Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SOME CARBONYL AND RELATED COMPLEXES CONTAINING THE LIGANDS $PhCH_2EMe_2$ (E=P or As)

R. L. BENNETT, M. I. BRUCE and F. G. A. STONE
Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)

(Received December 1st, 1971)

SUMMARY

The preparations and spectra of several transition metal (Mn, Fe, Ru, Rh, Ni, Pd, Pt) complexes derived from benzyldimethylphosphine and -arsine are described.

Recent work using *N,N*-dimethylbenzylamine as a ligand in transition metal complexes has shown[1,2] that *ortho*-metalation of the phenyl group, with formation of a five-membered chelate ring, often occurs. A natural consequence of this study was the extension to benzyldimethylphosphine and -arsine (I, E=P or As). Complexes in which metal–carbon σ bond formation has occurred have been obtained from *o*-tolylphosphine ligands, either directly[3], or by prior metalation of the ligand with an alkali metal[4]. In this paper, we describe several complexes of (I, E=P or As) which we have examined during the course of our related studies. The stereochemistry of these complexes was determined by a combination of infrared, Raman, and proton NMR spectrometry; the latter are discussed in detail below.

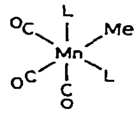
Reactions between these ligands and $MeMn(CO)_5$ afforded the disubstituted complexes $MeMn(CO)_3(PhCH_2EMe_2)_2$ (II, E=P; III, E=As) as yellow crystalline solids. The proton NMR spectrum of (II) (see below) suggested that the two phosphine ligands were mutually *trans*, and also *cis* to the methyl group; the ν(CO) region of the infrared spectrum (Table 1) showed three bands, with an intensity pattern consistent with the geometry shown. The infrared spectrum of (III) is similar, and this complex is assumed to have the same geometry as (II). From the reaction which afforded (II), a small amount of the dinuclear complex $[Mn(CO)_3(PhCH_2PMe_2)_2]_2$ (IV) was also obtained. In neither reaction was any evidence obtained for the formation of any acyl complexes.

Similar reactions with the bromide, $Mn(CO)_5Br$, afforded the disubstituted complexes $MnBr(CO)_3(PhCH_2EMe_2)_2$ (V, E=P; VI, E=As). For (V), the proton NMR spectrum showed that the ligands were mutually *trans*, and the infrared spectrum showed a similar pattern to that of (II).

The crude product from the reaction between the phosphine (I) and $Fe_2(CO)_9$ contained both $Fe(CO)_4(PhCH_2PMe_2)$ (VII) and $Fe(CO)_3(PhCH_2PMe_2)_2$ (VIII), as shown by its proton NMR spectrum. However, we were unable to obtain the mono-substituted derivative in a pure state. Complex (VIII) contains mutually

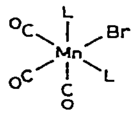
$PhCH_2EMe_2$

(I), E = P or As



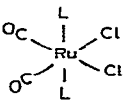
(II), L = $PhCH_2PMe_2$

(III), L = $PhCH_2AsMe_2$



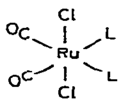
(V), L = $PhCH_2PMe_2$

(VI), L = $PhCH_2AsMe_2$

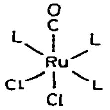


(XIII), L = $PhCH_2PMe_2$

(XIV), L = $PhCH_2AsMe_2$



(XV), L = $PhCH_2AsMe_2$



(XVIII), L = $PhCH_2PMe_2$

trans phosphine ligands, as expected. With the arsine, only $Fe(CO)_4(PhCH_2AsMe_2)$ (IX) was obtained.

Dodecacarbonyltriruthenium reacted readily with $PhCH_2PMe_2$ in refluxing cyclohexane to give deep purple crystals of $Ru_3(CO)_9(PhCH_2PMe_2)_3$ (X). Boiling this complex in chloroform gave a yellow solution from which $RuCl_2(CO)_3(PhCH_2PMe_2)$ (XI) was isolated. This suggests that one phosphine is coordinated to each metal atom in the cluster complex (X), probably in the equatorial position. In contrast with the reaction of triphenylarsine[5], the tris-substituted complex $Ru_3(CO)_9(PhCH_2AsMe_2)_3$ (XII) was obtained from the reaction of the arsine with $Ru_3(CO)_{12}$. This

