Rhodium(I), Rhodium(III), Palladium(II), and Platinum(II) Complexes containing Ligands of the Type PR_nQ_{3-n} (n = 0, 1, or 2; R = Me, Et, Bu^t, or Ph; Q = CH_2OCOMe or CH_2OH)

By **Joseph Chatt, G. Jeffery Leigh,* and Roger M. Slade,** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

We report the characterisation of the phosphines PR_nQ_{3-n} (n = 0, 1, or 2; R = Me, Et, Bu^t, or Ph; Q = CH_2OCOMe or CH_2OH) and of their complexes with halides of Pt^{II}, Pd^{II}, Rh^{I}, and Rh^{III}. The methylene protons of the acetoxymethyl- and hydroxymethyl-groups show no $^{31}P-^{1}H$ coupling in the complexes, and this is attributed to $|^2J(PH) + {}^4J(PH)|$ being accidentally nearly zero. Although the phosphines render the complexes more soluble in hydroxylic solvents than complexes of more conventional phosphines, and complexes derived from phosphines containing two or more hydroxymethyl groups are water soluble, the new complexes were not found to possess exceptional or unusual catalytic properties for the hydrogenation or isomerisation of olefins.

THE complexes of tertiary phosphines with the halides of metals of Group VIII are catalysts for reactions such as the isomerisation and the hydrogenation of olefins and acetylenes. However, their use is limited to organic solvents owing to the hydrophobic nature of the tertiary phosphines. The objects of this work were to prepare tertiary phosphine complexes soluble in water to see whether their catalytic properties could be exercised in aqueous solution and further, whether the water itself might participate in catalytic reaction of olefins. Hydroxymethylphosphines have been known for some time but their reactions with sodium chloropalladite or even with the halogen-bridged $[Pt_2Cl_4(PR_3)_2]$ (PR_3 = tertiary phosphine) generally lead to syrups. We found that phosphines of the type $PR(CH_2OH)_2$ (R = Me or Et) are difficult to obtain pure and we were often unable to prepare pure complexes from these phosphines. However, if complexes of the acetates of the hydroxyalkylphosphines are hydrolysed, the hydroxyalkylphosphine complexes so obtained are sufficiently pure to crystallise. We also succeeded in crystallising some complexes of $P(CH_2OH)_3$, and monohydroxyalkylphosphine complexes derived from $PPh_2(CH_2OCOMe)$. Many tertiary phosphines of the type PR_nQ_{3-n} (n = 0, 1, or 2; R = Me, Et, Pr^n, Bu^n, or Ph; Q = CH_2OCOMe or CH_2OH) are known [1-7] but only a few of their metal complexes.[8]

Preparation and Properties of the Phosphines.—We have prepared $P(CH_2OCOMe)_3$ and $P(CH_2OH)_3$ by established methods [1,9] and PRQ_2 and PR'_2Q (R = Me or Et; R' = Ph or Bu^t; Q = CH_2OCOMe) by the following routes (see Experimental section for full details).

Routes 1—4 are more convenient than the published methods and in some cases have led to new phosphines,

[1] Z. N. Mironova, E. N. Tsvetkov, A. G. Nikolaev, and M. I. Kabachnik, *Zhur. obshchei Khim.*, 1967, **37**, 2747.
[2] K. A. Petrov, V. A. Parshina, and A. F. Manuilov, *Zhur. obschchei Khim.*, 1965, **35**, 2062.
[3] K. A. Petrov, V. A. Parshina, and M. B. Luzanova, *Zhur. obshchei Khim.*, 1962, **32**, 553.
[4] E. I. Grinshtein, A. B. Bruker, and L. V. Soborovskii, *Doklady. Akad. Nauk. S.S.S.R.*, 1961, **139**, 1359.
[5] K. A. Petrov and V. A. Parshina, *Zhur. obshchei Khim.*, 1961, **31**, 3417.
[6] S. Trippet, *J. Chem. Soc.*, 1961, 2813.
[7] H. Hellman and O. Schumacher, *Angew. Chem.*, 1960, **72**, 211.
[8] N. Cahill and M. F. Lappert, unpublished observations.
[9] M. Reuter and L. Orthner, G.P. 1,035,135 (*Chem. Abs.*, 1960, **54**, 14125a.

e.g., $PMe(CH_2OCOMe)_2$, $PPh_2(CH_2OCOMe)$, $PBu^t_2(CH_2OCOMe)$, and $PMe_2(CH_2OCOMe)$.

The ^1H n.m.r. spectra of the complexes of the phosphines PR_nQ_{3-n} ($n = 0$, 1, or 2; R = Me, Et, Bu^t, or Ph; Q = CH_2OCOMe or CH_2OH) show interesting features which necessitated a study of the ^1H n.m.r. spectra of the phosphines themselves and details are given in Table 1. The $COCH_3$ protons always give rise to a singlet and for PQ_3 and PR_2Q (R = Ph, Bu^t, or Me; Q = CH_2OCOMe or CH_2OH) the P–CH_2–O protons give rise to a simple doublet due to ^{31}P–^1H coupling. The spectra of the compounds $PR(CH_2OCOMe)_2$ (R = Me or Et) show an ABX pattern for the P–CH_2–O protons (X = ^{31}P) indicating that the two protons of each P–CH_2–O group are non-equivalent. Similar behaviour has been reported for the di-isopropylphenylphosphine [10] but in this case the two methyl groups of each isopropyl group are non-equivalent. Many examples of such diastereotopic groups have been reported, for example, the two fluorine atoms in CF_2Br–$CHBrCl$.[11a] The Sn–CH_2–Ph protons of $PhCMe_2CH_2Sn(CH_2Ph)MeX$ (X = Cl, I, or Ph) are non-equivalent as are the $PhCMe_2CH_2$ protons.[11b]

$$P(CH_2OCOMe)_3 + [Et_3O]^+[BF_4]^- \xrightarrow{CH_2Cl_2} [PEt(CH_2OCOMe)_3]^+[BF_4]^- \xrightarrow{NaOH} PEt(CH_2OCOMe)_2 \quad (1)$$

$$PMe(CH_2OCOMe)_2 + MeOSO_2F \xrightarrow{CH_2Cl_2} [PMe_2(CH_2OCOMe)_2]^+[OSO_2F]^- \xrightarrow{NaOH} PMe_2(CH_2OCOMe) \quad (2)$$

$$P(CH_2OH)_3 + RX \longrightarrow [PR(CH_2OH)_3]^+X^- \xrightarrow{MeCOCl} [PR(CH_2OCOMe)_3]^+X^- \xrightarrow{NaOH} PR(CH_2OCOMe)_2 \quad (3)$$

$$PR'_2H \xrightarrow{HCHO} [PR'_2(CH_2OH)_2]^+Cl^- \xrightarrow[(ii)\ NaOH]{(i)\ MeCOCl} PR'_2CH_2(OCOMe) \quad (4)$$

(RX = MeI or EtBr; R′ = Ph or Bu^t)

Palladium(II) *and Platinum*(II) *Complexes.*—The complexes *cis*- or *trans*-$[MX_2L_2]$ {M = Pd or Pt; X = Cl, Br, or I; L = $P(CH_2OCOMe)_3$, $PMe(CH_2OCOMe)_2$, $PEt(CH_2OCOMe)_2$, $PMe_2(CH_2OCOMe)$, $PBu^t_2(CH_2OCOMe)$, $PPh_2(CH_2OCOMe)$, or $P(CH_2OH)_3$} were prepared by the addition of a phosphine (2 molar equivalents) to either sodium chloropalladite in methanol or potassium chloroplatinite in water–ethanol. Heating *cis*-$[PtCl_2L_2]$ {L = $PMe(CH_2OCOMe)_2$ or $PPh_2(CH_2OCOMe)$} in ethanol containing hydrochloric acid at reflux during 8 h gave *cis*-$[PtCl_2L'_2]$ {L′ = $PMe(CH_2OH)_2$ or $PPh_2(CH_2OH)$}. Ethyl acetate was detected in the solution at the end of the reaction. *cis*-$[PdCl_2\{PMe(CH_2OH)_2\}_2]$ was prepared in a similar manner from *trans*-$[PdCl_2\{PMe(CH_2OCOMe)_2\}_2]$.

