Coordination Chemistry Reviews, 68 (1985) 101–130
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ALKOXO DERIVATIVES OF PLATINUM METALS

R.C. MEHROTRA, S.K. AGARWAL * and YASH PAL SINGH

Chemical Laboratories, University of Rajasthan, Jaipur 302004 (India)

(Received 25 January 1985)

CONTENTS

A. INTRODUCTION

In spite of extensive work published on the alkoxy derivatives of main group and transition (including inner transition) metals during the last three decades, the chemistry of alkoxo derivatives of the later transition elements does not appear to have received much attention except for a number of publications from the authors' laboratories in recent years [1–12]. The above situation is also reflected in the review literature. Although there are a number of review articles [13–22] and recent books on the chemistry of alkoxy derivatives of metals in general [23] and lanthanide metals in particu-

---

* Present address: Banasthali Vidyapeeth 304022, India.

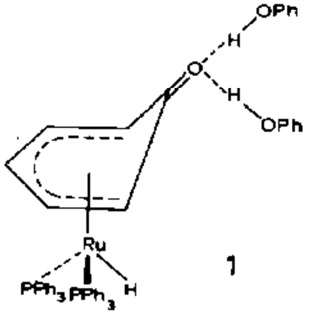
lar [24], there appears to be no review at all on alkoxy derivatives of platinum metals.

B. ALKOXO DERIVATIVES OF RUTHENIUM AND OSMIUM

The chemistry of ruthenium and osmium bears little resemblance to that of iron except in compounds such as sulphides or phosphides and complexes with ligands, such as CO, PR_3, η-C_5H_5, etc. This general difference in the chemistry of ruthenium and osmium is to some extent reflected in the chemistry of their alkoxo derivatives. Iron forms simple alkoxo derivatives with the general formula $[Fe(OR)_{2\ or\ 3}]_n$ [25–30] which are associated through alkoxy bridges only; no such compound for ruthenium or osmium has so far been reported.

Although the product could not be isolated, the formation of mononuclear ethoxo–hydrido species of ruthenium was proposed by Bendetti et al. [31] by the interaction of $[Ru(CO)_3Cl_2]_2$ with ethanol.

All the isolable alkoxy derivatives of ruthenium and osmium are either binuclear (with rather close resemblance to each other) or polynuclear (with marked differences among themselves). Besides the complexes in which the phenoxide moiety is bonded or bridged to the metal atom through its oxygen, a few complexes of ruthenium are also known in which the phenoxide ion is η-bonded [32] to ruthenium metal as illustrated (1). In this derivative, the CO group becomes more like a keto group and the bonding is delocalised similar to that in η-1,5-cyclohexadienyls; such compounds are regarded as η-1,5-oxocyclohexadienyls rather than as η-arenes.



1

(i) Binuclear derivatives

Binuclear alkoxo derivatives of ruthenium and osmium were prepared first by Stephenson et al. [33,34]. The work on ruthenium derivatives has been extended considerably, but only one compound of osmium $[(\eta$-$C_6H_6)_2Os_2(OMe)_3]^+$ has so far been prepared and characterised.

(a) Methods of preparation

The binuclear triple alkoxo-bridged derivatives were prepared [33,34] by refluxing the complex $[(\eta\text{-arene})_2Ru_2(OH)_3][BPh_4]$ in an alcohol ROH

$$[(\eta\text{-arene})_2Ru_2(OH)_3][BPh_4] + 3ROH \rightarrow [(\eta\text{-arene})_2Ru_2(OR)_3][BPh_4] + 3H_2O$$

$(R = Me, Et, Ph;\ \text{arene} = \eta\text{-}C_6H_6)$

An acetone adduct, $[(\eta\text{-arene})_2Ru_2(OH)_3][BPh_4]\cdot Me_2CO$ can be used in place of $[(\eta\text{-arene})_2Ru_2(OH)_3][BPh_4]$ as the starting material in the above reaction [34].

The mechanism of the above reactions presumably involves protonation of the OH bridges by the weak acid, ROH to form the cation $[Ru(H_2O)_3(C_6H_6)]^{2+}$ which then reacts rapidly with alkoxide anions giving monomeric alkoxide intermediates such as $[Ru(H_2O)_2(C_6H_6)(OR)]^+$ and $[Ru(H_2O)(C_6H_6)(OR)_2]$ the facile coupling reactions of which could give rise to the product cations $[Ru_2(C_6H_6)_2(OR)_3]^+$. The alkoxy derivatives of ruthenium and osmium have also been synthesised by reaction of the complexes $[M(\text{arene})Cl_2]_2$ with freshly prepared NaOR (R = Me, Et) in alcoholic solvents in the presence of $NaBPh_4$ [34]

$$[M(\text{arene})Cl_2]_2 \xrightarrow[ROH]{NaOR/NaBPh_4} [M_2(\text{arene})_2(OR)_3][BPh_4]$$

$(M = Ru;\ R = Me, Et, Ph;\ \text{arene} = C_6H_6:\ M = Ru;\ R = Me;$
$\text{arene} = C_6H_3Me_3, C_6Me_6:\ M = Os;\ R = Me;\ \text{arene} = C_6H_6)$

However, attempts to prepare branched/longer chain alkoxides, such as isopropoxides or n-butoxides using either of these routes led to extensive decomposition [34]; this has been ascribed to a facile β-elimination process with ruthenium hydride formation although the same should also have applied to ethoxy derivatives. The corresponding isopropoxide and n-butoxide derivatives have actually been isolated from the reaction of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ with the parent alcohol under mild conditions [35]

$$[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3H_2O][BPh_4] + 3ROH \rightarrow [Ru_2(\eta\text{-}C_6H_6)_2(OR)_3][BPh_4 + 4H_2O$$

$(R = i\text{-}C_3H_7 \text{ and } n\text{-}C_4H_9)$

(b) Properties

All the compounds containing the cation $[M_2(\eta\text{-arene})_2(OR)_3]^+$ are coloured crystalline solids, which behave as a 1 : 1 electrolyte in nitromethane. In contrast to other metal alkoxides in general, a striking feature of these alkoxides is their stability towards hydrolysis as water is often present in the synthetic routes adopted for these derivatives. The chemical reactions [35] of the triple-bridged alkoxo complexes, $[(\eta\text{-arene})_2Ru_2(OR)_3][PF_6]$ have been investigated with the help of ^1H NMR spectroscopy. These do not react with nitrogen donor ligands such as pyridine, 2,2′-bipyridyl and 1,10-phenanthroline under reflux. There is no reaction with PPh_3, but they do react with PPh_2Et to give a low yield (~ 5%) of $[Ru(\eta\text{-}C_6H_6)(PPh_2Et)_3][PF_6]_2$. $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ reacts with anhydrous HCl to give both $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BPh_4]$ and $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ while reaction with HX (X = Br, I) gives only $[Ru(\eta\text{-}C_6H_6)X_2]_2$.

Exchange reactions between 'OR' groups as well as between metal atoms also take place to give heterobridged (a) and heterometallic (b) compounds

$$\text{(a)}\quad [Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+ + [Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3]^+$$
$$\rightarrow [Ru_2(\eta\text{-}C_6H_6)_2(OMe)_2(OEt)]^+ + [Ru_2(\eta\text{-}C_6H_6)_2(OEt)_2(OMe)]^+$$

$$\text{(b)}\quad [Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+ + [Os_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+$$
$$\rightarrow 2[(\eta\text{-}C_6H_6)Ru(OMe)_3Os(\eta\text{-}C_6H_6)]^+$$

(c) Spectroscopic studies

The IR spectra of these complexes [34,35] show a strong broad band at ~ 1050 cm^{-1} due to the alkoxide group (νC–O) as well as characteristic bands for the various other groups present.

The ^1H NMR spectra of these complexes [34,35] are summarised in Table 1 and show the characteristic signals for $[BPh_4]$ (a multiplet centred at δ 6.90 and 7.30 ppm), η-arene and alkoxy protons.

The ^{13}C NMR spectrum of one derivative, $[Ru_2(\text{arene})_2(OR)_3][BPh_4]$ (arene = C_6H_6 and R = Pr^i), in CD_3NO_2 has been reported [35]. It shows three signals (in addition to the $[BPh_4]$ signal at 120–140 ppm) at δ 78.8, 33.8 and 19.7 ppm. The resonance at 78.8 ppm is readily assigned to η-C_6H_6, while the proton-coupled spectrum indicates that the signal at δ 33.8 ppm is for $O\underline{CH}(CH_3)_2$ and the signal at δ 19.7 ppm is for $OCH(\underline{CH_3})_2$ carbon atoms.

(d) X-ray structural analysis

X-ray structural analysis of one compound only has been reported [35]. The compound $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ crystallises in the monoclinic space group $P2_{1/\eta}$ with $a = 11.725(4)$, $b = 15.573$, $c = 18.739(2)$ Å, $\beta = 103.29(2)°$. The Ru–Ru distance of 3.005(2) Å is of similar magnitude to that found in the hydroxo bridged compound. The Ru–O distance lies between 2.044 and 2.080 Å and depicts an average value of 2.060(8) Å. The Ru–C distances for the two rings are 2.155(14) and 2.158(13) Å. The

