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Mononuclear d^7 complexes of platinum metals

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CONTENTS

ABBREVIATIONS

acacen	ethylenebis(acetylacetoneimine)
bipy	2,2′-bipyridyl
Bu	*n*-butyl
Bu^t	*tert*-butyl
create	creatinine
cod	cyclooctadiene
Cy	cyclohexyl
dbc	3,5-di-*tert*-butylcatecholate
diamsar	1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane

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dmgH	dimethylglyoxime monoanion
dpc	dipicolinic acid
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
ESR	electron spin resonance
ESCA	electron spectroscopy for chemical analysis
Et	ethyl
IR	infrared
Me	methyl
NMR	nuclear magnetic resonance
o-MeCys	cysteinate methylester
pc	phthalocyanine
pd	pentane-2,4-dionate
Ph	phenyl
phen	1,10-phenanthroline
psp	polymeric diphenylbenzylphosphine
pz	pyrazolyl
salen	N,N′-ethylenebis(salicylideniminate)
s-bqdi	*semi-o*-benzoquinonediimine
SCF-Xa-SW	self-consistent field-Xa-scattered wave
s-disn	*semi*-diiminosuccinonitrile
sep	1,3,6,8,10,13,6,19-octaazabicyclo[6.6.6]icosane
siphos	tris(trimethylsilylmethyl)phosphine
tacn	1,4,7-triazacyclononane
tmpp	tris(2,4,6-trimethoxyphenyl)phosphine
TMP	tetramesitylporphyrin(dianion)
TPP	tetraphenylporphyrin(dianion)
tren	2,2′,2″-triaminotriethylamine
ttcn	1,4,7-trithiacyclononane
XPS	X-ray photoelectron spectroscopy

A. INTRODUCTION

Coordination compounds of d^7 platinum metal ions have so far attracted less attention than those of d^5, d^6 metal ions of ruthenium and osmium, and d^6, d^8 metal ions of rhodium, iridium, palladium and platinum. There is a marked contrast in the behaviour of coordination compounds of d^7 metal ions between iron, cobalt and nickel on one hand and those of the platinum metals on the other. d^7 Platinum metal species are generally found in dinuclear systems. Dimerization is obtained either by direct metal–metal interaction or by metal–ligand–ligand–metal interaction. Assuming that metal–metal interaction requires location of the unpaired electron on the metal centre and that metal–ligand–ligand–metal interaction requires location of the unpaired electron on the ligand, then localization of the unpaired

electron either on the metal or on the ligand precludes stable monomeric d^7 platinum metal complexes. Spectroscopic studies of monomeric d^7 complexes reveal delocalization of the unpaired electron between the metal and the ligand. This hypothesis explains the stability of a number of monomeric d^7 platinum metal complexes.

Mononuclear d^7 platinum metal complexes have received only limited coverage [1–17] in books and periodicals on inorganic and organometallic chemistry; they are discussed here in much greater detail. The literature has been divided into four categories which are presented in the following sections. Section B describes the general preparative routes and structures of mononuclear compounds. Section C presents the reactivity of these complexes. Sections D and E provide the magnetic and spectroscopic data available on mononuclear d^7 complexes of platinum metals. Emphasis is primarily in the areas of magnetic susceptibility measurements, electron spin resonance (ESR) spectroscopy, vibrational spectroscopy, electronic absorption spectroscopy and X-ray photoelectron spectroscopy (XPS). Catalytic applications of these complexes are discussed in section F.

B. PREPARATION AND STRUCTURE

(i) Ruthenium(I) complexes

Very few monomeric complexes of ruthenium(I) are known. There are a number of early reports, without real evidence to support the claims, of the existence of RuCl [18–21], RuBr and RuI [19] as solution species. Gamma-ray irradiation of $K_4[Ru(CN)_6]\cdot 3H_2O$ single crystals at 77 K or X-ray irradiation at room temperature is reported to produce low spin ruthenium(I) species $[Ru(CN)_5(NC)]^{5-}$ and $[Ru(CN)_4(NC)_2]^{5-}$ [22]. Symon and Wilkinson [23] suggested that the cyanide ligand is merely tilted off axis, rather than rotated. Other ruthenium(I) species including $[Ru(CN)_5(H_2O)]^{4-}$, $[Ru(CN)_5X]^{5-}$ and $[Ru(CN)_4X_2]^{5-}$ (X = Cl or Br) have been detected upon γ-irradiation of $K_4[Ru(CN)_6]\cdot 3H_2O$ in alkali metal halide host lattices [23].

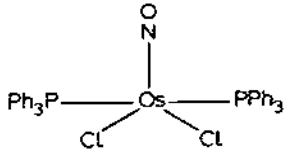
The bipyridine complex $[Ru(bipy)_3]^+$ is generated by controlled potential reduction of $[Ru(bipy)_3]^{2+}$ at -1.42 V [24–27]. The absorption spectrum of $[Ru(bipy)_3]^+$ is consistent with the formation of charged localized ruthenium(II)–bipyridine radical species and it is better formulated as $[Ru^{II}(bipy)_2(bipy)^-]^+$.

The nitrosyl complexes can be reduced chemically or electrochemically to give one-electron reduction products. The oxidation state assignment for transition metal nitrosyl complexes depends on the formalism used regarding the NO ligand. Nitric oxide could lose or gain one electron in its bonding interaction with transition metal ions to give the complexes of NO^+ or NO^- respectively. The NO ligand is assigned as NO^+ for the complexes discussed in this article. The black complex $[Ru(O)Cl(bipy)_2]I$ is prepared by the reaction of $[Ru(NO)Cl(bipy)_2](PF_6)_2$ with $[NBu_4]I$. The reduction of $[Ru(NO)(bipy)_2(CH_3CN)]^{3+}$ electrochemically yields $[Ru(NO)(bipy)_2(CH_3CN)]^{2+}$. These reduced ruthenium(I) nitrosyl complexes are

stable in deaerated acetonitrile, acetone or water solutions, but they react slowly with oxygen in solution [28, 29]. Nitrosyl chloride reacts with hydrated ruthenium trichloride in the presence of excess PPh_3 to give $[Ru(NO)Cl_2(PPh_3)]_2$, $NH_4[Ru(NO)Cl_5]$ and NH_4Cl. The complex $[Ru(NO)Cl_2(PPh_3)]_2$, on refluxing with excess PPh_3 in dichloromethane, yields $(Ru(NO)Cl_2(PPh_3)_2]$ [30]. The formation of $[Ru(NO)\ Cl_2(PPh_3)_2]$ as a minor side product in the preparation of $[Ru(NO)Cl_3(PPh_3)_2]$ has also been reported [31]. Reaction of NOCl with $RuCl_3 \cdot 3H_2O$ in the presence of excess $AsPh_3$ affords a greenish-yellow complex $[Ru(NO)Cl_2(AsPh_3)_2]$ and NH_4Cl [32]. On decreasing the amount of L (L = PPh_3, $AsPh_3$), the above reactions result in the formation of the complexes $[Ru(NO)Cl_3L_2]$. The possible structure of $[Ru(NO)Cl_2(PPh_3)]_2$ would be square pyramidal chloro-bridged [30]. Complexes of the type $[Ru(NO)I_2L_2]$ have been prepared by reaction of $[Ru(NO)I_2]_n$ with L (L = py, 1/2bipy, $AsMePh_2$) [33]. These complexes are essentially diamagnetic and are, therefore, tentatively formulated as the metal–metal bonded dimer $[Ru(NO)I_2L_2]_2$. The ruthenium(I) species $[RuCl(dppp)_2]$ has been prepared by the electroreduction of $[RuCl(dppp)_2](PF_6)$. $[Ru(NO)(dppp)_2](PF_6)$ also undergoes two-electron reversible reductions [34,35]. A report of $[RuClL_3]$ (L = PPh_3, $AsPh_3$) and $[RuBr(PPh_3)_3]$ is erroneous [36]; the complexes are hydridoruthenium(II) species [37].

(ii) Osmium(I) complexes

Only four complexes of osmium(I) have been reported so far. Electron bombardment of $[Os(CN)_6]^{4-}$ in a KCl matrix at 77 K results in the formation of $[Os(CN)_5]^{4-}$, detected by ESR spectroscopy [38]. The bright yellow osmium(I) hexamine complex $[Os(NH_3)_6]Br$ has been synthesized by the reduction of $[Os(NH_3)_6]Br_3$ with potassium in liquid ammonia [39]. The reaction of nitrosyl halides NOX (X = Cl or Br) with $OsCl_2(PPh_3)_3$ in the presence of triphenylphosphine in dichloromethane affords osmium(I) nitrosyl complexes $[Os(NO)ClX(PPh_3)_2]$ (X = Cl or Br) [40]. IR studies confirm the presence of a linear nitrosyl group in these complexes. Combining the rules which have been suggested by Ibers et al. [41] and Hoffmann et al. [42] for pentacoordinated nitrosyl complexes, with the empirical rules of stereochemistry, the geometry about the osmium atom can be best described as distorted trigonal bipyramid with axial phosphine ligands and two chloro ligands and the NO group occupying the equatorial plane (the molecule (I) has C_{2v} symmetry [43]. These pentacoordinated linear $\{OsNO\}^7$ complexes can be regarded as complexes between Os(I) and NO^+.

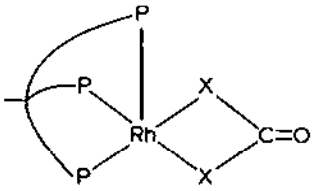


(I)

(iii) Rhodium(II) complexes

There are a number of reports of compounds believed to contain Rh(II), namely RhO [44], $Na_2[Rh(SO_3)_2]\cdot 2H_2O$ [45,46], "$3RhCl_2\cdot 2tren\cdot HCl\cdot 6H_2O$" [47], $RhCl_2$ [48,49], RhS [50] and $[RhCl(bipy)]X\cdot 2H_2O$ ($X=NO_3$, ClO_4) [51], but the significance of the oxidation state of the rhodium is uncertain.

A number of rhodium(II) complexes with sulphur donor ligands have been reported. Reaction of $Rh_2(O_2CCH_3)_4$ with sodium maleneonitriledithiolate in the presence of $(n\text{-}Bu_4N)OH$ in methanol gives a red solution and a green salt containing the anion $[Rh\{S_2C_2(CN)_2\}]^{2-}$ [52]. The reactions of $Rh_2(O_2CCH_3)_4$ with amino acids containing free Sh groups (L = 1-cystein, 1-cystein methyl ester and 1-penicillamine) yield monomeric square planar rhodium(II) complexes $[RhL_2]$. The absence of the ν(S–H) band at about 2500 cm^{-1}, present in the free ligands, indicates the formation of S–M bonds in all these complexes [53]. The $[Rh(ttcn)_2]^{3+}$ (ttcn = 1,4,7-trithiacyclononane) cation shows two reversible one-electron reductions at −0.64 and −1.0 eV vs. Fc^0/Fc^+ in acetonitrile assigned to the Rh^{III}/Rh^{II} and Rh^{III}/Rh^{I} redox complexes, respectively. Electrochemical reduction of $[Rh(ttcn)_2]^{3+}$ at −0.75 V [54] and at −0.8 V [55] affords the reduced product $[Rh(ttcn)_2]^{2+}$. Electrochemical reduction of $[Rh(ttcn)_2]^{3+}$ in CH_3NO_2 at a glassy carbon electrode at −0.5 V also gives the straw-coloured complex $[Rh(ttcn)_2]^{2+}$ [56]. One-electron reduction of $[(triphos)Rh(X_2CO)](BPh_4)$ (triphos = $MeC(CH_2PPh_2)_3$, X = S or Se) and $[(triphos)Rh(S_2CNPh)](BPh_4)$, gives the stable, square pyramidal rhodium(II) complexes [(triphos)Rh(X_2CO)] (II) and [(triphos)Rh(S_2CNPh)], respectively [57,58].



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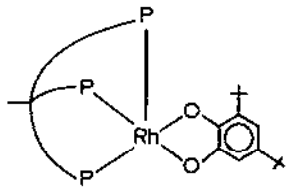
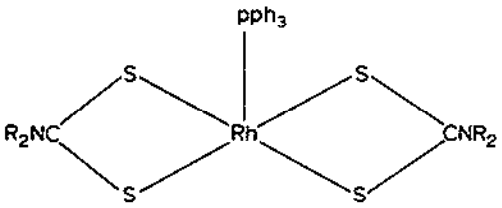


(III)

The rhodium(II) species [(triphos)Rh(dbc)] (III) (dbc = 3,5-di-*tert*-butylcatecholate) has been generated by the electrochemical reduction of $[(triphos)Rh(dbc)]^+$ in acetonitrile at −1.0 V [59].

Reaction of the rhodium nitrosyl complex $[Rh(NO)Cl_2(PPh_3)_2]$ with $Na(S_2CNR_2)\cdot xH_2O$ (R = Et or Me) in benzene under reflux yields the square planar complexes $[Rh(S_2CNR_2)]$. Similar reactions, on stirring the reaction mixture for 6 h without refluxing, give square pyramidal complexes $[Rh(S_2CNR_2)(PPh_3)]$ (IV) [60]. $[Rh(S_2CNR_2)]$ is also prepared by the reaction of $Rh(NO)Cl_3$ with $Na(S_2CNR_2)\cdot xH_2O$ in ethanol [61]. Another square pyramidal rhodium(II) complex is reported to be $[(np_3)Rh(\sigma\text{-}C{\equiv}CPh)](BPh_4)$ ($np_3 = N[CH_2CH_2PPh_2]_3$) (V) [62].



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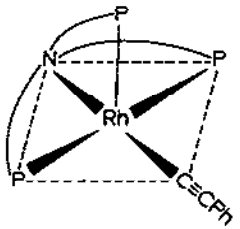
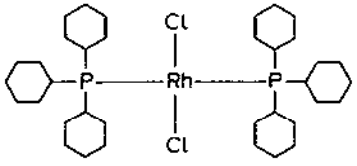


(V)

Bennett et al. reported the first example of a halogenophosphine rhodium(II) complex in 1966 [63]:

$$RhCl_3 \cdot 3H_2O + P(o\text{-}C_6H_4Me)_3(\text{excess}) \xrightarrow[EtOH]{25^\circ C} [RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$$

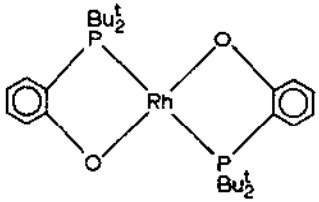
A trans, square planar structure was proposed for this blue-green complex by comparison of the far-infrared spectra with isomorphous Pd(II) and Pt(II) complexes. A mauve modification of the blue-green complex can be obtained either by performing the original reaction at 0°C or by evaporating in vacuo the dichloromethane solution of the blue-green complex. The purple complex is not isomorphous with the blue-green complex. If these preparations are carried out at high temperatures, *o*-metallation occurs [64]. The red-brown complex $[RhCl_2(PCy_3)_2]$ and the green complex $[RhBr_2(PCy_3)_2]$ are similarly prepared by the reduction of $RhX_3 \cdot 3H_2O$ (X = Cl or Br) with PCy_3 [65]. The reaction of halogens with $RhX(PCy_3)_2$ (X = Cl, Br, I) yields the Rh(II) complexes $[RhXY(PCy_3)_2]$ (X = Cl, Y = Cl, Br, I; X = Y = Br) [66]. These complexes are assigned a square planar, trans structure (VI)



(VI)

on the basis of the high ν(Rh–X). Carbon monoxide reacts with $[RhCl_2(PCy_3)_2]$ in the solid state to give a white Rh(II) carbonyl complex $[Rh(CO)Cl_2(PCy_3)_2]$ which was claimed as the first example of a paramagnetic Rh(II) carbonyl complex. This complex rapidly decays to give $[Rh(CO)Cl(PCy_3)_2]$ and $[Rh(CO)Cl_3(PCy_3)_2]$ [67]. Similarly the reactions of hydrated rhodium trichloride with bulky phosphines PBu^t_2R (R = Me, Et, Pr^n) in ethanol at room temperature give the rhodium(II) complexes, *trans*-$[RhCl_2(PBu^t_2R)_2]$ [68,69]. The complex $[RhHCl_2\{PBu^t_2(C{\equiv}CPh)\}_2]$ slowly decomposes in chloroform solution to give an orange, insoluble paramagnetic complex $[RhCl_2\{PBu^t_2(C{\equiv}CPh)\}_2]$ which appears to be binuclear [70]. Demethylation of the phosphine $PBu^t_2(o\text{-}C_6H_4OMe)$ was observed in the reaction

of $PBu^t_2(o\text{-}C_6H_4OMe)$ with hydrated rhodium trichloride. The product of the reaction is *trans*-$[Rh\{PBu^t_2(o\text{-}C_6H_4O)\}_2]$ (**VII**) [71].



