TITLE 1, 2-NAPHTHOQUINONE MONO-OXIMATO COMPLEXES OF RUTHENIUM

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INSTITUTION and DATE NORTH LONDON POLYTECHNIC (CNAA) 1988

1,2-NAPHTHOQUINONE MONO-OXIMATO COMPLEXES OF RUTHENIUM

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

by

William C. Stoten

The Polytechnic of
North London &
Johnson Matthey PLC

November 1988

To Margaret

'Give me a firm place to stand, and I will move the earth.'

Archimedes

Declaration

Whilst registered as a candidate for this degree the author has not been registered as a candidate for any other award.

W. C. Stoten

Abstract

The ruthenium(II) complexes $Ru(nqo)_2$ (nqoH = 1,2-naphthoquinone 1-oxime, or 2-oxime) were prepared by the interaction of the sodium salts of the 1,2-naphthoquinone mono-oximes with hydrated ruthenium(III) chloride in aqueous tetrahydrofuran. Reaction of ruthenium(III) chloride with the sodium salts of the oximes in aqueous pyridine gave complexes of type $Ru(nqo)_2(py)_2$; however reaction in ethanol or acetic acid afforded complexes of type $Na[Ru(nqo)_3]$ and $Ru(nqo)_2(nqoH)$ respectively. In all these reactions, reduction of the metal occurred, i.e. ruthenium(III) to ruthenium(II); for the system Na(1-nqo)/$RuCl_3$ in methanol, the oxidation product was identified as formaldehyde. Complexes of type $Ru(nqo)_2(PPh_3)_2$ were obtained from the reaction of $RuCl_2(PPh_3)_3$ with the sodium salts of the oximes. Nitrosation of 1-naphthol and 2-naphthol in the presence of ruthenium(III) chloride, gave complexes of approximate composition '$Ru(nqo)_2(NO)_2$' which on treatment with pyridine gave complexes of type $Ru(nqo)_2(py)_2$. The complexes $Ru(nqo)_2$ were also obtained from the reaction of $Ru(acac)_3$ with the sodium salts of the oximes.

The complexes of type $Ru(nqo)_2$ were resistant to dilute hydrochloric acid whereas the complexes $Ru(nqo)_2(nqoH)$ gave $Ru(nqo)_2$ and the protonated ligand. Reaction of $Ru(nqo)_2$ and $Ru(nqo)_2(nqoH)$ with Lewis bases gave 1:2 adducts of type $Ru(nqo)_2(LB)_2$ (LB = pyridine or triphenylphosphine).

All the ruthenium(II) complexes were diamagnetic. Infra-red studies indicated that the nqo ligands are essentially quinoneoximic in character. For the complex $Ru(1\text{-}nqo)_2(py)_2$, the quinoneoximic character has been confirmed by X-ray crystallography.

The complexes $Ru(nqo)_2$ catalysed the aerobic oxidation of cyclohexene, styrene and 1-octene. The complexes also catalysed hydration of the above alkenes to give alcohols which were further oxidised to give the respective carbonyl product (aldehyde or ketone). The homogeneous $Ru(nqo)_2$ catalysts gave insignificant induction times and very high yields of oxidation and hydration products. The turnover numbers are exceptionally high and, by a large margin, better than values reported to date. The oxidation and hydration reactions were mechanistically assessed. Dioxygen uptake by the complexes $Ru(nqo)_2$ was demonstrated in the case of $Ru(1\text{-}nqo)_2$.

Acknowledgements

I wish to thank Dr. J. Charalambous for his guidance in all parts of this work, Dr. K. Henrick for his help on X-ray crystallographic studies and Dr. D. Baluch for his advise and help in the oxidation experiments.

I also thank Dr. D. Thompson and Dr. A. Berzins of Johnson Matthey PLC. for their support and assistance.

I finally thank Inco Europe Ltd. for their support and encouragement through the latter part of this study.

Abbreviations

qoH	1,2-Quinone mono-oxime
1-nqoH	1,2-Naphthoquinone 1-oxime
2-nqoH	1,2-Naphthoquinone 2-oxime
nqoH	1-nqoH or 2-nqoH
4-ClqoH	4-Chloro-1,2-benzoquinone 2-oxime
3-MeOqoH	5-Methoxy-1,2-benzoquinone 2-oxime
3-MeqoH	3-Methyl-5-hydroxy-1,2-benzoquinone 2-oxime
$(Et_2NCS_2)^-$	Diethyl dithiocarbamate anion
acacH	Acetylacetone
salenH	Salicylaldimine
phenazinone	5-Hydroxy-dibenzo[b,i]phenazin-12(6H)one
PPh_3	Triphenylphosphine
Ph_3PO	Triphenylphosphine oxide
py	Pyridine
t.l.c.	Thin layer chromatography
g.l.c.	Gas/liquid chromatography
i.r.	Infra-red
u.v./vis.	Ultra-violet/visible
ICP-AES	Inductively coupled plasma/ atomic emission spectrometry
AAS	Atomic absorption spectrophotometry

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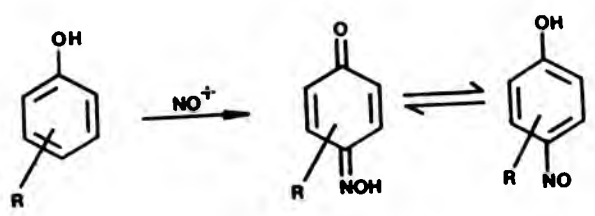
CHAPTER ONE

1,2-QUINONE MONO-OXIMES AND THEIR METAL COMPLEXES

1.1 Quinone mono-oximes

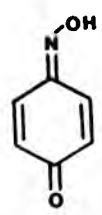
Ring nitrosation of aromatic compounds is difficult unless activating groups are attached to the aromatic ring, e.g. hydroxy or amino. A hydroxy group is a strong ortho/para director and can overwhelm the directing effect of other substituent groups. Nitrosation of phenols, thus, yield mixtures of 2- and 4- substituted isomers with the 4-isomer dominating. Nitrosation of naphthols, however, gives the 2-isomer as the main product. [1] The predominance of the 4-isomer in the nitrosation of phenols is due to the labile nature of the 2-isomer, which may undergo further reactions. These include oxidation to 2-nitrophenols and reaction with unreacted phenol to

give indophenols.[2] In consequence, only a small number of 2-nitrosophenols have been isolated. The major products, 4-nitrosophenols, can exist in tautomeric equilibrium with their 1,4-quinone mono-oximic form (Scheme 1.1).[3-5]

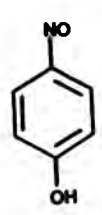


Scheme 1.1

For some compounds both forms have been isolated. For example, nitrosation of phenol affords a product from which colourless and yellow-green compounds may be recrystallised from water and acetone respectively. The coloured compound has been formulated as 1,4-benzoquinone mono-oxime (1.1), whilst the colourless form as 4-nitrosophenol (1.2).[4-9]

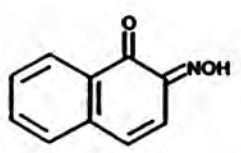


(1.1)



(1.2)

The 2-substituted isomer also results in some cases, e.g. the nitrosation products of naphthol (1.3) and 5-methoxyphenol (1.4). As in the case of the 4-substituted isomers, some 2-substituted isomers have been isolated in two forms.



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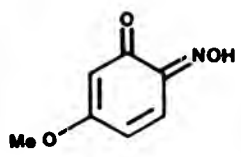
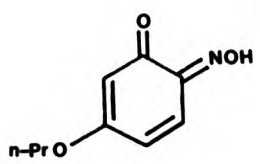


(1.4)

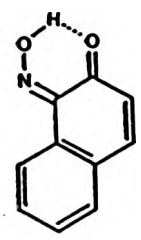
The quinoneoximic form of 5-methoxy-1,2-benzoquinone 2-oxime, has been shown by X-ray crystallography to exist in the *anti*-quinone form.[10] In contrast, 5-n-propoxy-1,2-benzoquinone 2-oxime (1.5), exists in the *syn*-quinoneoximic form.[11] In the *syn* form, the oximic oxygen is bent towards the quinoid oxygen, giving rise to hydrogen bonding between the two groups, whilst in the *anti* form, the oximic oxygen is bent away from the quinoid oxygen.

The *anti* form is not observed in 5-n-propoxy-1,2-benzoquinone 2-oxime, due to steric considerations, and in 5-methoxy-1,2-benzoquinone 2-oxime the *syn* form is not favourable for intra-molecular hydrogen bonding. In these structures, some contribution from the nitrosophenolic form is apparent for the *syn*-quinone oximic form.[12]



(1.5)

Only 1,2-naphthoquinone mono-oximes have been isolated in the nitrosation of 2-substituted naphthols. I.r.,[13] ^{1}H n.m.r.[14] and X-ray crystallographic studies,[15] have shown that 1,2-naphthoquinone 1-oxime (1.6) and 1,2-naphthoquinone 2-oxime (1.7) exist in the *syn* and *anti* form repectively.



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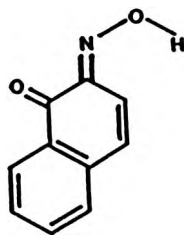


(1.7)

1.2 Metal chelates derived from the mono-oximes of 1,2-quinones.

The ability of 1,2-quinone mono-oximes to form chelates with metals is well known. Many complexes of 1st row transition elements, e.g. chromium, manganese, iron, cobalt, nickel, copper and zinc, have been

prepared.[14-24] Preparation of these chelates has been achieved by a number of methods which include: i) the direct reaction of the oxime with a metal salt or metal carbonyl, ii) nitrosation of a phenol or naphthol in the presence of a metal salt or more recently, iii) ligand exchange.

The direct reaction between ligand and metal salt involves the interaction of the metal salt with the appropriate 1,2-quinone mono-oxime in a suitable solvent (Reaction 1.1). Limitations in the number of 1,2-quinone mono-oxime available restrict this method of preparation.

$$ML_n + n(qoH) \xrightarrow{H_2O,\ MeOH} M(qo)_n + nLH$$

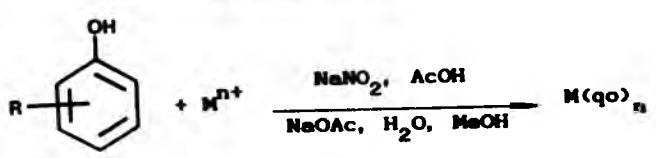
L= Cl , SO_4

qoH= 1,2-quinone mono-oxime

Reaction 1.1

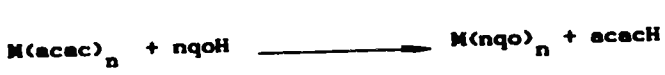
When a phenol is nitrosated in the presence of a metal salt, using sodium nitrite in acetic acid, the 2-substituted isomer is the preferred product.[15] A wide range of complexes have been prepared using this method and it is particularly useful when the appropriate 1,2-quinone mono-oxime is unavailable. The complexes afforded by this method are usually in high

yield. The reaction may be regarded as an electrophilic substitution by the nitrosonium ion NO^+ on the phenol followed by chelation of the product with the metal (Reaction 1.2). Complexes of many 1st row transition elements, e.g. iron(II), iron(III), nickel(II), chromium(III), manganese(III), copper(II), cobalt(III) and vanadium(IV), have been prepared by this technique. [12,14-17,22-24]



Reaction 1.2

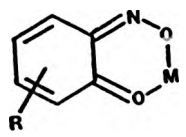
Recently, chelates have been prepared by ligand exchange. Thus, complexes of type $M(nqo)_n$ (e.g. M = Mn) have been synthesised by the reaction of the appropriate 1,2-naphthoquinone mono-oxime with the acetylacetonato complex of the metal (Reaction 1.3). [25]



Reaction 1.3

1,2-Quinone mono-oximato complexes of 2nd and 3rd row transition metals have received comparatively little attention. Recently, 1,2-naphthoquinone mono-oximato complexes of iridium, rhodium [27] and rhenium [28] have been reported. In the case of the iridium complex, its quinoneoximic character has been established by X-ray crystallography.

The structures of metal 1,2-benzoquinone and 1,2-naphthoquinone oximato complexes have been established by a variety of methods. X-ray crystallography has proved important in the clarification of structures of the complexes.[29-39] Prior to X-ray crystallographic studies, the mode of coordination of ligand to metal in these complexes was presumed to involve 6-membered chelate rings (1.8). Evidence obtained from the X-ray studies of several complexes, however, show 5-centred coordination in the vast majority of cases (1.9). This form of chelation occurs through the nitrogen atom of the oxime and the oxygen atom of the quinone group. So far, no complexes having 6-membe ed chelate rings have been identified by X-ray crystallography.



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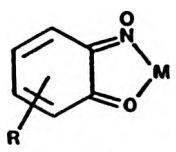
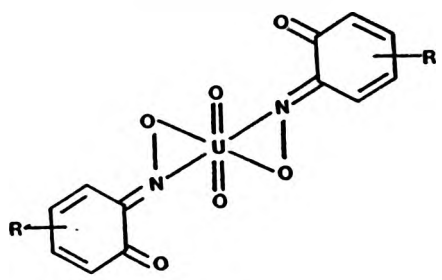


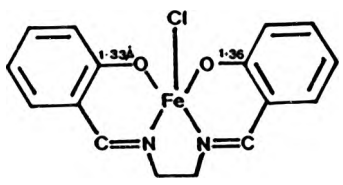
(1.9)

Recently, X-ray crystallographic studies of uranium quinoneoximic complexes, showed a novel form of bonding involving the oximic group only (1.10). Thus in diaquobis(1,2-naphthoquinone 2-oximato)dioxouranium-(VI)½trichloromethane, the ligand is bound to the metal solely through the oximato group.[38] Similarly, diaquobis(triphenylphosphine)(1,2-naphthoquinone 1-oximato)dioxouranium(VI) exhibits this mode of bonding.



(1.10)

All X-ray crystallographic studies to date, show that the ligand in the complexes is essentially quinoneoximic in character. For example, in bis(1,2-naphthoquinone 1-oximato)bis(acetone)copper(II),[30] the ring carbon bonds show a pattern of short and long bonds and the average bond length of the CO group is shorter than that of analogous bonds in the iron(III) complex of N,N-bis(salicylideneimine) (1.11).[36] Furthermore, the average CN bond length in quinone-oximato complexes, e.g. the iron complex of the sulphonated derivative of 1,2-naphthoquinone 2-oxime,[37] is shorter than that found for the analogous bond in nitrosonaphthalene (1.12).



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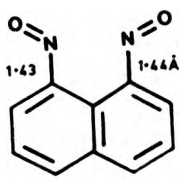


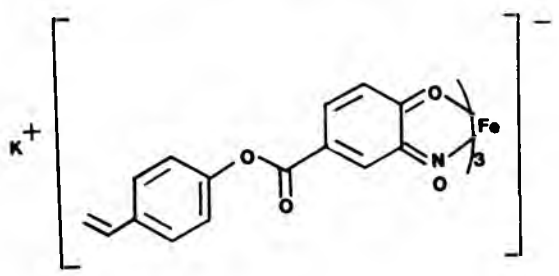
(1.12)

Other physical methods have also been utilised in the study of the structure of quinoneoximic complexes. I.r. spectrophotometry is of particular note. For all 1,2-quinone mono-oximes, the shift to lower wavenumbers for νCO, to *ca.* 1620 cm^{-1} from *ca.* 1630-1675 cm^{-1} in the protonated ligands, supports the coordination of the C=O group to the metal. [24]

Mass spectrometry has also provided information with regard to the mode of coordination. Fragmentation patterns from a number of complexes show $[M-NO]^+$ and $[M-O]^+$ ions, supporting the five-centred structure. [39] U.v./vis. data have been used in the examination of the complexes in solution. [23] Unfortunately, the strong charge tranfer region usually causes problems in the evaluation of the spectra. [35] Mössbauer spectra have been utilised to establish the oligomeric character of some iron complexes. [12,24]

1.3 Uses and applications of metal 1,2-quinone and 1,2-naphthoquinone mono-oximes.

Metal 1,2-quinone and 1,2-naphthoquinone mono-oxime complexes find a wide range of uses and applications in industry. [40-42,44-50] They are also biochemically important and may be found as naturally occuring compounds, e.g. ferroverdin (1.13). [43-45]



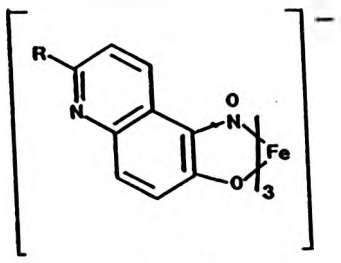
(1.13)

The reaction between some metal $M(qo)_n$ chelates and Lewis bases has been utilised in catalysis. [23] Their highly coloured nature make them particularly useful as dyes. The insolubility of some complexes also makes them extremely useful in the gravimetric analysis of various metals and their high molar absorbances in the spectrophotometric analysis of metals.

Recently, studies of the reactions of iron(III) and iron(II) complexes of 1,2-naphthoquinone 1-oxime with Lewis bases have led to an application involving the selective filtration of tobacco smoke. [40] Such complexes show strong affinity for Lewis bases found in the smoke, e.g. CO, NO and nicotine, thus allowing extraction of these toxic components from the smoke vapour. [42]

Iron complexes of 1,2-naphthoquinone 1-oxime, 5-methoxy-1,2-benzoquinone 1-oxime and 4-methyl-1,2-benzoquinone 2-oxime have found applications as dye materials. [12] A dye based on a soluble derivative of an

iron(II) trischelate (1.14) has recently been patented and acts specifically on polyamide fibres.[41]



(1.14)

1,2-Naphthoquinone mono-oximes are used in metal analysis.[44] For example, in 'superalloys', cobalt may be selectively determined in the presence of nickel by the interaction of 1,2-naphthoquinone 1-oxime in alcohol with an aqueous solution of the metal at low pH. Similarly copper, iron, nickel, and chromium may be determined via complexation with 1,2-naphthoquinone 1-oxime. Palladium may also be precipitated selectively in the presence of platinum, a feature which is particularly important in the analysis of platinum group metals. The sulphonated derivative of 1,2-naphthoquinone 1-oxime is also used in metal analysis.

Ruthenium may also be analysed spectrophotometrically via complexation with 1,2-naphthoquinone 1-oxime or 1,2-naphthoquinone 2-oxime.[47,48] The method has been used in the analysis of the metal for a number of years and was first used as a semi-quantitative test for the metal ion in solution. The requirement for faster, more accurate determination of ruthenium,

generated by the increased use of nuclear reactors, led to further development and improvement of the technique. In the early 1960's the method was considered to be superior in detection limit and accuracy to other means of determination of ruthenium available at that time.[49] Significantly, it was shown that ruthenium could be specifically analysed in the presence of uranium salts at quite high levels.[50] However, the resulting ruthenium complexes have received little attention and have not been isolated and characterised.

This work reports the first succesful synthesis and structural elucidation of these complexes. In addition, the redox and catalytic chemistry of the complexes has been explored.

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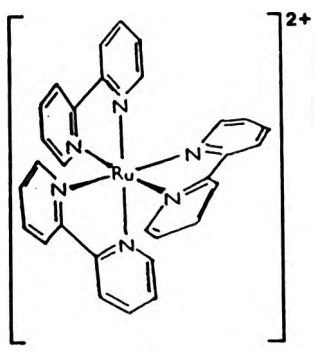
CHAPTER TWO

THE PREPARATION AND CHARACTERISATION OF COMPLEXES OF RUTHENIUM DERIVED FROM MONO-OXIMES OF 1,2-NAPHTHOQUINONE.

2.1 Introduction

Ruthenium has many oxidation states; ranging from -1 to +8. This work is concerned primarily, with chelate compounds derived from ruthenium(II) and ruthenium(III) complexes. A number of cationic and neutral complexes of both ruthenium(II) and ruthenium(III) have been previously reported, e.g. (2.1) - (2.4).[1,2]

The main synthetic routes to the complexes involve the reaction of i) $RuCl_3(H_2O)_n$ (n = 1-3) or ii) $RuCl_2(PPh_3)_3$ with chelating ligands. The latter type of reaction typically leads to Ru(II) chelates[1] whereas from the former either ruthenium(II) or ruthenium(III) complexes result.[2]



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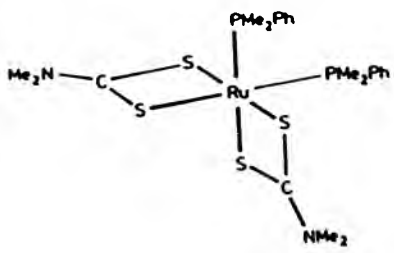
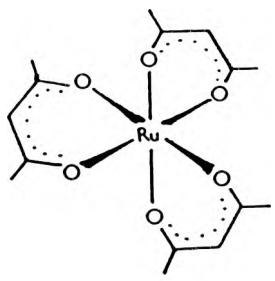
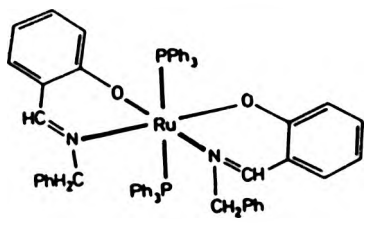


(2.2)



(2.3)



(2.4)

Ruthenium(II) chelates have also been prepared by reacting the ruthenium(III) chloride with the chelating ligand in the presence of a reducing agent. [3]

In the reactions which involve ruthenium(III) chloride and lead to ruthenium(II) complexes, reduction of the metal occurs. The nature of the oxidised species has only been identified in the reaction with 2,2'-bipyridyl where a dimer of the ligand has been noted. [4]

2.2 Complexes of ruthenium derived from mono-oximes of 1,2-naphthoquinone

Previously, the reaction between the mono-oximes of 1,2-naphthoquinone and ruthenium(III) salts has been utilised in the analysis of the metal. [8-9] However, the systematic study of these reactions has not been undertaken to any significant degree. Complexes formed in these reactions have not been isolated in the solid state, but have been characterised on the basis of spectrophotometric studies. [9,10]

In this work the reactions of hydrated ruthenium(III) chloride with the mono-oximes of 1,2-naphthoquinone or their sodium salts have been systematically examined. In addition a study of the reactions of the mono-oximes with dichlorotris-(triphenylphosphine)ruthenium(II) has been undertaken. The preparation of ruthenium complexes using the nitrosation method and the reaction of the sodium salt of the mono-oximes of 1,2-naphthoquinone with tris-(acetylacetonato)ruthenium(III) have also been studied. The results obtained are presented and discussed in the next sections of this chapter. In all cases it has been established that the products arising from the reactions are ruthenium(II) species.

2.3 The direct reaction between metal salts and 1,2-quinone mono-oximes or their sodium salts.

In this section, the direct reactions of hydrated ruthenium(III) chloride with 1,2-naphthoquinone 1-oxime or 2-oxime and their sodium salts are reported and discussed. In general, these reactions lead to ruthenium(II) complexes whose nature is strongly affected by the reaction conditions.

The direct reaction of the oxime with a metal salt in aqueous alcohol or in aqueous acetic acid has been used to prepare a wide range of quinone mono-oximic complexes of various metals. By far, most of the complexes prepared involve first row transition elements such as copper(II),[11] nickel(II),[12] iron(II),[13] manganese(III),[14] and cobalt(III),[15] e.g. Reaction 2.1.

$$Cu^{2+} + 2nqoH \longrightarrow Cu(nqo)_2$$

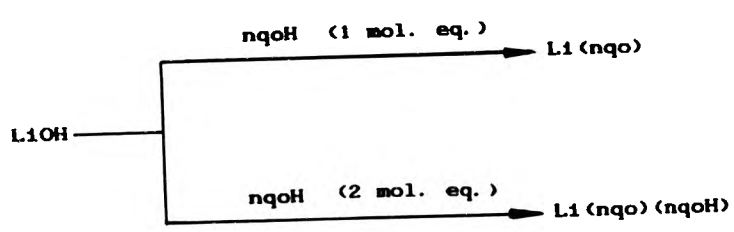
Reaction 2.1

Some attention has also recently been given to the preparation of complexes of the second and third row transition elements and of actinides, such as $Rh(nqo)_3$, $Ir(nqo)_3$,[16] $UO_2(nqo)_2(H_2O)_2 \cdot \frac{1}{2}(CHCl_3)$,[17] e.g. Reaction 2.2.

$$Ir^{3+} + 3Na(1\text{-nqo}) \xrightarrow{\text{acetone}} Ir(1\text{-nqo})_3$$

Reaction 2.2

Some complexes of non-transition metals have also been prepared by the direct method, but in this case the metal hydroxide has been used (Scheme 2.1).[18]



Scheme 2.1

Generally, the direct reaction of a 1,2-quinone mono-oxime with a transition metal salt in aqueous acetic acid or aqueous ethanol leads to neutral complexes of type $M(nqo)_n$. In some cases, the reaction involves change in the oxidation state of the metal. For example, reaction of cobalt(II) chloride with 1,2-naphthoquinone mono-oximes leads to cobalt(III) complexes of type $Co(nqo)_3$, (Reaction 2.3).[15]

$$CoCl_2 + 3nqoH \xrightarrow[\text{air}]{\text{aq. EtOH}} Co(nqo)_3$$

Reaction 2.3

In contrast, the reaction of iron(II) salts with mono-oximes of 1,2-naphthoquinone lead to both iron(II) and iron(III) complexes, (Reaction 2.4).[19,20]

$$FeSO_4 + 3nqoH \longrightarrow Fe(nqo)_3 + Fe(nqo)_2$$

Reaction 2.4

The reaction of the sodium salt of the mono-oxime with a metal salt in various solvents has been used to prepare a number of 1,2-naphthoquinone mono-oximato transition metal complexes, e.g. Reactions 2.5-2.7.[21,22]

$$FeSO_4 + 3Na(nqo) \longrightarrow Na[Fe(nqo)_3]$$

Reaction 2.5

$$CrCl_3 + 3Na(nqo) \longrightarrow Cr(nqo)_3$$

Reaction 2.6

$$MnCl_2 + 2Na(nqo) \longrightarrow Mn(nqo)_2$$

Reaction 2.7

From such reactions, neutral complexes of type $M(nqo)_n$ or anionic complexes such as $Na[M(qo)_n]$ or $K[M(nqo)_n]$ resulted.

Preliminary experiments indicated that the reaction between 1,2-naphthoquinone mono-oximes and ruthenium(III) chloride did not lead to complete substitution of the chloro ligands. Instead, complex mixtures of products were formed. Chromatographic separation of these mixtures suggested the presence of complexes of type $RuCl_{3-n}(nqo)_n$ amongst the reaction products. However, products formed in the preliminary experiments could not be reproduced when repeated on a larger scale. By using the sodium derivative of the mono-oxime, complete substitution of the chloro ligands and the isolation of pure products was achieved.

Complexes of type $Ru(nqo)_2$ were obtained from the reaction of ruthenium(III) chloride with the sodium salt of the respective 1,2-naphthoquinone mono-oxime in aqueous tetrahydrofuran (Reaction 2.8).

$$RuCl_3 + 2Na(nqo) \xrightarrow{H_2O/THF} Ru(nqo)_2$$

Reaction 2.8

When aqueous pyridine was used in place of aqueous tetrahydrofuran, complexes of type $Ru(nqo)_2(py)_2$ were obtained (Reaction 2.9).

$$RuCl_3 + 2Na(nqo) \xrightarrow{H_2O/pyridine} Ru(nqo)_2(py)_2$$

Reaction 2.9

Reaction in ethanol using 3 mole equivalents of the sodium salt of the oxime per mole equivalent of ruthenium(III) chloride hydrate, afforded complexes of the type $Na[Ru(nqo)_3]$ (Reaction 2.10) whereas in acetic acid complexes of the type $Ru(nqo)_2(nqoH)$ resulted (Reaction 2.11).

$$RuCl_3 + 3Na(nqo) \xrightarrow{\text{ethanol}} Na[Ru(nqo)_3]$$

Reaction 2.10

$$RuCl_3 + 3Na(nqo) \xrightarrow{\text{acetic acid}} Ru(nqo)_2(nqoH)$$

Reaction 2.11

As noted above, ruthenium(III) is reduced to ruthenium(II). Metal reduction has also been observed in the reaction between iron(III) salts and the sodium salts of 1,2-benzoquinone and 1,2-naphthoquinone monooximes. [19-21]

The formation of ruthenium(II) complexes involves reduction of the metal which must be accompanied by oxidation of the ligand and/or the solvent. As noted earlier, in the reactions involving ruthenium(III) chloride with various chelating ligands, reduction of the metal from +3 to +2 has been observed but the nature of the oxidised species has been overlooked or disregarded. On the other hand, studies of the reaction

of ruthenium(III) chloride with triphenylphosphine have indicated formation of aldehydes when the reactions are carried out in high boiling point alcohols. [23]

In this study the nature of the oxidised species originating from the reaction between ruthenium(III) chloride (1 mol. eq.) and the sodium salt of 1,2-naphthoquinone 1-oxime (3 mol. eq.), in methanol, was established by gas chromatography. Methanol was chosen as the solvent because the expected oxidation products, formaldehyde, formic acid or methyl formate are volatile. Oxygen was eliminated from the reaction mixture with a stream of nitrogen. The nitrogen also acted as a carrier for any volatile oxidised species which were collected in methanol at -80 °C. Gas chromatography of the resulting methanol solution showed the presence of formaldehyde. The gas chromatogram produced (Fig. 2.1) was well defined, the peak for the formaldehyde being separated well from that of the methanol indicating a high yield of formaldehyde (*ca.* 80%).

The solid product obtained from the reaction was diamagnetic and TLC suggested that it was a mixture of $Na[Ru(1\text{-nqo})_3]$ and $Ru(1\text{-nqo})_2$. As noted above in Section 2.1 of this chapter, reduction of the metal is also observed in the reactions of a number of other bidentate chelating ligands with ruthenium(III) chloride. These include 1,10-phenanthrolene,

2,2-dipyridyl,[4] diarsines,[24] diphosphines[25] and phosphothioic esters of dithioacyloin.[26]

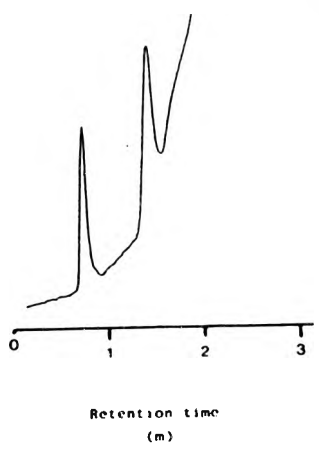


Fig. 2.1 **Chromatogram of the resultant solution from the reaction between $RuCl_3 \cdot 2H_2O$ and Na(1-nqo).**

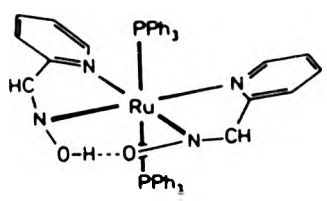
In contrast, no reduction is observed when ruthenium(III) chloride is treated with some other bidentate chelating ligands such as ethylenediamine, acetylacetone or α-benzil mono-oximes in ethanol.[27]

From the above observations, it is evident that the reaction between ruthenium(III) chloride and ligands which exhibit π-acceptor properties generally lead to ruthenium(II) complexes. In contrast, ligands with limited π-acceptor properties usually give rise to products where the metal oxidation state is unchanged.

Reduction of ruthenium(III) to ruthenium(II) is in accord with the strong ligand field effect of the 1,2-naphthoquinone mono-oximes.

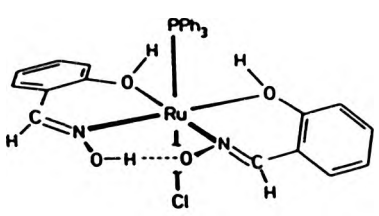
2.4 The reaction of dichlorotris(triphenylphosphine)-ruthenium(II) with the mono-oximes of 1,2-naphthoquinones and their sodium salts.

A number of complexes have been prepared by the reaction between dichlorotris(triphenylphosphine)-ruthenium(II) and chelating oximes such as α-dioximes, imino-oximes, pyridine oximes and α-carbonyl oximes, e.g. (2.5),[28] the latter of which are structurally related to 1,2-quinone mono-oximes. These reactions lead to complexes of type $RuCl_2(dioxH_2)(PPh_3)_2$, $RuCl_2(oxH)_2(PPh_3)_2$ or $Ru(ox)_2(PPh_3)_2$ ($dioxH_2$=dioxime; oxH= α-carbonyl oxime, α-imino oxime, pyridine oxime) involving either the neutral or anionic ligand.

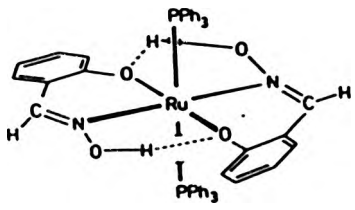


(2.5)

The nature of the product is strongly affected by the reaction conditions. For example, when the reaction is carried out in ethanol, a complex containing a neutral ligand is formed (2.6); however, when the reaction is carried out in the presence of sodium hydroxide, a complex involving anionic ligands results (2.7). When the oxime is chelated as a neutral species, the resultant complex also contains unsubstituted chloro ligands and has the general formula $RuCl(oxH)_2(PPh_3)$.



(2.6)



(2.7)

The reaction between 1,2-naphthoquinone 1-oxime or 1,2-naphthoquinone 2-oxime and dichlorotris(triphenylphosphine)ruthenium(II) in acetone, tetrahydrofuran or ethanol, afforded complex mixtures which could not be separated chromatographically or by recrystallisation. Similar mixtures resulted when the reaction between the sodium salts of the 1,2-naphthoquinone mono-oximes and dichlorotris(triphenylphosphine)ruthenium(II) was carried out in acetone. However, reaction of the sodium salt of the 1,2-naphthoquinone mono-oxime (2 mol. eq.)

