

SOME CARBONYL AND RELATED COMPLEXES CONTAINING THE LIGANDS $\text{PhCH}_2\text{EMe}_2$ ($\text{E} = \text{P}$ or As)

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SUMMARY

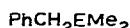
The preparations and spectra of several transition metal (Mn , Fe , Ru , Rh , Ni , Pd , Pt) complexes derived from benzyldimethylphosphine and -arsine are described.

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, $\text{E} = \text{P}$ or As). Complexes in which metal-carbon σ bond formation has occurred have been obtained from *o*-tolylphosphine ligands, either directly³, or by prior metalation of the ligand with an alkali metal⁴. In this paper, we describe several complexes of (I, $\text{E} = \text{P}$ 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.

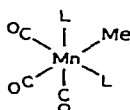
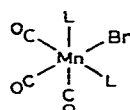
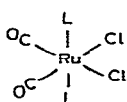
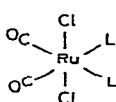
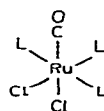
Reactions between these ligands and $\text{MeMn}(\text{CO})_5$ afforded the disubstituted complexes $\text{MeMn}(\text{CO})_3(\text{PhCH}_2\text{EMe}_2)_2$ (II, $\text{E} = \text{P}$; III, $\text{E} = \text{As}$) as yellow crystalline solids. The proton NMR spectrum of (II) (see below) suggested that the two phosphine ligands were mutually *trans*, and also *cis* to the methyl group; the $\nu(\text{CO})$ 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 $[\text{Mn}(\text{CO})_3(\text{PhCH}_2\text{PMe}_2)_2]_2$ (IV) was also obtained. In neither reaction was any evidence obtained for the formation of any acyl complexes.

Similar reactions with the bromide, $\text{Mn}(\text{CO})_5\text{Br}$, afforded the disubstituted complexes $\text{MnBr}(\text{CO})_3(\text{PhCH}_2\text{EMe}_2)_2$ (V, $\text{E} = \text{P}$; VI, $\text{E} = \text{As}$). 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 $\text{Fe}_2(\text{CO})_9$ contained both $\text{Fe}(\text{CO})_4(\text{PhCH}_2\text{PMe}_2)$ (VII) and $\text{Fe}(\text{CO})_3(\text{PhCH}_2\text{PMe}_2)_2$ (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



(I), E = P or As

(II), L = PhCH₂PMe₂(III), L = PhCH₂AsMe₂(V), L = PhCH₂PMe₂(VI), L = PhCH₂AsMe₂(XIII), L = PhCH₂PMe₂(XIV), L = PhCH₂AsMe₂(XV), L = PhCH₂AsMe₂(XVIII), L = PhCH₂PMe₂

trans phosphine ligands, as expected. With the arsine, only Fe(CO)₄(PhCH₂AsMe₂) (IX) was obtained.

Dodecacarbonyltriruthenium reacted readily with PhCH₂PMe₂ in refluxing cyclohexane to give deep purple crystals of Ru₃(CO)₉(PhCH₂PMe₂)₃ (X). Boiling this complex in chloroform gave a yellow solution from which RuCl₂(CO)₃(PhCH₂PMe₂) (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 triphenylarsine⁵, the tris-substituted complex Ru₃(CO)₉(PhCH₂AsMe₂)₃ (XII) was obtained from the reaction of the arsine with Ru₃(CO)₁₂. This