TABLE 1

CARBONYL STRETCHING FREQUENCIES

Complex[a]		*ν(CO) (cm^{-1})*	*Solvent*
(II)	$Mn(CO)_3(P^*)_2Me$	1988 w, 1904 s, 1867 m	$CHCl_3$
(III)	$Mn(CO)_3(As^*)_2Me$	1994 w, 1905 s, 1869 m	$CHCl_3$
(IV)	$[Mn(CO)_3(P^*)_2]_2$	2055 w, 1991 w, 1961 m, 1905 s, 1867 m	$CHCl_3$
(V)	$Mn(CO)_3(P^*)_2Br$	2031 w, 1945 s, 1907 m	C_6H_{12}
(VI)	$Mn(CO)_3(As^*)_2Br$	2028 w, 1960 s, 1912 m	C_6H_{12}
(VII)	$Fe(CO)_4(P^*)$	2051 m, 1977 m, 1943 (sh), 1934 vs	C_6H_{12}
(IX)	$Fe(CO)_4(As^*)$	2049 ms, 1975 m, 1944 (sh), 1937 vs	C_6H_{12}
(VIII)	$Fe(CO)_3(P^*)_2$	1884 (sh), 1875 vs, 1841 w	C_6H_{12}
(X)	$Ru_3(CO)_9(P^*)_3$	2043 w, 2017 w, 1973 s, 1937 m	C_6H_{12}
(XII)	$Ru_3(CO)_9(As^*)_3$	2043 vw, 2016 vw, 1982 s, 1971 s, 1935 m, 1921 m	C_6H_{12}
(XI)	$Ru(CO)_3(P^*)Cl_2$	2069 s, 2009 s, 1991 (sh)	$CHCl_3$
(XIII)	$Ru(CO)_2(P^*)_2Cl_2$	2050 s, 1986 s	$CHCl_3$
(XIV)	$Ru(CO)_2(As^*)_2Cl_2$	2047 s, 1985 s	$CHCl_3$
(XV)	$Ru(CO)_2(As^*)_2Cl_2$	2063 s, 2008 m	$CHCl_3$
(XVIII)	$Ru(CO)(P^*)_3Cl_2$	1981 s	$CHCl_3$
(XX)	$Rh(CO)(P^*)_2Cl$	1963 s	C_6H_{12}
(XXI)	$Rh(CO)(As^*)_2Cl$	1965 s	C_6H_{12}

[a] $P^* = PhCH_2PMe_2$; $As^* = PhCH_2AsMe_2$.

was the only complex obtained using a variety of conditions. Degradation of the complex with chloroform gave $RuCl_2(CO)_2(PhCH_2AsMe_2)_2$, identical with one of the isomers (XIV) obtained from the reaction between the arsine and $[Ru(CO)_3Cl_2]_2$ (see below).

In a reaction with the phosphine, the complex $[Ru(CO)_3Cl_2]_2$ afforded white $RuCl_2(CO)_2(PhCH_2PMe_2)_2$ (XIII). The infrared spectrum had two ν(CO) bands, suggesting that the carbonyl groups were *cis*. The proton NMR spectrum indicated that the two phosphine ligands were *trans*, thus unequivocally allowing the assignment of the illustrated structure. With the arsine, two products were obtained, both isomers of the complex $RuCl_2(CO)_2(PhCH_2AsMe_2)_2$. The isomer with ν(CO) at 2047 and 1985 cm^{-1} also showed bands at 629, 622 and 596 cm^{-1} in the Raman spectrum, assigned to ν(AsC), and indicating *trans* arsine ligands (XIV). The second isomer had ν(CO) at 2063 and 2008 cm^{-1}, and is probably (XV).

A variety of complexes has been obtained previously from reactions between hydrated ruthenium trichloride and phosphines or arsines. In our hands, reactions with either ligand (I) gave respectively $RuCl_2(PhCH_2EMe_2)_4$ (XVI, E=P; XVII, E=As). The solid complex (XVI) slowly turned green over a period of months. Reactions of (XVI) with CO gave yellow solutions which afforded crystals of the complex $RuCl_2(CO)(PhCH_2PMe_2)_3$ (XVIII). If a stream of hydrogen was passed into a refluxing dimethylacetamide solution of complex (XVII), a yellow solution, probably containing a complex carbonyl hydride, was formed. Subsequent treatment with CO, and recrystallisation from chloroform afforded crystalline $RuCl_2(CO)_2$-$(PhCH_2AsMe_2)_2$ (isomer XIV). The same compound was obtained by reaction of the arsine with the ruthenium carbonyl chloride obtained by heating hydrated ruthenium trichloride in 2-ethoxyethanol.