Complexes of $PBu^t_2(CH_2OH)$ could not be obtained in this way from *trans*-$[MCl_2\{PBu^t_2(CH_2OCOMe)\}_2]$ (M = Pd or Pt) even after 20 h at reflux. Presumably the bulky t-butyl groups prevent attack by H^+ and EtOH on the carbonyl group of the phosphines.

The palladium(II) and platinum(II) complexes of ligands with $-CH_2OCOMe$ substituents have physical and general chemical properties similar to those of complexes of dimethylphenylphosphine and trimethylphosphine.[12,13] Both types of complex are soluble

TABLE 1

^1H N.m.r. data [a] for some tertiary phosphines of the type $PR_n(CH_2OCOMe)_{3-n}$, ($n = 0$, 1, or 2; R = Me, Et, Bu^t, or Ph) and $P(CH_2OH)_3$

Phosphine	Solvent	P–CH_2–O τ	P–CH_2–O $\lvert^2J_{PH}\rvert$ (Hz)	COMe τ	Other resonances	Assignment
$P(CH_2OCOMe)_3$	$CDCl_3$	5·38d(2)	5·4	7·82(3)		
$P(CH_2OCOMe)_3$	CH_3CN	5·50d	5·3	Obscured		
$PMe(CH_2OCOMe)_2$	$CDCl_3$	5·57(2), 5·67(2) [b]	6·5, 5·5	7·94(6)	8·90d(3)	P–Me, $\lvert^2J_{PH}\rvert$ = 3·5 Hz
$PMe(CH_2OCOMe)_2$	CH_3CN	5·63, 5·73 [c]	6·5, 5·5	Obscured	Obscured	
$PMe(CH_2OCOMe)_2$	C_6H_6	5·59(2), 5·69(2) [b]	6·5, 5·5	7·98(6)	8·93d(3)	P–Me, $\lvert^2J_{PH}\rvert$ = 3·5 Hz
$PEt(CH_2OCOMe)_2$	$CDCl_3$	5·54(2), 5·65(2) [b,c]	6·3, 5·4	7·95(6)	8·42m(2) 8·95m(2)	P–CH_2CH_3 P–CH_2CH_3
$PPh_2(CH_2OCOMe)$	$CDCl_3$	5·23d(2)	5·6	8·14(3)	2·20—2·90m(10)	Phenyl protons
$PBu^t_2(CH_2OCOMe)$	C_6H_6	5·42d(2)	3·1	8·11(3)	8·76d(18)	P–Bu^t, $\lvert^3J_{PH}\rvert$ = 10·9 Hz
$P(CH_2OH)_3$	CH_3CN	5·88d(2)	5·0		6·52(1)	O–H
$PMe_2(CH_2OCOMe)$	C_6H_6	5·88(2)	7·1	8·20(3)	9·08(6)	P–Me

[a] Recorded at *ca.* 30° and 100 MHz. All resonances are singlets unless indicated otherwise; d = 1 : 1 doublet; m = complex multiplet. Relative intensities are given in parentheses. τ Values ±0·02. *J* Values ±0·5 Hz. [b] Resonance due to P–CH_2–O protons appears as an ABX pattern (X = ^{31}P), $^2J_{PH}$ = 12·8 Hz. [c] $\lvert^2J_{HH}\rvert$ = 12·9 Hz.

[10] W. McFarlane, *Chem. Comm.*, 1968, 229.

[11] (*a*) K. Mislow and M. Raban, *Topics Stereochem.*, 1967, **1**, 1; (*b*) D. V. Stynes and A. L. Allred, *J. Amer. Chem. Soc.*, 1971, **93**, 2666; see also G. J. D. Peddle and G. Redl, *J. Amer. Chem. Soc.*, 1970, **92**, 365.

[12] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

[13] D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc.* (*A*), 1969, 2134.

in acetone and chlorinated solvents (the palladium compounds are also soluble in benzene) and are only sparingly soluble in cold alcohols. The dichloro-complexes are readily converted into the dibromo- and di-iodo-species by simple anionic displacement.

The complexes of $P(CH_2OH)_3$ and $PMe(CH_2OH)_2$ are insoluble in chlorinated solvents but very soluble in alcohols, acetone, and water. However, *cis*-$[PtCl_2\{PPh_2(CH_2OH)\}_2]$ is soluble in dichloromethane, chloroform, and hot alcohols and is sparingly soluble in cold alcohols or water. Hence two $-CH_2OH$ substituents per phosphine are necessary to make these complexes soluble in water. *cis*-$[PdCl_2\{P(CH_2OH)_3\}_2]$ slowly decomposes in aqueous solution and palladium metal is deposited.

Infrared Spectra.—There is a strong band in the i.r. spectrum of all the complexes except those of $P(CH_2OH)_3$, $PMe(CH_2OH)_2$, and $PPh_2(CH_2OH)$ at *ca.* 1745 cm^{-1}. This is assigned to the carbonyl group(s) of the ligands. Metal–chlorine stretching frequencies could not always be assigned unambiguously because there are several bands other than those due to ν(M–Cl) between 380 and 230 cm^{-1}. For example, there is a very strong band at 367 cm^{-1} in the spectrum of *trans*-$[PdCl_2\{PEt(CH_2OCOMe)_2\}_2]$ which is much weaker in the spectrum of the corresponding dibromide. However, there are no other differences between the spectra of these complexes. Thus ν(Pd–Br) could not be assigned and the assignment of the band at 367 cm^{-1} to ν(Pd–Cl) must be tentative.

^1H N.M.R. Spectra (*see Tables* 2 *and* 3).—(a) *Acetoxymethylphosphine complexes.* The stereochemistries of these complexes are generally established by the ^1H n.m.r. spectra. Thus, the t-butyl resonances of $[MCl_2\{PBu^t_2(CH_2OCOMe)\}_2]$ (M = Pd or Pt) are triplets, indicating *trans*-structures with $|^2J(PP)| \gg |^3J(PH) + {}^5J(PH)|$.[14] The *P*-methyl and *P*-ethyl parts of the spectra of other complexes similarly indicate the stereochemistries.