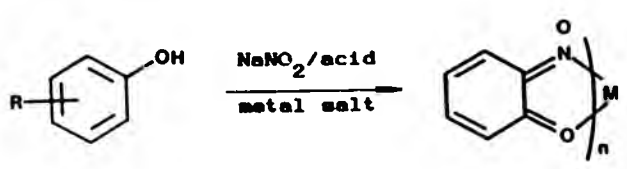
and dichlorotris(triphenylphosphine)ruthenium(II) (1 mol. eq.) in refluxing tetrahydrofuran, afforded complexes of type $Ru(nqo)_2(PPh_3)_2$ in high yield, (Reaction 2.12).

$$RuCl_2(PPh_3)_3 + 2Na(nqo) \longrightarrow Ru(nqo)_2(PPh_3)_2 + PPh_3$$

Reaction 2.12

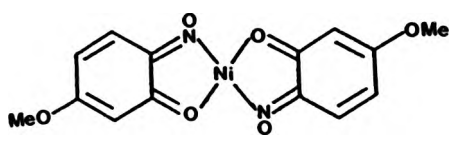
2.5 Nitrosation of phenols and naphthols in the presence of ruthenium(III) chloride.

Nitrosation of 1-naphthol or 2-naphthol, using sodium nitrite and acetic acid, in the presence of metal salts generally leads to 1,2-naphthoquinone mono-oximic complexes in high yield. Similarly, nitrosation of some phenols such as 3-methoxyphenol, 4-chlorophenol, 4-bromophenol give 1,2-benzoquinone mono-oximic complexes in high yield, e.g Reaction 2.13.



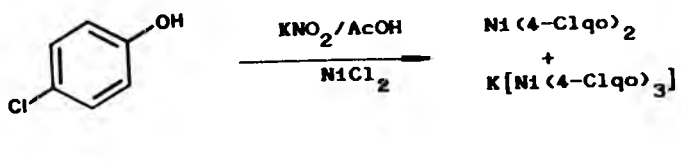
Reaction 2.13

In most cases the above reactions lead to neutral complexes of the type $M(qo)_x$ (x = 2 or 3). For example, when the nitrosation of 3-methoxyphenol is carried out in the presence of nickel(II) chloride, the neutral complex (2.8) results.



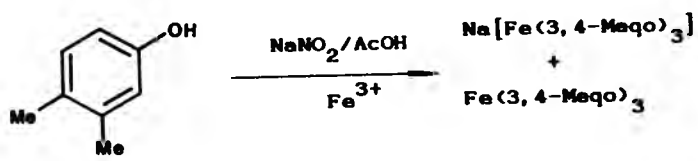
(2.8)

Similarly 4-chlorophenol, 4-methyl-phenol and 4-bromophenol give neutral chelate complexes of type $M(qo)_2$ when nitrosated in the presence of a metal(II) chloride. However, in some cases, anionic complexes are obtained together with the neutral complexes. For example, when 4-chlorophenol is nitrosated, using potassium nitrite and acetic acid, in the presence of nickel(II) chloride, $Ni(4\text{-}Clqo)_2$ and $K[Ni(4\text{-}Clqo)_3]$ (4-ClqoH = 4-chloro-1,2-quinone mono-oxime), is obtained (Reaction 2.14).[29] Complexes of type $Na[Co(qo)_2(NO_2)_2]$ have been obtained together with the neutral complex $Co(qo)_3$ when a number of phenols were nitrosated in the presence of cobalt(II) chloride.[30]



Reaction 2.14

In the reactions involving cobalt(II) salts, oxidation of the metal occurs. In contrast, when phenols are nitrosated in the presence of iron(III) salts, reduction of the metal occurs, to some extent, and mixtures of iron(II) and iron(III) result, e.g. Reaction 2.15. [19]



Reaction 2.15

In this study, when 2-naphthol was nitrosated in the presence of ruthenium(III) chloride, using sodium nitrite and acetic acid, a mixture of products resulted. The main product (solid A) was insoluble in water, methanol, acetone and toluene. Solid A was found to be diamagnetic and its i.r. spectrum showed typical peaks associated with chelated 1,2-naphthoquinone 1-oximato anions, e.g. 1610-1500 cm^{-1}. Significantly, the spectrum also had a peak at 1890 cm^{-1} (Fig. 2.2).

Elemental analysis of solid A indicated an approximate metal:nitrogen ratio of 1:4, which together with the i.r. data, suggested the formation of a nitrosyl derivative of approximate formulation $Ru(1\text{-nqo})_2(NO)_2$. Attempts to purify solid A were unsuccessful, as treatment with refluxing acetone led to the disappearance of the NO band at 1890 cm^{-1} and to a product (Solid B) of composition approximately corresponding to $Ru(1\text{-nqo})_2$. Solid B, on treatment with pyridine gave $Ru(1\text{-nqo})_2(py)_2$.

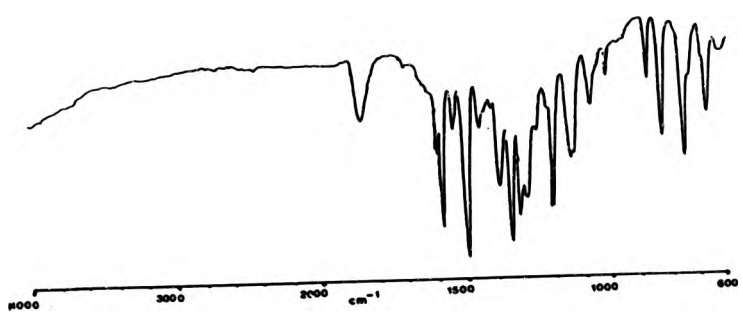


Fig 2.2 **I.r. spectrum of the product from the nitrosation of 2-naphthol.**

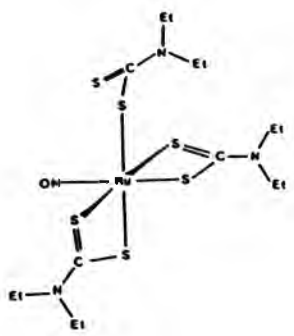
Similar results were obtained with 1-naphthol when nitrosated in the presence of ruthenium(III) chloride. However, when 4-chlorophenol or 4-methylphenol were treated in a similar fashion, tarry multicomponent mixtures resulted.

The formation of a nitrosyl 1,2-naphthoquinone mono-oximic complexes by ruthenium is not unexpected, as ruthenium(II) has a pronounced tendency to form nitrosyl compounds. This is demonstrated by the ease of formation of the complex $Na[Ru(NO)(NO_2)_4(OH)]$ by the action of nitrous acid on ruthenium(III) chloride (Reaction 2.16).[31]

$$RuCl_3 + NaNO_2 \xrightarrow{\text{acid}} Na[Ru(NO)(OH)(NO_2)_4]$$

Reaction 2.16

Of relevance is also the reaction of nitric oxide with chelates of ruthenium. For example, treatment of the dithiocarbamato complex $Ru(Et_2NCS_2)_3$ with nitric oxide gives rise to the complex $Ru(NO)(Et_2NCS_2)_3$.[32] An X-ray study of this complex shows that there are two bidentate dithiocarbamato ligands and one monodentate dithiocarbamato group *cis* to the nitrosyl group, giving an octahedral structure (2.9).[33]



(2.9)

2.6 The reaction between tris(acetylacetonato)-ruthenium(III) and the mono-oximes of 1,2-naphthoquinones.

Metal acetylacetonato complexes have been used extensively for the synthesis of other complexes via ligand exchange reactions. Generally, such reactions lead to mixed ligand complexes of type $M(acac)_x(L)_n$. For example when $Mn(acac)_3$ is treated with N,N'-disubstituted aminotroponimines (datiH) the complex $Mn(acac)(dati)_2$ is formed.[21] Recently, complexes of type $Mn(nqo)_3$ have been obtained from the reaction between $Mn(acac)_3$ and the mono-oximes of 1,2-naphthoquinone, (Reaction 2.17).[22]

$$Mn(acac)_3 + 3nqoH \longrightarrow Mn(nqo)_3 + 3acacH$$

Reaction 2.17

In this study it has been established that ligand exchange reactions involving tris(acetylacetonato)-ruthenium(III) and the sodium salts of 1,2-naphthoquinone mono-oximes in tetrahydrofuran, provide a convenient route to complexes of type $Ru(nqo)_2$, e.g. Reaction 2.18.

$$Ru(acac)_3 + 2Na(nqo) \longrightarrow Ru(nqo)_2$$

Reaction 2.18

These reactions involve reduction of the metal, but the oxidised species has not been identified.

2.7 Characterisation and structure of the complexes $Ru(nqo)_2$, $Na[Ru(nqo)_3]$ and $Ru(nqo)_2(nqoH)$.

2.7.1 Chemical properties.

All the complexes prepared during this study, i.e. $Ru(nqo)_2$, $Ru(nqo)_2(nqoH)$ and $Na[Ru(nqo)_3]$, showed stability towards aerial oxidation in the solid state as their i.r. spectra indicated no significant change over a period of several months.

The complexes $Ru(nqo)_2$ were resistant to attack from cold, dilute hydrochloric acid. In contrast, the complexes $Ru(nqo)_2(nqoH)$ afforded the bis chelate and free ligand on reaction with the acid, (Reaction 2.19).

$$Ru(nqo)_2(nqoH) \xrightarrow{\text{dil. HCl}} Ru(nqo)_2 + nqoH$$

Reaction 2.19

Pyridine and triphenylphosphine reacted with the complexes $Ru(nqo)_2$ to give the adducts $Ru(nqo)_2(LB)_2$ (LB = py, Ph_3P). These reactions and their products are described in detail in Chapter 3.

2.7.2 Physical properties and structure.

The room temperature magnetic susceptibility measurements show all the above complexes to be diamagnetic suggesting low spin d^6 configuration and supporting the suggested Ru(II) metal oxidation state.

Thermal gravimetric analysis and macroscale pyrolysis of the complexes $Ru(nqo)_2(nqoH)$ showed quantitative loss of nqoH at *ca.* 80-85 °C to give the bis chelates $Ru(nqo)_2$. Further heating of these compounds led to decomposition of $Ru(nqo)_2$ at *ca.* 290 °C. Decomposition temperatures for the complexes $Na[Ru(nqo)_3]$ and $Ru(nqo)_2$ are shown in Table 2.1.

Conductimetric measurements on the complexes $Na[Ru(1\text{-}nqo)_3]$ and $Na[Ru(2\text{-}nqo)_3]$ showed them to be 1:1 electrolytes. The molar conductances for the above complexes in ethanol at 21 °C were found to be 153 and 151 Ω^{-1} respectively. These are consistent with values reported for 1:1 electrolytes in the literature. [21,35]

The u.v./vis. spectra of all the complexes show intense charge transfer absorptions which tail into the visible region, e.g. Figs 2.3, 2.4, and values obtained for molar absorptivities are shown in Tables 2.2 and 2.3. In general, the spectra show close similarity to those reported earlier for ruthenium 1,2-naphthoquinone mono-oximic complexes erroneously formulated as ruthenium(III) species. [9,10]

Table 2.1 Thermal gravimetric analysis of the complexes $Ru(nqo)_2$, $Ru(nqo)_2(qoH)$ and $Na[Ru(nqo)_3]$.

Compound	Sample weight (mg)	Weight Loss Temp. (°C)	Weight Loss Found (mg)	Weight Loss Calc. (mg)	Decomp. Temp. (°C)
$Ru(1\text{-}nqo)_2$	100	-	-	-	319
$Ru(1\text{-}nqo)_2(1\text{-}nqoH)$	102	82[a]	23	28	-
$Na[Ru(1\text{-}nqo)_3]$	110	-	-	-	310
$Ru(2\text{-}nqo)_2$	113	-	-	-	307
$Ru(2\text{-}nqo)_2(2\text{-}nqoH)$	100	84[b]	22	28	-
$Na[Ru(2\text{-}nqo)_3]$	107	-	-	-	296

[a] = Loss of 1-nqoH

[b] = Loss of 2-nqoH

Table 2.2 Electronic absorption results for the complexes $Ru(1\text{-}nqo)_2$, $Ru(1\text{-}nqo)_2(1\text{-}qoH)$ and $Na[Ru(1\text{-}nqo)_3]$ at 20 °C.

Compound/ concentration (mol dm^{-3})/ solvent	λ_{max} (nm)	ϵ ($m^2 mol^{-1}$)
1-nqoH	390	320
2.9×10^{-4}	260	1750
ethanol	205	2000
$Ru(1\text{-}nqo)_2$	620	3200
2.2×10^{-4}	570	5800
ethanol	525	4050
	400	1400
	325	11200
$Ru(1\text{-}nqo)_2(1\text{-}nqoH)$	615	5900
3.3×10^{-4}	570	7800
ethanol	530	5250
	400	1750
	320	12600
$Na[Ru(1\text{-}nqo)_3]$	620	5100
3.2×10^{-4}	565	7300
ethanol	525	6100
	405	1350
	315	11900

Table 2.3 Electronic absorption results for the complexes $Ru(2\text{-nqo})_2$, $Ru(2\text{-nqo})_2(2\text{-qoH})$ and $Na[Ru(2\text{-nqo})_3]$ at 20 °C.

Compound/ concentration (mol dm^{-3})/ solvent	λ_{max} (nm)	ϵ ($m^2 mol^{-1}$)
2-nqoH	390	310
2.9×10^{-4}	260	1700
ethanol	205	2050
$Ru(2\text{-nqo})_2$	625	4000
2.2×10^{-4}	580	6400
ethanol	525	4600
	400	1050
	325	9800
$Ru(2\text{-nqo})_2(2\text{-nqoH})$	625	6500
3.3×10^{-4}	580	8000
ethanol	540	5250
	400	1750
	310	13300
$Na[Ru(2\text{-nqo})_3]$	620	4800
3.2×10^{-4}	580	7500
ethanol	535	5150
	405	1650
	315	10200

Fig 2.3 **U.v./vis. spectra of 1,2-naphthoquinone 1-oximato complexes of ruthenium.**

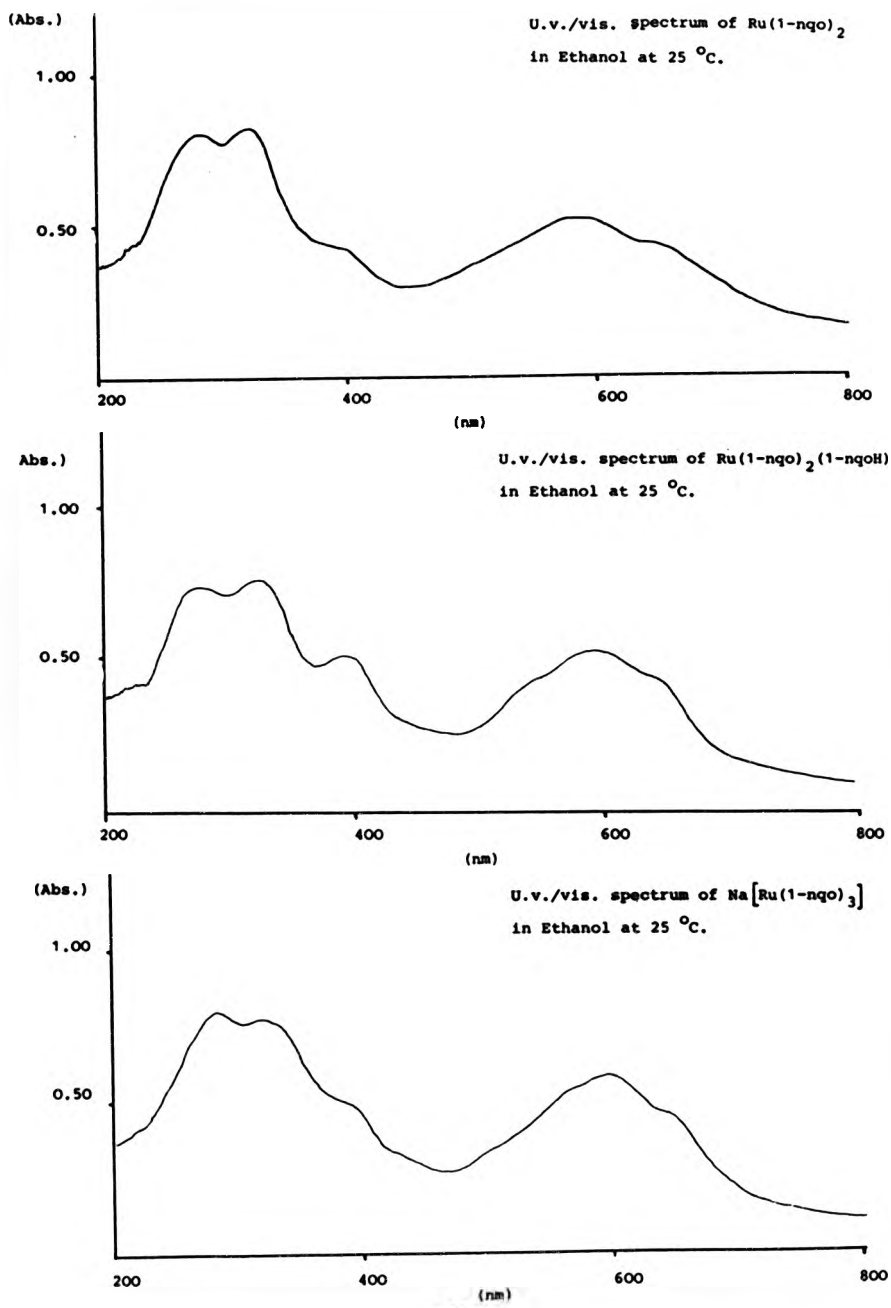
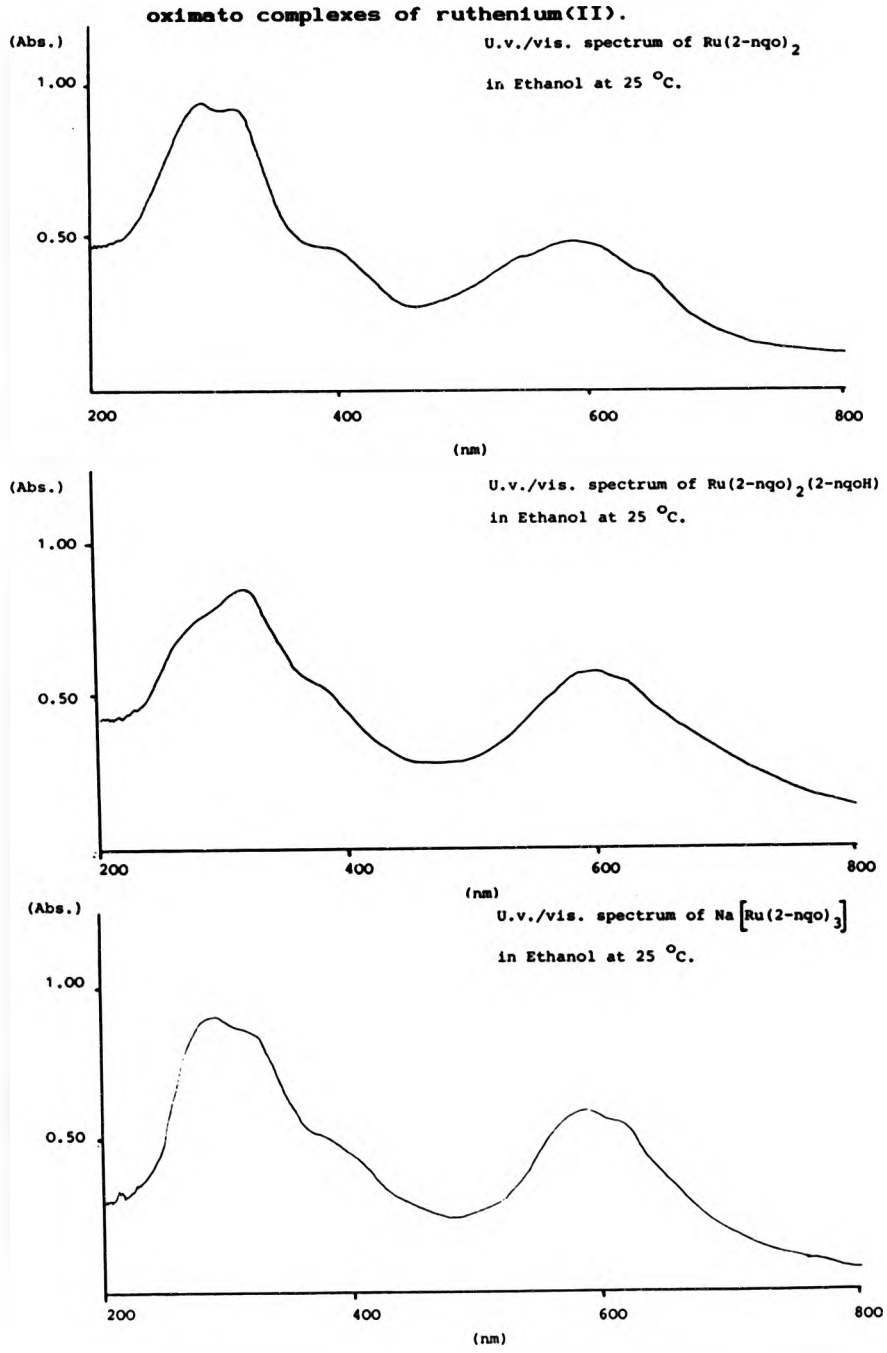


Fig 2.4 **U.v./vis. spectra of 1,2-naphthoquinone 2-oximato complexes of ruthenium(II).**



Some information regarding the structure of the ruthenium complexes and the nature of bonding of the ligands has been obtained from comparisons of their i.r. spectra with those of the free ligands and related compounds (Table 2.4, Figs. 2.5 and 2.6).[13,18,34-39] Generally, complexes containing anionic chelating 1,2-naphthoquinone mono-oximato ligands exhibit a shift of the absorption due to νCO to a lower frequency than that observed for the protonated ligand. In the case of the 1-nqo complexes, the shift is small (*ca.* 10 cm^{-1}), whilst in the 2-nqo complexes the shift is larger (*ca.* 50 cm^{-1}). This difference is due to the differing arrangements of the oximic group in the protonated ligands. In the 1,2-naphthoquinone 1-oxime, the NOH is *anti* to CO and νCO appear at *ca.* 1620cm^{-1}. In 1,2-naphthoquinone 2-oxime, the NOH is *syn* to CO and because of intra-molecular hygrogen bonding, the νCO appears at *ca.* 1660 cm^{-1}. The i.r. spectra of all the complexes show strong absorptions at 1610-1600 cm^{-1}, characteristic of chelated quinone mono-oximato ligands. In the case of the complex $Ru(1\text{-nqo})_2(py)_2$, this has been established by X-ray crystallography (see Chapter 4).

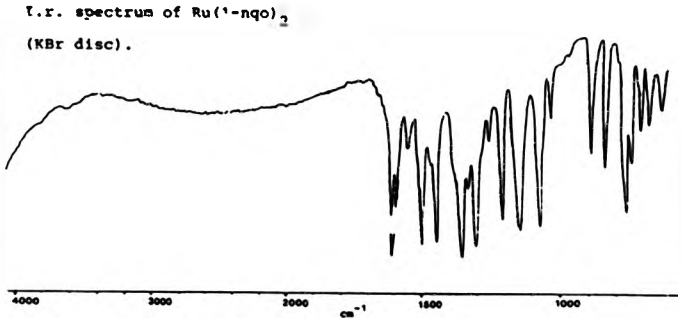
Table 2.4 vCO absorption of 1,2-naphthoquinone monooximes and their complexes

Compound	vCO (cm^{-1})	Ref.
1-nqoH	1618	36, 37
Li(1-nqo)	1620	18
$Cu(1\text{-}nqo)_2$	1610	38
$Fe(1\text{-}nqo)_3$	1610	13
Li(1-nqo)(1-nqoH)	1665, 1618	18
$Ru(1\text{-}nqo)_2$	1605	#
$Ru(1\text{-}nqo)_2(1\text{-}nqoH)$	1601	#
$Na[Ru(1\text{-}nqo)_3]$	1606	#
2-nqoH	1668	36, 37
Li(2-nqo)	1620	18
$Cu(2\text{-}nqo)_2$	1618	38
$Fe(2\text{-}nqo)_3$	1620	38
Li(2-nqo)(2-nqoH)	1670, 1618	18
$Ru(2\text{-}nqo)_2$	1604	#
$Ru(2\text{-}nqo)_2(2\text{-}nqoH)$	1601	#
$Na[Ru(2\text{-}nqo)_3]$	1605	#

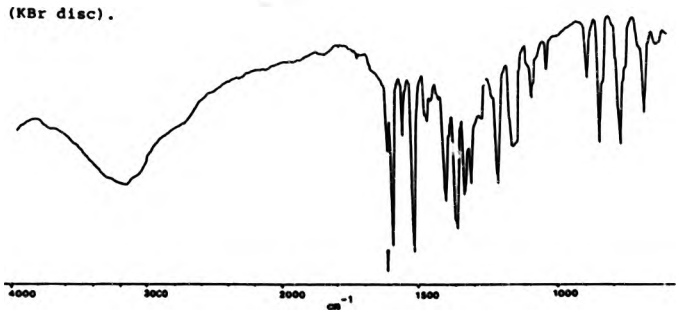
= this work

Fig. 2.5 **I.r. spectra of 1,2-naphthoquinone 1-oximato complexes of ruthenium(II).**

I.r. spectrum of $Ru(^1\text{-nqo})_2$ (KBr disc).



I.r. spectrum of $Ru(^1\text{-nqo})_2(1\text{-nqoH})$ (KBr disc).



I.r. spectrum of $Na\left[Ru(1\text{-nqo})_3\right]$ (Kbr disc).

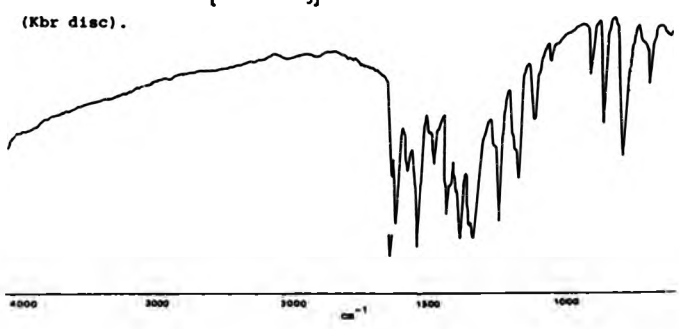
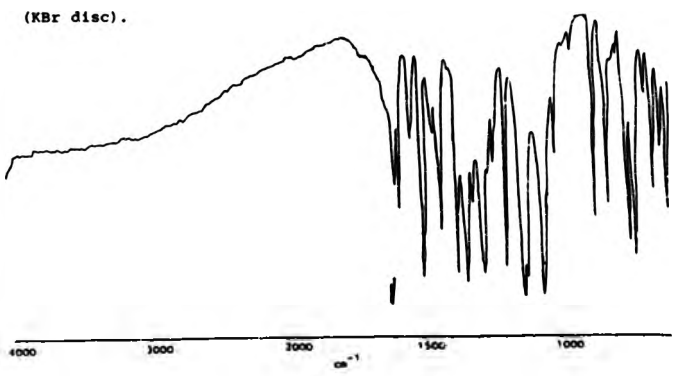
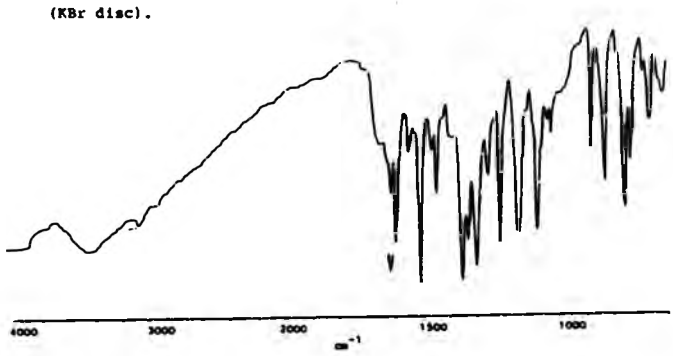


Fig. 2.6 I.r. spectra of 1,2-naphthoquinone 2-oximato complexes of ruthenium(II).

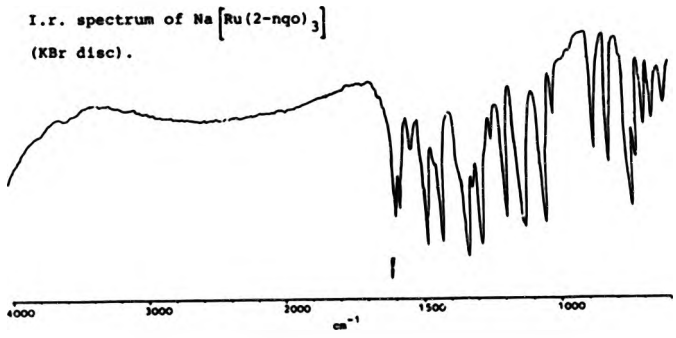
I.r. spectrum of $Ru(2\text{-nqo})_2$ (KBr disc).



I.r. spectrum of $Ru(2\text{-nqo})_2(2\text{-nqoH})$ (KBr disc).



I.r. spectrum of $Na\left[Ru(2\text{-nqo})_3\right]$ (KBr disc).



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CHAPTER THREE

THE REACTIONS OF 1,2-NAPHTHOQUINONE MONO-OXIMATO COMPLEXES OF RUTHENIUM WITH LEWIS BASES

3.1 Introduction

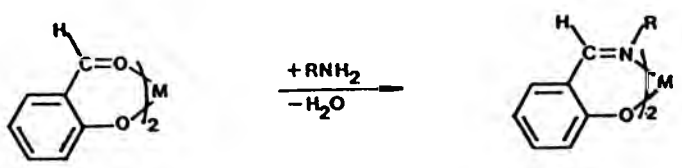
Transition metal chelates undergo three main types of reaction with Lewis bases. These are, i) adduct formation, ii) reaction with the coordinated ligand, or iii) internal redox reaction. The nature of the reaction between metal chelates and Lewis bases, has been shown to be affected by a number of factors which include the type of Lewis base, the chelating ligand, the metal and the solvent employed.

Metal chelates of type $M(chel)_2$ can form adducts with Lewis bases (Reaction 3.1). [1-4] This type of reaction involves an increase in the coordination number of the metal, whilst its oxidation state remains unchanged, e.g. Reaction 3.1. [2]

$$Cu(Et_2NCSS)_2 + 2PPh_3 \longrightarrow Cu(Et_2NCSS)_2(PPh_3)_2$$

Reaction 3.1

In reactions between Lewis bases and the chelated ligand there is no increase in the oxidation state of the metal and the coordination number usually does not change. These reactions are typified by the condensation of primary amines with metal chelates of salicylaldehyde (Reaction 3.2). [1]



Reaction 3.2

Internal redox reactions between chelates of type $M(chel)_2$ or $M(chel)_3$ and Lewis bases usually lead to a change in the oxidation state of the metal and liberation of a ligand as a radical, [3,4] e.g. Reaction 3.3. Internal redox reactions are also induced by light [7] and/or heat [8] (Reaction 3.4).

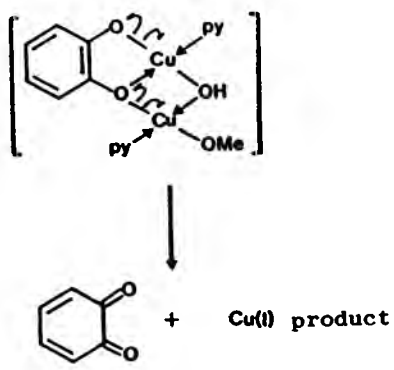
$$Fe(Et_2NCSS)_3 + RNC \longrightarrow Fe(Et_2NCSS)_2(RNC)_2 + Et_2NCSS^{\cdot}$$

Reaction 3.3

$$L_xM^{n}\!-\!L \xrightarrow{LB\ /\ h\nu/\ \Delta} L_xM^{n-1} + L^{\cdot}$$

Reaction 3.4

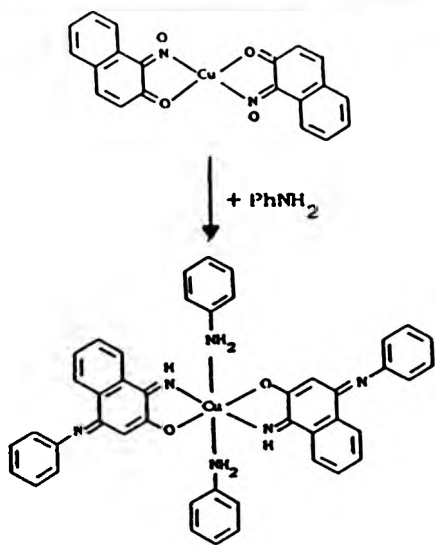
Internal redox reactions are important in various fields, such as synthesis, catalysis, and biological systems. For example, the role of copper in oxygenases has been succesfully accounted for in terms of internal redox behaviour. Oxygenases are a class of enzyme capable of oxidative opening of the aromatic ring in phenols and catechol, by inserting oxygen atoms (from O_2) into the substrate. Molecular oxygen is activated by its reaction with the metal. Using model systems, it has been shown that for the oxygenation of catechol, copper(II) is the active species. [9] The initial stages involve chelation of the metal through the hydroxy groups of the phenol or catechol. This is followed by reduction of copper(II) to copper(I) and the release of benzoquinone (Scheme 3.1). The benzoquinone reacts further with copper species present to give *cis, cis* muconic acid monomethyl ester.