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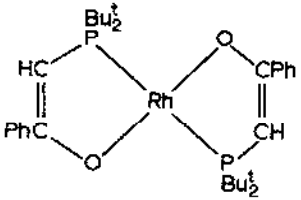
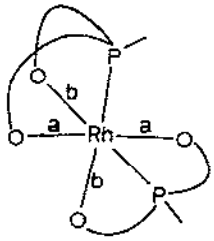


(VIII)

The green complex *trans*-$[RhCl_2\{PBu^t_2(R)\}_2]$ has been prepared by the reaction of $RhCl_3\cdot 3H_2O$ and $PBu^t_2(R)$ ($R = -CH_2(2\text{-Me-}5\text{-}OMeC_6H_3)$) at room temperature. The trans structure was proposed on the basis of spectral studies [72]. Reaction of hydrated rhodium trichloride with the keto phosphine $PBu^t_2(CH_2COPH)$ in the presence of sodium methoxide affords the rhodium(II) complex *trans*-$[Rh\{PBu^t_2(CHCOPh)\}_2]$ (**VIII**). In the absence of sodium methoxide, the same reaction yields a rhodium(III) complex containing the phosphenolate [73]. The reaction of dppe with the η^1-2-methallyl complex $[RhCl_2(\eta^1\text{-}C_3H_4Me)]$ in ethanol in an equimolar ratio results in the formation of the grey-green complex $[RhCl_2(dppe)]$, which is stable in air [74]. The carbethoxy tertiary phosphines $PBu^t_2(CH_2CH_2CO_2Et)$ and $PBu^t_2(Ch_2Ch_2CH_2CO_2Et)$ react with $RhCl_3\cdot 3H_2O$ to form four-coordinated rhodium(II) complexes in which the phosphorus atoms are only binding sites [75]. Hydrated rhodium(II) formate and acetate react with triphenylphosphine to give orange mononuclear rhodium(II) complexes [76]. Traces of a paramagnetic species believed to be an Rh(II) species are formed in addition to $[RhCl(PPh_3)_3]$ when PPh_3 reacts with $RhCl_3\cdot 3H_2O$ in ethanol [77]. Recently, Ogle et al. [78] have successfully isolated the paramagnetic species $[RhCl_2(PPh_3)_2]$. Reaction of two equivalents of triphenylphosphine with $Rh_2(CO)_2Cl_2$ in chloroform gives $[(cod)RhCl(PPh_3)]$. Recrystallization of $[(cod)RhCl(PPh_3)]$ in dichloromethane affords yellow crystals of $[RhCl_2(PPh_3)_2]$. The ^1H NMR spectrum of $[RhCl_2(PPh_3)_2]$ in C_6D_6 exhibits multiplet signals at 7.011 (3H) and 7.955 (2H) due solely to the phenyl proton. The molecule has a square planar environment for rhodium which consists of two phosphorus atoms in a trans arrangement. The Rh—P and Rh—Cl bond lengths are 2.323(2) Å and 2.428 Å, respectively [78].

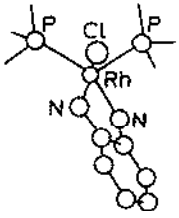
Reaction of an ethanolic solution of $RhCl_3\cdot 3H_2O$ with NO gives $Rh(NO)Cl_3$ in solution. The ESR spectrum of this solution consists of a broadened singlet at $g = 2.17$. Triphenylphosphine reacts with this solution to give a paramagnetic complex $[Rh(NO)Cl_3(PPh_3)_2]$, contaminated with $Rh(NO)Cl_2(PPh_3)_2$ [79]. A diamagnetic complex $[RhCl_2\{Sb(o\text{-}C_6H_4Me)_3\}]$ is prepared by the reaction of $RhCl_3\cdot 3H_2O$ with $Sb(o\text{-}C_6H_4Me)_2$. Its diamagnetism and the non-equivalence of the methyl protons in the ^1H NMR spectrum suggest a planar dimeric structure [80]. Reaction of tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) with $[Rh_2(CH_3CN)_{10}][BF_4]_4$ in methanol or

acetonitrile results in the formation of a purple complex $[Rh(tmpp)_2][BF_4]_2$. X-ray crystal structure determination showed the rhodium to be hexacoordinate. It has a distorted octahedral structure (**IX**) with four weak Rh–O bonds (Rh–O distances; $a = 2.398(5)$ Å, $b = 2.201(6)$ Å) and two strong Rh–P bonds (Rh–P bond distance, 2.216(2) Å).



(IX)

Each tmpp ligand is coordinated to the Rh atom via one phosphorus atom and two *ortho*-methoxy substituents. The very long Rh–O bonds, 2.398(5) Å, are evidently a consequence of Jahn–Teller distortion [81]. Reaction of rhodium trichloride with siphos (siphos = tris(trimethylsilylmethyl)phosphine) affords a chloro-bridged dimer $[Rh_2(siphos)_4Cl_4]$. In contrast, the reaction of rhodium tribromide with siphos gives a monomeric Rh(II) complex, $[RhBr_2(siphos)_2]$ [82]. $[RhCl(PPh_3)_3]$ reacts with *o*-phenylenediamine or diaminomaleonitrile in CH_3CN in the presence of air to give air-stable, green complexes $[RhCl(L)(PPh_3)_2$ (L = *semi-o*-benzoquinonediimine, *s*-bqdi; *semi*-diiminosuccinonitrile, *s*-disn). The X-ray crystal structure of [RhCl-(*s*-bqdi)$(PPh_3)_2$] has been determined. The rhodium atom is linked to two phosphorus atoms of triphenylphosphine, one chlorine atom and two nitrogen atoms of the *semi-o*-benzoquinonediimine and has a geometry between a square pyramid and a trigonal bipyramid (**X**) [83].



(X)

Organometallic compounds $[Rh(\eta^6\text{-}C_6Me_6)_2][AlX_4]_2$ (X = Cl, Br) are prepared by the reduction of rhodium trichloride [84,85]:

$$3RhCl_3 + 5AlX_3 + Al + 6C_6Me_6 \rightarrow 3[Rh(\eta^6\text{-}C_6Me_6)_2][AlX_4]_2$$

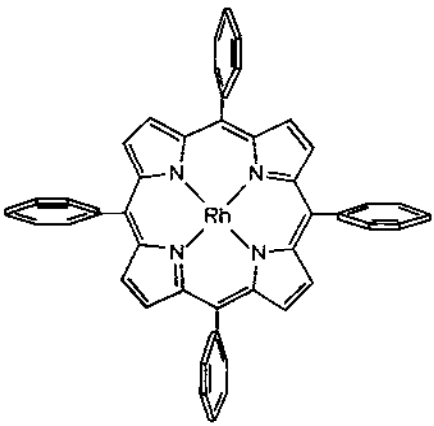
The stable, red complexes $[Rh(\eta^6\text{-}C_6Me_6)_2][PtCl_6]$ and $[Rh(\eta^6\text{-}C_6Me_6)_2][PF_6]_2$ can be isolated from $[Rh(\eta^6\text{-}C_6Me_6)_2][AlX_4]_2$ [84]. Rhodocene $[Rh(\eta^5\text{-}C_5H_5)]$ has been synthesized, but it is unstable [86,87]. Cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}C_2H_4)_2]^+$ [88] and the one-electron reduction product of $[(\eta^5\text{-}C_5H_5)Rh\{S_2C_2(CF_3)_2\}_2]$ [89] have also been prepared. The complex ion [{hydrotris(1-pyrazolyl)borato}(η^5-pentamethylcyclopentadienyl)rhodium(II)] is prepared by the reaction of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ with hydrotris(1-pyrazolyl)borate ions and isolated as the PF_6^- salt [90,91]. The X-ray crystal structure of $[(\eta^5\text{-}C_5Me_5)Rh(HB(pz)_3)](PF_6)$ consists of discrete cationic rhodium complexes and PF_6^- anions. Allyl and propadienyl–rhodium(III) complexes react with polyhalogenomethanes to give rhodium(II) species as reactive intermediates [92]:

$$CCl_3\cdot + [Rh(CO)Br_2(CH_2CH{=}CHR)(PMe_2Ph)_2]$$

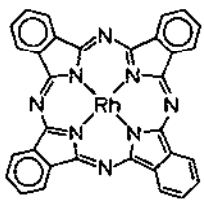
$$\rightarrow [Rh(CO)Br_2(PMe_2Ph)_2] + CCl_3CHRCH{=}CH_2$$

$$[Rh(CO)Br_2(PMe_2Ph)_2] + CBrCl_3 \rightarrow [Rh(CO)Br_3(PMe_2Ph)_2] + CCl_3\cdot$$

Synthesis and organometallic reactions of the monomeric rhodium(II) porphyrin complexes [Rh(por)] (por = dianion of porphyrin macrocycle) have been extensively investigated [93–105]. Reaction of $[Rh(CO)_2Cl]_2$ with H_2TPP in acetic acid results in the formation of [Rh(TPP)] (**XI**) [93].



(**XI**)

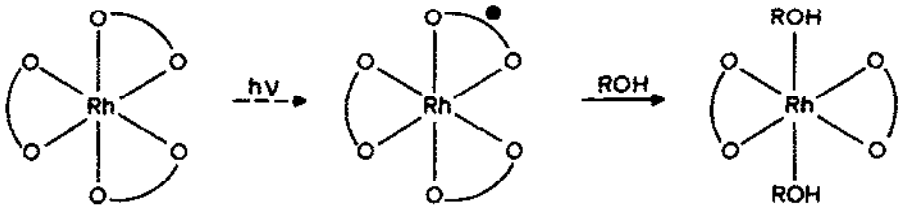


(**XII**)

[Rh(TPP)] may be also generated by the electrochemical reduction of $[(TPP)Rh(L)_2]^+Cl^-$, where L is dimethylamine [100]. This rhodium(II) radical reacts with another rhodium(II) radical to form a dimer. [Rh(TMP)] (H_2TMP = tetramethylporphyrinate) is generated by photolysis of a solution of $[(TMP)Rh(CH_3)]$ [104]. Ultraviolet irradiation of [Rh(pc)X] (pc = phthalocyanine; X = Cl, Br, I) yields a rhodium(II) complex [Rh(pc)] (**XII**) through the formation of a rhodium(III) intermediate [106(a)]. Surface-bound [Rh(II)Pc] is also obtained by the electrochemi-

cal reduction of surface-bound [ClRh(III)Pc] [106(b)]. The complex $[Rh(sep)]^{2+}$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane) is prepared by the electrochemical reduction or by pulse radiolysis of $[Rh(sep)]^{3+}$ [107]. The complex $[RhCl_2(py)_4]Cl$ undergoes reversible one-electron reduction in acetonitrile, acetonitrile–pyridine and pyridine to afford $[RhCl_2(py)_4]$ [108].

Monomeric rhodium(II) species have been postulated as transient intermediates in several studies using photolytic or radiolytic methods [109–114]. Flash photolysis of *trans*/*cis*-tris(1,1,1-trifluoropentane-2,4-dionate)rhodium(III) in alcoholic solvents produces a short-lived Rh(II) species which decays to a longer-lived intermediate [115,116]:



The pulse radiolytic reduction of $[RhCl(NH_3)_5]^{2+}$, $[Rh(H_2O)(NH_3)_5]^{3+}$ and $[RhBr_2(NH_3)_4]^{+}$ by the hydrated electron yields a transient intermediate $[Rh(NH_3)_4]^{2+}$ species [117]:

$$[RhCl(NH_3)_5]^{2+} + e_{aq}^- \rightarrow [RhCl(NH_3)_5]^{+}$$

$$[RhCl(NH_3)_5]^{+} + H_3O \rightarrow [Rh(NH_3)_4]^{2+} + Cl^- + NH_4^+ + H_2O$$

$[Rh(NH_3)_4]^{2+}$ exchanges ammonia for water:

$$[Rh(NH_3)_4]^{2+} + H_2O \rightarrow [Rh(H_2O)(NH_3)_3]^{2+} + NH_3$$

$$[Rh(H_2O)(NH_3)_3]^{2+} + H_2 \rightarrow [Rh(H_2O)_2(NH_3)_2]^{2+} + NH_3$$

$[Rh(NH_3)_4]^{2+}$ acts as a chain carrier in a photoinitiated thermal reaction that activates O_2 by coordination [118]. The formation of the pentaamine rhodium(II) $[Rh(NH_3)_5]^{2+}$ intermediate has been proposed in the photolysis of acidic aqueous solutions of $[Rh(N_3)(NH_3)_5]^{2+}$ [119]. The reaction of $[Rh(bipy)_3]Cl_3$ with radiation-generated radicals in aqueous solution results in the formation of $[Rh(bipy)_3]Cl_2$ which slowly loses bipy at room temperature to give $[Rh(bipy)_2]Cl_2$ [120]:

$$[Rh(bipy)_3]^{3+} + e_{aq}^- \rightarrow [Rh(bipy)_3]^{2+}$$

$$[Rh(bipy)_3]^{2+} \xrightarrow{slow} [Rh(bipy)_2]^{2+} + bipy$$

The photoinduced reactions of $[Ru(bipy)_3]^{2+}$ with $[Rh(bipy)_3]^{3+}$ produce $[Rh(bipy)_3]^{2+}$. The other known bipyridine rhodium(II) intermediate radicals are six-coordinate $[Rh(H_2O)_2(bipy)_2]^{2+}$ and five-coordinate $[Rh(H_2O)(bipy)_2]^{2+}$ [121–123]. Hydrogen gas is produced from the reduction of H_2O through the

proposed intermediate $[Rh(bipy)_3]^{2+}$ in the electron transfer reaction of $[Ru(bipy)_3]^{2+}$ with $[Rh(bipy)_3]^{3+}$ in aqueous solution [124,125]. Flash photolysis of $[Rh(dmgH)_2(PPh_3)]_2$ (dmgH is the monoanion of 2,3-butanedione dioxide or dimethylglyoxime) or allyl rhodoxime $[(i\text{-}C_3H_7)Rh(dmgH)_2(PPh_3)]$ produces $[Rh(dmgH)_2(PPh_3)]$ by homolytic cleavage of the Rh–Rh and Rh–C bonds, respectively [126,127]. Other known rhodium(II) species are $[RhH_6]^{4-}$, $[RhCl_6]^{4-}$, $[RhBr_6]^{4-}$, $[RhO_6]^{10-}$ and $[Rh(CN)_4Cl_2]^{4-}$. The short lifetimes of these species have been extended by trapping them within a crystal lattice [128–135].

(iv) Iridium(II) complexes

The first mononuclear iridium(II) nitrosyl complex $[Ir(NO)Br_3(PPh_3)_2]$ was prepared by Malatesta et al. [136]:

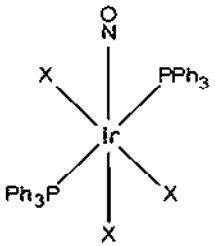
$$[Ir(NO)_2(PPh_3)_2] + 2Br_2 \rightarrow [Ir(NO)Br_3(PPh_3)_2] + \ldots$$

The iridium(II) complexes $[Ir(NO)X_3(PPh_3)_2]$ (X = Cl, Br) are also synthesized by the oxidation of iridium nitrosyl complexes with nitrosyl halides [137]:

$$[Ir(NO)Br_2(PPh_3)_2] + NOBr \rightarrow [Ir(NO)Br_3(PPh_3)_2] + \ldots$$

$$[Ir(NO)_2X(PPh_3)_2] + NOX \rightarrow [Ir(NO)X_3(PPh_3)_2] + \ldots$$

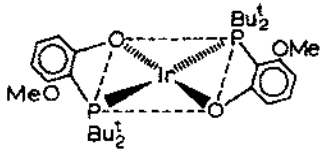
$[Ir(NO)Cl_3(PPh_3)_2]$ is isostructural with $[Ru(NO)Cl_3(PPh_3)_2]$ [138], which shows a linear Ru–N–O angle. It is therefore possible to assign the (**XIII**) structure to $\{IrNO\}^7$ complexes.



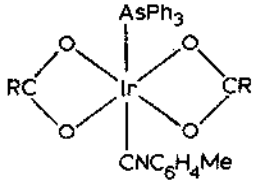
(**XIII**)

In air, a benzene solution of the iridium(I) complex $[Ir(CO)\{PBu^t_2(C_6H_4O)\}\{PBu^t_2(C_6H_4OH)\}]$ becomes blood-red and gives a deep red iridium(II) complex *trans*-$[Ir\{PBu^t_2(C_6H_4O)\}_2]$ together with a few percent of the purple iridium(III) complex $[IrH\{PBu^t_2(C_6H_4O)\}_2]$ and carbon dioxide. The crystals of $[Ir\{PBu^t_2(C_6H_4O)\}_2]$ belong to space group P_2/c with $a = 8.111$, $b = 11.926$, $c = 15.669$ Å, $\beta = 108.52°$; $Z = 2$, $D_m = 1.53$ and $D_c = 1.54$ g cm^{-3} [139]. Similarly, the

oxidation of $[IrH\{PBu^t_2(C_6H_3(OMe)O)\}_2]$ yields the red iridium(II) complex $[Ir\{PBu^t_2(C_6H_3(OMe)O)\}_2]$ (**XIV**).



