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# CHELATING DIOXYGEN COMPOUNDS OF THE PLATINUM METALS

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## CONTENTS

## ABBREVIATIONS

$\overline{P\quad P} = dp$ = 1, 2-bis(diphenylphosphino) ethane
2=phos = *cis*-1, 2-bis(diphenylphosphino) ethylene
P = triphenylphosphine
$RuO_2$ = $Ru(O_2)(NCS)(NO)(PPh_3)_2$
RuCO = $Ru(NCS)(CO)(NO)(PPh_3)_2$
DMG = dimethylglyoxime

## A. INTRODUCTION

The process whereby low-valent coordination compounds of transition metals are coordinated by molecular dioxygen has interested coordination chemists (and biochemists) for almost ten years. While such coordination does not necessarily activate the dioxygen for reaction (and indeed, in most cases does not appear to do so), the possibility of such activation, and hence catalysis by this route, does exist and is the subject of considerable current research. The most significant property of dioxygen complexes is their ability to catalyse the oxygenation of substrates under unusually mild conditions. However, at this stage it is not yet possible to synthesise a dioxygen compound which will catalyse the oxidation of a given substrate. It is hoped that further work will eliminate the hit-or-miss

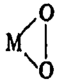
TABLE 1

The formation and characterisation of dioxygen compounds of transition metals

| Dioxygen compounds | Formation | Reversibility | $\mathrm{M}{<}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mid}}$ IR band (cm$^{-1}$) | Comments | Ref. |
|---|---|---|---|---|---|
| RuCl$_2$(AsPh$_3$)$_2$(O$_2$) | RuCl$_2$(AsPh$_3$)$_3$ in benzene rapidly absorbs O$_2$ at room temperature to give the dark brown complex |  | 880 | This dioxygen compound is unusual because it is paramagnetic whereas most others are diamagnetic. Not well characterised | 1 |
| RuX(NO)(PPh$_3$)$_2$(O$_2$) | The compound is readily formed from the corresponding RuX(NO)(PPh$_3$)$_2$, where X = OH, Br, I, NCS, NCO, N$_3$, CN |  | 800–900 | A well characterised series of compounds | 2 |
| RuCl(NO)(PPh$_3$)$_2$(O$_2$) | RuCl(NO)(CO)(PPh$_3$)$_2$ in solution absorbs O$_2$ readily to give the adduct | Irreversible | 875 | Well characterised crystalline solid | 3 |
| Ru(CO)(CNR)(PPh$_3$)$_2$(O$_2$) | Ru(CO)(CNR)(PPh$_3$)$_3$ + O$_2$ in solution (R = *p*-tolyl) | Can be reversed if heated in EtOH with PPh$_3$ | 835 | Analytical data confirm formulation | 4 |
| Ru(CO)$_2$(PPh$_3$)$_2$(O$_2$) | Ru(CO)$_2$(PPh$_3$)$_3$ + O$_2$ in solution | Can be reversed if heated in EtOH with PPh$_3$ | 849 | Brown crystals well characterised. Stable to air in the absence of light, which causes decomposition | 5 |
| Os(CO)$_2$(PPh$_3$)$_2$(O$_2$) | Os(CO)$_2$(PPh$_3$)$_3$ + O$_2$ in solution |  | 820 | The rate of O$_2$ uptake is very low. Well characterised | 5 |
| OsCl(NO)(PPh$_3$)$_2$(O$_2$) | OsHCl(ClO$_4$)(NO)(PPh$_3$)$_2$ + NaOH/MeOH → OsCl(NO)(PPh$_3$)$_2$ → OsCl(NO)(PPh$_3$)$_2$(O$_2$) |  | ca. 840 | Well characterised | 6 |

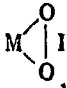
| | | | | | |
|---|---|---|---|---|---|
| $RhCl(CO)(OPPh_3)_2$<br>$RhCl(CO)(PPh_3)_2(O_2)$? | $Rh(CO)Cl(PPh_3)_2$ may form a 1:1 adduct with $O_2$ which enhances autoxidation of an organic substrate | Reversible | | The adduct has not been isolated but its existence is expected by analogy with the iridium analogue. The $O_2$ would be less tightly held and thus it might be more available for entry into an autoxidation process | 7–9 |
| $RhCl(AsPh_3)_2(O_2)$ | On passing $O_2$ into solutions of $RhCl(AsPh_3)_3$ in $CH_2Cl_2$ these become greenish-brown. Olive-brown solids are obtained on addition of $Et_2O$ | | 890 | Some solvent is coordinated as evidenced by high Cl analysis when sample is prepared in $CH_2Cl_2$. The suggested formulation is $RhCl(AsPh_3)_2O_2 \cdot n\text{-}CH_2Cl_2$ | 10 |
| $[Rh(dp)_2(O_2)]^+[PF_6]^-$ | The preparation is similar to that of the iridium analogue | Reversible | | The structure has been determined by X-ray analysis | 11 |
| $Rh(PPh_3)_3(O_2)$ | During the treatment of a solution of phenyl-(1,5-cyclooctadiene)-(triphenylphosphine)-rhodium and $PPh_3$ with $O_2$ in toluene, approximately 1 mole of $O_2$ was absorbed and yellow crystals were deposited | | 815 | Elemental analysis conforms to a composition $Rh(PPh_3)_3(O_2)$. Diamagnetism seems to suggest a dimeric structure | 12 |
| $Rh(PPh_3)(AsPh_3)_2(O_2)$ | Similar procedure | | 810 | | |
| $[Rh(PPhMe_2)_4(O_2)]^+$ | $[Rh(PPhMe_2)_4]^+$ (anion $PF_6^-$ or $ClO_4^-$) reacts slowly with $O_2$ in solid state but rapidly in solution | | | Not well characterised | 13 |

TABLE 1 (continued)

| Dioxygen compound | Formation | Reversibility |  IR band (cm$^{-1}$) | Comments | Ref. |
|---|---|---|---|---|---|
| $Rh^{II}-O_2^-$? | $[RhCl(C_8H_{14})_2]_2/Cl^-/DMA$ solution readily absorbs $O_2$ to a 1:1 ratio at ambient conditions | Irreversible | 895 (solution IR) | The solution shows an ESR signal thought to be due to $Rh^{II}-O_2^-$ | 14 |
| | The reaction of $RhCl(PPh_3)_3$ with $O_2$ in $CH_2Cl_2$ yields an adduct which has been reported by three groups of workers | | | In the most recent study[15], the structure of the isolated adduct was determined. This consists of dimeric units $[RhCl(PPh_3)_2O_2]_2$ situated at inversion centres in the crystals. The disordered $CH_2Cl_2$ molecules are not coordinated to the Rh atoms | |
| $Rh(Cl)(PPh_3)_2(O_2) . 1/2\ CH_2Cl_2$ (i)<br>$RhCl(PPh_3)_2(O_2) . CH_2Cl_2$ (ii)<br>$[RhCl(PPh_3)_2(O_2)]_n$ (iii) | | | ca. 900<br>ca. 845<br>ca. 876 | | (i) 16<br>(ii) 15<br>(iii) 17 |
| $IrX(CO)(PPh_3)_2(O_2)$ | $IrX(CO)(PPh_3)_2 + O_2 \xrightarrow{\text{solution}}$ adduct, where $X = Cl, Br, I, N_3$ | X = Cl, reversible<br>X = Br<br>X = I, irreversible | 858<br>861<br>862 | A well characterised series of compounds. Rate of reaction: Cl < Br < I | 18–22 |
| $IrCl(CO)(AsPh_3)_2(O_2)$ | $IrCl(CO)(AsPh_3)_2$ is extremely sensitive toward $O_2$ compared with $IrCl(CO)(PPh_3)_2$ | | | Not described in detail | 23, 24 |
| $IrI(CO)(AsPh_3)_2(O_2)$ | $IrI(CO)(AsPh_3)_2 + O_2 \xrightarrow[\text{2 h}]{\text{benzene}}$ adduct, | | 850 | Pink crystals. Elemental analysis confirms formulation | 25 |

| | | | | | |
|---|---|---|---|---|---|
| $IrCl(CO)L_2(O_2)$ | Formed from $IrCl(CO)L_2$ in chlorobenzene solution at 40°C, where L = $(p\text{-}ClC_6H_4)_3P$, $(p\text{-}MeC_6H_4)_3P$, $(p\text{-}MeOC_6H_4)_3P$, $(C_6H_{11})_3P$, $(n\text{-}C_4H_9)_3P$, $Et_3P$, $Ph_2EtP$ | Reversible | 800–900 | Well characterised compounds | 26, 27 |
| $Ir(C{\equiv}CR)(CO)(PPh_3)_2(O_2)$ | The solid $Ir(C{\equiv}CR)(CO)(PPh_3)_2$ reacts with air or $O_2$ slowly in the solid but rapidly in solution to afford the dioxygen adduct | | | Not well characterised | 28 |
| $[Ir(CO)(PPh_2Me)_3(O_2)]^+$ | The red solution in $CH_2Cl_2$/EtOH of $[Ir(CO)(PPh_2Me)_3]$-$[ClO_4]$ reacts slowly with $O_2$ to yield pale brown adduct | Irreversible | 840 | This well characterised compound catalyses the oxidation of $PPh_2Me$ to $OPPh_2Me$ | 29,30 |
| $[Ir(CO)(PPh_2Et)_3(O_2)]^+$ | Similar procedure | Irreversible | 845 | Well characterised | 29 |
| $IrCl(PPh_3)_2(C_2H_4)(O_2).C_6H_6$ | $IrCl(PPh_3)_2(C_2H_4) + O_2$ in benzene | | 880 | There is a broadened NMR resonance at $\tau$ 6.67 due to coordinated ethylene. This is the first known compound containing $O_2$ and an alkene ligand co-ordinated to one metal atom and may be considered as a model compound for an intermediate in the oxidation of alkenes by non-radical pathways | 31 |
| $IrCl(PPh_3)_3(O_2)$ | $IrCl(PPh_3)_2(C_2H_4)(O_2) + PPh_3$ | | 849 | | |
| $IrCl(PPh_3)_2(py)(O_2)$ | $IrCl(PPh_3)_2(C_2H_4)(O_2) + py$ (py = pyridine) | | 843 | | |