TABLE I

CARBONYL STRETCHING FREQUENCIES

Complex ^a		$\nu(\text{CO}) (\text{cm}^{-1})$	Solvent
(II)	Mn(CO) ₃ (P*) ₂ Me	1988 w, 1904 s, 1867 m	CHCl ₃
(III)	Mn(CO) ₃ (As*) ₂ Me	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*) ₂ Br	2031 w, 1945 s, 1907 m	C ₆ H ₁₂
(VI)	Mn(CO) ₃ (As*) ₂ Br	2028 w, 1960 s, 1912 m	C ₆ H ₁₂
(VII)	Fe(CO) ₄ (P*)	2051 m, 1977 m, 1943 (sh), 1934 vs	C ₆ H ₁₂
(IX)	Fe(CO) ₄ (As*)	2049 ms, 1975 m, 1944 (sh), 1937 vs	C ₆ H ₁₂
(VIII)	Fe(CO) ₃ (P*) ₂	1884 (sh), 1875 vs, 1841 w	C ₆ H ₁₂
(X)	Ru ₃ (CO) ₉ (P*) ₃	2043 w, 2017 w, 1973 s, 1937 m	C ₆ H ₁₂
(XII)	Ru ₃ (CO) ₉ (As*) ₃	2043 vw, 2016 vw, 1982 s, 1971 s, 1935 m, 1921 m	C ₆ H ₁₂
(XI)	Ru(CO) ₃ (P*)Cl ₂	2069 s, 2009 s, 1991 (sh)	CHCl ₃
(XIII)	Ru(CO) ₂ (P*) ₂ Cl ₂	2050 s, 1986 s	CHCl ₃
(XIV)	Ru(CO) ₂ (As*) ₂ Cl ₂	2047 s, 1985 s	CHCl ₃
(XV)	Ru(CO) ₃ (As*) ₂ Cl ₂	2063 s, 2008 m	CHCl ₃
(XVIII)	Ru(CO)(P*) ₃ Cl ₂	1981 s	CHCl ₃
(XX)	Rh(CO)(P*) ₂ Cl	1963 s	C ₆ H ₁₂
(XXI)	Rh(CO)(As*) ₂ Cl	1965 s	C ₆ H ₁₂

^a P* = PhCH₂PMe₂; As* = PhCH₂AsMe₂.

was the only complex obtained using a variety of conditions. Degradation of the complex with chloroform gave $\text{RuCl}_2(\text{CO})_2(\text{PhCH}_2\text{AsMe}_2)_2$, identical with one of the isomers (XIV) obtained from the reaction between the arsine and $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ (see below).

In a reaction with the phosphine, the complex $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ afforded white $\text{RuCl}_2(\text{CO})_2(\text{PhCH}_2\text{PMe}_2)_2$ (XIII). The infrared spectrum had two $\nu(\text{CO})$ 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 $\text{RuCl}_2(\text{CO})_2(\text{PhCH}_2\text{AsMe}_2)_2$. The isomer with $\nu(\text{CO})$ at 2047 and 1985 cm^{-1} also showed bands at 629, 622 and 596 cm^{-1} in the Raman spectrum, assigned to $\nu(\text{AsC})$, and indicating *trans* arsine ligands (XIV). The second isomer had $\nu(\text{CO})$ 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 $\text{RuCl}_2(\text{PhCH}_2\text{EMe}_2)_4$ (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 $\text{RuCl}_2(\text{CO})(\text{PhCH}_2\text{PMe}_2)_3$ (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 $\text{RuCl}_2(\text{CO})_2(\text{PhCH}_2\text{AsMe}_2)_2$ (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 $[(\pi\text{-C}_5\text{H}_5)_2\text{Ni}(\text{PhCH}_2\text{PMe}_2)_2]^+$ 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 $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}(\text{P}^i\text{Bu}_3)_2\text{X}$ (X=Cl, Br, I)⁸.

With $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, the expected complexes $\text{RhCl}(\text{CO})(\text{PhCH}_2\text{EMe}_2)_2$ (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, $\nu(\text{AsC})$ bands occurred at 551, 596 and 618 cm^{-1} , and a further band was found at 459 cm^{-1} .

Yellow $\text{RhCl}_3(\text{PhCH}_2\text{PMe}_2)_3$ (XXII) or $\text{RhCl}_3(\text{PhCH}_2\text{AsMe}_2)_3$ (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 $\text{PdCl}_2(\text{PhCH}_2\text{PMe}_2)_3$ (XXIV). Treatment of this complex with sodium tetraphenylborate gave a white solid analysing for $[\text{PdCl}(\text{PhCH}_2\text{PMe}_2)_3]\text{BPh}_4$ (XXV), suggesting that complexes (XXIV) and (XXV) are further examples of the relative rare cationic $[\text{PdClL}_3]^+$ complexes⁹. 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*-PdCl₂(PhCH₂PMe₂)₂ (XXVI). Similar reactions of the arsine resulted in the formation of yellow PdCl₂(PhCH₂AsMe₂)₂ (XXVII), shown to be the *cis* isomer by its Raman spectrum. This contained four $\nu(\text{AsC})$ 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 PtCl₂(PhCH₂PMe₂)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 PtCl₂-(PhCH₂AsMe₂)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, Me₂AsO(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 (³¹P) results in the methyl resonances appearing as a doublet [$J(\text{PH})$ 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 CH₂ 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 coupling¹⁰. 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 $|J_{\text{AX}} + J_{\text{AX}}'|$, 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)(PhCH₂PMe₂)₂, where a triplet of doublets is found. This arises from a rhodium–methyl coupling of about 1.1 Hz. With Mn(CO)₃(PhCH₂PMe₂)₂Me, the metal–methyl signal (resonating above TMS, at τ 10.7) also exhibits *cis* coupling with both phosphorus atoms [$J(\text{PMe})$ 7.8 Hz].