The resonance due to the $CO\mathit{CH}_3$ protons in the spectrum of every complex (found in the range τ 7·83—8·46) is a singlet, as in the free phosphines, and there is no ^{31}P–^1H coupling. In the palladium complexes, the P–CH_2–O protons also give rise to a singlet, or an AB pattern (two doublets), but there is again no indication of ^{31}P–^1H coupling, although it occurs in the free phosphines. The platinum complexes are similar except that the spectra are complicated by coupling to the ^{195}Pt, which occurs in a natural abundance of 33·3%. Where there is an ABX pattern, the coupling constant $|^3J(PtH)|$ to each proton is of course different. The situation is thus very different from that found in, say, *trans*-$[MX_2(PMe_2Ph)_2]$ (M = Pd or Pt; X = halogen) where ' virtual coupling ' occurs.[12,15]

The non-observance of phosphorus–hydrogen coupling could be due to phosphine exchange. This is, however, unlikely, because coupling to platinum seems unaffected. Also the addition of either $P(CH_2OCOMe)_3$ or $[Pd_2Cl_4(PBu^n_3)_2]$ to a solution of $[PdCl_2\{P(CH_2OCOMe)_3\}_2]$ does not affect the P–CH_2–O resonance. The explanation will be discussed further below.

The spectra occasionally have other *unusual* properties. The spectrum of $[PdCl_2\{PPh_2(CH_2OCOMe)\}_2]$ in deuteriochloroform solution has two pairs of peaks, the components of each pair being of different intensities, assigned to the P–CH_2–O and the C–O–CH_3 protons. The relative intensities of the members of a pair are solvent-dependent. Thus, addition of $[^2H_4]$methanol to a solution of $[PdCl_2\{PPh_2(CH_2OCOMe)\}_2]$ in deuteriochloroform caused the peaks at τ 4·78 and 8·38 to increase in intensity relative to those at τ 4·67 and 8·19. Deuteriobenzene had the opposite effect. These observations suggest that $[PdCl_2\{PPh_2(CH_2OCOMe)\}_2]$ exists in solution as a mixture of isomers. However, the corresponding dibromide exists entirely as the *cis*-isomer and the di-iodide entirely as the *trans*.

A further peculiarity is that $|^3J(PtH)|$ for the protons P–CH_2–O of *cis*-$[PtCl_2\{PPh_2(CH_2OCOMe)\}_2]$ is both concentration- and temperature-dependent. At about 70°, or in dilute solution, $|^3J(PtH)|$ is *ca.* 11·5 Hz, whereas at −10°, or in more concentrated solution, it falls to 9·8 Hz. We are unable to account for these observations.

TABLE 2

^1H N.m.r. and i.r. data [a] for complexes of the type *cis*- or *trans*-$[PdX_2PR_{3-n}Q_n]$, (X = Cl, Br, or I; *n* = 3, 2, or 1; R = Me, Et, Ph, or Bu^t; Q = CH_2OCOMe or CH_2OH)

Compound	τ(P–CH_2–O)	ν(C=O) cm^{-1}	ν(Pd–Cl) cm^{-1}
trans-$[PdCl_2\{P(CH_2OCOMe)_3\}_2]$	5·12(6)	1735	*b*
trans-$[PdBr_2\{P(CH_2OCOMe)_3\}_2]$	5·02(6)	1755	
trans-$[PdI_2\{P(CH_2OCOMe)_3\}_2]$	4·86(6)	1760	
trans-$[PdCl_2\{PMe(CH_2OCOMe)_2\}_2]$	5·18(2), 5·24(2) [c]	1748	367
trans-$[PdBr_2\{PMe(CH_2OCOMe)_2\}_2]$	5·11(2), 5·17(2) [c]	1749	
trans-$[PdI_2\{PMe(CH_2OCOMe)_2\}_2]$	4·94(2), 4·99(2) [c]	1747	
trans-$[PdCl_2\{PEt(CH_2OCOMe)_2\}_2]$	5·15(2), 5·20(2) [c]	1753	*b*
trans-$[PdBr_2\{PEt(CH_2OCOMe)_2\}_2]$	5·10(4)	1748	
trans-$[PdI_2\{PEt(CH_2OCOMe)_2\}_2]$	4·94(4)	1745	
trans-$[PdCl_2\{PPh_2(CH_2OCOMe)\}_2]$	4·67(2)	1749	356
cis-$[PdCl_2\{PPh_2(CH_2OCOMe)\}_2]$	4·77(2)	1749	
trans-$[PdBr_2\{PPh_2(CH_2OCOMe)\}_2]$	4·58(2)	1748	*d*
trans-$[PdI_2\{PPh_2(CH_2OCOMe)\}_2]$	4·44(2)	1748	
trans-$[PdCl_2\{PBu^t_2(CH_2OCOMe)\}_2$	5·16(2)	1738	354
cis-$[PdCl_2\{PMe_2(CH_2OCOMe)\}]$	5·12(2)		
trans-$[PdCl_2\{PMe_2(CH_2OCOMe)\}_2]$	5·26(2)		
cis-$[PdCl_2\{P(CH_2OH)_3\}_2]$ [e]	5·50(6)		
cis-$[PdCl_2\{PMe(CH_2OH)_2\}_2]$ [e]	5·54(2), 5·68(2) [e,f]		

[a] N.m.r. spectra were recorded at *ca.* 30° and 100 MHz in $CDCl_3$ solution unless indicated otherwise. Relative intensities are given in parentheses. τ Values ±0·02. I.R. data are from $CHCl_3$ solution [ν(C=O)] and Nujol mulls [ν(Pd–Cl)]. [b] Other bands in this region prevent the assignment of ν(Pd–Cl). [c] Resonance due to P–CH_2–O group appears as an AB quartet, $|^2J(H_AH_B)| = 13·5$ Hz. [d] ν(Pd–Br) Appears at 283 cm^{-1}. [e] Spectrum recorded in CD_3OD solution. [f] $|^2J(HH)| = 13·0$ Hz.

[14] B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 2976.

[15] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

TABLE 3

^{1}H N.m.r. and i.r. data [a] for complexes of the type *cis*- or *trans*-$[PtX_2(PR_{3-n}Q_n)_2]$ (X = Cl, Br, or I; n = 3, 2, or 1; R = Me, Et, Bu^t, or Ph; Q = CH_2OCOMe or CH_2OH)

Compound	^{1}H N.m.r. P–CH_2–O τ	$\lvert^3J(PtH)\rvert$	I.r./cm^{-1} ν(C=O)	ν(Pt–Cl)
cis-$[PtCl_2\{P(CH_2OCOMe)_3\}_2]$	5·01(6)	19·8	1760	*b*
cis-$[PtBr_2\{P(CH_2OCOMe)_3\}_2]$	4·98(6)	20·0	1755	
trans-$[PtBr_2\{P(CH_2OCOMe)_3\}_2]$	5·02(6)	13·7	1755	
trans-$[PtI_2\{P(CH_2OCOMe)_3\}_2]$	4·86(6)	15·3	1750	
cis-$[PtCl_2\{PMe(CH_2OCOMe)_2\}_2]$	5·12(4)	16·5	1751	*b*
cis-$[PtBr_2\{PMe(CH_2OCOMe)_2\}_2]$	5·07(4)	16·5	1749	
trans-$[PtBr_2\{PMe(CH_2OCOMe)_2\}_2]$	5·13(4)	7·5 [c]	1749	
trans-$[PtI_2\{PMe(CH_2OCOMe)_2\}_2]$	4·95(2), 5·04(2) [d]	13·9, 8·7	1747	
cis-$[PtCl_2\{PEt(CH_2OCOMe)_2\}_2]$	5·10—5·20(4) [e]		1752	314, 290
trans-$[PtBr_2\{PEt(CH_2OCOMe)_2\}_2]$	5·07(2), 5·13(2) [d,f]	14·8, 5·1	1748	
trans-$[PtI_2\{PEt(CH_2OCOMe)_2\}_2]$	4·85(4)	11·3	1748	
cis-$[PtCl_2\{PPh_2(CH_2OCOMe)\}_2]$	4·84(2)	9·8	1749	322, 293
cis-$[PtBr_2\{PPh_2(CH_2OCOMe)\}_2]$	4·82(2)	10·5	1750	
cis-$[PtI_2\{PPh_2(CH_2OCOMe)\}_2]$	4·86(2)	11·0	1749	
trans-$[PtI_2\{PPh_2(CH_2OCOMe)\}_2]$	4·46(2)	6·5	1749	
trans-$[PtCl_2\{PBu^t_2(CH_2OCOMe)\}_2]$	5·16(2)	23·1	1738	344vs
cis-$PtCl_2\{P(CH_2OH)_3\}_2$ [h]	5·50(6)	23·4		
cis-$[PtCl_2\{PMe(CH_2OH)_2\}_2]$ [h]	5·61(2), 5·69(2) [d,g]	22·9, 18·3		
cis-$[PtCl_2\{PPh_2(CH_2OH)\}_2]$	5·47d(2) [i]	23·5		