Refluxing a chloroform solution of nickelocene with the phosphine gave a red solution from which the tetraphenylborate of the $[(\pi\text{-}C_5H_5)Ni(PhCH_2PMe_2)_2]^+$ cation (XIX) could be obtained as an orange solid. Similar complexes containing triphenylphosphine, with counter ions such as F^- or $SnCl_3^-$ have been described[6,7], as have the halides $(\pi\text{-}C_5H_5)Ni(PBu_3)_2X$ (X=Cl, Br, I)[8].

With $[Rh(CO)_2Cl]_2$, the expected complexes $RhCl(CO)(PhCH_2EMe_2)_2$ (XX, E=P; XXI, E=As) were formed, the phosphine complex exhibiting a proton NMR spectrum consistent with the presence of mutually *trans* phosphine ligands. The same stereochemistry was found for the arsine complex on the basis of the Raman spectrum. In this, ν(AsC) bands occurred at 551, 596 and 618 cm^{-1}, and a further band was found at 459 cm^{-1}.

Yellow $RhCl_3(PhCH_2PMe_2)_3$ (XXII) or $RhCl_3(PhCH_2AsMe_2)_3$ (XXIII) separated on stirring an ethanolic solution of hydrated rhodium trichloride with the respective ligands overnight.

Refluxing a mixture of the phosphine and lithium tetrachloropalladate afforded a white complex, with analytical data corresponding to the formula $PdCl_2(PhCH_2$-$PMe_2)_3$ (XXIV). Treatment of this complex with sodium tetraphenylborate gave a white solid analysing for $[PdCl(PhCH_2PMe_2)_3]BPh_4$ (XXV), suggesting that complexes (XXIV) and (XXV) are further examples of the relative rare cationic $[PdClL_3]^+$ complexes[9]. This appears to be the first direct preparation of this type of compound from a simple palladium chloride; previously reported examples are obtained by multi-step syntheses. Heating complex (XXIV) in a higher-boiling solvent gave pale yellow *trans*-$PdCl_2(PhCH_2PMe_2)_2$ (XXVI). Similar reactions of the arsine resulted in the formation of yellow $PdCl_2(PhCH_2AsMe_2)_2$ (XXVII), shown to be the *cis* isomer by its Raman spectrum. This contained four ν(AsC) bands at 632, 620, 603 and 593 cm^{-1}.

With sodium tetrachloroplatinate, the phosphine afforded initially a product which was a 1/5 mixture of *cis* and *trans* isomers of $PtCl_2(PhCH_2PMe_2)_2$ (XXVIII), from which the pure *cis* isomer was isolated after refluxing the solid in 2-methoxyethanol. The arsine afforded pale yellow crystals of a single isomer (*cis*) of $PtCl_2(PhCH_2AsMe_2)_2$ (XXIX), as shown by the Raman spectrum.

The ligands (I) were very reactive colourless liquids which fumed in air. The phosphine readily formed the corresponding oxide (XXX) on aerial oxidation as white needles. The product was also isolated from several of the reactions described above (see Experimental). In contrast, the arsine suffered ready cleavage of the benzyl group, presumably as a result of hydrolysis, and white cacodylic acid, $Me_2AsO(OH)$, was obtained when the arsine came into contact with air, even for only short periods. Benzyltrimethylphosphonium iodide (XXXI) was prepared in order to compare its ^1H NMR spectrum with other derivatives of the phosphine.

PROTON NMR STUDIES

The proton NMR spectra of several products obtained in this work are listed in Table 2. Of most interest are the methyl and methylene resonances of the ligands, which occur in the regions τ 8.5–9.0 and τ 6.5–7.0, respectively. In the free phosphine, coupling with phosphorus (^{31}P) results in the methyl resonances appearing as a doublet [J(PH) 2.75 Hz]. A small coupling with the phosphorus atom, possibly also with some benzylic coupling, results in a broad singlet being observed for the CH_2 group. The corresponding oxide shows doublets for both resonances, with the considerably larger coupling constants expected for a phosphorus(V) compound. The methiodide is similar.

As observed previously in phosphine complexes, the nature of the resonances is affected by the stereochemistry of the complexes formed, and by the degree of internuclear coupling[10]. Thus the methyl and methylene resonances can be described as parts of $A_nXX'A'_n$ systems, with $n=6$ for the methyl group, and $n=2$ for the methylene group. In both cases, the XX′ part of the spectrum is not observed, arising from the phosphorus atoms. In our complexes, the resonances have not been fully resolved, both appearing as triplets, and the only measurable parameter is $|J_{AX}+J_{AX'}|$, which is also listed in Table 2.

