and in the top organic layer was the product. The organic layer was isolated via a separating funnel and the aqueous layer was extracted (3 x 100 cm³) with diethyl ether; the extracts were then added to the mother liquor. The organic layer was then dried over anhydrous $MgSO_4$ for ca. 2 hours after which time the organic solvent was filtered and removed via a rotary evaporator to leave a yellow solid. The product was crystallised from ethanol and toluene (5:1). Yield 18 gm (60%).

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<u>Transition Metal Complexes</u>[17]

An example of the preparation of molybdenum complex with the above ligand is outlined. This was repeated for the chromium and tungsten hexacarbonyls. The diphosphine (1g, 2.34 mmoles) was refluxed with molybdenum hexacarbonyl (0.62g 2.34 mmoles) in deoxygenated diglyme(b.p. 161°C) for ca. 30 mins. the solution was then left to cool and the solvent was removed under reduced pressure (0.5 mm Hg) to leave an oily residue. This was taken up by 20 cm³ dichloromethane and 40 cm³ methanol which was refluxed and left to cool overnight to deposit bright yellow crystals.

Yield 0.82g (55%). The chromium and tungsten analogues gave 58% and 66% respectively.

<u>Preparation of 1,1-bis(diphenylphosphino)ethene</u>[18].

Triphenylphosphine (80g, 0.30 moles) was dissloved in 700 cm³ THF in a three neck 2 litre flask equipped with a mechanical stirrer and water condenser. To the stirred reaction mixture were added thin strips of lithium (4.2g, 0.6 moles) and it was then left to stir overnight under nitrogen; this gave a deep-red colour. The solution was treated with 2-chloro-2-methylpropane (27.8g 0.3 moles) to remove phenyllithium, and left to stir for 15 mins. after which time the reaction mixture was decanted into a dropping funnel. The resulting solution of LiPPh$_2$ was then added dropwise, under nitrogen, to 1,1-dichloroethene (14.5g, 0.15 moles) in benzene (50 cm³). When the addition was complete, dilute HCl (200 cm³) was added such that a partition layer formed so that the top organic layer could be removed; the aqueous layer was then washed with diethyl ether (3 x 100 cm³) to remove any product left in the aqueous

layer. These washings were then added to the mother liquor and left to dry over anhydrous $MgSO_4$ for ca. 30 hrs. After removal of the organic solvents on a rotary evaporator an oily residue remained which crystallised on addition of absolute alcohol. The product was then further recrystallised from ethanol.

Yield 16 gm (27%).

Transition Metal Complexes.

Complexes of the above ligand were prepared with transition metal carbonyls in diglyme. However, the molybdenum complex for the prepared ligand required an alternative route rather than direct reaction of the metal hexacarbonyl with the diphosphine. This is demonstrated nicely by the reaction between the ligand $(Ph_2P)_2C=CH_2$ (1 g, 2.52 mmoles) with $Mo(CO)_4(pip)_2$ (0.95 g, 2.5 mmoles) in 10 cm^3 dichloromethane which is then stirred for 15 mins. after this time the solution is filtered and the solvent removed under reduced pressure (0.5 mmHg). To the oily residue CH_2Cl_2/MeOH was added (1:3) to effect crystallisation. Yield 0.93 g (61%). For the chromium and tungsten complexes the yields were 68% and 72% respectively.

Preparation of 2.3-bis(diphenylphosphino)butane[27,155]

To a 2 litre flask containing p-toluenesulphonyl chloride (134 g, 0.7 moles) was added with stirring dry pyridine (135 cm^3) at 0°C; to the stirred solution was then added 2,3-Butanediol (containing mixture of DL and meso-forms; 28.0 gm, 0.30 moles) over a period of 45 minutes. The solution set to a gelatinous mixture which was then allowed to stir at room temperature overnight for approximately 18 hours.

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After this time small portions of ice-water were added and after each addition the mixture was vigorously shaken. After about 90 minutes a solid formed. The product was then poured into another 2 litre flask containing ice and concentrated HCl (12 M, 130 cm³) and was then left to stir for 1 hour.

The solid was then collected over a Büchner funnel and washed thoroughly with water. It was then dissolved in methylene chloride, 200 cm³, and the solution was initially extracted with 0.5N HCl (2 x 100 cm³) and then with water, the process being carried out in a 2 litre separating funnel. The organic layer was then separated and dried over anhydrous MgSO₄ for ca. 2 hours after which time the solvent was stripped off on the rotary evaporator. To the orange/brown oil left behind was added n-propanol (100 cm³), and the mixture was left in a freezer overnight to give a fine crystalline product. The pure ditosylate was collected, washed with n-propanol and dried in vacuo. Yield 92 gm (76%).