(XIV)



(XV)

X-ray crystal structure analysis of these complexes reveals C_1 symmetry and planarity. The reaction of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ with carboxylic acids results in the formation of iridium(II) complexes $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$ (**XV**) (R = Me, p-ClC_6H_4, p-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$ and RCO_2 = pentane-2,4-dionate (pd)). A tetragonally distorted octahedral geometry was proposed for these complexes. The distortion increases with the ability of the planar ligands to delocalize the electron density of the iridium and thus, complex $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CMe)_2]$ is least distorted [140]. Allyl and propadienyl–iridium(III) complexes react with polyhalogenomethanes to give iridium(II) species as reactive intermediates [92]:

$$CCl_3\cdot + [Ir(CO)Cl_2(CH_2CH{=}CHR)(PMe_2Ph)_2]$$

$$\rightarrow [Ir(CO)Cl_2(PMe_2Ph)_2] + CCl_3CHRCH{=}CH_2$$

$$[Ir(CO)Cl_2(PMe_2Ph)_2] + CBrCl_3 \rightarrow [Ir(CO)Cl_2Br(PMe_2Ph)_2] + CCl_3\cdot$$

Complexes *trans*-$[Ir(R)(CO)(PPh_3)_2]$ (R = H, CH_3, CH_2CN, C_6H_5) are oxidized in 1,2-dichloroethane containing PPh_3 in two one-electron steps, the first involving addition of PPh_3 prior to reversible electron transfer. One-electron electrolysis produces the stable iridium(II) species $[Ir(R)(CO)(PPh_3)_3]^+$ [141]. The complex ion $[Ir(CO)I_3(COC_2H_5)]^-$ may be isolated as an isoquinoline salt during the carbonylation of ethanol using hydrated iridium trichloride as catalyst precursor with HI as a promotor [142]. Several diamagnetic carbonyl halide complexes $[Ir(CO)X_2(p\text{-toluidine})_2]$ (X = Cl, Br), $[AsPh_4][Ir(CO)X_3]$ (X = Br, I) and $[AsPh_4][Ir(CO)I_4]$, which must be regarded as iridium(II) complexes, have been reported [143–145]. It has been suggested that some type of metal–metal interaction is involved in these complexes.

$[Ir(\eta^5\text{-}C_5H_5)_2]$, the only cyclopentadienyl iridium complex so far analyzed, is dimeric under ordinary conditions and may be kept as a monomeric complex only under special conditions [86,87]:

$$[Ir(\eta^5\text{-}C_5H_5)_2]Cl + Na \rightarrow [Ir(\eta^5\text{-}C_5H_5)_2] + NaCl$$

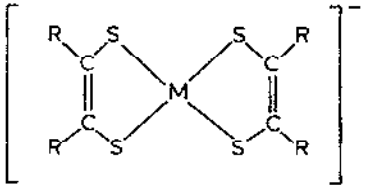
The reaction of quadridentate Schiff bases *N,N'*-ethylenebis(salicylideneimine)(Hsalene) and *N,N'*-ethylenebis(acetylacetoneimine)(acacen) with $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ result in the formation of iridium(II) complexes

$[Ir(AsPh_3)(salene)(CNC_6H_4Me\text{-}p)]$ and $[Ir(AsPh_3)(acacen)(CNC_6H_4Me\text{-}p)]$, respectively [146].

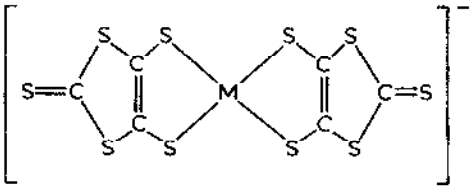
The synthesis of $IrBr_2$ and IrI_2 have been reported [147]. The existence of these halides as iridium(II) species is doubtful. The electron irradiation of $[IrCl_6]^{3-}$ in an NaCl host lattice generates the iridium(II) species $[IrCl_6]^{4-}$ [148]. Similar paramagnetic species $[IrCl_6]^{4-}$ and $[IrBr_6]^{4-}$ have been identified as products in the light-induced decomposition of Ir(III)-doped AgCl and AgBr single crystals [149]. Electron irradiation of $[Ir(CN)_6]^{3-}$ in a KCl lattice produces a paramagnetic Ir(II) species $[Ir(CN)_5]^{3-}$ [150].

(v) Palladium(III) and platinum(III) complexes

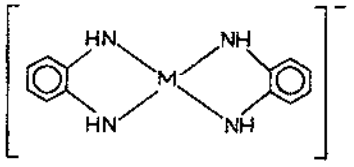
Several palladium(III) and platinum(III) complexes, which have been claimed, in the past, to contain the trivalent metals, are found to be either binuclear with metal–metal bonds containing M(II) and M(IV) (M = Pd or Pt) oxidation states or mononuclear containing the M(II) oxidation state with the unpaired electron on the ligand [151–164]. Examples of the first type of compounds are MX_3 (X = F, Cl, Br) and M(amine)Br_3, species consisting of two metals, one divalent and one tetravalent. The second type of compounds includes **(XVI)**–**(XX)** in which the unpaired electron resides in the π orbitals of the organic systems, the metals being present as M(II).



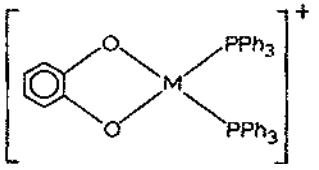
(XVI)



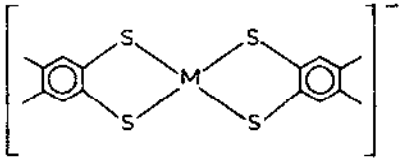
(XVII)



(XVIII)



(XIX)

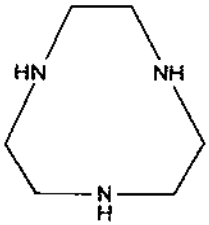


(XX)

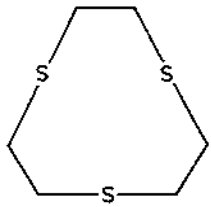
(a) Palladium(III) complexes

Very few examples of monomeric palladium(III) complexes have been reported in the literature [165–170]. Reaction of NaF with Pd_2F_6 at 600°C/70 bar results in the formation of $Na[PdF_4]$. The ESR spectrum of $Na[PdF_4]$ at 8 K indicates the presence of palladium(III) with the unpaired electron in the $4d_{z^2}$ orbital [166]. The syntheses of $K_2Li[PdF_6]$ and $K_2Na[PdF_6]$ have also been reported [167,168]. The crystal structure data for $K_2Na[PdF_6]$ indicate a tetragonal structure [168].

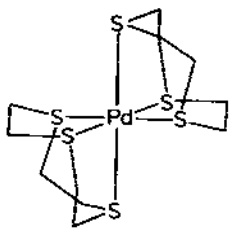
Microcycles such as L = tacn or ttcn (tacn = 1,4,7-triazacyclononane, (**XXI**); ttcn = 1,4,7-trithiacyclononane, (**XXII**) stabilize palladium(III).



(**XXI**)



(**XXII**)



(**XXIII**)

The complexes $[PdL_2](PF_6)_3$ are prepared by the oxidation of $[PdL_2](PF_6)_2$ [54,169–171]. The complex $[Pd(ttcn)_2](PF_6)_3$ is less stable than the complex $[Pd(tacn)_2](PF_6)_3$. The $[Pd(tacn)_2]^{3+}$ complex has a tetragonal distorted octahedral structure with $Pd-N_1 = 2.180(9)$ Å, $Pd-N_4 = 2.119(9)$ Å and $Pd-N_7 = 2.111(9)$ Å, which is consistent with a Jahn–Teller distorted d^7 complex. The X-ray crystal structure of $[Pd(ttcn)_2]^{3+}$ is related to that of $[Pd(tacn)_2]^{3+}$, with $Pd-S_1 = 2.5448(15)$ Å, $Pd-S_4 = 2.3358(15)$ Å and $Pd-S_7 = 2.3692(15)$ Å (**XXIII**). Greater tetragonal distortion has been observed in the structure of $[Ni(tacn)_2]^{3+}$ than in $[Pd(tacn)_2]^{3+}$, which may be due to the smaller size of Ni(III) [172,173]. The complex $[Pd(ttcn)_2](PF_6)_2$ shows a greater elongation of the axial bonds than $[Pd(ttcn)_2](PF_6)_3$. The mean differences between the axial and equatorial bond lengths in $[Pd(ttcn)_2](PF_6)_2$ and $[Pd(ttcn)_2](PF_6)_3$ are 0.631 Å and 0.182 Å, respectively. Decreasing the electron density on the $4d_{z^2}$ orbital of palladium on oxidising from Pd(II) to Pd(III), reduces the interaction of the Pd $4d_{z^2}$ electron with the axial thia-donor S_1, and as a result, S_1 is brought in towards the palladium(III) centre.

(b) Platinum(III) complexes

Muraveiskaya et al. [174] have reported the preparation of $[Pt(NH_3)_2(SCN)_2I]$ by the reaction of *cis*-$[Pt(NH_3)_2(SCN)_2]$ with iodine:

$$cis\text{-}[Pt(NH_3)_2(SCN)_2] + 1/2I_2 \xrightarrow{BuOH} cis\text{-}[Pt(NH_3)_2(SCN)_2I]$$

Uson and co-workers [175–178] reported the first, well-characterized complex $[NBu_4][Pt(C_6Cl_5)_4]$, which is prepared by the oxidation of the platinum(II) complex $[NBu_4]_2[Pt(C_6Cl_5)_4]$ with stoichiometric amounts of Cl_2 or Br_2:

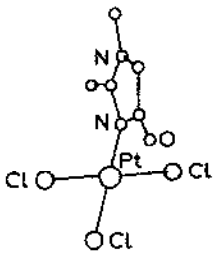
$$[NBu_4]_2[Pt(C_6Cl_5)_4] + 1/2X_2 \rightarrow [NBu_4][Pt(C_6Cl_5)_4] + NBu_4X$$

The complex $[NBu_4][Pt(C_6Cl_5)_4]$ can also be prepared in low yield by using I_2 or $TlCl_3$ as an oxidising agent:

$$[NBu_4]_2[Pt(C_6Cl_5)_4] + \tfrac{3}{2}TlCl_3 \rightarrow [NBu_4][Pt(C_6Cl_5)_4] + \tfrac{1}{2}TlCl + [NBu_4][TlCl_4]$$

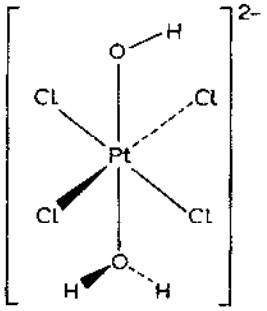
The X-ray crystal structure of $[Pt(C_6Cl_5)_4]^-$ shows a square planar geometry with Pt–C = 2.094(8) Å, C–C = 1.388(12) Å and C–Cl = 1.729 Å. The closest Pt–Pt distance is 9.7 Å, suggesting no evidence for the presence of Pt–Pt interaction [177].

$AgClO_4$ reacts with bis(diphenylglyoxime)platinum(IV) diiodide in benzene to give red-brown platinum(III) complexes $[Pt(dpg)_2](ClO_4)$ and $[Pt(dpg)_2](ClO_4)\cdot 1.5C_6H_6$. Both complexes are highly hygroscopic and change their colour to black-green in a humid atmosphere. The complex $[Pt(dpg)_2](ClO_4)$ has a tetragonal structure which consists of stacks of $[Pt(dpg)_2]^+$ cations with equidistant Pt–Pt separations of 3.259(4) Å [179]. The complex $[Pt(diamsar)]^{3+}$ (diamsar = 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) has an octahedral structure and is prepared by the γ-radiolysis of $[Pt(diamsar)]^{4+}$ at 77 K [180]. Electrochemical oxidation of $[Pt(ttcn)_2]^{2+}$ at 0.5 V affords a stable platinum(III) complex $[Pt(ttcn)_2]^{3+}$ [181]. The d^7 species $[Pt(ttcn)_2]^{3+}$ and $[Pd(ttcn)_2]^{3+}$ are more stable than the corresponding $[Rh(ttcn)_2]^{2+}$. This might be expected in view of the greater formal charge in the platinum(III) and palladium(III) species. Reaction of $[PtCl_4]^{2-}$ with an equimolar amount of creatinine (creat) results in the formation of (neutral, anionic and cationic) blue to green paramagnetic species. A green complex $[AsPh_4][PtCl_3(creat)]$ was isolated at pH 2.4 and an X-ray crystal structure has been determined. In the complex ion $[PtCl_3(creat)]^-$, the platinum atom is bound with three chloride ions and one creatinine ligand coordinated through the endogenic nitrogen (**XXIV**) [182].



(**XXIV**)

Several short-lived platinum(III) species are generated by electrochemical, photolytic, thermal non-complementary and radiolytic reactions of Pt(II) and Pt(IV) compounds [183–201]. Pulse radiolysis or flash photolysis of $[PtCl_6]^{2-}$ produces three species, $[PtCl_6]^{3-}$, $[PtCl_5]^{2-}$ and $[PtCl_4]^{-}$. Relativistic multiple scattering Xα molecular orbital calculations have been performed for these platinum(III) species and it was concluded that $[PtCl_4]^{-}$ is the more stable species. Photolysis of $[PtX_6]^{2-}$ (X = Cl, Br, SCN) in a system containing $[Ru(bipy)_3]^{2+}$ yields $[PtX_4]^{-}$ [202,203]. Photolysis of $[PtCl_6]^{2-}$ and $[PtCl_4(OH)_2]^{2-}$ in aqueous solution yields Pt(III) complexes $[PtCl_4(H_2O)_2]^{-}$ and $[PtCl_4(OH)(H_2O)]^{2-}$ (**XXV**), respectively.



(**XXV**)

The acid dissociation constant of $[PtCl_4(H_2O)_2]^{-}$ is 3.5 [204]. The formation of the intermediate Pt(III) species $[PtCl_5]^{2-}$ during the pulse laser photolysis of a $[PtCl_6]^{2-}$–methanol system has been reported [205]. Transient $[PtCl_5]^{2-}$ is a relatively long-lived species, which has a square pyramidal structure with elongated Pt–Cl bonds [206]. Multiple scattering Xα molecular orbital calculations have been performed for a number of Pt(III) complex ions containing aquo and chloro ligands: $[PtCl_4(OH)]^{2-}$, $[PtCl_4(OH)(H_2O)]^{2-}$ and *cis*- and *trans*-$[PtCl_3(OH)_2]^{2-}$ [207]. The peak positions for the intense charge transfer transitions occurring in the near UV–visible regions have been calculated for $[PtCl_4(OH)]^{2-}$, $[PtCl_4(OH)(H_2O)]^{2-}$, *cis*- and *trans*-$[PtCl_3(OH)_2]^{2-}$, $[PtCl_6]^{3-}$, $[PtCl_5]^{2-}$ and $[PtCl_4]^{-}$ [207] and compared with the experimentally observed absorption spectra [208]. Reaction of $[PtCl_4]^{2-}$ with the hydroxyl radical in water results in a Pt(III) intermediate $[PtCl_4(OH)(H_2O)]^{2-}$ which reacts with hydroxide ion in basic media to form $[PtCl_4(OH)_2]^{3-}$ and $[PtCl_2(OH)_2]^{-}$:

$$[PtCl_4]^{2-} + \cdot OH \text{ (radical)} \xrightarrow{H_2O} [PtCl_4(OH)(H_2O)]^{2-}$$

$$[PtCl_4(OH)(H_2O)]^{2-} + OH^- \rightarrow PtCl_4(OH)_2]^{3-} + H_2O$$

$$[PtCl_4(OH)_2]^{3-} \rightarrow [PtCl_2(OH)_2]^{-} + 2Cl^-$$

Reaction of the *tert*-butyl alcohol radical (generated by the reaction of the OH

radical with *tert*-butyl alcohol) with $[PtCl_6]^{2-}$ yields $[PtCl_2(OH)_2]^-$:

$$\cdot OH + (CH_3)_3COH \rightarrow H_2O + \cdot CH_2C(CH_3)_2OH$$

$$[PtCl_6]^{2-} + \cdot CH_2(CH_3)_2COH$$

$$\rightarrow [PtCl_2(OH)_2]^- + 3Cl^- + 2H^+ + ClCH_2(CH_3)_2COH$$

Reaction of $[PtCl_6]^{2-}$ with a hydrogen atom (at pH 2.2–2.7 in an argon-saturated media, the hydrated electron reacts rapidly with a proton to give a hydrogen atom) in aqueous solution gives $[PtCl_2(OH)_2]^-$ [208]:

$$H + [PtCl_6]^{2-} + 2H_2O \rightarrow [PtCl_2(OH)_2]^- + 4Cl^- + 3H^+$$

Grivin et al. [209] have studied the pulse laser photolysis of the $[PtCl_6]^{2-}$–creatinine–methanol system and demonstrated the formation of an intermediate $[PtCl_5(creat)]^{2-}$. In the photoreduction of the $[PtCl_6]^{2-}$ complex in methanol, using laser flash photolysis, electron transfer from the solvent molecules to the excited complex has been reported [210]:

$$[PtCl_6]^{2-} \xrightarrow{h\nu} [PtCl_6]^{2-*} \xrightarrow{CH_3OH} [PtCl_6]^{3-} + R + H^+$$

$$[PtCl_6]^{3-} \rightarrow [PtCl_5]^{2-} + Cl^-$$

C. REACTIVITY

The reactions of mononuclear d^7 complexes of platinum metals can be divided into two groups: (a) reaction at the metal centre and (b) reaction at the ligand. Reaction of $[Ru(NO)(CH_3CN)(bipy)_2]^{2+}$ with O_2 gives $[Ru(NO_2)(CH_3CN)(bipy)_2]^{1+}$ by the oxidation of the coordinated NO group [29]. The osmium nitrosyl complex $[Os(NO)Cl(PPh_3)_2]$, on refluxing with triphenylphosphine in benzene for 30 h, affords the green osmium(0) complex $[Os(NO)Cl(PPh_3)_3]$ [40].

