Transition Metal–Carbon Bonds. Part XLII.[1] Complexes of Nickel, Palladium, Platinum, Rhodium and Iridium with the Tridentate Ligand 2,6-Bis[(di-t-butylphosphino)methyl]phenyl †

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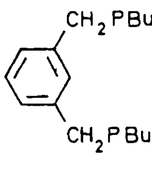
The bulky diphosphine 1,3-[(di-t-butylphosphino)methyl]benzene undergoes metallation very readily to give a new type of tridentate chelating system, 2,6-bis[di-t-butylphosphino)methyl]phenyl (pcp). Complexes prepared are of the types [MX(pcp)] (M = Ni, Pd, or Pt; X = Cl, Br, H, C⋮CPh, or CN; M = Rh, X = CO), [MHCl(pcp)] (M = Rh or Ir), and [IrHCl(CO)(pcp)]. [Ni(CO)(pcp)][BPh$_4$] was also prepared. ^{1}H- and ^{31}P- n.m.r. data and i.r. data are given.

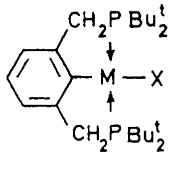
It is now well-established that bulky tertiary phosphine ligands generate unusual transition-metal chemistry. In particular, di-t-butylphosphines, PBu$^t_2$R (R = alkyl or aryl), promote hydride formation, internal *C*- or *O*-metallation, and co-ordinative unsaturation, and also stabilize unusual valency states such as iridium(II), or unusual compounds such as platinum dihydrides.[2,3] We have now synthesized the bulky diphosphine 1,3-bis[(di-t-butylphosphino)methyl]benzene (1) (*m*-xylenyldiphosphine) anticipating that it would undergo metallation at the aromatic carbon *ortho* to the two CH$_2$PBu$^t_2$ groupings thereby generating a new type of tridentate chelate system (pcp) which might be expected to give complexes of unusual types.

The new diphosphine was prepared in high yield by the quaternization of di-t-butylphosphine with 1,3-bis(dibromomethyl)benzene and subsequent treatment with base (sodium acetate) (see the Experimental section and Tables for details).

Tertiary di-t-butylphosphines, PBu$^t_2$R, are less strongly bonding ligands than tertiary phosphines which are less bulky (*e.g.* PEt$_2$R) and for example have little affinity for nickel(II) halides, *e.g.* addition of PEt$_3$ to an ethanolic solution of nickel chloride readily gives the dark red *trans*-[NiBr$_2$(PEt$_3$)$_2$] but a similar addition of PBu$^t_2$Et has no effect. However, when an ethanolic solution of hydrated nickel chloride is treated with one mole proportion of the diphosphine at 20 °C golden yellow needles of the nickel(II) complex [NiCl(pcp)] (2; M = Ni, X = Cl) precipitate after a few minutes. This complex is readily purified by sublimation under vacuum and also sublimes slowly at *ca.* 240 °C/1 atm onto the cover slip of a heated microscope slide, without any apparent decomposition. It is soluble in the common organic solvents. The assigned structure is based on the following evidence: (i) microanalytical and molecular weight data (Table 1); (ii) the occurrence of a t-butyl triplet and a methylene triplet pattern in the ^{1}H n.m.r. spectrum, characteristic of strong phosphorus–phosphorus coupling between *trans*-bonded and magnetically equivalent phosphorus donor atoms (Table 2); (iii) a singlet ^{31}P n.m.r. pattern (Table 2); (iv) the occurrence of one strong band at 214 cm^{-1} in the far-i.r. spectrum attributed to ν(Ni–Cl) and absent from the spectrum of the corresponding bromide. The bromo-complex [NiBr(pcp)] (2) was formed readily by treating hydrated nickel bromide with the diphosphine in ethanol.