Scheme 3.1

3.2 The reaction between metal complexes derived from mono-oximes of 1,2-naphthoquinone and Lewis bases.

Chelates of type $M(qo)_x$ (x = 2 or 3) undergo similar reactions with Lewis bases as those noted above for complexes of type $M(chel)_x$. Thus, reactions between coordinatively unsaturated 1,2-quinone mono-oximato metal chelates and Lewis bases can lead to adduct formation. Internal redox reactions generally lead to formation of derivatives of the ligand and a change of oxidation state or coordination number of the metal and, as in the case of other metal chelates, will usually occur if the metal in the complex can be easily reduced. [10] Reactions of the ligand with the Lewis base, without affecting the metal's oxidation state, have been also been reported (Reaction 3.5). [11]



Reaction 3.5

The nature of the Lewis base affects the type of reaction. For example, $Cu(nqo)_2$ reacts with triphenylphosphine to give the copper(I) complex $Cu(nqo)(PPh_3)_2$ (Reaction 3.6), [11] while the reaction of the complex with pyridine gives the copper(II) complex $Cu(nqo)_2(py)$ (Reaction 3.7). [12] The metal also affects the nature of the products. Thus, the reaction of $Fe(nqo)_3$ with pyridine (Reaction 3.8) gives a reduced metal complex and the free ligand, whilst in the analogous reaction with $Cu(nqo)_2$, the oxidation state is unaffected and an adduct results (Reaction 3.6). In the reaction between manganese(III) 1,2-naphthoquinone mono-oximato complexes and pyridine, an oxo-bridged complex of type $[Mn(nqo)_2]O$ is formed via an internal redox reaction (Reaction 3.9). [13]

$$Cu(nqo)_2 + PPh_3 \longrightarrow Cu(nqo)(PPh_3)_2 + \text{organic products}$$

Reaction 3.6

$$Cu(nqo)_2 + py \longrightarrow Cu(nqo)_2(py)$$

Reaction 3.7

$$Fe(1\text{-}nqo)_3 + py \longrightarrow Fe(1\text{-}nqo)_2(py)_2 + [1\text{-}nqo^{\cdot}]$$

$$[1\text{-}nqo^{\cdot}] \xrightarrow[\text{from solvent}]{\text{Abstraction of } H^{\cdot}} 1\text{-}nqoH$$

Reaction 3.8

$$Mn(nqo)_3 + py \xrightarrow{\text{air}} [Mn(nqo)_2O] + [nqo^{\cdot}]$$

$$[nqo^{\cdot}] \longrightarrow \text{other products}$$

Reaction 3.9

Studies of the reaction between 1,2-naphthoquinone mono-oximato complexes of 2nd and 3rd row transition elements, or of non-transition metals, with pyridine has been limited by the availability of well defined complexes. Recently, some complexes of this type have been prepared, i.e. $Ir(nqo)_3$, $Rh(nqo)_3$ [14,15] $Li(nqo)$, [14] and their reactivity towards pyridine has been examined. The trischelates of both iridium(III) and rhodium(III), do not react with pyridine. However, addition of pyridine to the mixture arising from the reaction of 1,2-naphthoquinone 1-oxime with hexachloriridic(III) acid leads to the well defined complex $[pyH][Ir(1\text{-}nqo)(py)Cl_3]$. [14] Lithium chelates derived from 1,2-naphthoquinone mono-oximes, i.e. $Li(nqo)$ and $Li(nqo)(nqoH)$, do not react with pyridine. [14]

Complexes of type $Ru(nqo)_2$ react readily with pyridine, to give the 1:2 adducts $Ru(nqo)_2(py)_2$ (Reaction 3.10). The complexes $Ru(nqo)_2(nqoH)$ also react readily with pyridine to give the adducts $Ru(nqo)_2(py)_2$ and free 1,2-naphthoquinone mono-oxime (Reaction 3.11). As noted in Chapter 2, the pyridine complexes may also be obtained in excellent yield by the interaction of ruthenium trichloride hydrate and the sodium salt of the appropriate 1,2-naphthoquinone mono-oxime in water, in the presence of pyridine (Reaction 3.12).

$$Ru(nqo)_2 + py \longrightarrow Ru(nqo)_2(py)_2$$

Reaction 3.10

$$Ru(nqo)_2(nqoH) + py \longrightarrow Ru(nqo)_2(py)_2 + nqoH$$

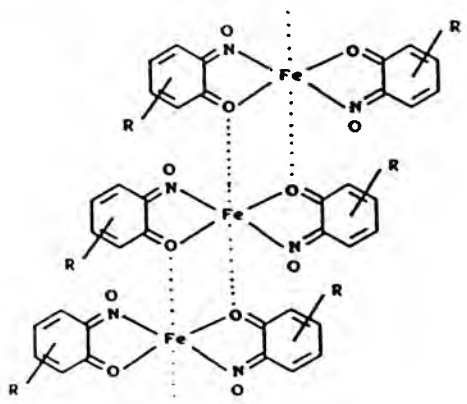
Reaction 3.11

$$RuCl_3 + Na(nqo) \xrightarrow{py/H_2O} Ru(nqo)_2(py)_2$$

Reaction 3.12

Internal redox reactions have not been observed in any of the above reactions between pyridine and the 1,2-naphthoquinone mono-oximato complexes of ruthenium(II).

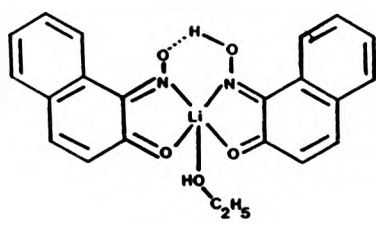
The readiness of reaction between chelates of type $Ru(nqo)_2$ and pyridine is noteworthy. Analogous 1,2-naphthoquinone mono-oximato complexes of iron(II) react slowly with pyridine at room temperature.[17] In the case of the iron(II) complexes, oligomerisation has been established by Mössbauer spectroscopy and magnetic studies (3.1).



(3.1)

The speed of reaction between the bischelates of type $Ru(nqo)_2$ and pyridine thus suggests that these complexes are not associated.

As noted above, there is no reaction between chelates of type Li(nqo)(nqoH) and pyridine, while complexes of type $Ru(nqo)_2(nqoH)$ react with pyridine to give the free ligand and $Ru(nqo)_2(py)_2$. In the former, intra-molecular hydrogen bonding has been demonstrated from i.r. and X-ray crystallographic studies (3.2).[15] Facile loss of the neutral ligand in ruthenium(II) chelates may be due, in part, to the absence of intra-molecular hydrogen bonding.

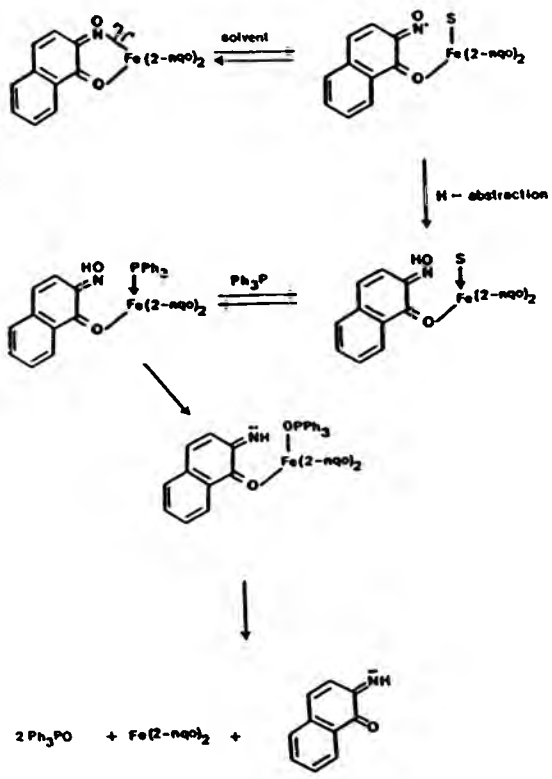


(3.2)

Previously, studies of the interaction of triphenylphosphine with metal chelates derived from mono-oximes of 1,2-naphthoquinones for a number of 1st row transition elements, e.g. copper(II), zinc(II), iron(III), chromium(III) and manganese(III) have shown that the Lewis base causes deoxygenation and/or an internal redox reaction, e.g. Reaction 3.13 and Scheme 3.2. [17-20,13]

Reaction 3.13

Studies of reactions between 2nd and 3rd row transition metal 1,2-naphthoquinone mono-oximic complexes and triphenylphosphine are limited to that of the trischelates of rhodium(III) and iridium(III). [15] In these cases no reaction occurs. This stability is explained in terms of the spin-paired d^6 configuration.



Scheme 3.2

Complexes of copper(II) and iron(III) undergo internal redox reactions with triphenylphosphine. In such systems, products arising from further reactions of the released ligand radical occur and are often complex. Thus, the reaction between $Cu(2\text{-nqo})_2$ and triphenylphosphine leads to the formation of 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine, 5-hydroxy-dibenzo[b,i]phenazin-12(6H)one and $Cu(2\text{-nqo})(PPh_3)_2$.[18]

In the reaction between $Cu(1\text{-}nqo)_2$ and triphenylphosphine, the main products are 1-amino-2-naphthol and $Cu(1\text{-}nqo)(PPh_3)_2$, with traces of 1-phenylamino-2-naphthol and 6-hydroxydibenzo[b,kl]-acridin-8-one. [18]

The reaction between $Ru(nqo)_2$ and triphenylphosphine in tetrahydrofuran afforded complexes of type $Ru(nqo)_2(PPh_3)_2$ (Reaction 3.14). No deoxygenation products are present even when reflux conditions are maintained for several days. Similarly $Ru(nqo)_2(nqoH)$ gives the bis triphenylphosphine complex in tetrahydrofuran together with the free 1,2-naphthoquinone mono-oxime (Reaction 3.15).

$$Ru(nqo)_2 + PPh_3 \xrightarrow[\text{reflux}]{\text{THF}} Ru(nqo)_2(PPh_3)_2$$

Reaction 3.14

$$Ru(nqo)_2(nqoH) + PPh_3 \xrightarrow[\text{reflux}]{\text{THF}} Ru(nqo)_2(PPh_3)_2 + nqoH$$

Reaction 3.15

This behaviour contrasts that of the first row transition metal complexes of 1,2-naphthoquinone mono-oximes which generally undergo deoxygenation of the ligand or reduction of the metal on treatment with triphenylphosphine. However, similar resistance towards

the phosphine is shown by the complexes $Rh(nqo)_3$ and as noted earlier, can be accounted for by the Ru(II) and Rh(III) low-spin d^6 configuration.

In contrast to $Ru(nqo)_2$, the analogous complexes of type $Fe(nqo)_2$ do not form adducts with triphenylphosphine.[17] This may be due, in part, to the strength of the inter-molecular bonds in the oligomeric structure.

When the above reactions are carried out in the presence of pyridine, the bis triphenylphosphine adduct is not formed. The metal containing product in both cases is $Ru(nqo)_2(py)_2$ (Reactions 3.16 and 3.17).

$$Ru(nqo)_2 + PPh_3 \xrightarrow[\text{reflux}]{\text{pyridine}} Ru(nqo)_2(py)_2$$

Reaction 3.16

$$Ru(nqo)_2(nqoH) + PPh_3 \xrightarrow[\text{reflux}]{\text{pyridine}} Ru(nqo)_2(py)_2 + nqoH$$

Reaction 3.17

3.3 Properties and structures of the complexes.

The pyridine adducts have been formulated on the basis of their elemental analysis and physico-chemical studies. The complex $Ru(1\text{-}nqo)_2(py)_2$ has also been recrystallised from pyridine:acetone to give crystals of *cis*-bis(1,2-naphthoquinone 1-oximato)dipyridine-ruthenium(II) with pyridine of crystallisation in the crystal lattice, for which an X-ray crystallographic structure has been derived (See Chapter 4).

The adducts $Ru(nqo)_2(py)_2$ were monomeric in acetone. Magnetic susceptibility measurements on the complexes at 20 °C indicated that the complexes were diamagnetic. Of interest, is the high thermal stability of these adducts. T.g.a. under nitrogen, indicated loss of pyridine between 240 and 280 °C, followed by decomposition of the ruthenium bis chelate at *ca.* 290 - 310 °C. Macroscale pyrolysis of $Ru(1\text{-}nqo)_2(py)_2$ and $Ru(2\text{-}nqo)_2(py)_2$, at *ca.* 270 °C, in *vacuo*, gave $Ru(1\text{-}nqo)_2$ and $Ru(2\text{-}nqo)_2$ respectively (Reaction 3.18).

$$Ru(nqo)_2(py)_2 \xrightarrow[0.1\ mm\ Hg]{270\ ^\circ C} Ru(nqo)_2 + 2py$$

Reaction 3.18

The complexes $Ru(nqo)_2(py)_2$ were soluble in ethanol (*ca.* 15 $g.dm^{-3}$). ^1H n.m.r. spectra (Fig. 3.1) in ethanol were obtained. The chemical shifts in the region 5.5-8.6 ppm, agree well with values obtained for analogous 1,2-naphthoquinone mono-oximic metal complexes.[16] The fine structure observed in the region 8.0-8.6 ppm is in accord with the presence of *cis*-arranged ligands.

The u.v./vis spectra of the adducts in ethanol, (Fig. 3.2), show intense charge transfer bands which tail off in the d-d region similar to those observed for the parent complexes $Ru(nqo)_2$, $Ru(nqo)_2(nqoH)$ and $Na[Ru(nqo)_3]$.

The i.r. spectra obtained for the complexes show bands in the region 1620-1200 cm^{-1} attributable to the 1,2-naphthoquinone mono-oximato ligands (Fig. 3.3), similar to those reported for the analogous iron,[17,21] nickel[22,19,20] and copper[23,24] complexes.

The complexes of type $Ru(nqo)_2(PPh_3)_2$ have been formulated on the basis of their elemental analysis, i.r., t.g.a. and magnetic measurements.

Treatment of complexes of type $Ru(nqo)_2(PPh_3)_2$ with pyridine gave the pyridine complexes $Ru(nqo)_2(py)_2$ and triphenylphosphine (Reaction 2.19).

Fig. 3.1 ^1H n.m.r. spectra of complexes of type $Ru(nqo)_2(py)_2$

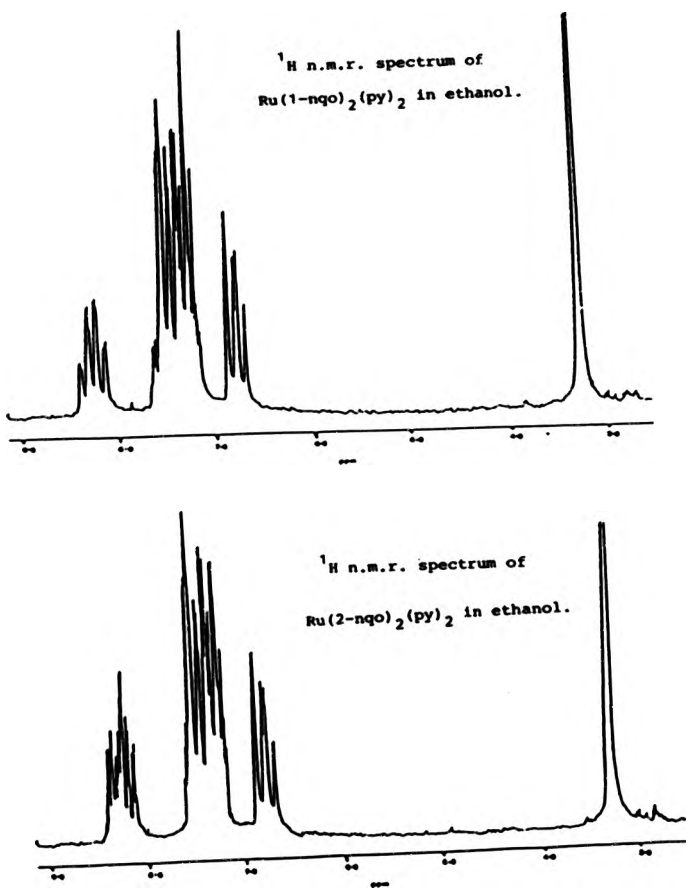
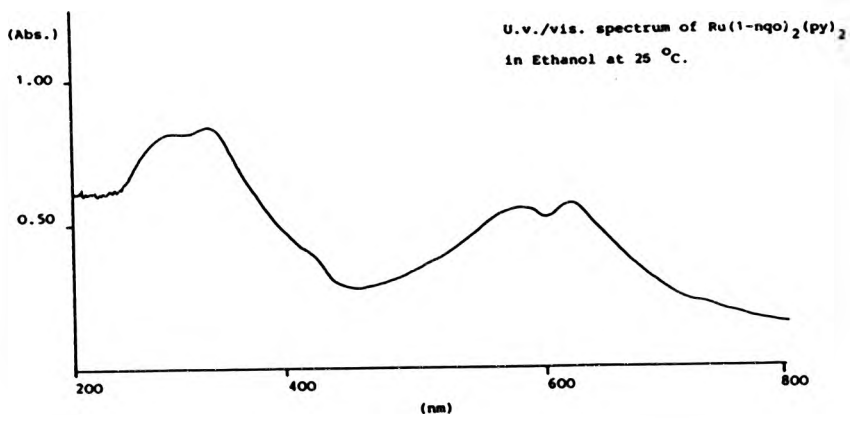


Fig. 3.2 U.v./vis spectra of complexes of type $Ru(nqo)_2(py)_2$



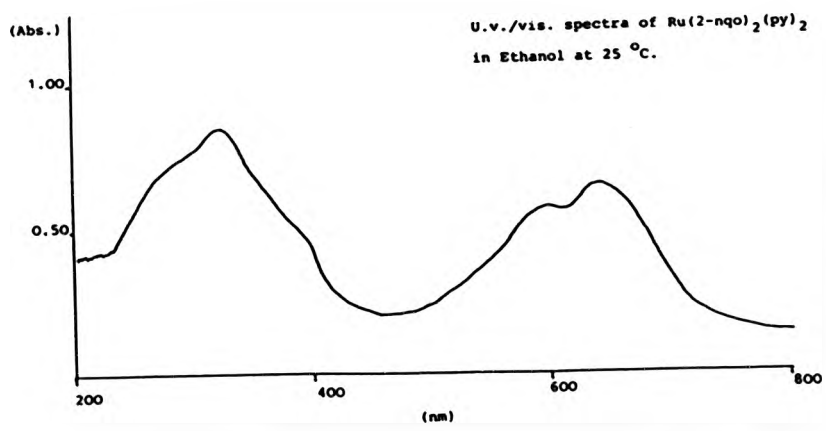
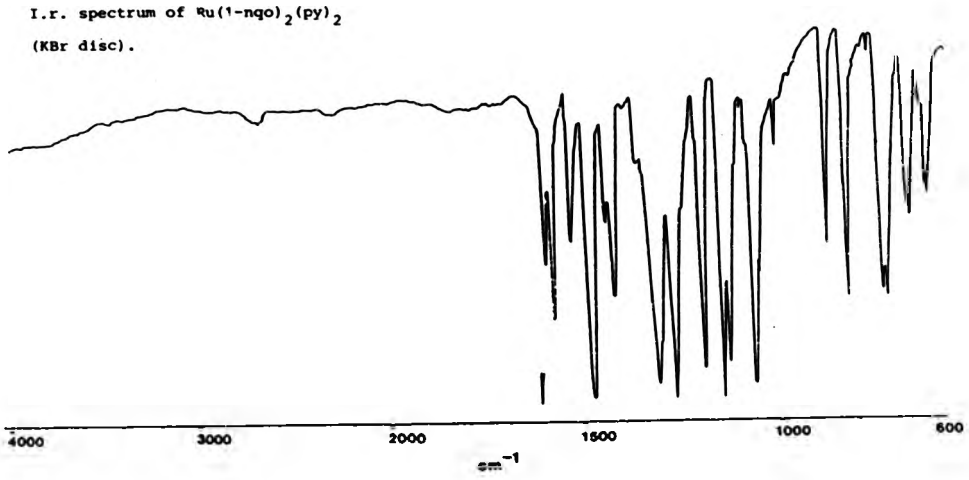
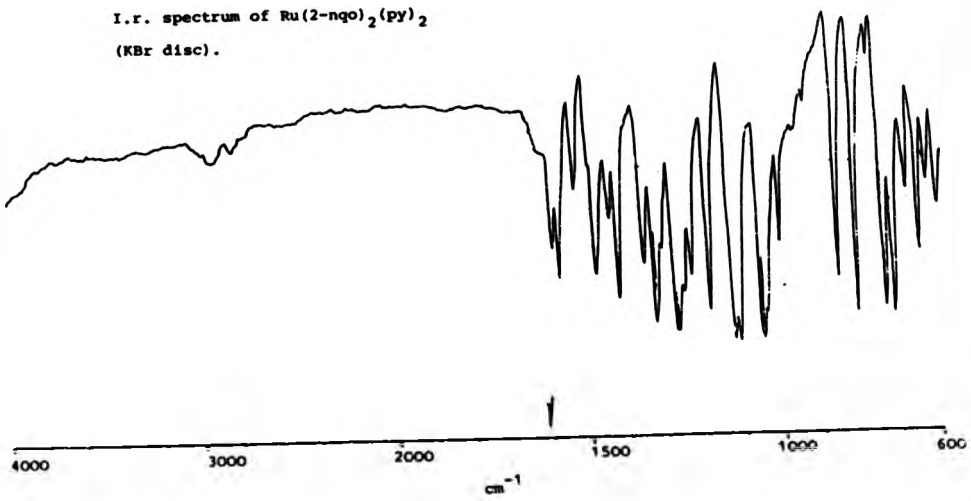


Fig. 3.3 I.r. spectra of complexes of type $Ru(nqo)_2(py)_2$

I.r. spectrum of $Ru(1\text{-}nqo)_2(py)_2$
(KBr disc).



I.r. spectrum of $Ru(2\text{-}nqo)_2(py)_2$
(KBr disc).



$$Ru(nqo)_2(PPh_3)_2 \xrightarrow{\text{pyridine}} Ru(nqo)_2(py)_2 + PPh_3$$

Reaction 2.19

T.g.a. of $Ru(1\text{-}nqo)_2(PPh_3)_2$ and $Ru(2\text{-}nqo)_2(PPh_3)_2$, indicates loss of both molecules of triphenylphosphine between 150 and 170 °C. Further heating to *ca.* 300 °C led to decomposition of the parent complexes.

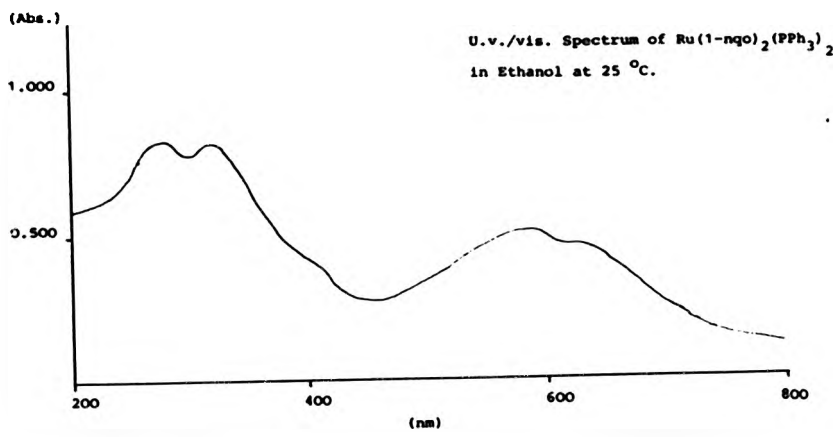
Magnetic susceptibility measurements on the complexes at 20 °C indicated the complexes to be diamagnetic.

The u.v./vis. solution spectra of the complexes in ethanol showed intense charge transfer bands which tail off into the d-d region, as observed for the precursor metal complexes (Fig. 3.4).

The i.r. spectra obtained for the complexes show bands in the region 1650-1200 cm^{-1}, attributable to quinone mono-oximic structures, similar to those reported for the analogous iron, [21,22] nickel [18,20] and copper [23,24] complexes (Fig. 3.5). Furthermore, the adducts exhibit bands attributable to the phosphine ligands similar to those observed in related ruthenium(II) complexes, such as $Ru(dioxH)_2(PPh_3)_2$. [27] Thus, bands present at 400-700 cm^{-1} which are absent in the parent complexes, are attributable to P-C vibrations (Table 3.1).

Fig. 3.4 U.v./vis spectra of complexes of type

$Ru(nqo)_2(PPh_3)_2$



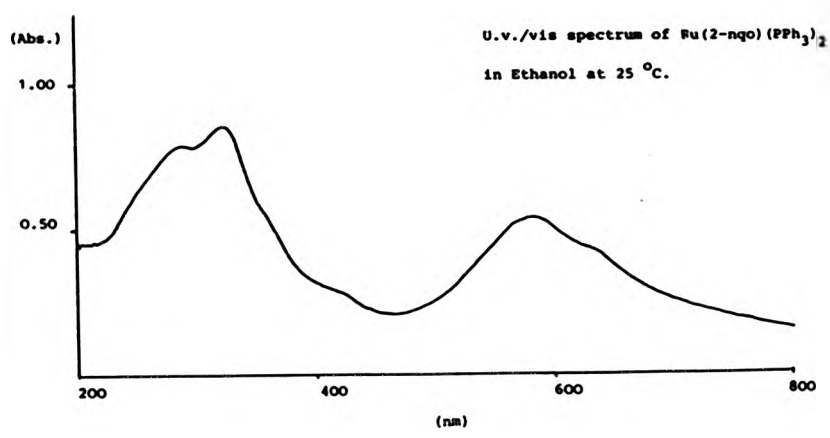
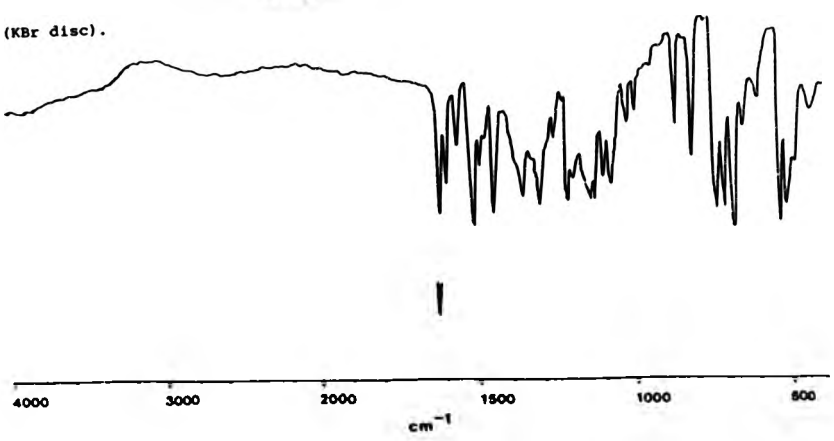


Fig. 3.5 I.r. spectra of complexes of type $Ru(nqo)_2(PPh_3)_2$

I.r. spectrum of $Ru(1\text{-}nqo)_2(PPh_3)_2$

(KBr disc).



I.r. spectrum of $Ru(2\text{-}nqo)_2(PPh_3)_2$

(KBr disc).

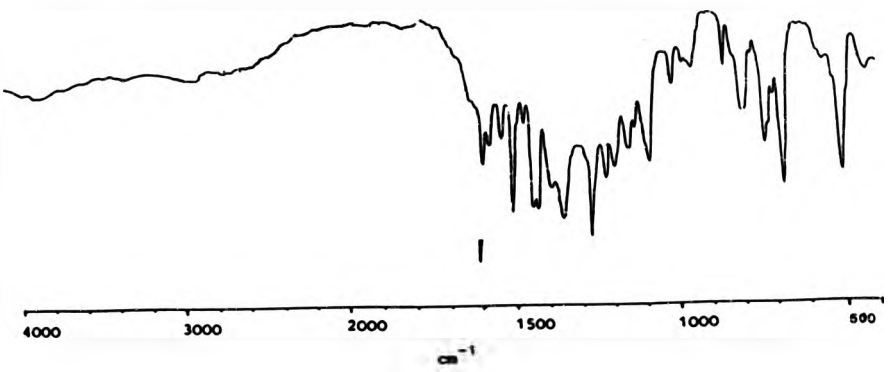


Table 3.1 I.r. bands for complexes of type $Ru(nqo)_2(PPh_3)_2$ compared with those for $RuCl_2(PPh_3)_2$.

wavenumbers (cm^{-1}).

Complex	Phosphine stretching region			Aromatic vibration		Phosphine stretch	vibration	
	ν(P-Ar)	ν(P-Ar)	ν(P-Ar)	ϑ(C-H)	ϑ(C-H)	ν(P-C)	ϑ(P-Ar)	ϑ(P-Ar)
$RuCl_2(PPh_3)_3$	1580	1477	1430	1190	1085	685	510	485
	s	m_2	m_2	s	m_+	m_+	s	m_2
$Ru(1\text{-}nqo)_2(PPh_3)_2$	1585	1477	1435	1200	1090	685	510	485
	m_2*	s	m_2*	m_2*	m_2	m_2	s	s
$Ru(2\text{-}nqo)_2(PPh_3)_2$	1585	1476	1434	1195	1092	685	508	487
	m_2*	s	m_2*	m_2*	m_2	m_2	s	s

Key:- m = multiplet (2 = two peaks, + = more than two peaks)
s = singlet
* = include nqo peaks

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CHAPTER FOUR

X-RAY CRYSTAL STRUCTURE OF BIS(1,2-NAPHTHOQUINONE-1-OXIMATO)DIPYRIDINERUTHENIUM(II).

4.1 Crystal preparation

The dipyridine complex of 1,2-naphthoquinone 1-oxime was prepared by stirring bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime)ruthenium(II) in pyridine under reflux. Recrystallisation of this complex from an acetone-pyridine mixture gave purple needle-like crystals of bis(1,2-naphthoquinone 1-oxime)dipyridineruthenium(II).1½pyridine. The crystal selected for this study had the dimensions 0.81 x 0.18 x 0.18 mm. The crystals were mounted in a single crystal X-ray diffraction camera and data were collected over a period of 24 hours.

4.2 Determination of the structure

A Philips PW1100 computer controlled, four circle, single crystal diffractometer with θ-2θ scan was used. A constant speed of scan at 0.05° s^{-1} and a scan width of 0.8° were used, with a background time equal to half the scan time. Three standard reflections were examined every 3 hours during the collection of data, showing no significant variation in intensity. In all, 25 reflections with $3.0<\theta<25.0°$ were examined and the crystals unit cell dimensions were found to be; a=16.321, b=11.519, c=9.354 (Å), α=102.41, β=102.2, γ=98.02 (°). From the unit cell dimensions and from the intensity relationships, the crystal was found to be triclinic, space group $P\bar{1}$. The measured reflections were 4114, out of which 4030 had $I>3\sigma(I)$ and used in the refinement of the structure. Corrections were made for Lorentz polarisation factors and for absorption. The structure was solved by the Patterson and Fourier methods and the positions of all the atoms, except hydrogen, were located. The hydrogen atoms were located in subsequent difference Fourier maps.

In the refinement of the structure by full matrix least square procedure, which converged to R=0.0505, ruthenium, nitrogen and oxygen were assigned anisotropic thermal parameters. The hydrogen atoms, which were assigned isotropic thermal parameters, were included in structure factors calculations but were not

refined. Neutral atom scattering factors were used throughout and calculations were done using the SHELX [1] programs. All the atomic coordinates, temperature factors, bond lengths, intra bond angles, inter and intra-molecular distances are given in Tables 1-7 in Appendix 1.

4.3 Results and discussion

The ruthenium atom is hexa- coordinated in a distorted octahedral environment, with two anionic 1,2-naphthoquinone 1-oximato ligands and two neutral pyridine ligands. The octahedral unit is monomeric, however, 1½ molecules of pyridine are associated in the crystal lattice. A view of the molecule with the atomic numbering scheme is shown in Fig. 4.1. Selected bond lengths and bond angles are given in Figs. 4.2 and 4.3 respectively. In the discussion, the bond lengths are given to two significant figures to allow comparison with other reported data. As noted earlier, previous studies have shown that 1,2-naphthoquinone 1-oxime has essentially a quinoneoximic structure involving intramolecular hydrogen bonding. This is shown by the short CN (1.31 Å), CO (1.25 Å), C3-C4 (1.33 Å) bond lengths and the long NO (1.36 Å), C1-C2 (1.48 Å) bond lengths (Fig. 4.4). [2] The CO bond distance compares well with that found in quinones, e.g. 1,4-benzoquinone (C=O, 1.22 Å), [3,4] and NO and CN bond lengths with

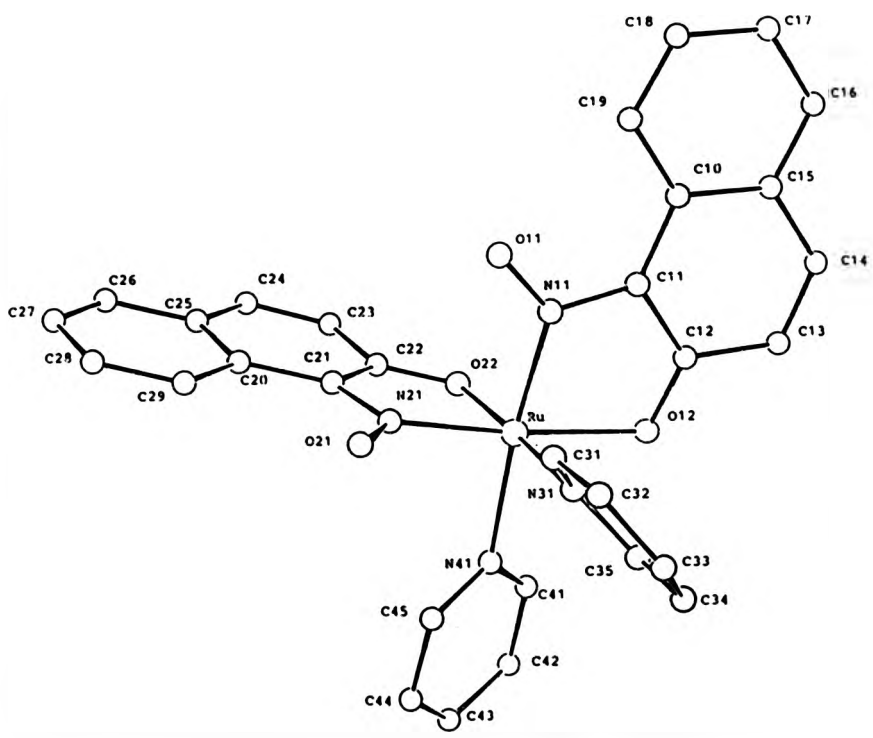

Fig. 4.1 A view of $Ru(1\text{-nqo})_2(py)_2$ with the atomic numbering scheme.