The reaction of O_2 with $[Rh(bipy)_3]^{2+}$ is an electron transfer reaction [120]:

$$[Rh(bipy)_3]^{2+} + O_2 \rightarrow [Rh(bipy)_3]^{3+} + O_2^-$$

The formation of an oxygen adduct in the reaction of O_2 with $[RhCl(NH_3)_5]^{2+}$ has been proposed [117]. At pH > 11, $[Rh(bipy)_3]^{2+}$ is susceptible to coordination by OH^-:

$$[Rh(bipy)_3]^{2+} + 2OH^- \rightleftharpoons [Rh(bipy)_2(OH)_2] + bipy$$

On heating the blue-green or purple complex $[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$, *o*-metallation occurs [64]. The reaction of $[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$ with sodium borohydride in the presence of excess $P(o\text{-}C_6H_4CH_3)_3$ in ethanol results in the formation of a greenish-brown diamagnetic complex $[RhH(BH_4)\{P(o\text{-}C_6H_4Me)_3\}]$ [211]. The rho-

dium(II) radical $[Rh(dmgH)_2(PPh_3)]$ undergoes rapid dimerization reforming the parent dimer. Reaction of $[Rh(dmgH)_2(PPh_3)]$ with the alkyl halide RX affords the rhodium(III) complex by halogen atom abstraction [126,127]:

$$[Rh(dmgH)_2(PPh_3)] + RX \rightarrow [RhX(dmgH)_2(PPh_3] + R\cdot$$

Cobalt(III) complexes of the type $CoX(dmgH)_2(PPh_3)$ and $[CoX(NH_3)_5]^{2+}$ where X is a halogen or pseudohalogen, oxidize $[Rh(dmgH)_2(PPh_3)]$ [212,213]:

$$Rh(dmgH)_2(PPh_3)] + [CoX(dmgH)_2(PPh_3)] \rightarrow [RhX(dmgH)_2(PPh_3)] + [Co(dmgH)_2(PPh_3)]$$

$$[Rh(dmgH)_2(PPh_3)] + [CoX(NH_3)_5]^{2+} \rightarrow [RhX(dmgH)_2(PPh_3)] + [Co(NH_3)_5]^{2+}$$

Carbon monoxide reacts with the rhodium(II) complex $[Rh(tmpp)_2][BF_4]$ to afford the rhodium(III) complex $[Rh(tmpp)_2][BF_4]_3$ and the rhodium(I) complex $[Rh(CO)_2(tmpp)_2][BF_4]$. The Rh(I) dicarbonyl complex, upon purging with an inert gas, loses one CO ligand to give $[Rh(CO)(tmpp)_2][BF_4]$ which also loses CO in a second redox reaction to reproduce the original $[Rh(tmpp)_2][BF_4]_2$ [214]:

$$2[Rh(tmpp)_2][BF_4]_2 + 2CO \rightarrow [Rh(tmpp)_2][BF_4]_3 + [Rh(CO)_2(tmpp)_2][BF_4]$$

$$[Rh(CO)_2(tmpp)_2][BF_4] \xrightarrow{\text{inert gas}} [Rh(CO)(tmpp)_2][BF_4] + CO$$

$$[Rh(tmpp)_2][BF_4]_3 + [Rh(CO)(tmpp)_2][BF_4] \rightarrow [Rh(tmpp)_2][BF_4]_2 + CO$$

[Rh(TPP)] reacts with CH_2Cl_2 to give the rhodium–carbon σ-bonded species $[(TPP)Rh(CH_2Cl)]$ [100]. Reaction of Rh(TPP) with alkyl halides (RX) in solution results in the formation of [(TPP)Rh(R)] and X^-. If [Rh(TPP)] attacks at the R–X bond, then, either loss of $X\cdot$ and formation of [(TPP)Rh(R)] or loss of X^- and formation of $[(TPP)Rh(R)]^+$ will occur [102]:

$$[(TPP)Rh] + RX \rightarrow [(TPP)Rh(R)] + X\cdot$$

$$[(TPP)Rh] + RX \rightarrow [(TPP)Rh(R)]^+ + X^-$$

$$[(TPP)Rh(R)]^+ + S \rightarrow [(TPP)Rh(R)] + S^+$$

$$X\cdot + S \rightarrow X^- + S^+$$

where S is an electron source other than the electrode. The reversible reaction of [(TMP)Rh] with carbon monoxide gives [(TMP)Rh(C·O)] which dimerizes by C–C bond formation [104]:

$$[(TMP)Rh] + CO \rightleftharpoons [(TMP)Rh{-}C\cdot O]$$

$$2[(TMP)Rh{-}C\cdot O] \rightleftharpoons [(TMP)Rh{-}C(O){-}C(O)Rh(TMP)]$$

[(TMP)Rh] reacts reversibly with methane in benzene to yield $[(TMP)Rh{-}CH_3]$

and [(TMP)Rh−H] [105]:

$$2[(TMP)Rh] + CH_4 \rightleftharpoons [(TMP)Rh{-}CH_3] + [(TMP)Rh{-}H]$$

Trans-$[Ir\{PBu^t_2C_6H_3(OMe)O\}_2]$ absorbs oxygen reversibly to give a purple product. The complexes $[Ir\{PBu^t_2C_6H_4O\}_2]$ and $[Ir\{PBu^t_2C_6H_3(OMe)O\}_2]$ react with carbon monoxide to form carbonyl complexes $[Ir(CO)\{PBu^t_2C_6H_4O\}_2]$ and $[Ir(CO)\{PBu^t_2C_6H_3(OMe)O\}_2]$, respectively. Reaction of $[Ir(PBu^t_2C_6H_4O)_2]$ with H_2 yields the hydrido-complex [139]:

$$2[Ir(PBu^t_2C_6H_4O)_2] + H_2 \rightarrow [IrH(PBu^t_2C_6H_4O)_2]$$

Reaction of nitric oxide with $[NBu_4][Pt(C_6Cl_5)_4]$ affords $[NBu_4][Pt(NO)(C_6Cl_5)_4]$. The anion $[Pt(C_6Cl_5)_4]^-$ is a distorted square pyramid with a linear Pt−N−O unit [178].

D. MAGNETIC PROPERTIES

(i) Magnetic measurements

The magnetic data obtained from the d^7 platinum metal complexes are listed in Table 1. The heavier elements tend to give low spin complexes [215]. As expected, the values of magnetic moment are consistent with a spin of 1/2 system and are characteristic of low spin d^7 configuration.

(ii) Electron spin resonance spectroscopy

There have been excellent review articles on transition metal ESR studies by McGarvey [216], Koenig [217], Kokoszka and Gorden [218], Fujiwara and Nagashima [219], Kuska and Rogers [220,221], Goodman and Raynor [222] and Abragan and Bleaney [223]. Mononuclear d^7 complexes of platinum metals exhibit a low spin configuration. The presence of a single unpaired electron in these compounds makes them attractive for study using ESR spectroscopy.

The octahedral complexes possess a $(t_{2g})^6(e_g)^1$ configuration and should be Jahn–Teller distorted. Axially distorted complexes possess an unpaired electron either in the d_{z^2} orbital (ground state, $^2A_{1g}$) or in the $d_{x^2-y^2}$ orbital (ground state, $^2B_{1g}$). In low symmetry molecules (due to Jahn–Teller distortion as well as inherent low symmetry of molecules with mixed ligands), the energy levels are either singly degenerate (symmetry A or B) or doubly degenerate (E).

The formation of a molecular orbital between the metal orbital containing the unpaired electron and the atomic orbitals on the ligand nuclei results in the transfer of some of the unpaired electron density from the metal to the ligands. The available ESR data for mononuclear d^7 platinum metal complexes (Table 2) suggest that g

TABLE 1

Magnetic properties of Ru(I), Os(I), Rh(II), Ir(II), Pd(III) and Pt(III) complexes

Complex	Magnetic moment, μ (B.M.)	Ref.
$[Ru(NO)Cl_2(PPh_3)_2]$	1.60	30
$[Ru(NO)Cl_2(AsPh_3)_2]$	1.62	32
$[Os(NH_3)_6]Br$	1.50	38
$[Os(NO)Cl_2(PPh_3)_2]$	1.52	40
$[Os(NO)ClBr(PPh_3)_2]$	1.46	40
$[Rh\{S_2C_2(CN)_2\}_2]^{2-}$	1.91	52
$[Rh(Cys)_2]$	1.85	53
$[Rh(o\text{-MeCys})_2]$	1.91	53
[Rh(penicillamine)$_2$]	1.87	53
Trans-$[RhBr_2(siphos)_2]$	1.50	82
$[Rh(S_2CNMe_2)_2]$	2.08	60
$[Rh(S_2CNEt_2)_2]$	2.12	60
$[Rh(S_2CNMe_2)_2(PPh_3)]$	2.10	60
$[Rh(S_2CNEt_2)_2(PPh_3)]$	2.02	60
Cis-$[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$	2.00	63
Trans-$[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$	2.30	63
$[RhCl_2(PCy_3)_2]$	2.24	65
$[RhBr_2(PCy_3)_2]$	2.24	65
Trans-$[RhCl_2(PBu^t_2Me)_2]$	1.15	68, 69
Trans-$[RhCl_2(PBu^t_2Et)_2]$	0.92	68, 69
Trans-$[RhCl_2(PBu^t_2Pr^n)_2]$	0.53	68, 69
$[Rh(tmpp)_2][BF_4]_2$	1.80	81
[Rh(TTP)]	1.20	93
$[Rh(\eta^6\text{-}C_6Me_6)_2]\ (AlCl_4)_2$	1.32	84, 85
$[Ir(NO)Cl_3(PPh_3)_2]$	1.30	137
$[Ir(NO)Br_3(PPh_3)_2]$	1.31	136
$[Ir\{PBu^t_2(C_6H_4O)\}_2]$	1.76	139
$[Ir\{PBu^t_2(C_6H_3(OMe)O)\}_2]$	1.76	139
$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$		
R = Me	1.66	140
R = *p*-ClC_6H_4	1.67	140
R = *p*-$MeOC_6H_4$	1.74	140
R = 2,4,6-$Me_3C_6H_3$	1.67	140
RCO_2 = pd	1.65	140
$[C_9H_8N][Ir(CO)_2I_3(COC_2H_5]$	1.33	142
$[Ir(AsPh_3)(salene)(CNC_6H_4Me\text{-}p)]$	1.76	146
$[Ir(AsPh_3)(acacen)(CNC_6H_4Me\text{-}p)]$	1.97	146
$(NBu_4)[Pt(C_6Cl_5)_4]$	2.57 at 260 K 2.42 at 80 K	177

shifts depend on the degree of covalency of the complex, (i.e. the amount of unpaired electron density on the ligands) and will decrease with increasing covalency.

All the six platinum metals possess nuclear spin (Table 3). The magnitude of hyperfine coupling depends mainly on (a) mixing of other metal orbitals with the metal orbital containing the unpaired electron, (b) the nature of the metal ligand bonds and (c) the influence of charge on the metal. Increasing covalency expands the d orbital and lowers the effective charge on the metal with a resultant increase in hyperfine coupling. However, admixture of a small amount of s-character to the orbital containing the unpaired electron reduces the unpaired electron density on the ligand nuclei and hence decreases hyperfine coupling. A superhyperfine coupling may sometimes be observed when there are ligands or other atoms in the molecule whose nuclei have magnetic moments. For a free ion, the hyperfine interactions increase as the charge on the metal increases, since the electrons are more tightly held. The dependence of $\langle r^{-3} \rangle$ on the nuclear charge for d^7 ions (Ru^+, Rh^{2+}, Pd^{3+}) [224,225] is presented in Fig. 1.

The ESR spectra of Ru(I) species obtained by γ-irradiation of $[Ru(CN)_6]^{4-}$ have been interpreted in terms of the species $[Ru(CN)_5(NC)]^{5-}$ at room temperature and $[Ru(CN)_4(NC)_2]^{5-}$ at liquid nitrogen temperature [22]. The formation of the Ru—NC linkage is supported by the observations of nitrogen superhyperfine splitting. The ESR spectra for the species, produced by γ-irradiation of $[Ru(CN)_6]^{4-}$ in various lattices, exhibit the form of g tensor as $g_{\parallel} = 2.0023$ and $g_{\perp} > 2.0023$, suggesting a $4d_{z^2}$ configuration [23]. $[Ru(bipy)_3]^+$ gives a single signal at $g = 2.00$ [24,25] which is similar to that in Na(bipy) where $g_{\parallel} = 2.0023$ and $g_{\perp} = 2.0046$. This suggests that the electron is almost entirely delocalized on the bipyridine ring system. The spectra of $[Ru(NO)Cl_2L_2]$ ($L = PPh_3$, $AsPh_3$) (Fig. 2) are very broad with $g_{av} \approx 2.10$. The

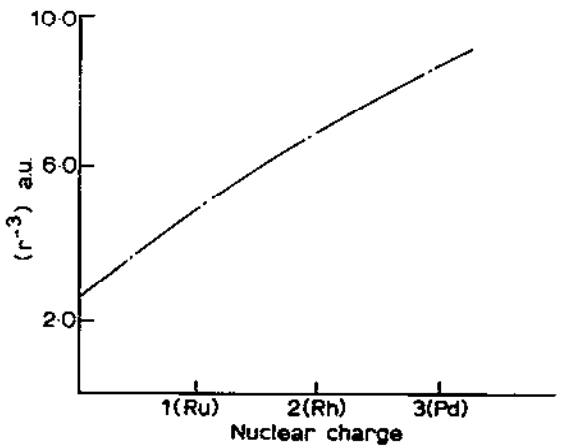


Fig. 1. Influence of nuclear charge on $\langle r^{-3} \rangle$ for d^7 ions.

TABLE 2

Electron spin resonance data for Ru(I), Os(I), Rh(II), Ir(II), Pd(III) and Pt(III) complexes

Complex	Conditions of measurement[a]	g tensor			Hyperfine tensor	Ref.
		g_{av}	$g_{\parallel}$	$g_{\perp}$	A (metal or ligands) (10^4 cm^{-1})	
$[Ru(CN)_5(HCN)]^{4-}$	77 K		1.991	2.0128 2.0138	(^{14}N) 5.3, 22.0, 17.0 (^{1}H) $A_{iso}=117$	22
$[Ru(CN)_4(NC)_2]^{5-}$	77 K		1.998	2.085	(^{14}N) $A_{iso}=3.0$	22
$[Ru(CN)_5(NC)]^{5-}$	298 K		1.998	2.088	(^{101}Ru) $A_{\parallel}=38.4$ $A_{\perp}=5.0$ (^{14}N) $A_{iso}=4.5$	22
$[Ru(CN)_4(CN')_2]^{5-}$	77 K, KCl lattice			2.078		23
$[Ru(CN)_4(CN')(H_2O)]^{5-}$	77 K, KCl lattice		1.998	2.077		23
$[Ru(CN)_4(CN')Cl]^{5-}$	77 K, KCl lattice		1.998	2.076		23
$[Ru(CN)_4Cl_2]^{5-}$	77 K, KCl lattice		1.990	2.266		23
$[Ru(CN)_4(CN')Br]^{5-}$	77 K, KBr lattice			2.085		23
$[Ru(CN)_4Br_2]^{5-}$	77 K, KBr lattice			2.091		23
$[RuCl(dppp)_2]$	243 K	2.058				34, 35
$[Ru(bipy)_3]^{+}$		2.000				24
$[Ru(NO)Cl_2(PPh_3)_2]$	295 K	2.120	2.000			30
$[Ru(NO)Cl_2(AsPh_3)_2]$	295 K	2.100	2.003			32
$[Os(CN)_5]^{4-}$	77 K, KCl matrix		1.975	2.153		38
$[Os(NO)Cl_2(PPh_3)_2]$	295 K	2.485	2.481	2.492		40
$[Os(NO)ClBr(PPh_3)_2]$	295 K	2.349	2.314	2.420		40
$[Rh\{S_2C_2(CN)_2\}_2]^{2-}$	Frozen solution		1.936	2.019 2.447		52
$[Rh(o\text{-MeCys})_2]$	RT		1.955	2.020 2.035		53