(1) (pcpH)



(2) [MX(pcp)]

This chloro-complex, [NiCl(pcp)] (2), fails to undergo metathesis to the corresponding bromide even on prolonged (4 h) refluxing with a large excess of lithium bromide in acetone. However, the bromo-complex [NiBr(pcp)] was slowly but essentially completely converted into the chloro-complex when treated with lithium chloride in acetone for 16 h at 20 °C. Usually bromide is a better ligand than chloride in transition metal–tertiary phosphine complexes (*e.g.* with ligands such as PBu$^n_3$, PEt$_2$Ph, PPh$_3$, *etc.*). The reversal in the usual order of affinities in these complexes with the very bulky pcp ligand is probably due to steric factors *i.e.* bromide is larger than chloride.

The palladium and platinum complexes (2; M = Pd or Pt; X = Cl) were made by heating [PdCl$_2$(PhCN)$_2$] or [PtCl$_2$(Bu^{t}CN)$_2$] with the diphosphine in 2-methoxyethanol. Both are volatile, thermally very stable, and soluble in common organic solvents. The structures are based on microanalytical, molecular weight, and spectroscopic data (see Tables and Experimental section for details). Values of ν(M–Cl) are 272 (Pd) and 283 cm^{-1} (Pt) typical for chlorine *trans* to σ-bonded carbon. Although the palladium complex was made in good yield and appeared to be the only metal-containing product the platinum complex (2) was accompanied by much petroleum-insoluble material. Much of this is soluble in dichloromethane and on addition of methanol it precipitates as a microcrystalline powder. This material appeared on microscopic examination to be a mixture. We could not separate it but the 60 MHz ^{1}H n.m.r. spectrum in deuteriochloroform shows a well-defined t-butyl 1 : 2 : 1 triplet at δ 1.42 with $|^3J(\mathrm{PH}) + {}^5J(\mathrm{PH}\,| = 14$ Hz, indicating mutually *trans* and equivalent phosphorus donor atoms.

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† No reprints available.

[1] Part XLI, B. L. Shaw, and M. M. Truelock, *J. Organometallic Chem.*, in the press.

[2] H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J.C.S. Dalton*, 1975, 1690.

[3] B. L. Shaw and M. F. Uttley, *J.C.S. Chem. Comm.*, 1974, 918.

In the far i.r. absorption spectrum there was only one band in the range 400—200 cm^{-1}. This was a very strong band at 333 cm^{-1}, a frequency typical of ν(Pt–Cl) with chlorine *trans* to chlorine.[4,5] The ^{1}H n.m.r. and far-i.r. data therefore suggest the product is a polymer *trans*-$[PtCl_2(Bu^t_2PC_8H_8PBu^t_2)]_x$, $x \geqslant 2$ (or a polymer mixture). However microanalytical data were in rather poor agreement with this formulation (Found: C, 45.15; H, 6.95; Cl, 8.2. $C_{24}H_{43}Cl_2P_2Pt$ requires C, 43.7; H, 6.6; Cl, 10.75%). We therefore cannot formulate this product mixture. On prolonged heating (10 h) in 2-methoxyethanol (b.p. 124 °C) it gave none of the metallated derivative (2) (M = Pt, X = Cl) and was recovered essentially unchanged.

TABLE 1

Colours, % yields, melting points, microanalytical, and molecular-weight data for some complexes containing the ligand 1,3-bis[(di-t-butylphosphino)methyl]phenyl (pcp)