TABLE 1 (continued)

| Dioxygen compound | Formation | Reversibility |  IR band (cm$^{-1}$) | Comments | Ref. |
|---|---|---|---|---|---|
| $IrCl(PPh_3)_2(O_2)$ | $IrCl(PPh_3)_3 + O_2$<br>(orange)<br>$\xrightarrow{\text{rapid}}$ adduct |  | ca. 840 | Even under anaerobic conditions it is difficult to obtain $IrCl(PPh_3)_3$ and $IrCl(SbPh_3)_3$ completely free from $O_2$ | 32 |
| $IrCl(SbPh_3)_2(O_2)$ | $IrCl(SbPh_3)_3 + O_2$<br>(maroon)<br>$\xrightarrow{\text{rapid}}$ adduct |  | ca. 840 |  |  |
| $Ir(PPh_3)_3(O_2)$ | $Ir(PPh_3)_3 + O_2$<br>(reddish)<br>$\xrightarrow{\text{fast}} Ir(PPh_3)_3(O_2)$<br>(salmon-coloured) | Irreversible | 852 | The compound is very stable. Well characterised | 32, 33 |
| $[Ir(dp)_2(O_2)]^+$ | $IrCl(CO)(PPh_3)_2$ +<br>2 dp $\rightarrow [Ir(CO)(dp)_2][Cl]$<br>$\Updownarrow$ heat<br>adduct $\xleftarrow{O_2} [Ir(dp)_2][Cl]$<br>(anion = Cl, $BPh_4$, I, $ClO_4$, $PF_6$) | Irreversible | 845 | The crystals of $[Ir(dp)_2][Cl]$ are moderately air-stable but do react slowly with $O_2$ on standing. In solution ($CHCl_3$, EtOH) a conversion to the cream-coloured adduct takes place in minutes. Well characterised | 22, 34–36 |
| $[M(2{=}phos)_2(O_2)]^+$ | $[M(2{=}phos)_2][A] + O_2$ in chlorobenzene (M = Co, Rh, Ir; A = Cl, I, $BF_4$, $BPh_4$) |  |  | Well characterised. The structure of the Co compound has been determined by X-ray analysis | 37, 38 |

| | | | | | |
|---|---|---|---|---|---|
| Ni($t$-BuNC)$_2$(O$_2$) | Ni($t$-BuNC)$_{4 \text{ or } 2}$ + O$_2$ | Irreversible | 898 | The compounds are diamagnetic and thermally unstable. They are insoluble in non-polar solvents and not monomeric in the solid state. IR, NMR, electronic spectra and magnetic data have been used to deduce the square-planar structure with intermolecular axial interaction through the O$_2$ ligand | 39, 40 |
| Ni(cyclo-C$_6$H$_{12}$NC)$_2$(O$_2$) | Similar reaction | Irreversible | 904 | | |
| Pd($t$-BuNC)$_2$(O$_2$) | Similar reaction | Irreversible | 893 | | |
| Pt(PPh$_3$)$_2$(O$_2$) | O$_2$ reacts rapidly with a benzene solution of Pt(PPh$_3$)$_4$ to yield Pt(PPh$_3$)$_2$(O$_2$) and 2 moles of OPPh$_3$ | Irreversible | 815 (shoulder at 824) | Stable. The platinum compound has been particularly well characterised | 41–44 |
| M(PPh$_3$)$_2$(O$_2$) | M(PPh$_3$)$_4$ + O$_2$ solution (M = Ni, Pd) | Irreversible | 800–900 | Stable | 41–44 |
| Co$^{II}$–O$_2$? | The reversible formation at low temperature of a 1:1 dioxygen adduct with cobalt(II) – tetrasulphophthalocyanine has been demonstrated by ESR spectroscopy | | | Not characterised | 45[a] |
| Fe(DMG)$_2$(base)$_2$(O$_2$) | Fe(DMG)$_2$ is capable of combining with O$_2$. The reaction occurs in a mixed solvent in the presence of added bases such as pyridine, ammonia, histidine and imidazole | Reversible | | The liberation of O$_2$ from the complexes has been studied manometrically. The complexes have not been characterised | 47 |

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[a] References to other biological model systems are cited in recent ESR[46a] and X-ray crystallographic studies[46b] on reversible oxygen-carrying cobalt(II) complexes. These show that the oxygen molecule is bound in an angular manner, and such compounds are not considered further in this review.

situation that exists at the present time.

This review is a survey of the field of chelating dioxygen compounds of the platinum metals and aims to cover the journal literature to December 1971. All the dioxygen compounds that have been reported are tabulated in Table 1 with a brief description of their formation and properties. Schiff base dioxygen carriers are not mentioned, nor are dinuclear dioxygen compounds and dioxygen bridged complexes included, since the oxygen atoms in these compounds are generally non-equivalent.

The findings of the major investigations of oxidations catalysed by dioxygen compounds are described briefly.

## B. THE INFRA-RED SPECTRA OF DIOXYGEN COMPOUNDS

Infra-red absorption bands due to the dioxygen group attached to a metal have been reported for a wide range of compounds. In general, the only band observed for this group is in the region 800–900 $\text{cm}^{-1}$; such bands have been assigned to the O–O stretch[18].

The assignment of the infra-red band in the region 800–900 $\text{cm}^{-1}$ has been confirmed for $IrCl(CO)(PPh_3)_2(O_2)$ (ref. 48) and for $M(O_2)(t\text{-BuNC})$ (M = Ni, Pd) (refs. 40, 49) by isotopic studies. Spectra of the corresponding complexes containing heavy dioxygen showed new bands at 800–900 $\text{cm}^{-1}$ (also additional unassigned bands at 480–550 $\text{cm}^{-1}$). For example, the band* at 856 $\text{cm}^{-1}$ for the iridium complex split into three absorption bands at 856, 836 and 808 $\text{cm}^{-1}$. These three bands can be explained in terms of O–O stretching since the dioxygen contains three molecular species, $^{16}O_2$, $^{16}O{-}^{18}O$ and $^{18}O_2$. Qualitatively the relative intensity of the three bands was found to be that expected from the isotopic composition of the dioxygen gas. Calculations on the assumption of free diatomic molecules gave the wave-numbers 856, 832 and 807 $\text{cm}^{-1}$.

The implication of this excellent agreement is that the band near 900 $\text{cm}^{-1}$ is assigned to the stretching vibration of the O–O bond. The agreement further implies that the oxygen atoms coordinate to a metal as a peroxy group forming an isosceles triangle.

$M(O_2)(t\text{-BuNC})_2$ (M = Ni, Pd) have been studied in a similar way[49]. The nickel complex shows a band at 898 $\text{cm}^{-1}$ (isotopic substitution gave 898, 873, 848 $\text{cm}^{-1}$) and for the palladium complex it is at 893 $\text{cm}^{-1}$ (isotopic substitution gave 893, 868, 837 $\text{cm}^{-1}$). The fact that substitution of nickel by palladium had little effect on the stretching frequency (consistent with the isosceles structure) suggests that mixing with other vibrations is slight or absent (but see below). A bent, linear or bridged form is thus excluded.

Otsuka et al.[40] concluded that the band at 800–900 $\text{cm}^{-1}$ is not solely due to "pure" O–O stretching, after calculating isotopic splitting and force constants for the assumed triangular geometry for a number of dioxygen complexes. The frequency of the so-called "O–O stretching" mode is increased by an increase in the M–O (M = metal) symmetric stretching frequency. The experimentally observed constancy of the "O–O stretching" vibration could be a consequence of two opposing forces; that is, an increase in the O–O force constant in most cases reduces the $M{-}O_2$ (M = metal) force constant.

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* The value obtained by Takao et al.[48] is different from that obtained by Vaska and Ibers (see Table 1).

The same conclusion was reached by Ibers and co-workers[21], who measured the O—O bond lengths for $IrX(O_2)(CO)(PPh_3)_2$. They decided that the assignment of the characteristic infra-red band as an O—O stretch did not explain why a difference of 0.2 Å in O—O bond length between the chloro and iodo compounds resulted in a change of only 4 $cm^{-1}$ in the position of the absorption. Normally the position of an absorption should vary greatly with the bond length and bond strength.

