

CHELATING DIOXYGEN COMPOUNDS OF THE PLATINUM METALS

V.J. CHOY and CHARMIAN J. O'CONNOR

Chemistry Department, University of Auckland, Auckland (New Zealand)

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ABBREVIATIONS

$\overline{\text{P}}-\text{P}$	=	1, 2-bis(diphenylphosphino) ethane
2=phos	=	<i>cis</i> -1, 2-bis(diphenylphosphino) ethylene
P	=	triphenylphosphine
RuO_2	=	$\text{Ru}(\text{O}_2)(\text{NCS})(\text{NO})(\text{PPh}_3)_2$
RuCO	=	$\text{Ru}(\text{NCS})(\text{CO})(\text{NO})(\text{PPh}_3)_2$
DMG	=	dimethylglyoxime

A. INTRODUCTION

The process whereby low-valent coordination compounds of transition metals are co-ordinated 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	$\begin{array}{c} \text{O} \\ \\ \text{M} - \text{O} \\ \\ \text{O} \end{array}$ IR band (cm^{-1})	Comments	Ref.
$\text{RuCl}_2(\text{AsPh}_3)_2(\text{O}_2)$	$\text{RuCl}_2(\text{AsPh}_3)_3$ 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
$\text{RuX}(\text{NO})(\text{PPh}_3)_2(\text{O}_2)$	The compound is readily formed from the corresponding $\text{RuX}(\text{NO})(\text{PPh}_3)_2$, where $\text{X} = \text{OH}, \text{Br}, \text{I}, \text{NCS}, \text{NCO}, \text{N}_3, \text{CN}$		800–900	A well characterised series of compounds	2
$\text{RuCl}(\text{NO})(\text{PPh}_3)_2(\text{O}_2)$	$\text{RuCl}(\text{NO})(\text{CO})(\text{PPh}_3)_2$ in solution absorbs O_2 readily to give the adduct	Irreversible	875	Well characterised crystalline solid	3
$\text{Ru}(\text{CO})(\text{CNR})(\text{PPh}_3)_2(\text{O}_2)$	$\text{Ru}(\text{CO})(\text{CNR})(\text{PPh}_3)_3 + \text{O}_2$ in solution ($\text{R} = p\text{-tolyl}$)	Can be reversed if heated in EtOH with PPh_3	835	Analytical data confirm formulation	4
$\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{O}_2)$	$\text{Ru}(\text{CO})_2(\text{PPh}_3)_3 + \text{O}_2$ 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
$\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{O}_2)$	$\text{Os}(\text{CO})_2(\text{PPh}_3)_3 + \text{O}_2$ in solution		820	The rate of O_2 uptake is very low. Well characterised	5
$\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{O}_2)$	$\text{OsHCl}(\text{ClO}_4)(\text{NO})(\text{PPh}_3)_2 + \text{NaOH}/\text{MeOH} \rightarrow \text{OsCl}(\text{NO})(\text{PPh}_3)_2 \rightarrow \text{OsCl}(\text{NO})(\text{Et})_2(\text{O}_2)$		ca. 840	Well characterised	6