The arsine does not exhibit this behaviour, but the similarities in chemical shifts and infrared spectra suggest that similar geometries obtain for these complexes.

In only one case has a further splitting of the methyl resonance been observed, namely for $RhCl(CO)(PhCH_2PMe_2)_2$, where a triplet of doublets is found. This arises from a rhodium–methyl coupling of about 1.1 Hz. With $Mn(CO)_3(PhCH_2PMe_2)_2Me$, the metal-methyl signal (resonating above TMS, at τ 10.7) also exhibits *cis* coupling with both phosphorus atoms [J(PMe) 7.8 Hz].

In the cation $[(\pi\text{-}C_5H_5)Ni(PhCH_2PMe_2)_2]^+$, it is unlikely that the two ligands are *trans*. Nevertheless, triplets are observed in these complexes for the CH_3 and CH_2 resonances, suggesting a fairly strong interaction between the phosphorus

TABLE 2

PROTON NMR DATA

			Chemical shifts (τ)			*Coupling constants* (*Hz*)[b]		
No.	*Complex*[a]	*Solvent*	*Me*	*CH_2*	*Ph*	*PMe*	*PCH_2*	*other*
(II)	$Mn(CO)_3(P^*)_2Me$[c]	$CDCl_3$	8.82 d	6.91 d	2.90 m	(6.4)	(4.4)	PMe 7.8
(III)	$Mn(CO)_3(As^*)_2Me$[d]	$CDCl_3$	8.94 s	6.95 s	2.91 m			
(IV)	$[Mn(CO)_3(P^*)_2]_2$	$CDCl_3$	8.80 d	6.89 d	2.82 m			
(V)	$Mn(CO)_3(P^*)_2Br$	$(CD_3)_2CO$	8.58 t	6.58 t	2.76 m	(7.7)	(6.2)	
(VI)	$Mn(CO)_3(As^*)_2Br$[g]	$CDCl_3$	8.79 d	6.73 d	2.72, 2.91 m	2.0	2.5	
(VII)	$Fe(CO)_4(P^*)$	$(CD_3)_2CO$	8.36 d	6.60 d	2.66 br	11	11	
(IX)	$Fe(CO)_4(As^*)$	$(CD_3)_2CO$	8.53 s	6.63 s	2.79 s			
(VIII)	$Fe(CO)_3(P^*)_2$	$(CD_3)_2CO$	8.53 d	6.71 d	2.66 br	(8)	(8)	
(X)	$Ru_3(CO)_9(P^*)_3$	$(CD_3)_2CO$	8.71 d	6.87 d	2.86, 3.08 m	8.5	7.0	
(XII)	$Ru_3(CO)_9(As^*)_3$	$(CD_3)_2CO$	8.71 s	6.74 s	2.80 m			
(XI)	$Ru(CO)_3(P^*)Cl_2$	$CDCl_3$	8.50 d	6.46 d	2.70, 2.90 m			
(XIII)	$Ru(CO)_2(P^*)_2Cl_2$	$CDCl_3$	8.52 t	6.50 t	2.85 m	(7)	(7.6)	
(XIV)	$Ru(CO)_2(As^*)_2Cl_2$	$(CD_3)_2CO$	8.63 s	6.52 s	2.80 m			
(XV)	$Ru(CO)_2(As^*)_2Cl_2$	$(CD_3)_2CO$	8.76 s	6.70 s	2.80 m			
(XVIII)	$Ru(CO)(P^*)_3Cl_2$	$CDCl_3$	8.65 d,	6.65 d,	2.78 m	7.4	5.25	
			8.56 t	6.51 t		(6.8)	(6.7)	
(XVI)	$RuCl_2(P^*)_4$	CS_2	8.68 s, br	6.74 s, br	2.95 m			
(XVII)	$RuCl_2(As^*)_4$	$CDCl_3$	8.73 s	6.62 s	2.79 m			
(XIX)	$[(\pi\text{-}C_5H_5)Ni(P^*)_2]BPh_4$[e]		8.78 t	6.98 t	2.86 m, 3.30 m	(9.0)	(11.0)	
(XX)	$Rh(CO)(P^*)_2Cl$	CS_2	8.68 td	6.79 t	2.90 s	6.0	7.5	RhMe 1.0
(XXI)	$Rh(CO)(As^*)_2Cl$	$CDCl_3$	8.70 s	6.65 s	2.76 m			
(XXIII)	$RhCl_3(As^*)_3$	CS_2	8.65 s	6.24 s	2.82 m, br			
(XXIV)	$PdCl_2(P^*)_3$	$CDCl_3$	8.60 br	6.60 br	2.80 br			
(XXVI)	$PdCl_2(P^*)_2$	$CDCl_3$	8.70 t	6.71 t	2.81 m			
(XXVII)	$PdCl_2(As^*)_2$	$CDCl_3$	8.78 s	6.80 s	2.86 m			
(XXVIIIa)	$PtCl_2(P^*)_2$-*cis*	$(CF_3)_2CHOH$	8.63 d	6.60 d	2.80 m	10.6	13.0	PtMe 35 $PtCH_2$ 30
(XXVIIIb)	$PtCl_2(P^*)_2$-*trans*	$(CF_3)_2CHOH$	8.52 tt	6.54 s	2.66 m	(6.4)		
(XXIX)	$PtCl_2(As^*)_2$	$CDCl_3$	8.77 s	6.70 d	2.81 m			
	$PhCH_2PMe_2$	$CDCl_3$	9.07 d	7.34 s	2.90 m	2.75		
	$PhCH_2AsMe_2$	$CDCl_3$	9.16 s	7.27 s	2.66–3.00 m			
	$PhCH_2P(O)Me_2$	CS_2	8.78 d	7.08 d	2.91 s	12.2	15.0	
	$PhCH_2PMe_3I$[f]	D_2O	8.13 d	6.28 d	2.58 m	14.2	16.0	

