Transition-metal Complexes Containing Phosphorus Ligands. Part XIII.[1] Dialkyl Phenylphosphonite and Alkyl Diphenylphosphinite Derivatives of Silver, Gold, and the Platinum Metals

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Reactions between metal halides, metal carbonyl halides, or metal olefin halides and dialkyl phenylphosphonite, $P(OR)_2Ph$, or alkyl diphenylphosphinite, $P(OR)Ph_2$, ligands (R = Me, Et) performed in polar or aromatic solvents afford a general route to an extensive series of uncharged complexes. Compounds isolated in this way include $RuCl_2(CO)_2L_2$, $RuCl_2(CO)L_3$, $OsCl_2(CO)_2L_2$, $IrHCl_2L_3$, *cis*-$PdCl_2L_2$, *cis*-$PtCl_2L_2$ *cis*-$PtBr_2L_2$ [L = $P(OR)Ph_2$, $P(OR)_2Ph$; R = Me, Et], $AgCl[P(OEt)Ph_2]_2$, $AgClL'$ [L' = $P(OR)_2Ph$, $P(OMe)Ph_2$], and $AuCl[P(OEt)Ph_2]$. ^1H and ^{31}P N.m.r. spectra are presented and discussed.

ALTHOUGH there has been widespread interest in the study of transition-metal complexes containing tertiary phosphine [2,3] and, to a lesser extent, tertiary phosphite [3,4] ligands, no systematic investigation of the co-ordinating ability of the closely related phosphonites, $P(OR)_2R'$, and phosphinites, $P(OR)R_2'$, toward class 'b' transition-metals has been described. We have recently commenced such an investigation and have reported[1] the synthesis and structure of complex cations of gold, silver, and the platinum metals containing some ligands of this type. We now report the synthesis and stereochemistry of some related uncharged complexes.

The new complexes were prepared either by direct reaction of the appropriate ligand with metal halides or metal carbonyl halides (*e.g.* AgCl, $[RuCl_2(CO)_2]_n$, $[OsCl_2(CO)_3]_2$), or by substitution of the ligand for olefin in metal olefin halide complexes (*e.g.* $PdCl_2(C_8H_{12})$, $PtCl_2(C_8H_{12})$, $[IrHCl_2(C_8H_{12})]_2$, $AuCl(C_8H_{14})$; C_8H_{12} = cyclo-octa-1,5-diene, C_8H_{14} = cyclo-octene). Some of

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[1] Part XII, D. A. Couch and S. D. Robinson, *Inorg. Chem.*, 1974, **13**, 456.

[2] G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.

[3] S. D. Robinson, *M.T.P. International Rev. of Science, Inorg. Chem. Series* 1, 1972, **6**, 121.

[4] D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta*, in the press, and references therein.

the products were obtained in low yield, because of their high solubility in most potential solvents and their tendency to form oils when subjected to recrystallisation procedures. This problem was particularly marked with the silver and gold complexes. These latter species are also light-sensitive. Several attempts to prepare rhodium derivatives from $[\mathrm{RhCl(C_7H_8)}]_2$ in dichloromethane or other solvents were unsuccessful; the products obtained were very labile and could not be obtained in a pure state.

All the complexes reported were fully characterised by elemental analysis, i.r., ^{1}H n.m.r., and, where appropriate, ^{31}P n.m.r. spectra. ^{1}H N.m.r. spectra of the $\mathrm{P(OEt)_2Ph}$ complexes are complicated and, where capable of interpretation, confirm the presence of intrinsically asymmetric methylene groups.