In the cation $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PhCH}_2\text{PMe}_2)_2]^+$, it is unlikely that the two ligands are *trans*. Nevertheless, triplets are observed in these complexes for the CH₃ and CH₂ resonances, suggesting a fairly strong interaction between the phosphorus

TABLE 2

PROTON NMR DATA

No.	Complex ^a	Solvent	Chemical shifts (τ)			Coupling constants (Hz) ^b		
			Me	CH ₂	Ph	PMe	PCH ₂	other
(II)	$\text{Mn}(\text{CO})_3(\text{P}^*)_2\text{Me}^c$	CDCl_3	8.82 d	6.91 d	2.90 m	(6.4)	(4.4)	PMe 7.8
(III)	$\text{Mn}(\text{CO})_3(\text{As}^*)_2\text{Me}^d$	CDCl_3	8.94 s	6.95 s	2.91 m			
(IV)	$[\text{Mn}(\text{CO})_3(\text{P}^*)_2]_2$	CDCl_3	8.80 d	6.89 d	2.82 m			
(V)	$\text{Mn}(\text{CO})_3(\text{P}^*)_2\text{Br}$	$(\text{CD}_3)_2\text{CO}$	8.58 t	6.58 t	2.76 m	(7.7)	(6.2)	
(VI)	$\text{Mn}(\text{CO})_3(\text{As}^*)_2\text{Br}^g$	CDCl_3	8.79 d	6.73 d	2.72, 2.91 m	2.0	2.5	
(VII)	$\text{Fe}(\text{CO})_4(\text{P}^*)$	$(\text{CD}_3)_2\text{CO}$	8.36 d	6.60 d	2.66 br	11	11	
(IX)	$\text{Fe}(\text{CO})_4(\text{As}^*)$	$(\text{CD}_3)_2\text{CO}$	8.53 s	6.63 s	2.79 s			
(VIII)	$\text{Fe}(\text{CO})_3(\text{P}^*)_2$	$(\text{CD}_3)_2\text{CO}$	8.53 d	6.71 d	2.66 br	(8)	(8)	
(X)	$\text{Ru}_3(\text{CO})_9(\text{P}^*)_3$	$(\text{CD}_3)_2\text{CO}$	8.71 d	6.87 d	2.86, 3.08 m	8.5	7.0	
(XII)	$\text{Ru}_3(\text{CO})_9(\text{As}^*)_3$	$(\text{CD}_3)_2\text{CO}$	8.71 s	6.74 s	2.80 m			
(XI)	$\text{Ru}(\text{CO})_3(\text{P}^*)\text{Cl}_2$	CDCl_3	8.50 d	6.46 d	2.70, 2.90 m			
(XIII)	$\text{Ru}(\text{CO})_2(\text{P}^*)_2\text{Cl}_2$	CDCl_3	8.52 t	6.50 t	2.85 m	(7)	(7.6)	