	Colour [a]	% Yield	M.p.[b] (θ_c/°C)	C (%)	H (%)	Cl (%)	M [d]
[NiCl(pcp)]	y	54	240—250s	58.9 (59.1)	8.9 (8.9)	7.1 (7.25)	500 (488)
[PdCl(pcp)]	w	75	270—294s	53.4 (53.85)	8.1 (8.1)	7.0 (6.6)	524 (535)
[PtCl(pcp)]	w	32	270—295s	46.5 (46.2)	6.8 (6.95)	6.0 (5.7)	626 (624)
[NiCN(pcp)]	y	54	240—260	62.2 (62.7)	9.1 (9.05)		
[Ni(C⋮CPh)(pcp)]	y	*ca.* 100	195—230	69.2 (69.45)	8.9 (8.75)		
[Ni(CO)(pcp)][BPh$_4$]	y	86	170—175 [c]	73.2 (73.6)	8.1 (7.95)	0 (0)	
[PdH(pcp)]	w	96	172—200 [c]	58.4, 55.5 (57.3)	9.15, 7.95 (8.85)	0 (0)	
[PtH(pcp)]	w	95	212—220	49.2 (48.9)	7.4 (7.5)		566 (590)
[Pd(C⋮CPh)(pcp)]	w	93	267—273 [c]	63.85 (63.95)	8.0 (8.05)		
[RhHCl(pcp)]	o	69	180—200s	54.1 (54.3)	8.35 (8.15)	6.5 (6.65)	558 (536)
[IrHCl(pcp)]	db	74	245—350s	46.5 (46.3)	7.15 (7.13)	5.6 (5.7)	652 (622)
[Rh(CO)(pcp)]	y	91	205—210	56.8 (57.2)	8.1 (8.25)		518 (524)
[IrHCl(CO)(pcp)]	w	*ca.* 100	210—214	51.0 (51.05)	7.3 (7.55)	6.2 (6.05)	

[a] w = white, y = yellow, o = orange, db = dark brown. [b] s = sublimes. [c] With decomposition. [d] Measured osmometrically in chloroform solution.

TABLE 2

^{1}H-[a] and ^{31}P-n.m.r.[b] and i.r. data [c]

	δ Bu^t	^{1}H δ CH$_2$	Other resonances	^{31}P $\delta_{H_3PO_4}$	I.r. data (cm^{-1})
[NiClpcp)]	1.48 (12.6)t	3.08 (7.4)t		74.65	NiCl 214s
[PdCl(pcp)]	1.42 (13.7)t	3.23 (7.8)t		72.5	PdCl 272s
[PtCl(pcp)]	1.37 (13.9)t	3.16 (7.6)t ^3J(PtH) = 21		64.95 ^1J(PtP) = 2 881	PtCl 283s
[NiCN(pcp)]	1.40 (13.0)t	3.21 (7.1)t			
[Ni(C⋮CPh)(pcp)]	1.40 (12.7)t	3.26 (7.4)t			C⋮C 2 075s
[Ni(CO)(pcp)][BPh$_4$]	1.32 (14.6)t	3.40 (8)t		106.07	C⋮O
[PdH(pcp)]	1.25 (13.2)t	3.41 (7.0)t	PdH −3.86 (13.5)t		PdH 1 730s
[PtH(pcp)]	1.30 (13.7)t	3.43 (7.8)t ^3J(PtH) = 16	PtH −2.40 (15.7)t ^1J(PtH) = 902		PtH 1 917s
[Pd(C⋮CPh)(pcp)]	1.43 (13.6)t	3.40 (8.8)t			C⋮C 2 095s
[RhHCl (pcp)]	1.40 (13.6)t	3.22 (7.4)t	RhH −27.5 (12.0) ^1J(RhH) = 52.8	74.9 ^1J(RhP) = 115	RhCl 275s
[IrHCl(pcp)]	1.37 (13.0)t	3.26 (7.5)t	IrH −43.0 (12.0)	67.5	IrCl 276s
[Rh(CO)(pcp)]	1.34 (12.6)t	3.43 (7.4)t		92.1 ^1J(RhP) = 147	C⋮O 1 925s
[IrHCl(CO)(pcp)]	1.55 (13.6)t 1.45 (13.6)t	3.22 (7.6)t	IrH −7.6 (15)		IrH 2 165s C⋮O 1 985vs IrCl 265s

[a] In CDCl$_3$ at *ca.* 34 °C. Coupling constants (Hz) to phosphorus shown in parentheses for Bu^t $|^3J(PH) + {^5J}(PH)|$ and for CH$_2$ $|^2J(PH) + {^4J}(PH)|$. δ-Values ±0.02, J-values ±1 Hz. [b] In CDCl$_3$ at *ca.* 25 °C. δ-values ±0.05, J-values ±1 Hz. [c] Nujol mulls.