$\text{RhCl}(\text{CO})(\text{OPPh}_3)_2$ $\text{RhCl}(\text{CO})(\text{PPh}_3)_2(\text{O}_2)?$	$\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ may form a 1:1 adduct with O_2 which enhances autooxidation 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 autooxidation process	7-9
$\text{RhCl}(\text{AsPh}_3)_2(\text{O}_2)$	On passing O_2 into solutions of $\text{RhCl}(\text{AsPh}_3)_3$ in CH_2Cl_2 these become greenish-brown. Olive-brown solids are obtained on addition of Et_2O		Some solvent is coordinated as evidenced by high Cl analysis when sample is prepared in CH_2Cl_2 . The suggested formulation is $\text{RhCl}(\text{AsPh}_3)_2\text{O}_2 \cdot n\text{-CH}_2\text{Cl}_2$	10
$[\text{Rh}(\text{dp})_2(\text{O}_2)]^+ [\text{PF}_6]^-$	The preparation is similar to that of the Iridium analogue	Reversible	The structure has been determined by X-ray analysis	11
$\text{Rh}(\text{PPh}_3)_3(\text{O}_2)$	During the treatment of a solution of phenyl-(1,5-cyclooctadiene)-(triphenylphosphino)-rhodium and PPh_3 with O_2 in toluene, approximately 1 mole of O_2 was absorbed and yellow crystals were deposited		Elemental analysis conforms to a composition $\text{Rh}(\text{PPh}_3)_3(\text{O}_2)$. Diamagnetism seems to suggest a dimeric structure	12
$\text{Rh}(\text{PPh}_3)(\text{AsPh}_3)_2(\text{O}_2)$ $[\text{Rh}(\text{PPh}_3)_2(\text{O}_2)]^+$	Similar procedure $[\text{Rh}(\text{PPh}_3)_2(\text{O}_2)]^+$ (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	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{M} \quad \text{O} \\ \text{(cm}^{-1}\text{)} \end{array}$ IR band	Comments	Ref.
$\text{Rh}^{\text{II}}-\text{O}_2^-?$	$[\text{RhCl}(\text{C}_6\text{H}_{14})_2]_2/\text{Cl}^-/\text{DMA}$ solution readily absorbs O_2 to a 1:1 ratio at ambient conditions The reaction of $\text{RhCl}(\text{PPh}_3)_3$ with O_2 in CH_2Cl_2 yields an adduct which has been reported by three groups of workers	Irreversible	895 (solution IR)	The solution shows an ESR signal thought to be due to $\text{Rh}^{\text{II}}-\text{O}_2^-$ In the most recent study ¹⁵ , the structure of the isolated adduct was determined. This consists of dimeric units $[\text{RhCl}(\text{PPh}_3)_2\text{O}_2]_2$ situated at inversion centres in the crystals. The disordered CH_2Cl_2 molecules are not coordinated to the Rh atoms	14
$\text{Rh}(\text{Cl})(\text{PPh}_3)_2(\text{O}_2)$, $1/2 \text{CH}_2\text{Cl}_2$ (i) $\text{RhCl}(\text{PPh}_3)_2(\text{O}_2) \cdot \text{CH}_2\text{Cl}_2$ (ii) $[\text{RhCl}(\text{PPh}_3)_2(\text{O}_2)]_n$ (iii)			ca. 900 ca. 845 ca. 876		(i) 16 (ii) 15 (iii) 17
$\text{IrX}(\text{CO})(\text{PPh}_3)_2(\text{O}_2)$	$\text{IrX}(\text{CO})(\text{PPh}_3)_2 + \text{O}_2$ solution $\xrightarrow{\text{adduct, where}}$ $\text{X} = \text{Cl, Br, I, N}_3$	$\text{X} = \text{Cl}$, reversible $\text{X} = \text{Br}$ $\text{X} = \text{I}$, irreversible	858 861 862	A well characterised series of compounds. Rate of reaction: $\text{Cl} < \text{Br} < \text{I}$	18--22
$\text{IrCl}(\text{CO})(\text{AsPh}_3)_2(\text{O}_2)$	$\text{IrCl}(\text{CO})(\text{AsPh}_3)_2$ is extremely sensitive toward O_2 compared with $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$			Not described in detail	23, 24
$\text{IrI}(\text{CO})(\text{AsPh}_3)_2(\text{O}_2)$	$\text{IrI}(\text{CO})(\text{AsPh}_3)_2 + \text{O}_2$ benzene $\xrightarrow{\text{adduct,}}$ 2 h		850	Pink crystals, Elemental analysis confirms formulation	25

$\text{IrCl}(\text{CO})\text{L}_2(\text{O}_2)$	Formed from $\text{IrCl}(\text{CO})\text{L}_2$ in chlorobenzene solution at 40°C , where $\text{L} = (p\text{-ClC}_6\text{H}_4)_3\text{P}$, $(p\text{-MeC}_6\text{H}_4)_3\text{P}$, $(p\text{-MeOC}_6\text{H}_4)_3\text{P}$, $(\text{C}_6\text{H}_{11})_3\text{P}$, $(n\text{-C}_4\text{H}_9)_3\text{P}$, Et_3P , Ph_2EtP	Reversible	800–900	Well characterised compounds	26, 27
$\text{Ir}(\text{C}\equiv\text{CR})(\text{CO})(\text{PPh}_3)_2(\text{O}_2)$	The solid $\text{Ir}(\text{C}\equiv\text{CR})(\text{CO})(\text{PPh}_3)_2$ reacts with air or O_2 slowly in the solid but rapidly in solution to afford the dioxygen adduct			Not well characterised	28
$[\text{Ir}(\text{CO})(\text{PPh}_2\text{Me})_3(\text{O}_2)]^+$	The red solution in $\text{CH}_2\text{Cl}_2/\text{EtOH}$ of $[\text{Ir}(\text{CO})(\text{PPh}_2\text{Me})_3]^-[\text{ClO}_4]^-$ 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
$[\text{Ir}(\text{CO})(\text{PPh}_2\text{Et})_3(\text{O}_2)]^+$	Similar procedure	Irreversible	845	Well characterised	29
$\text{IrCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)(\text{O}_2) \cdot \text{C}_6\text{H}_6$	$\text{IrCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4) + \text{O}_2$ in benzene		840	There is a broadened NMR resonance at τ 6.67 due to coordinated ethylene. This is the first known compound containing O_2 and an alkene ligand coordinated 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
$\text{IrCl}(\text{PPh}_3)_3(\text{O}_2)$	$\text{IrCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)(\text{O}_2) + \text{PPh}_3$		849		
$\text{IrCl}(\text{PPh}_3)_2(\text{py})(\text{O}_2)$	$\text{IrCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)(\text{O}_2) + \text{py}$ (py = pyridine)		843		

TABLE 1 (continued)