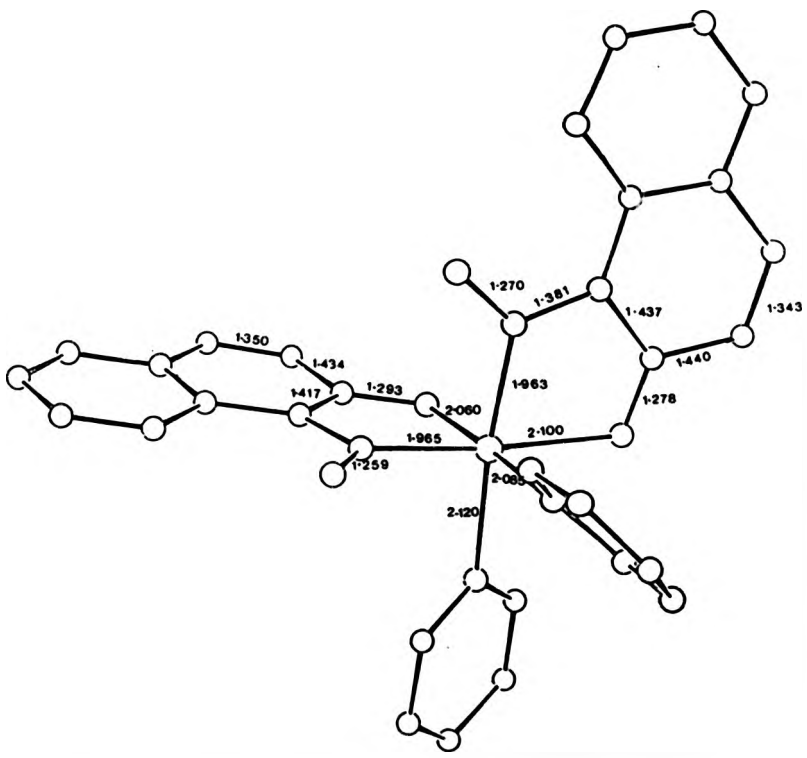

Fig. 4.2 A view of $Ru(1\text{-}nqo)_2(py)_2$ with selected bond lengths (Å).

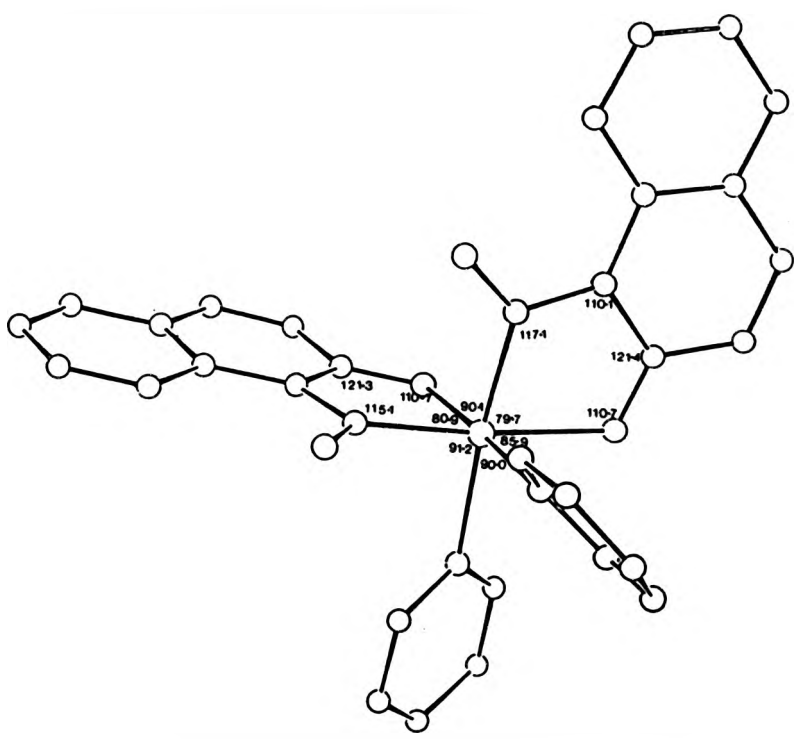

Fig. 4.3 A view of $Ru(1\text{-}nqo)_2(py)_2$ with selected bond angles (°).

those found in oximes,[5] e.g. acetoxime (C=N, 1.29 Å; N-O, 1.36 Å). The CO and CN bond lengths in 1,2-naphthoquinone 1-oxime are longer than the corresponding bonds in 1,2-quinone mono-oximes which do not exhibit intramolecular hydrogen bonding. For example, 1,2-naphthoquinone 2-oxime 5-sulphonic acid has a CO bond length of 1.24 Å and a CN bond length of 1.30 Å.[6]

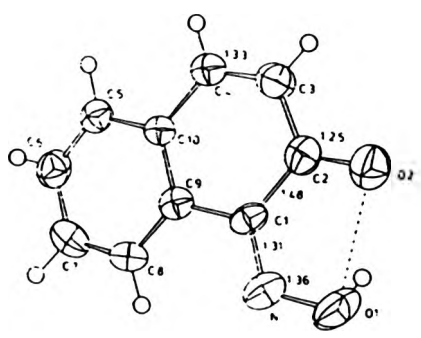

Fig. 4.4 Crystal structure of 1,2-naphthoquinone 1-oxime with the atomic numbering and selected bond lengths (Å).

Two types of complexes derived from naphthoquinone 1-oxime have been characterised by X-ray crystallography. Both types involve the anion of the ligand which either chelates or bonds to the metal via the NO group. In both cases the nature of the ligand is essentially quinoneoximic as shown by the C1-C2 and C3-C4 bond lengths which exhibit single and double bond character respectively, e.g Figs. 4.5 and 4.6.

Chelation involving a 5-membered ring has been established by X-ray crystallographic techniques in four 1,2-naphthoquinone 1-oximato complexes,[7-10] $Cu(1\text{-}nqo)_2.2Me_2CO$, $Cu(1\text{-}nqo)(PPh_3)_2$, $Li(1\text{-}nqo)$-$(1\text{-}nqoH).EtOH$ and $[pyH][Ir(1\text{-}nqo)(py)Cl_3]$. This type of bonding has also been established in several other 1,2-quinone-oximic ligands.[11-19]

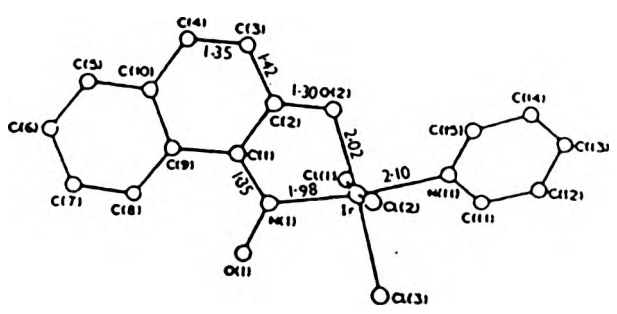

Fig. 4.5 **Crystal structure of $[pyH][Ir(1\text{-}nqo)(py)Cl_3]$ and selected bond lengths.**

Recently, bonding to the metal via the nitrogen and oxygen of the NO only has been identified for the complex $UO_2(1\text{-}nqo)_2(Ph_3PO).H_2O$ (Fig. 4.6).[20] In this complex, the CO is not involved in the bonding. Platinum complexes derived from 4-isonitroso-3(R)-isoxazol-5-one also exhibit bonding to the metal via

only the NO group, [21] but in this case, bonding is through the nitrogen atom only. In complexes involving the anionic chelated 1-nqo$^-$ ligand, the CO and CN bonds are longer than in the free ligand (Table 4.1), and are in agreement with the observed shift in the νCO absorption in the i.r. spectra as noted in earlier chapters. In contrast, the NO bond lengths in these complexes are shorter than that found in the free ligands, this being partly due to the absence of hydrogen bonding in the former. In the uranyl complex, the CN bond is longer than in the free ligand whilst, the CO bond, which does not take part in bonding to the metal, is slightly shorter than that of the free ligand.

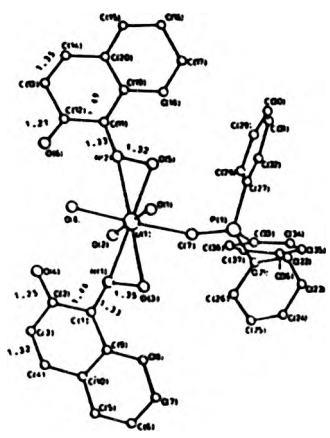

Fig. 4.6 Crystal structure of $UO_2(1\text{-nqo})_2(Ph_3PO).H_2O$ and selected bond lengths (Å).

Recently, the structure for a lithium complex derived from 1,2-naphthoquinone 1-oxime has been reported. In this complex, Li(1-nqo)(1-nqoH).EtOH, chelation to the metal is via an anionic ligand and a neutral ligand. In this case, the bond lengths for the neutral ligand are very similar to those of the free ligand. For the anionic ligand, the bond lengths agree well with other complexes with anionic ligands. Selected bond lengths for metal complexes derived from 1,2-naphthoquinone 1-oxime, are presented in Table 4.1.

In the complex $Ru(1\text{-}nqo)_2(py)_2$, both ligands are anionic and are quinoneoximic in character. The quinoneoximic character of the ligand is indicated by the long C1-C2 (1.43 ± 0.01 Å) and the short C3-C4 (1.34 ± 0.01 Å) average bond distances (Fig. 4.2). The CO (1.28 ±0.01 Å) average bond length is longer than that of the free ligand and is in agreement with those observed for the anionic ligands of the copper, iridium and lithium complexes. The NO (1.26 ± 0.01 Å) average bond length is shorter than that of the free ligand and similarly is in agreement with the above metal complexes. The CN (1.39 ± 0.01 Å) average bond length is longer than that of the free ligand and is slightly longer than observed for other metal complexes of this type. The 1,2-naphthoquinone 1-oximato ligands are found in a *cis* configuration.

Table 4.1 **Selected bond lengths (Å) of 1,2-naphthoquinone 1-oxime and its metal complexes.**

Compound	C-O	C-N	N-O	Ref.
1-nqoH	1.25	1.31	1.36	2
$Cu(1\text{-}nqo)_2 \cdot 2Me_2CO$	1.29	1.35	1.26	7
$Cu(1\text{-}nqo) \cdot (PPh_3)$	1.26	1.37	1.29	8
$Li(1\text{-}nqo)(1\text{-}nqoH) \cdot EtOH$	1.26	1.33	1.30	
	1.24	1.28	1.34	9
$[pyH][Ir(1\text{-}nqo)(py)Cl_3]$	1.30	1.35	1.27	10
$UO_2(1\text{-}nqo)_2(Ph_3PO) \cdot H_2O$	1.25	1.33	1.35	
	1.21	1.33	1.32	20
$Ru(1\text{-}nqo)_2(py)_2$	1.28	1.38	1.27	
	1.29	1.39	1.27	#

= This work.

In $Ru(1\text{-}nqo)_2(py)_2$, the pyridine ligands are found in a *cis* configuration. The Ru-N bond length for the pyridine molecule *trans* to the NO group (2.12 Å) is slightly longer than that observed for the bond *trans* to the CO group (2.08 Å).

This *cis*-pyridine arrangement is similar to that observed in the copper(II) complex $Cu(4\text{-}Clqo)_2(bipy)$ (4-ClqoH = 4-chloro-1-benzoquinone 2-oxime) (Fig. 4.7).[18] The 2,2'-bipyridine adduct is similarly found coordinated to the metal through one short (Cu-N3 2.01 Å) and one long (Cu-N4 2.18 Å) metal-nitrogen bond. In this case however, the long metal-nitrogen bond corresponds to the pyridine molecule *trans* to the CO group, while the short bond to that of the NO group of the quinone 2-oximato ligand.

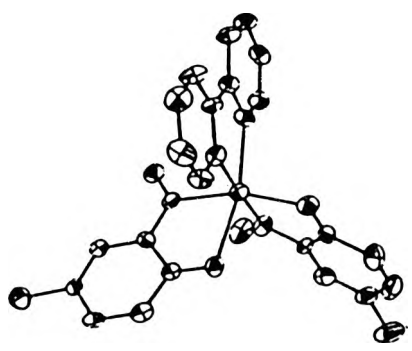

Fig. 4.7 **Crystal structure of $Cu(qo)_2(bipy)$**

In the complex under study, the average metal-pyridine bond length (2.10 Å) is identical to that observed in the complex [pyH][Ir(1-nqo)(py)Cl_3] (Fig. 4.5), (2.10 Å) and that of the average metal-2,2'-bipyridyl bonds, in the complex Cu(qo)$_2$(bipy) (2.10 Å) (Fig. 4.7). The similarity of the average metal-pyridine (M-N) bond lengths for the above complexes is noteworthy. Although the atomic radius of the atoms of the 1st, 2nd and 3rd row transition elements increase respectively, the metal-pyridine average bond length remains constant.

4.4 References

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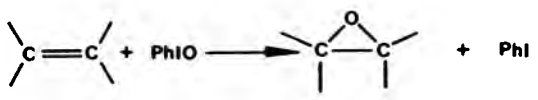
CHAPTER FIVE

RUTHENIUM COMPLEXES DERIVED FROM 1,2-NAPHTHOQUINONE MONO-OXIMES AS CATALYSTS FOR THE AEROBIC OXIDATION OF ALKENES

5.1 Introduction

Epoxidation of alkenes is commercially very important as it allows the simultaneous functionalisation of two adjacent carbon atoms.[1,2] In addition, the field is also of theoretical interest. A mechanistic understanding in this area can expedite understanding of biological oxygenation reactions, e.g. those involving cytochrome P-450[3,4] Consequently, epoxidation reactions are currently receiving intense attention.[5-24] Many transition metal complexes have been studied for the oxidation of organic substrates including complexes of cobalt,[25,26] copper,[27]

chromium,[28-30] iron,[31,32] manganese,[33,34] and ruthenium.[11,35] Generally, these systems do not give good yields in terms of alkene converted to oxidation products. Furthermore, they suffer from two other disadvantages. Firstly, oxidations involving dioxygen activation require the presence of a co-reductant. Secondly, in most studies, the important problem of dioxygen activation is bypassed and alternative oxygen sources such as iodosobenzene, hydroperoxides or hypochlorites are used.[20] The catalytic systems which based on the alternative oxygen sources are expensive and also have the drawback of stoichiometric coproduct formation (Reaction 5.1).[1]

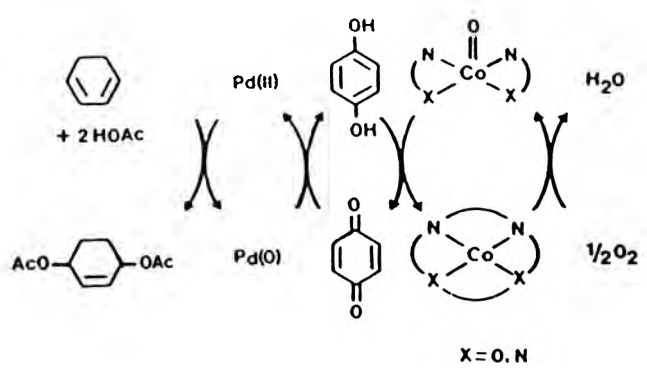


Reaction 5.1

Most of the catalytic systems cited above are based on porphyrins.[2] Development of non-porphyrin metal complexes as catalysts for alkene oxidation has received limited attention, particularly with regard to aerobic oxidation. The iodosobenzene epoxidation of alkenes catalysed by non-porphyrin complexes of type OsL^1PPh_3Cl, MnL^1Cl and MnL^2Cl has been reported [L^1H = 1,2-bis(pyridine-2-carboxamido)benzene and L^2H = 1,2-bis(pyridine-2-carboxamide)-4,5-dichlorobenzene].[19]

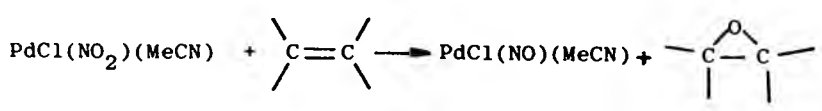
The aerobic oxidation of alkenes to aldehydes and ketones using a 1:4 mixture of $Pd(MeCN)_2(NO_2)$ and $CuCl_2$ as the catalyst, has been reported during the course of this study.[12]

Benzoquinones are well known oxidants in synthetic organic chemistry.[22] The 1,4-benzoquinone/hydroquinone redox couple has been used as part of a catalytic system involving the redox couples Pd(II)/Pd(0) and Co(TPP)(O)/Co(TPP) as catalysts (Scheme 5.1).[21]



Scheme 5.1

It has been also reported that systems based on the nitroso/nitro redox couple (Reactions 5.2 and 5.3) can catalyse the aerobic oxidation of alkenes to ketones and the stoichiometric oxidation of norbornene to exo-epoxynorbornane.[21]



Reaction 5.2

$$PdCl(NO)(MeCN) + \tfrac{1}{2}O_2 \longrightarrow PdCl(NO_2)(MeCN)$$

Reaction 5.3

The use of complexes derived from 1,2-naphthoquinone mono-oximes and involving transition metals such as iron, manganese, chromium etc., as catalysts for alkene oxidations is advantageous. In addition to the ability of the metal to activate dioxygen, the coordinated ligands in such complexes have quinoid and oximic features which can expediate catalytic oxidation. Furthermore, 1,2-naphthoquinone mono-oximato complexes are cheaper than metal porphyrin complexes.

Recently, it has been reported from this laboratory that the complexes $Mn(nqo)_3$ and $Mn(nqo)_2$ are efficient catalysts for the aerobic epoxidation of alkenes (Table 5.1).[34] The manganese catalysts are, however, susceptible to decomposition and the reactions involve long induction periods. In an effort to increase yield and reduce the induction period, the catalytic potential of the complexes $Ru(nqo)_2$ was investigated. Ruthenium has close similarities to iron which is known to be involved in the catalytic cycle of cytochrome P-450. In addition, the complexes $Ru(nqo)_2$ are more soluble than $Mn(nqo)_2$ and more stable than $Mn(nqo)_3$.

5.2 Oxidation of alkenes

Cyclohexene, styrene and 1-octene, were selected as substrates as they represent a range of reactivities with regard to aerobic oxidation. Furthermore, these olefins have been used as substrates by other workers and therefore yields and turnover numbers can be compared. All the oxidation reactions were carried out at room temperature and at 60 °C, under oxygen and in air. In addition, the oxidation of cyclohexene was also investigated at 20 °C in the presence of a small amount of pyridine.

Table 5.1 The epoxidation of alkenes with dioxygen at 60 °C, using manganese catalysts.

Catalyst	Alkene	Induction time (h)	% yield[a]/ turnover[b]
$Mn(1\text{-}nqo)_2$	cyclohexene	18	65/260
$Mn(2\text{-}nqo)_2$	cyclohexene	99	46/184
$Mn(1\text{-}nqo)_3$	cyclohexene	88	40/160
$Mn(2\text{-}nqo)_3$	cyclohexene	32	55/220
$Mn(1\text{-}nqo)_2$	styrene	32	21/82
$Mn(2\text{-}nqo)_2$	styrene	100	14/55
$Mn(1\text{-}nqo)_3$	styrene	94	17/67
$Mn(2\text{-}nqo)_3$	styrene	38	22/86
$Mn(1\text{-}nqo)_2$	1-octene	46	30/53
$Mn(2\text{-}nqo)_2$	1-octene	120	24/43
$Mn(1\text{-}nqo)_3$	1-octene	110	19/34
$Mn(2\text{-}nqo)_3$	1-octene	65	27/48

[a]Based on alkene. [b]Based on catalyst.

5.2.1 Oxidation of cyclohexene

When cyclohexene (1000 mol. eq.) and Ru(2-nqo)2 (1 mol. eq.) were stirred at 60 °C under oxygen, 1,2-epoxycyclohexane, cyclohexanol and cyclohexanone were obtained in yield/turnover of 34%/340, 37%/370 and 20%/200 respectively (Table 5.2). A small amount of cyclohexene was recovered unreacted (9%). The total yield/turnover of oxidation products was 91%/910. Catalyst decomposition was not observed (t.l.c.). The catalyst was recovered and re-used in a repeat of the above experiment. This led to 1,2-epoxycyclohexane, cyclohexanol and cyclohexanone in yield/turnover of 30%/300, 32%/320 and 14%/140 (Fig. 5.1). Cyclohexene (24%) was recovered unreacted. The total yield and turnover of oxidation products was 76%/760, i.e. the catalyst retained 86% of its activity.

When the above experiments were repeated using Ru(1-nqo)$_2$ as catalyst, similar results were obtained (Fig. 5.2). Thus, yield turnover of 1,2-epoxycyclohexane and cyclohexanol and cyclohexanone were 29%/290, 31%/310 and 12%/120, respectively; unreacted cyclohexene (28%) was recovered. The total yield/turnover of oxidation products was 72%/720. Once again catalyst decomposition was not observed and the catalyst was found to retain 90% of its original activity.

Table 5.2 Aerobic oxidation of cyclohexene catalysed by the complexes $Ru(nqo)_2$.[a]

Induction/reaction time (hours)	Products % yield[b]/turnover[c]			Total % yield/turnover of oxidation products
	Epoxide	Cyclohexanol	Cyclohexanone	
2/120[d, e]	34/340	21/210	10/100	65/650
1/120[d, f]	45/450	30/300	12/120	87/870
1/120[d, g]	34/340	37/370	20/200	91/910
2/120[h, e]	25/250	15/150	10/100	50/500
1/120[h, f]	38/380	27/270	13/130	78/780
1/120[h, g]	29/290	31/310	12/120	72/720

[a]Cyclohexene (initial concentration 225 mmol). [b]Yield based on cyclohexene. [c]Turnover based on catalyst. [d]Catalyst = $Ru(2\text{-}nqo)_2$ (initial concentration 0.225 mmol). [e]At 20 °C/O_2. [f]At 20 °C/O_2 in the presence of pyridine (1.27 mmol). [g]At 60 °C/O_2. [h]Catalyst $Ru(1\text{-}nqo)_2$ (initial concentration 0.225 mmol).

When cyclohexene (1000 mol. eq.) and $Ru(2\text{-nqo})_2$ (1 mol. eq.) or $Ru(1\text{-nqo})_2$ (1 mol. eq.) were stirred at 60 °C in air, no oxidation of the substrate occured.

At 20 °C, under oxygen, oxidation of cyclohexene by $Ru(2\text{-nqo})_2$ afforded 1,2-epoxycyclohexane, cyclohexanol and cyclohexanone in yield/turnover of 34%/340, 21%/210 and 10%/100 respectively (Fig. 5.3). The total yield/turnover was 65%/650.

At 20 °C, under oxygen, oxidation of cyclohexene by $Ru(1\text{-nqo})_2$ gave similar results to the corresponding reaction involving $Ru(2\text{-nqo})_2$. Thus 1,2-epoxycyclohexane, cyclohexanol and cyclohexanone were obtained in yield/turnover of 25%/250, 15%/150 and 10%/100 respectively (Fig. 5.4). The total yield/turnover being 50%/500.

When cyclohexene (1000 mol. eq.) and $Ru(2\text{-nqo})_2$ (1 mol. eq.) or $Ru(1\text{-nqo})_2$ (1 mol. eq.) were stirred at 20 °C in air, no oxidation of the substrate occured.

It has been reported that the addition of a small amount of pyridine, or substituted pyridines, increases the rate of alkene oxidation and the yield of oxidation products. This has been previously rationalised by proposing that electron donation by coordinated pyridine expedites formation of high-valent oxo-metal

intermediates. This 'pyridine effect' was observed in the catalyst systems involving the complexes $Mn(nqo)_2$ or $Mn(nqo)_3$.[37]

When the oxidation of cyclohexene was carried out in the presence of pyridine, with $Ru(2\text{-}nqo)_2$ as catalyst, a marked increase in the rate of oxidation and yield of oxidation products was observed relative to the corresponding reaction in the absence of pyridine. Thus, at 20 °C and under oxygen, the reaction afforded 1,2-epoxycyclohexane and cyclohexanol and cyclohexanone in yield/turnover of 45%/450, 30%/300 and 12%/120 respectively (Fig. 5.5) (the corresponding figures in the absence of pyridine were 34%/340, 21%/210 and 10%/100). The total yield/turnover was 87%/870 (in the absence of pyridine the total yield/turnover was 75%/750).

Similar results were obtained with $Ru(1\text{-}nqo)_2$ as the catalyst (Fig. 5.6). Thus at 20 °C, under oxygen and in the presence of pyridine, the oxidation of cyclohexene gave 1,2-epoxycyclohexane, cyclohexanol and cyclohexanone in yield/turnover of 38%/380, 27%/270, 13%/130 respectively (the corresponding figures in the absence of pyridine were 25%/250, 15%/150, 10%/100). The total yield/turnover being 78%/780 (in the absence of pyridine the total yield/turnover was 50%/500).

The yield/turnover of the oxidation products from the reactions involving $Ru(nqo)_2$ complexes and cyclohexene are better than the results reported using $Mn(nqo)_n$ (n = 2 or 3) as catalysts under identical conditions. In the case of the manganese complexes, turnover numbers for 1,2-epoxycyclohexane were in the range 160-260. The ruthenium complexes however, gave turnover numbers of 290 and 340 for the formation of the 1,2-epoxycyclohexane; whilst the turnover numbers for total oxidation products were 720-910. The manganese complexes are however, more selective and give the epoxides as the major products. It has been previously also reported that the MnL^1Cl - and MnL^2Cl - catalysed PhIO epoxidation of cyclohexene affords the epoxide in yields of 39-58 % and turnovers of 12-29. [13] Similarly, the Cr(salen) - catalysed PhIO epoxidation of cyclohexene affords the epoxide in yields of 2-22% (based on the amount of PhIO converted to PhI). [14] Thus, the total yield/turnover of 1,2-epoxycyclohexane and other oxidation products obtained in this study (Table 5.2) are better than those previously reported for other catalyst systems.

The complexes $Ru(nqo)_2$, behave similarly to the complexes $Mn(nqo)_3$ and $Mn(nqo)_2$, in that they catalyse the aerobic oxidation of cyclohexene at 60 °C. In contrast to the manganese catalysts, the complexes $Ru(nqo)_2$ also catalyse the aerobic oxidation of cyclohexene at 20 °C.

Fig. 5.1 Reaction profile for the oxidation of cyclohexene with dioxygen, at 60 °C, catalysed by the complex $Ru(2\text{-nqo})_2$.

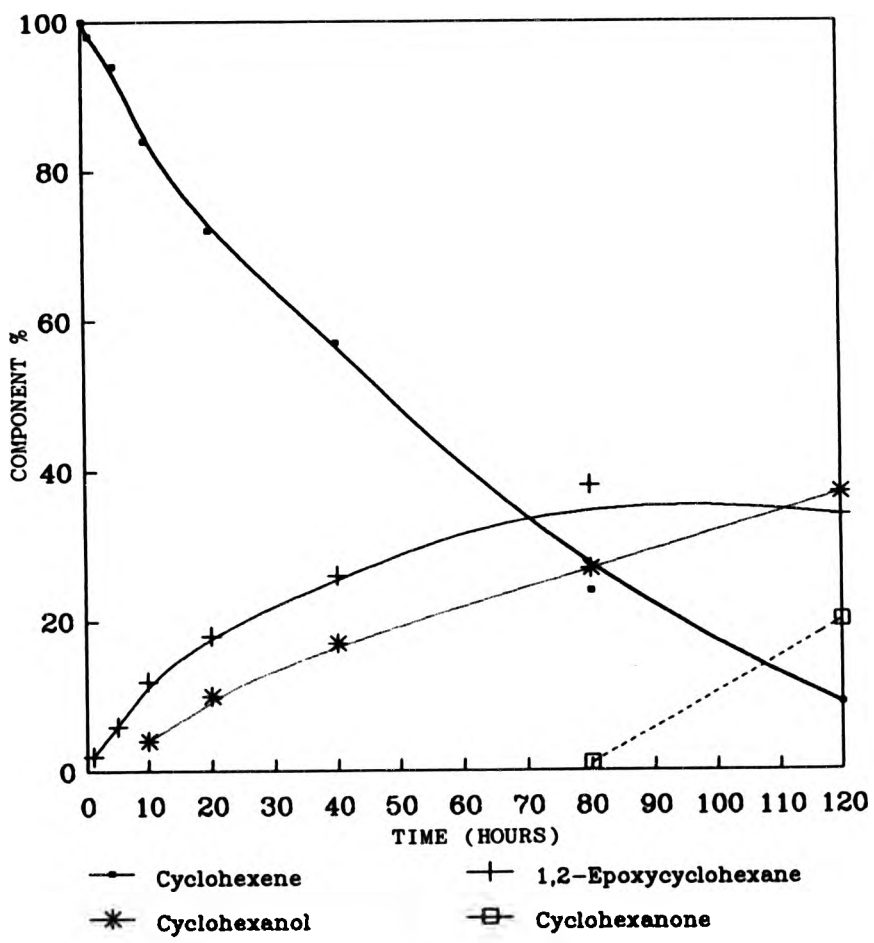


Fig. 5.2 Reaction profile for the oxidation of cyclohexene with dioxygen, at 60 °C, catalysed by the complex $Ru(1\text{-nqo})_2$.

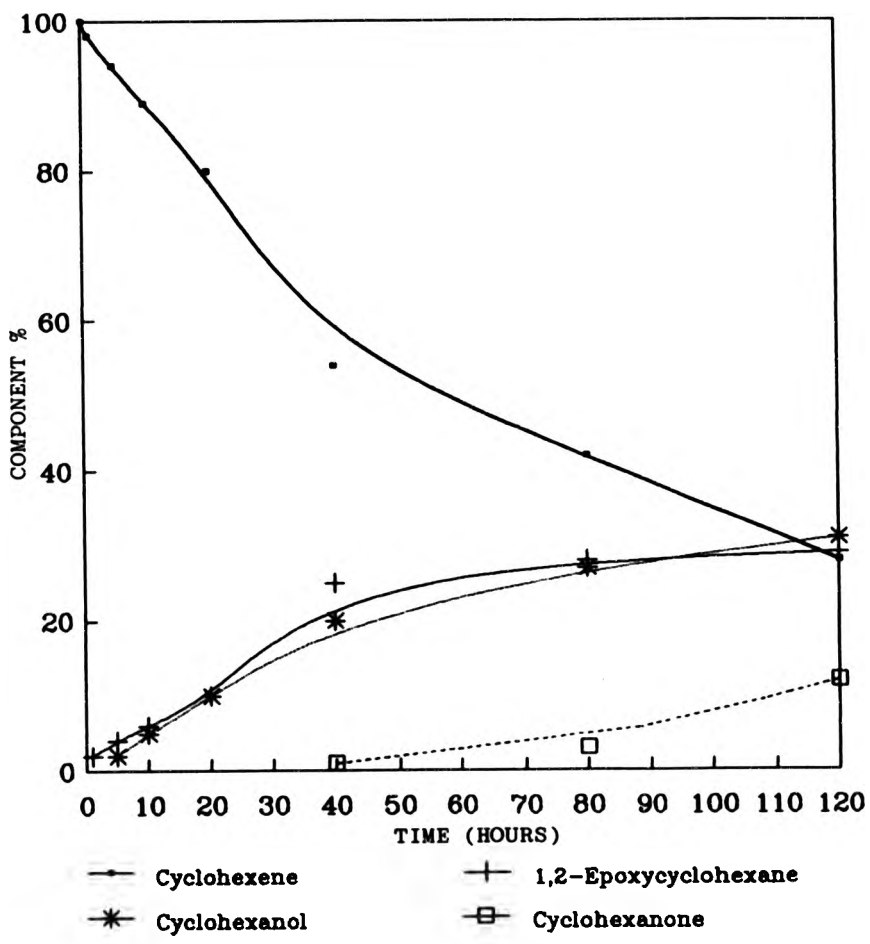


Fig. 5.3 Reaction profile for the oxidation of cyclohexene with dioxygen, at 20 °C, catalysed by the complex $Ru(2\text{-nqo})_2$.