The palladium(II) and platinum(II) complexes (2; X = Cl) were recovered unchanged after heating under reflux with a large excess of lithium bromide in 2-methoxyethanol. Presumably, because of its larger size, bromide fails to displace chloride. We have therefore attempted to displace the chloride ligand in complexes of type (2; X = Cl) by ligands X which are less sterically demanding than chloride. In this we were successful, as described below.

The chloride ligand in the platinum or palladium complexes (2) is readily replaced by hydride, by treatment under reflux with sodium borohydride in ethanol for *ca.* 1 h. The platinum hydride (2; M = Pt, X = H) is a readily soluble, colourless, crystalline, and stable material. The low value for ν(Pt–H) (1 917 cm^{-1}) is what one might expect for hydrogen *trans* to σ-bonded carbon. The hydride reacts rapidly with ethanolic hydrogen chloride to give back the chloride with dihydrogen evolution. The assigned structure for this hydride is based on (i) microanalytical and molecular weight data (Table 1), (ii) on the occurrence of a well defined t-butyl triplet pattern in the ^{1}H n.m.r. spectrum indicating mutually *trans* and equivalent phosphorus donor atoms, (iii) a 1 : 2 : 1 triplet hydride resonance at δ −2.40 with ^2J(P–H) = 15.7 Hz flanked by satellites, ^1J(Pt–H) = 902 Hz (see Table 2), (iv) a central singlet

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[4] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

[5] D. A. Dudell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

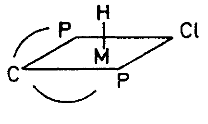
^{31}P n.m.r. with satellites due to platinum-195 coupling. The palladium hydride was not obtained analytically pure (Table 1) but the spectroscopic data (Table 2) show that it was formed and has the assigned structure.

Treatment of [NiCl(pcp)] with sodium borohydride in ethanol readily gives a yellow powder. The material contains no chlorine and the i.r. spectrum suggests it is the required hydride (2; M = Ni, X = H). Thus there is a very strong absorption band at 1 757 cm^{-1} and apart from bands due to ν(M–H) the rest of the spectrum from 4 000—200 cm^{-1} is very similar to those of the platinum or palladium hydrides. However, no hydride resonance was observed in the ^{1}H n.m.r. spectrum (δ −70 to +10). This is presumably due to an exchange effect. This nickel hydride complex was not obtained analytically pure.

Other ligands with small steric requirements which replace the chloride in complexes of type (2) are C≡CPh, C≡N, or C≡O. Thus the nickel complex [NiCl(pcp)], when treated with sodium cyanide in acetone, gave the corresponding cyano-complex and with lithium phenylacetylide in tetrahydrofuran the phenylacetylide [Ni(C⋮CPh)(pcp)] was formed in high yield. The microanalytical and spectroscopic data (Tables) confirm the structures. Both complexes were stable and soluble in common organic solvents and the cyano-complex could be sublimed under vacuum. A phenylacetylide of palladium was similarly made and characterized (see Experimental section and Tables). When an ethanolic solution of the chloro-complex [NiCl(pcp)] was treated with carbon monoxide in the presence of sodium tetraphenylborate the nickel(II) carbonyl salt [Ni(CO)(pcp)][BPh$_4$] was precipitated (see Experimental section, and Tables for characterizing data).

Complexes of Rhodium or Iridium formed from the m-*Xylenyldiphosphine* (1).—We have shown that bulky di-t-butyl(alkyl)phosphine and related ligands form unusual types of rhodium(III), rhodium(II), iridium(III), or iridium(II) complexes.[6,7] We have now investigated the action of the *m*-xylenyldiphosphine with rhodium and iridium chlorides. When a solution of rhodium trichloride in propan-2-ol was heated with the diphosphine the deep orange five-co-ordinate rhodium(III) hydride [RhHCl(pcp)] (3; M = Rh) was formed. This complex is soluble in the common organic solvents and sublimes easily under vacuum. The assigned structure is based on (i) microanalytical and molecular-weight data, (ii) the ^{1}H n.m.r. spectrum which shows a doublet of triplets at high field (δ −27.5) characteristic of a square pyramidal rhodium(III) hydride [6] and a t-butyl triplet characteristic of mutually *trans* and equivalent phosphorus donor atoms, (iii) a strong band at 275 cm^{-1} due to ν(Rh–Cl). [Absorption due to ν(Rh–H) was too weak to observe; possibly the hydrogen is surrounded by a ' cage ' of t-butyl groups and vibration is suppressed], and (iv) the ^{31}P n.m.r. spectrum which shows a doublet at 74.9 p.p.m., ^{1}J(Rh–P) = 115 Hz.