$[Rh(ttcn)_2](PF_6)_2$	77 K, CH_3CN glass		2.007	2.088		54
	77 K		2.010	2.082		55
				2.089		
	77 K, frozen glass		2.009	2.042		56
				2.085		
[(triphos)Rh(S_2CO)]	100 K, CH_2Cl_2 glass	2.062	1.990	2.092	(^{103}Rh) $A_{\parallel}=249$	58
					$A_{\perp}=213.3$	
[(triphos)Rh(Se_2CO)]	100 K, CH_2Cl_2 glass	2.065	1.998	2.086	(^{103}Rh) $A_{\parallel}=260$	58
					$A_{\perp}=210.7$	
[(triphos)Rh(S_2CNPh)]	298 K	2.062				58
[(triphos)Rh(dbc)]	100 K, CH_2Cl_2 glass		1.986	2.078	(^{103}Rh) $A_{\parallel}=262$ G	59
					$A_{\perp}=210$ G	
$[Rh(S_2CNMe_2)_2]$	295 K		1.9828	2.0135		60
				2.0523		
$[Rh(S_2CNEt_2)_2]$	295 K		1.9816	2.0148		60
				2.0529		
$[Rh(S_2CNMe_2)_2(PPh_3)]$	295 K		1.9858	2.0085		60
				2.0503		
$[Rh(S_2CNEt_2)_2(PPh_3)]$	295 K		1.9858	2.0073		60
				2.0516		
Cis-$[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$	300 K	2.03				63
Trans-$[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$	300 K		0.8	0.98		66
				4.23		
	93 K		0.92	1.21		66
				4.32		
$[RhCl_2(PCy_3)_2]$	300 K		1.27	1.58		65
				3.96		
	93 K		1.33	1.68		66
				4.02		
$[RhClBr(PCy_3)_2]$	300 K		1.20	1.56		66
				4.03		
$[RhClI(PCy_3)_2]$	300 K		1.18	1.65		66
				4.00		

TABLE 2 (*continued*)

Complex	Conditions of measurement[a]	*g* tensor			Hyperfine tensor	Ref.
		g_{av}	$g_{\parallel}$	$g_{\perp}$	*A* (metal or ligands) (10^4 cm^{-1})	
$[RhBr_2(PCy_3)_2]$	300 K		1.13	1.55 4.09		65
$[Rh(tmpp)_2][BF_4]_2$	8 K		2.004	2.250		81
[Rh(TTP)]	77 K		1.990	2.029 2.089		93
[Rh(TMP)]	90 K		1.915	2.650	(^{103}Rh) $A_{\parallel}=158$ $A_{\perp}=197$	104
$[RhCl_2(py)_4]$	133 K		2.00	2.28	(^{103}Rh) $A_{\parallel}=24$	108
$[RhCl_2(dppe)]$			1.988	2.019 2.087		74
$[RhCl_2(PPh_3)_2]$	RT		2.19	2.05		77
			2.17	2.05		78
$[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}C_2H_4)_2]^+$		1.9855				88
$[Rh(\eta^5\text{-}C_5H_5)_2]$		2.033	2.002			87
$[Rh(NO)Cl_3(EtOH)_n]$	RT	2.17				79
$[Rh(NO)Cl_3(PPh_3)_2]$	RT		2.03	2.01		79
$[Rh(CN)_4Cl_2]^{4-}$	77 K, KCl lattice		1.995	2.297	(^{103}Rh) $A_{\parallel}=43.6$ $A_{\perp}=39.5$	134
$[RhCl_6]^{4-}$	35 K, AgCl lattice		2.011	2.422		130
$[RhCl_6]^{4-}$	35 K, NaCl lattice		2.019	2.453		130
$[RhBr_6]^{4-}$	35 K, AgBr lattice		2.030	2.359	(^{103}Rh) $A_{\parallel}=13.6$ $A_{\perp}=69$	131
$[RhH_6]^{4-}$	77 K, LiH lattice		2.112	2.038	(^{103}Rh) $A_{\parallel}=26.2$ $A_{\perp}=14.5$	128

$[RhO_6]^{10-}$	4.2 K, MgO lattice		2.023	2.245	(^{103}Rh) $A_{\parallel}=7.5$	129
					$A_{\perp}=16.8$	132
$[Ir(NO)Br_3(PPh_3)_2]$	4.2 K		1.8128	1.9515		226
				2.0218		
$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$						
R = Me	RT	2.038			(^{75}As) $A_{iso}=31.31$	140
R = p-ClC_6H_4	RT	2.023	2.039	2.015	(^{75}As) $A_{\parallel}=31.38$	140
					$A_{\perp}=12.52$	
R = p-$MeOC_6H_4$	RT	2.023	2.039	2.015	(^{75}As) $A_{\parallel}=31.38$	140
					$A_{\perp}=12.52$	
R = 2,4,6-$Me_3C_6H_3$	RT	2.023	2.039	2.015	(^{75}As) $A_{\parallel}=31.38$	140
					$A_{\perp}=12.52$	
RCO_2 = pd	RT	2.027	2.06	2.011	(^{75}As) $A_{\parallel}=31.70$	140
					$A_{\perp}=4.12$	
$[Ir(\eta^5\text{-}C_5H_5)_2]$			2.033	1.977	(Ir) $A_{\parallel}=1$, $A_{\perp}=5.1$	86, 87
$[Ir(H)(CO)(PPh_3)_3]$	120 K		1.98	2.15	(Ir) $A_{\parallel}=200$	141
				2.22	$A_{\perp}=197$	
$[Ir(CH_3)(CO)(PPh_3)_3]$	120 K		1.97	2.19	(Ir) $A_{\parallel}=226$	141
				2.22	$A_{\perp}=163$	
$[Ir(CH_2CN)(CO)(PPh_3)_3]$	120 K		1.97	2.15	(Ir) $A_{\parallel}=232$	141
				2.24	$A_{\perp}=173$	
$[Ir(C_6H_5)(CO)(PPh_3)_3]$	120 K		1.97	2.16	(Ir) $A_{\parallel}=227$	141
				2.25	$A_{\perp}=171$	
$[Ir(AsPh_3)(acacen)(CNC_6H_4Me\text{-}p)]$	77 K		1.9	3.19		146
$[Ir(CN)_5]^{3-}$	77 K, KCl lattice		1.9665	2.2022		150
				2.2103		
$[IrCl_6]^{4-}$	AgCl lattice		1.904	2.813	(Ir) $A_{\parallel}=40.7$	149
					$A_{\perp}=66.0$	
$[IrBr_6]^{4-}$	AgBr lattice		1.91	2.69	(Ir) $A_{\parallel}=37.6$	149
					$A_{\perp}=62$	
$[Ir(py)_2Cl_4]^{2-}$	γ-Irradiation			2.566	(Ir) $A_{iso}=87.4$	230
					(^{14}N) $A_{iso}=12$	

TABLE 2 (*continued*)

Complex	Conditions of measurement[a]	*g* tensor			Hyperfine tensor	Ref.
		g_{av}	$g_{\parallel}$	$g_{\perp}$	*A* (metal or ligands) (10^4 cm^{-1})	
$[Ir(NO_2)_4Cl_2]^{4-}$	γ-Irradiation			2.431	(Ir) $A_{iso}=118.5$ (^{14}N) $A_{iso}=15.9$	230
Trans-$[Ir(phen)_2Br_2]^{4-}$	γ-Irradiation			2.314		230
$[Pd(tacn)_2](PF_6)_3$	77 K, frozen glass		2.007	2.123	(^{14}N) $A_{\parallel}=27$	169
	77 K, CH_3CN glass		2.007	2.115	$A_{\parallel}=26.2$ G	171
$[Pd(ttcn)_2](PF_6)_3$	77 K, CH_3CN glass	2.032	2.008	2.048		54
$[PtI(SCN)_2(NH_3)_2]$	293 K	2.18				174
$[Pt(C_{14}H_{34}N_8)]$	γ-Irradiation	2.0				200
$[Pt(ttcn)_2](PF_6)_3$	77 K, CH_3CN glass		1.987	2.044	(^{195}Pt) $A_{\parallel}=85$ $A_{\perp}=30$	181
$[AsPh_4][PtCl_3(creat)]$	pH = 2.4		1.96	2.36		182
$[PtCl_6]^{3-}$	77 K	2.43				210

[a] RT = room temperature.

TABLE 3
Natural abundance and nuclear spin of platinum metal nuclei

Isotope	Natural abundance	Spin I in multiples of $h/2\pi$
^{99}Ru	12.81	5/2
^{101}Ru	16.98	5/2
^{103}Rh	100	1/2
^{105}Pd	22.23	5/2
^{187}Os	1.64	1/2
^{189}Os	16.10	3/2
^{191}Ir	38.50	3/2
^{193}Ir	61.50	3/2
^{195}Pt	33.7	1/2

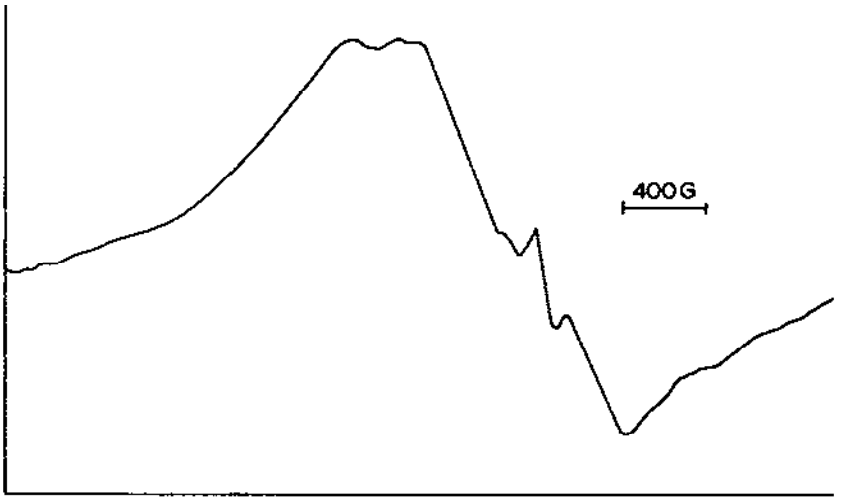


Fig. 2. ESR spectra of (a) $[Ru(NO)Cl_2(PPh_3)]_2$, (b) $[Ru(NO)Cl_2(PPh_3)_2]$ and (c) $[Ru(NO)Cl_2(AsPh_3)_2]$ at 295 K.

results indicate a ground state of $4d_{z^2}$ with the structure of the complexes being square pyramidal [30,32].

The ESR measurements of $[Os(CN)_5]^{4-}$ and $[Ir(CN)_5]^{3-}$ have shown these to be of C_{4v} symmetry with the unpaired electron in the $5d_{z^2}$ orbital [38,150]. For $[Os(CN)_5]^{4-}$ and $[Ir(CN)_5]^{3-}$ with the $5d^7$ configuration, the osmium(I) species is less covalent than the Ir(II). For a linear $\{MNO\}^7$ pentacoordinate system, the unpaired electron could be either in σ_{NO}–d_{z^2} in the case of tetragonal pyramidal geometry ($g_{\|} = 2.0$) or in $d_{x^2-y^2}$ in the case of distorted trigonal bipyramidal geometry ($g_{\perp} > 2.0$). The values of the g tensors for $[Os(NO)ClX(PPh_3)_2]$ (X = Cl, Br) (Fig. 3) suggest a distorted trigonal bipyramidal structure.

ESR studies of mononuclear Rh(II) systems were reviewed by Felthouse in

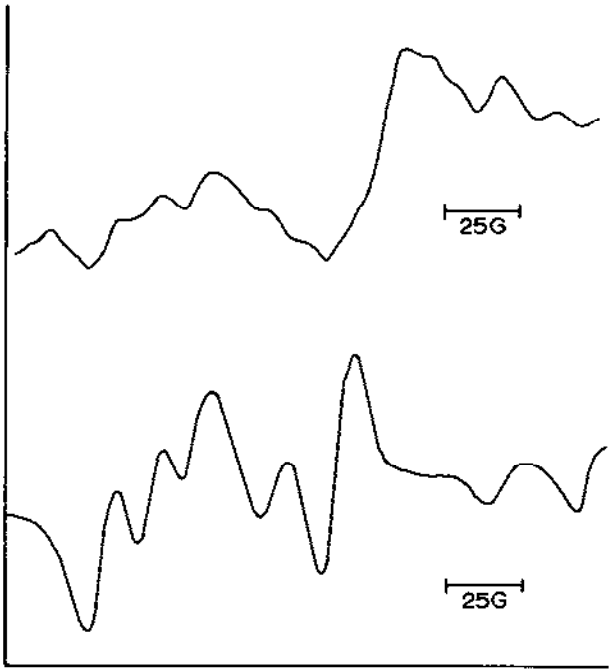


Fig. 3. ESR spectrum of $[Os(NO)ClBr(PPh_3)_2]$ at 295 K.

1982 [5]. Rh(II) exhibits two types of ESR spectra as seen in Table 3. Complexes exhibiting the first type have axial spectra with small anisotropy and the second type possess completely anisotropic g values. The ground state responsible for the type I ESR spectra can be described as $4d_{z^2}$ (with $g_\perp > g_\parallel = 2.00$), whereas for type II spectra, the ground state is $4d_{xz}$.

The ESR spectrum of the $[Rh(ttcn)_2]^{2+}$ complex ion exhibits $g = 2.046$ without resolved ^{103}Rh hyperfine splitting. Frozen solutions yield rhombic spectra. The complex [(triphos)Rh(S_2CO)] shows a single broad ESR signal (298 K) at $\langle g \rangle = 2.062$ ($\Delta H = 120$ G), indicative of a strong exchange interaction between nearest neighbours. A well-resolved spectrum is obtained in CH_2Cl_2 glass at 100 K. The large hyperfine splittings are due to a strong interaction with the apical phosphorus. Similar ESR spectra have been obtained for [(triphos)Rh(Se_2CO)], [(triphos)Rh(S_2CNPh)] and [(triphos)Rh(Dbc)] at freezing and room temperature [58,59]. The ESR powder spectra of the complexes $[Rh(S_2CNR_2)_2]$ and $[Rh(S_2CNR_2)_2(PPh_3)]$ (R = Me, Et) show three g values near 2.0 (Fig. 4) [60]. The ESR spectra of *trans*-$[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$ and $[RhXY(PCy_3)_2]$ exhibit large anisotropies with $g_y \approx 4$ and $g_x, g_z \approx 1$–1.6 [63,65,66]. The vibrations of the surrounding ligands cause mixing between $4d_{z^2}$ and $4d_{xz}$. The spectrum of $[RhCl_2(py)_4]$ shows an eight-line pattern signal for $g_\parallel$ with $A_\parallel = 24 \times 10^{-4}$ cm^{-1} due to coupling to one Rh (I = 1/2) and two Cl atoms (I = 3/2) [108]. ESR signals are detected in the species

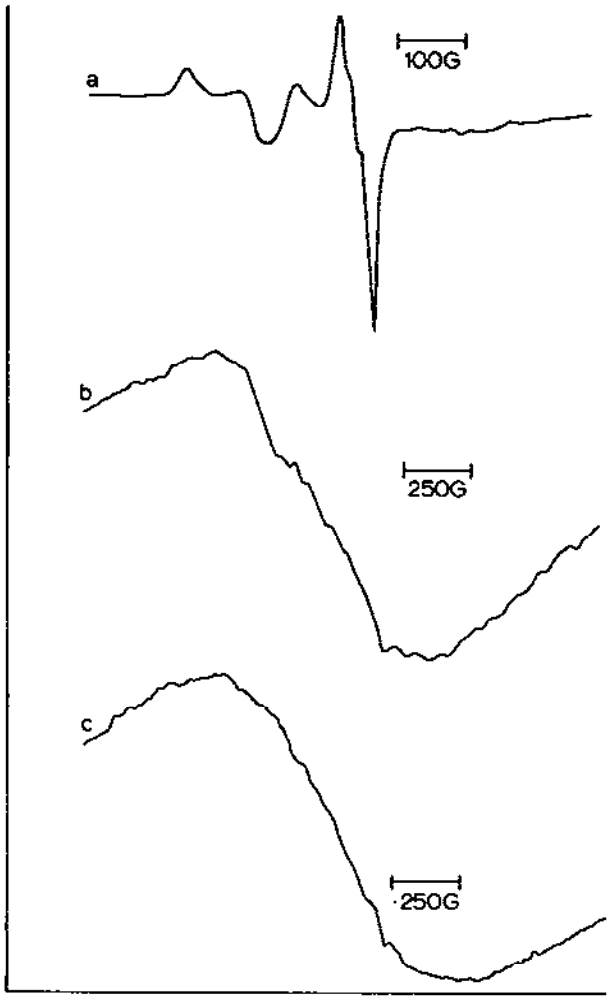


Fig. 4. ESR spectra of (a) $[Rh(S_2CNEt_2)_2(PPh_3)]$ and (b) $[Rh(S_2CNEt_2)_2]$ at 295 K.

thought to be $[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}C_2H_2)_2]^+$ [88] and also from the one-electron reduction product of $[(\eta^5\text{-}C_5H_5)Rh\{S_2C_2(CF_3)_2\}]$ [89]. In $[Rh(\eta^5\text{-}C_5H_5)_2]$, the unpaired electron occupies the A_{2u} ($4d_{z^2}$) orbital [87].