## C. THE STRUCTURE OF DIOXYGEN COMPOUNDS

It is generally accepted for dinitrogen complexes that the term covers any mode of preparation leading to the formation of a complexed dinitrogen moiety. Such unanimity does not occur in the case of dioxygen compounds where an attempt is usually made to distinguish between the coordinated dioxygen molecule and the related peroxo ($O_2^{2-}$) and superoxo ($O_2^-$) ligands. Platinum metal tertiaryphosphine dioxygen complexes[11, 20, 36, 50] and chromium, molybdenum and titanium peroxo complexes[51] have the dioxygen group symmetrically bonded (Fig. 1 (a)), whereas cobalt(III) amine and Schiff base peroxo and superoxo complexes, which are usually binuclear, have the less symmetrical geometry[52, 53] (Fig. 1(b)).

A few examples of chelating dioxygen compounds are shown in Fig. 2.

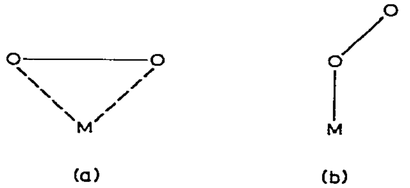


Fig. 1. The π-bonded (a) and non-linear (b) metal—dioxygen geometries.

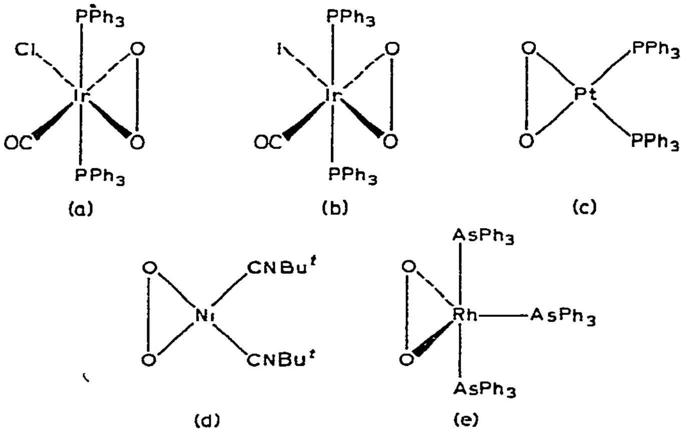


Fig. 2. Examples of dioxygen complexes.

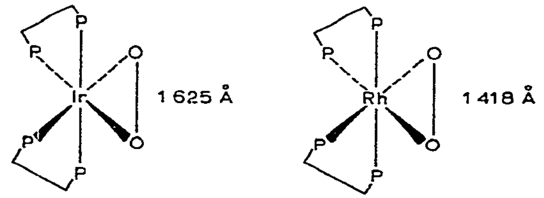
The equivalence of the oxygen atoms is consistent with Griffith's[54] model of the $\pi$-bonding of dioxygen to iron in haemoglobin. The fact that dioxygen uptake is reversible and that O—O bond length is significantly shorter than that in a typical peroxide is consistent with the view[55] that reversibility probably depends upon some electron transfer from metal to oxygen, though the transfer is not sufficient to bring about irreversible oxidation of the metal. In the case of Vaska's compound (Fig. 2(a)), this transfer amounts to approximately one electron since the O—O distance corresponds closely to $O_2^-$ (Table 2). Such evidence suggests that division of classification of compounds containing a complexed dioxygen moiety is unnecessary, and that explicit usage of the term dioxygen complexes for all such compounds would prevent confusion.

Structures of different compounds[11,36] which differ only in the central metal atom have analogous structures (Fig. 3). However, these structures have different structural parameters (the bond lengths) and different chemical properties (the reversibility of dioxygen addition). In the rhodium cation where the addition of dioxygen is reversible

TABLE 2

O—O bond lengths of dioxygen

| Compound | Bond length | Ref. |
|---|---|---|
| $O_2^+$ (bond order 2.5) | 1.123 | 56 |
| $O_2$ (bond order 2.0) | 1.207 | 57 |
| $O_2^-$ (bond order 1.5) | 1.28 | 56 |
| $O_2^{2-}$ (bond order 1.0) | 1.49 | 56 |
| $[Cr(O_2)_4]^{3-}$ | 1.405 | 58 |
| $[U(O_2)(O_2)_3]^{4-}$ | 1.51 | 59 |
| $K_2[Ti(O_2)(C_7H_3O_4N)]_2O \cdot 5H_2O$ | 1.45 | 51 |
| $[(NH_3)_5CoO_2Co(NH_3)_5][(SCN)_4]$ | 1.65 | 60 |
| $IrCl(CO)(PPh_2Et)_2(O_2)$ | 1.573 | 27 |
| $IrCl(CO)(PPh_3)_2(O_2)$ | 1.30 | 20, 50 |
| $IrI(CO)(PPh_3)_2(O_2)$ | 1.51 | 20, 50 |
| $[Ir(dp)_2(O_2)]^+$ | 1.625 | 11, 36 |
| $[Rh(dp)_2(O_2)]^+$ | 1.418 | 11, 36 |
| $[Pt(PPh_3)_2(O_2)]1.5\ C_6H_6$ | 1.45 | 44 |



(where $\overline{P\quad P}$ = 1,2-bis(diphenylphosphino)ethane)

Fig. 3. Structures of $[M(O_2)(\overline{P\quad P})_2]^+$ cations (M = Rh, Ir).

(Table 1), the Rh—O mean distance 2.025 Å is significantly longer than the corresponding Ir—O mean distance 1.976 Å. The weaker metal—dioxygen bond is accompanied by a stronger O—O bond (and a shorter O—O bond length, 1.418 Å). The addition of dioxygen to the iridium complex is irreversible. The stronger metal—dioxygen bond is accompanied by a weaker O—O bond (and a longer O—O bond length, 1.625 Å).

The dioxygen adduct formed from chlorotris(triphenylphosphine) rhodium(I) is $\{RhCl(O_2)(PPh_3)_2\}_2$. The structure[15] contains dimeric units situated at inversion centres in the crystal. The overall geometry of each rhodium atom can be described in terms of a distorted trigonal bipyramid (Fig. 4).

The O—O bond lengths of a series of dioxygen complexes are listed in Table 2 along with those of various oxidation states of dioxygen.

Ibers and co-workers[11, 36] discovered the remarkable trend in the O—O bond lengths that can be seen for the series of iridium complexes in Table 2. Both the O—O distance and the tendency to bind dioxygen increase as the ancillary ligands become more electron-releasing (dp > $PPh_2Et$ > $PPh_3$ and I > Cl).

## D. THE BONDING IN DIOXYGEN COMPOUNDS

The electron configuration[61] of the dioxygen molecule might be either

$$(\sigma_1)^2(\sigma_1^*)^2(\sigma_2)^2(\pi)^4(\pi^*)^2$$

or

$$(\sigma_1)^2(\sigma_1^*)^2(\pi)^4(\sigma_2)^2(\pi^*)^2$$

The bond order is predicted to be 2 and two unpaired electrons are expected. As expected on the basis of simple molecular orbital theory, removal of electrons strengthens the bond, while addition of electrons weakens the bond (Table 2).

The addition of dioxygen to $d^8$ systems can be discussed on the basis of the $\pi$-bonding scheme of Chatt and Duncanson[62] and Dewar[63] used to explain the coordination of the

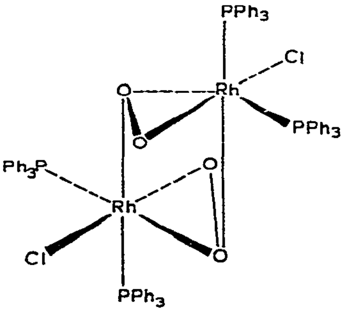


Fig. 4. The structure of $[RhCl(O_2)(PPh_3)_2]_2$.

ethylene molecule to platinum in Zeiss's salt. A $\sigma$-bond is formed by donation from a filled $\pi$-bonding orbital on the ligand to an unfilled metal *d* or hybrid orbital. Back-donation then occurs, to offset the resultant dipole, from a filled metal orbital to a $\pi^*$-antibonding orbital on the ligand molecule.

For the dioxygen molecule an early scheme was proposed in which electron transfer occurred to the ligand, which then assumed the character of the superoxide ion, $O_2^-$, or the peroxide ion, $O_2^{2-}$, depending on whether one or two electrons were transferred. However, the diamagnetism of the compound $IrCl(CO)(PPh_3)_2(O_2)$, in which the O–O bond length approximates that of $O_2^-$, suggests that there is no formal transfer of an electron to dioxygen.