[a] N.m.r. spectra were recorded at *ca.* 30° and 100 MHz in $CDCl_3$ solution unless indicated otherwise. Relative intensities are given in parentheses. τ Values ±0·02. J Values ±0·5 Hz. I.r. data are from $CHCl_3$ solution [ν(C=O)] and Nujol mulls [ν(Pt–Cl)]. [b] Other bands in this region prevent the assignment of ν(Pt–Cl). [c] Approximate value (±2 Hz) only since the ^{195}Pt satellites appear as shoulders on the resonances due to the *cis*-isomer. [d] Resonance due to P–CH_2–O protons appears as an AB quartet ($\lvert^2J(HH)\rvert$ = 13·4 Hz), 33·3% of which is further split by coupling to the ^{195}Pt nucleus to give an ABX pattern. [e] Complex multiplet. [f] $\lvert^2J(HH)\rvert$ = 13·9 Hz. [g] $\lvert^2J(HH)\rvert$ = 13·5 Hz. [h] Spectrum recorded in CD_3OD. [i] $\lvert^3J(HH)\rvert$ = 7·5 Hz.

TABLE 4

Values of $\lvert^2J(PH)\rvert$ (in Hz) for some tertiary phosphines, phosphonium cations and metal complexes

L	free L	$[LMe]^+$	*cis*- or *trans*-$[MX_2L_2]$	Ref.
PMe_2Ph	3·0	14·5	10—12	12, 21
PMe_3	2·5	15·0	10—12	13, 21
PBu^tMe_2	3·0	13·6	9—11	14
$PBu^t_2(CH_2CMe{=}CH_2)$	3·9	13·7	10—11	22
$P(CH_2OCOMe)_3$	5·4	4·0	Not resolved	This work
$PMe(CH_2OCOMe)_2$	6·5, 5·5 (P–CH_2–O)	4·6	Not resolved	This work

(b) *Hydroxymethylphosphine complexes.* The stereochemistry of these complexes in solution is often difficult to determine because they also do not exhibit P–CH_2–O coupling. The complexes $[MCl_2\{PMe(CH_2OH)_2\}_2]$ (M = Pd or Pt) are certainly *cis* since the methyl resonances are doublets; complexes $[MCl_2P\{(CH_2OH)_3\}_2]$ (M = Pd or Pt) are also probably *cis* in deuteriomethanol, especially as the solvent is polar.

The non-observance of ^{31}P–^{1}H coupling in the spectra of hydroxymethyl complexes is surprising because it is confined to the P–CH_2–O protons. Where the phosphines contain also methyl or t-butyl groups, the CH_3 protons exhibit the usual ' virtual coupling ' patterns with $\lvert^2J(PH) + {}^4J(PH)\rvert$ or $\lvert^3J(PH) + {}^5J(PH)\rvert$ of values similar to those observed in complexes of other methyl-, ethyl-, or *t*-butyl-phosphines.[12-14] Hence, in our *trans*-complexes, $\lvert^2J(PH) + {}^4J(PH)\rvert$ must be close to zero and therefore $^2J(PH)$ and $^4J(PH)$ probably have opposite signs. In the *cis*-complexes, the coupling constants are probably individually also close to zero.

In the phosphonium salts $[PR(CH_2OH)_3]X$ (R = CH_2OH, Me, or Et; X = Cl, Br, or I) and $[PBu^t_2(CH_2OH)_2]Cl$, $\lvert^2J(PH)\rvert$ can be observed directly and for the P–CH_2–O protons falls in the range 1·5—2·5 Hz. The values observed in the free phosphines, their phosphonium salts, and their complexes are compared with those of $\lvert^2J(PH)\rvert$ for derivatives of several other phosphines in Table 4.[12-14,16] Because alone the magnitude of $\lvert^2J(PH) + {}^4J(PH)\rvert$ in complexes is normally observable, $\lvert^2J(PH)\rvert$ has been estimated assuming that $^4J(PH)$ is 2—4 Hz for *trans*-compounds [17] and *ca.* 1 Hz for *cis*-compounds.[18]

From Table 4 it is evident that the magnitude of $\lvert^2J(PH)\rvert$ changes in a regular pattern as the phosphine is quaternised and co-ordinated. This coupling constant has been shown to be positive for free dimethylphenylphosphine, but it becomes negative upon quatern-

[16] W. McFarlane, *Chem. Comm.*, 1967, 58.
[17] A. Pidcock, *Chem. Comm.*, 1968, 92.
[18] R. J. Goodfellow, *Chem. Comm.*, 1967, 114.

isation [16] and co-ordination.[19] The changes are thus *ca.* −17 Hz in the former case and *ca.* −14 Hz in the latter. Evidently ^2J(PH) is the more negative the greater the positive charge on the phosphorus. Trimethyl-, t-butyldimethyl-, and di-t-butyl(2-methylallyl)-phosphines apparently fall into the same pattern.

Because $|^2J(PH)|$ for the P-CH_2-O protons of the phosphonium salts of the acetoxymethylphosphines does not exceed 5 Hz (and is probably negative), it is likely that $|^2J(PH)|$ in the complexes is very close to zero. $|^4J(PH)|$ is, in any case, likely to be small, so that the non-observation of ^{31}P–^1H coupling arises from the accident that $|^2J(PH) + {}^4J(PH)|$ is not large enough to give rise to the conventional ' virtual coupling ' patterns. Why groups like OH and OCOMe, which are electron withdrawing, have this effect on $|^2J(PH)|$ is not at all obvious.

Table 3 shows that $|^3J(PtH)|$ in our *trans*-complexes falls in the range 5—23 Hz, and in the range 9—23 Hz for the *cis*-complexes. No general trends are discernable. These values are lower than those observed for the Pt^{II} complexes with dimethylphenylphosphine and with trimethylphosphine. Again, the reason is not evident.