TABLE 1

^1H NMR data for some binuclear ruthenium and osmium alkoxo complexes at 298°K

S.No.	Compound	Solvent	η-arene δ(ppm)	Others δ(ppm)	Reference
1.	$[C_6H_6Ru(OMe)_3RuC_6H_6][BPh_4]$	$(CD_3)_2CO$	5.48(s)	4.42(s)	35
2.	$(C_6H_6Ru(OMe)_3RuC_6H_6][PF_6]$	$(CD_3)_2CO$	5.66	4.68(s)	34
3.	$[C_6H_6Ru(OEt)_3RuC_6H_6][BPh_4]$	$(CD_3)_2SO$	5.43(s)	4.50(q, CH_2) 1.35(t, CH_3) $^3J(CH_2CH_3$ 7.0 Hz)	35
4.	$[C_6H_6Ru(OEt)_3RuC_6H_6][PF_6]$	$(CD_3)_2CO$	5.50(s)	4.33(q), 1.58(t) $J(CH_2CH_3$ 7.0 Hz)	34
5.	$[C_6H_6Ru(OPh)_3RuC_6H_6][BPh_4]$	CD_3NO_2	5.12(s)	6.95(m)	34
6.	$[C_6Me_6Ru(OMe)_3RuC_6Me_6][BPh_4]$	$CDCl_3$	1.97	4.00(s)	34
7.	$[C_6H_6Os(OMe)_3OsC_6H_6][BPh_4]$	$(CD_3)_2CO$	6.15(s)	4.63(s)	34
8.	$[(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Ru_2(OMe)_3][BPh_4]$	CD_3NO_2	5.24 (H_AH_B 18 Hz; J 7.0 Hz) 2.82(sp $CHMe_2$); 2.20(s, CH_3) 1.32 (d, CH_3 of $CHMe_2$ J 7.0 Hz)	6.49	35
9.	$[Ru_2(\eta\text{-}1,4\text{-}Me\text{-}C_6H_4CHMe_2)_2(OEt)_3][BPh_4]$	CD_3NO_2	5.21 (H_AH_B, 26 Hz; J 6.0 Hz) 2.79(sp, $CHMe_2$); 2.18(s, CH_3) 1.31(d, CH_3 of $CHMe_2$; J 7.0 Hz)	4.60(q)	35
10.	$[Ru_2(\eta\text{-}C_6H_6)_2(OPr^i)_3][BPh_4]$	CD_3NO_2	5.46(s)	4.89(sp, CH) 1.48(d CH_3, $^3JCH(CH_3)_2$ 7.0 Hz)	35
11.	$[Ru_2(\eta\text{-}C_6H_6)_2(OBu^i)_3][BPh_4]$	CD_3NO_2	5.36(s)	1.12(d, CH_3 J 7.0 Hz) 4.27(d, CH_2) 2.28(m, CH)	35

s = Singlet, d = doublet, t = triplet, q = quartet, sp = septet, m = multiplet.

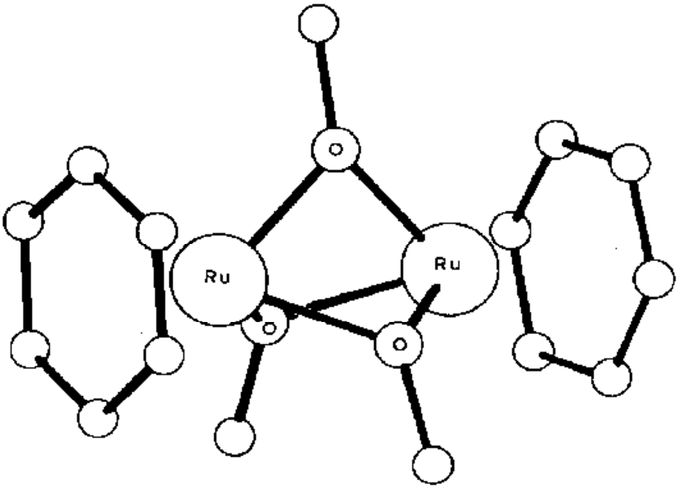


Fig. 1. Crystal structure of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$.

distances from the metal to the ring centroids are 1.643 and 1.646 Å respectively. The Ru–O–Ru angles are approximately 92.6° and the O–Ru–O angles lie between 71.4 and 74.9°. The two benzene rings are partially disordered over two positions. In the major site (80% occupancy) they are twisted (26°) with respect to one another giving an almost staggered conformation (Fig. 1).

(ii) Polynuclear derivatives

These derivatives have generally been obtained during recrystallisation of $Ru_3(CO)_{12}$ [36] or $Os_3(CO)_{12}$ [37] from the mother liquor obtained by the carbonylation of $RuCl_3 \cdot xH_2O$ (in methanol/ethanol) or OsO_4 (in methanol) and a number of interesting products have been isolated by chromatographic techniques. However, while the ruthenium products are generally tetranuclear, those of osmium are trinuclear. A brief account of spectroscopic data is presented below together with a X-ray crystallographic study of one compound.

(a) Spectroscopic studies

The IR spectra of tetranuclear and trinuclear alkoxo derivatives of ruthenium [36] and osmium [37] respectively show characteristic bands due to terminal νC–O (carbonyl groups) together with various bands due to methoxy groups (Table 2).

Mass spectral data for $[Ru_4(CO)_{10}Cl_2(OMe)OH]$, $[Ru_4(CO)_{10}Cl_2(OMe)_2]$, $[Ru_4(CO)_{10}Cl(OMe)_3]$, $[Ru_4(CO)_{10}Cl_2(OEt)(OH)]$ [36] and $[Os_3(CO)_{10}(OCH_3)_2]$ [37] have been reported. All the compounds show molecular ion peaks. The mass spectra of methoxy ruthenium derivatives do not show

TABLE 2

Molecular-ion values (M^+) (for ruthenium compounds only), IR spectra and ^1H NMR data for tetranuclear and trinuclear alkoxo compounds of ruthenium

S.No.	Compound	M^+	IR $\nu CO\ cm^{-1}$			^1H NMR spectra δ(ppm)	Reference
1.	$[Ru_4(CO)_{10}Cl_2(OMe)_2]$	818	2103 m	2022 vs		4.05(s) (C_6D_6)	
			2078 s	2002 w			
			2036 sh	1946 m		4.73(s) ($CDCl_3$)	
			2032 vs				
2.	$[Ru_4(CO)_{10}Cl(OMe)_3]$	814	2094 m	2006 w			
			2058 sh	1994 m			
			2029 vs	1951 w			
			2012 vs	1946 m			
3.	$[Ru_4(CO)_{10}Cl_2(OMe)(OH)]$	804	2094 w				
			2096 s				36
			2023 vs				
			2016 vs				
4.	$[Ru_4(CO)_{10}Cl(OMe)_2OH]$	800	2090 m	2010 s			
			2058 m	1990 m			
			2055 s	1943 m			
			2024 s				
			2019 vs				
5.	$[Os_3(CO)_{10}(OMe)_2]$		2107 m	2071 vs		4.0 (C_6H_6)	
			2056 s	2016 vs			
			1989 s	1928 m	1951 w	5.73 (CCl_4)	37
6.	$[HOs_3(CO)_{10}(OMe)]$		2112 vw	2072	2060 sh		
			2038 m	2025 vs	2000 m		
			1990 sh	1985 sh			

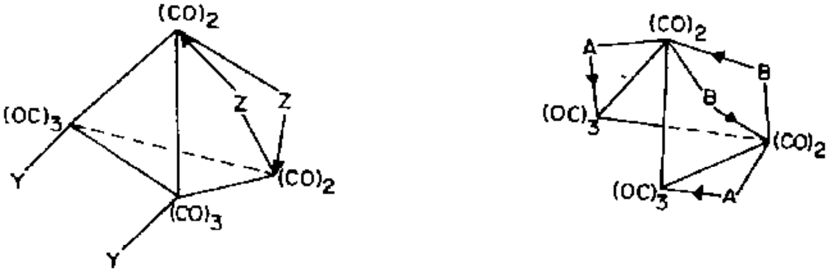


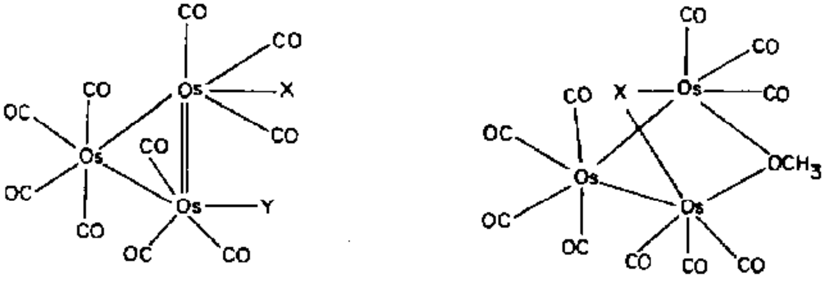
Fig. 2. Proposed structures for the tetranuclear $[Ru_4(CO)_{10}X_4]$ clusters.

stepwise loss of CO; for example, the mass spectrum of $[Ru_4(CO)_{10}Cl_2(OMe)_2]$ shows the ejection of 12 CO groups together with six hydrogen atoms, whereas the osmium compound [37] shows stepwise loss of carbon monoxide. No mononuclear or binuclear fragments are observed in the mass spectrum of $[Os_3(CO)_{10}(OCH_3)_2]$; the appearance of trinuclear fragments only therefore suggests a cyclic structure.

The ^1H NMR spectra [36] of these compounds have been recorded but due to the presence of solvent impurities, the assignment of $CH_3(OCH_3)$ in $[Ru_4(CO)_{10}Cl_2(OMe)_2]$ and of $CH_2(OC_2H_5)$ in $[Ru_4(CO)_{10}Cl_2(OEt)(OH)]$ only could be made. The ^1H NMR spectrum of $Os_3(CO)_{10}(OMe)_2$ [37] showed a singlet at δ 4.0 (in C_6H_6) or δ 4.73 ppm (in CCl_4) for the methoxy protons.

In the complexes, $[Ru_4(CO)_{10}Cl_2(OMe)_2]$ and $[Ru_4(CO)_{10}Cl_2(OEt)(OH)]$ [36], the absence of a bridging CO group indicates that the three ligands Cl, OH or OR (R = Me or Et) act as one electron (terminal) or three electron (bridging) ligands. Two distinct structural possibilities have been proposed (Fig. 2) for these compounds, but the final choice awaits X-ray crystal data.

On the basis of the effective atomic number rule as well as mass, IR and NMR spectroscopic data, two plausible structures have been proposed for derivatives $[HOs_3(CO)_{10}(OCH_3)]$ and $[Os_3(CO)_{10}(OCH_3)_2]$ (Fig. 3) [37]. A terminal configuration (Fig. 3(a)) is favoured by mass spectroscopic and



(a) (b)

Fig. 3. Possible structures for the compounds $[Os_3(CO)_{10}XY]$.

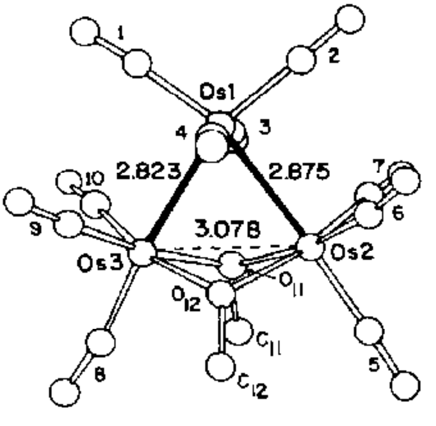


Fig. 4. Crystal structure of $[(OCH_3)_2Os_3(CO)_{10}]$.

vibrational data [38] since two force constants are different from the remainder. An X-ray crystal structure determination of $[Os_3(CO)_{10}(OMe)_2]$, however, reveals the existence of a bridging structure (Fig. 3(b)) [39].