(XIV)	$\text{Ru}(\text{CO})_2(\text{As}^*)_2\text{Cl}_2$	$(\text{CD}_3)_2\text{CO}$	8.63 s	6.52 s	2.80 m			
(XV)	$\text{Ru}(\text{CO})_2(\text{As}^*)_2\text{Cl}_2$	$(\text{CD}_3)_2\text{CO}$	8.76 s	6.70 s	2.80 m			
(XVIII)	$\text{Ru}(\text{CO})(\text{P}^*)_3\text{Cl}_2$	CDCl_3	8.65 d, 8.56 t	6.65 d, 6.51 t	2.78 m	7.4 (6.8)	5.25 (6.7)	
(XVI)	$\text{RuCl}_2(\text{P}^*)_4$	CS_2	8.68 s, br	6.74 s, br	2.95 m			
(XVII)	$\text{RuCl}_2(\text{As}^*)_4$	CDCl_3	8.73 s	6.62 s	2.79 m			
(XIX)	$[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{P}^*)_2]\text{BPh}_4^e$		8.78 t	6.98 t	2.86 m, 3.30 m	(9.0)	(11.0)	
(XX)	$\text{Rh}(\text{CO})(\text{P}^*)_2\text{Cl}$	CS_2	8.68 td	6.79 t	2.90 s	6.0	7.5	RhMe 1.0
(XXI)	$\text{Rh}(\text{CO})(\text{As}^*)_2\text{Cl}$	CDCl_3	8.70 s	6.65 s	2.76 m			
(XXIII)	$\text{RhCl}_3(\text{As}^*)_3$	CS_2	8.65 s	6.24 s	2.82 m, br			
(XXIV)	$\text{PdCl}_2(\text{P}^*)_3$	CDCl_3	8.60 br	6.60 br	2.80 br			
(XXVI)	$\text{PdCl}_2(\text{P}^*)_2$	CDCl_3	8.70 t	6.71 t	2.81 m			
(XXVII)	$\text{PdCl}_2(\text{As}^*)_2$	CDCl_3	8.78 s	6.80 s	2.86 m			
(XXVIIIa)	$\text{PtCl}_2(\text{P}^*)_2\text{-cis}$	$(\text{CF}_3)_2\text{CHOH}$	8.63 d	6.60 d	2.80 m	10.6	13.0	{ PtMe 35 PtCH ₂ 30
(XXVIIIb)	$\text{PtCl}_2(\text{P}^*)_2\text{-trans}$	$(\text{CF}_3)_2\text{CHOH}$	8.52 tt	6.54 s	2.66 m	(6.4)		
(XXIX)	$\text{PtCl}_2(\text{As}^*)_2$	CDCl_3	8.77 s	6.70 d	2.81 m			
	$\text{PhCH}_2\text{PMe}_2$	CDCl_3	9.07 d	7.34 s	2.90 m	2.75		
	$\text{PhCH}_2\text{AsMe}_2$	CDCl_3	9.16 s	7.27 s	2.66–3.00 m			
	$\text{PhCH}_2\text{P}(\text{O})\text{Me}_2$	CS_2	8.78 d	7.08 d	2.91 s	12.2	15.0	
	$\text{PhCH}_2\text{PMe}_3\text{I}^f$	D_2O	8.13 d	6.28 d	2.58 m	14.2	16.0	