Rhodium(I) *and Rhodium*(III) *Complexes.*—The complex $[\{RhCl(CO)_2\}_2]$ reacts with 4 molar equivalents of ligand, L, to give the complexes *trans*-$[RhCl(CO)L_2]$ {L = $P(CH_2OCOMe)_3$, $PMe(CH_2OCOMe)_2$, $PEt(CH_2OCOMe)_2$, $PPh_2(CH_2OCOMe)$, $PBu^t_2(CH_2OCOMe)$, or $P(CH_2OH)_3$}. ^1H N.m.r. and i.r. data for these complexes are given in Table 5. The tertiary phosphines in the complexes $[RhCl(CO)\{PR(CH_2OCOMe)_2\}_2]$ (R = Me or Et) are undergoing exchange in benzene solution at room temperature, because the ^1H n.m.r. spectra are very simple. When R = Me the P-CH_3 groups give rise to a singlet. For R = Et one triplet and one quartet are observed for the P-CH_2-CH_3 and P-CH_2 protons respectively. On cooling the solutions to 0° the expected ' virtually coupled ' patterns are observed, *i.e.* a triplet when R = Me and a quintet and a multiplet when R = Et. The ligands of *trans*-$[RhCl(CO)\{PBu^t_2(CH_2OCOMe)\}_2]$ are not exchanging at room temperature since the P-Bu^t resonance is a triplet. The pattern is unchanged at +60°.

Attempts to prepare *trans*-$[RhCl(CO)\{PMe(CH_2OH)_2\}_2]$ by hydrolysis of the corresponding acetate with concentrated hydrochloric acid–methanol at room temperatures gave instead a dark red water-soluble crystalline solid which analysed for $[Rh_2Cl_4\{PMe(CH_2OH)_2\}_4(CO)_n]$ (n = 1 or 2). The i.r. spectrum shows a strong band at 1740 cm^{-1} so that, compared with the starting material, the terminal carbonyl [ν(C≡O) at 1974 cm^{-1}] and the acetate carbonyl [ν(C=O) at 1735 cm^{-1}] have disappeared. The ^1H n.m.r. spectrum in $[^2H_4]$methanol shows only resonances due to the $PMe(CH_2OH)_2$ ligand. These results suggest a structure with bridging carbonyl ligand(s), either $[\{PMe(CH_2OH)_2\}_2ClRhCl_2CORhCl\{PMe(CH_2OH)_2\}_2]$ for n = 1 or $[\{PMe(CH_2OH)_2\}_2Cl_2Rh(CO)_2RhCl_2\ \{PMe(CH_2OH)_2\}_2]$ for n = 2. The compound is being investigated further.

Treatment of rhodium trichloride trihydrate with 3 molar equivalents of ligand, L, in boiling ethanol gives *mer*-$[RhCl_3L_3]$ {L = $P(CH_2OCOMe)_3$, $PMe(CH_2OCOMe)_2$, $PEt(CH_2OCOMe)_2$, or $PPh_2(CH_2OCOMe)$}. However, $P(CH_2OH)_3$ reacts with rhodium trichloride to give the *fac*-isomer. The relevant n.m.r. and i.r. data for these complexes are also given in Table 5, and analytical data in Table 7.

Catalytic Properties of the Complexes.—Platinum(II) compounds have been used as hydrosilylation and hydrogenation catalysts. However, *cis*-$[PtCl_2\{P(CH_2OCOMe)_3\}_2]$ does not react with triethylsilane in benzene. Addition of oct-1-ene did not promote any reaction. The complex does not catalyse the hydrogenation of cyclohexene. The palladium(II) complexes decompose in ethanol and water and were not tested as catalysts.

Rhodium complexes of the new phosphines were more effective as catalysts. The complex *trans*-$[RhCl(CO)\{P(CH_2OCOMe)_3\}_2]$ does not catalyse the isomerisation or the hydrogenation of oct-1-ene in benzene. However, 2 molar equivalents of sodium borohydride caused the colour of the solution to change from yellow to red-brown, after which slow isomerisation and hydrogenation took place at comparable rates. Similar results were obtained from solutions in 1 : 1 benzene–ethanol.

A mixture of $[\{RhCl(cyclohexene)_2\}_2]$ with 2 molar equivalents of $P(CH_2OH)_3$ in ethanol rapidly catalyses the hydrogenation and isomerisation of oct-1-ene. When the olefin has been entirely hydrogenated or isomerised to oct-2-ene, rhodium metal begins to precipitate. Colloidal rhodium may be the catalyst in this system, but after precipitation of the rhodium, dihydrogen uptake is very slow.

In acetone solution, the above mixture of rhodium complex and hydroxymethylphosphine quickly generates rhodium metal, which catalyses the slow hydrogenation and isomerisation of oct-1-ene. In water the mixture is not capable of catalysing the hydrogenation of even maleic acid. We conclude that these complexes show no obviously useful catalytic properties.

EXPERIMENTAL

All reactions were carried out under an atmosphere of pure, dry dinitrogen with reagent grade solvents. Tris(acetoxymethyl)phosphine, tris(hydroxymethyl)phosphine,[9] and di-t-butylphosphine,[20] were prepared by the reported methods. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer (Nujol mulls 250—4000 cm^{-1}) and a Grubb-Parsons DM4 spectrophotometer (Nujol mulls 200—500 cm^{-1}). ^1H N.m.r. spectra were recorded on a

[19] A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Comm.*, 1966, 89.
[20] W. Hoffmann and P. Schellenbeck, *Chem. Ber.*, 1966, **99**, 1134.
[21] K. Alford, D.Phil. Thesis, University of Sussex, 1971.
[22] J. Chatt, W. Hussain, and G. J. Leigh, unpublished observations.

TABLE 5

^{1}H N.m.r. and i.r. data [a] for complexes of the type *trans*-[RhCl(CO(L$_2$] and *mer*-[RhCl$_3$L$_3$] [L = P(CH$_2$OCOMe)$_3$, PMe(CH$_2$OCOMe)$_2$, PEt(CH$_2$OCOMe)$_2$, PPh$_2$(CH$_2$OCOMe), PBu$^t_2$(CH$_2$OCOMe), or P(CH$_2$OH)$_3$]

L	τ(P–*CH*$_2$–O)	τ(CO–*Me*)	Other resonances	Assignment	ν(C=O) cm^{-1}	ν(C≡O) cm^{-1}
trans-[RhCl(CO)L$_2$]						
P(CH$_2$OCOMe)$_3$ [b]	4·98(2)	8·19(3)			1755 [b]	1985
PMe(CH$_2$OCOMe)$_2$ [c]	5·37(4)	8·38(6)	8·71dt(3)	P–Me (J* 6·7, |^3J(RhH| = 1·0)	1751 [b]	1974
PEt(CH$_2$OCOMe)$_2$ [c]	5·23(4)	8·28(6)	8·16m(2)	P–*CH*$_2$–CH$_3$	1750 [c]	1965
			8·87q(3)	P–CH$_2$–*CH*$_3$ (J** 18·0, |^3J(HH)| = 7·6)		
PPh$_2$(CH$_2$OCOMe)	4·64(2)	8·12(3)	2·00—2·70m (10)	Phenyl protons	1745	1979
PBu$^t_2$(CH$_2$OCOMe)	5·06(2)	7 90(3)	8·50t(18)	P–*Bu*^{t} (J** 13·4)	1739	1954
P(CH$_2$OH)$_3$ [g]	5·62(2)		5·22(1)	O–*H*		1950 [f]
mer-[RhCl$_3$L$_3$]						
P(CH$_2$OCOMe)$_2$	4·72(4)	7·83 } (8)			1760	
	4·80(2)	7·85 }				
PMe(CH$_2$OCOMe)$_2$	4·92(8)	7·86 } (18)	8·18d } (9)	P–*Me* (J* 10·8)	1750	
	5·08(4)	7·88 }	8·26t }	P–*Me* (J* 7·5)		
PEt(CH$_2$OCOMe)$_2$	4·80(4) [d]	7·88(18)	7·65m(6)	P–*CH*$_2$–CH$_3$	1735 [e]	
	4·90(4)		8·65m(9)	P–CH$_2$–*CH*$_3$		
	4·98(4)					
PPh$_2$(CH$_2$OCOMe)	3·96(4)	8·45 } (9)	2·24—3·20m	Phenyl protons	1741 [e]	
	4·82(2)	8·50 }	(30)			