The ^{13}C NMR spectral data [40] show that in the compound $[Os_3(CO)_{10}(OEt)_2]$, two pseudo-equatorial carbonyl ligands exchange their positions, whereas the remaining carbonyls are unaffected. The photoelectron spectrum of $[HOs_3(CO)_{10}(OMe)]$ has also been reported [41].

(b) X-ray structural analysis

An X-ray structure determination (Fig. 4) of $[(OCH_3)_2Os_3(CO)_{10}]$ [39] shows that the two methoxy groups bridge two osmium metal atoms separated by 3.07 Å. The formal metal–metal bond order, as calculated by the 18 electron rule [42], is zero whereas in the analogous compounds, $[H_2Os_3(CO)_{10}]$ and $[H(SC_2H_5)Os_3(CO)_{10}]$, the formal bond orders are two and one respectively [39].

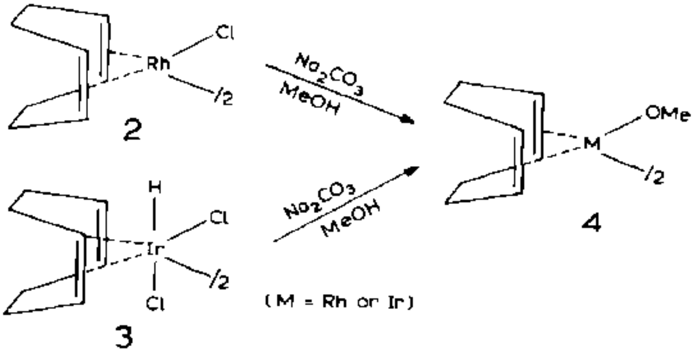
C. ALKOXO DERIVATIVES OF RHODIUM AND IRIDIUM

In contrast to Co^{III}, reduction of Rh^{III} and Ir^{III} complexes does not in general give rise to divalent complexes. The alkoxy chemistry of the last two metals has been studied mainly for their +1 oxidation state, obtained initially by the reduction of their salts in +3 states and stabilised by ligation with π-acceptor ligands such as cyanide, carbon monoxide, phosphine, olefin and diolefin. Of the two, iridium does not appear to exist in the +2 state and triply-bridged phenoxy derivatives of Rh^{II} only have been described.

The first alkoxy derivative of rhodium(I), i.e. $[(cod)Rh(OMe)]_2$ (cod = 1,5-cyclooctadiene) was synthesised as early as 1957 [43], but its true nature was established only in 1965 [44]; this work has been followed by a few publications, summarised below:

(i) Methods of preparation

In 1965, Robinson and Shaw [44] prepared the methoxy derivatives of these metals by extending the method of Chatt et al. [43], (**2**–**4**). (cod)$RhCl_2$ [43] and $[(cod)IrHCl_2]_2$ [44] were obtained by treating $RhCl_3 \cdot xH_2O$ and $H_3IrCl_6 \cdot xH_2O$ respectively with ethanol in the presence of 1,5-cyclooctadiene (cod). However, the iridium analogue of $[(cod)RhCl]_2$ was prepared [45] by the reduction of $IrCl_3 \cdot 3H_2O$ with isopropanol in the presence of cod. This compound $[(cod)IrCl]_2$ has successfully been used for the synthesis of not only the methoxy but a series of higher alkoxy and even phenoxy derivatives [46]



2

3

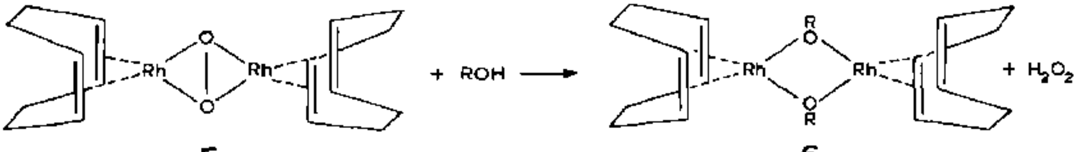
4

(M = Rh or Ir)

$$[(cod)IrCl]_2 \xrightarrow[ROH]{Na_2CO_3} [(cod)Ir(OR)]_2$$

$(R = CH_3, C_2H_5, n\text{-}C_3H_7, i\text{-}C_3H_7, n\text{-}C_4H_9, i\text{-}C_4H_9, C_8H_{17}$ and $C_6H_5)$

A more reactive starting material $[(cod)Rh]_2O_2$, obtained by the anion exchange reaction of $[(cod)RhCl]_2$ with KO_2, has also been used for the synthesis of alkoxo derivatives of rhodium (**5** → **6**) [47].



5

6

$(R = CH_3$ or $C_2H_5)$

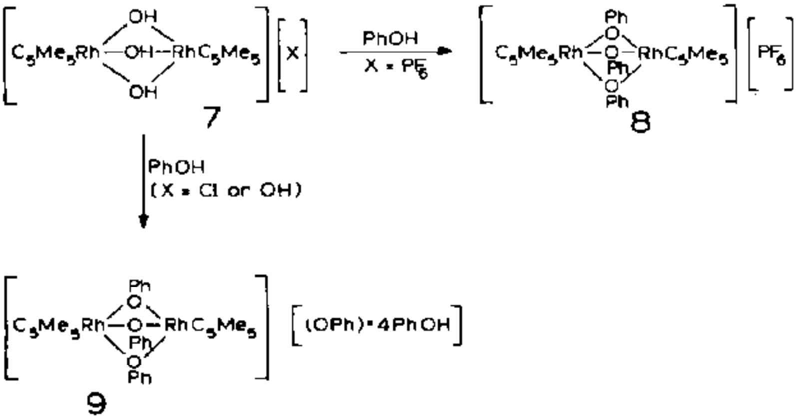
The chemistry of phenoxo derivatives of rhodium in both the +1 and +2 states has been investigated further. A reddish-brown compound, phenoxy(triphenylphosphine)rhodium(I) $(Ph_3P)_3Rh(OPh)$, was obtained [48] from the reaction of PhOH and $(PPh_3)_3RhR$ (R = Me, Ph) by liberating the corresponding hydrocarbon in 65 and 95% yields respectively

$$(Ph_3P)_3RhR + PhOH \rightarrow (Ph_3P)_3RhOPh + RH$$

$(R = Me, Ph)$

The product $(Ph_3P)_3RhOPh$ on being stirred under petroleum appears to lose a molecule of PPh_3 yielding $(Ph_3P)_2Rh(OPh)$ which is presumably dimeric and analogous to $Rh_2(CO)_4Cl_2$.

The tri-μ-phenoxo dirhodium complexes, $[\{Rh(C_5Me_5)\}_2(OPh)_3][PF_6]$ and $[\{Rh(C_5Me_5)(OPh)_2(PhOH)_2\}_n]$ have been synthesised by the reaction of $[\{Rh(C_5Me_5)\}_2(OH)_3][PF_6]$ and $[\{Rh(C_5Me_5)\}_2(OH)_3][X]$ $(X = Cl$ or $OH)$ with phenol. On the basis of ^{13}C NMR spectra, the complex $[\{Rh(C_5Me_5)(OPh)_2(PhOH)_2\}_n]$ can be formulated as the tri-μ-phenoxodirhodium complex, $[\{Rh(C_5Me_5)\}_2(OPh)_3][(OPh)\cdot 4PhOH]$ [49], (**7** → **8**,**9**).



(ii) Structure and properties

The structural features of $[(cod)M(OR)]_2$ $(M = Rh$ or $Ir)$ have been elucidated by IR and NMR spectroscopy and the crystal structure of the rhodium derivatives has been determined.

The infrared spectroscopic data [44,46] for alkoxo derivatives of rhodium and iridium have been reported. A sharp band in the region 1470 cm^{-1} may be due to the $\nu C{=}C$ mode (of the cod moiety); a characteristic band at ~ 1050 cm^{-1} for the $\nu C{-}O$ mode has also been observed, as well as other absorbances (Table 3 for iridium complexes only).

The ^1H NMR spectra [44,46] of the complexes $[(cod)Rh(OR)]_2$ $(R = Me, Et)$ and $[(cod)Ir(OR)]_2$ $(R = Me, Et, Pr^i, Bu^t)$ have been reported (Table 4). The signals for cyclooctadiene protons are complex but the total number of olefinic protons and protons on the saturated carbon atom could be esti-

TABLE 3

IR spectral data of some alkoxo iridium complexes

Methoxy	Ethoxy	Propoxy	Butoxy	Octoxy	Phenoxy
					3070
					3050
					3030
					3015
		2975			
2968	2970	2965	2970	2970	2970
2950		2950	2940	2950	2965
	2930		2930	2930	2935
		2920		2920	
2918					
	2910		2910		2910
2878		2875	2875	2875	2880
	2870	2864			2870
2858				2858	
2828	2830	2830	2830	2830	2835
2810					
2100					
					1580
					1482
					1472
1468	1468	1467	1469	1468	
	1449	1457	1450		1446
1443	1437	1442	1437	1442	
	1422	1425	1425		
1372	1372	1375	1372	1370	
		1360			
1352	1342	1352	1350	1350	
		1333		1335	1322
1320	1317	1318	1318	1318	
1295	1293	1294	1295	1292	1295
			1290		
		1267			
		1252			1250
1228	1224	1225	1227	1225	1222
1201	1200	1200	1203	1200	
		1175			
1168	1167		1167	1168	
					1157
1152	1148	1150	1150	1152	
	1087	1092	1088	1088	
	1073				
1051	1048	1063	1048	1068	1066
				1050	
				1030	
				1010	1018

TABLE 3 (continued)

Methoxy	Ethoxy	Propoxy	Butoxy	Octoxy	Phenoxy
1000	1000	1000	1002		1004
				998	
		975			978
966	968	964	968	971	
				917	922
905	900	904	900	905	900
891	890	890	890	889	894
868	868	870	870	870	870
					845
				830	
820	820	820	822		825
806	802	805	804	806	
778	775	788	777	778	773
				721	752
				721	
718					694
					598
					580
		562		560	
548	540	535	542		535
522	515	515	518	517	
501	498	498	498	498	496
		485			
	463		460	472	462
422	420	422	420	422	420
			392		392
358		368	370		
326	320	324	320		

mated readily by integration and were found in the ratio of 4 : 8. Resonances due to other protons were observed as sharp signals.