Dioxygen compound	Formation	Reversibility	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{M} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ IR band (cm^{-1})	Comments	Ref.
$\text{IrCl}(\text{PPh}_3)_2 (\text{O}_2)$	$\text{IrCl}(\text{PPh}_3)_3 + \text{O}_2$ (orange) rapid \longrightarrow adduct		ca. 840	Even under anaerobic conditions it is difficult to obtain $\text{IrCl}(\text{PPh}_3)_3$ and $\text{IrCl}(\text{SbPh}_3)_3$ completely free from O_2	32
$\text{IrCl}(\text{SbPh}_3)_2 (\text{O}_2)$	$\text{IrCl}(\text{SbPh}_3)_3 + \text{O}_2$ (maroon) rapid \longrightarrow adduct		ca. 840		
$\text{Ir}(\text{PPh}_3)_3 (\text{O}_2)$	$\text{Ir}(\text{PPh}_3)_3 + \text{O}_2$ (reddish) fast \longrightarrow $\text{Ir}(\text{PPh}_3)_3 (\text{O}_2)$ (salmon-coloured)	Irreversible	852	The compound is very stable. Well characterised	32, 33
$[\text{Ir}(\text{dp})_2 (\text{O}_2)]^+$	$\text{IrCl}(\text{CO})(\text{PPh}_3)_2 + 2 \text{ dp} \rightarrow [\text{Ir}(\text{CO})(\text{dp})_2] [\text{Cl}]$ adduct $\xrightarrow[\text{heat}]{\text{O}_2}$ $[\text{Ir}(\text{dp})_2] [\text{Cl}]$ (anion = Cl, BPh ₄ , I, ClO ₄ , PF ₆)	Irreversible	845	The crystals of $[\text{Ir}(\text{dp})_2] [\text{Cl}]$ 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
$[\text{M}(\text{2-phen})_2 (\text{O}_2)]^+$	$[\text{M}(\text{2-phen})_2] [\text{A}] + \text{O}_2$ 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(<i>t</i> -BuNC) ₂ (O ₂) Ni(cyclo-C ₆ H ₁₂ NC) ₂ (O ₂) Pd(<i>n</i> -BuNC) ₂ (O ₂)	Ni(<i>t</i> -BuNC) ₄ or 2 + O ₂ Similar reaction Similar reaction	Irreversible Irreversible Irreversible	898 904 893	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
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) Co ^{II} -O ₂ ?	M(PPh ₃) ₄ + O ₂ solution (M = Ni, Pd) The reversible formation at low temperature of a 1:1 dioxygen adduct with cobalt(II) - tetrasulphophthalocyanine has been demonstrated by ESR spectroscopy	Irreversible Irreversible	800-900	Stable Not characterised	41-44 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

^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 $800\text{--}900\text{ cm}^{-1}$; such bands have been assigned to the O—O stretch¹⁸.

The assignment of the infra-red band in the region $800\text{--}900\text{ cm}^{-1}$ has been confirmed for $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{O}_2)$ (ref. 48) and for $\text{M}(\text{O}_2)(t\text{-BuNC})$ ($\text{M} = \text{Ni}, \text{Pd}$) (refs. 40, 49) by isotopic studies. Spectra of the corresponding complexes containing heavy dioxygen showed new bands at $800\text{--}900\text{ cm}^{-1}$ (also additional unassigned bands at $480\text{--}550\text{ cm}^{-1}$). For example, the band* at 856 cm^{-1} for the iridium complex split into three absorption bands at 856, 836 and 808 cm^{-1} . These three bands can be explained in terms of O—O stretching since the dioxygen contains three molecular species, $^{16}\text{O}_2$, $^{16}\text{O}\text{--}^{18}\text{O}$ and $^{18}\text{O}_2$. 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 cm^{-1} .

The implication of this excellent agreement is that the band near 900 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.

$\text{M}(\text{O}_2)(t\text{-BuNC})_2$ ($\text{M} = \text{Ni}, \text{Pd}$) have been studied in a similar way⁴⁹. The nickel complex shows a band at 898 cm^{-1} (isotopic substitution gave 898, 873, 848 cm^{-1}) and for the palladium complex it is at 893 cm^{-1} (isotopic substitution gave 893, 868, 837 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 $800\text{--}900\text{ cm}^{-1}$ 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 ($\text{M} = \text{metal}$) 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—O₂ ($\text{M} = \text{metal}$) force constant.

* 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-workers²¹, who measured the O—O bond lengths for $\text{IrX}(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$. 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 peroxy (O_2^{2-}) and superoxy (O_2^-) ligands. Platinum metal tertiaryphosphine dioxygen complexes^{11, 20, 36, 50} and chromium, molybdenum and titanium peroxy complexes⁵¹ have the dioxygen group symmetrically bonded (Fig. 1 (a)), whereas cobalt(III) amine and Schiff base peroxy and superoxy 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.

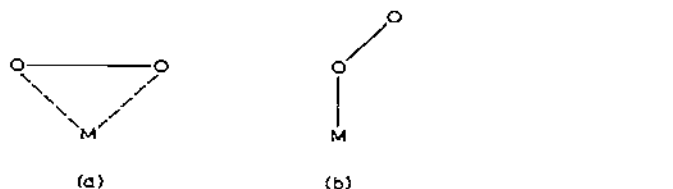


Fig. 1. The π -bonded (a) and non-linear (b) metal—dioxygen geometries.

