Some Complexes of Platinum, Palladium, Rhodium, and Iridium formed from the Bulky Ligand (Phenylethynyl)di-t-butylphosphine †

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The new phosphine $PBu^t_2(C\equiv CPh)$ (L) gives complexes of the type $trans$-$[MX_2L_2]$ (M = Pd or Pt, X = Cl or I) which exist as conformers due to restricted rotation around the phosphorus–metal bonds. The complexes are very resistant to nucleophilic attack but $trans$-$[PtCl_2L_2]$ can be protonated, $e.g.$, in CF_3CO_2H, $[PtCl_2L\{PBu^t_2(CH=CPh)\}]^+$ forms reversibly and with dry hydrogen chloride $[PtCl_2\{PBu^t_2[CH=C(Cl)Ph]\}_2]$ is obtained. The complexes cis-$[PtMe_2L_2]$ and $trans$-$[PtCl(Me)L_2]$ are prepared by displacing cyclo-octa-1,5-diene (cod) from $[PtMe_2(cod)]$, $etc.$, but with 2 mol of L $[PtCl_2(cod)]$ readily gives $[PtCl_2(cod)L]$ in which only one of the cod double bonds is co-ordinated. The complexes $trans$-$[MCl(CO)L_2]$ (M = Rh or Ir) have also been prepared and the iridium complex converted into $[IrHCl_2(CO)L_2]$ with HCl. With $trans$-$[MCl(CO)L_2]$ one rotamer is much preferred over the other two. Treatment of H_2IrCl_6 with L gives five-co-ordinate $[IrHCl_2L_2]$ which appears to be trigonal bipyramidal, whereas $RhCl_3$ gives $[RhHCl_2L_2]$ which is square pyramidal. Treatment of $trans$-$[MCl(CO)L_2]$ (M = Rh or Ir) with sodium propan-2-olate in propan-2-ol gives the chelate complexes $[M(CO)\{(PBu^t_2[CH=C(O)Ph]\}L]$.

With sodium methoxide in methanol both acetylenic bonds are attacked giving $[Ir(CO)\{PBu^t_2[CH=C(O)Ph]\}\{PBu^t_2[CH=C(OMe)Ph]\}]$. Infrared, ^1H, ^{31}P, and some ^{13}C n.m.r. data are given.

TRANSITION-METAL COMPLEXES with tertiary di-t-butyl-phosphines, PBu^t_2R (R = alkyl or aryl), frequently show unusual chemistry and n.m.r. phenomena including low co-ordination numbers,[1,2] unusual valency states,[3] stable multihydrides,[4] metallation reactions,[5] very large chelate rings,[6] or rotamers caused by restricted rotation about phosphorus–metal bonds.[7] It therefore was of interest to study ligands of the type $PBu^t_2(C\equiv CR)$ for two main reasons. (i) There is a very large difference in the steric requirements of the t-butyl and the linear acetylenic group: one would therefore expect unusually large energy barriers to rotation about the phosphorus–metal bonds. Some of the chemical phenomena, $e.g.$ metallation and large-ring formation, seem to be dependent on the size of these energy barriers. (ii) The acetylenic bonds of the phosphines might undergo reactions after co-ordination to give other unusual products.

We chose to study as ligand (phenylethynyl)di-t-butylphosphine which was prepared from phenylethynyl-lithium and chlorodi-t-butylphosphine. This solid phosphine was characterized by its methiodide salt and by microanalyses and i.r. and n.m.r. spectroscopy (see Experimental section). The ^{13}C n.m.r. data on this new phosphine in $CDCl_3$ solution are, with the assignment shown in (I) : 30.3(d), ^2J(PH) 14, b; 33.3(d), ^1J(PH)

(I)

18, a; 88.9(d), ^2J(PH) 24 Hz, d; 106.6(s), c; 124.3(s), p; 128.8(s), o; and 131.9(s) p.p.m., m; the resonance for C^1 was probably obscured by the peak at δ 131.9 p.p.m. Shifts are relative to $SiMe_4$.

Platinum and Palladium Complexes.—Treatment of $trans$-$[PtCl_2(NCBu^t)_2]$ or $trans$-$[PdCl_2(NCPh)_2]$ with 2
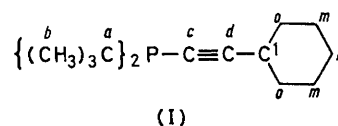
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† No reprints available.

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TABLE 1

Yields, colours, m.p.s, and analytical data (calculated values in parentheses) for some complexes of $PBu^t_2(C{\equiv}CPh)$, L