A number of ESR spectra of Rh(II) ions doped in various diamagnetic hosts have been reported. $[Rh(CN)_4Cl_2]^{4-}$ in a KCl host shows tetragonal distortion having a $4d_{z^2}$ ground state. The large value of the ^{103}Rh hyperfine splitting for $[Rh(CN)_4Cl_2]^{4-}$ suggests a large amount of spin density at the rhodium nucleus [134]. The spectrum of $[RhH_6]^{4-}$ in LiH crystals from 77 to 300 K shows two g values. Superhyperfine interactions with the octahedrally coordinated H^- ions have been observed [128]. The g values indicate a $^2B_1$ ($4d_{x^2-y^2}$) ground state. A dynamic

Jahn–Teller distortion occurs in $[RhX_6]^{4-}/AgX$ (X = Cl or Br) at temperatures > 200 K. At 35 K, the Rh(II) ions are covalently bonded to six halide ions, interacting with two axially opposed ligands more effectively than with those in the equatorial positions. At 200 K, the unpaired electron occupies a wavefunction which is an equal amount of $\psi(d_{x^2-y^2})$ and $\psi(d_{z^2})$ [130,131]. The ESR spectrum of $[RhO_6]^{10-}$ in an MgO host shows a single isotropic g value from 12–77 K but at 4.2 K, the spectrum consists of two g values [108,111]. For $[RhX_6]^{4-}$ (X = H, Cl, Br) and $[RhO_6]^{10-}$, the total electron density transferred from the Rh(II) ion increases as H^- (0.11) < Cl^- (0.19) < Br^- (0.23) < O^{2-} (0.33). The total covalency in the Rh–H bonds is rather small compared to halide and oxide complexes.

At room temperature, the spectrum of $[Ir(NO)Br_3(PPh_3)_2]$ has a broad unresolved resonance. At 4.2 K, the spectrum is well-resolved with three g values [226] whose trend is diagnostic of an electronic state similar to that observed in trapped NO centres [227]. Series of complexes [140] $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$, where R = Me, p-ClC_6H_4, p-$MeOC_6H_4$ and 2,4,6-$Me_3C_6H_3$ and RCO_2 = pentane-2,4-dionate, give interesting ESR spectra with ^{75}As superhyperfine splitting. The g value patterns ($g_{\parallel} > g_{\perp} > 2.0$) suggest that the unpaired electron is in a $5d_{x^2-y^2}$ orbital. The magnitude of the tetragonal distortion decreases from $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(pd)]$ to $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CMe)_2]$ which gives an isotropic resonance. A small metal hyperfine coupling is detected for $[Ir(\eta^5\text{-}C_5H_5)_2]$ [87].

The ESR spectra of $[Ir(R)(CO)(PPh_3)_3]^+$ (R = H, CH_3, CH_2CN, C_6H_5) are insensitive to the nature of R and consist of a doublet at room temperature and a triplet of doublets at 120 K. The unpaired electron on iridium in these complexes seems to couple with non-axial phosphorus. The iridium hyperfine splitting becomes smaller as the ligand becomes more covalent [141]. The complexes $[Ir(AsPh_3)(L)(CNC_6H_4Me\text{-}p)]$ (L = salen and acacen) exhibit broad resonance. The spectrum of the salen complex is too broad to be resolved, whereas at low temperature, the spectrum of the acacen complex is resolved into two g values [146] which are similar to those for the isoelectronic cobalt complex [228].

Similar to Ru(I) and Rh(II) ions, several reports have appeared on the ESR spectra of Ir(II) ions doped into diamagnetic hosts [149,150,229,230]. The ESR data for $[IrX_6]^{4-}$ (X = Cl, Br) in AgX hosts are consistent with an unpaired electron in a $5d_{z^2}$ orbital interacting with two equivalent halogen atoms and iridium nuclei. The g values for the Ir(II) complexes, produced by γ-irradiation of Ir(III) complexes, decrease with the ligand as Cl > py > NO_2 > phen [230].

The ESR spectrum of $[Pd(tacn)_2]^{3+}$ in aqueous solution gives a broad isotropic signal ($g_{iso} = 2.08$ at room temperature and $g_{iso} = 2.077$ at 77 K). Increasing the ionic strength and decreasing the pH of the solution yields a resolved ESR spectrum for $[(Pd(tacn)_2]^{3+}$ with $g_{\parallel} = 2.007$ ($A_{\parallel} = 26.2$ G) and $g_{\perp} = 2.115$ [171]. ^{14}N Superhyperfine couplings to two nitrogen donors are observed with $A_{\parallel} = 27$ G. Similar ^{14}N superhyperfine splitting to two nitrogen donors has been observed for Ni(III) macrocyclic complexes [231]. The complexes $[M(ttcn)_2](PF_6)_3$ (M = Pd, Pt) show resolved

ESR spectra at 77 K. The isotropic signal near $g=2.00$ for $[Pt(C_{14}H_{34}N_8)]$ suggests an octahedral environment of the macrocyclic ligand around the Pt(III) ion [181].

E. SPECTROSCOPIC STUDIES

(i) Infrared studies

Infrared spectroscopy provides the most convenient method for characterization of the ligand binding modes from which the molecular structure of a complex can be deduced. The important infrared frequencies for various complexes are presented in Table 4.

The corrected NO stretching frequencies for the nitrosyl complexes $[Ru(NO)Cl_2L_2]$ ($L=PPh_3$, $AsPh_3$), $[Os(NO)ClX(PPh_3)_2]$, $[Rh(NO)Cl_3(PPh_3)_2]$ and $[Ir(NO)X_3(PPh_3)_2]$ ($X=Cl$, Br) (Table 4) lie above 1610 cm^{-1}. This is evidence for the presence of a linear nitrosyl group and the complexes can be regarded as complexes between metals and NO^+ [138]. However, the complexes $[Ru(NO)Cl(bipy)_2]I$ and $[Ru(NO)(CH_3CN)(bipy)_2]^{2+}$ exhibit corrected nitrosyl stretching frequencies below 1610 cm^{-1}. The presence of an unpaired electron on the nitrosyl group has been proposed for these complexes.

The binding sites of the amino acids to rhodium in the complexes $[RhL_2]$ (L = Cys, *o*-MeCys, penicillamine) are deduced from their infrared spectra. The absence of SH stretching frequencies at about 2500 cm^{-1}, present in the free ligands, suggests the formation of M–S bonds in these complexes.

The identification of metal–halide stretching vibrations has assisted in the assignment of coordination geometries for the halophosphine complexes. The bands in the range 355–300 cm^{-1} are assigned to ν(M–Cl) (Cl trans to Cl) and thus a trans stereochemistry is suggested for $[RhCl_2(PR_3)_2]$. The far-IR spectrum of *trans*-$[RhCl_2(PPh_3)_2]$ shows bands at 406, 423, 444 and 454 cm^{-1} due to ν(Rh–P) [78].

In the infrared spectra of complexes $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$, which have been prepared from $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$, the bands due to ν(Ir–H) disappear and the bands due to ν(CN) shift to a higher frequency of 2135 cm^{-1} [140]. The CN stretching bands in $[Ir(AsPh_3)(salene)(CNC_6H_4Me\text{-}p)]$ and $[Ir(AsPh_3)(acacen)(CNC_6H_4Me\text{-}p)]$ are insensitive to the reduction from Ir(III) to Ir(II) [146]. The vibrational spectra of these complexes are consistent with the carboxylate ligand as bidentate.

(ii) Electronic absorption studies

All the known mononuclear d^7 complexes of platinum metals exhibit a low spin configuration. The ground term for low spin d^7 is ^2E_g and should be Jahn–Teller distorted. Axially distorted complexes possess an unpaired electron either in the d_{z^2} orbital (ground state, $^2A_{1g}$) or in the $d_{x^2-y^2}$ orbital (ground state, $^2B_{1g}$) [232].

TABLE 4

Important IR frequencies (cm^{-1}) for Ru(I), Os(I), Rh(II) and Ir(II) complexes

Complex	ν(NO)	ν(CO)	ν(M–X)	ν(NH)	ν(COO)	Ref.
$[Ru(NO)Cl_2(PPh_3)_2]$	1868		340			30
$[Ru(NO)Cl_2(AsPh_3)_2]$	1860					32
$[Ru(NO)Cl(bipy)_2]I$	1611					28, 29
$[Ru(NO)(CH_3CN)(bipy)_2]^{2+}$	1655					28, 29
$[Os(NO)Cl_2(PPh_3)_2]$	1845		325			40
$[Os(NO)ClBr(PPh_3)_2]$	1842		320			40
$[Rh(NO)Cl_3(PPh_3)_2]$	1660					79
$[Ir(NO)Cl_3(PPh_3)_2]$	1732					137
$[Ir(H)(CO)(PPh_3)_3]$		1990				141
$[Ir(CH_3)(CO)(PPh_3)_3]$		2008				141
$[Ir(CH_2CN)(CO)(PPh_3)_3]$		2015				141
$[Ir(C_6H_5)(CO)(PPh_3)_3]$		2010				141
$[Rh(Cys)_2]$				3100	1710	53
$[Rh(o\text{-}MeCys)_2]$				3230	1730	53
				3215		
[Rh(penicillamine)$_2$]				3200	1705	53
[RhCl(*s*-bqdi)(PPh$_3$)$_2$]				3335		83
				3290		
				3260		
[RhCl(*s*-disn)(PPh$_3$)$_2$]				3340		83
				3325		
				3230		
Trans-$[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$			351			63
$[RhCl_2(PCy_3)_2]$			354, 343			65
$[RhBr_2(PCy_3)_2]$			288, 270			65
$[RhClBr(PCy_3)_2]$			335, 271			66
$[RhClI(PCy_3)_2]$			325			66
$[Rh(CO)Cl_2(PCy_3)_2]$		2000	300			67
Trans-$[RhCl_2(PBu^t_2Me)_2]$			352, 348			68, 69
Trans-$[RhCl_2(PBu^t_2Et)_2]$			360, 334			68, 69
$[RhCl_2\{PBu^t_2(C{\equiv}CPh)_2]$			295			70
$[RhCl_2(dppe)]$			262			74
$[RhCl_2(PPh_3)_2]$			310			78

There is a close similarity between the electronic spectra of low spin six-coordinate d^7 complexes and those of low spin five-coordinate square pyramidal and low spin four-coordinate square planar complexes. The ground state in a low spin trigonal bipyramidal d^7 complex will be 2e′ and is subject to Jahn–Teller distortion. For trigonal bipyramidal complexes, the lower energy transition will be a transition from a component of e′ to a'_1. Since much less work has been done (Table 5), some of the important features for these complexes are discussed briefly.

The electronic spectra of $[Ru(NO)Cl_2L_2]$ ($L = PPh_3$ or $AsPh_3$) show four

TABLE 5

Electronic spectroscopic data for monomeric d^7 platinum metal complexes

Complex	λ_{max}[a] (nm)	Ref.
$[Ru(NO)Cl_2(PPh_3)_2]$	425, 335, 330, 282	30
$[Ru(NO)Cl_2(AsPh_3)_2]$	420, 335, 300, 275	32
$[Ru(NO)Cl(bipy)_2](PF_6)$	350(5400), 310 sh, 293(26 000)	28, 29
$[RuCl(dppp)_2]$	530	34, 35
$[Ru(bipy)_3]^+$	495–510	24, 25
$[Os(NO)Cl_2(PPh_3)_2]$	805(5.56), 750(16.5), 675(43.5)	40
$[Os(NO)ClBr(PPh_3)_2]$	810(13.58), 770(23.8), 682(52.3)	40
$[Rh\{S_2C_2(CN)_2\}_2]^{2-}$	1282(30), 633(4000)	52
$[Rh(Cys)_2]$	575	53
$[Rh(o\text{-}MeCys)_2]$	575	53
[Rh(penicillamine)$_2$]	575	53
$[Rh(ttcn)_2]^{2+}$	268(22 300)	55
$[Rh(S_2CNMe_2)_2]$	430(2320), 312(44 080), 281(29 190)	60
$[Rh(S_2CNEt_2)_2]$	430(2060), 314(45 090), 280(26 370)	60
$[Rh(S_2CNMe_2)_2(PPh_3)]$	430(1930), 306(31 430), 280(32 860)	60
$[Rh(S_2CNEt_2)_2(PPh_3)]$	426(1830), 315(36 360), 280(20 860)	60
Trans-$[RhCl_2(PBu^t_2Me)_2]$	559(125), 446(481)	68, 69
Trans-$[RhCl_2(PBu^t_2Pr^n)_2]$	583(147), 484(110)	68, 69
$[Rh(tmpp)_2][BF_4]_2$	540(2050), 329(13 405), 298(15 280) 285 (17 518)	81
$[RhCl(s\text{-}bqdi)(PPh_3)_2]$	650(5170), 500(2010), 390(3690)	83
[Rh(TTP)]	601, 568, 531, 418	93
$[RhCl_2(dppe)]$	405(1700), 267(19 900)	74
$[Rh(bipy)_3]^{2+}$	485(1000)	120
$[Rh(CN)_4Cl_2]^{4-}$	575	134
$[Ir(NO)Br_3(PPh_3)_2]$	885	136
$[C_9H_8N][Ir(CO)_2I_3(COC_2H_5)]$	326(9240)	142
$[Pd(ttcn)_2]^{3+}$	476(5350), 341(16 100), 230(8100)	54
$[Pd(tacn)_2]^{3+}$	387(590), 314(1240), 196(11 200)	171
$[Pt(ttcn)_2]^{3+}$	401(3500)	181
$[PtCl_4(H_2O)_2]^-$	410	204
$[PtCl_4(OH)(H_2O)]^{2-}$	450	204
$[PtCl_5]^{2-}$	530(2690), 370(5265)	205, 210
$[PtCl_6]^{3-}$	260	208
$[PtCl_4(OH)]^{2-}$	450	207, 208
$[PtCl_4]^-$	620, 410	203, 207
Trans-$[PtCl_2(OH)_2]^-$	408	207, 208
Cis-$[PtCl_2(OH)_2]^-$	415	207
$[PtCl_3(OH)]^-$	414, 395	207

[a] ε_{max} (mol^{-1} dm^3 cm^{-1}) in parentheses.

absorption bonds around 420, 330, 300 and 280 nm (Fig. 5). The last three bands are assigned to charge transfer transitions. The band around 420 nm may be assigned to a d–d transition ($e_g \rightarrow a_{1g}$) with the occupied metal orbital having some ligand character [30,32]. $[Ru(bipy)_3]^+$ exhibits a band due to the $d\pi$ (Ru)→*(bipy) transition at 495–510 nm [24,25].

The electronic spectra of $[Rh(S_2CNR_2)]$ and $[Rh(S_2CNR_2)(PPh_3)]$ (R = Me or Et) complexes show intense absorption bands in the vicinity of 315–280 nm ($\varepsilon = 10^4$ mol^{-1} dm^3 cm^{-1}) which have been assigned to π–π^* transitions. A weak absorption band in the region 425 nm, which is stronger for four-coordinated complexes, is a transition from the lower filled orbitals e_g to the empty b_{1g} antibonding orbital [60]. *Trans*-$[RhCl_2(PBu^t_2R)_2]$ (R = Me or Pr^n) show two maxima in their electronic absorption spectra in the visible region which are assigned to d_{xz}, $d_{yz} \rightarrow d_{z^2}$ and $d_{xy} \rightarrow d_{z^2}$ [68,69]. $[Rh\{S_2C_2(CN)\}_2]^{2-}$ shows a band around 1282 nm which has been assigned to an $a_{1g} \rightarrow b_{1g}$ transition [52]. A band at 505 nm for $[Rh(CN)_4Cl_2]^{4-}$ is assigned to an $e_g \rightarrow a_{1g}$ transition [134]. The rhodium(II) monomeric complexes

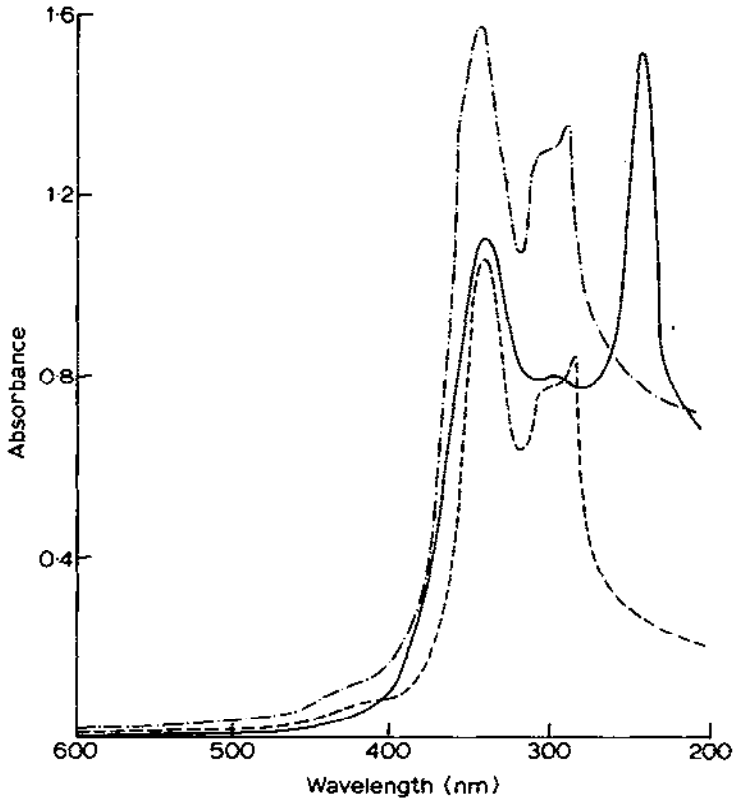


Fig. 5. Electronic spectra (ca. 10^{-4} M solution in benzene) of: —, $[Ru(NO)Cl_3(PPh_3)_2]$; $[Ru(NO)Cl_2(PPh_3)_2]$; – – –, $[Ru(NO)Cl_2(PPh_3)]_2$.