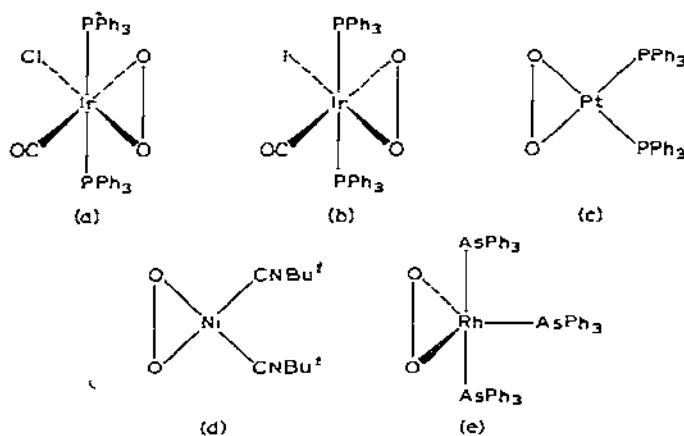


Fig. 2. Examples of dioxygen complexes.

The equivalence of the oxygen atoms is consistent with Griffith's⁵⁴ model of the π -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 view⁵⁵ 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
$K_2[Ti(O_2)(C_7H_3O_4N)_2] \cdot 5H_2O$	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
$[Pt(PPh_3)_2(O_2)] \cdot 1.5 C_6H_6$	1.45	44

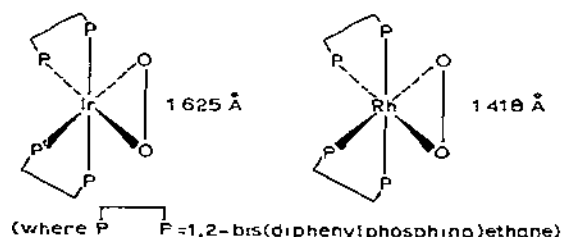


Fig. 3. Structures of $[M(O_2)(P-P)_2]^+$ cations ($M = Rh, Ir$).

(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).

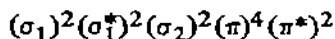
The dioxygen adduct formed from chlorotris(triphenylphosphine) rhodium(I) is $\{\text{RhCl}(\text{O}_2)(\text{PPh}_3)_2\}_2$. The structure¹⁵ contains dimeric units situated at inversion centres in the crystal. The overall geometry of each rhodium atom can be described in terms of a distorted trigonal 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.

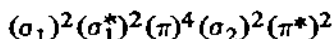
Ibers and co-workers^{11, 36} discovered the remarkable trend in the O—O bond lengths that can be seen for the series of iridium complexes in Table 2. Both the O—O distance and the tendency to bind dioxygen increase as the ancillary ligands become more electron-releasing ($\text{dp} > \text{PPh}_2\text{Et} > \text{PPh}_3$ and $\text{I} > \text{Cl}$).

D. THE BONDING IN DIOXYGEN COMPOUNDS

The electron configuration⁶¹ of the dioxygen molecule might be either



or



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 π -bonding scheme of Chatt and Duncanson⁶² and Dewar⁶³ used to explain the coordination of the

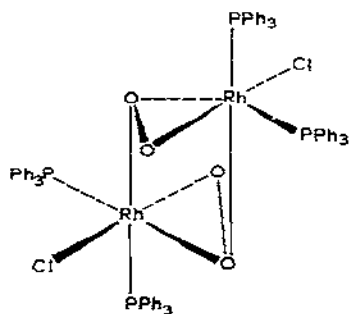


Fig. 4. The structure of $\{\text{RhCl}(\text{O}_2)(\text{PPh}_3)_2\}_2$.

ethylene molecule to platinum in Zeiss's salt. A σ -bond is formed by donation from a filled π -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 π^* -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 Griffith⁵⁴ for oxygenated haem. This theory has been discussed further by Ibers²¹ 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 σ -bond and one π -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 π -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 π^* -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 π -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 π -bonding orbitals to form a σ -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 π -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.

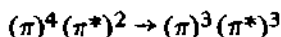
The two complexes $IrX(CO)(PPh_3)_2(O_2)$ ($X = Cl$ or I) are expected to show changes in uptake properties and molecular geometry analogous to those observed above. The energy

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 Mingos⁶⁴ 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 π and π^* (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 π (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, Mason⁶⁵ compared the coordinated dioxygen with the excited states of dioxygen gas. If the bonding of O_2 is similar to the bonding in other π -complexes, the dioxygen electron configuration would be similar to the one corresponding to the excitation



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 felt¹¹ 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.

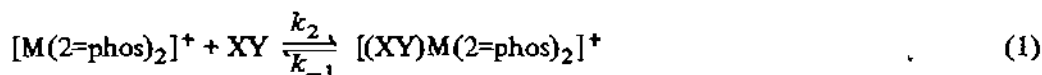
In $\{RhCl(O_2)(PPh_3)_2\}_2$, the Rh— O_2 bonding¹⁵ can be rationalised using the conventional molecular orbital scheme for dioxygen. Within this framework the O_2 has an electron configuration $(\pi^*)^2 (\pi^*)^0$ rather than the ground state electron configuration $(\pi^*)^1 (\pi^*)^1$. The bonding within the rhodium—oxygen—oxygen triangle is then described by ligand-to-metal donation from a fully occupied π -orbital and back-donation to the empty π^* -orbital. The full π^* -orbital of the μ -bonded dioxygen molecule is perpendicular to the rhodium—oxygen—oxygen triangle and is available for the formation of a σ -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 made³⁷. Vaska et al. studied the reactions in eqn. (1) and the results show an unexpected reactivity order $Co > Ir > Rh$.