Powder diffraction X-ray patterns for four iridium complexes $[(\mathrm{cod})\mathrm{Ir(OR)}]_2$ (R = CH_3, C_2H_5, i-C_3H_7 and Ph) have been reported [46].

Single crystal X-ray studies of one complex only of the series, $[(\mathrm{cod})\mathrm{Rh(OMe)}]_2$ have been carried out (Fig. 5) [50]. The compound crystallises in triclinic form with space group *P1* and cell dimensions $a = 7.347(4)$, $b = 6.471(3)$, $c = 9.554(6)$ Å, $\alpha = 87.06(4)$, $\beta = 82.50(5)$, and $\gamma = 77.48(4)°$. The geometry of the rhodium atom is square planar. The two Rh–O bond lengths, 2.051(5) and 2.063(5) Å are similar to the values found in (cod)Rh(acac) (2.054(5) and 2.066(5) Å) [51] and $[\mathrm{Rh(acac)(CO)_2}]$ (2.06 and 2.05 Å) [52].

The reaction of the iridium derivative $[(\mathrm{cod})\mathrm{Ir(OMe)}]_2$ (**10**) [44] with HCl in methanol has been shown to yield the $[(\mathrm{cod})\mathrm{IrHCl_2}]_2$ derivative (**11**). It

TABLE 4

^{1}H NMR spectroscopic data for alkoxo derivatives of rhodium and iridium

Products		δ(ppm); attributions, integrations: (p)						Reference
		Protons (olefinic)	–O–R			Cyclooctadiene protons		
Methoxy	(Ir)	=C–H 3.4–3.6 m.c. (8p)	$-OCH_3$ 3.20 singlet (6p)			$-CH_2-$ 2.05–2.35 m.c. (8p)	 1.25–1.5 m.c. (8p)	44
	(Rh)	3.6 (8p)	2.7 (8p)			2.5 (8p)	1.7 (8p)	44
Ethoxy	(Ir)	=C–H 3.4–3.6 m.c. (8p)	$-OCH_2-CH_3$ 3.3 quadriplet (4p) $J(CH_2-CH_3)$ 17 Hz	$-O-CH_2-CH_3$ 1.1 triplet (6p)		$-CH_2-$ 2–2.24 m.c. (8p) 2.5 (8p)	1.2–1.6 m.c. (8p) 1.65 (8p)	46 47
	(Rh)	3.53 (8p)	2.5 (4p)	1.1 (triplet) (6p)				
Propoxy	(Ir)	=C–H 3.4–3.6 m.c. (8p)	$O-CH_2-$ 3.2 triplet (4p) $J(CH_2-CH_2) = 7$ Hz	CH_2- 1.1–1.8 m.c. (4p)	CH_3- 0.6–0.9 triplet (6p)	$-CH_2-$ 2–2.5 m.c. (8p)	1.1–1.8 m.c. (8p)	46
Butoxy	(Ir)	=C–H 3.4–3.6 m.c. (8p)	$O-CH_2-$ 3.2 triplet (4p) $J(CH_2-CH_2) = 7$ Hz.	CH_2-CH_2- 1.1–1.8 m.c. (8p)	CH_3- 0.8–1.1 (6p)	$-CH_2-$ 2–2.5 m.c. (8p)	1.1–1.8 m.c. (8p)	46

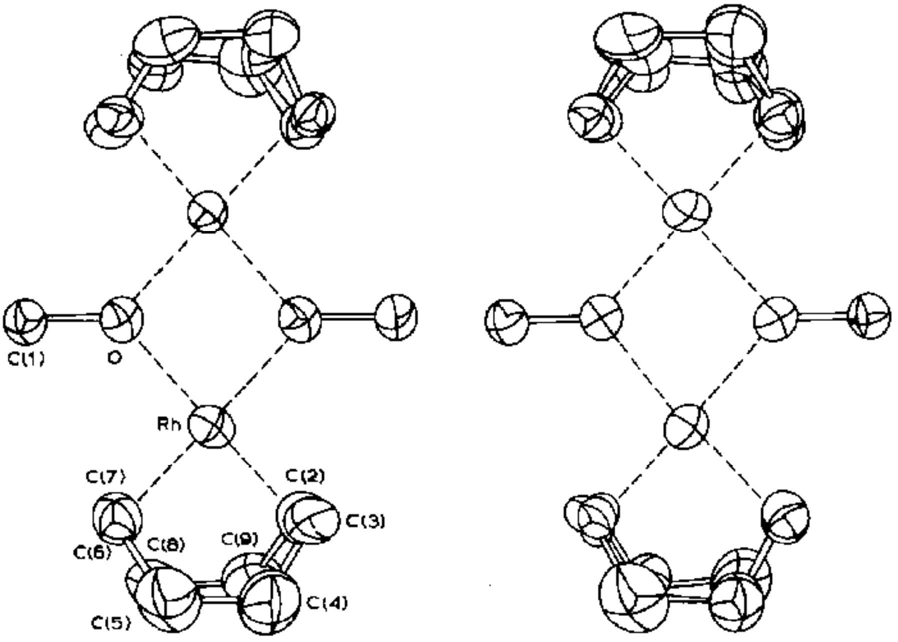
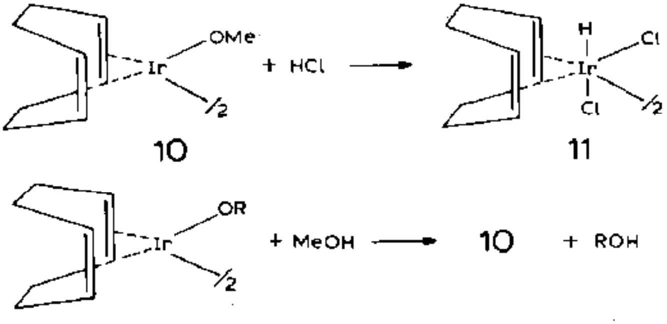


Fig. 5. X-ray crystal structure of [(cod)Rh(OMe)]$_2$.

has also been shown that the derivatives [(cod)Ir(OR)]$_2$ (**12**) (R = i-Bu and Oct) are converted into methoxides (**10**) on treatment with methanol [46].



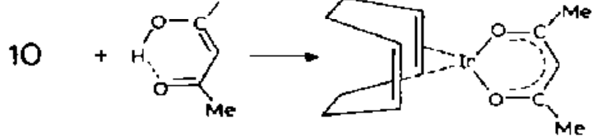
10

11

12

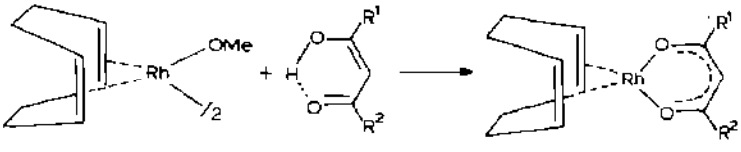
(R = $i\text{-}C_4H_9$; C_8H_{17})

Further [(cod)Ir(OMe)]$_2$ (**10**) reacts with acetylacetone [44] and Schiff bases [53] yielding the corresponding derivatives (**13**) which are monomeric, the metal attaining 4-coordination through chelation of the ligands.



13

A large variety of rhodium complexes (**15**) have also been synthesised recently by reaction of $[(cod)Rh(OMe)]_2$ (**14**) with β-diketones [54].

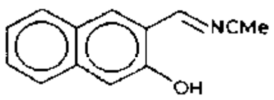


14 15

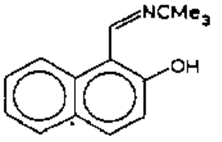
(R^1 = Me, R^2 = Me; R^1 = Ph, R^2 = Me; R^1 = Ph, R^2 = Ph)

(iii) Applications

Rhodium and iridium alkoxo complexes have been used as catalysts for various reactions. The rhodium complex $[(cod)Rh(OMe)]_2$ in the presence of Schiff base **16** or **17** catalyses the hydrogen transfer from isopropanol to cyclohexane or acetophenone [55].



16



17

The complex $[(cod)Ir(OMe)]_2$ has been used as a catalyst for the carbonylation of methanol to acetic acid [56]

$$CH_3OH + CO \rightarrow CH_3COOH$$

D. ALKOXO DERIVATIVES OF PALLADIUM AND PLATINUM

Only a limited number of palladium(II) and platinum(II) complexes containing metal–oxygen bonds have been isolated. Nevertheless these are presumed to play an important role as intermediates in diverse synthetic/catalytic reactions, e.g. hydration of nitriles [57] and oxidation of ethylene [58] and alcohols [59]. In addition, interest in platinum(II) complexes in general has been renewed recently due to their anti-cancer properties [60].

Only two alkoxy derivatives of these soft metals, *trans*-$[(PEt_3)_2Pd(OCH_3)CN]$ [61] and $[Pt(C_6H_9)(OMe)(PPh_2CH_2CH_2PPh_2)]$ [62] were known before 1976. The complex $Pt(GePh_3)(OR)(PEt_3)_2$, which was reported in 1965 [63] has now been shown, by a single X-ray crystal study to be $Pt(Ph)[Ge(OR)(Ph)_2](PEt_3)_2$ [64].