In a 2 litre 3-neck flask were placed lithium strips (6.5 gm, 0.93 moles) and triphenylphosphine (123 gm, 0.47 moles) in dry tetrahydrofuran (300 cm³) which generated a solution of lithium diphenylphosphide when left to stir overnight. The phenyl lithium generated during the course of the reaction was destroyed by addition of tertiary butyl chloride (43.7 gm, 0.47 moles). The resulting deep orange solution was cooled to -4°C and a solution of 2,3-butanediol di-p-toluenesulphonate (53.8gm, 0.134 moles) in dry tetrahydrofuran (75 cm³) was added with stirring over a period of 45 minutes. The reaction mixture was then left to stir for 1 hour. Deoxygenated water (175 cm³) was then added, dropwise, to the reaction mixture until the lithium salts were taken up in the water layer. The mixture was then decanted into a 2 litre

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separating funnel and the aqueous layer was separated and washed with diethyl ether (2 x 100 cm³) which was then added to the main organic layer. This was then dried over anhydrous magnesium sulphate for ca. 2 hours and the solvent was removed on the rotary evaporator. The yellow oily material in the flask was taken up in industrial methylated spirits (200 cm³) and then left to crystallise (3-4 weeks). This afforded 14.5 gm (26.3%) of the diphosphine as pure white small colourless prisms.

1,2-bis(diphenylphosphino)propane[41]

The procedure adopted in the previous synthesis was repeated except that 51.7 gm of the ditosylate derivative, OTsCH(CH₃)CH₂OTs, from a yield of 89 g (75%) was required to give the expected diphosphine. Yield 18 gm (32.5%).

1,3-bis(diphenylphosphino)butane

The appropriate amount of the ditosylate, OTsCH(CH₃)CH₂CH₂OTs, 52 gm and 2 moles lithium diphenyl phosphide gave, after the work up procedure, a white-powdery solid. Yield 15 gm (27%).

1,2-bis(diphenylphosphino)butane

A solution of diphenyl phosphide (0.47 moles) was generated from the appropriate amount of lithium and triphenyl phosphine. To the cold and stirred solution was added 52 gm ditosylate, OTsCH(CH₂CH₃)CH₂OTs. The reaction was worked up as previously described to give an oily residue. This was characterised by ¹³C, ¹H and ³¹P n.m.r. Yield 18g (32%).

1,4-bis(diphenylphosphino)pentane

A solution of diphenylphosphide (0.12 moles) was generated from equivalent amounts of lithium and triphenyl phosphine. To the deep-red phosphide solution was added dropwise tert-butyl chloride (11.26 g, 0.12 moles) after complete addition, with stirring, 1,4-dibromopentane (14 g, 0.06 moles) was added until the solution turned to a light yellow colour. To the reaction mixture was added deoxygenated water, dropwise, until two layers were seen to form. The aqueous layer containing the lithium salts was removed from the separating funnel leaving behind the organic layer containing the product. This was then left to dry over anhydrous magnesium sulphate. After 2 hours the solvent was filtered and then removed in vacuo leaving behind a yellow oil, which was then taken up in ethanol and left in the refrigerator to crystallise. The product (3.2 gm, 27.8%) was obtained as pure-white sharp crystals which did not require further recrystallisation m.p. 115°C.

Transition Metal Complexes

$M[Ph_2P(CH_2)_n(CH_3)CHPPh_2](CO)_4$, $M[Ph_2PCH(CH_2CH_3)CH_2PPh_2](CO)_4$ and $M[Ph_2PCH(CH_3)CH(CH_3)PPh_2](CO)_4$; where $n=1,2,3$ and $M=Cr,Mo,W$.

An example for the preparation once of the following complexes is given below: $W(CO)_6$ (0.85 gm, 2.41 moles) was reacted with the ligand 1,2-bis(diphenylphosphino)butane (1 gm, 2.42 moles) in refluxing diglyme (b.p. 161°C) for 45 minutes. The mixture was then cooled and the solvent was removed under reduced pressure (0.5mm Hg) leaving behind an oily residue which was then taken up in 40 cm³ toluene, under reflux, to which was then added 40 cm³ methanol. The

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product was then allowed to cool overnight at ambient temperature after which time yellow lustrous crystals were deposited. Yield 1.2 gm (69.8%).

The chromium and molybdenum complexes were obtained similarly in 72% and 65% yield respectively. Analogous procedures were adopted for the corresponding Cr, Mo and W complexes for the above-mentioned ligands.