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

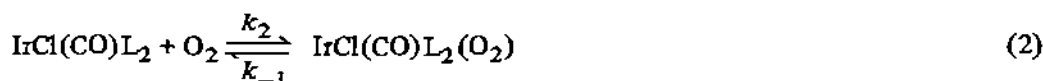
The unmistakable order of attraction of the univalent cations to dioxygen, $Co \gg Ir > Rh$, is shown in Table 3. It was suggested³⁷ that the reactivity of the $d^8 M^I$ complexes is directly dependent on their field stabilisation energies. This could be a guide for predicting the relative energetics 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 ($M^{-1} \text{sec}^{-1}$)	ΔH_2^\ddagger (kcal.mole ⁻¹)	ΔS_2^\ddagger (e.u.)
Co	1.7×10^4	3.4	-28
Rh	0.12	11.6	-24
Ir	0.47	6.5	-38

Vaska and Chen²⁶ have also found that the rates of dioxygen addition



(where L = tertiary phosphine)

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

$$K_2 = k_2/k_{-1} = [\text{IrCl}(\text{CO})\text{L}_2(\text{O}_2)] / [\text{IrCl}(\text{CO})\text{L}_2][\text{O}_2] \quad (3)$$

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*- $\text{IrCl}(\text{CO})\text{L}_2$ in chlorobenzene at 40°C

L	$k_2 \times 10^2$ ($M^{-1} \cdot \text{sec}^{-1}$)	ΔH_2^\ddagger (kcal. mole $^{-1}$)	ΔS_2^\ddagger (e.u.)
1 $(\text{C}_6\text{H}_{11})_3\text{P}$	0.127	9.5	-42
2 $(p\text{-ClC}_6\text{H}_4)_3\text{P}$	3.10	10.8	-31
3 $(\text{C}_6\text{H}_5)_3\text{P}$	9.93	9.5	-33
4 $(\text{C}_6\text{H}_5)_3\text{As}$	14.2	8.1	-37
5 $(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)\text{P}$	14.2	8.4	-36
6 $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$	21.6	9.3	-32
7 $(\eta\text{-C}_4\text{H}_9)_3\text{P}$	26.1	9.0	-33
8 $(\text{C}_2\text{H}_5)_3\text{P}$	33.8	8.5	-34
9 $(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$	48.4	8.5	-33

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

where k_2 = rate of oxygenation (second-order rate constant) and $\sigma(\text{X})$ = Hammett constant for the *para* substituent in the arylphosphine ligand $(p\text{-XC}_6\text{H}_4)_3\text{P}$.

Recently we have studied³⁰ the uptake of dioxygen by $[\text{Ir}(\text{CO})(\text{PPh}_2\text{CH}_3)_3][\text{ClO}_4]$ in acetone and dichloromethane, and the rate law fits the expression

$$-d[\text{Ir}(\text{CO})(\text{PPh}_2\text{CH}_3)_3^+] / dt = k_1 [\text{Ir}(\text{CO})(\text{PPh}_2\text{CH}_3)_3^+][\text{O}_2]$$

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

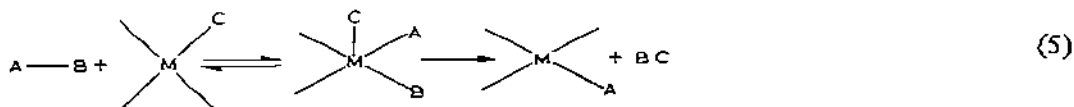
TABLE 5

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

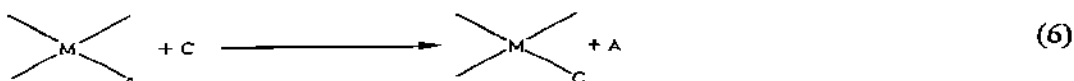
Solvent	k_2 ($M^{-1} \cdot sec^{-1}$)	ΔH_2^\ddagger (kcal mole $^{-1}$)	ΔS_2^\ddagger (e.u.)
Acetone	0.33	7.99	-34.0
Dichloromethane	0.61	9.71	-27.1

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 sites⁶⁶. Such processes can be imagined to embody as discrete steps oxidative addition, migratory insertion, and reductive elimination.



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



Reactions between singlet molecules and free (triplet) dioxygen usually experience high activation energies⁶⁷ because of the problem of spin conservation⁶⁸. 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