[a] $P^* = PhCH_2PMe_2$; $As^* = PhCH_2AsMe_2$. [b] Values in parentheses indicate separation of two outer lines of "virtually-coupled" triplets. [c] MnMe at τ 10.71 t. [d] MnMe at τ 10.74 s. [e] π-C_5H_5 at τ 4.81 s; BPh_4 at τ 2.86 m. [f] Chemical shifts originally measured relative to H_2O (assumed τ 5.25). [g] Mixture of isomers (?).

atoms. Similar results were obtained earlier with the ruthenium complexes $(\pi\text{-}C_5H_5)Ru(PMePh_2)_2X$, which probably have a similar configuration[11]. No interaction of the phosphorus atoms with the π-C_5H_5 protons occurs, a sharp singlet at τ 4.81 being found for these protons.

In the spectrum of complex (XVIII), doublet and triplet resonances, with relative intensities 1/2, are found for both the methyl and methylene protons. This enables the stereochemistry of the three phosphine ligands to be established as shown. The Raman spectrum shows bands at 329 [ν(RuCl) asym] and 285 cm^{-1}

[ν(RuCl) sym], confirming a *cis* Cl–Ru–Cl geometry, and the overall structure as shown in (XVIII).

EXPERIMENTAL

General experimental and instrumental methods are similar to those reported in other papers from these laboratories. All reactions were carried out under nitrogen,