The Sulphides of the Chiral Ligands.

2,3-bis(diphenylphosphino)butane (1 gm, 2.3 moles) and sulphur (0.15 gm, 4.7 moles) were refluxed in deoxygenated benzene (10 cm^3) for ca. 40 minutes. The solution was then filtered and reduced to half its volume in vacuo to which was added methanol (10 cm^3). This was then left to crystallise overnight in the refrigerator. Yield 0.6 gm (70%). This procedure was repeated for the above-mentioned chiral ligands.

The Selenides of the Chiral Ligands.

Similarly, 2,3-bis(diphenylphosphino)butane (1 gm, 2.3 moles) and selenium (0.37 gm, 4.7 moles) were refluxed in toluene for (10 cm^3) ca. 40 mins after which time the solution was filtered and evaporated. The oily residue was then taken up in methanol (25cm^3); this was then left to crystallise overnight. Yield 0.94 gm (68.5%).

In a similar fashion, the selenides of the corresponding chiral ligands mentioned above were prepared.

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Complexes of 1,2-bis(diphenylphosphino)benzene.

where M=Mo, W
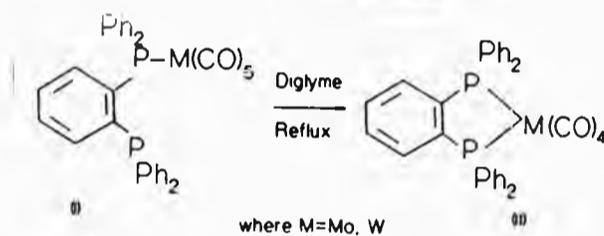
Irradiation[155] of a mixture of W(CO)$_6$ (2 gm, 5.7 moles) in THF (70 cm^3) overnight generated the species, W(CO)$_5$.[THF]. In a 100 cm^3 flask, fitted with side arm and equipped with a magnetic stirrer, was placed 1,2-bis(diphenylphosphino)benzene (0.5 gm, 1.2 moles) in THF (20 cm^3). To the stirred solution was added W(CO)$_5$.[THF] (14 cm^3); this was then left overnight to give the pentacarbonyl species (I). Complete conversion of the free-ligand to (I) was monitored by ^{31}P n.m.r.. The solvent was then removed under reduced pressure and the product was crystallised from CH$_2$Cl$_2$/MeOH (1:2). To the recrystallised product was added diglyme (20 cm^3) and the mixture was refluxed for ca. 35 minutes to achieve complete conversion to the five-membered ring compound (II) as confirmed by ^{31}P n.m.r.. On standing at room temperature the product recrystallised out as fine-white crystals, no further recrystallisation being necessary. Yield 0.53 gm (63.7%) based on the free ligand. In a similar fashion the chromium analogue was prepared. Yield 0.49 gm (71.6%).

For the corresponding five-membered molybdenum complex this could not be prepared by the above-mentioned method owing to difficulties in the generation of the species, Mo(CO)$_5$.[THF]. A sample of Et$_4$N$^+$[Mo(CO)$_5$.THF]$^-$Br (1.2 mmoles) were prepared by the method of Abel et al[156,157] and was left as a suspension in 40/60

petroleum ether (40 cm³). A solution of 1,2-bis(diphenylphosphino)benzene (0.54 gm, 1.2 mmoles) in CH₂Cl₂ (25 cm³) and then AlCl₃ (0.48 gm, 3.6 mmol) were added successively and the mixture stirred overnight. The reaction mixture was then filtered and the solvent reduced to half its volume to which was added methanol and left overnight in the refrigerator to crystallise. The species (I) was then collected and dried under vacuo; to this was added diglyme (20 cm³) and refluxed for ca. 45 minutes to give the corresponding five-membered ring structure when left to stand at room temperature. These complexes were characterised by ³¹P n.m.r. when the solution was still hot and also by mass spectra of the crystals. Yield 0.52 gm (66%).

Preparation of [2,2-bis(diphenylphosphino)ethyl]phenylphosphine.

1,1-bis(diphenylphosphino)ethene (3.2g, 8.1 mmoles) and a catalytic amount of BᵗuO⁻ K⁺(0.9g, 8.1 mmoles) was magnetically stirred to which was added PhPH₂,[158-160](0.89g, 8.1 mmoles) in 20 cm³ THF, in a dropwise manner. When the addition was complete the reaction mixture was stirred for a further 20 mins. and the solution was then filtered and removed under reduced pressure (0.5 mmHg). Addition of CH₂Cl₂/MeOH (1:3) to the oily residue resulted in the formation of white crystals, when left in the fridge.