Ruthenium and Osmium Complexes.—$\mathrm{MCl_2(CO)_2L_2}$. These white, air-stable, crystalline complexes each show two strong carbonyl absorptions in their i.r. spectra (Table 2) typical of *cis*-dicarbonyl species. The far-i.r. spectrum of each complex shows two bands attributable to *sym* and *asym* vibrations of a *cis*-$\mathrm{MCl_2}$ group. Finally the ^{1}H n.m.r. spectra of the $\mathrm{P(OMe)Ph_2}$ and $\mathrm{P(OMe)_2Ph}$ complexes each contain a triplet [virtual coupling, $|^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})|$ *ca.* 12 Hz] arising from the methyl protons, thus indicating[5] that the two ^{31}P nuclei are strongly coupled and probably occupy mutually *trans* co-ordination sites. Stereochemistry (I) (M = Ru, Os) is the only one consistent with these observations. The methyl protons in each of the ethyl diphenylphosphinite and diethyl phenylphosphonite complexes generate a simple triplet pattern, $^3J(\mathrm{HH'})$ *ca.* 7 Hz. However, the methylene protons display more interesting spectroscopic behaviour. Those in the ethyl diphenylphosphinite complexes $\mathrm{MCl_2(CO)_2[P(OEt)Ph_2]_2}$ are intrinsically equivalent (Figure 1) and give rise to a temperature and field independent pattern comprising nine equally spaced sharp lines. This pattern may be analysed as the expected quartet of triplets if we make the entirely feasible assumption that $^3J(\mathrm{HH'})$ and $|^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})|$ are coincidently equal to *ca.* 7·0 Hz. In contrast the methylene groups in the diethyl phenylphosphonite derivatives show intrinsic asymmetry (Figure 2); therefore an AB type n.m.r. pattern arising from mutual coupling of *gem*-methylene protons is expected. Each member of the AB pattern should be further split by couplings to the methyl protons and the ^{31}P nuclei. The observed spectrum (90 MHz, $\mathrm{CDCl_3}$) for $\mathrm{OsCl_2(CO)_2[P(OEt)_2Ph]_2}$ contains a symmetrical group of 19 equally spaced lines attributable to the methylene protons. At 220 MHz this pattern resolves into an AX pattern,* with further fine structure due to ^{31}P nuclei and methyl protons.

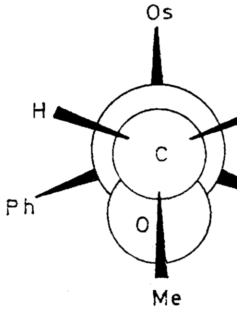


FIGURE 1

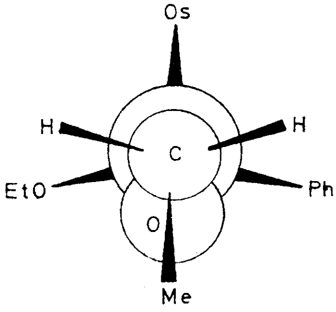
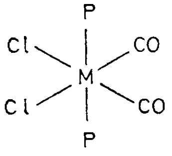
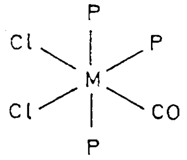


FIGURE 2

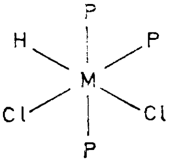
Using the chemical shift separation ($\Delta\nu$ = *ca.* 23 Hz at 90 MHz) deduced from the AX pattern and employing values of $^3J(\mathrm{HH'})$ and $|^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})|$ similar to those derived from the spectra of $\mathrm{OsCl_2(CO)_2[P(OEt)_2Ph]_2}$ and $\mathrm{OsCl_2(CO)_2[P(OEt)Ph_2]_2}$ respectively, the overall patterns observed for the methylene protons of $\mathrm{OsCl_2(CO)_2[P(OEt)_2Ph]_2}$ at 90 MHz may be simulated. The observed spectra are therefore entirely consistent with the structure and stereochemistry proposed for the osmium complexes. However, the spin systems present in these compounds are complex and the interpretation given may be an oversimplification of the situation. The analogous ruthenium complexes give essentially similar though less clearly resolved spectra.



(I)



(II)



(III)

$\mathrm{RuCl_2(CO)L_3}$. The phosphonite and phosphinite ligands, L, each react with $[\mathrm{RuCl_2(CO)_2}]_n$ in boiling alcohol to afford a mixture of the mono- and di-carbonyl species $\mathrm{RuCl_2(CO)L_3}$ and $\mathrm{RuCl_2(CO)_2L_2}$ respectively, which, on treatment with carbon monoxide in boiling benzene, is converted into the corresponding dicarbonyl, *cis*-$\mathrm{RuCl_2(CO)_2L_2}$, in good yield. One monocarbonyl complex, $\mathrm{RuCl_2(CO)[P(OEt)Ph_2]_3}$ was isolated in a pure state. Its i.r. spectrum shows a strong carbonyl absorption (1986 cm^{-1}) and two ν(M–Cl) bands attributable to a *cis*-$\mathrm{RuCl_2}$ group. The ^{1}H n.m.r. spectrum contains two triplets, relative intensities 2 : 1, attributable to the methyl protons of the $\mathrm{P(OEt)Ph_2}$ ligands. On the basis of this evidence the complex is assigned stereochemistry (II) (M = Ru).