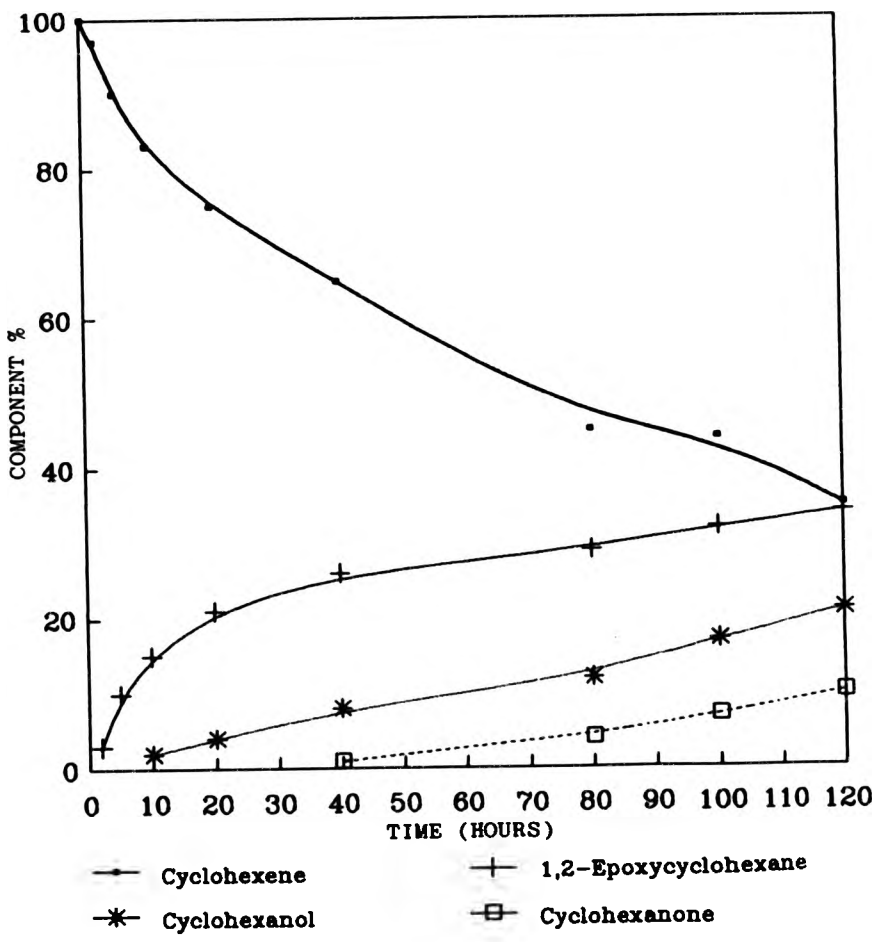


Fig. 5.4 Reaction profile for the oxidation of cyclohexene with dioxygen, at 20 °C, catalysed by the complex $Ru(1\text{-}nqo)_2$.

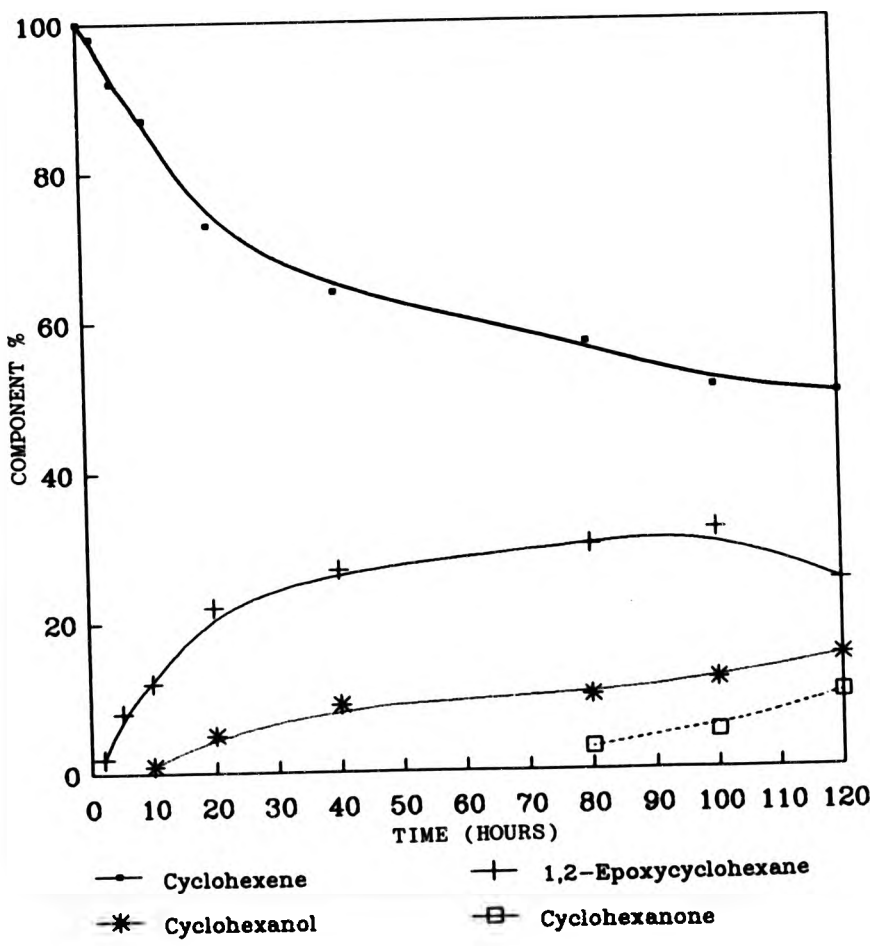


Fig. 5.5 Reaction profile for the oxidation of cyclohexene with dioxygen, at 20 °C in the presence of pyridine, catalysed by the complex $Ru(2\text{-}nqo)_2$.

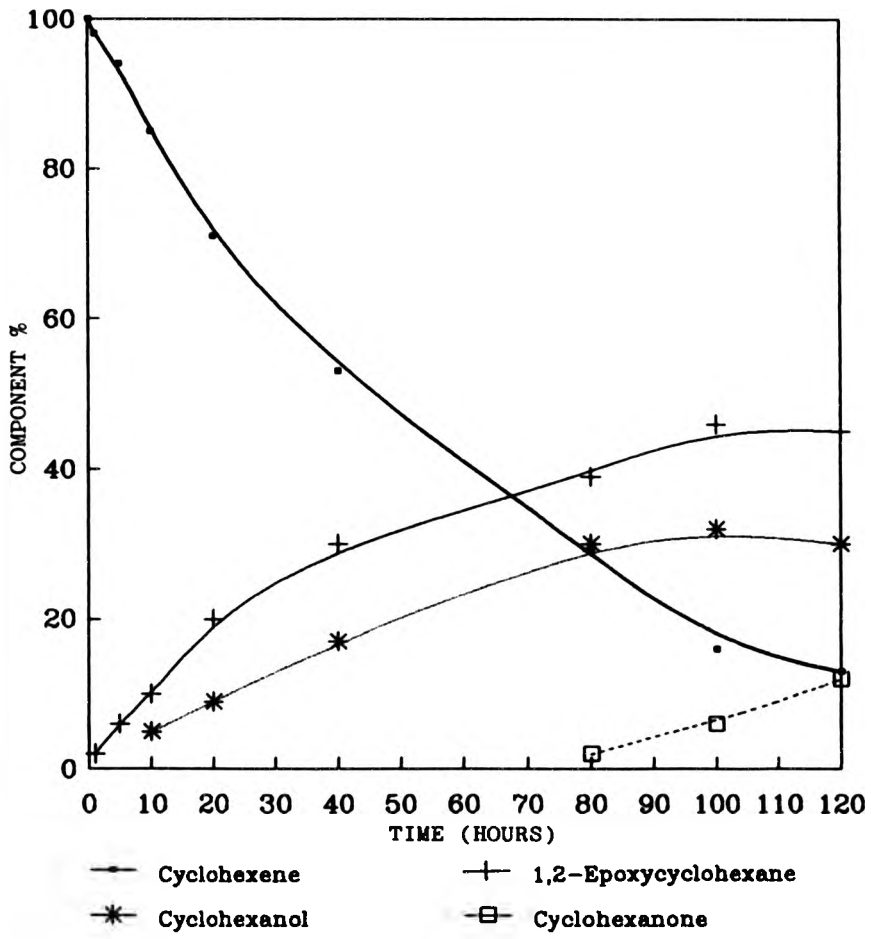
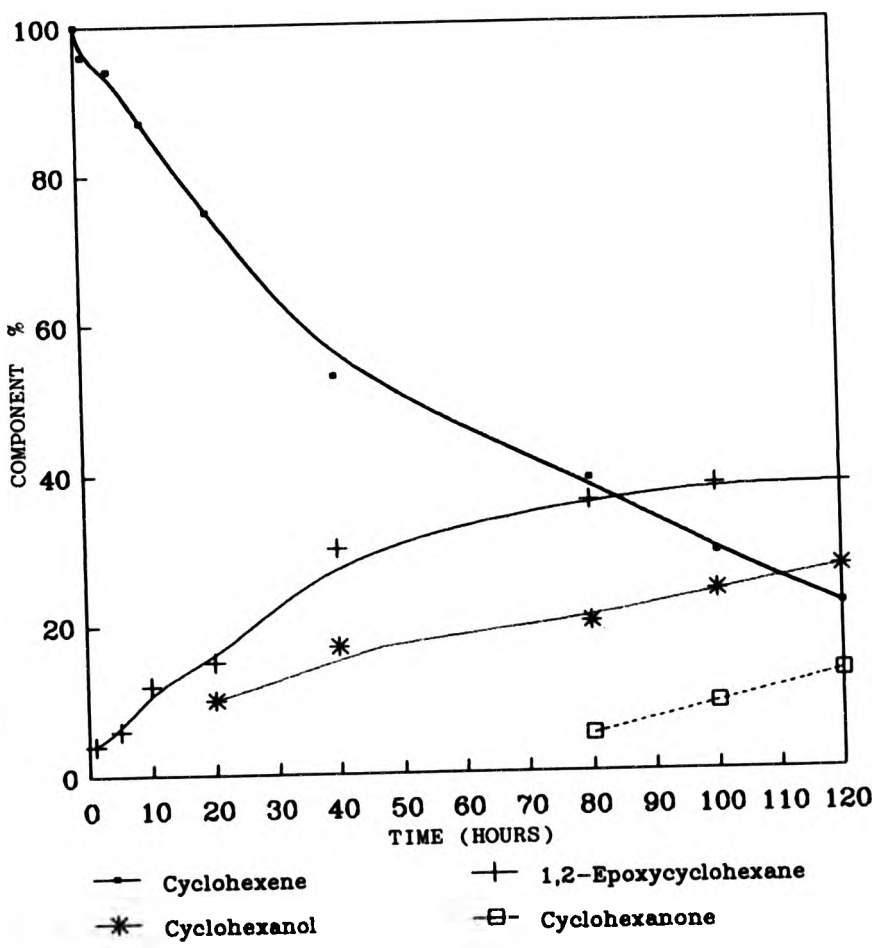


Fig. 5.6 Reaction profile for the oxidation of cyclohexene with dioxygen, at 20 °C in the presence of pyridine, catalysed by the complex Ru(1-nqo)2.



As in the case of the manganese complexes, the ruthenium complexes do not catalyse aerobic oxidation of cyclohexene in air at 20 °C or at 60 °C.

The manganese catalysts $Mn(nqo)_3$ and $Mn(nqo)_2$, afford the 1,2-epoxide as the major oxidation product with only minor amounts of other products. In the case of the ruthenium catalysts, three products are formed over a similar reaction time: an epoxide, an alcohol and a ketone. In this study, the oxidation of cyclohexene by the ruthenium catalysts $Ru(nqo)_2$ affords identical products to those reported previously for the aerobic oxidation of cyclohexene using porphyrin complexes of ruthenium(II) as catalyst. [31]

5.2.2 Oxidation of styrene

When styrene (1000 mol. eq.) and $Ru(2\text{-}nqo)_2$ (1 mol. eq.) were stirred at 60 °C, complete oxidation of the styrene was observed after 180 h to give styrene epoxide and phenylacetaldehyde in yields/turnover of 5%/50 and 80%/800 respectively (Fig. 5.7), plus four unidentified minor products. The reaction profile showed that initially the epoxide plus an unidentified component were the major oxidation products in the reaction mixture. Formation of phenylacetaldehyde starts to occur only after an induction period of 10 h.

Formation of aldehydes in styrene epoxidation has been previously reported to occur via decomposition of the styrene epoxide.

Similar results were obtained when $Ru(1\text{-}nqo)_2$ was used as catalyst. Thus, when styrene (1000 mol. eq.) and $Ru(1\text{-}nqo)_2$ (1 mol. eq.) were stirred at 60 °C for 200 h, styrene epoxide and phenylacetaldehyde were obtained in yield/turnover of 4%/40, and 78%/780 respectively (Fig. 5.8). Unidentified components accounted for the remainder of the mixture with yield/turnover of approximately 15%/150. The reaction profile of the $Ru(1\text{-}nqo)_2$ system showed a similar behaviour to the $Ru(2\text{-}nqo)_2$ system with regard to product variation.

When styrene (1000 mol. eq.) and $Ru(1\text{-}nqo)_2$ (1 mol. eq.) or $Ru(2\text{-}nqo)_2$ (1 mol. eq.) were stirred at 20 °C under oxygen, oxidation of the substrate did not occur. Similarly, when the reaction was repeated in air at 20 °C and at 60 °C, no oxidation of the styrene was observed.

The yield/turnover of products from the oxidation of styrene was high compared to previously reported values. Thus, the catalysts $Mn(nqo)_n$ (n = 2 or 3) give 14-22 % conversion of styrene to styrene epoxide with total turnover figures of 55-86. The $Ru(nqo)_2$/styrene system leads to complete oxidation of the substrate and total turnovers of 820-850.

Fig. 5.7 Reaction profile for the oxidation of styrene with dioxygen, at 60 °C, catalysed by the complex $Ru(2\text{-nqo})_2$.

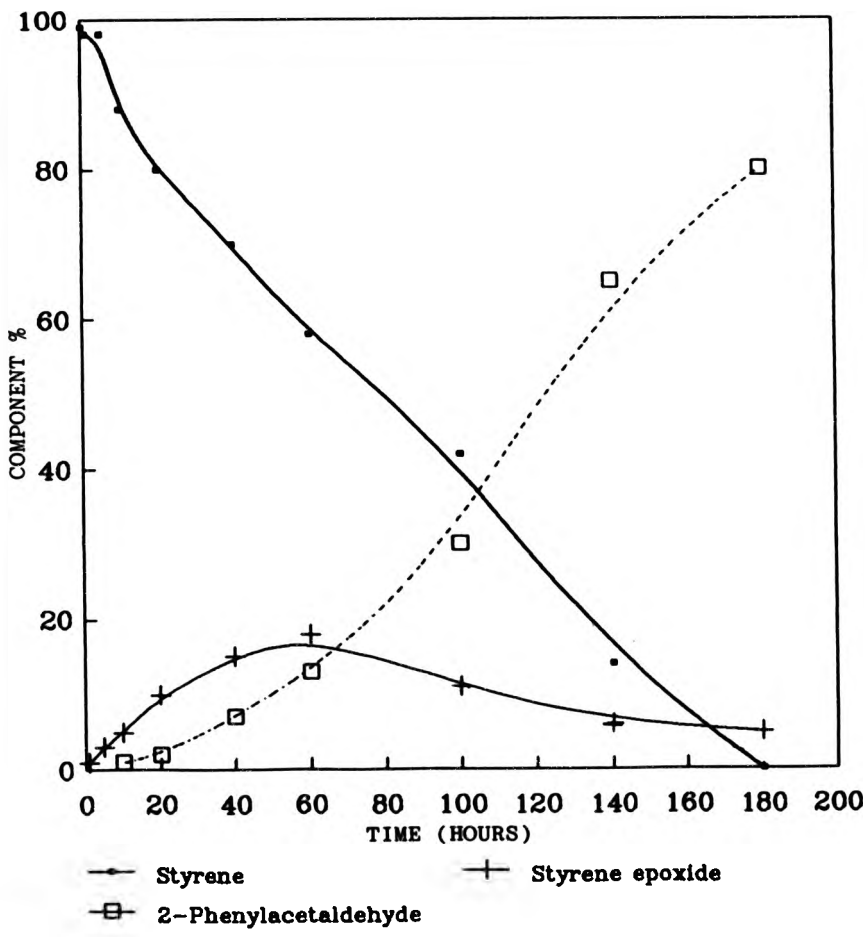
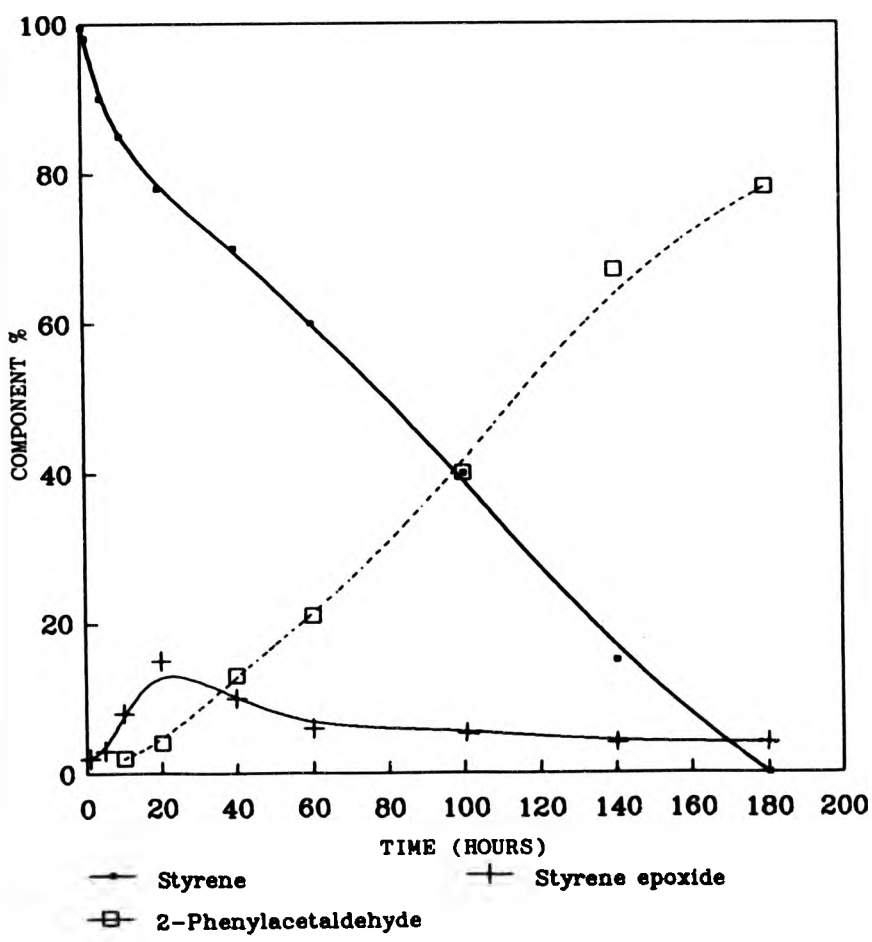


Fig. 5.8 Reaction profile for the oxidation of styrene with dioxygen, at 60 °C, catalysed by the complex $Ru(1\text{-nqo})_2$.



5.2.3 The oxidation of 1-octene

When 1-octene (1000 mol. eq.) and $Ru(2\text{-nqo})_2$ (1 mol. eq.) were stirred at 60 °C, under an atmosphere of oxygen, complete oxidation of 1-octene was observed after 180 h to give 1,2-epoxyoctane, 1-octanol and octanal in yields/turnover of 2%/200, 28%/280 and 70%/700 respectively. Continuous g.c. monitoring of the reaction showed formation of 1,2-epoxyoctane during the early stages of the reaction (Fig. 5.9). The quantity of the epoxide was, however, never more than 5% of the total reaction composition.

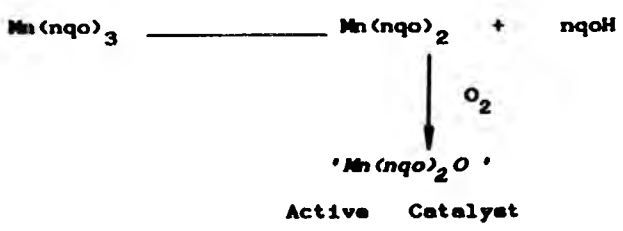
Similar results were obtained when $Ru(1\text{-nqo})_2$ was used as the catalyst. Thus, when 1-octene (1000 mol. eq.) and $Ru(1\text{-nqo})_2$ (1 mol. eq.) were stirred at 60 °C under oxygen for 180 h, 1,2-epoxyoctane, 1-octanol and octanal were obtained in yields/turnover of 1%/10, 25%/250 and 74%/740 respectively. The reaction profile of the $Ru(1\text{-nqo})_2$ system was similar to the $Ru(2\text{-nqo})_2$ system with regard to product variation (Fig. 5.10).

The oxidation of 1-octene (1000 mol. eq.) with $Ru(2\text{-nqo})_2$ (1 mol. eq.) at 20 °C, under an atmosphere of oxygen, led to 1,2-epoxyoctane, 1-octanol and octanal in yields/turnover of 12%/120, 34%/340 and 7%/70 respectively, after 180 h. 1-octene (47%) was recovered unreacted. Continuous g.c. monitoring of the reaction showed rapid formation of 1,2-epoxyoctane

during the early stages of the reaction, but after the initial increase, leveled off at *ca.* 14%. (Fig. 5.11).

The complex $Ru(1\text{-}nqo)_2$ (1 mol. eq.) also catalysed the oxidation of 1-octene (1000 mol. eq.) at 20 °C under oxygen. Thus after 180 h, 1,2-epoxyoctane, 1-octanol and octanal was obtained in yield/turnover 12%/120, 29%/290 and 4%/40. The reaction profile was similar to that obtained for the reaction between 1-octene and $Ru(2\text{-}nqo)_2$ (Fig. 5.12).

Catalyst decomposition was not detected in any of the above oxidation reactions. In contrast, the complexes $Mn(nqo)_3$ decompose during oxidation reactions. This is because the manganese trischelates act as catalysts via an internal redox process during which a ligand is discharged (Reaction 5.4). This has the disadvantage of co-product formation, i.e. nqoH. The ruthenium(II) catalysts do not suffer from this problem.



Reaction 5.4

Fig. 5.9 Reaction profile for the oxidation of octene with dioxygen, at 60 °C, catalysed by the complex $Ru(2\text{-nqo})_2$.

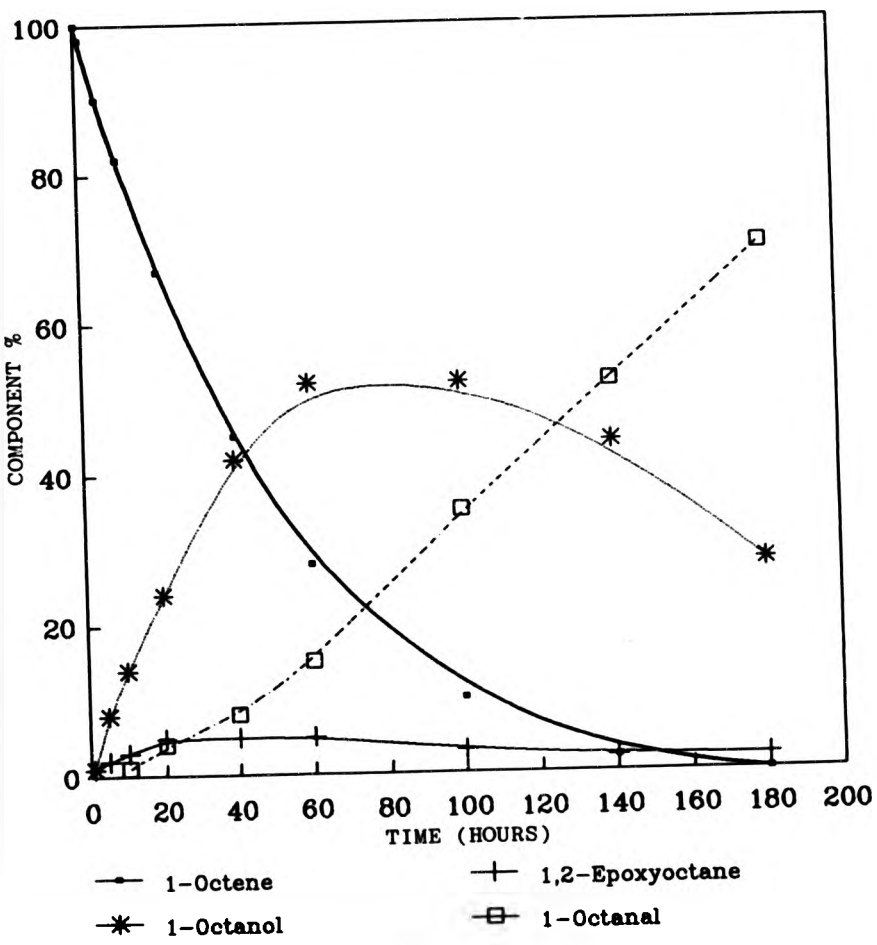


Fig. 5.10 **Reaction profile for the oxidation of octene with dioxygen, at 60 °C, catalysed by the complex Ru(1-nqo)2.**

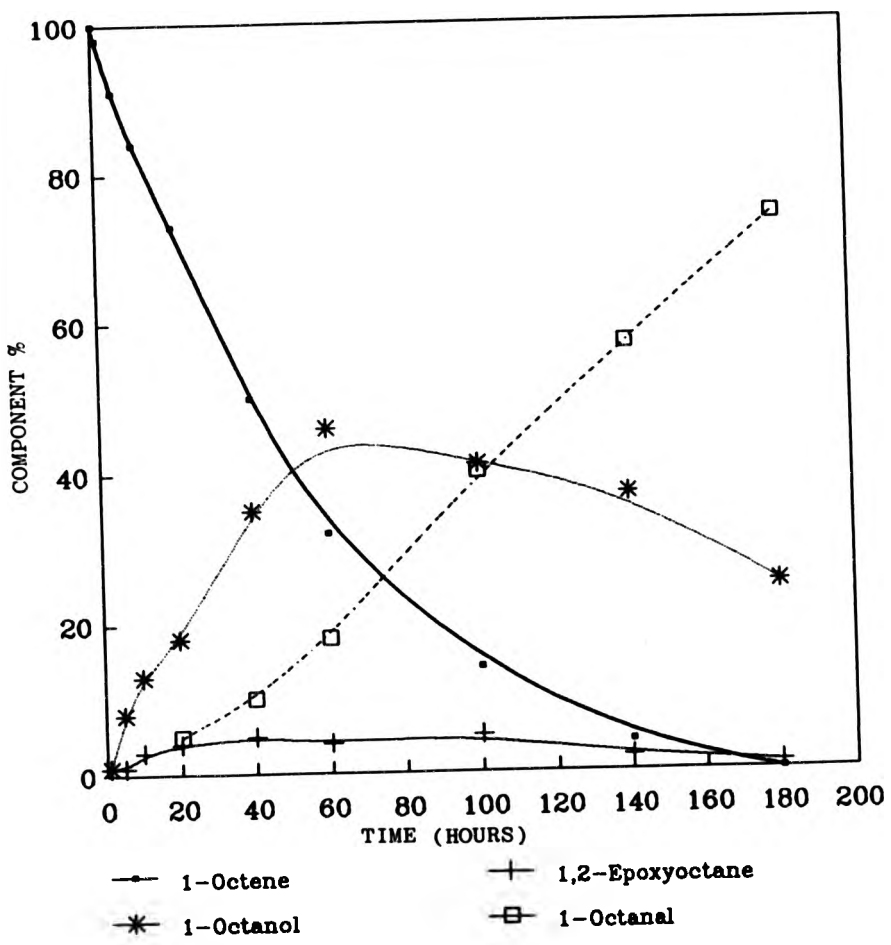


Fig. 5.11 **Reaction profile for the oxidation of octene with dioxygen, at 20 °C, catalysed by the complex $Ru(2\text{-}nqo)_2$.**

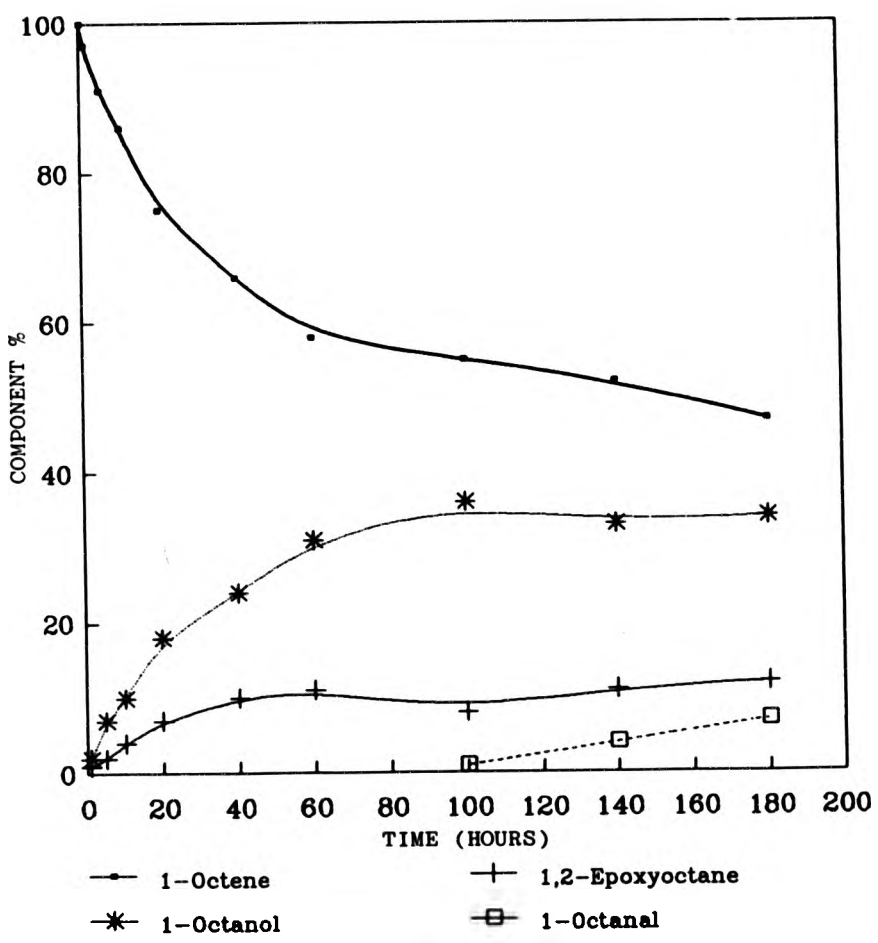
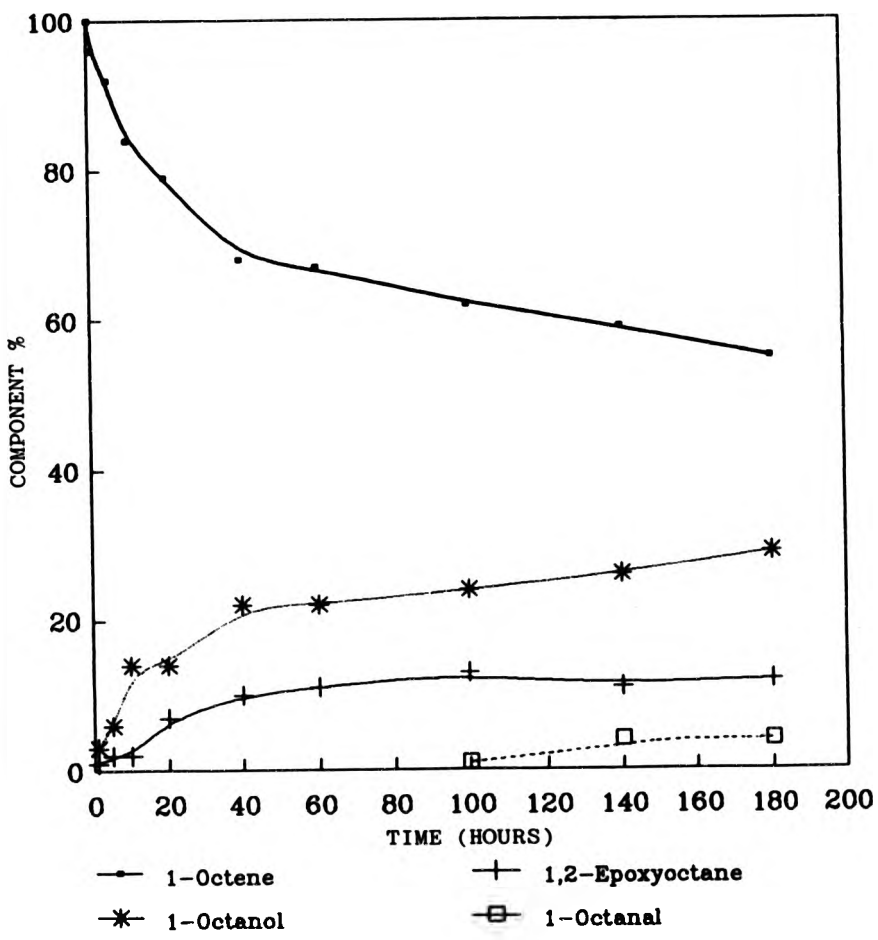
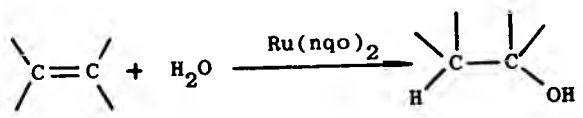


Fig. 5.12 Reaction profile for the oxidation of octene with dioxygen, at 20 °C, catalysed by the complex $Ru(1\text{-nqo})_2$.