The most reasonable explanation of the bonding in dioxygen compounds is analogous to that proposed by Griffith[54] for oxygenated haem. This theory has been discussed further by Ibers[21] in terms of the complex $IrCl(CO)(PPh_3)_2O_2$. The processes discussed are theoretical and have no semblance to the chemical intermediates of the oxygenation reaction. Prior to bonding, the $O_2$ group forms its valence state, i.e. the oxygen atoms are $sp^2$-hybridised and the molecule has two lone electron pairs on each oxygen atom with one $\sigma$- bond and one $\pi$-bond, both occupied by one pair of electrons. In this state the $O_2$ molecule is diamagnetic. The $O_2$ molecule acts as a ligand by donating one pair of electrons from the $\pi$-bond to iridium (and thus the O–O axis must be at right angles to the direction of coordination). Prior to oxygenation, the central atom $Ir^I$, a $d^8$ system, was $dsp^2$-hybridised. The valence state of iridium can be considered to be $dsp^3$-hybridised with one directional vacant orbital which, in oxygenation, receives the pair of electrons from the $O_2$ group. In conjunction with the formation of this bond, there is back-donation from one of the filled iridium *d*-orbitals to the $\pi^*$-orbital of the $O_2$ group. As electrons begin to be donated to iridium from dioxygen, a dipole is set up which tends to stop further donation; the back-donation reduces this dipole and thus the overall bond strength depends very largely upon the degree of back-donation that is possible.

For the dioxygen molecule to form a $\pi$-bond with the metal substrate several conditions must be fulfilled. Firstly, there must be available on the substrate an empty orbital of the correct energy and symmetry to overlap with the dioxygen $\pi$-bonding orbitals to form a $\sigma$-bond. Similarly, an essentially non-bonding, filled *d*-orbital (or hybrid orbital) must exist on the substrate through which electron density can be back-donated to the dioxygen ligand into the $\pi$-antibonding orbitals. The degree of back-bonding which occurs will depend upon the relative energies and the amount of overlap between the orbitals.

The two complexes containing bis-chelating phosphine ligands (Table 2) may be considered in these terms[11, 36]. In the iridium complex there is extensive back-donation to the ligand. This is manifested both in the long O–O bond (1.625 Å) and in the strong, short Ir–O bonds (mean, 1.976 Å). Thus, the orbital energies are exceptionally favourable for overlap, and extensive back-donation occurs. This effectively reduces the bond order of the $O_2$ to less than 1.0. In the rhodium complex, the overlap between the ligand and the substrate orbitals is less owing to the higher energies of the rhodium *d*-orbitals compared with those of iridium. The O–O bond length is now 1.418 Å, and the mean Rh–O distance is 2.025 Å.

The two complexes $IrX(CO)(PPh_3)_2(O_2)$ (X = Cl or I) are expected to show changes in uptake properties and molecular geometry analogous to those observed above. The energy of the substrate orbitals is varied by the change in the halide substituent. With the more electronegative chlorine atom the overlap between the orbitals is such that back-donation to the $O_2$ only occurs to the extent that the O—O bond is lengthened to 1.30 Å. With the less electronegative iodine substituent the O—O distance is 1.51 Å.

Comparison of $IrCl(CO)(PPh_3)_2(O_2)$ and $IrCl(CO)(PPh_2Et)_2(O_2)$ shows that the more basic, ethyl-substituted phosphine results in more residual electron density on Ir, again leading to a longer O—O bond.

The symmetry arguments outlined by Mingos[64] support Griffith's model of the dioxygen ligand in its valence state and its bonding arrangement to the metal. The bonding is interpreted in terms of a second-order Jahn—Teller effect which suggests that changes in geometry during complex formation between Lewis acids and bases depend solely on the direct product of the symmetries of the donor and acceptor orbitals. This treatment implies that only the dioxygen $\pi$ and $\pi^*$ (valence) orbitals need be considered because the approximation has been used that only the ground and first excited states of the complex contribute significantly to the second-order Jahn—Teller effect. In dioxygen complexes, symmetric coordination of dioxygen is expected because a prerequisite of bond formation is that the ligand filled $\pi$ (valence) orbital has the same symmetry as the empty metal orbital, and therefore their direct product must be totally symmetric.

In a more theoretical approach, Mason[65] compared the coordinated dioxygen with the excited states of dioxygen gas. If the bonding of $O_2$ is similar to the bonding in other $\pi$-complexes, the dioxygen electron configuration would be similar to the one corresponding to the excitation

$$(\pi)^4(\pi^*)^2 \rightarrow (\pi)^3(\pi^*)^3$$

in the free molecule. The precise amount of electron density transferred to the antibonding orbitals on the dioxygen through the metal will depend on the remaining ligands in the complex. The difference in the O—O distance for different sets of ligands reflects the donor and acceptor relations of these ligands with the metal. However, it is felt[11] that the range of O—O distances is too great to allow easy allocation of a different excited state of $O_2$ to the dioxygen in each complex.

In $\{RhCl(O_2)(PPh_3)_2\}_2$, the Rh—$O_2$ bonding[15] can be rationalised using the conventional molecular orbital scheme for dioxygen. Within this framework the $O_2$ has an electron configuration $(\pi^*)^2(\pi^*)^0$ rather than the ground state electron configuration $(\pi^*)^1(\pi^*)^1$. The bonding within the rhodium—oxygen—oxygen triangle is then described by ligand-to-metal donation from a fully occupied $\pi$-orbital and back-donation to the empty $\pi^*$-orbital. The full $\pi^*$-orbital of the $\mu$-bonded dioxygen molecule is perpendicular to the rhodium—oxygen—oxygen triangle and is available for the formation of a $\sigma$-bond to the second rhodium atom.

This particular view of the bonding of the central $Rh_2O_4$ unit does not allow an immediate discussion of the O—O distance because the participation of both orbitals of each $O_2$ produces opposite effects, i.e. there is a force tending to increase the O—O distance and an opposing force tending to decrease it. The relative effect of these two forces is not known.

## E. FORMATION DATA OF DIOXYGEN COMPOUNDS

The electronic factors affecting dioxygen uptake by coordination compounds now appear to be well understood. An increase in electron density at the metal caused by changing the ligands or the metal improves uptake properties. It is impossible to predict precisely whether or not a substrate will have molecular orbitals of energy and symmetry suitable for overlap with the $O_2$ orbitals. However, the present range of complexes could be extended. For example, in $IrBr(CO)(PPh_3)_2(O_2)$ the O—O distance is expected to be between the O—O distance of the chloro and iodo analogues. Intermediate uptake properties for $IrBr(CO)(PPh_3)_2$ are expected. Other series of complexes have been studied to obtain further important reactivity orders.

The reactivities of three different transition metals in the same periodic group have been compared by Vaska et al.[37]. In simple addition reactions, the reactivity of the activator complex and the stability of the adduct are generally observed to follow the sequence third-row > second-row transition metal. However, comparison with the first-row metal has not been possible until recently when the series of compounds $[M(2{=}phos)_2]^+$ (M = Co, Rh, Ir) was made[37]. Vaska et al. studied the reactions in eqn. (1) and the results show an unexpected reactivity order Co > Ir > Rh.

$$[M(2{=}phos)_2]^+ + XY \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} [(XY)M(2{=}phos)_2]^+ \qquad (1)$$

where $XY = O_2$, HCl, $H_2$, CO, $SO_2$, $k_2$ = second-order rate constant, $k_{-1}$ = first-order rate constant.

The unmistakable order of attraction of the univalent cations to dioxygen, Co ≫ Ir > Rh, is shown in Table 3. It was suggested[37] that the reactivity of the $d^8$ $M^I$ complexes is directly dependent on their field stabilisation energies. This could be a guide for predicting the relative energetics of analogous addition reactions.

TABLE 3

Kinetic and activation parameters for the addition of $O_2$ to $[M(2{=}phos)_2]^+$ in chlorobenzene at 25°C

| M | $k_2$ ($M^{-1}$.sec$^{-1}$) | $\Delta H_2^{\ddagger}$ (kcal.mole$^{-1}$) | $\Delta S_2^{\ddagger}$ (e.u.) |
|---|---|---|---|
| Co | $1.7 \times 10^4$ | 3.4 | −28 |
| Rh | 0.12 | 11.6 | −24 |
| Ir | 0.47 | 6.5 | −38 |

Vaska and Chen[26] have also found that the rates of dioxygen addition

$$IrCl(CO)L_2 + O_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} IrCl(CO)L_2(O_2) \qquad (2)$$

(where L = tertiary phosphine)

to *trans*-$[IrCl(CO)(R_3P)_2]$ ($R_3P$ = tertiary phosphine) and the stability, viz.

$$K_2 = k_2/k_{-1} = [\mathrm{IrCl(CO)L_2(O_2)}] \;/\; [\mathrm{IrCl(CO)L_2}][\mathrm{O_2}] \tag{3}$$

of the resulting dioxygen adduct increase with the basicity of the substituent R. This is true only if the ligands are isostructural or nearly so (2, 3, 6, 9 in Table 4). The geometry of R exerts a profound effect on the dynamics of these reactions.

The data in Table 4 can be summarised in linear free-energy relationships (eqn. (4)) which are new in organometallic chemistry but are expected to become increasingly important.