Iridium Complexes.—$\mathrm{IrHCl_2L_3}$. These white, air-stable, crystalline solids show in their i.r. spectra a sharp band at *ca.* 2180—2200 cm^{-1} (Table 2) consistent with the presence of a hydride ligand *trans* to halide in an octahedral iridium(III) complex.[6] The high-field ^{1}H n.m.r. spectra of these compounds each exhibit a hydride resonance (Table 2), comprising an apparent quartet [L = $\mathrm{P(OR)Ph_2}$] or a resolved doublet of triplets [L = $\mathrm{P(OR)_2Ph}$], and are indicative of three phosphorus nuclei *cis* to the hydride ligand. Stereochemistry (III) (M = Ir) is assigned to the complexes

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* The pattern is not fully first order, both components retain slight asymmetry.

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

[6] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231 and references therein.

Table 1

Analytical and m.p. data of phosphonite and phosphinite complexes

Compound	C(%)[a]	H(%)[a]	M.p. (t/°C)
$RuCl_2(CO)_2[P(OEt)Ph_2]_2$	52·25 (52·35)	4·5 (4·4)	218—221
$RuCl_2(CO)_2[P(OMe)Ph_2]_2$	51·25 (50·9)	4·2 (4·0)	180—185
$RuCl_2(CO)_2[P(OEt)_2Ph]_2$	42·5 (42·3)	4·95 (4·85)	99—100
$RuCl_2(CO)_2[P(OMe)_2Ph]_2$	38·45 (38·05)	3·95 (3·9)	138—140
$RuCl_2(CO)[P(OEt)Ph_2]_3$	57·3 (57·75)	5·1 (5·1)	209—210
$OsCl_2(CO)_2[P(OEt)Ph_2]_2$	46·2 (46·35)	3·95 (3·9)	250—252
$OsCl_2(CO)_2[P(OMe)Ph_2]_2$	45·05 (44·85)	3·4 (3·5)	207—208
$OsCl_2(CO)_2[P(OEt)_2Ph]_2$	37·4 (37·05)	4·25 (4·25)	144—145
$OsCl_2(CO)_2[P(OMe)_2Ph]_2$	33·1 (32·9)	3·3 (3·4)	164—165
$IrHCl_2[P(OEt)Ph_2]_3$	52·75 (52·8)	4·85 (4·85)	Decomp. >100
$IrHCl_2[P(OMe)Ph_2]_3$	52·05 (51·3)	4·6 (4·45)	118—121
$IrHCl_2[P(OEt)_2Ph]_3$	41·85 (41·95)	5·45 (5·4)	133—134 (Decomp. 122°)
$IrHCl_2[P(OMe)_2Ph]_3$			Decomp. >80
$PdCl_2[P(OEt)Ph_2]_2$	52·4 (52·7)	4·8 (4·7)	208—211 (Decomp.)
$PdCl_2[P(OEt)_2Ph]_2$	41·8 (41·85)	5·25 (5·3)	169—170
$PdCl_2[P(OMe)Ph_2]_2, \frac{1}{2}CH_2Cl_2$	48·35 (48·8)	4·1 (4·2)	Decomp. >184
$PdCl_2[P(OMe)_2Ph]_2$	36·9 (37·15)	4·15 (4·3)	Decomp. >160
$PtCl_2[P(OEt)Ph_2]_2$	46·35 (46·3)	4·25 (4·15)	221—222
$PtCl_2[P(OEt)_2Ph]_2$[b]	36·45 (36·25)	4·5 (4·25)	171
$PtCl_2[P(OMe)Ph_2]_2, \frac{1}{2}CH_2Cl_2$[c]	43·2 (42·95)	3·5 (3·7)	215
$PtCl_2[P(OMe)_2Ph]_2$	32·15 (31·7)	3·65 (3·65)	181—183
$PtBr_2[P(OEt)Ph_2]_2$			232—233
$PtBr_2[P(OEt)_2Ph]_2$	32·35 (31·95)	3·95 (4·0)	163—164
$PtBr_2[P(OMe)Ph_2]_2$	40·1 (39·65)	3·35 (3·3)	202—204
$PtBr_2[P(OMe)_2Ph]_2$			Decomp. >160°
$\{AgCl[P(OEt)Ph_2]_2\}_2$	55·95 (55·7)	5·2 (5·0)	115—118
$AgCl[P(OMe)Ph_2]$	44·15 (43·4)	3·75 (3·65)	
$AgCl[P(OEt)_2Ph]$	34·95 (35·15)	4·45 (4·45)	
$AgCl[P(OMe)_2Ph]$	30·15 (30·65)	3·55 (3·55)	
$AuCl[P(OEt)Ph_2]$	36·75 (36·35)	3·3 (3·25)	140—141