5.3 Mechanistic aspects of oxidation reactions

As noted in section 5.2, oxidation of alkenes by the catalysts $Ru(nqo)_2$ leads to three types of product; namely an epoxide, an alcohol and a carbonyl compound (ketone or aldehyde). The question arises as to whether the alcohol and carbonyl products are formed through decomposition of the epoxide or via some other route. For instance, the alcohol can be formed by means of a hydration reaction catalysed by the complexes $Ru(nqo)_2$ or by a high valent oxo-ruthenium species (Reaction 5.5).

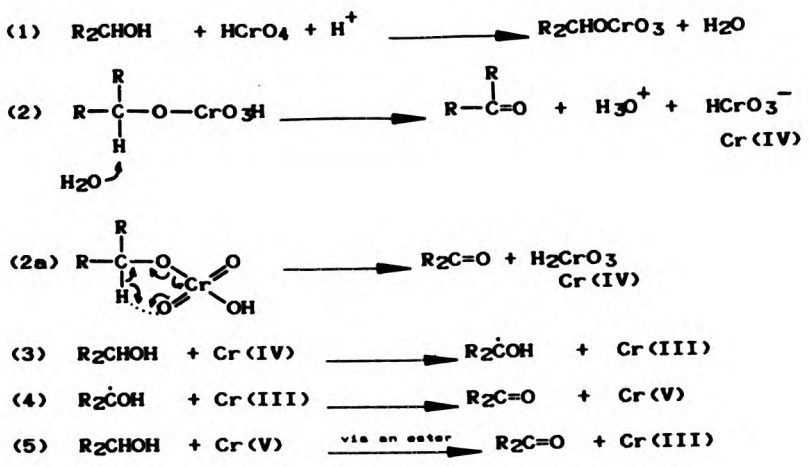


Reaction 5.5

The alcohol could then be oxidised to the respective ketone by a high-valent oxo-ruthenium species. Oxidation of alcohols by high valent oxo-metal complexes is well known, e.g. the use of CrO_3 in glacial acetic acid (Scheme 5.2).[37]

In these reactions, it is believed that high valent oxo-chromium species form a chromate ester intermediate (1) which loses a proton and a $HCrO_3^-$ anion to form a ketone (2). At this stage, loss of a

proton to an oxygen of the ester group can result in a cyclic mechanism (2a). Further alcohol is then oxidised (3)-(5) with the metal finishing as Cr(III).



Scheme 5.2

Alternatively, the ketone could arise via an intramolecular rearrangement of the epoxide (Scheme 5.3).

Scheme 5.3

In order to decide between the two alternatives proposed above, aerobic oxidation reactions of 1,2-epoxycyclohexane and cyclohexanol were investigated with $Ru(1\text{-}nqo)_2$ as catalyst.

When 1,2-epoxycyclohexane (225 mol. eq.) and $Ru(1\text{-}nqo)_2$ (1 mol. eq.) were stirred at 20 °C under oxygen for 7 days, no oxidation products were formed. When cyclohexanol (218 mol. eq.) and $Ru(1\text{-}nqo)_2$ (1 mol. eq.) were stirred at 20 °C under oxygen for for 7 days, cyclohexanone was obtained in yield/turnover of 28%/59.

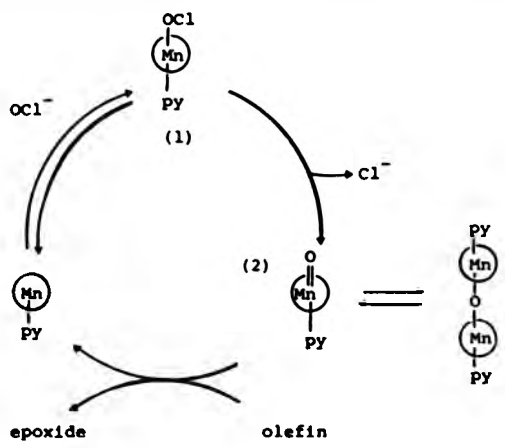
The above results indicate that the formation of alcohols in the aerobic oxidation of alkenes by the catalysts $Ru(nqo)_2$ is a result of hydration of the alkene. In addition, the formation of the carbonyl group is a result of oxidation of the alcohol (Reaction 5.6) and not of rearrangement of the epoxide.

Significantly, the catalytic hydration of cyclohexene by the catalysts $Ru(nqo)_2$ requires the presence of water in the reaction mixture. A similar feature has been noted previously in the catalytic oxidation of cyclohexene when bipyridyl-ruthenium(II)-aquo complexes were used as catalysts.[11] In order to assess the effect of high concentrations of water in the system, the aerobic oxidation of cyclohexene in water was investigated with $Ru(1\text{-}nqo)_2$ as catalyst.

When cyclohexene (1000 mol. eq.), water (280 mol. eq.) and $Ru(1\text{-}nqo)_2$ (1 mol. eq.) were stirred at 20 °C under oxygen for 7 days, 1,2-epoxycyclohexane, cyclohexanol (218 mol. eq.) and cyclohexanone were formed in yield/turnover 10%/100 , 21%/210 and 33%/330 respectively (the corresponding figures without the addition of water were 25%/250, 15%/150 and 10%/100). This shows that addition of water decreases the yield/turnover of the epoxide and increases the yield/turnover of alcohol and ketone.

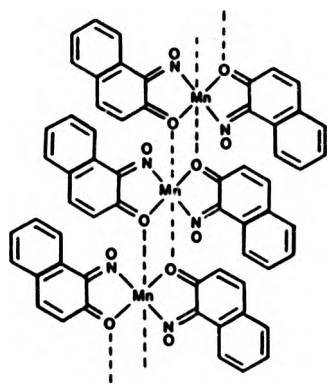
Generally, there is agreement amongst workers in the field of catalytic oxidation of organic substrates that high-valent oxo-metal intermediates are the active catalytic species. Thus, it has been reported that the rate determining step in alkene epoxidation, by the mono-oxygenase model (tetra-p-tolylporphinato)-manganese(III) acetate/sodium hypochlorite, is the conversion of the manganese(III) hypochlorite complex (1) into a high valent oxo-manganese(V) species (2) (Scheme 5.4).[18]

In the case of $Mn(nqo)_n$ (n = 2 or 3) catalysts, it has been suggested that the induction period observed in the catalytic epoxidation of cyclohexene, styrene and 1-octene represent the time required for the formation of catalytically active high-valent oxo-manganese intermediates.[18] The manganese catalysts give long induction periods because the complexes $Mn(nqo)_3$ and $Mn(nqo)_2$ are coordinately saturated.



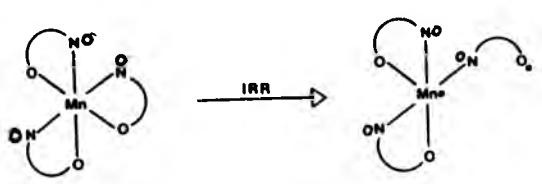
Scheme 5.4

The manganese bischelates can form oxo-manganese intermediates only after their polymeric structure (5.1) breaks down. [34]



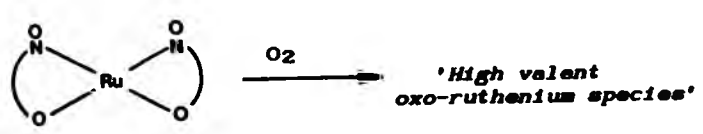
(5.1)

Similarly, the trischelates can only form the catalytically active intermediates after one of the ligands is discharged or becomes monodentate by means of an internal redox reaction (Reaction 5.6).



Reaction 5.6

In contrast to the manganese complexes, the ruthenium catalysts do not require significant induction periods as shown by the reaction profiles (see Figs. 5.1-5.12). This can be rationalised in terms of weak inter-molecular association in the ruthenium catalysts, i.e. $Ru(nqo)_2$ (see Chapter 3). The ruthenium bischelates can, therefore readily react with dioxygen to give active oxo-intermediates (Reaction 5.7).



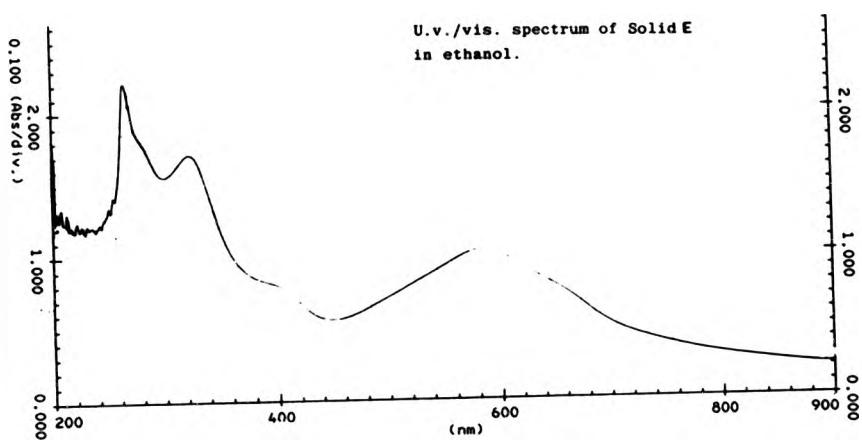
Reaction 5.7

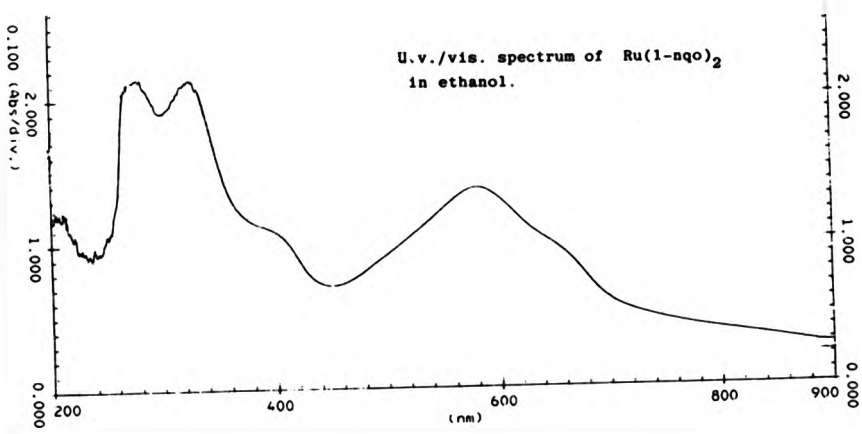
Evidence for the formation of an active oxo-ruthenium intermediate would substantiate the proposed mechanism for epoxidation and hydration of the alkene. With this in mind, the effect of oxygen on the catalyst in ethanol was investigated.

As noted earlier in Chapter 2, the complexes of type $Ru(nqo)_2$ are diamagnetic. When $Ru(1\text{-}nqo)_2$ was stirred in ethanol under an atmosphere of oxygen for 3 days, the solid (Solid E) obtained upon evaporation of the solvent was found to be paramagnetic ($X_g = 8.5 \times 10^{-7}$). In addition, the u.v./vis. spectrum of Solid E was significantly different from that of $Ru(1\text{-}nqo)_2$ (Fig. 5.13).

It was thought that Solid E could be a species of type $Ru(1\text{-}nqo)_2O_n$ or $Ru(1\text{-}nqo)_2(O_2)_n$ (n = 1 or 2). These species would be expected to be paramagnetic. It has been previously reported that dioxygen adducts lose the coordinated dioxygen upon heating under nitrogen. In contrast, complexes of type $Ru(1\text{-}nqo)_2O_n$ (n = 1 or 2) do not undergo any deoxygenation under identical conditions.[2] When Solid E was heated under reflux in toluene in an atmosphere of nitrogen for 24h, the solid obtained upon evaporation of the solvent was a diamagnetic species. This solid had i.r. and u.v./vis. spectra identical with that of $Ru(1\text{-}nqo)_2$ and was, thus, identified as such.

Fig. 5.13 U.v./vis. spectra of Solid E and Ru(1-nqo)2





These results indicate that Solid E is a dioxygen adduct. This is the first reported example of adduct formation between dioxygen and a complex of type $M(qo)_n$ (M = any metal). This result is also in agreement with papers which have reported the formation of active high-valent oxo-ruthenium species through the intermediate formation of ruthenium dioxygen adducts. [2]

To conclude, catalytic oxidation and hydration of unsaturated organic substrates is very important and, therefore, the results obtained in this study are of particular significance. This study has discovered potent oxidation/hydration catalysts which give turnover figures approaching 1000.

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CHAPTER SIX

EXPERIMENTAL

6.1 Reagents

Triphenylphosphine was recrystallised twice from toluene. Pyridine was purified by distillation and stored over KOH. The commercial grade ruthenium trichloride hydrate was supplied by Johnson Matthey as $RuCl_3.1\%H_2O$. Tris(acetylacetonato)ruthenium(III) and dichlorotris(triphenylphosphine)ruthenium(II) were prepared as described in the literature.[1,2]

6.2 Solvents

The solvents used were GPR grade. These were purified prior to use by fractional distillation. Ethanol and methanol were dried over sodium, distilled

and the distillate kept in the presence of molecular sieves (grade 4A).

The silica gel used for column chromatography was Merk silica gel 60, 70-230 mesh. Precoated Merck Kiselgel 60, F_{294} silica gel plates were used for thin layer chromatography.

6.3 Analytical techniques

Carbon, hydrogen and nitrogen analyses were carried out by the microanalytical services of the Polytechnic of North London and Pascher Laboratorie, GBR (courtesy of Johnson Matthey Research). For the determination of ruthenium, the sample (0.05 - 0.1 g) was ashed in the presence of sodium carbonate (1.0 g) in a zirconium or nickel crucible. Sodium peroxide (0.5 g) was added to the cooled melt. The mixture is further heated until the melt is at red heat (*ca.* 650-750 °C) and all components were completely dissolved. Water (25 cm^3) was added to the cold mixture and the mixture warmed to ensure complete hydrolysis. This was followed by careful addition of 1:1 hydrochloric acid (25 cm^3). The resultant solution was made up to 100 cm^3 in a grade A volumetric flask. Atomic absorption spectro-photometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the ruthenium content of the solution. For the determination of sodium, the sample (0.1 - 0.2 g) was warmed with

conc. nitric acid (5 cm^3) and heated to dryness. Concentrated sulphuric acid (5 cm^3) was added and the mixture heated strongly to destroy the acid. 1:1 *aqua regia* (5 cm^3) was added to the residue and the mixture was warmed to destroy the excess nitric acid. The resultant solution was made up to 100 cm^3 in a grade A volumetric flask and AAS or ICP-AES was used to determine the sodium content of the solution.

6.4 Physical techniques

Infra-red spectra in the region 4000-400 cm^{-1} were recorded on a Pye-Unicam SP2000 spectrophotometer. The spectra were recorded as nujol or hexachlorobutadiene mulls (with KBr or KCl windows) or as KBr discs. The KBr was dried in air at 130 °C and stored in dessicators over dried silica gel. Ultraviolet and visible solution spectra in the region 200-800 nm were recorded on a Pye-Unicam SP1800 Spectrophotometer. Fourier Transform ^1H n.m.r. spectra were recorded on a Bruker WP 80 MHz spectrometer. Tetramethylsilane was used as a reference standard and the spectra were recorded in ethanol.

Conductivity measurements were carried out with a PT 1-18 digital conductivity meter. Thermal gravimetric analyses were carried out on a Stanton HT-Sm Thermobalance. A downward flow of nitrogen was maintained in the oven. A linear rise in temperature of 100 °C h^{-1} was used. Room temperature magnetic moments

were determined using a Gouy balance, employing a permanent magnet of field strength 3600 Oersted, and on a Johnson Matthey magnetic susceptibility balance. Both instruments were calibrated with mercury(II) tetrathiocyanatocobaltate(II).

Gas-liquid chromatography was carried out using a Perkin-Elmer instrument with i) Chromosorb W-HP/10% OV101 and ii) 5% carbowax columns; column temp. 150 °C, injection temp. 100 °C and oven temp. 150 °C. The reaction profiles in the oxidation experiments were generated as best-fit curves on data obtained with the above instrument.

6.5 Reactions

6.5.1 Reaction of ruthenium trichloride hydrate with 1,2-naphthoquinone 1-oxime in methanol

Ruthenium trichloride hydrate (0.24 g, 1.0 mmol) in ethanol (25 cm^3) was added to a solution of 1,2-naphthoquinone 1-oxime (0.52 g, 3.0 mmol) in 2:1 ethanol (50 cm^3) and the mixture was stirred under reflux for 24h. Removal of the solvent afforded a black residue (0.69 g). The residue was stirred in hot water (100 cm^3) and filtered. A solid (0.65 g) (Found: C, 48.2; H, 3.3; N, 5.7; Cl, 14.3; Ru, 14.1 %) (ill defined by i.r. and multicomponent by t.l.c.) was filtered off, washed with cold methanol (50 cm^3) and dried *in vacuo*.

Similarly, reaction of ruthenium trichloride hydrate (0.24 g, 1.0 mmol) with 1,2-naphthoquinone 2-oxime (0.52 g, 3.0 mmol) afforded a solid (0.68 g) which was ill defined by i.r. and multicomponent by t.l.c.

6.5.2 Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 1-oximate in aqueous tetrahydrofuran.

Ruthenium trichloride hydrate (1.2 g, 5.0 mmol) in water (50 cm^3) was added to a stirred suspension of sodium 1,2-naphthoquinone 1-oximate (2.0 g, 10.0 mmol) in 2:1 water:tetrahydrofuran (100 cm^3) and the mixture was stirred at 20°C for 24h. Purple-brown *bis(1,2-naphthoquinone 1-oximato)ruthenium(II)* (2.2 g, 98%) (Found C, 53.6; H, 2.7; N, 6.1; Ru, 22.4. $C_{20}H_{12}N_2O_4Ru$ requires: C, 53.6; H, 2.7; N, 6.3; Na, 3.6; Ru, 22.7%) was filtered off, washed by stirring with cold 2:1 water:methanol (200 cm^3) and dried at 20 °C *in vacuo*. Analysis showed the presence of sodium (0.23 g, 10 mmol) and chlorine (0.53 g, 15 mmol) in the acidic (pH 3.5) filtrate.

6.5.3 Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 2-oximate in aqueous tetrahydrofuran.

Ruthenium trichloride hydrate (1.2 g, 5.0 mmol) in water (50 cm^3) was added to a stirred suspension of sodium 1,2-naphthoquinone 2-oximate (2.0 g, 10.0 mmol) in 2:1 water/tetrahydrofuran (100 cm^3) and the mixture was stirred at 20°C for 24h. Brown *bis(1,2-naphthoquinone 2-oximato)ruthenium(II)* (2.1 g, 95%) (Found C, 53.8; H, 2.4; N, 6.0; Ru, 22.6. $C_{20}H_{12}N_2O_4Ru$ requires: C, 53.6; H, 2.7; N, 6.3; Ru, 22.7%) was filtered off, washed by stirring with ice cold 2:1 water:methanol (200 cm^3) for 1 h, and dried *in vacuo* at 20 °C. Analysis showed the presence of sodium (0.23 g, 10 mmol) and chlorine (0.52 g, 15 mmol) in the acidic (pH 3.7) filtrate .

6.5.4 Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 1-oximate in aqueous pyridine.

Ruthenium trichloride hydrate (1.0 g, 4.1 mmol) in water (50 cm^3) was added to a solution of sodium 1,2-naphthoquinone 1-oximate (1.9 g, 9.7 mmol) in 10:1 water:pyridine (220 cm^3) and the mixture was stirred under reflux for 24h. Purple *bis(1,2-naphthoquinone 1-oximato)dipyridineruthenium(II)* (2.1 g, 82%) (Found: C, 59.6; H, 3.4; N, 9.4; Ru, 17.1. $C_{30}H_{22}N_4O_4Ru$

requires: C, 59.7; H, 3.6; N, 9.3; Ru, 16.7%) was filtered off, washed with 2:1 water:methanol (100 cm^3) and dried *in vacuo* at 20 °C. Analysis showed the presence of sodium (0.21 g, 9 mmol) and chlorine (0.42 g, 12 mmol) in the neutral filtrate. Concentration of the filtrate afforded a further crop of bis(1,2-naphthoquinone 1-oximato)dipyridineruthenium(II) (0.29 g, 11%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.5 Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 2-oximate in aqueous pyridine

Ruthenium trichloride hydrate (1.0 g, 4.1 mmol) in water (50 cm^3) was added to a solution of sodium 1,2-naphthoquinone 2-oximate (1.9 g, 9.7 mmol) in 10:1 water:pyridine (220 cm^3) and the mixture was stirred under reflux for 24h. Purple *bis(1,2-naphthoquinone 2-oximato)dipyridineruthenium(II)* (1.8 g, 71%) (Found: C, 60.1; H, 3.6; N, 9.1; Ru, 16.8. $C_{30}H_{22}N_4O_4Ru$ requires: C, 59.7; H, 3.6; N, 9.3; Ru, 16.7%) was filtered off, washed with cold 2:1 water:methanol (100 cm^3) and dried at 20 °C/1.0 mm Hg. Analysis showed the presence of sodium (0.21 g, 9 mmol) and chlorine (0.42 g, 12 mmol) in the neutral filtrate. Concentration of the filtrate gave further bis(1,2-naphthoquinone 2-oximato)dipyridineruthenium(II) (0.65 g, 25%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.6 Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 1-oximate in ethanol.

Ruthenium trichloride hydrate (2.1 g, 8.05 mmol) in ethanol (100 cm^3) was added to a stirred solution of sodium 1,2-naphthoquinone 1-oximate (5.8 g, 29.7 mmol) in ethanol (150 cm^3) and the mixture was stirred under reflux for 24h. On cooling purple *sodium tris-(1,2-naphthoquinone 1-oximato)ruthenate(II)* (4.89 g, 89%) (Found C, 55.8; H, 3.0; N, 6.4; Na, 3.5; Ru, 16.1. $C_{30}H_{18}N_3NaO_6Ru$ requires: C, 56.2; H, 2.8; N, 6.6; Na, 3.6; Ru, 15.8%) was filtered off, washed with 2:1 methanol:water (200 cm^3) and dried *in vacuo* at 20 °C. The filtrate on concentration afforded further crop of sodium tris(1,2-naphthoquinone 1-oximato)ruthenate(II) (0.5 g, 9%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.7 Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 2-oximate in ethanol.

Ruthenium trichloride hydrate (1.0 g, 4.3 mmol) in ethanol (50 cm^3) was added to a stirred solution of sodium 1,2-naphthoquinone 2-oximate (3.0 g, 15.4 mmol) in ethanol (100 cm^3) and the mixture was stirred under reflux for 24h. The mixture was cooled and blue *sodium tris(1,2-naphthoquinone 2-oximato)ruthenate(II)* (2.14 g,

79%) (Found C, 56.1; H, 2.7; N, 6.5; Na, 3.5; Ru, 15.7. $C_{30}H_{18}N_3NaO_6Ru$ requires: C, 56.2; H, 2.8; N, 6.6; Na, 3.6; Ru, 15.8%) was filtered off, washed with 2:1 methanol:water (100 cm^3) and dried *in vacuo* at 20 °C. On further concentration the filtrate gave a further crop of sodium tris(1,2-naphthoquinone 2-oximato)-ruthenate(II) (0.5 g, 9%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.8 Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 1-oximate in aqueous acetic acid.

Ruthenium trichloride hydrate (2.1 g, 8.05 mmol) in 2:1 acetic acid:water (50 cm^3) was added to a solution of sodium 1,2-naphthoquinone 1-oximate (5.8 g, 30.0 mmol) in glacial acetic acid (250 cm^3) and the mixture was heated under reflux with stirring for 24h. Violet-blue *bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime)ruthenium(II)* (4.82 g, 92%) (Found: C, 56.2; H, 3.1; N, 6.7; Ru, 16.2. $C_{30}H_{19}N_3O_6Ru$ requires: C, 58.3; H, 3.1; N, 6.8; Ru, 16.2%) was filtered off, washed with hot water (4 x 25 cm^3) and dried *in vacuo* at 20 °C. The filtrate on concentration afforded a further crop of bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime)ruthenium(II) (0.4 g, 7%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.9 **Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 2-oximate in aqueous acetic acid.**

Ruthenium trichloride hydrate (1.0 g, 4.3 mmol) in 2:1 acetic acid:water (30 cm^3) was added to a stirred solution of sodium 1,2-naphthoquinone 2-oximate (3.0 g, 15.3 mmol) in glacial acetic acid (100 cm^3) and the mixture was refluxed for 24h. Blue *bis(1,2-naphthoquinone 2-oximato)(1,2-naphthoquinone 2-oxime)-ruthenium(II)* (2.0 g, 79%) (Found: C, 56.9; H, 2.9; N, 6.9; Ru, 16.5. $C_{30}H_{19}N_3O_6Ru$ requires: C, 58.3; H, 3.1; N, 6.8; Ru, 16.2%) was filtered off, washed with hot water (4 x 25 cm^3) and dried *in vacuo* at 20 °C. Concentration of the filtrate afforded further bis(1,2-naphthoquinone 2-oximato)(1,2-naphthoquinone 2-oxime)ruthenium(II) (0.45 g, 17%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.10 **Reaction of ruthenium trichloride hydrate with sodium 1,2-naphthoquinone 1-oximate in methanol under nitrogen.**

Deoxygenated methanol (50 cm^3) was added dropwise to a mixture of ruthenium trichloride hydrate (2.1 g, 8.1 mmol) and sodium 1,2-naphthoquinone 1-oximate (4.7 g, 24.1 mmol) under a flow of nitrogen 100 cm^3 m^{-1}. The mixture was stirred under reflux and the nitrogen flow continued for 4 h. The carrier nitrogen was passed

though a trap at -80 °C to collect any volatile compounds. The collected distillate (5.4 g) contained methanol (5.2 g) and formaldehyde (0.18 g, 75%) (identified by g.c. with authentic samples). The reaction mixture was filtered. The filtrate contained further formaldehyde (0.04 g, 16%) and methanol (42.1 g) (identified by g.c.). The residue was washed with water and a solid (4.80 g) was obtained (mixture by t.l.c. - sodium tris(1,2-naphthoquinone 1-oximato)ruthenate(II) (major) and bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) (trace) - cellulose/ethyl acetate; identified by comparative t.l.c. with authentic samples). The washings contained sodium chloride (0.39 g).

6.5.11 Reaction of dichlorotris(triphenylphosphine)-ruthenium(II) with 1,2-naphthoquinone 1-oxime in acetone.

Dichlorotris(triphenylphosphine)ruthenium(II) (1.0 g, 1.0 mmol) and 1,2-naphthoquinone 1-oxime (0.35 g, 2.0 mmol) were stirred in acetone (50 cm^3) under reflux for 24 h. The mixture was cooled and filtered. The solid (1.3 g) (mixture by t.l.c.) was washed with diethyl ether (25 cm^3) followed by cold water (4 x 25 cm^3) and dried *in vacuo*.

Similarly, reaction of dichlorotris(triphenylphosphine)-ruthenium(II) (1.0 g, 1.0 mmol) and 1,2-naphthoquinone

1-oxime or 1,2-naphthoquinone 2-oxime (0.35 g, 2.0 mmol) in acetone, tetrahydrofuran or ethanol afforded complex mixtures (by t.l.c.).

6.5.12 Reaction of dichlorotris(triphenylphosphine)-ruthenium(II) with sodium 1,2-naphthoquinone 1-oxime in acetone.

Dichlorotris(triphenylphosphine)ruthenium(II) (1.0 g, 1.0 mmol) and sodium 1,2-naphthoquinone 1-oximate (0.4 g, 2.1 mmol) were stirred in acetone (50 cm^3) under reflux for 24 h. The mixture was cooled and filtered. The solid (1.2 g) (mixture by t.l.c.) was washed with diethyl ether (25 cm^3) followed by cold water (4 x 25 cm^3) and dried *in vacuo*.

Similarly, reaction of dichlorotris(triphenylphosphine)-ruthenium(II) (1.0 g, 1.0 mmol) and sodium 1,2-naphthoquinone 2-oxime (0.35 g, 2.0 mmol) in acetone afforded a complex mixture (by t.l.c.).

6.5.13 Reaction of dichlorotris(triphenylphosphine)-ruthenium(II) with sodium 1,2-naphthoquinone 1-oximate in tetrahydrofuran.

Dichlorotris(triphenylphosphine)ruthenium(II) (1.0 g, 1.0 mmol) and sodium 1,2-naphthoquinone 1-oximate (0.4 g, 2.1 mmol) were stirred in tetrahydrofuran

(50 cm^3) under reflux for 24 h. The mixture was cooled and filtered. The solid was washed with diethyl ether (25 cm^3) followed by cold water (4 x 25 cm^3) and dried *in vacuo* to give black *bis(1,2-naphthoquinone 1-oximato)bis(triphenylphosphine)ruthenium(II)* (0.86 g, 82%) (Found: C, 70.4; H, 3.9; N, 2.7; P, 6.3; Ru, 10.5. $C_{56}H_{42}N_2O_4P_2Ru$ requires C, 69.3; H, 4.3; N, 2.9; P, 6.5; Ru, 10.5%).

6.5.14 Reaction of dichlorotris(triphenylphosphine)-ruthenium(II) with sodium 1,2-naphthoquinone 2-oximate in tetrahydrofuran.

Dichlorotris(triphenylphosphine)ruthenium(II) (0.5 g, 0.52 mmol) and sodium 1,2-naphthoquinone 2-oximate (0.2 g, 1.0 mmol) were stirred in tetrahydrofuran (50 cm^3) under reflux for 24 h. The mixture was cooled and blue-black *bis(1,2-naphthoquinone 2-oximato)bis(triphenylphosphine)ruthenium(II)* (0.35 g, 70%) (Found: C, 70.4; H, 3.9; N, 2.7; P, 6.8; Ru, 10.5. $C_{56}H_{42}N_2O_4P_2Ru$ requires C, 69.3; H, 4.3; N, 2.9; P, 6.5; Ru, 10.5%) was filtered off, washed with diethyl ether (25 cm^3) followed by cold water (4 x 25 cm^3) and dried *in vacuo*.

6.5.15 **Nitrosation of 2-naphthol in the presence of ruthenium trichloride hydrate.**

Ruthenium trichloride hydrate (1.2 g, 5.0 mmol) in water (50 cm^3) was added to a stirred solution of 2-naphthol (2.0 g, 13.9 mmol), acetic acid (20 cm^3) and sodium acetate (5g) in 2:1 ethanol:water (100 cm^3). Sodium nitrite (1.0 g) in water (25 cm^3) was added portionwise and the mixture stirred for 7 days. A black solid (Solid A) (1.2 g) (Found: C, 45.3; H, 3.0; N, 11.5; Ru, 19.2) was filtered off and washed with hot water (25 cm^3) followed by ethanol (2 x 50 cm^3). The filtrate was dried *in vacuo*. Extraction of the residue with chloroform showed the presence of 1,2-naphthoquinone 1-oxime (identified by comparative t.l.c. with an authentic sample). Solid A was stirred in acetone (50 cm^3) for 4 h. A brown solid (Solid B) (1.0 g) (Found C, 52.1; H, 3.2; N, 6.0; Ru, 21.3%) was filtered off, washed with 2:1 water:methanol (50 cm^3) for 1 h, and dried *in vacuo* at 20 °C. Solid B was stirred in pyridine (25 cm^3) and the mixture evaporated to dryness. The residue (1.4 g) was stirred in acetone (50 cm^3) for 4 h and filtered. Evaporation of the filtrate at 50 °C *in vacuo* gave bis(1,2-naphthoquinone 1-oximato)dipyridineruthenium(II) (1.3 g, 40%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.16 **Nitrosation of 1-naphthol in the presence of ruthenium trichloride hydrate.**

Ruthenium trichloride hydrate (1.20 g, 5.0 mmol) in water (50 cm^3) was added to a stirred solution of 1-naphthol (2.0 g, 13.9 mmol), acetic acid (20 cm^3) and sodium acetate (5g) in 2:1 ethanol:water (100 cm^3). Sodium nitrite (1.0 g) in water (25 cm^3) was added portionwise and the mixture stirred for 7 days. A black solid (Solid C) (1.68 g) (Found: C, 46.3; H, 2.8; N, 10.6; Ru, 20.0) was filtered off and washed with hot water (4 x 25 cm^3) followed by ethanol (2 x 50cm^3). The filtrate was dried *in vacuo* and extraction of the residue with chloroform showed the presence of 1,2-naphthoquinone 2-oxime (confirmed by comparative t.l.c. with an authentic sample). Solid C was stirred in acetone (50 cm^3) for 4 h. A brown solid (Solid D) (1.40 g) (Found C, 52.5; H, 3.0; N, 6.5; Ru, 22.9%) was filtered off, washed with ice cold 2:1 water:methanol (100 cm^3) for 1 h, and dried *in vacuo* at 20 °C. Solid D was stirred in pyridine (25 cm^3) for 1 h and the pyridine removed *in vacuo*. The residue (1.7 g) was stirred in acetone (50 cm^3) for 4 h and filtered. Evapoation of the filtrate at 50 °C *in vacuo* gave bis(1,2-naphthoquinone 2-oximato)dipyridineruthenium(II) (1.6 g, 58%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.17 **Nitrosation of phenols in the presence of ruthenium trichloride hydrate.**

Nitrosation of 4-chlorophenol or 4-methylphenol (15 mmol) in the presence of ruthenium trichloride hydrate (1.2 g, 5.0 mmol) was carried out in a similar way to the nitrosation of 2-naphthol. Filtration afforded a black tar which was ill defined by i.r. and multicomponent by t.l.c. Atomic spectroscopy indicated that most of the ruthenium was present in the solid.