Complex	Yield (%)	Colour	M.p. (θ_c/°C)	C	H	Cl
(1) [PtCl₂L₂]	86	Yellow	243	51.1(50.65)	6.1(6.1)	9.5(9.35)
(2) [PdCl₂L₂]	98	Yellow	218—221	57.35(57.35)	6.8(6.9)	10.55(10.6)
(3) [PtI₂L₂]	94	Orange	286—288	41.1(40.8)	4.9(4.9)	27.1(26.95) [a]
(4) [PdI₂L₂]	90	Purple	253—260	45.4(45.05)	5.45(5.45)	30.1(29.75) [a]
(5) [Pd₂Cl₄L₂]	79	Orange	220—224	45.8(45.35)	5.5(5.45)	17.1(16.25)
(6) [PtCl₂{PBu$^t_2$[CH=C(Cl)Ph]}₂]	75	White	187—192	46.5(46.2)	5.8(5.8)	16.8(17.05)
(7) [PtMe₂L₂]	78	White	137—142 [b]	57.4(56.9)	7.4(7.3)	0(0)
(8) [PtCl(Me)L₂]	76	White	198—202	53.7(53.7)	6.7(6.7)	5.0(4.8)
(9) [PtCl₂(cod)L]	46	White	145—150	47.1(46.45)	5.8(5.7)	11.8(11.4)
(10) [IrCl(CO)L₂]	78	Yellow	202—205	52.9(52.95)	6.1(6.2)	5.1(4.75)
(11) [IrHCl₂(CO)L₂]	38	White	182—184	50.0(50.5)	6.1(6.05)	9.3(0.05)
(12) [RhCl(CO)L₂]	62	Yellow	194—197	60.2(60.15)	6.8(7.05)	5.6(5.4)
(13) [IrHCl₂L₂]	15	Red	160—165	50.7(50.8)	6.2(6.25)	9.7(9.35)
(14) [RhHCl₂L₂]	45	Red	140—145	57.8(57.6)	6.9(7.1)	10.5(10.6)
(15) [Rh₂Cl₄L₂]	47	Orange	133—140	45.6(45.75)	5.7(5.5)	17.3(16.9)
(16) [Ir(CO){PBu$^t_2$[CH=C(O)Ph]}L]	94	Yellow	195—199	54.1(54.3)	6.4(6.5)	0(0)
(17) [Rh(CO){PBu$^t_2$[CH=C(O)Ph]}L]	95	Yellow	174—178	61.7(61.85)	7.4(7.4)	0(0)
(18) [Ir(CO){PBu$^t_2$[CH=C(O)Ph]}-{PBu$^t_2$[CH=C(OMe)Ph]}]	90	Yellow	155—159	52.4(53.6)	6.6(6.75)	0.5(0)

[a] Iodine analysis. [b] Gas evolved on heating.

TABLE 2

Spectral data

	¹H N.m.r.[a]			³¹P N.m.r.[c]		I.r. (cm⁻¹) [d]		
	Bu^t							
	$\delta \pm 0.2$ p.p.m.	$J^{[b]} \pm 0.5$ Hz	Other resonances	$\delta \pm 0.1$ p.p.m.	J(PtP) $\pm$ Hz	ν(C≡C)	ν(M–Cl)	Other bands
Platinum and palladium								
(1) [e]	1.62(t)	15.4		26.5 / 33.2	2 628 / 2 607	2 196s	338s	
(2)	1.61(t)	15.5		35.1(br) / 41.7(br)	f	2 189s	351s	
(3)	1.64(t)	15.4		13.2 / 26.0	2 477 / 2 451	2 178s		
(4)	1.62(t)	15.6			g	2 183s		
(5)	1.62(d)	16.8		52.1		2 160s		
(6)	1.62(t)	13.7	6.18(t) [h] (7.2, 30.0)	29.1	2 585		334s	1 569m[ν(C=C)]
(7) [i]	1.70(d)	13.2 [j]	1.47(b) [k] (—, 70.5)	28.5	1 858 ⎫	2 178m		
(8) [i]	1.87(t)	15.0	1.49(t) [k] (14.0, 80.0)	36.3	3 274 ⎬ [l]	2 184s	258s	
(9) [i]	1.62(d)	16.3	2.75, 3.45, 4.95, 5.56 [m]	28.2	3 342 ⎭	2 167s	320s, 292s, 274s	
Iridium and rhodium								
	δ	$J^{[b]}$		δ	J	ν(C≡C)	ν(M–Cl)	ν(C≡O)
(10)	1.58(t)	15.1		f		2 181	313s	1 942s
(11)	1.60(t) / 1.71(t)	15.8 / 16.2	−16.2(t) (Ir–H) ²J(PH) 12.6	f		2 184	252s, 313s	2 035s
(12)	1.58(t)	12.8		f		2 183m	308s	1 954s
(13)	{1.44(d) / 1.70(d)}	15.7 / 15.8	−31.3(t) (Ir–H) ²J(PH) 21.6	15.0 [n]		2 178m	268s, 304s	
(14) [i]	1.79(t)	14.8	−29.8(dt), ¹J(RhH) 27.0 ²J(PH) 30.6	47.3	¹J(RhP) 105	2 193m	295s	
							ν(C=C)	
(16)	f		f	43.9 / 78.6	²J(PP) 293	2 178m	1 525m	1 922a
(17)	f		f	42.8 / 86.0	¹J(RhP) 127 ²J(PP) 284 / ¹J(RhP) 137	2 171m	1 519m	1 932s
(18)	f		f	45.2, 76.7	²J(PP) 292	1 526s		1 923s

[a] At 35 °C and 60 MHz in CDCl₃ unless stated otherwise; d = doublet, t = triplet. [b] |³J(PH) + ⁵J(PH)|. [c] At ambient temperature and 36.43 MHz in CDCl₃ unless otherwise stated. Shifts relative to 85% H₃PO₄; br = broad. [d] As Nujol mulls; w = weak, m = medium, s = strong. [e] The numbers refer to the complexes in Table 1. [f] See text. [g] Not recorded. [h] CH=C, ²J(PH) and ³J(PtH) in parentheses. [i] Hydrogen-1 n.m.r. in C₆H₆ or C₆H₆–C₆D₆. [j] J(PH). [k] δ(Me). [l] In C₆H₆–C₆D₆. [m] CH–C of cod. [n] In C₆D₆.