[a] Required figures given in parentheses. [b] Cl = 10·9 (10·7) %. [c] Cl = 14·95 (14·4) %.

Table 2

^{1}H N.m.r.[a] and i.r.[b] data of phosphonite and phosphinite complexes

Complex	τ(Me)	$\tau(CH_2)$	τ(Ph)[e]	τ(MH)	$J(HH^1)$	N[c]	^1J(PH)	ν(MH)	ν(CO)	ν(MCl)
$RuCl_2(CO)_2[P(OEt)Ph_2]_2$	8·76 (t)	5·99(m)[d]	1·91—2·71 (m)		6·75	ca. 7·0			2065s, 2005s	304m, 280m
$RuCl_2(CO)_2]P(OMe)Ph_2]_2$	6·26 (t, vc)		1·93—2·69 (m)			12·3			2067s 2020s	310m 305sh 280m
$RuCl_2(CO)_2[P(OEt)_2Ph]_2$	8·64 (t)	5·63 (m)[d]	2·13—2·60 (m)		7·05	ca. 7·0			2070s 2015s	310m 282m
$RuCl_2(CO)_2[P(OMe)_2Ph]_2$	6·08 (t, vc)		2·25—2·72 (m)			11·75			2070s 2000s	318m 283m
$RuCl_2(CO)[P(OEt)Ph_2]_3$	9·03 (t)[f] 9·13 (t)[g]	6·33—6·84 (m)	1·93—2·84 (m)		6·45 7·05				1986s 1939w	305m 280sh 260m
$OsCl_2(CO)_2[P(OEt)Ph_2]_2$	8·75 (t)	5·96 (m)[d]	1·96—2·75 (m)		7·05	ca. 7·0			2055s 1974s	307m 280m
$OsCl_2(CO)_2[P(OMe)Ph_2]_2$	6·27 (t, vc)		1·98—2·59 (m)			12·3			2048s 1981s 1965w	309m 280m
$OsCl_2(CO)_2[P(OEt)_2Ph]_2$	8·64 (t)	5·78 (m)[d]	2·22—2·69 (m)		7·05	ca. 7·0			2045s 1968s, 1955s	317m, 292m, 280m
$OsCl_2(CO)_2[P(OMe)_2Ph]_2$	6·11 (t, vc)		2·13—2·71 (m)			11·5			2050s, 1971s, 1958s	317m, 285m
$IrHCl_2[P(OEt)Ph_2]_3$	9·15 (t)[f] 8·84 (t)[g]	5·8—6·8 (m)[d]	2·13—2·93 (m)	28·41 (q)	7·1 7·1		14·7	2200w		
$IrHCl_2[P(OMe)Ph_2]_3$	6·78 (t, vc)[f] 6·61 (d)[g]		2·16—2·90 (m)	28·64 (q)		10·6 12·4[h]	ca. 15·0	2200m		
$IrHCl_2[P(OEt)_2Ph]_3$	8·76 (t)	5·58—6·49 (m)[d]	2·07—2·78 (m)	29·0 (d of t)	6·75		17·6 (d) 12·6 (t)	2185m		
$IrHCl_2[P(OMe)_2Ph]_3$	6·32 (t, vc)[f] 6·61 (d)[g]		2·15—2·88 (m)	28·8 (d of t)		12·4[h]	16·7 (d) 13·0 (t)	2200w		
$PdCl_2[P(OEt)Ph_2]_2$	9·01 (t)	6·29 (m)[d]	2·10—2·66 (m)		7·05	ca. 7·0				315m, 285m
$PdCl_2[P(OMe)Ph_2]_2, \frac{1}{2}CH_2Cl_2$[i]	6·66 (d, vc)		2·12—2·63 (m)			12·3				308m, 290m, 280m
$PdCl_2[P(OEt)_2Ph]_2$	8·65 (t)	5·54—6·09 (m)[d]	2·09—2·60 (m)		7·05	ca. 7·0				320m, 297 m,280sh
$PdCl_2[P(OMe)_2Ph]_2$	6·21 (d, vc)		2·13—2·60 (m)			12·9				310sh, 295m, 270m
$PtCl_2[P(OEt)Ph_2]_2$	8·99 (t)	6·24 (m)[d]	2·09—2·76 (m)		7·0	ca. 7·0				313m, 290m, 282sh
$PtCl_2[P(OMe)Ph_2]_2, \frac{1}{2}CH_2Cl_2$[i]	6·67 (d, vc)		2·07—2·70 (m)			12·5				316m, 291m, 285sh
$PtCl_2[P(OEt)_2Ph]_2$	8·69 (t)	5·87 (m)[d]	2·11—2·71 (m)		7·05	ca. 7·0				317m, 295m, 280sh
$PtCl_2[P(OMe)_2Ph]_2$	6·29 (d, vc)		2·13—2·63 (m)			12·3				315m, 290m, 285sh
$PtBr_2[P(OEt)Ph_2]_2$	9·00 (t)	6·27 (m)[d]	2·11—2·67 (m)		7·05	ca. 7·0				
$PtBr_2[P(OMe)Ph_2]_2$	6·70 (d, vc)		2·10—2·70 (m)			12·0				
$PtBr_2[P(OEt)_2Ph]_2$	8·68 (t)	5·90 (m)[d]	2·11—2·64 (m)		7·05	ca. 7·0				
$PtBr_2[P(OMe)_2Ph]_2$	6·33 (d, vc)		2·10—2·70 (m)							
$\{AgCl[P(OEt)Ph_2]_2\}_2$	8·82 (t)	6·00 (d of q)	2·18—2·78 (m)		7·05	9·4[h]				
$AgCl[[P(OMe)Ph_2]$	6·22 (d)		2·11—2·73 (m)			15·8[h]				
$AgCl[P(OEt)_2Ph]$	8·64 (t)	5·85 (qn)	2·05—2·56 (m)		7·05	7·0[h]				
$AgCl[P(OMe)_2Ph]$	6·29 (d)		2·17—2·81 (m)			13·2[h]				
$AuCl[P(OEt)Ph_2]$	8·60 (t)	5·84 (d of q)	2·14—2·67 (m)		7·05	9·4[h]				