(i) Methods of preparation

A general method of synthesis for mononuclear alkoxo derivatives of these metals consists of the *trans* replacement of the halogen in the derivatives

$M(R)(Cl)(PPh_3)_2$ with alkoxy groups by the metathesis reaction [65,66]

$M(R)(Cl)(PPh_3)_2 + NaOMe \rightarrow M(R)(OMe)(PPh_3)_2 + NaCl$

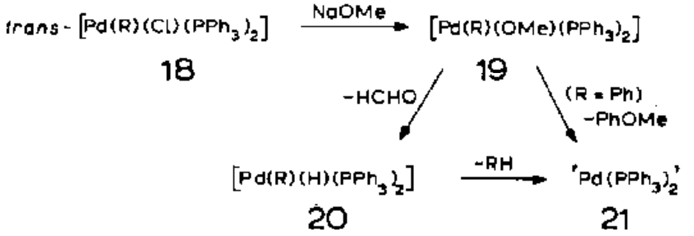
($M = Pd$ or Pt; $R = C_6F_5$, $CCl{=}CCl_2$, $CH{=}CCl_2$ or Ph)

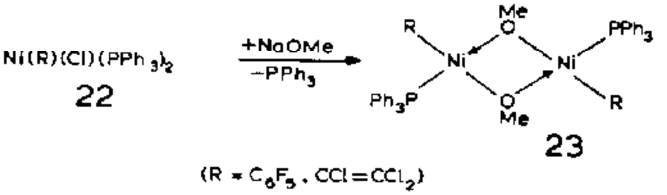
$M(R)(Cl)L_2 + NaOMe \rightarrow M(R)(OMe)L_2 + NaCl$

($M = Pt$; $R = CH_2CN$, CF_3 or CH_2CF_3; $L_2 = 2PPh_3$ or diphosphine)

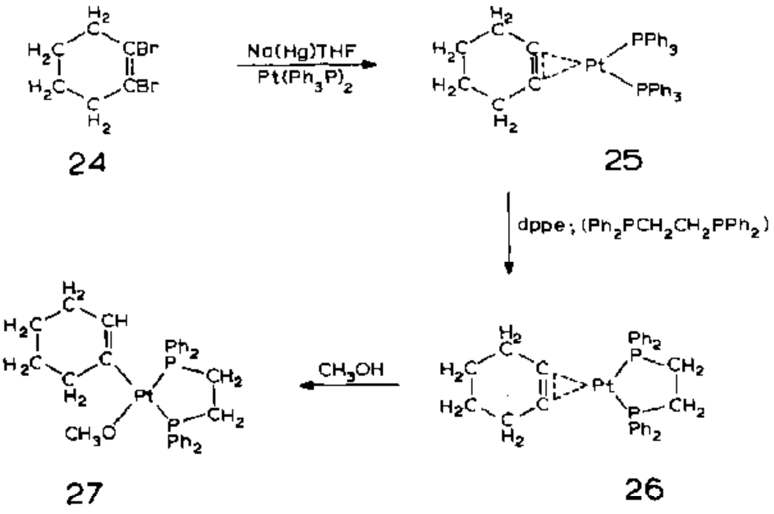
Success in prepararing these mononuclear methoxo complexes depends on the nature of the alkyl ligand R; a more electronegative R increases the effective positive charge on the metal and consequently, lowering the density on the OCH_3 group should increase the covalent character of the $M{-}OCH_3$ bond. The stability of the M–OR bond thus appears to be in the order: $Pt > Pd$; $C_6F_5 > CCl{=}CCl_2 > CH{=}CCl_2 > Ph$.

The reaction of *trans*-$[Pd(R)(Cl)(PPh_3)_2]$ ($R = Ph$ or $CH{=}CCl_2$) with NaOMe in toluene did not yield the expected methoxo complex; instead $[Pd(PPh_3)_2]_n$ was obtained, which produces "$Pd(PPh_3)_4$" on addition of 2 mol. of PPh_3. The species "$Pd(PPh_3)_2$" could also be obtained directly from *trans*-$[Pd(Ph)(OMe)(PPh_3)_2]$ together with the coupling product anisole (**18** → **21**). The formation of $[Pd(PPh_3)_2]_n$ may be accounted for by β-hydrogen elimination from the methoxo group in the initial product $Pd(R)(OMe)(PPh_3)_2$ giving HCHO and $Pd(R)(H)(PPh_3)_2$, which subsequently undergoes reductive elimination of RH. In contrast to mononuclear palladium(II) and platinum(II) complexes, the analogous nickel derivatives, $Ni(R)(Cl)(PPh_3)_2$ (**22**) yield binuclear bridged methoxo nickel derivatives [67] (**23**).

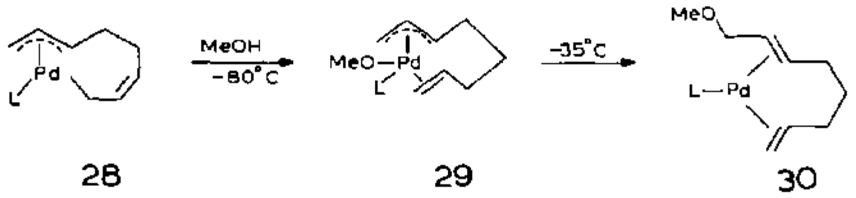




A thermally stable, diamagnetic colourless mononuclear methoxy platinum(II) complex (**27**) $Pt(OCH_3)(C_6H_9)(dppe)$ ($dppe = Ph_2PCH_2CH_2PPh_2$) has been synthesised [68] in 50% yield by the reaction of methanol with a cyclic alkylplatinum(0) complex (**26**) $Pt(C_6H_8)(dppe)$, which can be prepared as shown. The reaction of methanol with the complex **25**, on the other hand, gives a colourless hydrido complex of formula $PtH(C_6H_9)(PPh_3)_2$ in 69% yield. By contrast, the complex **27** shows no tendency to decompose to a hydrido complex. The thermal stability of this alkoxo complex is rather surprising because the thermal decomposition of intermediate alkoxides by β-elimination is thought to be responsible for the ready formation of hydrido complexes of these metals in basic alcoholic media.

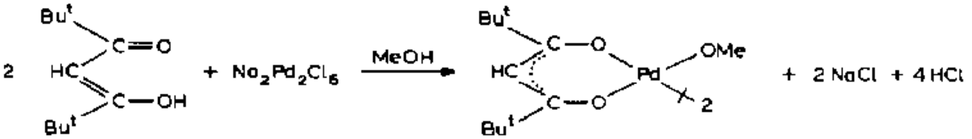


The interaction of the η^1,η^3-octadienediylpalladium compounds (**28**) with methanol has been reported [69] to yield mononuclear methoxo complexes (**29**) at −80° which change to **30** at −35°C.



(L = Me_3P, tricyclohexylphosphine)

The reaction of 2,2,6,6-tetramethylheptane-3,5-dione with disodium hexachlorodipalladate in 1:1 molar ratio in methanol yields the dimeric methoxy complex **31** [70] almost quantitatively. However, increasing yields of the bis(2,2,6,6-tetramethylheptane-3,5-dionato)palladium complex, $Pd(Bu^tCOCHCOBu^t)_2$ along with **31** were obtained as the molar ratio of β-diketone in the reaction mixture was increased. It has, therefore, been conjectured that the reaction of pentane-2,4-dione with disodium hexachlorodipalladate also proceeds via an analogue of complex **31** although the product in the latter case (in all molar ratios) is mainly the bis-complex, $Pd(CH_3COCHCOCH_3)_2$.

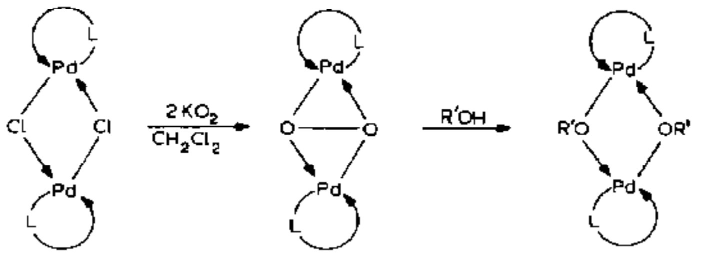


31

Recently, the synthesis of another binuclear palladium complex, $Pd_2(\mu\text{-}OCH_3)_2(F_6acac)_2$ by the reaction of $Pd(F_6acac)_2$ with methanol at room temperature has been reported [71]. Similarly $Pd_2(\mu\text{-}CD_3O)_2(F_6acac)_2$ was also prepared by using CD_3OD. Efforts to prepare higher homologues of $Pd_2(\mu\text{-}OCH_3)_2(F_6acac)_2$ failed, which might again be ascribed to the presence of an abstractable hydrogen in these alkoxy groups.

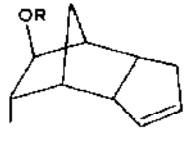
Thermal decomposition of the complex $Pd_2(\mu\text{-}OCH_3)_2(F_6acac)_2$ was found to be a disproportionation reaction and yielded palladium metal, $Pd(F_6acac)_2$, methanol, methylformate and a small amount of dimethoxymethane.

The binuclear alkoxo-bridged palladium products **34** have been obtained [72,73] by the reaction of methanol with dioxygen-bridged complexes **33**, which in turn were synthesised by reaction of the corresponding dichloro-bridged palladium(II) complexes **32** with potassium superoxide in dichloromethane.

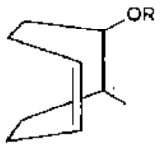


32 33 34

Q =

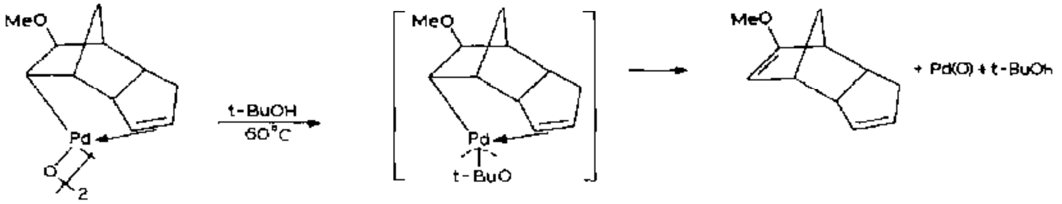


Q' =



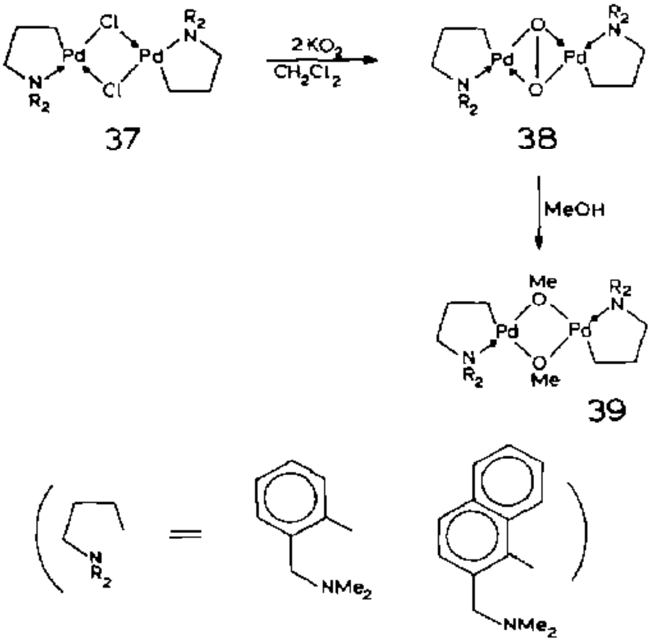
(L = Q(R = Me), R' = Me ; Q(R = Me), R' = Et , Q'(R = Me),
R' = Et ; Q'(R = Et), R' = Me)

Treatment of μ-peroxo complex **35** with t-butyl alcohol at 60°C caused decomposition into the free ligand and metallic palladium(0). It has been suggested that steric repulsion between the Me-DiCp ligand and the bulky alkoxo groups forces the β-elimination of Pd–H forming a coordinatively-unsaturated intermediate **36** which decomposes further.