mol equivalents of $PBu^t_2(C{\equiv}CPh)$ (L) gave *trans*-$[MCl_2L_2]$ (M = Pt or Pd) (see Experimental section and Table 1). Both complexes have the *trans* configuration from the i.r. and ^1H n.m.r. data (Table 2). The ^{31}P n.m.r. spectrum of *trans*-$[PtCl_2L_2]$ at 300 K in $CDCl_3$ shows two approximately equally intense peaks with satellites at δ 26.5 [^1J(PtP) 2 628] and 33.2 p.p.m. [^1J(PtP) 2 607 Hz]. These species are very probably due to the conformers (rotamers) (II) and (III) (although we cannot say which is which). As the temperature is

(II)   (III)
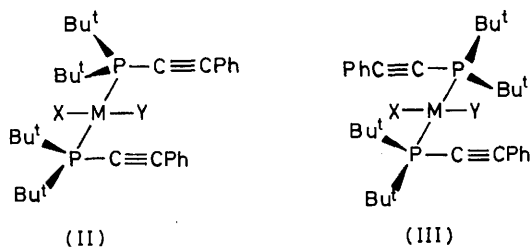
increased these peaks broaden reversibly, *e.g.* at 328 K two broad singlets are observed. This broadening is caused by some rotation about the platinum–phosphorus bonds. The ^{31}P spectrum of *trans*-$[PdCl_2L_2]$ at 300 K consists of two broad singlets at δ 35.1 and 41.7 p.p.m. which become very sharp at 233 K (δ 33.4 and 40.7 p.p.m.) but collapse into one broad singlet at 328 K (δ 39.4 p.p.m.). The effects of temperature changes are reversible. The complex *trans*-$[PtCl_2L_2]$ was very resistant to attack by iodide ion, *e.g.* it was recovered unchanged after treatment with sodium iodide in refluxing acetone for 17 h. However, after reflux for 3 h with NaI in 2-methoxyethanol the di-iodo-complex was formed in 94% yield. The ^{31}P n.m.r. spectrum of this di-iodide at 300 K shows the presence of two conformers (II) and (III) [δ 13.2, ^1J(PtP) 2 477; 26.0 p.p.m., ^1J(PtP) 2 451 Hz]. Metathesis of *trans*-$[PdCl_2L_2]$ with NaI in acetone at 20 °C gave red-brown *trans*-$[PdI_2L_2]$. Treatment of *trans*-$[PdCl_2(PBu^t_2Ph)_2]$ with NaI in acetone under similar conditions gives the bridged complex $[Pd_2I_4(PBu^t_2Ph)_2]$ with loss of phosphine, *i.e.* $PBu^t_2(C{\equiv}CPh)$ probably has a smaller steric requirement with respect to an iodide ligand than does PBu^t_2Ph. The chloro-bridged binuclear complex $[Pd_2Cl_4\{PBu^t_2(C{\equiv}CPh)\}_2]^2$ was readily prepared by mixing equimolar amounts of $Na_2[PdCl_4]$ and L. The bridging system is split by pyridine to give $[PdCl_2L(py)]$ which must have the two chlorines mutually *trans* since it shows just one strong band, at 351 cm^{-1}, in the far-i.r. spectrum.

We attempted to effect both nucleophilic and electrophilic attack on the acetylenic groups of the co-ordinated phosphines in *trans*-$[PtCl_2L_2]$. However, essentially quantitative recoveries of this complex were obtained after the following treatments: (*i*) sodium acetate in refluxing methanol for 1 d; (*ii*) $Na[O_2CMe]$ in refluxing methanol–benzene for 1 d; (*iii*) sodium methoxide (10 mol) in refluxing methanol for 3 h; and (*iv*) sodium

propan-2-olate (10 mol) in refluxing propan-2-ol for 15 min. Treatment of the complex with sodium propan-2-olate (10 mol) for 24 h gave a mixture which could not be separated. The i.r. spectrum showed a band at 2 184m cm^{-1} due to ν(C${\equiv}$C) and one at 1 534s cm^{-1} assigned to ν(C=C), indicating some attack on the acetylene bond(s). The complex *trans*-$[PtCl_2L_2]$ is converted into $[PtCl_2\{PBu^t_2[CH=C(Cl)Ph]\}_2]$ by a solution of hydrogen chloride in dry diethyl ether. The ^1H n.m.r. spectrum shows a ' virtually ' coupled 1 : 2 : 1 triplet due to the t-butyl hydrogens at δ 1.62 p.p.m. [|^3J(PH) + ^5J(PH)| 7.2 Hz] with platinum satellites [J(PtH) 30.0 Hz] due to the two vinylic hydrogens. The ^{31}P n.m.r. and i.r. spectra data (Table 2) also confirm the *trans* configuration of the phosphines and chlorines. We suggest that addition of hydrogen chloride occurs *via* initial electrophilic attack at the α-carbon atom of the alkyne followed by quenching of the carbonium ion by chloride. This would be entirely analogous to the addition of hydrohalogenic acids to diphenylacetylene [8] or propyne.[9] The ^1H n.m.r. spectrum of *trans*-$[PtCl_2L_2]$ in deuteriochloroform–trifluoroacetic acid (1 : 1) shows two doublets for the t-butyls, indicating inequivalent phosphine ligands, and a triplet at δ 6.60 p.p.m., with an intensity corresponding to one hydrogen [J(PH) 6.0 Hz], with platinum satellites [J(PtH) 27.6 Hz]. The ^{31}P n.m.r. spectrum shows an AB + ABX pattern (Table 2), the value of $J(P_AP_B)$ 375 Hz indicating *trans*-phosphorus nuclei. We therefore suggest that the cation *trans*-$[PtCl_2L\{PBu^t_2(CH=CPh)\}]^+$ is formed in CF_3CO_2H. Attempts to precipitate this cation as the tetraphenylborate salt were unsuccessful, the i.r. spectrum indicating that much of the complex *trans*-$[PtCl_2L_2]$ was present in the precipitate. When *trans*-$[PtCl_2L_2]$ was heated under reflux in CF_3CO_2H for 4 h and the solution evaporated to dryness, the unchanged dichloro-complex was recovered. Treatment of the free phosphine $PBu^t_2(C{\equiv}CPh)$ with a solution of hydrogen chloride in diethyl ether gives $[PBu^t_2(C{\equiv}CPh)H]Cl$ there being no evidence of addition to the triple bond. In contrast to the platinum complex, the palladium complex in $CDCl_3$–CF_3CO_2H (1 : 1) shows two broad resonances in the t-butyl region, and no signal due to vinyl hydrogens was observed.