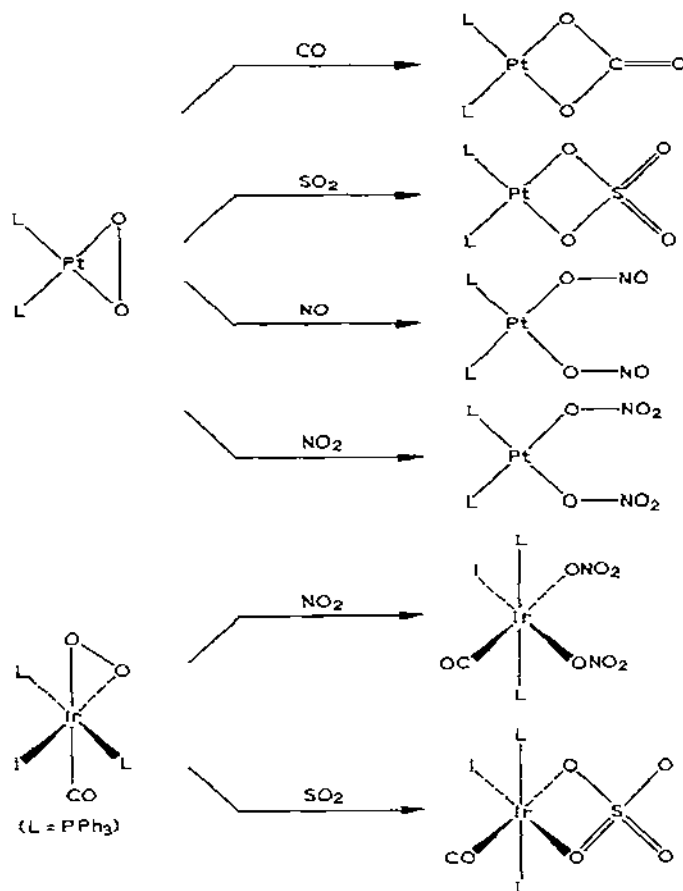
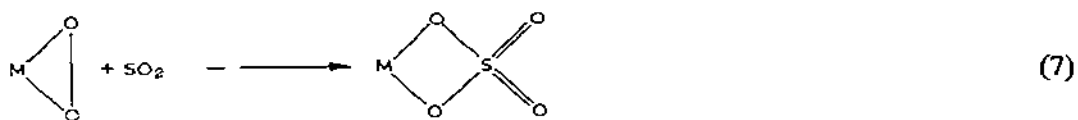
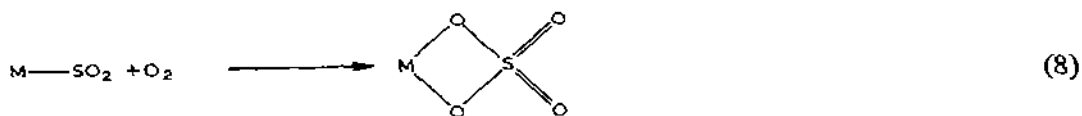


Fig. 5. Reactions of dioxygen compounds with non-metal oxides^{25, 69, 70}.

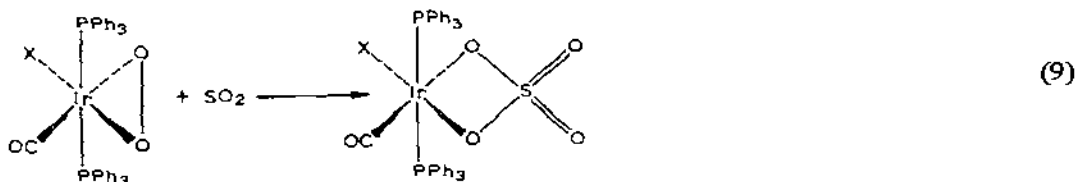


is believed to be a reaction characteristic of all dioxygen complexes. In several instances free dioxygen also reacts with the metal-SO₂ complexes (eqn. (8)).

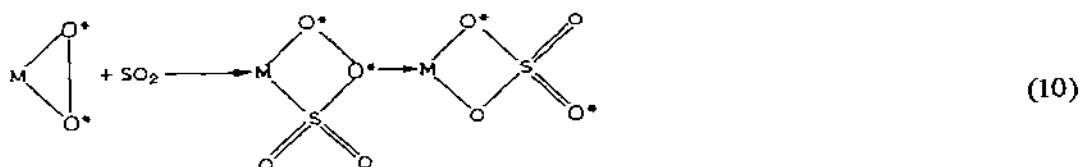


but this does not always happen.

The mechanism of eqn. (9) has been partially clarified through a study employing ^{18}O isotopic labelling²².



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.



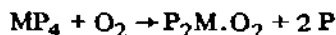
On the basis of infra-red studies²² and the apparent coordinative saturation, chelated sulphate structures have been assigned to all these complexes³³.

Similar reactions of dioxygen complexes with NO_2 , CO and NO to give dinitrates, carbonates and dinitrites 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 synthesise²⁵ an extended range of nitro, nitrate 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 ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{P} = \text{PPh}_3$) react with dioxygen to form dioxygen compounds^{41, 73}, viz.



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-workers⁷⁴. 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.

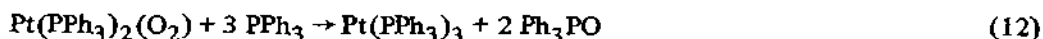
The reaction with dioxygen which yields the complex $Pt(PPh_3)_2(O_2)$, in accord with



has the rate law

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

where $k_1 = 2.6 \pm 0.1 M^{-1} \cdot sec^{-1}$. The rate of this reaction was unaffected by addition of up to $3 \times 10^{-3} M$ excess phosphine but, confirming the earlier work⁷³, it was found that $Pt(PPh_3)_2(O_2)$ does react further with excess phosphine to regenerate $Pt(PPh_3)_3$, i.e.