[a] N.m.r. spectra were recorded *ca.* 30° and 100 MHz in CDCl$_3$ solution unless indicated otherwise. All resonances are singlets unless indicated otherwise; d = 1 : 1 doublet, dt = two 1 : 2 : 1 triplets, m = complex multiplet, q = 1 : 4 : 6 : 4 : 1 quintet, t = 1 : 2 : 1 triplet. Relative intensities are given in parentheses. τ Values ±0·02. J Values ±0·5 Hz. J* = |^2J(PH) + ^4J(PH)|; J** = |^3J(PH) + ^5J(PH)|. I.r. data are from CHCl$_3$ solution. [b] Recorded in benzene solution. [c] Recorded in C$_7$D$_8$ at 0°. [d] Resonance due to P–*CH*$_2$–O protons appears as an AB quartet (|^2J(HH)| = 13·9 Hz). [e] Nujol mull. [f] KBr disc. [g] Recorded in CD$_3$OD solution.

TABLE 6

Analytical, melting point, and molecular weight data for some complexes of the type *cis*- or *trans*-[MX$_2$L$_2$], [M = Pd or Pt; X = Cl, Br, or I; L = P(CH$_2$OCO Me)$_3$, PMe(CH$_2$OCOMe)$_2$, PEt(CH$_2$OCOMe)$_2$, PPh$_2$(CH$_2$OCOMe), PBu$^t_2$(CH$_2$OCOMe), P(CH$_2$OH)$_3$, PMe(CH$_2$OH)$_2$, or PPh$_2$(CH$_2$OH)]

M	X	L	Configuration	% Yield	Colour	Analytical data [a] C	H	Halogen	M [a,b]	M.p./°C
Pd	Cl	P(CH$_2$OCOMe)$_3$	*trans*	80	Yellow	31·8(31·9)	4·5(4·5)	11·0(10·5)	700(678)	161—163
Pd	Br	P(CH$_2$OCOMe)$_3$	*trans*	60	Orange	28·5(28·2)	4·0(3·9)		830(767)	179—181
Pd	I	P(CH$_2$OCOMe)$_3$	*trans*	90	Red	25·3(25·1)	3·5(3·5)	29·5(29·5)	809(861)	170—172
Pt	Cl	P(CH$_2$OCOMe)$_3$	*cis*	82	White	28·6(28·2)	4·2(4·0)	9·2(9·3)		135—138
Pt	Br	P(CH$_2$OCOMe)$_3$	*trans*	64	Yellow	25·3(25·3)	3·6(3·5)	18·6(18·7)		174—175
Pt	I	P(CH$_2$OCOMe)$_3$	*trans*	93	Yellow	23·5(22·8)	3·3(3·2)	26·6(26·7)	993(949)	167—169
Pd	Cl	PMe(CH$_2$OCOMe)$_2$	*trans*	84	Yellow	30·0(29·9)	4·7(4·7)	13·0(12·6)	599(561)	137—139
Pd	Br	PMe(CH$_2$OCOMe)$_2$	*trans*	90	Orange	26·2(25·9)	4·3(4·0)	24·6(24·6)	676(650)	104—106
Pd	I	PMe(CH$_2$OCOMe)$_2$	*trans*	61	Red	22·6(22·6)	3·6(3·5)	33·6(34·1)	758(745)	78—81
Pt	Cl	PMe(CH$_2$OCOMe)$_2$	*cis*	91	White	26·1(25·9)	4·1(4·0)	11·3(10·9)	711(650)	157—159
Pt	Br	PMe(CH$_2$OCOMe)$_2$	*cis*	88	White	22·5(22·7)	3·5(3·6)	21·9(21·6)	799(739)	113—114
Pt	I	PMe(CH$_2$OCOMe)$_2$	*trans*	95	Yellow	20·3(20·2)	3·2(3·2)	30·3(30·5)	854(833)	93—95
Pd	Cl	PEt(CH$_2$OCOMe)$_2$	*trans*	92	Yellow	32·9(32·6)	5·3(5·1)		602(590)	100—104
Pd	Br	PEt(CH$_2$OCOMe)$_2$	*trans*	70	Orange	28·3(28·3)	4·6(4·5)	24·1(23·6)	700(679)	94—95
Pd	I	PEt(CH$_2$OCOMe)$_2$	*trans*	83	Red	24·9(25·0)	3·9(4·0)	32·6(32·9)	780(773)	83—85
Pt	Cl	PEt(CH$_2$OCOMe)$_2$	*cis*	94	White	28·3(28·3)	4·6(4·5)	11·0(10·5)		140—142
Pt	Br	PEt(CH$_2$OCOMe)$_2$	*trans*	71	Yellow	25·4(25·1)	4·1(3·9)	21·2(20·8)	841(767)	88—90
Pt	I	PEt(CH$_2$OCOMe)$_2$	*trans*	65	Yellow	22·7(22·3)	3·6(3·5)	29·1(29·5)	897(861)	91—93
Pd	Cl	PPh$_2$(CH$_2$OCOMe)	*trans*	88	Yellow	52·0(51·9)	4·6(4·4)	10·3(10·2)	705(694)	193—197 [c]
Pd	Br	PPh$_2$(CH$_2$OCOMe)	*trans*	92	Yellow	46·1(46·0)	4·0(3·9)		813(783)	216—218
Pd	I	PPh$_2$(CH$_2$OCOMe)	*trans*	90	Orange	40·9(41·1)	3·5(3·4)	28·5(28·9)	909(877)	210—212
Pt	Cl	PPh$_2$(CH$_2$OCOMe)	*cis*	76	White	46·5(46·1)	4·0(3·9)	9·5(9·1)	809(783)	214—217
Pt	Br	PPh$_2$(CH$_2$OCOMe)	*cis*	95	White	41·4(41·4)	3·6(3·9)	18·2(18·3)	952(871)	225—228
Pt	I	PPh$_2$(CH$_2$OCOMe)	*cis*	90	Yellow	37·0(37·3)	3·2(3·1)	25·8(26·3)	1005(965)	206—209
Pd	Cl	PBu$^t_2$(CH$_2$OCOMe)	*trans*	87	Yellow	43·3(43·1)	7·6(7·6)			222—235 [c]
Pt	Cl	PBu$^t_2$(CH$_2$OCOMe)	*trans*	91	Yellow	37·6(37·6)	6·7(6·6)	10·8(10·1)	707(702)	250—255 [c]
Pd	Cl	P(CH$_2$OH)$_3$	*cis*	60	Yellow	17·2(16·9)	4·4(4·3)	16·9(16·7)		146—149
Pt	Cl	P(CH$_2$OH)$_3$	*cis*	56	White	14·2(14·0)	3·7(3·5)			122—126
Pd	Cl	PMe(CH$_2$OH)$_2$	*cis*	79	White	18·4(18·3)	4·6(4·6)	18·3(18·0)		150—160 [c]
Pt	Cl	PMe(CH$_2$OH)$_2$	*cis*	84	White	15·0(15·0)	3·8(3·8)	14·5(14·7)		197—200
Pt	Cl	PPh$_2$(CH$_2$OH)	*cis*	60	White	44·9(44·7)	3·8(3·8)	10·3(10·1)		205—208 [c]
Pd	Cl	PMe$_2$(CH$_2$OCOMe)	*cis*	51	Cream	27·3(27·0)	5·2(5·0)			133—135

[a] Theoretical values given in parentheses. [b] Measured in 1,2-dichloroethane solution. [c] Melt with decomposition.