Nucleophilic attack at the triple bond of the palladium complex was also attempted but decomposition to very dark products occurred on treatments with sodium propan-2-olate in propan-2-ol for 15 min or with sodium hydroxide in refluxing ethanol for 5 min.

We also attempted to replace the chloride ligands or to attack the triple bonds of *trans*-$[MCl_2\{PBu^t_2(C{\equiv}CPh)\}_2]$ by methyl groups using methyl-lithium. The dichloro-platinum complex was heated with an excess of LiMe (5 mol) in benzene at 80 °C for 2 h. The resulting white solid product was a mixture which could not be separated; however, it had only 2% chlorine by micro-analysis so it probably contained some of the required

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[9] H. Hunziker, R. Meyer, and H. H. Gunthard, *Helv. Chim. Acta*, 1966, **49**, 497.

methyl complex(es). Treatment of trans-[PdCl$_2$L$_2$] with LiMe (2 mol) in benzene gave an intense green solution and what appeared to be green crystals. Attempts to isolate solids from such reactions led to decomposition, e.g. the green crystals immediately decomposed on washing with dry air-free diethyl ether. A large excess (×10) of LiMe gave deep blue crystals and an intense green solution, but attempts to isolate these deep blue crystals led to decomposition. We successfully prepared the complexes cis-[PtMe$_2$L$_2$], however, by displacing cyclo-octa-1,5-diene (cod) from [PtMe$_2$(cod)] with the ligand L (2 mol) in benzene. This formulation follows from the microanalytical and ^{1}H and ^{21}P n.m.r. data (Tables 1 and 2).

The displacement of cod by PBu$^t_2$(C≡CPh) (2 mol) in benzene was followed by observing the disappearance of the t-butyl ^{1}H n.m.r. doublet of free PBu$^t_2$(C≡CPh) and the appearance of the doublet of the product (the solutions were ca. 10^{-1} mol dm^{-3}). Reaction is complete in ca. 15 min at 34 °C. No intermediate could be detected by ^{1}H n.m.r. spectroscopy. Treatment of [PtMe$_2$(cod)] with only 1 equivalent of L gives a 50% yield of cis-[PtMe$_2$L$_2$] and unchanged [PtMe$_2$(cod)], which stays in solution. The product cis-[PtMe$_2$L$_2$] is one of the few examples of a complex containing two phosphines with di-t-butyl substituents which are of cis configuration. Complexes of the type trans-[MX$_2$-(PBu$^t_2$H)$_2$] (M = Pd or Pt; X = Cl or Br) are isomerized photochemically to the corresponding cis complexes [10] and the chelating ligand C$_6$H$_4$(CH$_2$PBu$^t_2$)$_2$-1,2 forms chelate complexes with Pt^{II}.[11]

The complex cis-[PtCl(Me)(cod)] reacts with 2 mol equivalents of L to give trans-[PtCl(Me)L$_2$] as white prisms. The formulation is based on the analytical and spectroscopic data, e.g. a strong i.r. absorption peak at 258 cm^{-1} is typical of ν(Pt–Cl) (trans-methyl) and triplets in the ^{1}H n.m.r. spectrum due to the Bu^t and PtMe groups also indicate the trans configuration. The ^{31}P n.m.r. spectrum shows a peak at δ 36.3 p.p.m. [^1J(PtP) 3 274 Hz].

Treatment of cis-[PtCl$_2$(cod)] with L (2 mol) in benzene gives cis-[PtCl$_2$(cod)L] as white prisms. The formulation is based on the analytical and spectroscopic data (Tables 1 and 2). The ^{1}H n.m.r. spectrum shows a t-butyl doublet, two broad resonances at δ 2.75 and 3.45 p.p.m. due to eight methylene hydrogens on the cod, and resonances at 4.95 and 5.56 p.p.m. each of intensity two corresponding to the vinylic hydrogens. We suggest that only one of the cod double bonds is co-ordinated and that the resonance at δ 5.56 p.p.m. corresponds to the hydrogens on an unco-ordinated double bond. The ^{31}P n.m.r. spectrum shows a peak at δ 28.2 p.p.m. [^1J(PtP) 3 343 Hz]. The i.r. spectrum shows a peak at 2 167 cm^{-1} due to ν(C≡C) and peaks at 320, 292, and 274 cm^{-1} due to ν(Pt–Cl). The complex

is non-conducting in nitrobenzene. When treated with iodomethane in acetone, yellow cis-[PtI$_2$(cod)] precipitated and the phosphonium salt [PMeBu$^t_2$(C≡CPh)]I was isolated from the mother liquor. The phosphine ligand is thus labile.