^a $\text{P}^* = \text{PhCH}_2\text{PMe}_2$; $\text{As}^* = \text{PhCH}_2\text{AsMe}_2$. ^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 $\pi\text{-C}_5\text{H}_5$ 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 $(\pi\text{-C}_5\text{H}_5)\text{-Ru}(\text{PMePh}_2)_2\text{X}$, which probably have a similar configuration¹¹. No interaction of the phosphorus atoms with the $\pi\text{-C}_5\text{H}_5$ 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 [$\nu(\text{RuCl})$ asym] and 285 cm^{-1}

[$\nu(\text{RuCl})$ 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 ₂ PMe ₂) ₂ Me	170–171	57.55 (57.55)	6.35 (6.35)				456 (456)
(III)	Mn(CO) ₃ (PhCH ₂ AsMe ₂) ₂ Me	123–125	47.5 (48.1)	5.15 (5.3)				
(IV)	[Mn(CO) ₃ (PhCH ₂ PMe ₂) ₂] ₂	150–151	56.65 (56.8)	5.95 (5.85)				
(V)	Mn(CO) ₃ (PhCH ₂ PMe ₂) ₂ Br	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 ₂ AsMe ₂) ₂ Br	140–141	41.65 (41.8)	4.15 (4.3)				
(VIII)	Fe(CO) ₃ (PhCH ₂ PMe ₂) ₂	86– 87	56.65 (56.7)	6.05 (5.85)				444 (444)
(IX)	Fe(CO) ₃ (PhCH ₂ AsMe ₂)	49– 50	42.9 (42.85)	3.55 (3.55)				364 (364)
(X)	Ru ₃ (CO) ₉ (PhCH ₂ PMe 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 ₂ AsMe ₂) ₃	217–218	37.75 (37.75)	3.25 (3.4)		19.5 (19.65)		
(XI)	Ru(CO) ₃ (PhCH ₂ PMe ₂)Cl ₂	226–227 d	34.8 (35.3)	3.5 (3.2)				
(XIII)	Ru(CO) ₂ (PhCH ₂ PMe ₂) ₂ Cl ₂	186–187	44.9 (45.15)	4.9 (4.9)	13.05 (13.35)			534 (534)
(XIV)	Ru(CO) ₂ (PhCH ₂ AsMe ₂) ₂ Cl ₂	149–150	38.65 (38.75)	4.05 (4.2)	11.6 (11.45)			622 (622)
(XV)	Ru(CO) ₂ (PhCH ₂ AsMe ₂) ₂ Cl ₂	146–147	39.1	4.2	11.3			
(XVIII)	Ru(CO)(PhCH ₂ PMe ₂) ₃ Cl ₂	153–154	51.25 (51.2)	6.0 (5.95)				
(XVI)	RuCl ₂ (PhCH ₂ PMe 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 ₂ AsMe ₂) ₄	155–156	45.5 (45.8)	5.35 (5.55)				
(XIX)	[(π -C ₅ H ₅)Ni(PhCH ₂ PMe ₂) ₂] ₂ BPh ₄	129–130	74.55 (74.45)	6.85 (6.8)				
(XX)	Rh(CO)(PhCH ₂ PMe ₂) ₂ Cl	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 ₂ AsMe ₂) ₂ Cl	86– 87	41.2 (41.5)	4.9 (4.7)				
(XXII)	RhCl ₃ (PhCH ₂ PMe ₂) ₃	270–271	48.55 (48.6)	5.8 (5.85)	15.4 (15.8)			
(XXIII)	RhCl ₃ (PhCH ₂ AsMe 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)	$\text{PdCl}_2(\text{PhCH}_2\text{PMe}_2)_3$	144–145	50.7 (51.1)	6.2 (6.15)	11.15 (11.2)	14.5 (14.5)	Pd 16.75 (16.75)	
(XXV)	$[\text{PdCl}(\text{PhCH}_2\text{PMe}_2)_3]\text{BPh}_4$	154–156 d	66.45 (66.7)	6.2 (6.1)				
(XXVI)	$\text{PdCl}_2(\text{PhCH}_2\text{PMe}_2)_2$	196–197	44.4 (44.9)	5.55 (5.2)	14.7 (14.75)			
(XXVII)	$\text{PdCl}_2(\text{PhCH}_2\text{AsMe}_2)_2$	156–157	38.3 (37.95)	4.75 (4.55)	12.1 (12.45)			
(XXVIII)	$\text{PtCl}_2(\text{PhCH}_2\text{PMe}_2)_2$	151–152	37.7 (37.9)	4.4 (4.55)	12.6 (12.45)			
(XXIX)	$\text{PtCl}_2(\text{PhCH}_2\text{AsMe}_2)_2$	167–168	33.05 (32.85)	4.05 (3.95)	11.1 (10.8)			
(XXX)	$\text{PhCH}_2\text{P}(\text{O})\text{Me}_2$	94–95°	63.55 (63.8)	7.7 (7.7)				168 (168)
(XXXI)	$\text{PhCH}_2\text{PMe}_3\text{I}$	199–200°	41.6 (40.9)	5.3 (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.

Benzyl dimethylphosphine, $\text{PhCH}_2\text{PMe}_2$. The ligand was prepared¹² by reduction of dibenzyl dimethylphosphonium bromide with lithium aluminium hydride. It is a colourless liquid, b.p. 95–97°/12 mm.

Benzyl dimethylarsine, $\text{PhCH}_2\text{AsMe}_2$. 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 benzyl dimethylphosphine

(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 $\text{PdCl}_2\text{-(PhCH}_2\text{PMe}_2)_3$ (XXIV) (739 mg, 58.5 %).