Varian HA 100 spectrometer at *ca.* 30° with tetramethylsilane used to provide the field–frequency lock. M.p.s were determined on an Electrothermal apparatus. Molecular weights were determined on a Hitachi–Perkin-Elmer 115 apparatus in 1,2-dichloroethane solution (43°).

Preparation of Tertiary Phosphines.—Bis(acetoxymethyl)ethylphosphine. (a) To a solution of tris(hydroxymethyl)phosphine (27 g) in methanol (25 ml), bromoethane (30 g) was added and the mixture boiled for 6 h. Excess of bromoethane and the solvent were removed by vacuum distillation to leave a white solid. The solid was suspended in glacial acetic acid (20 ml) and acetyl chloride (66 ml) was added dropwise during 2 h. The mixture was boiled for 2 h and then the excess of acetyl chloride and acetic acid were removed by vacuum distillation. To the residual oil, benzene (50 ml) and water (50 ml) were added and the mixture was neutralised to phenolphthalein with 2N-sodium hydroxide solution. The organic layer was removed and the water layer extracted with benzene (3 × 50 ml). The combined extracts were dried over sodium sulphate and the benzene removed by vacuum distillation. The residue was distilled *in vacuo* to yield *bis(acetoxymethyl)ethylphosphine* (27 g; 60%), b.p. 74—78°, 1 mmHg.

(b) Triethyloxonium tetrafluoroborate (19·4 g) dissolved in dichloromethane (60 ml) was added to tris(acetoxymethyl)phosphine (18·9 g) in dichloromethane (40 ml). The mixture was stirred at room temperature for 12 h and the solvent was removed by vacuum distillation to leave an off-white oil. The oil was taken up in water (10 ml) and benzene (50 ml) and neutralised to phenolphthalein with 2N-sodium hydroxide solution. The organic layer was removed and the water layer extracted with benzene (3 × 50 ml). The combined extracts were dried over sodium sulphate and the benzene removed by vacuum distillation. The residue was distilled *in vacuo* to yield bis(acetoxymethyl)ethylphosphine (9·5 g; 61%).

(Acetoxymethyl)dimethylphosphine was prepared in a manner similar to (b) from bis(acetoxymethyl)methylphosphine and methylfluorosulphinate (yield 10%; b.p. 66—67°, 22 mmHg).

Bis(acetoxymethyl)methylphosphine was prepared as in (a) from tris(hydroxymethyl)phosphine, iodomethane, and acetyl chloride (yield 60%; b.p. 74—76°, 2 mmHg).

(Acetoxymethyl)di-t-butylphosphine. A mixture of di-t-butylphosphine (9·8 g), aqueous formaldehyde (11 ml of *w/v* solution), concentrated hydrochloric acid (7·5 ml) and methanol (15 ml) was boiled for 6 h. Removal of the solvent by vacuum distillation left a white solid which was treated with acetic acid (45 ml) and acetyl chloride (45 ml) for 6 h. The acetic acid and the excess of acetyl chloride were removed by vacuum distillation. To the residual oil, benzene (50 ml) and water (50 ml) were added and the mixture was neutralised to phenolphthalein using 2N-sodium hydroxide solution. The organic layer was removed and the water layer extracted with benzene (3 × 50 ml). The combined extracts were dried over sodium sulphate and the benzene removed by vacuum distillation. The residue was distilled *in vacuo* to yield *(acetoxymethyl)di-t-butylphosphine* (10·5 g; 60%, b.p. 57—58°, 0·1 mmHg).

(Acetoxymethyl)diphenylphosphine was prepared in a similar manner from diphenylphosphine. The phosphine was not distilled but the pale yellow oil obtained when the benzene had been removed was filtered and used for further reactions. The ^{1}H n.m.r. spectrum of this oil in deuteriochloroform showed only resonances due to Ph, $-CH_2-O$, and $-COCH_3$ groups. Yield 9 g; 67%.

Preparation of Palladium(II) *and Platinum*(II) *complexes* (*see Table* 6).—Trans-*Bis{bis(acetoxymethyl)methylphosphine}dichloropalladium*(II). To a solution of sodium chloropalladite (1·07 g) in methanol (20 ml) was added bis(acetoxymethyl)methylphosphine (1·46 g, 2 mol) in methanol (5 ml). After 1 h the *solid* was filtered off and recrystallised from dichloromethane–methanol as prisms (1·70 g).

The following five compounds were prepared in a similar manner from sodium chloropalladite and the appropriate phosphine: trans-*dichlorobis{tris(acetoxymethyl)phosphine}palladium*(II); trans-*bis{(acetoxymethyl)diphenylphosphine}dichloropalladium*(II); trans-*bis{bis(acetoxymethyl)ethylphosphine}dichloropalladium*(II); trans-*bis{(acetoxymethyl)di-t-butylphosphine}dichloropalladium*(II); cis-*dichlorobis{tris(hydroxymethyl)phosphine}palladium*(II).

trans-*Bis{bis(acetoxymethyl)methylphosphine}dibromopalladium*(II). A mixture of *trans*-bis{bis(acetoxymethyl)-

TABLE 7

Analytical, melting point, and molecular weight data for complexes of the type *trans*-[RhCl(CO)L_2], *mer*-[$RhCl_3L_3$] and *fac*-[$RhCl_3\{P(CH_2OH)_3\}_3$] {L = $P(CH_2OCOMe)_3$, $PMe(CH_2OCOMe)_2$, $PEt(CH_2OCOMe)_2$, $PPh_2(CH_2OCOMe)$, $PBu^t_2(CH_2OCOMe)$ or $P(CH_2OH)_3$}

L	% Yield	Colour	Analytical data [a] C	H	Cl	*M* [a,b]	M.p./°C
trans-[RhlC(CO)L_2]							
$P(CH_2OCOMe)_3$	68	Yellow	34·1(34·2)	4·7(4·5)	5·3(5·3)	689(667)	115—116
$PMe(CH_2OCOMe)_2$	80	Yellow	32·6(32·7)	5·0(4·8)	6·9(6·4)		89—90
$PEt(CH_2OCOMe)_2$	60	Yellow	35·4(35·3)	5·4(5·2)	6·4(6·1)		68—70
$PPh_2(CH_2OCOMe)$	70	Yellow	54·5(54·5)	4·6(4·4)	5·1(5·2)	661(683)	126—128
$PBu^t_2(CH_2OCOMe)$	84	Yellow	46·2(45·8)	7·9(7·7)	6·1(5·9)	609(603)	192—194
$P(CH_2OH)_3$	55	Yellow	20·8(20·3)	4·5(4·4)	8·9(8·6)		
mer-[$RhCl_3L_3$]							
$P(CH_2OCOMe)_3$	55	Orange	33·8(33·8)	4·8(4·7)	11·5(11·1)	1066(960)	148—153
$PMe(CH_2OCOMe)_2$	66	Orange	32·2(32·1)	5·1(5·0)	13·7(13·6)	814(786)	127—129
$PEt(CH_2OCOMe)_2$	52	Orange	34·8(34·8)	5·5(5·5)	13·1(12·9)	814(828)	109—111
$PPh_2(CH_2OCOMe)$	53	Orange	54·6(54·9)	4·8(4·6)			165—171
fac-[$RhCl_3\{P(CH_2OH)_3\}_3$]	50	Yellow	18·8(18·6)	4·8(4·7)	18·2(18·3)		155—165(d.)