When a propan-2-ol solution of hydrated iridium trichloride and the *m*-xylenyldiphosphine is heated under reflux for 20 h a mixture of complexes is produced. The light-petroleum-soluble fraction yields dark brown needles of [IrHCl(pcp)] analogous to the rhodium complex described above and characterized in a similar manner (see Experimental section and Tables). The light-petroleum-insoluble fraction showed a strong band at 2 180 cm^{-1} presumably due to ν(Ir–H) but we were unable to separate pure material from this fraction, which was almost insoluble in benzene or chlorinated solvents. The material was probably not mononuclear.



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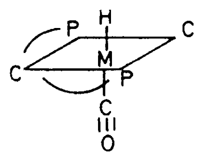

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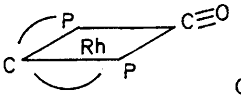

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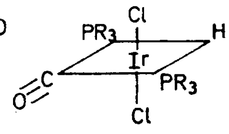

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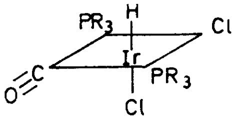

(7)

The complexes [MHCl(pcp)] (M = Rh or Ir) are co-ordinatively unsaturated and might be expected to react with small rod-like molecules such as carbon monoxide. When the deep red-brown solution of [IrHCl(pcp)] in benzene is treated with carbon monoxide, a colourless solution forms rapidly. The colourless crystalline product isolated from this solution is shown to have the structure (4; M = Ir) from microanalytical and spectroscopic data (see Tables). A similar treatment of the rhodium complex [RhHCl(pcp)] (3) with carbon monoxide probably gave the adduct (4) but this is unstable and easily loses the elements of hydrogen chloride to give the rhodium(I) carbonyl [Rh(CO)(pcp)] (5) and possibly other products. Thus an orange benzene solution of [RhHCl(pcp)] when treated with carbon monoxide rapidly turns pale yellow but only mixtures could be obtained from this solution. A freshly prepared sample of this pale yellow solution shows a broad proton resonance at δ −7.5 which decreases in intensity with time and has disappeared after 30 min at *ca.* 34 °C. The carbonylated solution shows i.r. absorptions at 2 020 and 1 928 cm^{-1}, but the higher frequency band decreases in intensity with time.

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[6] C. Masters and B. L. Shaw, *J. Chem. Soc.* (*A*), **1971**, 3679.

[7] C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 209.

The band at 1 928 cm^{-1} was probably due to the rhodium(I) carbonyl species [Rh(CO)(pcp)] (5), for if an alcoholic solution of [RhHCl(pcp)] is treated with sodium ethoxide and carbon monoxide this canary-yellow rhodium(I) carbonyl complex is formed. It is crystalline, readily soluble in common organic solvents, and is very easily sublimed. Its structure is shown by microanalytical and spectroscopic data (see Tables). It was recovered unchanged when treated with chlorine in carbon tetrachloride. An attempt to prepare the corresponding iridium(I) carbonyl complex by an analogous method failed. Impure [IrHCl(CO)(pcp)] (4) only was obtained. There is an analogy here with the behaviour of complexes of the type [$IrHCl_2(CO)(PR_3)_2$] of configuration (6) which do not dehydrochlorinate with base, whereas those of configuration (7) readily dehydrochlorinate (hydrogen *trans* to chlorine).[8] Rhodium is much more labile than iridium and a rhodium complex of configuration (4) possibly dehydrochlorinates after isomerization.