[a] N.m.r. spectra recorded for solutions in deuteriochloroform and referenced to internal tetramethylsilane; d = doublet; t = triplet; q = quartet; qn = quintet; m = multiplet; vc = virtual coupling. Coupling constants ±0·2 Hz. [b] I.r. spectra recorded for Nujol mulls. [c] $N = |^3J\text{ (PH)} + {}^5J\text{ (PH)}|$. [d] See text for discussion of pattern. [e] Usually resolved into 2 multiplets ratio 2(m-protons): 3(o- and p-protons). [f] Resonance due to two equivalent ligands. [g] Resonance due to unique ligand. [h] These values are for ^3J(PH). [i] CH_2Cl_2, $\tau(CH_2) = 4{\cdot}71$.

$IrHCl_2L_3$ on the basis of the above evidence and is confirmed by the proton decoupled ^{31}P n.m.r. spectra (Table 3) each of which shows a doublet and a triplet [$^2J(PP')$ *ca.* 24 Hz] with relative intensities 2 : 1. Two ^1H n.m.r. resonances with relative intensities 2 : 1, observed for the methyl protons in these complexes, further confirm the proposed stereochemistry. The n.m.r. pattern arising from the methylene protons appears as a broad ill-resolved multiplet which cannot be fully analysed, but is not inconsistent with the proposed stereochemistry.