6.5.18 **Reaction of tris(acetylacetonato)ruthenium (III) with sodium 1,2-naphthoquinone 1-oximate in tetrahydrofuran.**

Tris(acetylacetonato)ruthenium(III) (0.5 g, 1.2 mmol) and sodium 1,2-naphthoquinone 1-oximate (2.0 g, 10 mmol) was stirred in tetrahydrofuran (25 cm^3) at 20 °C for 7 days. On removal of the solvent a solid resulted (1.9 g). The solid was washed with toluene (2 x 25 cm^3), cold methanol (2 x 25 cm^3) and dried *in vacuo* to give bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.35, 63%) (identified by comparative t.l.c. and i.r. with an authentic sample). The filtrate contained unreacted sodium 1,2-naphthoquinone 1-oximate and tris(acetylacetonato)ruthenium(III) (identified by comparative t.l.c. and i.r. with authentic samples).

6.5.19 **Reaction of tris(acetylacetonato)ruthenium (III) with sodium 1,2-naphthoquinone 2-oximate in tetrahydrofuran.**

Tris(acetylacetonato)ruthenium(III) (0.5 g, 1.2 mmol) and sodium 1,2-naphthoquinone 2-oximate (1.9 g, 10 mmol) was stirred in tetrahydrofuran (25 cm^3) at 20 °C for 7 days. On removal of the solvent a solid resulted (1.9 g). The solid was washed with toluene (2 x 25 cm^3), cold methanol (2 x 25 cm^3) and dried *in vacuo* to give bis(1,2-naphthoquinone 2-oximato)ruthenium(II) (0.35, 63%) (identified by comparative t.l.c. and i.r. with an authentic sample). The washings contained unreacted sodium 1,2-naphthoquinone 2-oximate and tris(acetylacetonato)ruthenium(III) (identified by comparative t.l.c. and i.r. with authentic samples).

6.5.20 **Reaction of bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) with dilute hydrochloric acid.**

Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.45 g, 1 mmol) was suspended in dilute hydrochloric acid (50 cm^3) (10%) and stirred at 50 °C for 6 h. The mixture was cooled and bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) (0.45 g, 99%) (identified by comparative i.r. with an authentic sample) was filtered off.

6.5.21 Reaction of bis(1,2-naphthoquinone 2-oximato)-ruthenium(II) with dilute hydrochloric acid.

Bis(1,2-naphthoquinone 2-oximato)ruthenium(II) (0.45 g, 1 mmol) was suspended in dilute hydrochloric acid (50 cm^3) (10%) and stirred at 50 °C for 6 h. The mixture was cooled and bis(1,2-naphthoquinone 2-oximato)-ruthenium(II) (0.45 g, 99%) (identified by comparative i.r. with an authentic sample) was filtered off.

6.5.22 Reaction of bis(1,2-naphthoquinone 1-oximato)-(1,2-naphthoquinone 1-oxime)ruthenium(II) with dilute hydrochloric acid.

A suspension of bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime)ruthenium(II) (0.6 g, 1 mmol) was stirred in dilute hydrochloric acid (50 cm^3) (10%) at 50 °C for 6 h. Bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) (0.42 g, 92%) (identified by comparative i.r. with an authentic sample) was filtered off washed with ethanol (2 x 25 cm^3) and dried *in vacuo*. An extract of the filtrate was obtained in diethyl ether (25 cm^3). Removal of the solvent at 20 °C under nitrogen gave 1,2-naphthoquinone 1-oxime (0.15 g, 88%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.23 Reaction of bis(1,2-naphthoquinone 2-oximato)-(1,2-naphthoquinone 2-oxime)ruthenium(II) with dilute hydrochloric acid.

Bis(1,2-naphthoquinone 2-oximato)(1,2-naphthoquinone 2-oxime)ruthenium(II) (0.62 g, 1 mmol) was suspended in dilute hydrochloric acid (50 cm^3) (10%) and stirred at 50 °C for 6 h. Bis(1,2-naphthoquinone 2-oximato)-ruthenium(II) (0.45 g, 99%) (identified by comparative i.r. with an authentic sample) was filtered off, washed with ice-cold ethanol (2 x 25 cm^3) and dried at 20 °C/1.0 mm. A diethyl ether extract of the filtrate afforded (1,2-naphthoquinone 2-oxime (0.16 g, 92%) (identified by comparative t.l.c. and i.r. with an authentic sample) on removal of the solvent at 20 °C under nitrogen.

6.5.24 Pyrolysis of bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime) ruthenium(II)

Bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime)ruthenium(II) (0.62 g, 1 mmol) was heated at 80 °C/0.1 mm Hg for 4 h. Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.45 g, 99%) (identified by comparative i.r. with an authentic sample) was obtained. The sublimate, 1,2-naphthoquinone 1-oxime (0.14 g, 85%) (identified by comparative t.l.c. with an authentic sample) was collected in a trap at -80 °C.

6.5.25 **Pyrolysis of bis(1,2-naphthoquinone 2-oximato)(1,2-naphthoquinone 2-oxime) ruthenium(II)**

Bis(1,2-naphthoquinone 2-oximato)(1,2-naphthoquinone 2-oxime)ruthenium(II) (0.62 g, 1 mmol) was heated at 80 °C/0.1 mm Hg for 4 h. Bis(1,2-naphthoquinone 2-oximato)ruthenium(II) (0.43 g, 99%) (identified by comparative i.r. with an authentic sample) was obtained. The sublimate 1,2-naphthoquinone 2-oxime (0.11 g, 60%) (identified by comparative t.l.c. and i.r. with an authentic sample) was collected in a trap at -80 °C.

6.5.26 **Reaction of bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) with pyridine.**

Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.50 g, 1.1 mmol) was dissolved in pyridine (25 cm^3) and heated under reflux for 2 h. Evaporation of pyridine at 70 °C/1.0 mm gave bis(1,2-naphthoquinone 1-oximato)-dipyridineruthenium(II) (0.67 g, 99%) (identified by comparative t.l.c. and i.r. with an authentic sample).

6.5.27 **Reaction of bis(1,2-naphthoquinone 2-oximato)-ruthenium(II) with pyridine.**

Bis(1,2-naphthoquinone 2-oximato)ruthenium(II) (0.50 g, 1.1 mmol) was dissolved in pyridine (25 cm^3) and heated

under reflux for 2 h. Removal of the solvent at 70 °C/1.0 mm Hg gave bis(1,2-naphthoquinone 2-oximato)-dipyridineruthenium(II) (0.68 g, 99%) (identified by t.l.c. and i.r. with an authentic sample).

6.5.28 Reaction of bis(1,2-naphthoquinone 1-oximato)-(1,2-naphthoquinone 1-oxime)ruthenium(II) with pyridine.

Bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime)ruthenium(II) (0.68 g, 1.1 mmol) was stirred in pyridine (30 cm^3) at 20 °C for 4 h. Evaporation of the mixture afforded a solid (0.88 g). The solid was stirred in diethyl ether (50 cm^3) for 2 h. and bis-(1,2-naphthoquinone 1-oximato)dipyridineruthenium(II) (0.64 g, 99%) (identified by comparative t.l.c. and i.r. with an authentic sample) was filtered off. The filtrate on removal of the solvent, gave 1,2-naphthoquinone 1-oxime (0.16 g, 84%) (identified by comparative t.l.c. with an authentic sample).

6.5.29 Reaction of bis(1,2-naphthoquinone 2-oximato)-(1,2-naphthoquinone 2-oxime)ruthenium(II) with pyridine.

Bis(1,2-naphthoquinone 2-oximato)(1,2-naphthoquinone 2-oxime)ruthenium(II) (0.62 g, 1.0 mmol) was stirred in pyridine (25 cm^3) at 20 °C for 4 h. Evaporation of the

mixture afforded a solid (0.80 g). The solid was stirred in diethyl ether (40 cm^3) for 2 h. Bis(1,2-naphthoquinone 2-oximato)dipyridineruthenium(II) (0.60 g, 99%) (identified by comparative t.l.c. and i.r. with an authentic sample) was filtered off. The filtrate on evaporation under nitrogen gave 1,2-naphthoquinone 2-oxime (0.13 g, 75%) (identified by comparative t.l.c. with an authentic sample).

6.5.30 Reaction of bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) with triphenylphosphine in tetrahydrofuran.

Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.5 g, 1.1 mmol) and triphenylphosphine (1.1 g, 4.0 mmol) in tetrahydrofuran (50 cm^3) were stirred under reflux for 7 days. The mixture was cooled and filtered. The residue was washed with cold methanol (4 x 25 cm^3) and dried *in vacuo* to give bis(1,2-naphthoquinone 1-oximato)-bis(triphenylphosphine)ruthenium(II) (0.84 g, 79%) (identified by comparative i.r. with an authentic sample).

6.5.31 Reaction of bis(1,2-naphthoquinone 2-oximato)-ruthenium(II) with triphenylphosphine in tetrahydrofuran

Bis(1,2-naphthoquinone 2-oximato)ruthenium(II) (0.5 g, 1.1 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) in tetrahydrofuran (50cm^3) were stirred under reflux for 7 days. The mixture was cooled and black bis-(1,2-naphthoquinone 2-oximato)bis(triphenylphosphine)-ruthenium(II) (0.69 g, 65%) (identified by comparative i.r. with an authentic sample) was filtered off, washed with methanol (4 x 25 cm^3) and dried *in vacuo*.

6.5.32 Reaction of bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) with triphenylphosphine in pyridine

Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.5 g, 1.1 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) in pyridine (25 cm^3) were stirred under reflux for 7 days. The mixture was cooled and filtered. Removal of the solvent afforded a dark purple solid (1.7 g). The solid was stirred in toluene (50 cm^3) for 2 h. Filtration of the mixture gave bis(1,2-naphthoquinone 1-oximato)-dipyridineruthenium(II) (0.60 g, 90%) (identified by comparative t.l.c. and i.r. with an authentic sample). The filtrate contained unreacted triphenylphosphine (identified by comparative t.l.c. with an authentic sample).

6.5.33 Reaction of bis(1,2-naphthoquinone 2-oximato)-ruthenium(II) with triphenylphosphine in pyridine

Bis(1,2-naphthoquinone 2-oximato)ruthenium(II) (0.5 g, 1.1 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) in pyridine (25 cm^3) were stirred under reflux for 7 days. Removal of the solvent afforded a dark blue solid (1.65 g). The solid was stirred in toluene (50 cm^3) for 2 h. Filtration of the mixture gave bis(1,2-naphthoquinone 1-oximato)dipyridineruthenium(II)(0.65 g, 97%) (identified by comparative t.l.c. and i.r. with an authentic sample). The filtrate contained unreacted triphenylphosphine (identified by comparative t.l.c. with an authentic sample).

6.5.34 Pyrolysis of bis(1,2-naphthoquinone 1-oximato)dipyridineruthenium(II)

Bis(1,2-naphthoquinone 1-oximato)dipyridineruthenium(II) (0.61 g, 1 mmol) was heated at 270 °C/0.1 mm Hg. for 4 h. Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.45 g, 99%) (identified by comparative i.r. with an authentic sample) was obtained. Pyridine (0.12 g, 75%) (identified by comparative i.r. with an authentic sample) was collected in a trap at -80 °C.

6.5.35 Pyrolysis of bis(1,2-naphthoquinone 2-oximato)dipyridineruthenium(II)

Bis(1,2-naphthoquinone 2-oximato)dipyridineruthenium(II) (0.61 g, 1 mmol) was heated at 270 °C/0.1 mm Hg for 4 h. Bis(1,2-naphthoquinone 2-oximato)ruthenium(II) (0.45 g, 99%) (identified by comparative i.r. with an authentic sample) was obtained. The sublimate, pyridine (0.13 g, 80%) (identified by comparative i.r. with an authentic sample) was collected in a trap at -80 °C.

6.5.36 Reaction of bis(1,2-naphthoquinone 1-oximato)-bis(triphenylphosphine)ruthenium(II) with pyridine.

Bis(1,2-naphthoquinone 1-oximato)bis(triphenylphosphine)ruthenium(II) (0.2 g, 0.2 mmol) was stirred in pyridine (25 cm^3) at 20 °C for 24 h. The solution contained triphenylphosphine and bis(1,2-naphthoquinone 2-oximato)dipyridineruthenium(II) (identified by comparative t.l.c. and i.r. with authentic samples).

6.5.37 **Reaction of bis(1,2-naphthoquinone 2-oximato)-bis(triphenylphosphine)ruthenium(II) with pyridine.**

Bis(1,2-naphthoquinone 2-oximato)bis(triphenylphosphine)ruthenium(II) (0.2 g, 0.2 mmol) was dissolved in pyridine (25 cm^3) and the mixture stirred for 24 h. The solution contained bis(1,2-naphthoquinone 2-oximato)-dipyridineruthenium(II) and triphenylphosphine (identified by comparative t.l.c. and i.r. with authentic samples).

6.5.38 Oxidation reactions

(a) **Catalytic oxidations of alkenes**

Alkene and catalyst were stirred at 60 °C in an oxygen atmosphere, in quantities specified in Table 6.1. Samples (1 cm^3) were taken at intervals and analysed for oxidation products by g.l.c. (5% Carbowax 20M on Chromosorb W-HP).

Table 6.1 Catalytic oxidations of alkenes

Aerobic oxidation of cyclohexene at 20 °C after 120 h.

Catalyst g/mmol	alkene g/mmol	oxidation products	g/mmol
$Ru(2\text{-}nqo)_2$	cyclohexene	1,2-epoxycyclohexene	7.5/76
0.10/0.225	18.4/225	cyclohexanol	4.7/47
		cyclohexenone	2.2/22
$Ru(1\text{-}nqo)_2$	cyclohexene	1,2-epoxycyclohexene	5.5/56
0.10, 0.225	18.4/225	cyclohexanol	3.4/34
		cyclohexenone	2.2/22

Aerobic oxidation of cyclohexene at 60 °C after 120 h.

Catalyst g/mmol	alkene g/mmol	oxidation products	g/mmol
$Ru(2\text{-}nqo)_2$	cyclohexene	1,2-epoxycyclohexene	7.6/77
0.10/0.225	18.4/225	cyclohexanol	8.4/84
		cyclohexenone	4.4/45
$Ru(1\text{-}nqo)_2$	cyclohexene	1,2-epoxycyclohexene	6.4/65
0.10, 0.225	18.4/225	cyclohexanol	7.0/70
		cyclohexenone	2.6/27

Aerobic oxidation of cyclohexene at 20 °C in the presence of pyridine after 120 h.

Catalyst g/mmol	alkene g/mmol	oxidation products	g/mmol
Ru(2-nqo)2 0.10/0.225	cyclohexene 18.4/225	1,2-epoxycyclohexene	9.9/101
		cyclohexanol	6.8/68
		cyclohexanone	2.6/27
Ru(1-nqo)2 0.10,0.225	cyclohexene 18.4/225	1,2-epoxycyclohexene	8.4/86
		cyclohexanol	6.1/61
		cyclohexanone	2.9/29

Aerobic oxidation of styrene at 60 °C after 200 h.

Catalyst g/mmol	alkene g/mmol	oxidation products	g/mmol
Ru(2-nqo)2 0.10/0.225	styrene 23.5/225	styrene epoxide	0.9/11
		phenylacetaldehyde	21.6/180
Ru(1-nqo)2 0.10/0.225	styrene 23.5/225	styrene epoxide	1.1/9.0
		phenylacetaldehyde	21.1/176

Aerobic oxidation of 1-octene at 60 °C after 180 h.

Catalyst g/mmol	alkene g/mmol	oxidation products	g/mmol
Ru(2-nqo)2	1-octene	1,2-epoxyoctane	0.6/4.5
0.10/0.225	25.2/225	1-octanol	8.8/63
		1-octanal	22/157
Ru(1-nqo)2	1-octene	1,2-epoxyoctane	1.6/2.2
0.10/0.225	25.2/225	1-octanol	7.9/56
		1-octanal	23/167

Aerobic oxidation of 1-octene at 20 °C after 180 h.

Catalyst g/mmol	alkene g/mmol	oxidation products	g/mmol
Ru(2-nqo)2	1-octene	1,2-epoxyoctane	3.7/27
0.10/0.225	25.2/225	1-octanol	11/77
		1-octanal	2.2/16
Ru(1-nqo)2	1-octene	1,2-epoxyoctane	3.7/27
0.10,0.225	25.2/225	1-octanol	9.1/65
		1-octanal	1.2/9.0

(b) **Reaction of 1,2-epoxycyclohexane with oxygen in the presence of bis(1,2-naphthoquinone 1-oximato)-ruthenium(II)**

Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.1 g, 0.22 mmol) and 1,2-epoxycyclohexane (4.8 g, 49.3 mmol) were stirred at 20 °C under oxygen for 7 days. The epoxide was returned in full (by comparative g.l.c. with an authentic sample).

(c) **Reaction of cyclohexanol with oxygen in the presence of bis(1,2-naphthoquinone 1-oximato)-ruthenium(II)**

Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.1 g, 0.22 mmol) and cyclohexanol (4.8 g, 48.0 mmol) were stirred at 20 °C under oxygen for 7 days. The mixture contained cyclohexanone (1.3 g, 27.6%) and cyclohexanol (3.5 g, 72.4%) (by comparative g.l.c. with authentic samples).

(d) **Reaction of bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) with oxygen in ethanol.**

Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.5 g, 1.1 mmol) and ethanol (25 cm^3) were stirred at 20 °C under oxygen for 3 days. Removal of the solvent at 20 °C under a stream of nitrogen afforded a solid (Solid E) (0.6 g). Solid E was dissolved in toluene (25 cm^3) and the mixture stirred under reflux for 24 h in a nitrogen

atmosphere. Removal of the solvent under a stream of nitrogen gave bis(1,2-naphthoquinone 1-oximato)-ruthenium(II) (0.5 g) (identified by comparative i.r. and u.v. with an authentic sample)

(e) Catalytic oxidation of cyclohexene in the presence of bis(1,2-naphthoquinone 1-oximato)ruthenium(II) and water

Bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (0.1 g, 0.22 mmol), water (5 g, 278 mmol) and cyclohexene (18.4 g, 225 mmol) were stirred at 20 °C under oxygen for 7 days. The mixture contained 1,2-epoxycyclohexane (10.0%), cyclohexanol (21.5%), cyclohexanone (33.1%) and cyclohexene (4.5%) (identified by comparative g.l.c. with authentic samples) and an unidentified component (30.9%).

6.6 References

1. G. A. Barberi, *Atti Acad. Linc.*, 1914, **23**(5), 336.
2. T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.

APPENDIX

X-ray crystallographic data

Table 1. Fractional atomic coordinates and thermal parameters (Å)

Atom	x	y	z	Uiso or Ueq
Ru	0.19314(3)	0.12474(4)	0.28527(5)	0.0395(3)
O(12)	0.0881(2)	0.1726(3)	0.1543(4)	0.047(2)
C(12)	0.1112(3)	0.2699(5)	0.1164(6)	0.044(3)
C(11)	0.1976(3)	0.3369(5)	0.1708(6)	0.041(3)
N(11)	0.2488(3)	0.2763(4)	0.2536(5)	0.044(3)
O(11)	0.3283(3)	0.3195(4)	0.3034(6)	0.077(3)
C(13)	0.0524(4)	0.3157(6)	0.0149(7)	0.056(4)
C(14)	0.0773(4)	0.4196(6)	-0.0209(7)	0.062(4)
C(15)	0.1612(4)	0.4914(5)	0.0403(7)	0.054(4)
C(16)	0.1808(5)	0.6018(6)	0.0052(8)	0.075(5)
C(17)	0.2605(6)	0.6717(7)	0.0649(10)	0.098(6)
C(18)	0.3211(5)	0.6359(6)	0.1644(9)	0.082(5)
C(19)	0.3046(4)	0.5259(5)	0.2019(7)	0.063(4)
C(10)	0.2231(4)	0.4516(5)	0.1394(6)	0.047(3)
O(22)	0.1786(2)	0.2183(3)	0.4894(4)	0.053(2)
C(22)	0.2434(3)	0.2213(5)	0.5979(6)	0.046(3)
C(21)	0.3099(3)	0.1591(5)	0.5713(6)	0.041(3)
N(21)	0.2959(3)	0.1002(4)	0.4193(5)	0.044(3)
O(21)	0.3480(3)	0.0377(4)	0.3774(5)	0.066(3)
C(23)	0.2486(4)	0.2892(6)	0.7484(7)	0.060(4)
C(24)	0.3165(4)	0.2936(6)	0.8619(7)	0.065(4)
C(25)	0.3851(4)	0.2301(6)	0.8391(7)	0.057(4)
C(26)	0.4530(4)	0.2337(7)	0.9634(7)	0.067(5)
C(27)	0.5159(4)	0.1697(6)	0.9467(8)	0.068(5)

Table 1. Fractional atomic coordinates and thermal parameters (Å)

cont.

Atom	x	y	z	Uiso or Ueq
C(28)	0.5144(4)	0.1005(6)	0.8033(8)	0.066(4)
C(29)	0.4998(3)	0.0947(5)	0.6794(7)	0.052(4)
C(20)	0.3830(3)	0.1599(5)	0.6932(6)	0.045(3)
N(31)	0.2075(3)	0.0254(4)	0.0808(5)	0.041(3)
C(31)	0.2836(4)	0.0325(5)	0.0434(7)	0.052(4)
C(32)	0.2919(4)	-0.0296(6)	-0.0953(7)	0.065(4)
C(33)	0.2221(5)	-0.1033(6)	-0.1965(8)	0.071(5)
C(34)	0.1438(5)	-0.1114(6)	-0.1616(8)	0.065(4)
C(35)	0.1389(4)	-0.0452(5)	-0.0288(7)	0.052(4)
N(41)	0.1194(3)	-0.0323(4)	0.3117(5)	0.048(3)
C(41)	0.0394(4)	-0.0334(6)	0.3195(8)	0.065(4)
C(42)	-0.0105(5)	-0.1274(8)	0.3488(9)	0.087(6)
C(43)	0.0236(7)	-0.2246(8)	0.3747(9)	0.096(7)
C(44)	0.1060(6)	-0.2272(7)	0.3620(9)	0.088(6)
C(45)	0.1519(4)	-0.1288(6)	0.3318(7)	0.066(4)
C(51)	1.0680(5)	0.4667(7)	0.4502(9)	0.088(2)
C(52)	0.9868(5)	0.4205(6)	0.3587(8)	0.078(2)
C(53)	0.9183(5)	0.4520(7)	0.4076(9)	0.086(2)
C(61)	0.5984(7)	0.4583(9)	0.3579(12)	0.139(4)
C(62)	0.6792(7)	0.4223(9)	0.3698(12)	0.147(4)
C(63)	0.6971(5)	0.3248(8)	0.4057(10)	0.106(3)
C(64)	0.6369(7)	0.2449(8)	0.4268(11)	0.133(3)
C(65)	0.5519(6)	0.2682(8)	0.4158(10)	0.121(3)
C(66)	0.5335(5)	0.3741(8)	0.3824(10)	0.113(3)

Table 2. Fractional atomic coordinates for the hydrogen atoms

Atom	x	y	z
H(13)	-0.0124	0.2657	-0.0316
H(14)	0.0320	0.4496	-0.1004
H(16)	0.1329	0.6305	-0.0703
H(17)	0.2762	0.7559	0.0345
H(18)	0.3824	0.6955	0.2150
H(19)	0.3536	0.4975	0.2763
H(23)	0.1981	0.3364	0.7703
H(24)	0.3199	0.3462	0.9742
H(26)	0.4545	0.2886	1.0735
H(27)	0.5669	0.1731	1.0430
H(28)	0.5646	0.0501	0.7902
H(29)	0.4496	0.0400	0.5699
H(31)	0.3394	0.0889	0.1256
H(32)	0.3531	-0.0186	-0.1229
H(33)	0.2282	-0.1567	-0.3025
H(34)	0.0871	-0.1676	-0.2415
H(35)	0.0778	-0.0503	0.0051
H(41)	0.0124	0.0442	0.3012
H(42)	-0.0758	-0.1236	0.3523
H(43)	-0.0128	-0.2975	0.4043
H(44)	0.1337	-0.3054	0.3742
H(45)	0.2171	-0.1296	0.3247

Table 3. Anisotropic thermal parameters (Å)

Atom	U11	U22	U33	U23	U13	U12
Ru	0.0339(2)	0.0441(3)	0.0407(3)	0.0131(2)	0.0070(2)	0.0076(2)
O(12)	0.036(2)	0.053(2)	0.053(2)	0.016(2)	0.007(2)	0.008(2)
C(12)	0.040(3)	0.049(3)	0.043(3)	0.010(3)	0.011(3)	0.012(3)
C(11)	0.042(3)	0.042(3)	0.039(3)	0.010(3)	0.010(3)	0.013(2)
N(11)	0.035(2)	0.048(3)	0.050(3)	0.010(2)	0.003(2)	0.006(2)
O(11)	0.039(2)	0.070(3)	0.121(4)	0.043(3)	-0.008(3)	-0.002(2)
C(13)	0.048(3)	0.068(4)	0.051(4)	0.018(3)	0.005(3)	0.022(3)
C(14)	0.061(4)	0.066(4)	0.058(4)	0.025(3)	0.012(3)	0.029(3)
C(15)	0.063(4)	0.048(3)	0.052(4)	0.016(3)	0.015(3)	0.019(3)
C(16)	0.090(5)	0.062(4)	0.074(5)	0.030(4)	0.014(4)	0.015(4)
C(17)	0.141(8)	0.061(5)	0.092(6)	0.044(5)	0.029(6)	0.021(5)
C(18)	0.090(5)	0.063(5)	0.094(6)	0.032(4)	0.001(5)	-0.011(4)
C(19)	0.077(5)	0.050(4)	0.062(4)	0.021(3)	0.009(4)	0.004(3)
C(10)	0.057(4)	0.043(3)	0.041(3)	0.008(3)	0.013(3)	0.014(3)
O(22)	0.046(2)	0.064(3)	0.050(2)	0.010(3)	0.015(2)	0.020(2)
C(22)	0.044(3)	0.047(3)	0.046(3)	0.012(3)	0.014(3)	0.011(3)
C(23)	0.058(4)	0.068(4)	0.053(4)	0.003(3)	0.018(3)	0.021(3)
C(24)	0.067(4)	0.084(5)	0.044(4)	-0.004(3)	0.014(3)	0.012(4)
C(25)	0.057(4)	0.070(4)	0.043(4)	0.009(3)	0.011(3)	0.013(3)
C(26)	0.061(4)	0.099(5)	0.040(4)	0.003(4)	0.001(3)	0.004(4)
C(27)	0.054(4)	0.093(5)	0.057(5)	0.019(4)	0.001(3)	0.010(4)
C(28)	0.047(4)	0.084(5)	0.066(5)	0.024(4)	0.007(3)	0.019(3)

Table 3. Anisotropic thermal parameters (Å)

cont.

Atom	U11	U22	U33	U23	U13	U12
C(29)	0.048(3)	0.059(4)	0.050(4)	0.019(3)	0.010(3)	0.015(3)
C(20)	0.043(3)	0.048(3)	0.043(3)	0.012(3)	0.009(3)	0.005(3)
N(31)	0.045(3)	0.038(2)	0.039(3)	0.014(2)	0.007(2)	0.006(2)
C(31)	0.053(4)	0.049(3)	0.053(4)	0.024(3)	0.017(3)	0.012(3)
C(32)	0.067(4)	0.071(4)	0.057(4)	0.026(4)	0.025(4)	0.029(4)
C(33)	0.091(5)	0.075(5)	0.045(4)	0.008(4)	0.011(4)	0.033(4)
C(34)	0.073(5)	0.065(4)	0.057(4)	0.007(4)	-0.001(4)	0.011(4)
C(35)	0.049(3)	0.051(4)	0.055(4)	0.009(3)	0.007(3)	0.011(3)
N(41)	0.046(3)	0.053(3)	0.046(3)	0.018(2)	0.009(2)	0.004(2)
C(41)	0.060(4)	0.066(4)	0.069(5)	0.011(4)	0.024(4)	-0.005(3)
C(42)	0.078(5)	0.104(6)	0.079(6)	0.005(5)	0.033(5)	-0.026(5)
C(43)	0.124(8)	0.098(7)	0.064(5)	0.033(5)	0.011(5)	-0.043(6)
C(44)	0.116(7)	0.067(5)	0.081(6)	0.037(4)	-0.012(5)	-0.016(5)
C(45)	0.071(4)	0.060(4)	0.066(5)	0.027(4)	0.003(4)	0.004(3)

Table 4. Bond lengths (Å)

Ru	-O(12)	2.100(3)	Ru	-N(11)	1.963(5)
Ru	-O(22)	2.060(4)	Ru	-N(21)	1.965(4)
Ru	-N(31)	2.085(4)	Ru	-N(41)	2.120(4)
O(12)	-C(12)	1.278(6)	C(12)	-C(11)	1.437(7)
C(12)	-C(13)	1.440(7)	C(11)	-N(11)	1.381(6)
C(11)	-C(10)	1.439(7)	N(11)	-O(11)	1.270(5)
C(13)	-C(14)	1.343(8)	C(14)	-C(15)	1.427(8)
C(15)	-C(16)	1.392(8)	C(15)	-C(10)	1.417(8)
C(16)	-C(17)	1.363(10)	C(17)	-C(18)	1.380(10)
C(18)	-C(19)	1.392(8)	C(19)	-C(10)	1.408(8)
O(22)	-C(22)	1.293(6)	C(22)	-C(21)	1.417(7)
C(22)	-C(23)	1.434(8)	C(21)	-N(21)	1.393(7)
C(21)	-C(20)	1.463(7)	N(21)	-O(21)	1.259(5)
C(23)	-C(24)	1.350(8)	C(24)	-C(25)	1.447(8)
C(25)	-C(26)	1.416(8)	C(25)	-C(20)	1.420(8)
C(26)	-C(27)	1.360(9)	C(27)	-C(28)	1.399(9)
C(28)	-C(29)	1.376(8)	C(29)	-C(20)	1.419(7)
N(31)	-C(31)	1.355(7)	N(31)	-C(35)	1.343(7)
C(31)	-C(32)	1.384(8)	C(32)	-C(33)	1.358(9)
C(33)	-C(34)	1.381(9)	C(34)	-C(35)	1.381(8)
N(41)	-C(41)	1.321(7)	N(41)	-C(45)	1.329(7)
C(41)	-C(42)	1.373(9)	C(42)	-C(43)	1.362(11)
C(43)	-C(44)	1.378(12)	C(44)	-C(45)	1.384(9)
C(51)	-C(52)	1.379(10)	C(52)	-C(53)	1.360(9)
C(61)	-C(62)	1.427(12)	C(61)	-C(66)	1.424(11)
C(62)	-C(63)	1.292(11)	C(63)	-C(64)	1.327(11)
C(64)	-C(65)	1.437(11)	C(65)	-C(66)	1.378(10)

Table 5. Bond Angles (°)

N(11)	-Ru	-O(12)	79.7(2)	O(22)	-Ru	-O(12)	95.0(1)
O(22)	-Ru	-N(11)	90.1(2)	N(21)	-Ru	-O(12)	173.3(2)
N(21)	-Ru	-N(11)	95.0(2)	N(21)	-Ru	-O(22)	80.9(2)
N(31)	-Ru	-O(12)	85.9(2)	N(31)	-Ru	-N(11)	91.4(2)
N(31)	-Ru	-O(22)	178.3(2)	N(31)	-Ru	-N(21)	98.4(2)
N(41)	-Ru	-O(12)	93.9(2)	N(41)	-Ru	-N(11)	173.3(2)
N(41)	-Ru	-O(22)	88.5(2)	N(41)	-Ru	-N(21)	91.2(2)
N(41)	-Ru	-N(31)	90.0(2)	C(12)	-O(12)	-Ru	110.7(3)
C(11)	-C(12)	-O(12)	121.4(5)	C(13)	-C(12)	-O(12)	121.4(5)
C(13)	-C(12)	-C(11)	117.2(5)	N(11)	-C(11)	-C(12)	110.9(5)
C(10)	-C(11)	-C(12)	122.1(5)	C(10)	-C(11)	-N(11)	127.0(5)
C(11)	-N(11)	-Ru	117.1(3)	O(11)	-N(11)	-Ru	123.6(4)
O(11)	-N(11)	-C(11)	119.3(5)	C(14)	-C(13)	-C(12)	120.6(6)
C(15)	-C(14)	-C(13)	122.8(6)	C(16)	-C(15)	-C(14)	119.6(6)
C(10)	-C(15)	-C(14)	119.9(5)	C(10)	-C(15)	-C(16)	120.5(6)
C(17)	-C(16)	-C(15)	120.0(7)	C(18)	-C(17)	-C(16)	120.4(7)
C(19)	-C(18)	-C(17)	121.6(7)	C(10)	-C(19)	-C(18)	118.7(6)
C(15)	-C(10)	-C(11)	117.1(5)	C(19)	-C(10)	-C(11)	124.1(5)
C(19)	-C(10)	-C(15)	118.7(5)	C(22)	-O(22)	-Ru	110.7(3)
C(21)	-C(22)	-O(22)	121.3(5)	C(23)	-C(22)	-O(22)	119.6(5)
C(23)	-C(22)	-C(21)	119.1(5)	N(21)	-C(21)	-C(22)	111.8(5)
C(20)	-C(21)	-C(22)	122.1(5)	C(20)	-C(21)	-N(21)	126.2(5)
C(21)	-N(21)	-Ru	115.1(5)	O(21)	-N(21)	-Ru	125.2(4)
O(21)	-N(21)	-C(21)	119.7(4)	C(24)	-C(23)	-C(22)	119.9(6)
C(25)	-C(24)	-C(23)	122.5(6)	C(26)	-C(25)	-C(24)	120.1(6)
C(20)	-C(25)	-C(24)	120.3(5)	C(20)	-C(25)	-C(26)	119.5(6)

Table 5. Bond Angles (°) cont.