TABLE 3

ANALYTICAL DATA

No.	*Complex*	*M.p.* (°C)	*Analyses: found (calcd.) (%)*					*Mol.wt.*[a] *found* (*calcd.*)
			C	*H*	*Halogen*	*P or As*	*Other*	
(II)	$Mn(CO)_3(PhCH_2PMe_2)_2Me$	170–171	57.55 (57.55)	6.35 (6.35)				456 (456)
(III)	$Mn(CO)_3(PhCH_2AsMe_2)_2Me$	123–125	47.5 (48.1)	5.15 (5.3)				
(IV)	$[Mn(CO)_3(PhCH_2PMe_2)_2]_2$	150–151	56.65 (56.8)	5.95 (5.85)				
(V)	$Mn(CO)_3(PhCH_2PMe_2)_2Br$	159–160	48.35 (48.2)	5.05 (4.95)	15.5 (15.3)	12.0 (11.85)	Mn 10.55 (10.4)	
(VI)	$Mn(CO)_3(PhCH_2AsMe_2)_2Br$	140–141	41.65 (41.8)	4.15 (4.3)				
(VIII)	$Fe(CO)_3(PhCH_2PMe_2)_2$	86– 87	56.65 (56.7)	6.05 (5.85)				444 (444)
(IX)	$Fe(CO)_4(PhCH_2AsMe_2)$	49– 50	42.9 (42.85)	3.55 (3.55)				364 (364)
(X)	$Ru_3(CO)_9(PhCH_2PMe_2)_3$	171–172	42.9 (42.65)	3.75 (3.85)		9.1 (9.2)	Ru 29.75 (29.95)	998[b] (1011)
(XII)	$Ru_3(CO)_9(PhCH_2AsMe_2)_3$	217–218	37.75 (37.75)	3.25 (3.4)		19.5 (19.65)		
(XI)	$Ru(CO)_3(PhCH_2PMe_2)Cl_2$	226–227 d	34.8 (35.3)	3.5 (3.2)				
(XIII)	$Ru(CO)_2(PhCH_2PMe_2)_2Cl_2$	186–187	44.9 (45.15)	4.9 (4.9)	13.05 (13.35)			534 (534)
(XIV)	$Ru(CO)_2(PhCH_2AsMe_2)_2Cl_2$	149–150	38.65 (38.75)	4.05 (4.2)	11.6 (11.45)			622 (622)
(XV)	$Ru(CO)_2(PhCH_2AsMe_2)_2Cl_2$	146–147	39.1	4.2	11.3			
(XVIII)	$Ru(CO)(PhCH_2PMe_2)_3Cl_2$	153–154	51.25 (51.2)	6.0 (5.95)				
(XVI)	$RuCl_2(PhCH_2PMe_2)_4$	165–166	55.5 (55.4)	6.65 (6.65)	9.65 (9.1)	14.65 (15.9)	Ru 13.65 (12.95)	
(XVII)	$RuCl_2(PhCH_2AsMe_2)_4$	155–156	45.5 (45.8)	5.35 (5.55)				
(XIX)	$[(\pi\text{-}C_5H_5)Ni(PhCH_2PMe_2)_2]BPh_4$	129–130	74.55 (74.45)	6.85 (6.8)				
(XX)	$Rh(CO)(PhCH_2PMe_2)_2Cl$	76– 77	48.6 (48.4)	5.65 (5.5)	7.35 (7.55)	13.4 (13.15)	Rh 21.65 (21.85)	470 (470)
(XXI)	$Rh(CO)(PhCH_2AsMe_2)_2Cl$	86– 87	41.2 (41.5)	4.9 (4.7)				
(XXII)	$RhCl_3(PhCH_2PMe_2)_3$	270–271	48.55 (48.6)	5.8 (5.85)	15.4 (15.8)			
(XXIII)	$RhCl_3(PhCH_2AsMe_2)_3$	186–187	40.75 (40.6)	4.9 (4.85)	13.0 (13.35)			

(*Table continued*)

TABLE 3 (*continued*)

No.	*Complex*	*M.p.* (°*C*)	*Analyses: found (calcd.) (%)*					*Mol.wt.*[a] *found* (*calcd.*)
			C	*H*	*Halogen*	*P or As*	*Other*	
(XXIV)	$PdCl_2(PhCH_2PMe_2)_3$	144–145	50.7	6.2	11.15	14.5	Pd 16.75	
			(51.1)	(6.15)	(11.2)	(14.5)	(16.75)	
(XXV)	$[PdCl(PhCH_2PMe_2)_3]BPh_4$	154–156 d	66.45	6.2				
			(66.7)	(6.1)				
(XXVI)	$PdCl_2(PhCH_2PMe_2)_2$	196–197	44.4	5.55	14.7			
			(44.9)	(5.2)	(14.75)			
(XXVII)	$PdCl_2(PhCH_2AsMe_2)_2$	156–157	38.3	4.75	12.1			
			(37.95)	(4.55)	(12.45)			
(XXVIII)	$PtCl_2(PhCH_2PMe_2)_2$	151–152	37.7	4.4	12.6			
			(37.9)	(4.55)	(12.45)			
(XXIX)	$PtCl_2(PhCH_2AsMe_2)_2$	167–168	33.05	4.05	11.1			
			(32.85)	(3.95)	(10.8)			
(XXX)	$PhCH_2P(O)Me_2$	94–95°	63.55	7.7				168
			(63.8)	(7.7)				(168)
(XXXI)	$PhCH_2PMe_3I$	199–200°	41.6	5.3				
			(40.9)	(5.1)				

[a] Mass spectrometry. [b] Chloroform (osmometric).

and chromatography was on columns of Florisil, initially packed in light petroleum. Analytical and m.p. details are collected in Table 3.

Benzyldimethylphosphine, $PhCH_2PMe_2$. The ligand was prepared[12] by reduction of dibenzyldimethylphosphonium bromide with lithium aluminium hydride. It is a colourless liquid, b.p. 95–97°/12 mm.

Benzyldimethylarsine, $PhCH_2AsMe_2$. The arsenic analogue was obtained from benzylmagnesium chloride and dimethylarsenic iodide, as a colourless liquid, b.p. 110–112°/15 mm.