Iridium and Rhodium Complexes.—We attempted to prepare [IrHCl$_2$(CO)L$_2$] of configuration (IV) by adding the phosphine (2 equivalents) to a solution prepared by the action of carbon monoxide on a boiling ethanolic solution of hexachloroiridic(IV) acid.[12] The solid product was a mixture of the required product contaminated with trans-[IrCl(CO)L$_2$]. This iridium(I) complex was readily prepared by treating the mixture with triethylamine in ethanol, and characterized in the usual way (Tables 1 and 2). As expected this complex consisted of rotamers due to restricted rotation about the iridium–phosphorus bonds, e.g. the ^{31}P n.m.r. spectrum at 300 K consisted of two broad resonances and at 223 K of six sharp resonances, two singlets and one AB pattern corresponding to (II; X = Cl, Y = CO), (II; X = CO, Y = Cl), and (III; X = Cl, Y = CO). For the AB

(IV)
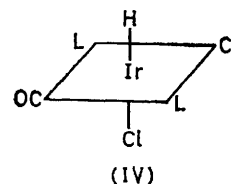
pattern J(PP) 334 Hz. One of the singlets is very strong, one very weak, and the AB pattern is of intermediate intensity. It is likely that the preferred conformation is (II; X = Cl, Y = CO) since an X-ray structure of trans-[IrCl(CO){Bu$^t_2$PC≡C(CH$_2$)$_5$C≡CPBu$^t_2$}][13] shows that only the conformer with C≡O and C≡C adjacent is present in the solid state, and the ^{31}P n.m.r. spectrum shows that virtually all the complex is present as one conformer. The complex trans-[IrCl(CO)L$_2$] was recovered unchanged after treatment with sodium tetrahydroborate in ethanol.

The complex [IrHCl$_2$(CO)L$_2$], configuration (IV), was prepared by treating the iridium(I) complex with hydrogen chloride. The i.r. spectrum showed bands at 2 261, 2 184, 2 035, 313, and 252 cm^{-1} due to ν(Ir–H), ν(C≡C), ν(C≡O), and ν(Ir–Cl) (two bands), respectively. As expected, the ^{1}H n.m.r. pattern showed a 1:2:1 triplet hydride pattern and two t-butyl 1:2:1 triplets.

The complex trans-[RhCl(CO)L$_2$] was readily prepared from [Rh$_2$Cl$_2$(CO)$_4$] and the phosphine. As with the iridium complex, this rhodium complex consisted of conformers in solution with two A$_2$X and one ABX pattern in the ^{31}P n.m.r. spectrum (Table 2) at 253 K. As before, one conformer is present in only small amounts, i.e. (II; X = CO, Y = Cl), and one is preferred (II; X = Cl, Y = CO).

Treatment of H$_2$IrCl$_6$ with 4 mol equivalents of PBu$^t_2$(C≡CPh) in refluxing propan-2-ol gives the five-
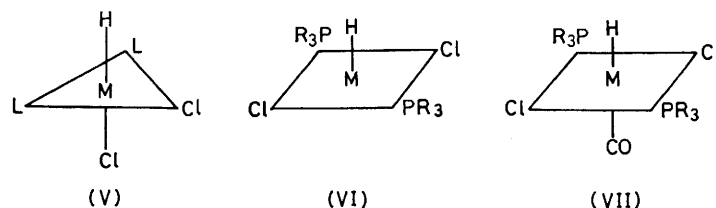
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co-ordinate [IrHCl$_2$L$_2$] as a red solid. The ^{1}H n.m.r. spectrum shows two doublets due to the t-butyls and a high-field triplet at δ −31.3 p.p.m., with a large coupling constant of 21.6 Hz due to IrH. The ^{31}P n.m.r. spectrum is a singlet. The i.r. spectrum shows a band at 2 178 cm^{-1} due to ν(C≡C), two bands due to ν(Ir–Cl) (at 304 and 268 cm^{-1}), but no band due to ν(Ir–H). In iridium hydrides with very bulky tertiary phosphines a band due to ν(Ir–H) is often very weak or not observed.[3] We formulate this iridium(III) hydride complex as trigonal-bipyramidal (V) with the phosphines in the

configuration (VIII) was formed. The i.r. spectrum shows bands at 2 178, 1 922, and 1 525 cm^{-1} due to ν(C≡C), ν(C≡O), and ν(C=C) respectively. The ^{31}P n.m.r. spectrum shows an AB pattern at δ 43.9 and 78.6 p.p.m. [J(PP) 293 Hz] showing trans-phosphines, and the ^{1}H n.m.r. spectrum four equally intense peaks centred at δ 1.46 p.p.m. due to the t-butyl hydrogens (separations ca. 2, 12.5, and 2 Hz) and a doublet of doublets for the vinyl hydrogen at δ 4.8 p.p.m. [J 3.0 and 5.0 Hz]. A rhodium complex was similarly prepared and characterized (see Table 2 for ^{31}P n.m.r. and i.r. data). The vinyl

(V)   (VI)   (VII)
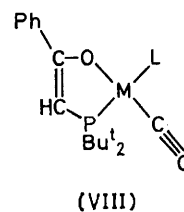
trigonal plane and cis-chlorides. In agreement with this formulation, the red complex (V) reacts readily with carbon monoxide to give the colourless complex (IV). We have made several other co-ordinatively unsaturated iridium(III) hydrides [IrHCl$_2$(PR$_3$)$_2$] (PR$_3$ is a very bulky tertiary phosphine such as PMeBu$^t_2$) but these have all had configuration (VI) and react with CO to give a six-co-ordinate carbonyl hydride of configuration (VII). Presumably the relatively small steric requirements of C≡CPh allows the P–Ir–P angle to be considerably less than 180° as in (V), whereas ligands such as PEtBu$^t_2$ are preferentially trans, as in (VI).