Transition-Metal Complexes of [2,2-bis(diphenylphosphino)ethyl]phenylphosphine

[1]   PhPH₂ (2.4 gm) was irradiated in THF (70 cm³) overnight. An aliquot of the generated species (28 cm³) was added to the appropriate amount of catalyst, ᵗBu⁻OK⁺, and refluxed.   To   the   refluxing   solution   [1,1-bis(diphenylphosphino)ethene]Tungsten tetracarbonyl (1 gm, 1.4 mmoles) in

THF (15 cm³) was added dropwise and left to reflux overnight. After this period, the reaction mixture was then filtered and the solvent was removed under reduced pressure; to the oily residue methanol (30 cm³) was added and the mixture was refluxed; this was then left overnight at 0°C to give light green furry crystals of [2,2-bis(diphenylphosphino)ethyl] 2,2-Tungsten tetracarbonyl phenylphosphine. Yield 0.61 gm (53%).

Similarly, the chromium analogue was prepared by refluxing an aliquot of irradiated PhPH₂/[THF] (34 cm³) with the chromium complex (1.0 gm, 1.78 moles) and working up the reaction as described above.

[2]   W(CO)₆ (3.5 gm, 9.95 mmoles) was irradiated overnight in THF (70 cm³) to generate the species W(CO)₅.[THF]. Phenylphosphine (1 gm, 9.0 mmoles) was syringed through the side-arm of the u.v. irradiation apparatus and the mixture allowed to stir for ca. 3 hours. The solution was then filtered, reduced under vacum and crystallised from methanol (20cm³), to give W(CO)₅.PPhH₂, overnight.

W(CO)₅.PPhH₂ (0.5 gm, 1.5 mmoles) was dissolved in THF (12 cm³) and the appropriate amount of 'Bu⁻OK⁺ added and stirred until the solution was orange. To the stirred solution 1,1-bis(diphenylphosphino)ethene (0.45 gm, 1.2 moles) was added dropwise; this was then left to stir for ca. 30 minutes. The solution was then filtered and the solvent removed under vacuo. To the residue methanol (20 cm³) was added and the mixture refluxed for 10 minutes after

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which time the solution was left to cool overnight in the refrigerator. Yield 0.45 gm (47%).

[3] Mo(CO)$_4$(pip)$_2$[161](0.4g, 1.0 mmol) and the above ligand (Ph$_2$P)$_2$CHCH$_2$PPhH (0.5g, 1.0 mmol) were refluxed in 10 cm^3 CH$_2$Cl$_2$ for ca. 30 mins.. This resulted in the predominant formation of the diastereomeric mixture (1:1) and also small quantities of the four-membered ring structure; the solution was then filtered and 30 cm^3 MeOH added to effect crystallisation. ^{31}P n.m.r. showed the presence of the diastereomeric species as well as the four-membered ring structure. Further attempts were made to isolate these separately but proved unsuccessful.

[4] W(CO)$_6$ (0.5gm, 1.1 mmol) was dissolved in propionitrile (40 cm^3) under reflux for ca. 80 hrs. to give fac-W(CO)$_3$(EtCN)$_3$ in solution[112]. To this was added a solution of [2,2-bis(diphenylphosphino)ethyl]phenylphosphine (0.54gm, 1.1 mmol) in CH$_2$Cl$_2$ (15 cm^3) dropwise, and the reaction mixture refluxed for ca. 40 mins.
The solution was then filtered and the solvent removed under vacum to leave a yellow/brown solid; this required a further two recrystallisations from CH$_2$Cl$_2$/MeOH (1:3). This resulted in yellow crystalls. Yield 0.2 gm (45% based on the free triphosphine ligand).

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Pentaphosphine Complexes formed from [1,1-bis(diphenylphosphino)ethene]M(CO)₄

The pentaphosphine complex [[1,1-bis(diphenylphosphino)ethyl]molybdenum tetracarbonyl]₂phenyl phosphine was prepared by refluxing [1,1-bis(diphenylphosphino)ethene]molybdenum tetracarbonyl (0.1 gm, 16.6 mmoles) and phenylphosphine (18.2 mg, 16.6 mmoles) with the appropriate amount of tert-potassium butoxide in THF (12 cm³) for ca. 15 minutes. The reaction mixture was then filtered and the solvent was removed under reduced pressure; to the residue was added methanol (10 cm³) to effect crystallisation. Yield 0.14g (64%). In a similar fashion the chromium and tungsten pentaphosphines were formed. Yield 68% and 72% respectively.

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