[a] Theoretical values given in parentheses. [b] In 1,2-dichloroethane solution.

methylphosphine}dichloropalladium(II) (0·22 g) and lithium bromide (9·60 g, 13 mol) was stirred in acetone (50 ml) for 2 h. The solvent was removed at 12 mmHg and the required product isolated with dichloromethane. It formed *prisms* from dichloromethane–methanol (0·23 g).

The following fifteen compounds were prepared in a similar manner from the appropriate dichloro-complex and an excess of lithium bromide or sodium iodide: trans-*dibromobis{tris(acetoxymethyl)phosphine}palladium*(II); trans-*di-iodobis{tris(acetoxymethyl)phosphine}palladium*(II); trans-*dibromobis{tris(acetoxymethyl)phosphine}platinum*(II); trans-*di-iodobis{tris(acetoxymethyl)phosphine}platinum*(II); trans-*bis{bis(acetoxymethyl)methylphosphine}di-iodopalladium*(II); cis-*bis{bis(acetoxymethyl)methylphosphine}dibromoplatinum*(II); trans-*bis{bis(acetoxymethyl)methylphosphine}-di-iodoplatinum*(II); trans-*bis{bis(acetoxymethyl)ethylphosphine}dibromopalladium*(II); trans-*bis{bis(acetoxymethyl)-ethylphosphine}di-iodopalladium*(II); trans-*bis{bis(acetoxymethyl)ethylphosphine}dibromoplatinum*(II); trans-*bis{bis-(acetoxymethyl)ethylphosphine}di-iodoplatinum*(II); trans-*bis{(acetoxymethyl)diphenylphosphine}dibromopalladium*(II); trans-*bis{(acetoxymethyl)diphenylphosphine}di-iodopalladium*(II); cis-*bis{(acetoxymethyl)diphenylphosphine}dibromoplatinum*(II); cis-*bis{(acetoxymethyl)diphenylphosphine}di-iodoplatinum*(II).

cis-*Bis{bis(acetoxymethyl)methylphosphine}dichloroplatinum*(II). To a solution of potassium chloroplatinite (1·78 g) in water (25 ml) was added bis(acetoxymethyl)methylphosphine (1·73 g, 3·4 mol) in methanol (10 ml). The mixture was stirred for 2 h and the resultant solid filtered off. Recrystallisation from dichloromethane–methanol gave the desired *product* as prisms (2·55 g).

The following five compounds were prepared in a similar manner from potassium chloroplatinite and the appropriate phosphine: cis-*dichlorobis{tris(acetoxymethyl)phosphine}-platinum*(II); cis-*bis{bis(acetoxymethyl)ethylphosphine}di-chloroplatinum*(II); cis-*bis{(acetoxymethyl)diphenylphosphine}dichloroplatinum*(II); trans-*bis{(acetoxymethyl)di-t-butylphosphine}dichloroplatinum*(II); cis-*dichlorobis{tris-(hydroxymethyl)phosphine}platinum*(II).

cis-*Bis{bis(hydroxymethyl)methylphosphine}dichloroplatinum*(II). *cis*-Bis{bis(acetoxymethyl)methylphosphine}-dichloroplatinum(II) (0·16 g) was boiled in ethanol (25 ml) containing concentrated hydrochloric acid (0·5 ml) for 6 h. The solvent was removed by vacuum distillation and the residue recrystallised from isopropyl alcohol to give the product as *prisms* (0·10 g).

The following compounds were prepared from the corresponding acetoxymethyl complexes in a similar manner: cis-*bis{bis(hydroxymethyl)methylphosphine}dichloropalladium*(II), (recrystallised from methanol); cis-*dichlorobis-{(hydroxymethyl)diphenylphosphine}platinum*(II), (recrystallised from dichloromethane–methanol).

Preparation of Rhodium Complexes.—trans-*Carbonylchlorobis{tris(acetoxymethyl)phosphine}rhodium*(I). Tetracarbonyldi-μ-chloro-dirhodium(I) (0·44 g) was dissolved in benzene (15 ml) and tris(acetoxymethyl)phosphine (1·12 g, 2·0 mol) in benzene (10 ml) added. A brown solution and yellow precipitate formed immediately. The yellow *crystals* (1·0 g) were filtered off, washed with hexane and dried at 10^{-3} mmHg.

In a similar fashion were synthesised trans-*bis{bis(acetoxymethyl)methylphosphine}carbonylchlororhodium*(I); trans-*bis{bis(acetoxymethyl)ethylphosphine}carbonylchlororhodium*-(I); trans-*bis{(acetoxymethyl)diphenylphosphine)}carbonylchlororhodium*(I); trans-*bis(acetoxymethyldi-t-butylphosphine)carbonylchlororhodium*(I).

trans-*Carbonylchlorobis{tris(hydroxymethyl)phosphine}-rhodium*(I).—Tris(hydroxymethyl)phosphine (0·33 g, 2·0 mol) was placed in a dinitrogen-filled flask together with di-μ-chloro-tetracarbonyldirhodium(I) (0·26 g). Dioxygen-free methanol (38 ml) was added and the mixture stirred for 0·5 h. The solution turned yellow, and was taken to dryness at 0·5 mmHg to yield a yellow solid, which was recovered from isopropyl alcohol as yellow *crystals* (0·31 g). These were washed with isopropyl alcohol and diethyl ether and dried at 10^{-3} mmHg.

mer-*Trichlorotris{tris(acetoxymethyl)phosphine}rhodium*-(III). Tris(acetoxymethyl)phosphine (2·07 g, 3·0 mol) was added to rhodium(III) chloride trihydrate (0·69 g) dissolved in methanol (40 ml). There was an immediate reaction and a yellow solid separated. The mixture was stirred during 18 h at 25°, after which time a yellow solid in a red-orange solution was present. The yellow *crystals* (1·40 g) were filtered off, washed with methanol and diethyl ether to which a small amount of the phosphine had been added, and dried at 10^{-3} mmHg.

Similarly were prepared mer-*tris{bis(acetoxymethyl)-methylphosphine}trichlororhodium*(III); mer-*tris{bis(acetoxymethyl)ethylphosphine}trichlororhodium*(III); mer-*tris{(acetoxymethyl)diphenylphosphine{trichlororhodium*(III).

fac-*Trichlorotris{tris(hydroxymethyl)phosphine}rhodium*-(III). Cyclo-octene (2·8 ml, *ca.* 10 mol) was added to rhodium(III) chloride trihydrate (0·51 g) in methanol (15 ml). Tris(hydroxymethyl)phosphine (0·78 g, 3·2 mol) was added and the mixture set aside for 0·75 h. A precipitate formed and slowly redissolved. The mixture was heated at reflux for 0·75 h and then cooled to 0° for three months. The yellow crystals (0·58 g) were filtered off, washed with methanol and diethyl ether, and dried in air.

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