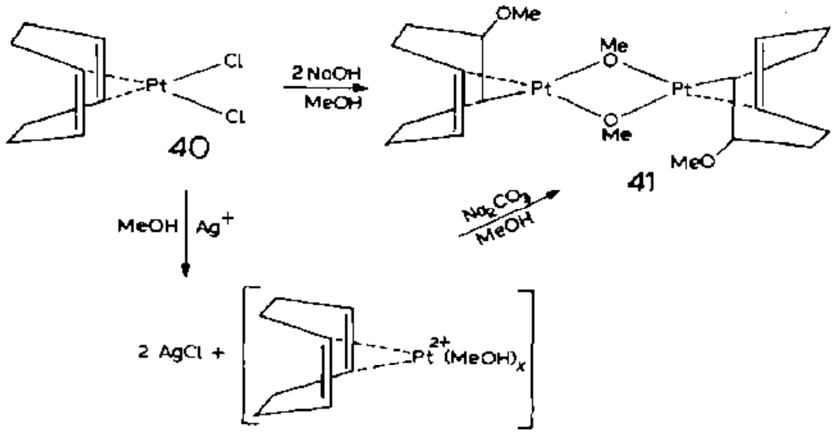
35 36

Similarly, the methoxo palladium complexes **39** have been prepared from the peroxo complexes **38** which can be obtained by anion exchange of the corresponding μ-chloro complexes [74] **37**.



37 38 39

The most convenient methods [75,76] for preparation of a stable binuclear platinum(II) complex **41** containing bridging methoxy groups $Pt_2(\mu\text{-}OCH_3)_2(\text{cod-}OCH_3)_2$ are the treatment of $(\text{cod})\cdot PtCl_2$ **40** with two equiv-

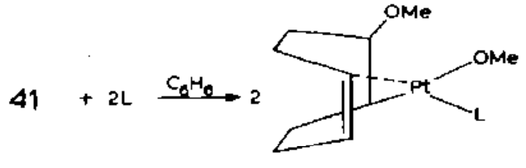


40 41

alents of sodium hydroxide in aqueous methanol or with sodium carbonate in methanol in the presence of silver nitrate.

A closely-related and possibly identical compound was reported in 1957 by Chatt et al. [77] without characterisation and was referred to as "α-dimethoxide". Attempts to prepare the dicyclopentadiene anologue failed and led to complex mixtures of products and/or extensive decomposition.

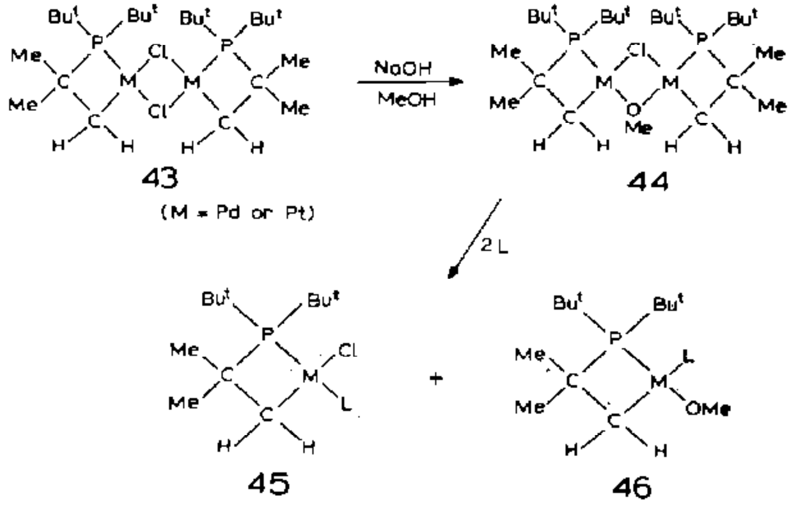
The methoxy bridges of **41** can be cleaved by tertiary phosphines (L) to give mononuclear methoxy complexes **42**.



42

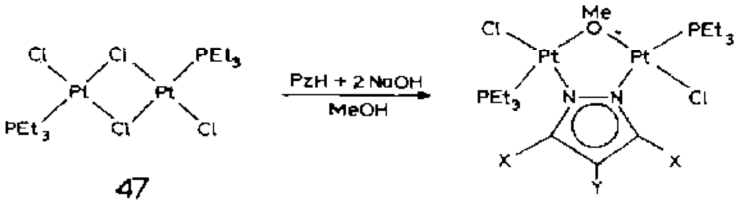
($L = Ph_3P$, $i\text{-}Pr_3P$, Cy_3P, $(p\text{-tolyl})_3P$)

The stable mixed methoxy- and chloro-bridged binuclear palladium(II) and platinum(II) complexes **44** are formed when the corresponding chloro-bridged binuclear complexes **43** suspended in methanol are allowed to react with an equimolar amount of sodium hydroxide [78,79]. The reaction of tertiary phosphines ($L = Ph_3P$, $(PhO)_3P$, $t\text{-}Bu_2PhP$ or $i\text{-}Pr_3P$) with **44** gives mononuclear chloro and methoxo complexes **45** and **46**.



(M = Pd or Pt)

Some interesting binuclear platinum(II) complexes of the type **48** have been synthesised by the reaction of $Pt_2Cl_4(PEt_3)_2$ **47** with pyrazole and sodium hydroxide in methanol [80].



47

48

(where X = H, Y = H; X = CH_3, Y = H or X = CH_3, Y = Br)

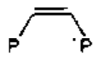
(ii) Properties

All mononuclear methoxo complexes of these metals are susceptible to hydrolysis [65,66] readily producing hydroxo complexes in contrast to binuclear methoxo complexes which are fairly stable towards water. The hydrolysis was accelerated by the addition of a small amount of potassium hydroxide or triethylamine.

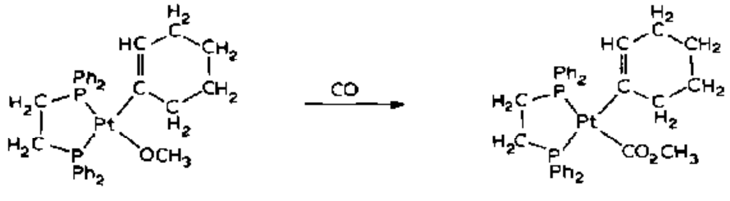
The platinum–oxygen bonds undergo facile insertion with CNR′, CO, COS, CS_2 and SO_2. The insertion reaction of isocyanides (CNR′) with methoxy–alkyl mononuclear platinum(II) complexes, $[Pt(OCH_3)(R)(Ph_2PCH{=}CHPPh_2)]$ (R = CF_3, CH_2CN) (**49**) affords insertion products $[PtC(OCH_3){=}NR'(R)(Ph_2PCH{=}CHPPh_2)]$ (**50**) [81].

49

50

(R = CF_3, CH_2CN;  = *cis*-$Ph_2PCH{=}CHPPh_2$;
R′ = methyl, *p*-methoxyphenyl or 2,6-dimethylphenyl)

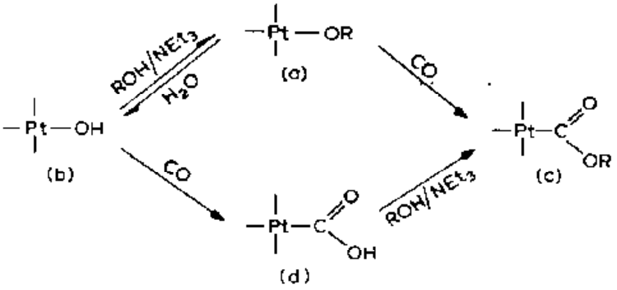
The preparation of $Pt(COOCH_3)(C_6H_9)(Ph_2PCH_2CH_2PPh_2)$ (**52**) via CO insertion into the $Pt{-}OCH_3$ bond of **51** has been reported [68].



51

52

In order to gain more information on the nature of the Pt–O bond in the methoxy alkyl mononuclear platinum complexes $Pt(OCH_3)(R)L_2$ (R = CF_3, CH_2CN; $L_2 = 2PPh_3$, diphosphine), their insertion reactions [66] with CO,



Scheme 1

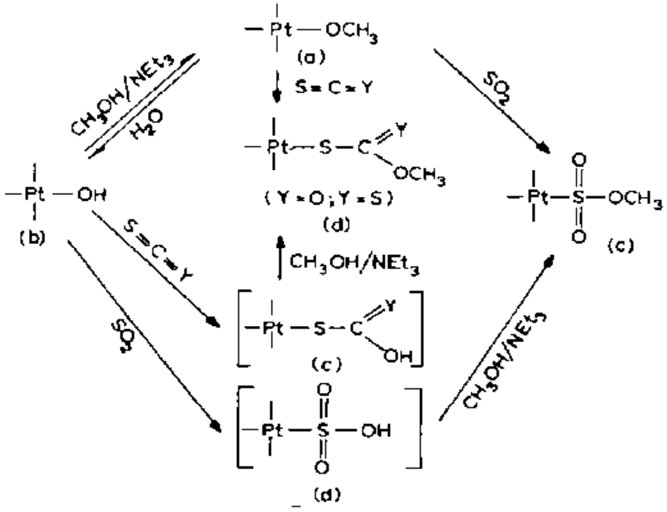
COS, CS_2 and SO_2 have been studied. These reactions are summarised in schemes 1 and 2.

Schemes 1 and 2 indicate two possible routes for the ROH/NEt_3 basic solution, i.e. formation of the alkoxo derivative (a) by the equilibrium (b) $\rightleftharpoons$ (a), and/or esterification of the carboxylato, thiocarbonato, dithiocarbonato or sulphinato intermediate complex (d).

(iii) Spectroscopic studies

In the infrared spectra of most of the complexes, a sharp band in the region 1050–1100 cm^{-1} has been assigned to the ν(C–O) mode of the methoxo group. In platinum complexes a sharp band at ~530 cm^{-1} has been attributed to ν(Pt–O).