TABLE 4

Kinetic and activation parameters for the reversible reactions of $O_2$ with *trans*-$\mathrm{IrCl(CO)L_2}$ in chlorobenzene at 40°C

| L | $k_2 \times 10^2$ ($M^{-1}$. sec$^{-1}$) | $\Delta H_2^{\ddagger}$ (kcal. mole$^{-1}$) | $\Delta S_2^{\ddagger}$ (e.u.) |
|---|---|---|---|
| 1 $(C_6H_{11})_3P$ | 0.127 | 9.5 | -42 |
| 2 $(p\text{-}ClC_6H_4)_3P$ | 3.10 | 10.8 | -31 |
| 3 $(C_6H_5)_3P$ | 9.93 | 9.5 | -33 |
| 4 $(C_6H_5)_3As$ | 14.2 | 8.1 | -37 |
| 5 $(C_6H_5)_2(C_2H_5)P$ | 14.2 | 8.4 | -36 |
| 6 $(p\text{-}CH_3C_6H_4)_3P$ | 21.6 | 9.3 | -32 |
| 7 $(n\text{-}C_4H_9)_3P$ | 26.1 | 9.0 | -33 |
| 8 $(C_2H_5)_3P$ | 33.8 | 8.5 | -34 |
| 9 $(p\text{-}CH_3OC_6H_4)_3P$ | 48.4 | 8.5 | -33 |

$$\log k_2 = 0.194 - 14.1\sigma(X) \tag{4}$$

where $k_2$ = rate of oxygenation (second-order rate constant) and $\sigma(X)$ = Hammett constant for the *para* substituent in the arylphosphine ligand $(p\text{-}XC_6H_4)_3P$.

Recently we have studied[30] the uptake of dioxygen by $[\mathrm{Ir(CO)(PPh_2CH_3)_3}][\mathrm{ClO_4}]$ in acetone and dichloromethane, and the rate law fits the expression

$$-\mathrm{d}[\mathrm{Ir(CO)(PPh_2CH_3)_3}^+] \;/\; \mathrm{d}t = k_1\, [\mathrm{Ir(CO)(PPh_2CH_3)_3}^+][\mathrm{O_2}]$$

The results (Table 5) are similar to those found by previous workers.

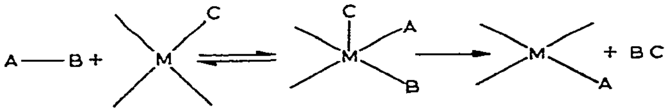
TABLE 5

Kinetic and activation parameters for the addition of $O_2$ to $[Ir(CO)(PPh_2CH_3)_3][ClO_4]$ in acetone and dichloromethane at 25°C

| Solvent | $k_2$ ($M^{-1}$. $sec^{-1}$) | $\Delta H_2^{\ddagger}$ (kcal. $mole^{-1}$) | $\Delta S_2^{\ddagger}$ (e.u.) |
|---|---|---|---|
| Acetone | 0.33 | 7.99 | −34.0 |
| Dichloromethane | 0.61 | 9.71 | −27.1 |

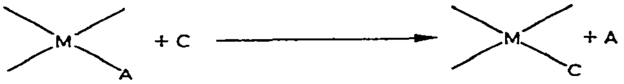
## F. THE REACTIONS OF DIOXYGEN COMPOUNDS

The interest in reactions of coordinated dioxygen derives from the realisation that a broad class of atom transfer redox reactions can be promoted by a metal which holds both reductant and oxidant in adjacent coordination sites[66]. Such processes can be imagined to embody as discrete steps oxidative addition, migratory insertion, and reductive elimination.



(5)

The overall reaction becomes catalytic if ligand replacement of the reduced fragment A by the reductant C occurs.



(6)

Reactions between singlet molecules and free (triplet) dioxygen usually experience high activation energies[67] because of the problem of spin conservation[68]. Apparently this "symmetry barrier" may be overcome by forming singlet complexes between the transition metals and dioxygen. The long O—O bond length and diamagnetic character of these dioxygen complexes suggests some similarity to singlet dioxygen which is 23 kcal more energetic than the ground state dioxygen.

The most significant property of the dioxygen complexes is their ability to oxygenate substrates under unusually mild conditions. Both catalytic and stoichiometric oxidations are possible.

### *(i) Stoichiometric reactions*

Stoichiometric oxidations of gaseous non-metal oxides occur readily (Fig. 5). The formation of bidentate sulphate with sulphur dioxide

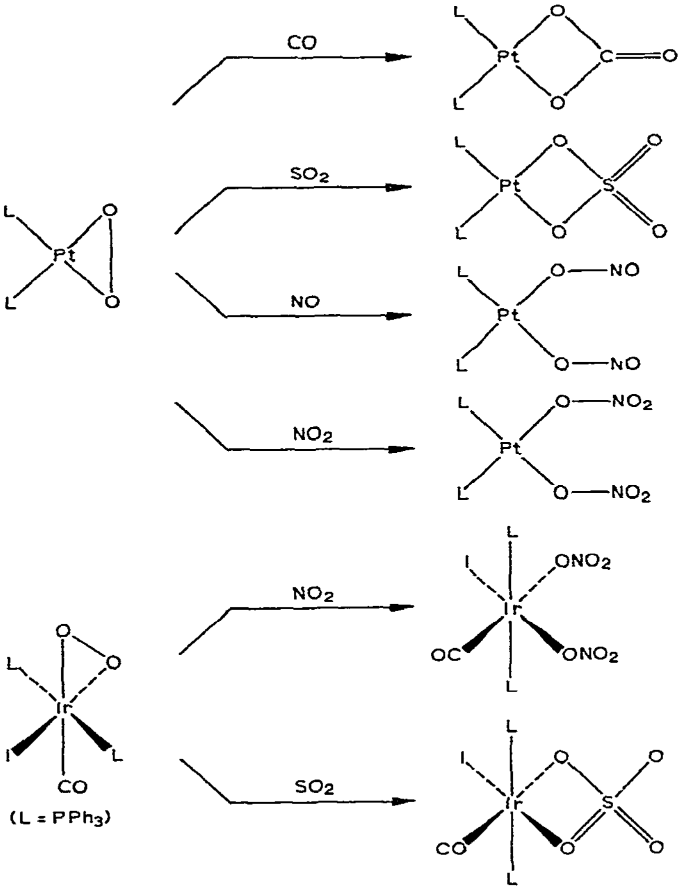
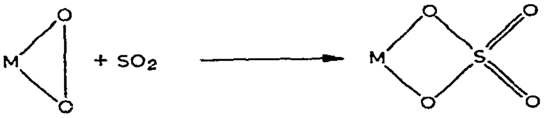


Fig. 5. Reactions of dioxygen compounds with non-metal oxides[25, 69, 70].



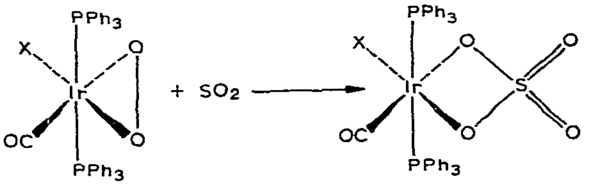
(7)

is believed to be a reaction characteristic of all dioxygen complexes. In several instances free dioxygen also reacts with the metal–$SO_2$ complexes (eqn. (8)).

(8)

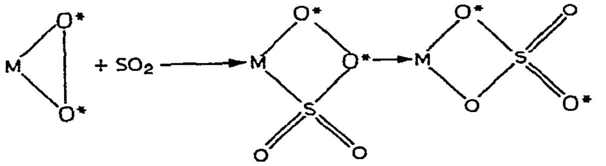
but this does not always happen.

The mechanism of eqn. (9) has been partially clarified through a study employing $^{18}O$ isotopic labelling[22].



(9)

This study showed that one oxygen atom from the $O_2$ and one originally from the $SO_2$ are attached to the iridium atom. The mechanism probably occurs in the manner shown in eqn. (10) (where O* denotes isotopic labelling) through the formation of a postulated peroxysulphate intermediate.



(10)

On the basis of infra-red studies[22] and the apparent coordinative saturation, chelated sulphate structures have been assigned to all these complexes[33].

Similar reactions of dioxygen complexes with $NO_2$, CO and NO to give dinitrates, carbonates and dinitrates respectively are known[25, 69–71]. The reactions with other unsaturated molecules such as $CO_2$, $CS_2$, aldehydes, ketones, acetone oxime and thiourea have been studied by Hayward et al.[72]. These reactions can be used to synthesise[25] an extended range of nitro, nitrato and sulphato complexes of platinum metals.

### *(ii) Homogeneous catalytic oxygenation*

Catalytic oxidations are more important than the stoichiometric reactions discussed above and the kinetics of some of these have been investigated. For any complex to function effectively as a homogeneous catalyst it must fulfil a number of requirements. It must (*i*) provide vacant coordination sites for the reactants; (*ii*) orient the reactants into the position required for atom transfer; (*iii*) activate the reactants and (*iv*) readily release the products so the cycle can continue. Because complexes of Group VIII metals possess these properties they are particularly suitable for use as catalysts and have been the principal subjects for the investigations discussed below. Well-characterised complexes have been used in these kinetic studies to determine equilibrium constants, rate constants, and activation parameters, and to establish mechanisms.

Solutions of $MP_4$ (M = Ni, Pd, Pt; P = $PPh_3$) react with dioxygen to form dioxygen compounds[41, 73], viz.

$$MP_4 + O_2 \rightarrow P_2M.O_2 + 2\,P$$

The dioxygen molecule coordinated to the zerovalent metal seems to be very reactive. The dioxygen compounds catalyse the oxidation of phosphine to phosphine oxide and of isocyanide to isocyanate[42, 74–77].