When RhCl$_3$·3H$_2$O is treated with 4 mol equivalents of PBu$^t_2$(C≡CPh) at 20 °C the red five-co-ordinate rhodium(III) hydride [RhHCl$_2$L$_2$] is formed. The ^{1}H and ^{31}P n.m.r. and i.r. evidence (Table 2) indicates that this complex probably has the square-pyramidal structure (VI) as found previously for complexes of the type [RhHCl$_2$(PR$_3$)$_2$].[14] It is not clear why the configuration should be different from that of the corresponding iridium complex described above. The complex [RhHCl$_2${PBu$^t_2$(C≡CPh)}$_2$] slowly decomposes in chloroform solution to give an orange insoluble complex which appears to be a binuclear complex of Rh^{II} of type [Rh$_2$Cl$_4$L$_2$]. This complex was too insoluble for molecular-weight determinations. The ^{1}H n.m.r. spectrum of a deuteriochloroform solution of [RhHCl$_2$L$_2$] slowly changes at 34 °C. After 20 min a doublet at δ 1.42 p.p.m. (J 12.4 Hz) is just visible: this corresponds to the free phosphine L. However, the resolution soon deteriorates, which we interpret as being due to the formation of paramagnetic species [i.e. the rhodium(II) complex]. When [RhHCl$_2$L$_2$] in benzene is treated with CO it rapidly gives trans-[RhCl(CO)L$_2$].

When the complex trans-[IrCl(CO)L$_2$] was treated with a solution of sodium propan-2-olate in propan-2-ol the chelate complex [Ir(CO){PBu$^t_2$[CH=C(O)Ph]}L] of

hydrogen formed a multiplet at δ 4.67 p.p.m. (CDCl$_3$). It is not clear whether small amounts of water in the

(VIII)

propan-2-ol–sodium propan-2-olate mixture were responsible for this hydration reaction or whether it involved breakdown of the propan-2-ol (or isopropoxide) possibly as shown in the Scheme. We have found for example
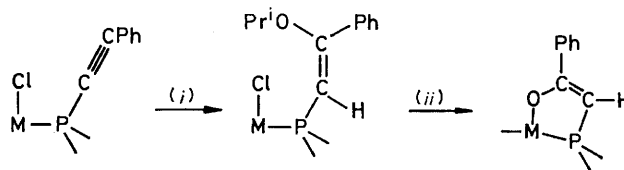
Scheme   (i) [OPr^i]$^-$ followed by Pr^{i}OH;   (ii) O-metallation, −Pr^{i}Cl

that the phosphine oxide PBu$^t_2$(C≡CEt)O with sodium propan-2-olate gives PBu$^t_2$[CH=C(OPr^i)Et]O.[15] Carty et al.[16] showed that cis-[PdCl$_2${PPh$_2$(C≡CCF$_3$)}$_2$] reacts with water to give a variety of products including [Pd{PPh$_2$[CH=C(O)CF$_3$]}$_2$] and suggested that the initial step is nucleophilic attack by water on the β-carbon followed by protonation and intramolecular hydrogen-chloride elimination.

Treatment of trans-[IrCl(CO)L$_2$] with sodium methoxide in refluxing methanol gave [Ir(CO){PBu$^t_2$[CH=C(O)-Ph]}{PBu$^t_2$[CH=C(OMe)Ph]}] (trans-phosphorus donor atoms). This product was not obtained analytically pure, but the i.r. and ^{31}P n.m.r. data (Table 2) and

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[15] D. Pawson and B. L. Shaw, unpublished work.

[16] A. J. Carty, S. Jacobson, R. T. Simpson, and N. J. Taylor, J. Amer. Chem. Soc., 1975, 97, 7254.

¹H n.m.r. data (below) agree with the formulation: four peaks due to the t-butyl hydrogens centred at δ 1.46 p.p.m., a singlet at 3.25 p.p.m. due to OMe, and sets of resonances due to the two vinylic protons at 4.83 [J(PH) 3.6 and 7.2] and 5.22 p.p.m. [J(PH) 2.4 and 6 Hz]. As was the case with reaction in propan-2-ol, the chelate ring might have been formed by a mechanism analogous to that shown in the Scheme or because of trace amounts of water in the sodium methoxide–methanol solution.

EXPERIMENTAL

All the operations involving PBut₂(C≡CPh) were carried out under argon. The analytical and spectroscopic data are recorded in the Tables.