$[Rh(Cys)_2]$, $[Rh(o\text{-}MeCys)_2]$ and [Rh(penicillamine)$_2$] show a weak band around 575 nm which may be assigned to an $e_g \rightarrow a_{1g}$ transition [53]. The absorption at 885 cm^{-1} for $[Ir(NO)Br_3(PPh_3)_2]$ can be assigned to a d–d transition with some $Ir(d\pi)$–$\pi^*(NO)$ character [136].

Electronic spectra of a number of Pt(III) complexes containing chloro, aquo and hydroxo ligands have been derived from both experimental and theoretical considerations [207,208]. From these data, $[PtCl_6]^{3-}$ should exhibit an intense maximum near 260 nm. Absorption bands near 450 and 250 nm have been observed for $[PtCl_4(OH)(H_2O)]^{2-}$. These bands are assigned to HO→Pt(III) (16a′→18a′) and H_2O→Pt(III) (10a′→18a′) charge transfer transitions. *Cis*- and *trans*-$[PtCl_2(OH)_2]^-$ are found to exhibit HO→Pt(III) charge transfer transitions, $6b_2 \rightarrow 3a_2$ (cis) and $6b_u \rightarrow 4b_g$ at 415 nm [207].

(iii) X-ray photoelectron spectral studies

X-ray photoelectron spectroscopy (also called ESCA) has proven to be a useful tool for the determination of the electronic structure of matter [233,234]. For a set of complexes in which the ligands are similar, the core electron binding energies for the metal can be correlated with the oxidation state. Only a few monomeric Ru(I), Rh(II) and Os(I) complexes have been studied by XPS (Table 6). Binding energies for rhodium $3d_{5/2}$ electrons in rhodium(II) complexes are in the region of 308.9 to 309.1 eV [235,236]. Core electron binding energies for Ru $3d_{5/2}$ electrons and Os $4f_{7/2}$ electrons in the complexes $[M(NO)Cl_2(PPh_3)_2]$ and $[M(NO)Cl_3(PPh_3)_2]$

TABLE 6

Metal core binding energies (eV) of the complexes

Complex	Oxidation state	Metal core binding energy Ru $3d_{5/2}$ or Rh $3d_{5/2}$ or Os $4f_{7/2}$	Ref.
$[Ru(NO)Cl_2(PPh_3)_2]$	+1	281.8[a]	238
$[Ru(NO)Cl_3(PPh_3)_2]$	+2	282.3[a]	238
		281.3	237
$[Ru(NO)Cl(bipy)_2]I$	+1	280.5	29
$[Os(NO)Cl_2(PPh_3)_2]$	+1	53.3[a]	238
$[Os(NO)Cl_3(PPh_3)_2]$	+2	53.8[a]	238
Trans-$[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$	+2	308.9	235
[Rh(psp)Cl_2][b]	+2	309.1	235
[Rh(dpc)]·$3H_2O$[c]	+2	308.8	236
$RhCl_3 \cdot 3H_2O$	+3	309.7	235

[a]Calculated value.

[b]psp = polymeric diphenylbenzylphosphine.

[c]dpc = 2,6-pyridinedicarboxylate.

(M = Ru, Os) were calculated by the method of Feltham and Brant [237,238]. One can infer from the experimental values for the rhodium complexes and the calculated values for the ruthenium and osmium complexes that metal core binding energies for d^7 configurations are lower than the metal core binding energies for d^8 configurations and hence, the unpaired electron in d^7 complexes will be in an orbital largely metal in character.

F. CATALYTIC APPLICATIONS

So far only the catalytic activities of rhodium(II) complexes have been reported. The existence of rhodium(II) complexes as intermediates in olefin oxidations has been proposed in a number of studies [239–241]. The rhodium(II) complexes $[RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2]$ and $[RhCl_2(PCy_3)_2]$ catalyze the hydrogenation and hydrosilation of various olefins and acetylenes [242]. The formation of equal amounts of cis and trans isomers in the hydrosilation of 1-hexyne suggests that these rhodium(II) complexes are not stereospecific.

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REFERENCES

1 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th edn., Wiley, New York, 1988, pp. 912, 931.
2 M. Schroder and T.A. Stephenson, in G. Wilkinson (Ed.) Comprehensive Coordination Chemistry, Vol. 4, Pergamon Press, Oxford, 1987, p. 277.
3 E.A. Seddon and K.R. Seddon, The Chemistry of Ruthenium, Elsevier, Amsterdam, 1984.
4 M.A. Bennett, M.I. Bruce and T.W. Matheson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon Press, Oxford, 1982, p. 651.
5 T.R. Felthouse, Prog. Inorg. Chem., 29 (1982) 73.
6 E.B. Boyer and S.D. Robinson, Coord. Chem. Rev., 50 (1983) 109.
7 S.E. Livingstone, in J.C. Bailar, Jr., H.J. Emelius, R.S. Nyholm and A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Vol. 3, Pergamon Press, Oxford, 1973, pp. 1163, 1244.
8 D.J. Woollins and P.F. Kelley, Coord. Chem. Rev., 65 (1985) 115.
9 F.R. Hartley, The Chemistry of Platinum and Palladium, Applied Science, London, 1971, p. 71.
10 R. Uson and J. Fornies, Adv. Organomet. Chem., 28 (1988) 219.
11 W.P. Griffith, in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Vol. 4, Pergamon Press, Oxford, 1987, p. 519.
12 F.H. Jardine and P.S. Sheridon, in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Vol. 4, Pergamon Press, Oxford, 1987, p. 932.

13 N. Serpone and M.A. Jamienson, in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Vol. 4, Pergamon Press, Oxford, 1987, p. 1020.
14 U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, New York, 1974, p. 166.
15 J.A. McCleverty, Prog. Inorg. Chem., 10 (1968) 49.
16 G.J. Leigh and R.L. Richards, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 5, Pergamon Press, Oxford, 1982, p. 557.
17 N.N. Greenwood and A. Earnshaw, Chemistry of Elements, Pergamon Press, Oxford, 1984, p. 1340.
18 W. Manchot and J. Duesing, Z. Anorg. Allg. Chem., 212 (1933) 21.
19 W. Manchot and H. Schmid, Chem. Ber., 64 (1931) 2672.
20 R. Remy and M. Koehn, Z. Anorg. Allg. Chem., 137 (1924) 365.
21 L. Woehler and P. Balz, Z. Anorg. Allg. Chem., 139 (1924) 411.
22 R.S. Eachus and F.G. Herring, Can. J. Chem., 50 (1972) 162.
23 M.C.R. Symons and J.G. Wilkinson, J. Chem. Soc. Dalton Trans., (1973) 965.
24 H.S.C. DeVille and H. DeBray, C. R. Acad. Sci., 83 (1976) 926.
25 K.C. Dewhirst, W. Keim and C.A. Reilly, Inorg. Chem., 7 (1968) 819.
26 A.A. Diamantis and G.J. Sparrow, J. Chem. Soc. D, (1970) 819.
27 A.A. Diamantis and G.J. Sparrow, J. Colloid Interface Sci., 47 (1974) 455.
28 R.W. Challan, G.M. Brown and T.J. Meyer, J. Am. Chem. Soc., 97 (1975) 894.
29 R.W. Challan and T.J. Meyer, Inorg. Chem., 16 (1977) 574.
30 K.K. Pandey, S.R. Ahuja, N.S. Poonia and S. Bharti, J. Chem. Soc. Chem. Commun., (1982) 1268.
31 S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton Trans., (1972) 1.
32 S.R. Ahuja, Ph.D. Thesis, D.A. University, Indore, 1985.
33 J. Irving and P.J. Laye, J. Chem. Soc. A, (1966) 16.
34 G. Zotti, G. Pilloni, M. Bressan and M. Martelli, J. Electroanal. Chem. Interfacial Electrochem., 75 (1975) 607.
35 G. Pilloni, G. Zotti, C. Corvaja and M. Martelli, J. Electroanal. Chem. Interfacial Electrochem., 91 (1978) 385.
36 L. Vaska and E.M.S. Sloane, J. Am. Chem. Soc., 82 (1960) 1263.
37 L. Vaska and J.W. Diluzio, J. Am. Chem. Soc., 83 (1961) 1262.
38 N.V. Vugman, A.N. Rossi and J. Danon, J. Chem. Phys., 68 (1978) 3152.
39 G.W. Watt, E.M. Potrafke and D.S. Klett, Inorg. Chem., 2 (1963) 868.
40 K.K. Pandey and S.R. Ahuja, Inorg. Chem., 24 (1985) 2855.
41 B.L. Haymore and J.A. Ibers, Inorg. Chem., 14 (1975) 2610.
42 R. Hoffmann, M.M.L. Chen, M. Elian, A.R. Rossi and D.M.P. Mingos, Inorg. Chem., 13 (1974) 2666.
43 A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365.
44 C. Claus, J. Prakt. Chem., 80 (1860) 297.
45 H. Reinlen and W. Huhn, Z. Anorg. Allg. Chem., 214 (1933) 190.
46 K. Seubert and K. Kobbe, Chem. Ber., 23 (1890) 2558.
47 F.G. Mann and W.J. Pope, Proc. R. Soc. London Ser. A, 109 (1925) 452.
48 L. Pauling, Proc. Natl. Acad. Sci. U.S.A., 15 (1929) 132.
49 L. Wohler and W. Mueller, Z. Anorg. Allg. Chem., 149 (1925) 132.
50 Gmelin's Handbuch der Anorganischen Chemie Rhodium, No. 64, Verleg-Chemi, Berlin, 1938.
51 B. Martui, W.R. McWhinnie and G.M. Waind, J. Inorg. Nucl. Chem., 23 (1961) 207.
52 E. Billing, S.I. Saupack, J.H. Waters, R. Williams and H.B. Gray, J. Am. Chem. Soc., 86 (1964) 926.

53 G.P. Kakis and P. Saroulis, Inorg. Chim. Acta, 46 (1980) 97.
54 A.J. Blake, A.J. Holder, T.I. Hyde and M. Shroeder, J. Chem. Soc. Chem. Commun., (1987) 987.
55 A.J. Blake, R.O. Gould, A.J. Holder, T.I. Hyde and M. Schroeder, J. Chem. Soc. Dalton Trans., (1988) 1861.
56 S.C. Rawle, R. Yagbasan, K. Prout and S.R. Cooper, J. Am. Chem. Soc., 109 (1987) 6181.
57 C. Bianchini, A. Meli and F. Vizza, Angew. Chem. Int. Ed. Engl., 26 (1987) 767.
58 C. Bianchini, A. Meli, F. Laschi, F. Vizza and P. Zanelli, Inorg. Chem., 28 (1989) 227.
59 C. Bianchini, P. Frediani, F. Laschi, A. Meli, F. Vizza and P. Zonello, Inorg. Chem., 29 (1990) 3402.
60 K.K. Pandey, D.T. Nehete and R.B. Sharma, Polyhedron, 9 (1990) 2013.
61 K.K. Pandey and S. Puri, unpublished work, 1990.
62 C. Bianchini, F. Laschi, F. Otta Wani, M. Peruzzini and P. Zanelli, Organometallics, 7 (1988) 1660.
63 M.A. Bennett, R. Bramley and P.A. Longstaff, J. Chem. Soc. Chem. Commun., (1966) 806.
64 M.A. Bennett and P.A. Longstaff, J. Am. Chem. Soc., 91 (1969) 6266.
65 F.G. Moers, J.A.M. DeJong and P.M.G. Beaumont, J. Inorg. Nucl. Chem., 35 (1973) 1915.
66 H.L.M. VanGall, J.M.J. Verlaak and T. Posno, Inorg. Chim. Acta, 23 (1977) 23.
67 G. Valentini, G. Braca, G. Sbrana and A. Colligiani, Inorg. Chim. Acta, 69 (1983) 221.
68 B.L. Shaw, C. Masters, W.S. McDonalt and G. Raper, J. Chem. Soc. Chem. Commun., (1971) 210.
69 C. Masters and G.L. Shaw, J. Chem. Soc. A, (1971) 3679.
70 H.D. Empsall, E.M. Hyde, E. Mentzer and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1977) 2285.
71 H.D. Empsall, E.M. Hyde, C.E. Jones and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1974) 1980.
72 H.D. Empsall, P.N. Heys and B.L. Shaw, Transition Met. Chem., 3 (1978) 165.
73 H.D. Empsall, S. Johnson and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1980) 302.
74 F. Pruchnik, Inorg. Nucl. Chem. Lett., 10 (1974) 661.
75 T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer and G. Wilkinson, J. Chem. Soc., (1965) 3632.
76 H.D. Empsall, E.M. Hyde, D. Pawson and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1977) 1292.
77 J.A. Osborn, F.J. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
78 C.A. Ogle, T.C. Masterman and J.L. Hubbard, J. Chem. Soc. Chem. Commun., (1990) 1733.
79 M.C. Baird, Inorg. Chim. Acta, 5 (1971) 46.
80 C.A. McAuliffe, I.E. Niven and R.V. Parish, Inorg. Nucl. Chem. Lett., 12 (1976) 855.
81 K.R. Dunbar, H.C. Haefner and L.E. Pense, J. Am. Chem. Soc., 111 (1989) 5504.
82 A.T.T. Hsich, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. Dalton. Trans., (1972) 1966.
83 S.-M. Peng, K. Peters, E.-M. Peters and A. Simon, Inorg. Chim. Acta, 101 (1985) L35.
84 E.O. Fischer and H.H. Linder, J. Organomet. Chem., 1 (1964) 307.
85 M.R. Thomson, J. Am. Chem. Soc., 102 (1980) 2979.
86 E.O. Fischer and H. Wawersik, J. Organomet. Chem., 5 (1966) 559.
87 H.J. Killer and H. Wawersik, J. Organomet. Chem., 8 (1967) 185.
88 R.E. Dessy, R.B. King and M. Waldrop, J. Am. Chem. Soc., 88 (1966) 5112.
89 R.E. Dessy, R. Kornmann, C. Smith and R. Hayter, J. Am. Chem. Soc., 90 (1968) 2001.
90 D.J. O'Sullivan and F.J. Lalor, J. Organomet. Chem., 57 (1973) C58.
91 R.J. Restivo, G. Ferguson, D.J. O'Sullivan and F.J. Lalor, Inorg. Chem., 14 (1975) 3046.