Thus, if a mixture of $MP_4$ (M = Ni, Pd, Pt; P = $PPh_3$) and an excess of $PPh_3$ in toluene is allowed to react with dioxygen at such a temperature that the dioxygen compound decomposes again, the triphenylphosphine is oxidised catalytically to triphenylphosphine oxide[41, 42, 73–77].

The mechanism of the above reaction has been studied by Halpern and co-workers[74]. The predominant species present in a benzene solution of $Pt(PPh_3)_4$ is the tris complex $Pt(PPh_3)_3$, and both dissociation (i.e. to $Pt(PPh_3)_2$) and association (i.e. to $Pt(PPh_3)_4$) are very small over a wide range of phosphine concentrations.

The reaction with dioxygen which yields the complex $Pt(PPh_3)_2(O_2)$, in accord with

$$Pt(PPh_3)_3 + O_2 \rightarrow Pt(PPh_3)_2(O_2) + PPh_3 \qquad (11)$$

has the rate law

$$-d[Pt(PPh_3)_3]/dt = k_1[Pt(PPh_3)_3][O_2]$$

where $k_1 = 2.6 \pm 0.1\ M^{-1}.\mathrm{sec}^{-1}$. The rate of this reaction was unaffected by addition of up to $3 \times 10^{-3}\ M$ excess phosphine but, confirming the earlier work[73], it was found that $Pt(PPh_3)_2(O_2)$ does react further with excess phosphine to regenerate $Pt(PPh_3)_3$, i.e.

$$Pt(PPh_3)_2(O_2) + 3\ PPh_3 \rightarrow Pt(PPh_3)_3 + 2\ Ph_3PO \qquad (12)$$

so that a catalytic cycle for the oxidation of triphenylphosphine to triphenylphosphine oxide is established. The second reaction has the rate law

$$d[Pt(PPh_3)_3]/dt = k_2[Pt(PPh_3)_2(O_2)][PPh_3]$$

where $k_2 = 0.15 \pm 0.01\ M^{-1}.\mathrm{sec}^{-1}$.

The rate laws are consistent with the postulated mechanism but do not unambiguously establish how the initial reaction between $Pt(PPh_3)_3$ and $O_2$ proceeds. This may take place as depicted above or by alternative reactions

$$Pt(PPh_3)_3 + 1.5\ O_2 \rightarrow Pt(PPh_3)_2(O_2) + Ph_3PO \qquad (13)$$

or

$$Pt(PPh_3)_3 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} Pt(PPh_3)_2 \xrightarrow{O_2} Pt(PPh_3)_2(O_2) \qquad (14)$$

since $Pt(PPh_3)_2$ is known to coexist with $Pt(PPh_3)_3$ in solution[75].

A study of the rate of consumption of dioxygen[76] and the excellent agreement between the measured and calculated values of this rate over a wide range of conditions lends strong support to the mechanism depicted by eqns. (11), (12). A significant contribution from a step with stoichiometry corresponding to eqn. (13) (instead of eqn. (11))would be reflected in a higher value of rate than that calculated from eqns. (11), (12). The possibility of a significant contribution from eqn. (14) would be reflected in a departure (which was not observed) from the dependence on $[PPh_3]$.

The general features of the mechanism for the $Pt(PPh_3)_3$-catalysed oxidation of triphenylphosphine are firmly established. However, the detailed mechanisms of the individual steps, particularly of eqn. (12), which has been interpreted in terms of a dissociative "oxygen insertion" sequence[74] shown in Fig. 6 remain to be fully elucidated.

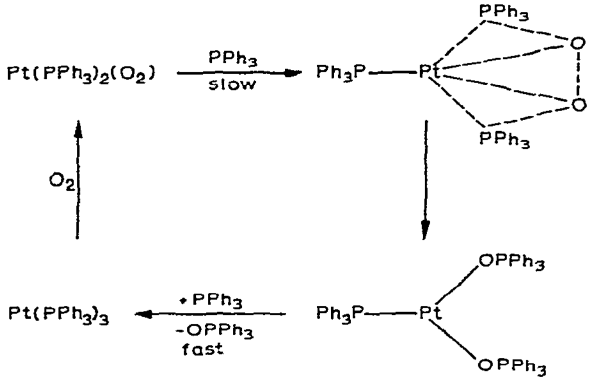


Fig. 6. Scheme for catalysed oxidation of triphenylphosphine by $Pt(PPh_3)_3$.

The above observations have been extended to dioxygen complexes of different coordination number and geometry[2,78]. $Ru(NCS)(CO)(NO)(PPh_3)_2$ and $Ru(O_2)(NCS)(NO)(PPh_3)_2$ were found to be efficient catalysts for the oxidation of triphenylphosphine. The reaction sequence proposed is shown in Fig. 7.

The actual catalytic cycle involves the steps II → III → IV → V → II. The rate equations for the mechanism are

$$-\frac{d[PPh_3]}{dt} = \frac{k_1K_2[RuO_2][P]}{1+K_2[P]}$$

for the dioxygen compound, and

$$-\frac{d[PPh_3]}{dt} = \frac{k_1K_1K_2[RuCO][O_2][P]}{[CO]+K_1[O_2]+K_1K_2[P][O_2]}$$

for the carbonyl compound, where $P = PPh_3$, $RuO_2 = Ru(O_2)(NCS)(NO)(PPh_3)_2$, and $RuCO = Ru(NCS)(CO)(NO)(PPh_3)_2$. Analysis of the data on the basis of these equations yields $k_1 = 1.26 \pm 0.03 \times 10^{-2}$ sec$^{-1}$ and $K_2 = 1.63 \pm 0.04\,M^{-1}$.

In contrast to the rate law observed by Halpern and co-workers[74], where the rate of oxidation of triphenylphosphine by $Pt(O_2)(PPh_3)_2$ depended on $[PPh_3]$, the above two rate equations require that the reciprocal of the rate depends on $[PPh_3]^{-1}$. Similar in-

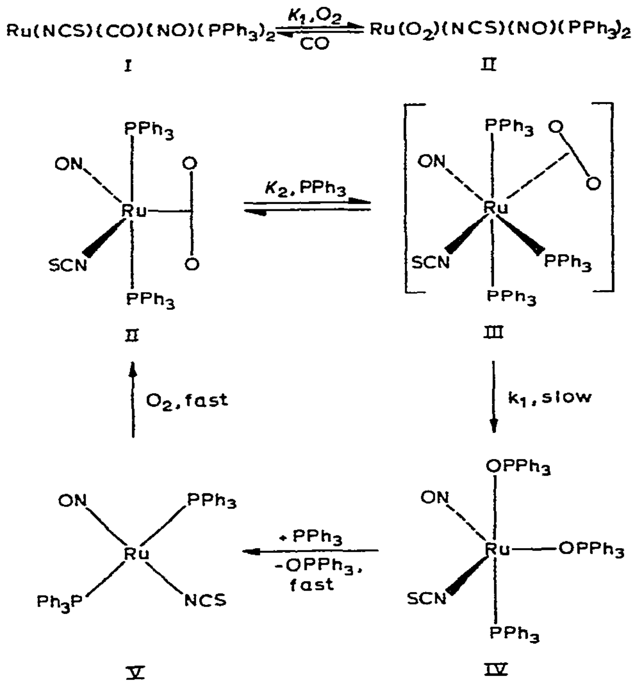


Fig. 7. Scheme for catalysed oxidation of triphenylphosphine by $Ru(NCS)(CO)(NO)(PPh_3)_2$ and $Ru(O_2)(NCS)(NO)(PPh_3)_2$.

verse dependence has also been observed for the homogeneous oxidation of *t*-butylisocyanide using $Ni(t\text{-}BuNC)_4$ as catalyst[79].

The catalytic cycle is initiated by the entry of $PPh_3$ into II to form III. The intermediate III is reasonably formulated as a six-coordinate derivative of $Ru^{II}$, the nitrosyl ligand being bound as $NO^-$. The rate-determining step is the oxygen atom transfer process to give a $OPPh_3$ complex IV. This species must be unstable and readily undergoes exchange to produce the coordinatively unsaturated $Ru^0$ complex V which, in turn, readily takes up dioxygen to re-form the catalyst II. Thus two molecules of $PPh_3$ are oxidised to $OPPh_3$ by one molecule of dioxygen in one catalytic cycle.

Another dioxygen $Ru^{II}$ complex has been reported[1]. $Ru(O_2)Cl_2(AsPPh_3)_3$ appears to be the first example of a paramagnetic 1:1 dioxygen complex of a $d^6$ system. In benzene solution, it appears to oxidise triphenylphosphine to triphenylphosphine oxide. However, this is yet to be studied fully.