(Phenylethynyl)di-t-butylphosphine.— n-Butyl-lithium (0.153 mol) in hexane (82 cm³) was added dropwise over 0.5 h to a well stirred solution of ethynylbenzene (15.6 g, 16.8 cm³, 0.153 mol) in diethyl ether (50 cm³). The resulting white suspension was heated under reflux for 2 h then added over 10 min to a cooled (−10 °C) solution of chlorodi-t-butylphosphine (18.4 g, 0.102 mol) in diethyl ether (70 cm³). The mixture was then heated under reflux for 20 h and hydrolyzed with water. The product was isolated by distillation, b.p. 188 °C (bath temperature) (27 mmHg),* white prisms, m.p. 46—49 °C, yield 80% (Found: C, 77.6; H, 9.2. C₂₀H₁₅P requires C, 78.0; H, 9.4%), ν(C≡C) in Nujol at 2 181s cm⁻¹. N.m.r. spectra in CDCl₃: ³¹P, δ 12.6 p.p.m.; ¹H, δ 1.28(d) p.p.m. [³J(PH) 12.5 Hz], But. With methyl iodide in acetone the compound readily gave the methiodide salt as needles, m.p. 150—155 °C, yield 69% (Found: C, 52.3; H, 6.8; I, 32.4. C₂₁H₁₈IP requires C, 52.6; H, 6.75; I, 32.7%).

trans-*Dichlorobis[(phenylethynyl)di-t-butylphosphine]-platinum*(II).—A suspension of dichlorobis(t-butyl cyanide)-platinum(II) (1.26 g, 2.67 mmol) in toluene (10 cm³) was treated with PBut₂(C≡CPh) (1.39 g, 5.60 mmol) and the mixture was stirred for 5 min at 20 °C. The resulting clear solution was diluted with light petroleum (b.p. 80—100 °C) to give the *product* (1.75 g, 2.30 mmol) as yellow prisms. trans-*Dichlorobis[(phenylethynyl)di-t-butylphosphine]-palladium*(II) was prepared similarly from dichlorobis-(benzonitrile)palladium(II) as orange prisms from toluene–light petroleum (b.p. 80—100 °C).

trans-*Iodobis[(phenylethynyl)di-t-butylphosphine]plati-num*(II).—A solution of *trans*-[PtCl₂{PBut₂(C≡CPh)}₂] (0.08 g, 0.11 mmol) in 2-methoxyethanol (5 cm³) containing sodium iodide (0.174 g, 1.1 mmol) was heated under reflux for 3.5 h. The resulting yellow solution was evaporated and the residual oil extracted with toluene. The extract was diluted with light petroleum (b.p. 80—100 °C) to give the *product* (0.094 g, 0.10 mmol) as yellow prisms.

trans-*Iodobis[(phenylethynyl)di-t-butylphosphine]palla-dium*(II).—A solution of *trans*-[PdCl₂{PBut₂(C≡CPh)}₂] (0.24 g, 0.35 mmol) in acetone (7 cm³) containing NaI (0.54 g, 3.54 mmol) was stirred for 16 h at 20 °C. The mixture was then cooled to *ca.* −15 °C giving the *product* as red-brown prisms. These were washed with water and dried, yield 0.27 g (0.32 mmol).

Di-μ-chloro-bis{chloro[(phenylethynyl)di-t-butylphosphine]-palladium(II)}.—A solution of PBut₂(C≡CPh) (0.45 g, 1.81 mmol) in methanol (5 cm³) was added to a solution of

disodium tetrachloropalladate(II) (0.64 g, 30.1% Pd, 1.81 mmol) in methanol (8 cm³). The resulting suspension was stirred for 16 h at 20 °C. The *product* (0.61 g, 1.45 mmol) was filtered off as orange prisms.

trans-*Dichlorobis[(2-chloro-2-phenylvinyl)di-t-butylphos-phine]platinum*(II).—A solution of *trans*-[PtCl₂{PBut₂-(C≡CPh)}₂] (0.10 g, 0.13 mmol) in dichloromethane (5 cm³) was treated with a solution of hydrogen chloride (13.2 mmol) in dry diethyl ether (3 cm³). The suspension was stirred for 16 h at 20 °C. The resulting clear solution was cooled to *ca.* 15 °C giving the *product* (0.083 g, 0.10 mmol) as white prisms.

cis-*Dimethylbis[(phenylethynyl)di-t-butylphosphine]-platinum*(II).—(Phenylethynyl)di-t-butylphosphine (0.098 g, 0.40 mmol) was added to a solution of *cis*-(cyclo-octa-1,5-diene)dimethylplatinum(II) (0.064 g, 0.20 mmol) in benzene (2 cm³). The mixture was stirred for 15 min at 20 °C to give a clear solution, and the solvent was removed under reduced pressure. The resulting oil was treated with light petroleum (b.p. 60—80 °C) and the *product* (0.11 g, 0.15 mmol) formed as white prisms.

trans-*Chloro(methyl)bis[(phenylethynyl)di-t-butylphos-phine]platinum*(II).—A solution of *cis*-chloro(cyclo-octa-1,5-diene)methylplatinum(II) (0.082 g, 0.23 mmol) in benzene (1 cm³) was treated with PBut₂(C≡CPh) (0.12 g, 0.46 mmol). The solvent was removed under reduced pressure. The resulting oil was treated with light petroleum (b.p. 60—80 °C) and the *product* (0.13 g, 0.17 mmol) formed as white prisms.