The ^1H, ^{31}P and ^{19}F NMR spectra of palladium(II) and platinum(II)



Scheme 2

TABLE 5

^{1}H NMR spectral data for alkoxo derivatives of palladium and platinum

S.No.	Compound	^{1}H NMR data δ(ppm)	Reference
1.	*cis*-[Pt(C_6H_5)(OMe)(PPh_3)$_2$]	4.05(d)(OMe), 6.4[^4J(HP)] 54 ·0[^3J(HPt)], 7.50(m), 6.80(m)(Ph)	65
2.	*cis*-[Pt(CCl=CCl_2)(OMe)(PPh_3)$_2$]	4.13(d)(OMe), 6.8[^4J(HP)] 55 ·0[^3J(HPt)], 7.6(m), 6.90(m)(Ph)	65
3.	*trans*-[Pt(CH=CCl_2)(OMe)(PPh_3)$_2$]	2.97(s)(OMe), 0[^4J(HP)], 27·0[^3J(HPt)] 7.95(m), 7.05(Ph)	65
4.	*trans*-[Pd(C_6F_5)(OMe)(PPh_3)$_2$]	3.08(t)(OMe), 1.8[^4J(HP)] 7.90(m), 7.00(m)(Ph)	65
5.	*trans*-[Pd(CCl=CCl_2)(OMe)(PPh_3)$_2$]	2.78(t)(OMe), 1.4[^4J(HP)], 8.06(m), 7.10(m)(Ph)	65
6.	Pt(OMe)(CH_2CN)($Ph_2PCH=CHPPh_2$)	3.76(dd)(OMe), 44.1[^3J(PtOCH)] 1.0(*cis*), 5.9(*trans*)[^4J(PPtOCH)] 1.61(dd)(CH_2CN), 78.5[^2J(PtCN)] 4.2(*cis*), 9.9(*trans*)[^3J(PPtCH)]	66

7.	$Pt(OMe)(CF_3)(Ph_2PCH{=}CHPPh_2)$	3.65(d)(OMe), 48.5[^3J(PtOCH)], 7.0[^3J(PPtOCH)]	66
8.	*trans*-$[Pt(OMe)(CF_3)(PPh_3)_2]$	2.0(s)(OMe), 19.7[^3J(PtOCH)]	66
9.	$Pt(OMe)(C_6H_9)(dppe)$	3.95(d)(OMe), 5.6[^4J(HP)(*trans*)], 52[^3J(PtH)]	68
10.	$Pd_2(\mu\text{-}OMe)_2(F_6acac)_2$	2.41(s)(OMe), 6.14(s)(F_6acac)	71
11.	$Pd_2(\mu\text{-}OMe)_2(MeO\text{–}diCp)_2$	3.18(s)(C–OMe), 3.40(s)(Pt–OMe) 5.10(m), 5.63(m)(olefinic)	72
12.	$Pt_2(\mu\text{-}OMe)_2(MeO\text{–}cod)_2$	5.25(s)(C–OMe), 3.55(s)(Pt–OMe) 1.0-2.9(m)(olefinic)(9H)	75, 76
13.	$Pd_2(\mu\text{-}Cl)(\mu\text{-}OMe)(t\text{-}Bu_2PCMe_2CH_2)_2$	3.78(t)(OMe), 2.2[J(PH)]; 1.37(d)(t-Bu_2P) 13.4[J(PH)]; 1.23(d)(P–CMe_2); 13.4[J(PH)] 1.16(d)(CH_2–Pd), 12.7[J(PH)]	78
14.	$Pt_2(\mu\text{-}Cl)(\mu\text{-}OMe)(t\text{-}Bu_2PCMe_2CH_2)_2$	3.49(t)(OMe), 2.2[J(PH)], 32.2[J(PtH)] 1.46(d)(t-Bu_2P), 13.2[J(PH)], 1.43(d)(P–CMe_2) 13.9[J(PH)]; 1.35(d)(CH_2–Pt), 6.8[J(PH)]	79
15.	$Pt_2Cl_2(PEt_3)_2(\mu\text{-}OMe)(C_3H_3N_2)$	3.59(q)(OMe), 46[^3J(PtH)]; 7.94(s) 6.33(H in pyrazole)	80
16.	$Pt_2Cl_2(PEt_3)_2(\mu\text{-}OMe)(C_5H_7N_2)$	2.98(q)(OMe), 48[^3J(PtH)], 2.47 5.81 (Me, H in pyrazole)	80
17.	$Pt_2Cl_2(PEt_3)_2(\mu\text{-}OMe)(C_5H_6N_2Br)$	3.01(q)(OMe), 48[^3J(PtH)], 2.48(Me in pyrazole)	80

s = Singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet.

TABLE 6

^{19}F and ^{31}P NMR spectral data for alkoxo derivatives of palladium and platinum

S. No.	Compound	^{19}F and ^{31}NMR data δ(ppm)	Reference
1.	$Pt(OMe)(CF_3)(Ph_2PCH{=}CHPPh_2)$ (^{19}F)	-27.9(dd)(CF_3), 603·0[^2J(PtCF)] 9·0(*cis*), 58·0(*trans*)[^3J(PPtCF)]	66
2.	$Pd_2(\mu\text{-}OMe)_2(F_6acac)_2$ (^{19}F)	75.0(s)	71
3.	$Pt_2(\mu\text{-}Cl)(\mu\text{-}OMe)(t\text{-}Bu_2PCMe_2CH_2)_2$ (^{31}P)	-22.42(s)(metalated t-Bu_2P), 3306·0[J(PtP)]	79
4.	$Pt_2Cl_2(PEt_3)_2(\mu\text{-}OMe)(C_3H_3N_2)$ (^{31}P)	0.67 (*trans* PEt_3), 3501·0[^1J(PtP)]	80
5.	$Pt_2Cl_2(PEt_3)_2(\mu\text{-}OMe)(C_5H_7N_2)$ (^{31}P)	1.01 (*trans* PEt_3), 3477·0[^1J(PtP)]	80
6.	$Pt_2Cl_2(PEt_3)_2(\mu\text{-}OMe)(C_5H_6N_2Br)$ (^{31}P)	1.07 (*trans* PEt_3), 3537·0[^1J(PtP)]	80

Abbreviations as in Table 5.

complexes have been studied and the results summarised in Tables 5 and 6 respectively.

(iv) X-ray structural analysis

The crystal structure of the complex, $Pd_2(\mu\text{-}OCH_3)_2(F_6acac)_2$ has been determined [71]. The crystal was monoclinic with the space group $P^2_{1/c}$; the

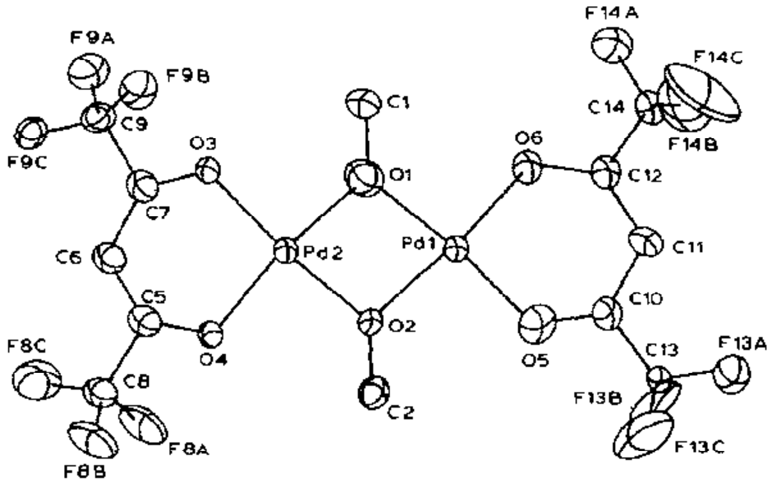


Fig. 6. The crystal structure of $Pd_2(\mu\text{-}OCH_3)_2(F_6acac)_2$.

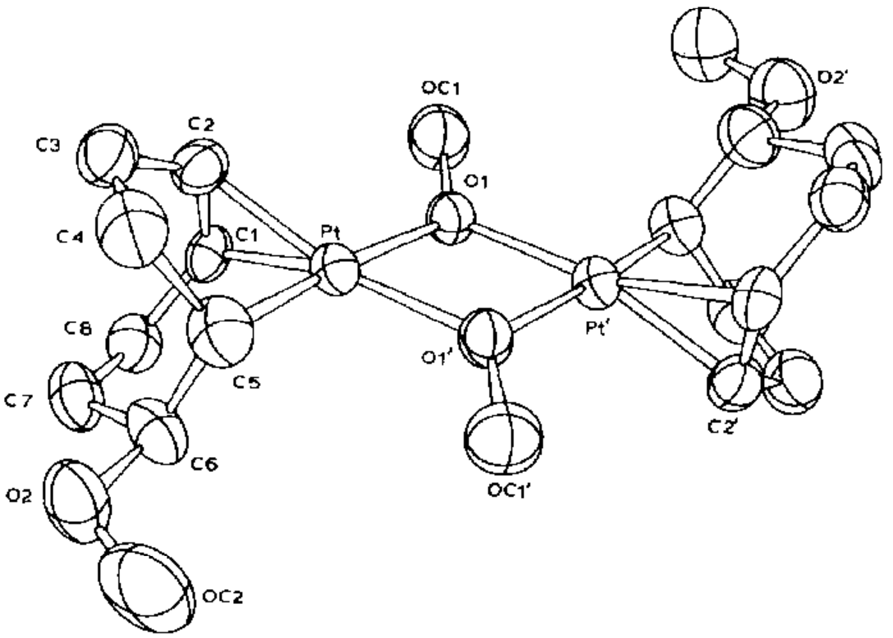


Fig. 7. The crystal structure of $Pt_2(\mu\text{-}OCH_3)_2(C_8H_{12}OCH_3)_2$.

values of unit cell dimensions are $a = 8.945(4)$, $b = 7.149(6)$, $c = 29.36(1)$ Å, $\beta = 93.89(3)°$ and $V = 1873$ Å^3. The calculated density is 2.443 g cm^{-3} with the assumption of $Z = 4$ (Fig. 6).

TABLE 7

Crystallographic data for $Pt_2(OMe)_2(C_8H_{12}OMe)_2$

Mol. formula	$C_{10}H_{18}O_2Pt_2$	$C_{10}H_{18}O_2Pt_2$
Mol.wt.	730.6	730.6
Crystal group	monoclinic	monoclinic
Space group	$P2_{1/c}$	$P2_{1/c}$
a (Å)	6.67(1)	6.648(2)
b (Å)	14.26(2)	14.186(5)
c (Å)	12.53(2)	14.237(4)
β(degrees)	113.0(1)	126.30(2)
V (Å^3)	1097	–
Z	2	2
d calcd. (g cm^{-3})	2.21	–
d exptl. (g cm^{-3})	2.19	–
F(000)	688	–
(M_oK_α) cm^{-1}	134	–
Reference	76	75

The crystal structure of the platinum(II) complex $Pt_2(\mu\text{-}OCH_3)_2(C_8H_{12}OCH_3)_2$ has been determined by Goel et al. [75] and Vitagliano et al., [76] in 1981 (Fig. 7) and results are summarised in Table 7.