92 A.E. Crease, B.D. Gupta, M.D. Johnson and S. Moorhouse, J. Chem. Soc. Dalton Trans., (1978) 1821.
93 B.R. James and D.V. Stynes, J. Am. Chem. Soc., 94 (1972) 6225.
94 B.B. Wayland and K.D. Rossi, J. Organomet. Chem., 276 (1984) C27.
95 M. Hoshino, K. Yasufuku, S. Konishi and M. Imamura, Inorg. Chem., 23 (1984) 1982.
96 S. van Voorhees and B.B. Wayland, Organometallics, 4 (1985) 1887.
97 K.D. Rossi and B.B. Wayland, J. Am. Chem. Soc., 107 (1985) 7941.
98 R.S. Paonessa, N.C. Thomas and J. Halpern, J. Am. Chem. Soc., 107 (1985) 4333.
99 K.M. Kadish, C.-L. Yao, J.E. Anderson and P. Cocolias, Inorg. Chem., 24 (1985) 4515.
100 J.E. Anderson, C.-L. Yao and K.M. Kadish, Inorg. Chem., 25 (1986) 718.
101 B.B. Wayland, B.A. Woods and V.L. Coffin, Organometallics, 5 (1986) 1059.
102 J.E. Anderson, C.-L. Yao and K.M. Kadish, J. Am. Chem. Soc., 109 (1987) 1106.
103 J.E. Anderson, C.-L. Yao and K.M. Kadish, Organometallics, 6 (1987) 706.
104 A.E. Sherry and B.B. Wayland, J. Am. Chem. Soc., 111 (1989) 5010.
105 A.E. Sherry and B.B. Wayland, J. Am. Chem. Soc., 112 (1990) 1259.
106 (a) G. Ferraudi, S. Muralidharan and K. Schmatz, Abstracts 182nd National Meeting of the Am. Chem. Soc., New York, 1981, Inorg. 152.
(b) Y.-H. Tse, P. Seymour, N. Kobayashi, H. Lam, C.C. Leznoff and A.B.P. Lever, Inorg. Chem., 30 (1991) 4453.
107 J. MacB. Harrowfield, A.J. Herlt, P.A. Lay, A.M. Sargenson, A.M. Bond, W.A. Mulac and J.C. Sullivan, J. Am. Chem. Soc., 105 (1983) 5503.
108 J.E. Anderson and T.P. Gregory, Inorg. Chem., 28 (1989) 3905.
109 H. Arzoumanian, A.A. Blanc, J. Metzger and J.E. Vincent, J. Organomet. Chem., 82 (1974) 261.
110 H.L. Bott, E.J. Bounsall and A.J. Poe, J. Chem. Soc. A, (1966) 1275.
111 T.L. Kelly and J.F. Endicott, J. Am. Chem. Soc., 94 (1972) 797.
112 T.L. Kelly and J.F. Endicott, J. Am. Chem. Soc., 92 (1970) 5733.
113 G. Pilloni, G. Schiovou, G. Zotti and S. Zecchiu, J. Organomet. Chem., 134 (1977) 305.
114 B.H. Van Vugt, N.J. Koole, W. Drenth and F.P.J. Kuijpers, Recl. Trav. Chim. Pays-Bas, 92 (1973) 1321.
115 F. Ferraudi, P.A. Grutsch and C. Kutal, J. Chem. Soc. Chem. Commun., (1979) 15.
116 C. Kutal, P.A. Grutsch and G. Ferraudi, J. Am. Chem. Soc., 101 (1979) 6884.
117 J. Lilie, M.G. Simic and J.F. Enidcott, Inorg. Chem., 14 (1975) 2129.
118 J.F. Endicott, C.L. Wong, T. Inoue and P. Natarajan, Inorg. Chem., 18 (1979) 450.
119 J. Read, H.D. Gainey and F. Basolo, J. Am. Chem. Soc., 96 (1974) 1363.
120 Q.G. Mullazzani, S. Emmi, M.Z. Hoffman and M. Menturi, J. Am. Chem. Soc., 103 (1981) 3362.
121 M.A. Hoselton, C.T. Lin, H.A. Schwarz and N. Sutin, J. Am. Chem. Soc., 100 (1978) 2383.
122 G.M. Brown, S.F. Chan, C. Creutz, H.A. Schwarz and N. Sutin, J. Am. Chem. Soc., 101 (1979) 7638.
123 H.A. Schwarz and C. Creutz, Inorg. Chem., 22 (1983) 707.
124 J.M. Lehn and J.P. Sauvage, Nouv. J. Chem., 1 (1977) 449.
125 M. Kirch, J.M. Lehn, J.P. Sauvage, Helv. Chim. Acta, 62 (1979) 1345.
126 U. Tinner and J.H. Espenson, J. Am. Chem. Soc., 103 (1981) 2120.
127 J.H. Espenson and U. Tinner, J. Organomet. Chem., 212 (1981) C43.
128 G.C. Abell and R.C. Bowman, Jr., J. Chem. Phys., 70 (1979) 2611.
129 J.T. Suss, A. Raizman, S. Szapiro and W. Low, J. Magn. Reson., 6 (1972) 438.
130 J.R. Shock and M.T. Rogers, J. Chem. Phys., 62 (1975) 2640.
131 R.S. Eachus and R.E. Graves, J. Chem. Phys., 61 (1974) 2860.

132 Z. Luz, A. Raiman and J.T. Suss, Solid State Commun., 21 (1977) 849.
133 M.D. Sastry, K. Savitri and B.D. Joshi, J. Chem. Phys., 73 (1980) 5568.
134 R.P.A. Muniz, N.V. Vugman and J. Danon, J. Chem. Phys., 54 (1971) 1284.
135 S.C. Jain, K.V. Reddy and T.R. Reddy, J. Chem. Phys., 62 (1975) 4366.
136 L. Malatesta, M. Angoletta and G. Caglio, Angew. Chem. Int. Ed. Engl., 2 (1963) 739.
137 B.L. Haymore and J.A. Ibers, J. Am. Chem. Soc., 96 (1974) 3325.
138 B.L. Haymore and J.A. Ibers, Inorg. Chem., 14 (1975) 3060.
139 R. Mason, K.M. Thomas, H.D. Empsall, S.R. Fletcher, P.N. Heys, E.M. Hyde, C.E. Jones and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1974) 612.
140 A. Araneo, F. Morazzoni and T. Napoletano, J. Chem. Soc. Dalton Trans., (1975) 2039.
141 S. Zecchin, G. Zotti and G. Pilloni, J. Organomet. Chem., 294 (1985) 379.
142 S. Padhye, R. Yerande, R.P. Patil, A.A. Kelkar and R.V. Chaudhari, Inorg. Chim. Acta, 156 (1989) 23.
143 W. Hieber, H. Lagally and A. Mayr, Z. Anorg. Allg. Chem., 246 (1941) 138.
144 L. Malatesta and F. Canziani, J. Inorg. Nucl. Chem., 19 (1961) 81.
145 L. Malatesta, L. Naldini and F. Cariati, J. Chem. Soc., (1964) 961.
146 G. Mercati and F. Morazzoni, J. Chem. Soc. Dalton Trans., (1979) 569.
147 F. Krauss and H. Gerlach, Z. Anorg. Allg. Chem., 143 (1925) 268, 277.
148 G. Yoneda and D.M. Blake, J. Organomet. Chem., 190 (1980) C71.
149 R.S. Eachus and R.E. Graves, J. Chem. Phys., 65 (1976) 1530.
150 N.V. Vugman, A.O. Caride and J. Danon, J. Chem. Phys., 59 (1973) 4418.
151 A. Davison, N. Edelstein, R.H. Holm and A.H. Maki, J. Am. Chem. Soc., 85 (1963) 2029.
152 A. Davison, M. Edelstein, R.H. Holm and A.H. Maki, Inorg. Chem., 2 (1963) 1227.
153 A. Davison, N. Edelstein, R.H. Holm and A.H. Maki, Inorg. Chem., 3 (1964) 814.
154 J.F. Weiher, L.R. Melby and R.E. Benson, J. Am. Chem. Soc., 86 (1964) 4329.
155 R. Williams, E. Billig, J.H. Waters and H.B. Gray, J. Am. Chem. Soc., 88 (1966) 43.
156 A.L. Balch and R.H. Holm, J. Am. Chem. Soc., 88 (1966) 520.
157 A.S. Foust and R.H. Soderberg, J. Am. Chem. Soc., 89 (1967) 5507.
158 N.S. Garifiyanov, I.I. Kalinichenko, I.V. Ovchinnikov and Z.F. Mantyanova, Dokl. Chem. (Engl. Transl.), 176 (1967) 795.
159 A.L. Balch, J. Am. Chem. Soc., 95 (1973) 2723.
160 A.Y. Girgis, Y.S. Sohn and A.L. Balch, Inorg. Chem., 14 (1975) 2327.
161 R. Kirmse and W. Dietzch, J. Inorg. Nucl. Chem., 38 (1976) 255.
162 R. Kirmse, W. Dietzch and B.V. Solovev, J. Inorg. Nucl. Chem., 39 (1977) 1157.
163 R. Kirmse, J. Stach, W. Dietzch, G. Steimeck and E. Hoyer, Inorg. Chem., 19 (1980) 2679.
164 G.A. Bowmaker, P.D.W. Boyed and G.K. Campbell, Inorg. Chem., 22 (1983) 1208.
165 R.S. Eachus and R.E. Groves, J. Chem. Phys., 65 (1976) 5445.
166 A. Tressaud, S. Khairoun, J.M. Dance, J. Grannec, G. Demazeau and P. Hagenmuller, C.R. Acad. Sci., Paris Ser. II, 295 (1982) 183.
167 A Tressaud, J Darriet, P. Lagassie, J. Grannec and P. Hagenmuller, Mater. Res. Bull., 19 (1984) 983.
168 S. Khairoun, J.M. Dance, J. Grannec, G. Demazeau and A. Tressaud, Rev. Chim. Miner., 20 (1983) 871.
169 A.J. Blake, A.J. Holder, T.I. Hyde and M. Schroeder, J. Chem. Soc. Chem. Commun., (1988) 1452.
170 A.J. Blake, A.J. Holder, T.I. Hyde, Y.V. Roberts, A.J. Lavery and M. Schroeder, J. Organomet. Chem., 323 (1987) 261.
171 A. McAuley and T.W. Whitecombe, Inorg. Chem., 27 (1988) 3090.
172 K. Wieghardt, W. Walz, B. Nuber, J. Weiss, A. Ozarowski, H. Stratemeier and D. Reinen, Inorg. Chem., 25 (1986) 1650.

173 V.J. Thoem, J.C.A. Boeyens, G.J. McDougall and R.D. Hancock, J. Am. Chem. Soc., 106 (1984) 3198.
174 G.S. Muraveiskaya, G.M. Larin and V.F. Sorokina, Zh. Neorg. Khim., 13 (1968) 1466.
175 R. Uson, J. Fonies, F. Martinez and M. Tomas, J. Chem. Soc. Dalton Trans., (1980) 888.
176 R. Uson, J. Fonies, F. Martinez, M. Tomas and I. Reyo, Organometallics, 2 (1983) 1386.
177 R. Uson, J. Fonies, M. Tomas, B. Menjon, K. Suenkel and R. Bau, J. Chem. Soc. Chem. Commun., (1984) 751.
178 R. Uson, J. Fonies, M. Tomas, B. Menjon, R. Bau, K. Suenkel and E. Kuwabara, Organometallics, 5 (1986) 1576.
179 H. Endres, H.J. Keller, H. Van de Sand and V. Dong, Z. Naturforsch. Teil B, 33 (1978) 843.
180 H.A. Boucher, G.A. Lawrance, P.A. Lay, A.M. Sargenson, A.M. Bond, D.M. Sangster and J.C. Sullivan, J. Am. Chem. Soc., 105 (1983) 4652.
181 A.J. Blake, R.O. Gould, A.J. Holder, T.I. Hyde, M.O. Odulate, A.J. Lavery and M. Schroeder, J. Chem. Soc. Chem. Commun., (1987) 118.
182 P.R. Bontchev, M. Metewa and G. Gentcheva, Pure Appl. Chem., 61 (1989) 897.
183 J.R. Hall and R.A. Plowman, Aust. J. Chem., 8 (1955) 158.
184 R.L. Rich and H. Taube, J. Am. Chem. Soc., 76 (1954) 2608.
185 G.E. Adams, R.K. Broskiewice and B.D. Michael, Trans. Faraday Soc., 64 (1968) 1256.
186 M.A.S. Ghosh and E.J. Hart, Int. J. Radiat. Phys. Chem., 1 (1969) 165.
187 T. Krigas and M.T. Rogers, J. Chem. Phys., 55 (1971) 3035.
188 J.C. Wright and G.S. Laurence, J. Chem. Soc. Chem. Commun., (1972) 132.
189 A. Peloso, Coord. Chem. Rev., 10 (1973) 123.
190 D.K. Storer, W.L. Waltz, J.C. Brodovitch and R.L. Eager, Int. J. Radiat. Phys. Chem., 7 (1975) 693.
191 A.V. Loginov, G.A. Shagisultanova, Zh. Prikl. Khim., 49 (1976) 2353.
192 R.K. Broszkiewciz and J. Grodkowski, Int. J. Radiat. Phys. Chem., 8 (1976) 359.
193 J.C. Brodovitch, D.K. Storer, W.L. Waltz and R.L. Eager, Int. J. Radiat. Phys. Chem., 8 (1976) 465.
194 J.S. Miller and A. Epstein, Prog. Inorg. Chem., 20 (1976) 1.
195 C. Amano and S. Fujiwara, Bull Chem. Soc. Jpn., 50 (1977) 1437.
196 G.V. Buxton and R.M. Sellers, Coord. Chem. Rev., 22 (1977) 195.
197 A. Stasicka and A. Marchaj, Coord. Chem. Rev., 23 (1977) 131.
198 W.L. Waltz, J.C. Brodovitch and K.P. Kundu, Int. J. Radiat. Phys. Chem., 10 (1977) 77.
199 W.L. Waltz, R.J. Woods and K.D. Whitburn, Photochem. Photobiol., 28 (1978) 681.
200 W.L. Waltz, J. Lilie, R.T. Waters and R.J. Woods, Inorg. Chem., 19 (1980) 3284.
201 H.M. Khan, W.L. Waltz, J. Lilie and R.J. Woods, Inorg. Chem., 21 (1982) 1489.
202 A. Goursot, H. Chermette, E. Penigault, M. Chanon and W.L. Waltz, Inorg. Chem., 23 (1984) 3618.
203 A. Goursot, H. Chermette, M. Chanon and W.L. Waltz, Inorg. Chem., 24 (1985) 1014.
204 K.P. Balashev, I.I. Blinov and G.A. Shigisultanava, Zh. Neorg. Khim., 32 (1987) 2470.
205 K.P. Balashev, I.I. Blinov and G.A. Shigisultanava, Koord. Khim., 13 (1987) 1674.
206 A. Goursot, A.D. Kirk, W.L. Waltz, G.B. Porter and D.K. Sharma, Inorg. Chem., 26 (1987) 14.
207 A. Goursot, H. Chermette, W.L. Waltz and J. Lilie, Inorg. Chem., 28 (1989) 2241.
208 W.L. Waltz, J. Lilie, A. Goursot and H. Chermette, Inorg. Chem., 28 (1989) 2247.
209 V.P. Grivin, V.F. Plyusnin, I.V. Khmelinski and N.M. Bazhin, Photochem. Photobiol., 51A (1990) 371.
210 V.P. Grivin, I.V. Khmelinski and V.F. Plyusnin, Photochem. Photobiol., 51A (1990) 389.

211 D.G. Holah, A.N. Hughes and B.C. Hui, Can. J. Chem., 53 (1975) 3669.
212 K.R. Howes, A. Bakac and J.H. Espenson, Inorg. Chem., 27 (1988) 3147.
213 K.R. Howes, A. Bakac and J.H. Espenson, Inorg. Chem., 28 (1989) 579.
214 K.R. Dunbar, S.C. Haefner and P.N. Swepston, J. Chem. Soc. Chem. Commun., (1991) 460.
215 F.E. Mabbs and D.J. Machin, Magnetism and Transition Metal Complexes, Chapman and Hall, London, 1973.
216 B.R. McGarvey, Transition Met. Chem., 3 (1966) 89.
217 E. Koenig, Physical Methods of Advanced Inorganic Chemistry, Wiley-Interscience, New York, 1968.
218 G.F. Kokoszka and G. Gordon, Tech. Inorg. Chem., 7 (1968) 151.
219 S. Fujiwara and K. Nagashima, Anal. Chem., 38 (1966) 1464.
220 H.A. Kuska and M.T. Rogers, Radical Ions, Wiley-Interscience, New York, 1968.
221 H.A. Kuska and M.T. Rogers, in A.E. Martell (Ed.), Coordination Chemistry, Vol. I, Van Nostrand, New York, 1971, p. 186.
222 B.A. Goodman and J.B. Raynor, Adv. Inorg. Radiochem., 13 (1970) 135.
223 A. Abragan and B. Bleaney, Electron Paramagnetic Resonance of Transition Metal Ions, Oxford University Press, London, 1970.
224 H. Basch and H.B. Gray, Theor. Chim. Acta, 4 (1966) 367.
225 A.J. Freeman and R.E. Watson, in G.T. Rodo and H. Suhl (Eds.), Magnetism, Vol. II, Academic Press, New York, 1965, p. 167.
226 M. Angoletta, T. Beringhelli and F. Morazzoni, Spectrochim. Acta Part A, 38 (1982) 1177.
227 M.B.D. Bloom, J.B. Raynor and M.C.R. Symons, J. Chem. Soc. A, (1972) 3843.
228 F. Cariati, F. Morazzoni, C. Busetto, G.D. Piero and A. Zazzette, J. Chem. Soc. Dalton Trans., (1976) 342.
229 A. Raizman, J.T. Suss and W. Low, Phys Rev. B, 15 (1977) 5184.
230 S. Fujiwara, T. Watanabe and T. Inoue, Chem. Lett., (1974) 755.
231 F.V. Lovecchio, E.S. Gore and D.H. Busch, J. Am. Chem. Soc., 96 (1974) 3109.
232 A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd edn., Elsevier, Amsterdam, 1984, p. 490.
233 K. Sieghbahn, C. Nordling, G. Johansson, J. Hedman, P. Hedan, K. Hamrin, U. Gelius, T. Bergmark, L. Werme, R. Manne and Y. Baer, ESCA Applied to Free Radicals, North-Holland, Amsterdam, 1969.
234 W.L. Jolly, Coord. Chem. Rev., 13 (1974) 47.
235 T. Imanaka, K. Kaneda, S. Teranishi and M. Terasawa, Proc. 6th Int. Congress on Catalysis, Vol. 2, The Chemical Society, London, 1977, p. 509.
236 R.W. Matthews, A.D. Hamer, D.L. Hoof, D.G. Tisley and R.A. Walton, J. Chem. Soc. Dalton Trans., (1973) 1033.
237 R.D. Feltham and P. Brant, J. Am. Chem. Soc., 104 (1982) 641.
238 K.K. Pandey, S.R. Ahuja and M. Goyal, Indian J. Chem., 24A (1985) 1059.
239 L.D. Tyutchenkova, L.G. Privalova, Z.K. Maizus and I.M. Emanuel, Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., (1975) 40.
240 L.D. Tyutchenkova, V.S. Vinogradova and Z.K. Maizus, Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., (1978) 666.
241 B.H. Van Vugt and W. Drenth, Recl. Trav. Chim. Pays-Bas, 96 (1977) 225.
242 J.P. Howe, K. Lung and T.A. Nile, J. Organomet. Chem., 208 (1981) 401.