C(27)	-C(26)	-C(25)	121.4(6)	C(28)	-C(27)	-C(26)	119.5(6)
C(29)	-C(28)	-C(27)	121.0(6)	C(20)	-C(29)	-C(28)	120.9(6)
C(25)	-C(20)	-C(21)	116.1(5)	C(29)	-C(20)	-C(21)	126.1(5)
C(29)	-C(20)	-C(25)	117.7(5)	C(31)	-N(31)	-Ru	122.8(4)
C(35)	-N(31)	-Ru	119.8(4)	C(35)	-N(31)	-C(31)	117.4(5)
C(32)	-C(31)	-N(31)	122.4(6)	C(33)	-C(32)	-C(31)	119.2(6)
C(34)	-C(33)	-C(32)	119.5(6)	C(35)	-C(34)	-C(33)	118.8(6)
C(34)	-C(35)	-N(31)	122.8(6)	C(41)	-N(41)	-Ru	119.9(4)
C(45)	-N(41)	-Ru	122.6(4)	C(45)	-N(41)	-C(41)	117.4(6)
C(42)	-C(41)	-N(41)	123.6(7)	C(43)	-C(42)	-C(41)	119.3(8)
C(44)	-C(43)	-C(42)	118.1(8)	C(45)	-C(44)	-C(43)	119.0(8)
C(44)	-C(45)	-N(41)	122.7(7)	C(53)	-C(52)	-C(51)	119.6(7)
C(66)	-C(61)	-C(62)	114.7(9)	C(63)	-C(62)	-C(61)	125.0(1)
C(64)	-C(63)	-C(62)	120.0(1)	C(65)	-C(64)	-C(63)	120.2(5)
C(66)	-C(65)	-C(64)	119.4(9)	C(65)	-C(66)	-C(61)	119.9(9)

Table 6. Intermolecular distances (Å)

Atom 1	Atom 2	dist	S	a	b	c
H(35)	...C(12)	2.81	-1	0.0	0.0	0.0
H(24)	...C(11)	2.99	1	0.0	0.0	0.0
C(42)	...C(13)	3.49	-1	0.0	0.0	0.0
C(43)	...C(13)	3.46	-1	0.0	0.0	0.0
C(44)	...H(13)	3.05	-1	0.0	0.0	0.0
C(14)	...C(14)	3.37	-1	0.0	1.0	0.0
H(14)	...C(14)	2.76	-1	0.0	1.0	0.0
C(43)	...C(14)	3.49	-1	0.0	0.0	0.0
H(23)	...C(15)	2.99	1	0.0	0.0	1.0
C(52)	...H(16)	2.86	-1	1.0	1.0	0.0
C(53)	...H(16)	2.99	-1	1.0	1.0	0.0
C(32)	...H(17)	2.98	1	0.0	-1.0	0.0
C(33)	...H(17)	3.03	1	0.0	-1.0	0.0
C(27)	...H(18)	2.97	-1	1.0	1.0	1.0
C(28)	...H(18)	2.75	-1	1.0	1.0	1.0
H(24)	...C(19)	2.71	1	0.0	0.0	1.0
H(24)	...C(10)	2.67	1	0.0	0.0	1.0
H(42)	...O(22)	2.73	-1	0.0	0.0	1.0
H(28)	...C(21)	2.98	-1	1.0	0.0	1.0
H(42)	...C(23)	3.01	-1	0.0	0.0	0.0
C(32)	...C(25)	3.40	-1	0.0	0.0	-1.0
H(32)	...C(25)	2.95	1	0.0	0.0	-1.0
H(32)	...C(26)	2.98	1	0.0	0.0	-1.0
C(66)	...H(26)	2.80	1	0.0	0.0	-1.0
H(32)	...C(27)	3.04	1	0.0	0.0	-1.0
C(32)	...H(27)	3.03	-1	1.0	0.0	1.0

Table 6. Intermolecular distances (Å) cont.

Atom 1	Atom 2	dist	S	a	b	c
H(32)	...C(28)	3.08	1	0.0	0.0	-1.0
C(31)	...H(28)	3.02	-1	1.0	0.0	1.0
H(32)	...C(29)	3.05	1	0.0	0.0	-1.0
H(32)	...C(20)	3.00	1	0.0	0.0	-1.0
C(63)	...C(33)	3.46	-1	1.0	0.0	0.0
C(63)	...H(33)	2.55	-1	1.0	0.0	0.0
C(64)	...H(33)	2.90	-1	1.0	0.0	0.0
H(41)	...C(34)	2.89	-1	0.0	0.0	0.0
C(52)	...H(34)	2.87	-1	1.0	0.0	0.0
C(42)	...C(41)	3.42	-1	0.0	0.0	1.0
C(53)	...H(43)	2.96	1	1.0	1.0	0.0
C(51)	...H(43)	2.76	-1	1.0	0.0	1.0
C(52)	...H(43)	2.87	-1	1.0	0.0	1.0
C(51)	...H(44)	2.98	1	1.0	1.0	0.0
C(51)	...C(51)	2.72	-1	2.0	1.0	1.0
C(52)	...C(51)	2.38	-1	2.0	1.0	1.0
C(53)	...C(51)	1.41	-1	2.0	1.0	1.0
C(52)	...C(52)	2.78	-1	2.0	1.0	1.0
C(53)	...C(52)	2.43	-1	2.0	1.0	1.0
C(53)	...C(53)	2.78	-1	2.0	1.0	1.0

Table 7. Intramolecular distances (Å)

C(12)	...Ru	2.82	C(11)	...Ru	2.87
O(11)	...Ru	2.87	C(13)	...Ru	4.23
C(22)	...Ru	2.79	C(21)	...Ru	2.85
O(21)	...Ru	2.85	C(23)	...Ru	4.19
C(31)	...Ru	3.04	H(31)	...Ru	3.10
C(35)	...Ru	2.99	H(35)	...Ru	3.01
C(41)	...Ru	3.00	H(41)	...Ru	3.01
C(45)	...Ru	3.05	H(45)	...Ru	3.10
C(11)	...O(12)	2.37	N(11)	...O(12)	2.60
C(13)	...C(12)	2.37	H(13)	...O(12)	2.64
O(22)	...C(12)	3.07	N(31)	...O(12)	2.85
C(35)	...C(12)	3.02	H(35)	...O(12)	2.61
N(41)	...C(12)	3.09	C(41)	...O(12)	3.20
H(41)	...C(12)	2.59	N(11)	...C(12)	2.32
H(13)	...C(12)	2.18	C(14)	...C(12)	2.42
C(15)	...C(12)	2.85	C(10)	...C(12)	2.52
N(31)	...C(12)	3.40	O(11)	...C(11)	2.29
C(13)	...C(11)	2.46	C(14)	...C(11)	2.78
C(15)	...C(11)	2.44	C(19)	...C(11)	2.51
H(19)	...C(11)	2.78	C(19)	...N(11)	3.06
H(19)	...N(11)	2.80	C(10)	...N(11)	2.52
O(22)	...N(11)	2.85	C(22)	...N(11)	3.43
N(21)	...N(11)	2.91	N(31)	...N(11)	2.90
C(31)	...N(11)	3.26	H(31)	...N(11)	2.97
C(19)	...C(11)	2.79	H(19)	...O(11)	2.11
C(10)	...C(11)	2.87	N(21)	...O(11)	2.98
H(31)	...O(11)	2.87	C(66)	...O(11)	3.21

Table 7. Intramolecular distances (Å) cont.

H(14)	...C(13)	2.09	C(15)	...C(13)	2.43
C(10)	...C(13)	2.86	C(14)	...H(13)	2.10
C(16)	...C(14)	2.44	H(16)	...C(14)	2.65
C(10)	...C(14)	2.46	C(15)	...H(14)	2.16
C(16)	...H(14)	2.65	H(16)	...C(15)	2.14
C(17)	...C(15)	2.38	C(18)	...C(15)	2.76
C(19)	...C(15)	2.43	H(17)	...C(16)	2.12
C(18)	...C(16)	2.38	C(15)	...C(16)	2.80
C(10)	...C(16)	2.44	C(17)	...H(16)	2.13
H(18)	...C(17)	2.12	C(19)	...C(17)	2.42
C(10)	...C(17)	2.79	C(18)	...H(17)	2.13
H(19)	...C(18)	2.15	C(10)	...C(18)	2.41
C(19)	...H(18)	2.14	C(10)	...H(19)	2.17
C(21)	...O(22)	2.36	N(21)	...O(22)	2.61
C(23)	...O(22)	2.36	H(23)	...O(22)	2.62
N(41)	...O(22)	2.92	C(41)	...O(22)	3.28
N(21)	...O(22)	2.33	H(23)	...C(22)	2.18
C(24)	...O(22)	2.41	C(25)	...C(22)	2.84
C(20)	...C(22)	2.52	O(21)	...C(21)	2.29
C(23)	...C(21)	2.46	C(24)	...C(21)	2.80
C(25)	...C(21)	2.45	C(29)	...C(21)	2.57
H(29)	...C(21)	2.82	C(29)	...N(21)	3.12
H(29)	...N(21)	2.86	C(20)	...N(21)	2.55
N(31)	...N(21)	3.07	C(31)	...N(21)	3.39
H(31)	...N(21)	2.96	N(41)	...N(21)	2.92
C(45)	...N(21)	3.11	H(45)	...N(21)	2.65
C(29)	...O(21)	2.84	H(29)	...O(21)	2.17

Table 7. Intramolecular distances (Å) cont.

C(20)	...O(21)	2.88	N(31)	...O(21)	3.17
C(31)	...O(21)	3.06	H(31)	...O(21)	2.53
C(45)	...O(21)	3.38	H(45)	...O(21)	2.55
H(24)	...C(23)	2.10	C(25)	...C(23)	2.45
C(20)	...C(23)	2.89	C(24)	...H(23)	2.11
C(26)	...C(24)	2.48	H(26)	...C(24)	2.68
C(20)	...C(24)	2.49	C(25)	...H(24)	2.18
C(26)	...H(24)	2.69	H(26)	...C(25)	2.16
C(27)	...C(25)	2.42	C(28)	...C(25)	2.79
C(29)	...C(25)	2.43	H(27)	...C(26)	2.12
C(28)	...C(26)	2.38	C(29)	...C(26)	2.78
C(20)	...C(26)	2.45	C(27)	...H(26)	2.12
H(28)	...C(27)	2.15	C(29)	...C(27)	2.41
C(20)	...C(27)	2.82	C(28)	...H(27)	2.16
H(29)	...C(28)	2.13	C(20)	...C(28)	2.43
C(29)	...H(28)	2.13	C(20)	...H(29)	2.16
H(31)	...N(31)	2.09	C(32)	...N(31)	2.40
C(33)	...N(31)	2.77	C(34)	...N(31)	2.39
H(35)	...N(31)	2.08	N(41)	...N(31)	2.97
C(45)	...N(31)	3.43	H(32)	...C(31)	2.14
C(33)	...C(31)	2.37	C(34)	...C(31)	2.71
C(35)	...C(31)	2.31	C(32)	...H(31)	2.13
H(33)	...C(32)	2.12	C(34)	...C(32)	2.37
C(35)	...C(32)	2.71	C(33)	...H(32)	2.12
H(34)	...C(33)	2.15	C(35)	...C(33)	2.38
C(34)	...H(33)	2.14	H(35)	...C(34)	2.13
C(35)	...H(34)	2.14	N(41)	...C(35)	3.19

Table 7. Intramolecular distances (Å) cont.

N(41)	...H(35)	2.76	H(41)	...N(41)	2.06
C(42)	...N(41)	2.37	C(43)	...N(41)	2.77
C(44)	...N(41)	2.38	H(45)	...N(41)	2.07
H(42)	...C(41)	2.13	C(43)	...C(41)	2.36
C(44)	...C(41)	2.68	C(45)	...C(41)	2.26
C(42)	...H(41)	2.12	H(43)	...C(42)	2.13
C(44)	...C(42)	2.35	C(45)	...C(42)	2.69
C(43)	...H(42)	2.13	H(44)	...C(43)	2.14
C(45)	...C(43)	2.38	C(44)	...H(43)	2.15
H(45)	...C(44)	2.13	C(45)	...H(44)	2.15
C(53)	...C(51)	2.37	C(63)	...C(61)	2.42
C(64)	...C(61)	2.79	C(65)	...C(61)	2.43
C(64)	...C(62)	2.27	C(65)	...C(62)	2.71
C(66)	...C(62)	2.40	C(65)	...C(63)	2.40
C(66)	...C(63)	2.78	C(66)	...C(64)	2.43

8754 Pergamon : Poly Ms. 1916

Polyhedron Vol. 8, No. 8, pp. [illegible], 1989
Printed in Great Britain

0277-5387/89 $3.00 + .00

COMPLEXES OF RUTHENIUM(II) WITH THE MONO-OXIMES OF 1,2-NAPHTHOQUINONE: X-RAY CRYSTAL STRUCTURE OF BIS(1,2-NAPHTHOQUINONE 1-OXIMATO)DIPYRIDINE RUTHENIUM(II)

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(*Received* 12 *April* 1988; *accepted* 25 *July* 1988)

Abstract—The ruthenium(II) complexes $Ru(nqo)_2$ [nqoH = 1,2-naphthoquinone 1-oxime (1-nqoH) or 1,2-naphthoquinone 2-oxime (2-nqoH)] were prepared by the interaction of the quinone oxime with hydrated ruthenium(III) chloride. Reaction of the chloride with the sodium salts of the oximes in ethanol or acetic acid afforded complexes of the type $Na[Ru(nqo)_3]$ and $Ru(nqo)_2(nqoH)$, respectively. The complex $Ru(nqo)_2$ reacted with pyridine or triphenylphosphine to give 1:2 adducts but showed no tendency to react with hydrochloric acid. The adduct $Ru(1\text{-}nqo)_2(py)_2 \cdot 1.5py$ was characterized by X-ray crystallography.

RESULTS AND DISCUSSION

Complex formation between ruthenium salts and 1,2-naphthoquinone 1-oxime (1-nqoH) and 1,2-naphthoquinone 2-oxime (2-nqoH) (the abbreviation nqoH will be used to denote both 1-nqoH and 2-nqoH) in aqueous media has been known for some time and it has been successfully used for the spectrophotometric determination of ruthenium.[1-3] Although the species arising from these systems have not been isolated, characterized, or otherwise studied to any significant extent, they have been generally formulated as ruthenium(III) complexes.[4,5] As a continuation of our studies of complexes derived from 1,2-quinone mono-oximes,[6-9] we now report on the reactions of hydrated ruthenium trichloride with the mono-oximes of 1,2-naphthoquinone or their sodium salts and the characterization and study of the ruthenium(II) complexes arising from them. We also report on the crystal and molecular structure of the complex bis(1,2-naphthoquinone 1-oximato)di(pyridine)ruthenium(II). Several ruthenium(II) oximic complexes have previously been obtained from the reaction of the oxime with dichlorotris(triphenylphosphine)ruthenium(II).[10]

The complexes $Ru(1\text{-}nqo)_2$ and $Ru(2\text{-}nqo)_2$ were obtained from the reaction of ruthenium(III) chloride with the sodium salt of the spective 1,2-naphthoquinone mono-oxime in aqueous tetrahydrofuran. Reaction in ethanol using 3 mol equiv. of the sodium salts afforded complexes of the type $Na[Ru(nqo)_3]$ whereas in acetic acid complexes of the type $Ru(nqo)_2(nqoH)$ resulted. The formulation of the products of the above reactions as ruthenium(II) complexes is indicated by their diamagnetic character. The formation of ruthenium(II) complexes in the reactions involving ruthenium(III) chloride and the naphthoquinone oximes or their sodium salts reflects the high ligand field effect and π-acceptor properties of quinone oximato ligands. Ruthenium(II) complexes have also been obtained from the reactions of ruthenium(III) chloride with triphenylphosphine,[11] dipyridine,[12] 1,10-phenanthroline[13] and sodium thiocarbamates[14] which are ligands also noted for their strong ligand-field effect and π-acceptor properties. In contrast, reactions of the ruthenium(II) chloride with the weaker ligand field species acetylacetone,[15] edta[16] and ethylene diamine[17] lead to ruthenium(III) complexes unless a strong reductant is present: e.g. zinc. Reduction of the metal is also observed in reactions involving iron(III) mono-oximes of 1,2-naphthoquinone.[18] However, in these cases iron(III)

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complexes $Fe(nqo)_3$ accompany the iron(II) products.

The complexes $Ru(nqo)_2$ did not react with hydrochloric acid whereas the complexes $Ru(nqo)_2(nqoH)$ did exhibit some degree of decomposition to give $Ru(nqo)_2$ and the protonated ligand. The inertness of the complexes $Ru(nqo)_2$ towards hydrochloric acid parallels that of the corresponding rhodium(III) chelates,[9] and contrasts the facile acidolysis of first row transition metal complexes of the quinoneoximic ligands.[19]

Pyridine and triphenylphosphine reacted with the complexes $Ru(nqo)_2$ to give the adducts $Ru(nqo)_2(LB)_2$ (LB = py or Ph_3P). Significantly, the reaction with triphenylphosphine did not lead to deoxygenation of the naphthoquinoneoximic ligand or reduction of the metal. This behaviour contrasts with that of first row transition metal complexes of quinonemonooximes which generally undergo deoxygenation of the ligand and/or reduction of the metal on treatment with triphenylphosphine.[6,20] However, similar resistance towards the phosphine is shown by the complexes $Rh(nqo)_3$,[9] and can be accounted for by the Ru^{II} and Rh^{III} low-spin d^6 configuration.

All the complexes $Ru(nqo)_3$, $Ru(nqo)_2$, $Ru(nqo)_2$ qoH) and $Na[Ru(nqo)_4]$ are diamagnetic suggesting a low-spin d^6 configuration. Their IR spectra show strong absorptions at 1540–1610 cm^{-1}, characteristic of chelated quinoneoximato ligands. The complexes of the type $Ru(nqo)_2(nqoH)$ also exhibit bands at *ca* 2800 cm^{-1} in accord with the presence of a protonated nqoH ligand. The UV–vis spectra of all the complexes show intense charge-transfer absorptions at 530–580 and 615–645 nm which tail into the visible region. In general the spectra show very close similarity to those reported earlier for ruthenium quinoneoximic complexes erroneously formulated as ruthenium(III) species.[2-5] Thermal gravimetric analysis (Table 1) on the pyridine adducts showed that pyridine is lost quantitatively at *ca* 260°C to give $Ru(nqo)_2$ which decomposes at *ca* 300°C.

Crystal and molecular structure of $Ru(1\text{-}nqo)_2(py)_2$

Crystal data. $C_{36}H_{22}RuN_4O_4 \cdot 1.5(C_5H_5N)$. The crystals were obtained by slow crystallization from pyridine–acetone. Triclinic, $P\bar{1}$, $a = 16.321(4)$, $b = 11.519(4)$, $c = 9.354(5)$ Å, $\beta = 102.22(3)$, $U = 1646.90$ Å, $D_c = 1.22$ g cm^{-3}, $Z = 2$. A crystal of size 0.81 × 0.18 × 0.18 mm was used in the data collection. Data were collected in the θ-range 3–25° with a scan width of 0.8°, on a Philips PW1100 four-circle diffractometer using graphite monochromated Mo-K_α radiation. The structure was solved and refined using 4030 unique reflections [$I > 3\sigma(I)$] out of 4114. The coordinates of the metal atom were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. The hydrogen atoms were located in a difference-Fourier synthesis calculated using data with $\sin\theta < 0.35$ and were included in the structure factor calculations but were not further refined. Ru, N and the carbonyl O atoms were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement which converged at $R = 0.0505$, with weights of $w = 1/\sigma 2F_o$. The bond lengths and the angles are listed in Tables 2 and 3, and the atomic numbering is explained in Fig. 1.

As with other 1,2-quinone oximato-complexes of *d*-block metals the chelate ring in bis(1,2-naphthoquinone 1-oximato)di(pyridine)ruthenium(II) is five-membered. The bond lengths in the chelate ring

Table 2. Bond lengths (Å) for $Ru(1\text{-}nqo)_2(py)_2$

Ru—O(12)	2.100(3)	Ru—N(11)	1.963(5)
Ru—O(22)	2.060(4)	Ru—N(21)	1.965(4)
Ru—N(31)	2.085(4)	Ru—N(41)	2.120(4)
O(12)—C(12)	1.278(6)	C(11)—N(11)	1.381(6)
N(11)—O(11)	1.270(5)	O(22)—C(22)	1.293(6)
C(21)—N(21)	1.393(7)	N(21)—O(21)	1.259(5)
N(31)—C(31)	1.355(7)	N(31)—C(35)	1.343(7)
N(41)—C(41)	1.321(7)	N(41)—C(45)	1.329(7)

Table 1. Thermal gravimetric analysis

Compound	Weight of sample (mg)	T (°C)	Weight loss[a] (mg) Found	Calc.	Decomposition temperature (°C) of $Ru(nqo)_2$
$Ru(1\text{-}nqo)_2(py)_2$	99	270	25	24	310
$Ru(2\text{-}nqo)_2(py)_2$	101	245	25	24	296

[a] Loss of pyridine.

Table 3. Bond angles (°) for $Ru(1\text{-nqo})_2(py)_2$

N(11)—Ru—O(12)	79.7(2)	O(22)—Ru—O(12)	95.0(1)
O(22)—Ru—N(11)	90.1(2)	N(21)—Ru—O(12)	173.3(2)
N(21)—Ru—N(11)	95.0(2)	N(21)—Ru—O(22)	80.9(2)
N(31)—Ru—O(12)	85.9(2)	N(31)—Ru—N(11)	91.4(2)
N(31)—Ru—O(22)	178.3(2)	N(31)—Ru—N(21)	98.4(2)
N(41)—Ru—O(12)	93.9(2)	N(41)—Ru—N(11)	173.3(2)
N(41)—Ru—O(22)	88.5(2)	N(41)—Ru—N(21)	91.2(2)
N(41)—Ru—N(31)	90.0(2)	C(12)—O(12)—Ru	110.7(3)
C(11)—N(11)—Ru	117.1(3)	O(11)—N(11)—Ru	123.6(4)
C(22)—O(22)—Ru	110.7(3)	C(21)—N(21)—Ru	115.1(5)
O(21)—N(21)—Ru	125.2(4)	C(35)—N(31)—Ru	119.8(4)
C(31)—N(31)—Ru	122.8(4)	C(41)—N(41)—Ru	119.9(4)
C(45)—N(41)—Ru	122.6(4)	C(11)—C(12)—O(12)	121.4(5)
C(13)—C(12)—O(12)	121.4(5)	N(11)—C(11)—C(12)	110.9(5)
C(10)—C(11)—N(11)	127.0(5)	O(11)—N(11)—C(11)	119.3(5)
C(14)—C(13)—C(12)	120.6(6)	C(21)—C(22)—O(22)	121.3(5)
C(23)—C(22)—O(22)	119.6(5)	N(21)—C(21)—C(22)	111.8(5)
C(20)—C(21)—N(21)	126.2(5)	O(21)—N(21)—C(21)	119.7(4)
C(35)—N(31)—C(31)	117.4(5)	C(32)—C(31)—N(31)	122.4(6)
C(34)—C(35)—N(31)	122.8(6)	C(45)—N(41)—C(41)	117.4(6)
C(42)—C(41)—N(41)	123.6(7)	C(44)—C(45)—N(41)	122.7(7)

agree well with results for other 1,2-naphthoquinone oximato complexes and the short C(3)—C(4) bond lengths provide additional evidence for the quinone oximic character.[20-22] The NO groups of the two chelating ligands are in a *cis* arrangement whereas in other related complexes, e.g. $Cu(1\text{-nqo})_2(Me_2CO)_2$,[21] the arrangement is *trans*.

EXPERIMENTAL

IR and UV–vis spectra were recorded with Pye–Unicam SP 2000 and 1200 spectrophotometers,

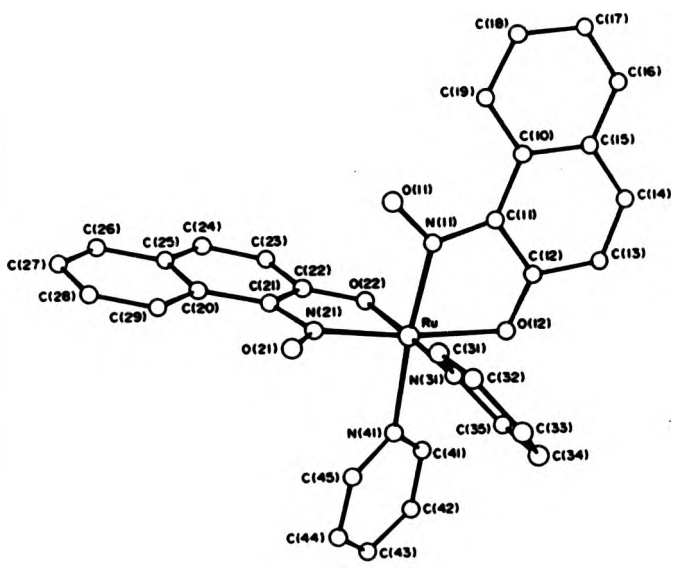

Fig. 1.

respectively. Magnetic measurements were made at room temperature using a Gouy balance equipped with a permanent magnet of 3600 Oe. Thermal gravimetric measurements were made using a Stanton HT-SM thermobalance, programmed for a linear rise between 20–400°C at a rate of 4.5°C min^{-1}. A downward flow of nitrogen (5 dm^3 h^{-1}) was maintained. Hydrated ruthenium(III) chloride, $RuCl_3 \cdot 2H_2O$, was provided by Johnson Matthey.

Reaction of hydrated ruthenium(III) trichloride with the sodium salts of the mono-oximes of 1,2-naphthoquinone in aqueous THF

A solution of hydrated ruthenium(III) chloride (1.21 g, 5 mmol) in water (50 cm^3) was added to a stirred suspension of sodium 1,2-naphthoquinone 1-oximate (1.96 g, 10 mmol) in 1:1 water–THF mixture (100 cm^3) with stirring. After 4 h the mixture was filtered to give purple–brown bis(1,2-naphthoquinone 1-oximato)ruthenium(II) (2.18 g, 98%). (Found: C,53.6; H, 2.7; N, 6.1; Ru, 22.4. $C_{20}H_{12}N_2O_4Ru$ requires: C, 53.6; H, 2.7; N, 6.3; Ru, 22.7%.)

Similarly, sodium 1,2-naphthoquinone 2-oximate gave brown bis(1,2-naphthoquinone 2-oximato)ruthenium(II) (2.10 g, 92%). (Found: C, 53.8; H, 2.4; N, 6.0; Ru, 22.6. $C_{20}H_{12}N_2O_4Ru$ requires: C, 53.6; H, 2.7; N, 6.3; Ru, 22.7%.)

Reaction of hydrated ruthenium(III) chloride with sodium 1,2-naphthoquinone mono-oximates in ethanol

A solution of hydrated ruthenium(III) chloride (2.08 g, 8.5 mmol) in ethanol (100 cm^3) was added to a solution of sodium 1,2-naphthoquinone (5.8 g, 27 mmol) in ethanol (150 cm^3) and heated under reflux for 24 h. After cooling, filtration gave purple sodium tris(1,2-naphthoquinone 1-oximato)ruthenate(II) (4.89 g, 89%). (Found: C, 55.8; H, 3.0; N, 6.4; Na, 3.5; Ru, 16.1. $C_{30}H_{18}N_3NaO_6Ru$ requires: C, 56.2; H, 2.8; N, 6.6; Na, 3.6; Ru, 16.1%.)

Similarly, sodium 1,2-naphthoquinone 2-oximate gave blue sodium tris(1,2-naphthoquinone 2-oximato)ruthenate(II) (2.14 g, 81%). (Found: C, 56.1; H, 2.7; N, 6.5; Na, 3.5; Ru, 15.7. $C_{30}H_{18}N_3NaO_6Ru$ requires: C, 56.2; H, 2.8; N, 6.6; Na, 3.6; Ru, 16.1%.)

Reaction of hydrated ruthenium(III) chloride with sodium 1,2-naphthoquinone mono-oximates in acetic acid

A solution of hydrated ruthenium(III) chloride (2.08 g, 8.5 mmol) in dilute acetic acid (30%, 50 cm^3) was added to a solution of sodium 1,2-naphthoquinone 1-oximate (5.85 g, 27.5 mmol) in glacial acetic acid (250 cm^3) and the mixture was heated under reflux for 24 h. Filtration gave blue–violet bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime)ruthenium(II). (Found: C, 57.9; H, 3.0; N, 6.7; Ru, 16.2. $C_{30}H_{19}N_3O_6Ru$ requires: C, 58.3; H, 3.1; N, 6.8; Ru, 16.2%.)

Similarly, sodium 1,2-naphthoquinone 2-oximate gave blue bis(1,2-naphthoquinone 2-oximato)(1,2-naphthoquinone 2-oxime)ruthenium(II) (79%). (Found: C, 57.9; H, 2.9; N, 6.9; Ru, 16.5. $C_{30}H_{19}N_3O_6Ru$ requires: C, 58.3; H, 3.1; N, 6.8; Ru, 16.2%.)

Reaction of $Ru(1\text{-nqo})_2(1\text{-nqoH})$ *and* $Ru(2\text{-nqo})_2(2\text{-nqoH})$ *with dilute hydrochloric acid*

Bis(1,2-naphthoquinone 1-oximato)(1,2-naphthoquinone 1-oxime) ruthenium(II) (0.62 g, 1 mmol) was heated in dilute hydrochloric acid (10%, 100 cm^3) for 6 h. Filtration of the mixture yielded bis(1,2-naphthoquinone 1-oximato)ruthenium(II) 0.45 g, 99%) (identified by TLC and IR) and 1,2-naphthoquinone 1-oxime (0.16 g, 99%) (identified by TLC and IR).

Similarly, bis(1,2-naphthoquinone 2-oximato) (1,2-naphthoquinone 2-oxime) ruthenium(II) gave (1,2-naphthoquinone 2-oximato)ruthenium(II) (97%) (identified by TLC and IR) and 1,2-naphthoquinone 2-oxime (91%) (identified by TLC and IR).

Attempted reactions of $Ru(1\text{-nqo})_2$ *or* $Ru(2\text{-nqo})_2$ *with concentrated hydrochloric acid*

$Ru(1\text{-nqo})_2$ or $Ru(2\text{-nqo})_2$ (*ca* 0.50 g) was recovered in *ca* 99% yield after being heated with concentrated hydrochloric acid (20 cm^3) for 7 days.

Reaction of $Ru(1\text{-nqo})_2$ *and* $Ru(2\text{-nqo})_2$ *with pyridine*

Bis(1,2-naphthoquinone 1-oximato)ruthenium (II) (0.45 g, 1 mol) was stirred in pyridine (50 cm^3) at 20°C for 4 h. Removal of the solvent 1-oximato)di(pyridine)ruthenium(II) (0.61 g, 99%). (Found: C, 59.6; H, 3.4; N, 9.4; Ru, 17.1. $C_{30}H_{22}N_4O_4Ru$ requires: C, 59.7; H, 3.6; N, 9.3; Ru, 16.7%.)

Similarly, bis(1,2-naphthoquinone 2-oximato)ruthenium(II) gave violet bis(1,2-naphthoquinone 2-oximato)di(pyridine)ruthenium(II) (97%). (Found: C, 60.1; H, 3.6; N, 9.1; Ru, 16.8. $C_{30}H_{22}N_4O_4Ru$ requires: C, 59.7; 3.6; N, 9.3; Ru, 17.1%.)

Reaction of Ru(1-nqo)$_2$ *and* Ru(2-nqo)$_2$ *with triphenylphosphine*

Bis(1,2-naphthoquinone 1-oximato)ruthenium (II) (0.5 g, 1.1 mmol) and triphenylphosphine (1.1 g, 4 mmol) were heated under reflux in THF (50 cm^3) for 7 days. Filtration of the mixture afforded bis(1,2-naphthoquinone 1-oximato)bis (triphenylphosphine)ruthenium(II) (0.72 g, 69%). (Found: C, 70.4; H, 3.9; N, 2.7; P, 6.2; Ru, 10.5. $C_{56}H_{42}N_2O_4P_2Ru$ requires: C, 69.3; H, 4.3; N, 2.9; P, 6.5; RU, 10.5%.)

Similarly, bis(1,2-naphthoquinone 2-oximato) ruthenium(II) gave bis(1,2-naphthoquinone 2-oximato)bis(triphenylphosphine)ruthenium(II)(85%). (Found: C, 70.0; H, 4.1; N, 2.8; P, 5.9; Ru, 10.8. $C_{56}H_{42}N_2O_4P_2Ru$ requires: C, 69.3; H, 4.3; N, 2.9; P, 6.5; Ru, 10.5%.)

Acknowledgements—We thank Dr D. T. Thompson, Dr A. A. Berzins and Johnson Matthey Technology Centre, for their advice and interest in this work.

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TITLE 1, 2-NAPHTHOQUINONE MONO-OXIMATO COMPLEXES OF RUTHENIUM

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INSTITUTION and DATE NORTH LONDON POLYTECHNIC (CNAA) 1988