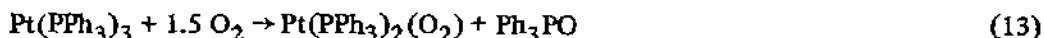


so that a catalytic cycle for the oxidation of triphenylphosphine to triphenylphosphine oxide is established. The second reaction has the rate law

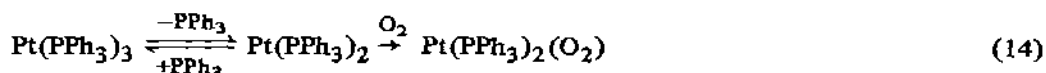
$$d[Pt(PPh_3)_3]/dt = k_2 [Pt(PPh_3)_2(O_2)] [PPh_3]$$

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

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



or



since $Pt(PPh_3)_2$ is known to coexist with $Pt(PPh_3)_3$ in solution⁷⁵.

A study of the rate of consumption of dioxygen⁷⁶ 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 $[\text{PPh}_3]$.

The general features of the mechanism for the $\text{Pt}(\text{PPh}_3)_3$ -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" sequence⁷⁴ shown in Fig. 6 remain to be fully elucidated.

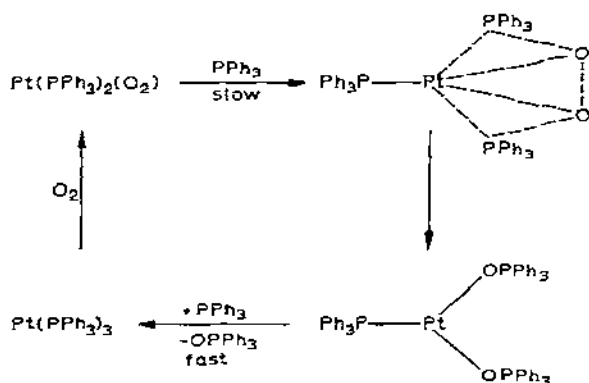


Fig. 6. Scheme for catalysed oxidation of triphenylphosphine by $\text{Pt}(\text{PPh}_3)_3$.

The above observations have been extended to dioxygen complexes of different coordination number and geometry^{2,78}. $\text{Ru}(\text{NCS})(\text{CO})(\text{NO})(\text{PPh}_3)_2$ and $\text{Ru}(\text{O}_2)(\text{NCS})(\text{NO})(\text{PPh}_3)_2$ 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 $\text{II} \rightarrow \text{III} \rightarrow \text{IV} \rightarrow \text{V} \rightarrow \text{II}$. The rate equations for the mechanism are

$$-\frac{d[\text{PPh}_3]}{dt} = \frac{k_1 K_2 [\text{RuO}_2] [\text{P}]}{1 + K_2 [\text{P}]}$$

for the dioxygen compound, and

$$-\frac{d[\text{PPh}_3]}{dt} = \frac{k_1 K_1 K_2 [\text{RuCO}] [\text{O}_2] [\text{P}]}{[\text{CO}] + K_1 [\text{O}_2] + K_1 K_2 [\text{P}] [\text{O}_2]}$$

for the carbonyl compound, where $\text{P} = \text{PPh}_3$, $\text{RuO}_2 = \text{Ru}(\text{O}_2)(\text{NCS})(\text{NO})(\text{PPh}_3)_2$, and $\text{RuCO} = \text{Ru}(\text{NCS})(\text{CO})(\text{NO})(\text{PPh}_3)_2$. Analysis of the data on the basis of these equations yields $k_1 = 1.26 \pm 0.03 \times 10^{-2} \text{ sec}^{-1}$ and $K_2 = 1.63 \pm 0.04 \text{ M}^{-1}$.

In contrast to the rate law observed by Halpern and co-workers⁷⁴, where the rate of oxidation of triphenylphosphine by $\text{Pt}(\text{O}_2)(\text{PPh}_3)_2$ depended on $[\text{PPh}_3]$, the above two rate equations require that the reciprocal of the rate depends on $[\text{PPh}_3]^{-1}$. Similar in-

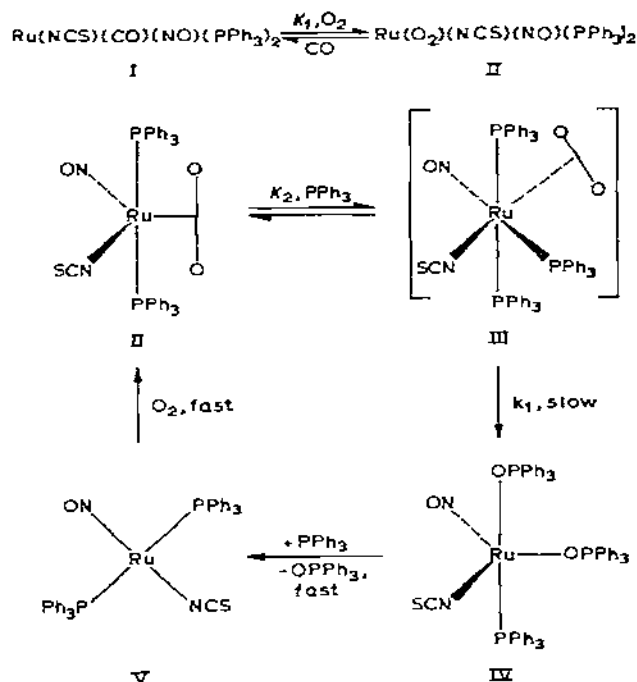


Fig. 7. Scheme for catalysed oxidation of triphenylphosphine by $\text{Ru(NCS)(CO)(NO)(PPh}_3)_2$ and $\text{Ru(O}_2\text{)(NCS)(NO)(PPh}_3)_2$.