$Ru(PPh_3)_3Cl_2$ is an effective catalyst for the oxidation of $PPh_3$ to $OPPh_3$ at room temperature and atmospheric pressure[80]. For example, at 20°C in benzene (20 ml), $Ru(PPh_3)_3Cl_2$ (0.15 m*M*) oxidised $PPh_3$ (1.5 m*M*) nearly quantitatively in about 15 min, under a pure atmosphere of dioxygen. The dioxygen is probably activated when it reacts with the $Ru^{II}$ complex

$$Ru(PPh_3)_3Cl_2 \rightleftharpoons Ru(PPh_3)_2Cl_2 + PPh_3 \qquad (15)$$

$$Ru(PPh_3)_2Cl_2 + O_2 \rightarrow Ru(PPh_3)_2Cl_2(O_2) \quad (16)$$

However, the proposed dioxygen compound has not been isolated to date. Evidence for eqn. (15) is provided by the induction time which was observed in all experiments; the presence of excess phosphine makes the dissociation of $Ru(PPh_3)_3Cl_2$ into the active species more difficult. The mechanism (Fig. 8) of this oxidation is now under study, but it is expected to be like the one proposed by O'Connor and co-workers[2, 78].

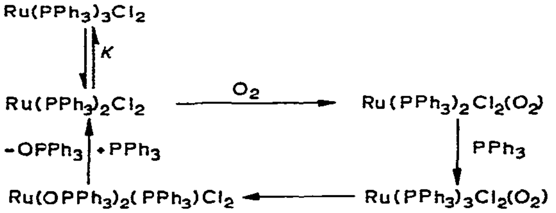


Fig. 8. Postulated scheme for catalysed oxidation of triphenylphosphine by $Ru(PPh_3)_3Cl_2$.

Japanese workers[81] have studied the oxidation reactions of styrene and triphenylphosphine catalysed by various iridium complexes. Triphenylphosphine is oxidised easily by the Vaska complexes $(IRX(CO)(PPh_3)_2$, X = Cl, Br, I) to afford triphenylphosphine oxide catalytically, and the catalyst is recovered with decomposition after the reaction. The yield increases in the order: X = Cl < I < Br. The fact that the Vaska complexes coordinate with dioxygen easily under a dioxygen atmosphere suggests that the reaction proceeds via an iridium dioxygen complex.

According to La Placa and Ibers[20] and McGinnety et al.[21] the O—O bond lengths of the dioxygen complexes prepared by Vaska et al. are 1.30 Å and 1.51 Å for the chloride complex and the analogous iodide complex respectively.. That increasing bond length of O—O increases the yield of oxide formed seems to show that the oxygen molecule is highly activated by coordinating with the iridium(I) metal. Heating of the dioxygen complexes in the absence of dioxygen resulted in the formation of triphenylphosphine oxide.

These results suggest the mechanism shown in Fig. 9. The catalysed oxidation may pro-

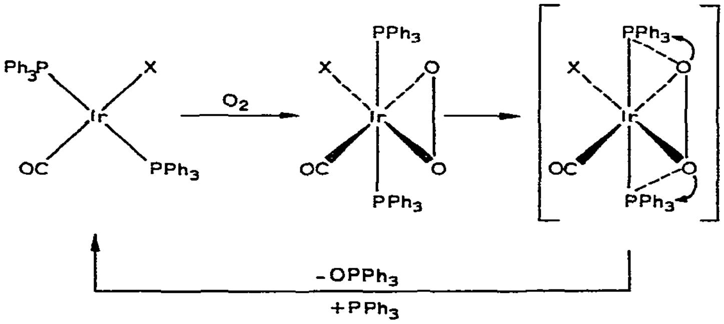


Fig. 9. Postulated scheme for catalysed oxidation of triphenylphosphine by Vaska complexes $(IrX(CO)(PPh_3)_2$.

ceed through the coordination of both dioxygen and triphenylphosphine to iridium(I) metal followed by oxygen atom transfer and by the replacement of $OPPh_3$ ligands by phosphine.

The Vaska complexes[81] can also cause the oxidation of styrene to give acetophenone in considerable yields. In the absence of the complexes no oxidation product was formed so they function as catalysts. The yield of acetophenone increases in the order: $X = I < Br < Cl$ which is different from that observed in the oxidation of triphenylphosphine. This can be explained by considering the steric hindrance between the halide ligand and the coordinated styrene (Fig. 10).

The complexes $RhX(PPh_3)_3$ (X = Cl, Br, I), especially $RhCl(PPh_3)_3$, can oxidise styrenes in the presence of oxygen to produce carbonyl compounds[82]. A remarkable solvent effect is observed in the reaction and this is consistent with the postulated reaction sequence (Fig. 10). It seems that the species $RhCl(PPh_3)_2$ which is derived from the dissociation of $RhCl(PPh_3)_3$ has an important role in the reaction. This species has a vacant site which is essential to catalytic activity and will be coordinated easily with dioxygen under a dioxygen atmosphere.

Recent communications have reported the oxidation of cyclohexene to cyclohexenone catalysed by rhodium[66] and iridium[83] phosphine complexes. Although in the first paper on this subject[66] a *cis*-coordinative interaction between the alkene and dioxygen was suggested, subsequent investigations[69,83,84] have clearly established the radical nature of the autoxidation of cyclohexene catalysed by low oxidation state phosphine complexes.

The action of the phosphine metal complexes does not involve a catalytic dioxygen activation which favours the formation of hydroperoxides but only a radical transformation of the hydroperoxides already present in the reaction mixture[85]. It follows that the postulated unique dioxygen activation by these complexes in hydrocarbon oxidation gen-

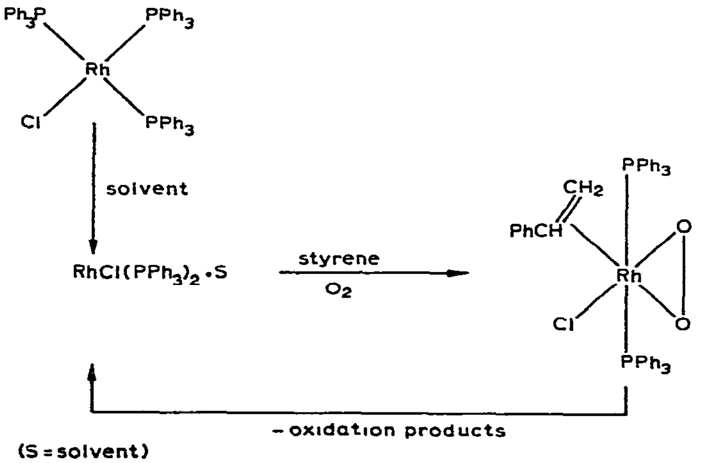


Fig. 10. Postulated scheme for catalysed oxidation of styrene by $RhCl(PPh_3)_3$.

erally does not take place, in contrast with the phosphine oxidation. The metal complexes do not take part in chain initiation and their effect becomes possible only after the appearance of peroxides.

The mechanisms of these metal ion-promoted autoxidations remain to be clarified. However, the existence of numerous oxygenases, metalloenzymes which catalyse the direct oxygenation of organic substrates (at least in some instances by non-radical pathways), sustains the expectation that non-radical, atom transfer oxidations of organic substrates by metal—dioxygen complexes will be discovered.

A rather novel homogeneous catalytic reaction has been reported by Vaska and Tadros[86]. They describe what appears to be a homogeneous catalytic combination of molecular hydrogen and dioxygen to form water in the presence of some triphenylphosphine complexes of platinum, iridium, rhodium and ruthenium, in toluene solutions under ambient conditions.

Most of the complexes showed autocatalysis which demonstrates that in these cases the active catalytic species are different from the starting materials. This may indicate the formation of dioxygen adducts. Although their evidence supports the premise that the reactions are not surface-catalysed by traces of colloidal metal, Vaska and Tadros have not provided absolute proof for the homogeneity of the catalyses.

## G. SUMMARY

Dioxygen in dioxygen complexes may be bound reversibly or irreversibly. The interest in these compounds lies mainly in their structural properties and the insights which they might give to bonding and coordination requirements in oxyhaemoglobin, oxygenase enzymes and oxidation processes in general. There is good reason to believe that investigations of the coordination of molecules such as $O_2$ and $N_2$ in complexes of transition metals, and an understanding of their reactions, especially those of homogeneous catalysis, will aid in the understanding of the processes by which metallo-enzymes function. This review has dealt specifically with the properties of the chelating dioxygen complexes of the platinum metals.

## REFERENCES

1 M.M. Taqui Khan, R.K. Andal and P.T. Manoharan, *Chem. Commun.*, (1971) 561.
2 B.W. Graham, K.R. Laing, C.J. O'Connor and W.R. Roper, *Chem. Commun.*, (1970) 1272.
3 K.R. Laing and W.R. Roper, *Chem. Commun.*, (1968) 1556, 1568.
4 D.F. Christian and W.R. Roper, *Chem. Commun.*, (1971) 1271.
5 B.E. Cavit, K.R. Grundy and W.R. Roper, *Chem. Commun.*, (1972) 60.
6 K.R. Laing and W.R. Roper, personal communication.
7 L. Vaska and J.W. DiLuzio, *J. Amer. Chem. Soc.*, 83 (1961) 2784.
8 J. Kiji and J. Furawaka, *Chem. Commun.*, (1970) 977.
9 L.W. Fine, M. Grayson and V.H. Suggs, *J. Organometal. Chem.*, 22 (1970) 219.
10 J.T. Mague and G. Wilkinson, *J. Chem. Soc. A*, (1966) 1736.
11 J.A. McGinnety, N.C. Payne and J.A. Ibers, *J. Amer. Chem. Soc.*, 91 (1969) 6301.
12 M. Takesada, H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Jap.*, 41 (1968) 270.