Preparation of the complexes

The complexes were generally prepared by heating solutions of the ligand with the transition metal precursor. Details of these reactions are gathered together in Tables 4 and 5. Some other reactions which were not straight-forward are described below.

Reactions of benzyldimethylphosphine

(*a*). *With nickelocene.* Reaction of the phosphine (250 mg, 1.64 mmoles) with nickelocene (310 mg, 1.64 mmoles) in refluxing chloroform (25 ml) for 2 h gave a red oil after removal of solvent. This was dissolved in ethanol and treated with $NaBPh_4$ to give an orange precipitate (XIX), which was collected and washed with ethanol and ether (589 mg, 48 %).

(*b*). *With Li_2PdCl_4.* A mixture of the phosphine (610 mg, 4 mmoles) with Li_2PdCl_4 (520 mg, 2 mmoles) was refluxed in methanol (50 ml) for 12 h. Evaporation and recrystallisation (benzene) of the residue afforded white crystals of $PdCl_2(PhCH_2PMe_2)_3$ (XXIV) (739 mg, 58.5%).

TABLE 4

REACTIONS OF BENZYLDIMETHYLPHOSPHINE

Reactant (mmole)		*Phosphine (mmole)*	*Solvent (temp./h)*	*Recrystd. from*	*Product*	*Colour*	*Yield (%)*
$Mn(CO)_5Br$	1.82	1.82	Cyclohexane 11 h/reflux	Light petrol/ benzene	$MnBr(CO)_3(PhCH_2PMe_2)_2$ (V)	Yellow	58
$Mn(CO)_5Me$	2.0	2.0	Heptane 3 h/reflux	Benzene/ heptane	$Mn(CO)_3(PhCH_2PMe_2)_2Me$ (II)	Yellow	22
$Fe_2(CO)_9$	1.0	2.0	Light petrol 3 h/reflux	Hexane	$Fe(CO)_3(PhCH_2PMe_2)_2$ (VIII)	Pale yellow	33
$Ru_3(CO)_{12}$	0.78	2.35	Cyclohexane 7 h/reflux	Benzene/ heptane[a]	$Ru_3(CO)_9(PhCH_2PMe_2)_3$ (X)	Dark reddish-purple	60
$RuCl_3 \cdot nH_2O$ (200 mg)		2.87	Methanol 7 h/reflux		$RuCl_2(PhCH_2PMe_2)_4$ (XVI)	Orange	33
$[Ru(CO)_3Cl_2]_2$	0.45	0.9	Chloroform 30 min/reflux	Benzene/ heptane	$RuCl_2(CO)_2(PhCH_2PMe_2)_2$ (XIII)	White	18
$[Rh(CO)_2Cl]_2$	1.3	2.58	Cyclohexane 3 h/reflux	Hexane	$RhCl(CO)(PhCH_2PMe_2)_2$ (XX)	Yellow	52
$RhCl_3 \cdot 3H_2O$	2.03	10.7	Ethanol 22 h/20°		$RhCl_3(PhCH_2PMe_2)_3$ (XXII)	Yellow	37

[a] After chromatography (Florisil; eluted with 20/1 light petroleum/ether).

TABLE 5

REACTIONS OF BENZYLDIMETHYLARSINE

Reactant (mmole)	*Arsine (mmole)*	*Solvent (h/temp.)*	*Recrystallised from*	*Product*	*Colour*	*Yield (%)*
$Mn(CO)_5Br$, 0.91	1.82	Ether 6 h/reflux		$MnBr(CO)_3(PhCH_2AsMe_2)_2$ (VI)	Bright yellow	45
$Mn(CO)_5Me$, 2.0	2.0	Heptane 3 h/reflux	Heptane	$Mn(CO)_3(PhCH_2AsMe_2)_2Me$ (III)	Bright yellow	12
$Fe_2(CO)_9$, 1.0	2.0	Light petrol 3 h/reflux	Hexane	$Fe(CO)_4(PhCH_2AsMe_2)$ (IX)	Bright yellow	40
$Ru_3(CO)_{12}$, 0.78	2.35	Cyclohexane 30 min/reflux	Benzene/heptane	$Ru_3(CO)_9(PhCH_2AsMe_2)_3$ (XII)	Purple	78
$RuCl_3 \cdot nH_2O$ (208 mg)	4.0	Methanol 7 h/reflux		$RuCl_2(PhCH_2AsMe_2)_4$ (XVII)	Red brown	54
$[Ru(CO)_3Cl_2]_2$, 0.45	0.9	Chloroform 30 min/reflux	Benzene/heptane	$RuCl_2(CO)_2(PhCH_2AsMe_2)_2$ (XIV+XV)	Yellow	52
$[Rh(CO)_2Cl]_2$, 0.65	2.60	Ether 1 h/reflux	Ether/hexane	$RhCl(CO)(PhCH_2AsMe_2)_2$ (XXI)	Bright yellow	68
$RhCl_3 \cdot 3H_2O$, 2.03	5.26	Ethanol 24 h/20°		$RhCl_3(PhCH_2AsMe_2)_3$ (XXIII)	Yellow	35
Li_2PdCl_4, 2.0	4.0	Methanol 3 h/20°	Benzene/heptane	$PdCl_2(PhCH_2AsMe_2)_2$ (XXVII)	Yellow	61
Na_2PtCl_4, 1.5	3.0	Methanol 3 h/reflux	Benzene/heptane	$PtCl_2(PhCH_2AsMe_2)_2$ (XXIX)	Pale yellow	52