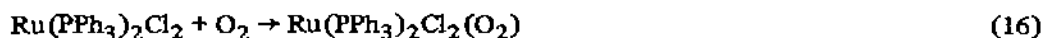
verse dependence has also been observed for the homogeneous oxidation of *t*-butylisocyanide using $\text{Ni}(t\text{-BuNC})_4$ as catalyst⁷⁹.

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 reported¹. $\text{Ru(O}_2\text{)Cl}_2(\text{AsPPh}_3)_3$ 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.

$\text{Ru(PPh}_3)_3\text{Cl}_2$ is an effective catalyst for the oxidation of PPh_3 to OPPh_3 at room temperature and atmospheric pressure⁸⁰. For example, at 20°C in benzene (20 ml), $\text{Ru(PPh}_3)_3\text{Cl}_2$ (0.15 mM) oxidised PPh_3 (1.5 mM) 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





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 $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ 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}.

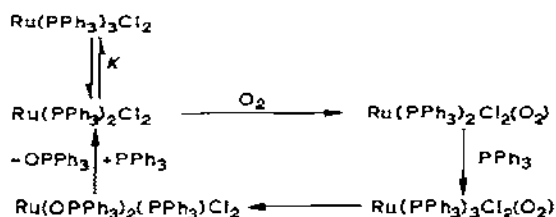


Fig. 8. Postulated scheme for catalysed oxidation of triphenylphosphine by $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$.

Japanese workers⁸¹ have studied the oxidation reactions of styrene and triphenylphosphine catalysed by various iridium complexes. Triphenylphosphine is oxidised easily by the Vaska complexes $(\text{IrX}(\text{CO})(\text{PPh}_3)_2)$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$ to afford triphenylphosphine oxide catalytically, and the catalyst is recovered with decomposition after the reaction. The yield increases in the order: $\text{X} = \text{Cl} < \text{I} < \text{Br}$. 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 Ibers²⁰ 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-

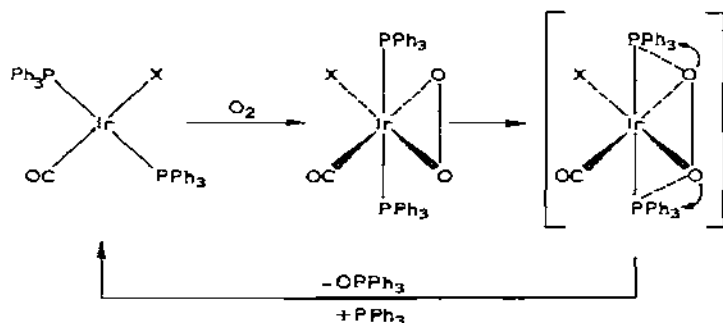


Fig. 9. Postulated scheme for catalysed oxidation of triphenylphosphine by Vaska complexes $(\text{IrX}(\text{CO})(\text{PPh}_3)_2)$.

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 complexes⁸¹ 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: $\text{X} = \text{I} < \text{Br} < \text{Cl}$ 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 $\text{RhX}(\text{PPh}_3)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), especially $\text{RhCl}(\text{PPh}_3)_3$, can oxidise styrenes in the presence of oxygen to produce carbonyl compounds⁸². 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 $\text{RhCl}(\text{PPh}_3)_2$ which is derived from the dissociation of $\text{RhCl}(\text{PPh}_3)_3$ 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 rhodium⁶⁶ and iridium⁸³ phosphine complexes. Although in the first paper on this subject⁶⁶ 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 mixture⁸⁵. It follows that the postulated unique dioxygen activation by these complexes in hydrocarbon oxidation gen-

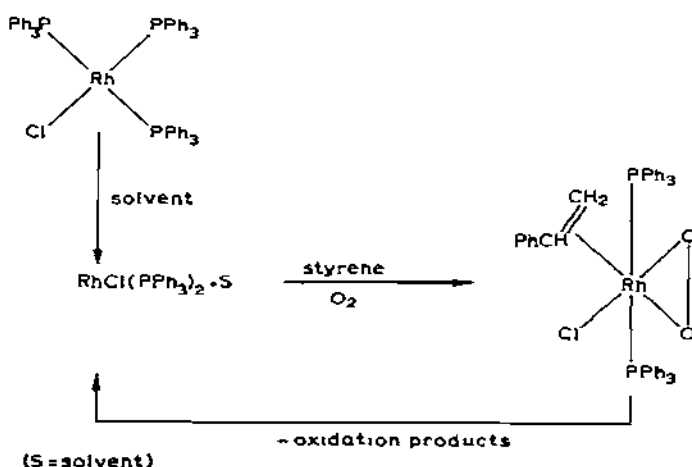


Fig. 10. Postulated scheme for catalysed oxidation of styrene by $\text{RhCl}(\text{PPh}_3)_3$.

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 Tadros⁸⁶. 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.

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