Palladium and Platinum Complexes.—MX_2L_2. These pale yellow ($M = Pd$; $X = Cl$) or white ($M = Pt$; $X = Cl$, Br) crystalline complexes each show a single ^{31}P n.m.r. resonance (Table 3) and thus exist as single isomers. The chloro derivatives MCl_2L_2 are identified as *cis* isomers on the basis of their far-i.r. spectra (Table 2) each of which shows two ν(M–Cl) bands attributable to a *cis*-MCl_2 group. Complexes containing $P(OMe)Ph_2$ or $P(OMe)_2Ph$ ligands are also assigned *cis* stereochemistry on the basis of their ^1H n.m.r. spectra (Table 2) each of which contains a virtual coupling doublet pattern, $|^3J(PH) + {}^5J(PH)|$ 12·5 Hz, indicative of a small $^2J(PP')$ coupling. The values of $|^3J(PH) + {}^5J(PH)|$ observed for these complexes agree well with those reported for the related trimethyl phosphite complexes *cis*-$PtX_2[P(OMe)_3]_2$.[7]

TABLE 3

^{31}P [a] N.m.r. data of phosphonite and phosphinite complexes

Complex	δ	$^2J(PP')$
$RuCl_2(CO)_2[P(OEt)Ph_2]_2$	−105·8 (s)	
$OsCl_2(CO)_2[P(OEt)Ph_2]_2$	−74·7 (s)	
$IrHCl_2[P(OEt)Ph_2]_3$	−84·8 (d)	17·9
	−67·7 (t)	
$IrHCl_2[P(OMe)Ph_2]_3$	−85·8 (d)	23·8
	−71·9 (t)	
$IrHCl_2[P(OEt)_2Ph]_3$	−102·8 (d)	23·8
	−85·3 (t)	
$IrHCl_2[P(OMe)_2Ph]_3$	−105·4 (d)	23·8
	−92·5 (t)	
$PdCl_2[P(OEt)_2Ph]_2$	−135·8 (s)	
$PtCl_2[P(OEt)_2Ph]_2$	−92·2 (s)	*b*
$PtBr_2[P(OEt)_2Ph]_2$	−92·2 (s)	*c*
$AgCl[P(OEt)Ph_2]_2$	−110·5 (s)	
$AgCl[P(OEt)_2Ph]$	−111·3 (s)	

[a] Spectra taken at 36·43 MHz in $CDCl_3$ solution and referenced to external H_3PO_4; all ^1H nuclei decoupled; $CDCl_3$ used to provide a ^2D field/frequency lock. [b] $^1J(PtP)$ 4817 Hz. [c] $^1J(PtP)$ 4770 Hz.

The methylene protons in the ethyl diphenylphosphinite complexes $MCl_2[P(OEt)Ph_2]_2$ ($M = Pd$, Pt) are equivalent and give rise to a single, field independent, complex n.m.r. pattern which appears to consist of a quartet of overlapping virtual coupling doublets with $^3J(HH') = |^3J(PH) + {}^5J(PH)|$. The methylene protons in the corresponding diethyl phenylphosphonite complexes $MCl_2[P(OEt)_2Ph]_2$ are intrinsically non-equivalent and give rise to a field dependent n.m.r. pattern. The basic AB pattern observed at 90 MHz is resolved at 220 MHz into an essentially AX pattern * each member of which shows coupling to the methyl protons and ^{31}P nuclei.

Silver and Gold Complexes.—$MClL_2$. Ethyl diphenylphosphinite reacts with silver chloride to afford the 1 : 2 complex $\{AgCl[P(OEt)Ph_2]_2\}_2$; this product was obtained even when a deficiency of ligand is employed.

MClL. The other phosphinite and phosphonite ligands afford 1 : 1 complexes AgClL which presumably contain linear two-co-ordinate silver(I). The very soluble, light-sensitive, white, crystalline complex $AuCl[P(OEt)Ph_2]$ was also isolated and characterised; however all attempts to prepare related gold complexes containing the other phosphinite or phosphonite ligands were unsuccessful.

EXPERIMENTAL

Platinum metal salts and phosphorus ligands were purchased from Johnson Matthey and Maybridge Chemical Co. respectively. All reactions were performed under nitrogen. Analyses were by the Microanalytical laboratory, University College, London.

N.m.r. spectra were taken using Bruker 90 MHz and Varian 220 MHz spectrometers. I.r. spectra were recorded on a Perkin-Elmer 457 grating spectrometer and calibrated against polystyrene film.