Treatment of this complex with sodium tetraphenylborate in ethanol gave an immediate white precipitate of $[PdCl(PhCH_2PMe_2)_3]BPh_4$ (XXV).

Heating complex (XXIV) (150 mg) in 2-methoxyethanol or diglyme for 24 h, followed by removal of solvent and recrystallisation (benzene/heptane), afforded pale yellow *trans*-$PdCl_2(PhCH_2PMe_2)_2$ (XXVI) (65 mg, 56%).

(*c*). *With Na_2PtCl_4.* A mixture of Na_2PtCl_4 (570 mg, 1.5 mmoles) and the phosphine (456 mg, 3 mmoles) in methanol (30 ml) was stirred for 1 h. The product separated as a white solid, which was filtered and washed with methanol and ether to give a mixture (1/5) of *cis*- and *trans*-$PtCl_2(PhCH_2PMe_2)_2$ (571 mg, 67%).

Refluxing this product (150 mg) in 2-methoxyethanol for 24 h, evaporation and recrystallisation of the residue from a benzene/heptane mixture afforded silver-white crystals of *cis*-$PtCl_2(PhCH_2PMe_2)_2$ (XXVIII) (80 mg, 53%).

Benzyldimethylphosphine oxide. In some reactions of the phosphine, varying amounts of a white crystalline solid were obtained, which was shown to be benzyldimethylphosphine oxide by comparison with an authentic sample. This was best prepared by drawing a stream of air through a light petroleum solution of the phosphine. Evaporation and sublimation (90°/0.1 mm) gave white needles of the oxide in quantitative yield.

Oxidation of benzyldimethylarsine. Drawing a stream of air through a light petroleum solution of benzyldimethylarsine caused precipitation of a white solid, identified as $Me_2AsO(OH)$ by comparison with an authentic sample, m.p. and mixed m.p. 199–200°.

Reaction of complex (X) with chloroform. A solution of complex (X) (100 mg, 1 mmole) was refluxed in chloroform (30 ml) for 24 h, to give a yellow solution. Evaporation and recrystallisation gave yellow $RuCl_2(CO)_3(PhCH_2PMe_2)$ (XI) (80 mg, 66%).

ACKNOWLEDGEMENT

R.L.B. thanks the S.R.C. for a Research Studentship. We thank Dr. P. L. Goggin for help in obtaining and interpreting the Raman spectra.

REFERENCES

1. A. Kasahara and T. Izumi, *Bull. Chem. Soc. Japan*, 42 (1969) 1765.
2. M. I. Bruce, M. Z. Iqbal and F. G. A. Stone, unpublished work.
3. M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 91 (1969) 6983.
4. G. Longoni, P. Chini, F. Canziani and P. Fantucci, *Chem. Commun.*, (1971) 470.
5. M. I. Bruce, C. W. Gibbs and F. G. A. Stone, *Z. Naturforsch. B*, 23 (1968) 1543.
6. P. A. McArdle and A. R. Manning, *Chem. Commun.*, (1967) 417.
7. M. van den Akker and F. Jellinek, *J. Organometal. Chem.*, 10 (1967) P37.
8. M. Sato, F. Sato and T. Yoshida, *J. Organometal. Chem.*, 27 (1971) 273; 31 (1971) 415.
9. D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton and J. G. Smith, *J. Chem. Soc.* (*A*), (1970) 545.
10. R. K. Harris, *Can. J. Chem.*, 42 (1964) 2275; J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, (1966) 770.
11. T. Blackmore, M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A*, (1971) 2376.
12. W. J. Bailey and S. A. Buckler, *J. Amer. Chem. Soc.*, 79 (1957) 3567.