TABLE 4
REACTIONS OF BENZYLDIMETHYLPHOSPHINE

Reactant (mmole)	Phosphine (mmole)	Solvent (temp./h)	Recrystd. from	Product	Colour	Yield (%)
Mn(CO) ₅ Br	1.82	1.82	Cyclohexane 11 h/reflux	MnBr(CO) ₃ (PhCH ₂ PMc ₂) ₂ (V)	Yellow	58
Mn(CO) ₅ Me	2.0	2.0	Heptane 3 h/reflux	Mn(CO) ₃ (PhCH ₂ PMc ₂) ₂ Me (II)	Yellow	22
Fe ₂ (CO) ₉	1.0	2.0	Light petrol 3 h/reflux	Fe(CO) ₃ (PhCH ₂ PMc ₂) ₂ (VIII)	Pale yellow	33
Ru ₃ (CO) ₁₂	0.78	2.35	Cyclohexane 7 h/reflux	Ru ₃ (CO) ₉ (PhCH ₂ PMc ₂) ₃ (X)	Dark reddish-purple	60
RuCl ₃ ·nH ₂ O (200 mg)	2.87	2.87	Methanol 7 h/reflux	RuCl ₃ (PhCH ₂ PMc ₂) ₄ (XVI)	Orange	33
[Ru(CO) ₃ Cl ₂] ₂	0.45	0.9	Chloroform 30 min/reflux	RuCl ₂ (CO) ₂ (PhCH ₂ PMc ₂) ₂ (XIII)	White	18
[Rh(CO) ₂ Cl] ₂	1.3	2.58	Cyclohexane 3 h/reflux	RhCl(CO)(PhCH ₂ PMc ₂) ₂ (XX)	Yellow	52
RhCl ₃ ·3H ₂ O	2.03	10.7	Ethanol 22 h/20°	RhCl ₃ (PhCH ₂ PMc 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 (%)
$(\text{Mn}(\text{CO})_5\text{Br}, 0.91$	1.82	Ether 6 h/reflux		$\text{MnBr}(\text{CO})_3(\text{PhCH}_2\text{AsMe}_2)_2$ (VI)	Bright yellow	45
$(\text{Mn}(\text{CO})_5\text{Me}, 2.0$	2.0	Heptane 3 h/reflux	Heptane	$\text{Mn}(\text{CO})_3(\text{PhCH}_2\text{AsMe}_2)_2\text{Me}$ (III)	Bright yellow	12
$(\text{Fe}_2(\text{CO})_9, 1.0$	2.0	Light petrol 3 h/reflux	Hexane	$\text{Fe}(\text{CO})_4(\text{PhCH}_2\text{AsMe}_2)$ (IX)	Bright yellow	40
$(\text{Ru}_3(\text{CO})_{12}, 0.78$	2.35	Cyclohexane 30 min/reflux	Benzene/ heptane	$\text{Ru}_3(\text{CO})_9(\text{PhCH}_2\text{AsMe}_2)_3$ (XII)	Purple	78
$[\text{RuCl}_3 \cdot n\text{H}_2\text{O} (208 \text{ mg})$	4.0	Methanol 7 h/reflux		$\text{RuCl}_2(\text{PhCH}_2\text{AsMe}_2)_4$ (XVII)	Rcd brown	54
$[\text{Ru}(\text{CO})_3\text{Cl}_2]_2, 0.45$	0.9	Chloroform 30 min/reflux	Benzene/ heptane	$\text{RuCl}_2(\text{CO})_2(\text{PhCH}_2\text{AsMe}_2)_2$ (XIV + XV)	Yellow	52
$[\text{Rh}(\text{CO})_2\text{Cl}]_2, 0.65$	2.60	Ether 1 h/reflux	Ether/ hexane	$\text{RhCl}(\text{CO})(\text{PhCH}_2\text{AsMe}_2)_2$ (XXI)	Bright yellow	68
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}, 2.03$	5.26	Ethanol 24 h/20°		$\text{RhCl}_3(\text{PhCH}_2\text{AsMe}_2)_3$ (XXIII)	Yellow	35
$\text{Li}_2\text{PdCl}_4, 2.0$	4.0	Methanol 3 h/20°	Benzene/ heptane	$\text{PdCl}_2(\text{PhCH}_2\text{AsMe}_2)_2$ (XXVII)	Yellow	61
$[\text{Na}_2\text{PtCl}_4, 1.5$	3.0	Methanol 3 h/reflux	Benzene/ heptane	$\text{PtCl}_2(\text{PhCH}_2\text{AsMe}_2)_2$ (XXIX)	Pale yellow	52

Treatment of this complex with sodium tetraphenylborate in ethanol gave an immediate white precipitate of $[\text{PdCl}(\text{PhCH}_2\text{PMe}_2)_3]\text{BPh}_4$ (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*- $\text{PdCl}_2(\text{PhCH}_2\text{PMe}_2)_2$ (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*- $\text{PtCl}_2(\text{PhCH}_2\text{PMe}_2)_2$ (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*- $\text{PtCl}_2(\text{PhCH}_2\text{PMe}_2)_2$ (XXVIII) (80 mg, 53%).

Benzyl dimethylphosphine oxide. In some reactions of the phosphine, varying amounts of a white crystalline solid were obtained, which was shown to be benzyl dimethylphosphine 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 benzyl dimethylarsine. Drawing a stream of air through a light petroleum solution of benzyl dimethylarsine caused precipitation of a white solid, identified as $\text{Me}_2\text{AsO}(\text{OH})$ 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 $\text{RuCl}_2(\text{CO})_3(\text{PhCH}_2\text{PMe}_2)$ (XI) (80 mg, 66%).

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