Dichlorodicarbonylbis(ethyl diphenylphosphinite)ruthenium.—Ruthenium trichloride trihydrate (0·45 g) was heated under reflux in 2-methoxyethanol (50 ml) for 24 h with a stream of carbon monoxide bubbling through the solution. The solution was cooled to room temperature, ethyl diphenylphosphinite (0·94 g) added dropwise, and the solution again heated under reflux for 5 min with a stream of carbon monoxide bubbling through it. The solution was cooled to −10 °C, when white crystals were formed. These were filtered off, washed with ethanol and hexane, and dried *in vacuo* to yield the required product as *white crystals*, 0·68 g (59%).

Dichlorodicarbonylbis(methyl diphenylphosphinite)ruthenium.—Ruthenium trichloride trihydrate (0·455 g) was heated under reflux in 2-methoxyethanol (50 ml) for 24 h with a stream of carbon monoxide bubbling through the solution. The solution was cooled to room temperature, methyl diphenylphosphinite (0·9 g) added dropwise, and the solution again heated under reflux for 10 min with a stream of carbon monoxide bubbling through it. The solution was cooled to room temperature, and 2-methoxyethanol removed on a rotary evaporator until crystallisation just commenced. Methanol (20 ml) was added, and the solution set aside to crystallise for 24 h. The white crystals formed were filtered off, washed with methanol and hexane, and dried *in vacuo* to yield the required product, 0·57 g (50%).

Similarly prepared as white crystals were *dichlorodicarbonylbis(diethyl phenylphosphonite)ruthenium* (25%), and *dichlorodicarbonylbis(dimethyl phenylphosphonite)ruthenium* (16%).

Dichlorocarbonyltris(ethyl diphenylphosphinite)ruthenium.—*catena*-Dichlorodicarbonylruthenium (0·09 g) was heated under reflux with ethyl diphenylphosphinite (0·5 ml) in ethanol (50 ml) for 45 min with a stream of carbon monoxide bubbling through the solution. During this time the yellow colour was practically discharged. The solution was cooled to room temperature, and then stored at −10 °C

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* See note p. 1310.

[7] M. J. Church and M. J. Mays, *J. Inorg. Nuclear Chem.*, 1971, **33**, 253.

overnight, when a mixture of pale yellow and white crystals were deposited. These were filtered off and shown to be a mixture of dichlorodicarbonylbis(ethyl diphenylphosphinite)ruthenium and dichlorocarbonyltris(ethyl diphenylphosphinite)ruthenium. The filtrate was evaporated to dryness on a steam-bath, and the resultant white solid washed with ethanol and hexane. Recrystallisation from dichloromethane–ethanol afforded *white crystals* of the required product, 0·09 g (25%).

Alternative Preparation of Dichlorodicarbonylbis(methyl diphenylphosphinite)ruthenium.—*catena*-Dichlorodicarbonylruthenium (0·228 g) and methyl diphenylphosphinite (0·52 g) were heated under reflux in methanol (20 ml) for 5 min. A yellow precipitate was formed on cooling to room temperature, and this was filtered off, washed with methanol and hexane, and dried *in vacuo*. This mixture of dichlorodicarbonylbis(methyl diphenylphosphinite)ruthenium and dichlorocarbonyltris(methyl diphenylphosphinite)ruthenium was heated under reflux in benzene (50 ml) for 5 h with a stream of carbon monoxide bubbling through the solution. The solvent was removed under reduced pressure, and the resulting white solid was recrystallised from dichloromethane–methanol to give *white crystals* of the required product, 0·135 g (31%).

Dichlorodicarbonylbis(ethyl diphenylphosphinite)osmium.—Di-μ-chloro-dichlorohexacarbonyldiosmium (0·345 g), dissolved in hot ethanol (20 ml), was added to a stirred boiling solution of ethyl diphenylphosphinite (0·5 g) in ethanol (10 ml), and heating continued for 10 min. The solution was cooled to room temperature, when white crystals precipitated. The precipitate was filtered off, washed with ethanol and hexane, and dried *in vacuo* to give *white crystals* of the required product, 0·40 g (51%).

Similarly prepared as white crystals were *dichlorodicarbonylbis(diethyl phenylphosphonite)osmium* (14%), and in methanol, *dichlorodicarbonylbis(methyl diphenylphosphinite)osmium* (43%), and *dichlorodicarbonylbis(dimethyl phenylphosphonite)osmium* (precipitated with hexane) (41%).