ACKNOWLEDGEMENT

The authors thank the Department of Science and Technology, New Delhi for financial assistance.

REFERENCES

1 B.P. Baranwal, P.C. Bharara and R.C. Mehrotra, Transition Met. Chem., 2 (1977) 204.
2 B.P. Baranwal and R.C. Mehrotra, Transition Met. Chem., 3 (1978) 220.
3 B.P. Baranwal and R.C. Mehrotra, Z. Anorg. Allg. Chem., 443 (1979) 284.
4 B.P. Baranwal, G.K. Parashar and R.C. Mehrotra, Z. Naturforsch., Teil B, 34 (1979) 459.
5 B.P. Baranwal and R.C. Mehrotra, Aust. J. Chem., 33 (1980) 37.
6 J.V. Singh, N.C. Jain and R.C. Mehrotra, Z. Naturforsch., Teil B, 35 (1980) 1555.
7 J.V. Singh, B.P. Baranwal and R.C. Mehrotra, Z. Anorg. Chem., 477 (1981) 235.
8 J.V. Singh and R.C. Mehrotra, Inorg. Chem., 23 (1984) 1046.
9 J.V. Singh and R.C. Mehrotra, Z. Anorg. Allg. Chem., 512 (1984) 221.
10 J.V. Singh and R.C. Mehrotra, Can. J. Chem., 62 (1984) 1003.
11 J.V. Singh and R.C. Mehrotra, Transition Met. Chem., 9 (1984) 148.
12 J.V. Singh and R.C. Mehrotra, J. Coord. Chem., 13 (1984) 273.
13 D.C. Bradley, Adv. Chem. Ser., 23 (1959) 10.
14 D.C. Bradley in F.A. Cotton (Ed.), Progress in Inorganic Chemistry, Interscience, New York, Vol. 2, 1960.
15 D.C. Bradley in F.G.A. Stone and W.G.A. Graham (Eds.), Inorganic Polymers, Academic Press, New York, 1962.
16 J.Ya. Turova and A.V. Novoselova, Usp. Khim., 34 (1965) 385; Chem. Abstr., 62 (1965) 14213b.
17 R.C. Mehrotra, Ist International Symposium on Organosilicon Chemistry, Prague (1965), Pure Appl. Chem., 13 (1966) 111.
18 D.C. Bradley, Coord. Chem. Rev., 2 (1967) 229.
19 R.C. Mehrotra, Inorg. Chim. Acta Rev., 1 (1967) 99.
20 R.C. Mehrotra, J. Sci. Ind. Res., 28 (1969) 326.
21 R.C. Mehrotra, Coordination Chemistry (IUPAC), 21 (1981) 1131. (Special Main Lecture delivered at XXI International Conference of Coordination Chemistry, Toulouse, France 1981).
22 R.C. Mehrotra, in H.J. Emeleus and A.G. Sharpe (Eds.), Recent Advances in Inorganic and Radiochemistry, 26 (1983) 269.
23 R.C. Mehrotra, D.P. Gaur and D.C. Bradley, Chemistry of Metal Alkoxides, Academic Press, London, 1978.
24 J.M. Batwara, P.N. Kapoor and R.C. Mehrotra, Coord. Chem. Rev., 31 (1980) 67.
25 R.W. Adams, C.G. Baraclough, R.L. Martin and G. Winter, Inorg. Chem., 5 (1966) 346.
26 C.J. Lundman and T.C. Waddington, J. Chem. Soc. A, (1966) 1816.
27 D.C. Bradley, R.K. Multani and W. Wardlaw, J. Chem. Soc., (1958) 126 and 4153.
28 P.P. Sharma and R.C. Mehrotra, Ind. J. Chem., 5 (1967) 456.
29 P.P. Sharma and R.C. Mehrotra, J. Indian Chem. Soc., 44 (1967) 74.

30 P.P. Sharma and R.C. Mehrotra, J. Indian Chem. Soc., 45 (1968) 736.

31 E. Benedetti, G. Braca, G. Sbrana, F. Salvetti and M. Grassi, J. Organomet. Chem., 37 (1972) 361.

32 D.J. Cole-Hamilton, R.J. Young and G. Wilkinson, J. Chem. Soc., (1976) 1995.

33 D.R. Robertson and T.A. Stephenson, J. Organomet. Chem., 157 (1978) C47.

34 T. Arthur, D.R. Robertson, D.A. Tocher and J.A. Stephenson, J. Organomet. Chem., 208 (1981) 389.

35 R.O. Gould, T.A. Stephenson and D.A. Tocher, J. Organomet. Chem., 263 (1984) 375.

36 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc., (1977) 477.

37 B.F.G. Johnson, J. Lewis and P.A. Kilty, J. Chem. Soc. A, (1968) 2859.

38 D. Hartley, P.A. Kilty and M.J. Ware, J. Chem. Soc. Chem. Commun., (1968) 493.

39 V.F. Allen, R. Mason and P.B. Hitchcock, J. Organomet. Chem., 140 (1977) 297.

40 E.C. Bryan, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Chem. Commun., (1977) 329.

41 C.F. Brucker, T.N. Rhodin, Wijeyesckar, G.St. George and J.R. Shapley, J. Chim. Phys. Phys. Chim. Biol., 78 (1981) 897; Chem. Abstr., 97 (1982) 153421.

42 R. Mason and M.P. Mingos, J. Organomet. Chem., 50 (1979) 53.

43 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735; W.P. Griffith, The Chemistry of the Rarer Platinum Metals, Interscience, New York, 1967, p. 397.

44 S.D. Robinson and B.L. Shaw, J. Chem. Soc., (1965) 4997.

45 G. Pannetier, R. Bonnaire and P. Fougeroux, J. Less-Common Metals, 21 (1970) 437.

46 G. Pannetier, P. Fougeroux, R. Bonnaire and N. Platzer, J. Less-Common Metals, 24 (1971) 83.

47 F. Sakurai, H. Suzuki, Y. Moro-oka and T. Ikawa, J. Am. Chem. Soc., 102 (1980) 1749.

48 W. Keim, J. Organomet. Chem., 14 (1968) 179.

49 A. Nutton and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1981) 2335.

50 I. Tanaka, N. Jin-No, T. Kushida, N. Tsutsui, T. Ashida, H. Suzuki, H. Sakurai, Y. Moro-oka, and T. Ikawa, Bull. Chem. Soc. Jpn., 56 (1983) 637.

51 P.A. Tucker, W. Scutcher and D.R. Russel, Acta Crystallogr., Sect. B, 36 (1975) 592.

52 N.A. Bailey, E. Coates, G.B. Robertson, F. Bonati and R. Ugo, J. Chem. Soc. Chem. Commun., (1967) 1041.

53 A.C. Sievert and E.L. Muetterties, Inorg. Chem., 20 (1981) 489.

54 S.K. Agarwal and R.C. Mehrotra, unpublished results.

55 R. Sariego, M. Valderroma, I. Carkovic and M. Martinez, Bol. Soc. Chil. Quim., 27 (1982) 117.

56 D. Brodzki, B. Denise and G. Pannetier, J. Mol. Catal., 2 (1977) 149; Chem. Abstr., 87 (1977) 133393.

57 M.A. Bennett and T. Yoshida, J. Am. Chem. Soc., 95 (1973) 3030.

58 P.E. Maitlis, The Organic Chemistry of Palladium, Academic Press, New York, Vol. 2, 1971, p. 82.

59 F.R. Hartley, The Chemistry of Platinum and Palladium, Holsted Press, New York, 1973, 172.

60 F.R. Hartley, Coord. Chem. Rev., 35 (1981) 143.

61 F. Glocking and E.H. Brooks, Prepr. Pap. Nat. Meeting Div. Petr. Chem., 14 (1969) B 135.

62 M.A. Bennett, G.B. Robertson, P.O. Whimp and T. Yoshida, J. Am. Chem. Soc., 95 (1973) 3028.

63 R.J. Cross and F. Glocking, J. Chem. Soc., (1965) 5422.

64 R.J.D. Gee and H.M. Powell, J. Chem. Soc., (1971) 1956.

65 T. Yoshida, T. Okano and S. Otsuka, J. Chem. Soc. Dalton Trans., (1976) 993.

66 R.A. Michelin, M. Napoli and R. Ros, J. Organomet. Chem., 175 (1979) 239.

67 H.F. Klein, and H.H. Karsch, Chem. Ber., 106 (1973) 1433.

68 M.A. Bennett and T. Yoshida, J. Am. Chem. Soc., 100 (1978) 1750.

69 A. Doehring, P.W. Jolly, R. Mynott, K.P. Schick and G. Wilke, Z. Naturforsch., Teil B, 36 (1981) 1198.

70 D.A. White, J. Chem. Soc. A, (1971) 143.

71 A.R. Siedle and L.H. Pignolet, Inorg. Chem., 21 (1982) 3090.

72 H. Suzuki, K. Mizutani, Y. Moro-Oka and T. Ikawa, J. Am. Chem. Soc., 101 (1979) 748.

73 R. Sugimoto, H. Eikawa, H. Suzuki, Y. Mora-Oka and T. Ikawa, Bull. Chem. Soc., Jpn., 54 (1981) 2849.

74 P.J. Chung, Gakujutsu Ronbunshu-Chosen Shogakkai, 9 (1979) 226.

75 A.B. Goel, S. Goel and D.G. Vanderveer, Inorg. Chim. Acta, 54 (1981) L169.

76 F. Giordano and A. Vitagliano, Inorg. Chem., 20 (1981) 633.

77 J. Chatt, L.M. Vallarino and L.M. Venanzi, J. Chem. Soc., (1957) 2436; U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, New York, 1974.

78 A.B. Goel and S. Goel, Transition Met. Chem., 5 (1980) 378.

79 H.C. Clark and A.B. Goel, J. Organomet. Chem., 178 (1979) C27.

80 F. Bonati, H.C. Clark and C.S. Wong, Can. J. Chem., 58 (1980) 1435.

81 R.A. Michelin, J. Organomet. Chem., 169 (1979) C42.