13 L.M. Haines, *Inorg. Chem.*, 10 (1971) 1685.
14 B.R. James and F.T.T. Ng, *Chem. Commun.*, (1970) 908.
15 M.H. Bennett and P.B. Donaldson, *J. Amer. Chem. Soc.*, 93 (1971) 3307.
16 M.C. Baird, D.N. Lawson, J.T. Mague, J.A. Osborn and G. Wilkinson, *Chem. Commun.*, (1966) 129.
17 J. Blum, H. Rosenman and E.D. Bergman, *Tetrahedron Lett.*, (1967) 3665.
18 L. Vaska, *Science*, 140 (1963) 809.
19 P.B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 88 (1966) 3511.
20 S.J. La Placa and J.A. Ibers, *J. Amer. Chem. Soc.*, 87 (1965) 2581.
21 J.A. McGinnety, R.J. Doedens and J.A. Ibers, *Inorg. Chem.*, 6 (1967) 2243.
22 R.W. Horn, E. Weissberger and J.P. Collman, *Inorg. Chem.*, 9 (1970) 2367.
23 J.P. Collman and W.R. Roper, *Advan. Organometal. Chem.*, 7 (1968) 63.
24 J.P. Collman and W.R. Roper, unpublished results quoted by J.P. Collman, F.D. Vastine and W.R. Roper, *J. Amer. Chem. Soc.*, 90 (1968) 2282.
25 J.J. Levison and S.D. Robinson, *J. Chem. Soc. A*, (1971) 762.
26 L. Vaska and L.S. Chen, *Chem. Commun.*, (1971) 1080.
27 M.S. Weininger, I.F. Taylor and E.L. Amma, *Amer. Chem. Soc. Nat. Meet., 162nd, Washington, D.C. Abstr.*, INORG (1971) 176.
28 C.K. Brown and G. Wilkinson, *Chem. Commun.*, (1971) 70.
29 G.R. Clark, C.A. Reed, W.R. Roper, B.W. Skelton and T.N. Waters, *Chem. Commun.*, (1971) 758.
30 V.J. Choy and C.J. O'Connor, *J. Chem. Soc. Dalton*, (1972) in the press.
31 H. van Gaal, H.G.A. Cuppers and A. Van der Ent, *Chem. Commun.*, (1970) 1694.
32 M.A. Bennett and D.L. Milner, *J. Amer. Chem. Soc.*, 91 (1969) 6983.
33 J. Valentine, D. Valentine, Jr. and J.P. Collman, *Inorg. Chem.*, 10 (1971) 219.
34 L. Vaska and D.L. Catone, *J. Amer. Chem. Soc.*, 88 (1966) 5324.
35 A. Sacco, M. Rossi and C.F. Nobile, *Chem. Commun.*, (1966) 589.
36 J.A. McGinnety and J.A. Ibers, *Chem. Commun.*, (1968) 235.
37 L. Vaska, L.S. Chen and W.V. Miller, *J. Amer. Chem. Soc.*, 93 (1971) 6671.
38 N.W. Terry, E.L. Amma and L. Vaska, *J. Amer. Chem. Soc.*, 94 (1972) 653.
39 S. Otsuka, A. Nakamura and Y. Tatsuno, *Chem. Commun.*, (1967) 836.
40 S. Otsuka, A. Nakamura and Y. Tatsuno, *J. Amer. Chem. Soc.*, 91 (1969) 6994.
41 C.D. Cook and G.S. Jauhal, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 31.
42 K. Sonogashira and N. Hagihara, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, 22 (1965) 165.
43 R. Ugo, G. La Monica, F. Cariati, S. Cenini and F. Conti, *Inorg. Chim. Acta*, 4 (1970) 390.
44 T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi and N. Hagihara, *Chem. Commun.*, (1969) 743.
45 E.W. Abel, J.M. Pratt and R. Whelan, *Chem. Commun.*, (1971) 449.
46 (a) D.L. Diemente, B.M. Hoffman and F. Basolo, *Chem. Commun.*, (1970) 467; (b) G.A. Rodley and W.T. Robinson, *Nature*, 235 (1972) 438.
47 J.F. Drake and R.J.P. Williams, *Nature*, 182 (1958) 1084; M.J. Cowen, J.M.F. Drake and R.J.P. Williams, *Discuss. Faraday Soc.*, 27 (1959) 217.
48 K. Takao, Y. Fujiwara, T. Imanaka, M. Yamamoto, K. Hirota and S. Teranishi; *Bull. Chem. Soc. Jap.*, 43 (1970) 2249.
49 K. Hirota, M. Yamamoto, S. Otsuka, A. Nakamura and Y. Tatsuno, *Chem. Commun.*, (1968) 533.
50 J.A. Ibers and S.J. La Placa, *Science*, 145 (1964) 920.
51 D. Schwarzenbach, *Inorg. Chem.*, 9 (1970) 2391.
52 B.M. Hoffman, D.L. Diemente and F. Basolo, *J. Amer. Chem. Soc.*, 92 (1970) 61.
53 W.P. Schaefer, R.E. Marsh and G.G. Christoph, *Inorg. Chem.*, 8 (1969) 291.
54 J.S. Griffith, *Proc. Roy. Soc., Ser. A*, 235 (1956) 23.
55 A.E. Martell and M. Calvin, *Chemistry of Metal Chelate Compounds*, Prentice-Hall, Englewood Cliffs, N.J., 1952, p. 352.
56 S.C. Abrahams, *Quart. Rev., Chem. Soc.*, 10 (1956) 407.
57 H.K. Higginbotham, *Diss. Abstr.*, (1965) 2779.
58 J.A. Connor and E.A.V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, 6 (1964) 279.
59 N.W. Alcock, *Chem. Commun.*, (1966) 536.

60 N.G. Vannerberg, *Acta Crystallogr.*, 18 (1965) 449.
61 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd edn., Wiley, London, 1966, p. 91.
62 J. Chatt and L.A. Duncanson, *J. Chem. Soc., London*, (1953) 2939.
63 M.J.S. Dewar, *Bull. Soc. Chim. Fr.*, 18 (1951) C71.
64 D.M.P. Mingos, *Nature*, 230 (1971) 154.
65 R. Mason, *Nature*, 217 (1968) 543.
66 J.P. Collman, M. Kubota and J.W. Hosking, *J. Amer. Chem. Soc.*, 89 (1947) 4809.
67 S. Fallab, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 496.
68 H. Taube, in D. Rittenberg (Ed.), *Oxygen, Proceedings of a Symposium, sponsored by the N.Y. Heart Foundation*, Little, Brown, Boston, 1965, p. 29.
69 J.P. Collman, *Accounts Chem. Res.*, 1 (1968) 136.
70 (a) N.H.B. Stiddard and R.E. Townsend, *Chem. Commun.*, (1969) 1372; (b) J.J. Levison and S.D. Robinson, *Chem. Commun.*, (1967) 198.
71 C.D. Cook and G.S. Jauhal, *J. Amer. Chem. Soc.*, 89 (1967) 3066.
72 P.J. Hayward, D.M. Blake, G. Wilkinson and C.J. Nyman, *J. Amer, Chem. Soc.*, 92 (1970) 5873.
73 G. Wilke, H. Schott and P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 92.
74 J.P. Birk, J. Halpern and A.L. Pickard, *J. Amer. Chem. Soc.*, 90 (1968) 4491.
75 J.P. Birk, J. Halpern and A.L. Pickard, *Inorg. Chem.*, 7 (1968) 2672.
76 J. Halpern and A.L. Pickard, *Inorg. Chem.*, 9 (1970) 2798.
77 S. Takabashi, K. Sonogashira and N. Hagihara, *Nihon Kagaku Zasshi*, 87 (1966) 610.
78 B.W. Graham, K.R. Laing, C.J. O'Connor and W.R. Roper, *J. Chem. Soc. Dalton*,(1972) 1237.
79 S. Otsuka, personal communication.
80 S. Cenini, A. Fusi and G. Capparella, *J. Inorg. Nucl. Chem.*, 33 (1971) 3576.
81 K. Takao, Y. Fujiwara, T. Imanaka and S. Teranishi, *Bull. Chem. Soc. Jap.*, 43 (1970) 1153.
82 K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka and S. Teranishi, *Bull. Chem. Soc. Jap.*, 43 (1970) 3898.
83 V.P. Kurkov, J.Z. Pasky and J.P. Lavigne, *J. Amer. Chem. Soc.*, 90 (1968) 4743.
84 R. Ugo, *Coord. Chem. Rev.*, 3 (1968) 319.
85 A. Fusi, R. Ugo, F. Fox, A. Pasini and S. Cenini, *J. Organometal. Chem.*, 28 (1971) 417.
86 L. Vaska and M.E. Tadros, *J. Amer. Chem. Soc.*, 93 (1971) 7099.