Dichlorohydridotris(ethyl diphenylphosphinite)iridium.—Di-μ-chloro-dichlorodihydrido(cyclo-octa-1,5-diene)diiridium (0·2 g) and ethyl diphenylphosphinite (0·38 g) were heated under reflux in benzene (5 ml) for 30 min. The solution was cooled to room temperature and filtered. Hexane was added slowly with shaking to produce a white solid, which was filtered off and washed thoroughly with hexane. Recrystallisation from dichloromethane–ethanol afforded the required product as *white crystals*, 0·28 g (54%).

Similarly prepared as white solids were *dichlorohydridotris(diethyl phenylphosphonite)iridium* (recrystallised from diethyl ether–hexane) (52%), *dichlorohydridotris(methyl diphenylphosphinite)iridium* (57%), and *dichlorohydridotris(dimethyl phenylphosphonite)iridium* (56%).

Dichlorobis(ethyl diphenylphosphinite)palladium.—Dichloro(cyclo-octa-1,5-diene)palladium (0·368 g) and ethyl diphenylphosphinite (0·6 ml) were stirred together vigorously in benzene (10 ml) at room temperature for 20 min. A white precipitate soon formed, and precipitation was completed by the addition of hexane (30 ml). The precipitate was filtered off, washed with ethanol and hexane, and recrystallised from dichloromethane–ethanol to yield *pale yellow crystals* of the required product, 0·61 g (97%).

Similarly prepared as pale yellow crystals were *dichlorobis(methyl diphenylphosphinite)palladium* (as a dichloromethane solvate) (38%), *dichlorobis(diethyl phenylphosphonite)palladium*, and *dichlorobis(dimethyl phenylphosphonite)palladium* (28%).

Dichlorobis(diethyl phenylphosphonite)platinum.—Dichloro(cyclo-octa-1,5-diene)platinum (1·0 g) and diethyl phenylphosphonite (1·2 g) were refluxed in benzene (20 ml) for 30 min. The solution was filtered hot, concentrated on a rotary evaporator, and hexane (50 ml) added to complete precipitation. The white solid obtained was filtered off, washed with ethanol and hexane, and recrystallised from dichloromethane–ethanol to give *white crystals* of the required product, 0·76 g (39%).

Similarly prepared as white crystals were *dichlorobis(methyl diphenylphosphinite)platinum* (as a dichloromethane solvate) (95), *dichlorobis(ethyl diphenylphosphinite)platinum* (90%), and *dichlorobis(dimethyl phenylphosphonite)platinum* (38%).

Dibromobis(ethyl diphenylphosphinite)platinum.—Dibromo(cyclo-octa-1,5-diene)platinum (0·87 g) and ethyl diphenylphosphinite (1 ml) were stirred together in benzene (10 ml) at room temperature for 1 h. A white precipitate formed, and precipitation was completed by the addition of hexane. The solid was filtered off, washed with ethanol and hexane, and dried *in vacuo* to yield the required product, 1·48 g (95%).

Similarly prepared as white solids were *dibromobis(methyl diphenylphosphinite)platinum* (53%), *dibromobis(diethyl phenylphosphonite)platinum* (68%), and *dibromobis(dimethyl phenylphosphonite)platinum* (45%).

Chlorobis(ethyl diphenylphosphinite)silver.—Freshly prepared silver chloride (0·65 g) and ethyl diphenylphosphinite (2 ml) were stirred in ethanol (20 ml) with warming, until a clear solution formed. The solution was filtered hot, concentrated on a rotary evaporator, diluted with n-hexane, then cooled to −10 °C. A white precipitate formed, which was filtered off, washed with ethanol and hexane, and dried *in vacuo* to yield *white crystals* of the required product (80%).

The following were similarly prepared using the appropriate ligands and alcoholic solvents: *chloro(methyl diphenylphosphinite)silver* as white crystals (80%), *chloro(diethyl phenylphosphonite)silver* as white crystals (32%), and *chloro(dimethyl phenylphosphonite)silver* (78%).

Chloro(ethyl diphonylphosphinite)gold.—Freshly prepared chloro(cyclo-octene)gold (0·31 g) and ethyl diphenylphosphinite (0·4 g) were shaken together under an atmosphere of nitrogen for 15 min in benzene (15 ml). The solution was filtered, then concentrated on a rotary evaporator until crystallisation commenced. Hexane (10 ml) was added, and the solution cooled to −10 °C. The resulting white crystals were filtered off, washed thoroughly with ethanol, and dried *in vacuo* to yield the required product, 0·2 g (48%).

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