Dichloro(cyclo-octa-1,5-diene)[(phenylethynyl)di-t-butyl-phosphine]platinum(II).—A suspension of *cis*-dichloro(cyclo-octa-1,5-diene)platinum(II) (0.19 g, 0.52 mmol) in benzene (5 cm³) was treated with PBut₂(C≡CPh) (0.13 g, 0.52 mmol). The mixture was stirred for 30 min at 20 °C. The resulting colourless solution was evaporated and the residual oil extracted with methanol. The *product* formed as white prisms (0.15 g, 0.24 mmol).

trans-*(Carbonyl)chlorobis[(phenylethynyl)di-t-butylphos-phine]iridium*(I).—A solution of hexachloroiridic(IV) acid (1.10 g, 42.8% Ir, 2.44 mmol) in absolute ethanol (20 cm³) and rhodium trichloride trihydrate (0.007 g, 0.03 mmol) was stirred in a carbon monoxide atmosphere for 24 h under slow reflux. (Phenylethynyl)di-t-butylphosphine (1.26 g, 5.13 mmol) was then added to the resulting yellow solution. The suspension was then stirred for 2 h at 20 °C. Filtration gave a cream solid (1.54 g) which was found to be a *ca.* 1 : 1 mixture of *trans*-[IrCl(CO){PBut₂(C≡CPh)}₂] and carbonyl-dichlorohydridobis[(phenylethynyl)di-t-butylphosphine]-iridium(III) (see text). A suspension of the mixture (1.54 g) in absolute ethanol (3 cm³) was treated with triethylamine (0.12 g, 1.20 mmol) and the mixture was heated under reflux for 5 min then cooled to *ca.* −15 °C giving the *product* (1.43 g, 1.90 mmol) as yellow prisms.

trans-*Carbonyldichlorohydridobis[(phenylethynyl)di-t-butyl-phosphine]iridium*(III).—A solution of *trans*-[IrCl(CO)-{PBut₂(C≡CPh)}₂] (0.16 g, 0.22 mmol) in dichloromethane (3 cm³) was treated with a solution of hydrogen chloride (0.24 mmol) in diethyl ether (0.75 cm³). The resulting colourless solution was diluted with absolute ethanol (3 cm³) then cooled to *ca.* −15 °C giving the *product* (0.066 g, 0.085 mmol) as white prisms.

trans-*Carbonylchlorobis[(phenylethynyl)di-t-butylphos-phine]rhodium*(I).— (Phenylethynyl)di-t-butylphosphine (0.25 g, 1.04 mmol) was added to a methanol solution (2 cm³) of di-μ-chloro-bis[dicarbonylrhodium(I)] (0.096 g,

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

0.49 mmol Rh). The required *product* (0.20 g, 0.31 mmol) separated as yellow prisms.

Dichlorohydridobis[(phenylethynyl)di-t-butylphosphine]-iridium(III).—A solution of H_2IrCl_6 (0.44 g, 0.97 mmol) in propan-2-ol (10 cm³) was heated for 5 min until it became brownish green. The solution was cooled and PBu^t_2-(C≡CPh) (0.98 g, 3.97 mmol) added under argon. The resulting green slurry was then heated under reflux for 5 h. The suspension obtained was filtered and the filtrate was cooled to ca. −15 °C giving the *product* (0.11 g, 0.15 mmol) as red prisms.

Dichlorohydridobis[(phenylethynyl)di-t-butylphosphine]-rhodium(III).—(Phenylethynyl)di-t-butylphosphine (0.76 g, 3.1 mmol) was added to a solution of $RhCl_3 \cdot 3H_2O$ (0.19 g, 0.77 mmol) in absolute ethanol (15 cm³). The resulting deep red solution was stirred for 20 min at 20 °C then cooled to ca. −15 °C giving the *product* (0.23 g, 0.35 mmol) as red prisms.

Di-µ-chloro-bis{chloro[(phenylethynyl)di-t-butylphosphine]-rhodium(II)}.—A solution of $[RhHCl_2\{PBu^t_2(C≡CPh)\}_2]$ (0.11 g, 0.16 mmol) in chloroform (1 cm³) was stirred for 16 h at 20 °C. The *product* was filtered off as orange prisms (0.03 g, 0.07 mmol).

Carbonyl[2-(di-t-butylphosphino)-1-phenylethyleneoxo-OP][(phenylethynyl)di-t-butylphosphine]iridium(I).— The complex *trans*-[IrCl(CO){PBu^t_2(C≡CPh)}$_2$] (0.15 g, 0.20 mmol) was treated with a solution of sodium propan-2-olate in propan-2-ol (11.4 cm³, 0.14 mol dm⁻³) under reflux for 16 h. The resulting suspension was evaporated to an oil which was then treated with water. The *product* (0.13 g, 0.18 mmol) was filtered off as yellow prisms.

Carbonyl[2-(di-t-butylphosphino)-1-phenylethyleneoxo-OP][(phenylethynyl)di-t-butylphosphine]rhodium(I).—A suspension of *trans*-[RhCl(CO){PBu^t_2(C≡CPh)}$_2$] (0.11 g, 0.16 mmol) in a solution of sodium propan-2-olate in propan-2-ol (9.4 cm³, 0.1 mol dm⁻³) was heated under reflux for 16 h. The resulting suspension was evaporated to an oil which was then treated with water. The *product* (0.10 g, 0.15 mmol) was filtered off as yellow prisms.

Carbonyl[2-(di-t-butylphosphino)-1-phenylethyleneoxo-OP][(2-methoxy-2-phenylvinyl)di-t-butylphosphine]iridium(I). —The complex *trans*-[IrCl(CO){PBu^t_2(C≡CPh)}$_2$] (0.15 g, 0.20 mmol) was treated with a solution of sodium methoxide in methanol (2.1 cm³, 0.8 mol dm⁻³) under reflux for 22 h. The resulting suspension was then evaporated to an oil *in vacuo* and water was added. The *product* (0.14 g, 0.18 mmol) was filtered off as yellow prisms and could be recrystallized from dichloromethane–methanol.