EXPERIMENTAL

The general techniques and instruments used are the same as those described in a previous paper.[2]

o-*Phenylenedimethylbis(di-t-butylphosphonium) Dibromide*.—A mixture of di-t-butylphosphine (0.828 g, 5.67 mmol) and 1,3-bis(bromomethyl)benzene (0.749 g, 2.84 mmol) in acetone (3 ml) was heated under reflux with stirring for 45 min. The mixture was then cooled to 5 °C, giving the product as white prisms (1.57 g, 2.83 mmol, *ca.* 100%).

1,3-*Bis[(di-t-butylphosphino)methyl]benzene*.—A solution of the above-mentioned diphosphonium salt (4.3 g, 7.79 mmol) in degassed water (10 ml) was treated with a solution of sodium acetate (4 g, 48 mmol) in degassed water (10 ml). The precipitated diphosphine was isolated with ether and distilled (135—140 °C/0.01 mmHg) on a Kugelrohr as a colourless liquid which slowly crystallized (yield 2.97 g, 7.53 mmol, 97%).

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}chloronickel*.—A solution of nickel chloride hexahydrate (2.25 g, 9.45 mmol) in water (4 ml) was added to a solution of the diphosphine (3.83 g, 9.6 mmol) in ethanol (20 ml). The mixture was then heated to *ca.* 80 °C for 5 min and then cooled to 5 °C. This gave the required product as golden-yellow needles (2.47 g, 5.06 mmol, 54%). The corresponding bromide was made similarly.

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}chloropalladium*.—Bis(benzonitrile)dichloropalladium (2.06 g, 5.38 mmol) was added to a suspension of the diphosphine (2.13 g, 5.39 mmol) in 2-methoxyethanol (14 ml). The resultant mixture was refluxed for 25 min and the product isolated by evaporation and recrystallization from ethanol; it formed needles (2.16 g, 75%).

The corresponding *platinum* complex was similarly prepared as *needles* from light petroleum (b.p. 60—80 °C).

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}cyanonickel*.—A mixture of sodium cyanide (0.017 g, 0.337 mmol) and the chloro-complex (0.138 g, 0.282 mmol) was stirred for 35 min in acetone. The required product was isolated by evaporation and extraction with benzene. It formed yellow needles (0.12 g, 0.24 mmol, 87%) from light petroleum (b.p. 60—80 °C).

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}hydridoplatinum*.—Sodium tetrahydroborate (0.10 g) was added to a stirred suspension of the chloro-complex (0.21 g, 0.33 mmol) in ethanol (2 ml). The mixture was refluxed for 1.5 h, four further quantities of sodium borohydride (0.10 g) being added at *ca.* 20-min intervals. The mixture was cooled and the product precipitated with water. It formed white needles from light petroleum (b.p. 60—80 °C) (yield 0.19 g, 0.31 mmol, 95%).

The analogous *palladium* complex was prepared and isolated similarly; the reflux time was 1 h and the product formed white needles (yield 96%).

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}hydridonickel*.—Sodium tetrahydroborate (0.1 g) was added to a suspension of the chloro-complex (0.173 g, 0.354 mmol) in a mixture of benzene (5 ml) and ethanol (5 ml). The mixture was stirred for 20 h at 20 °C after which a further quantity of sodium tetrahydroborate (0.1 g) was added. The mixture was stirred for a further 3 h after which water and benzene were added. The product was isolated from the benzene by evaporation as a yellow microcrystalline solid (0.164 g, 0.358 mmol, *ca.* 100%).

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}phenylethynylpalladium*.—The corresponding chloro-complex was added to a mixture of phenylacetylene (0.09 g, 0.87 mmol), n-butyl-lithium (0.87 mmol in 0.47 ml of a hexane solution), and benzene (2 ml). The mixture was refluxed for 4 h, cooled, water was added, and the product was isolated with benzene. It formed white prisms from light petroleum (b.p. 60—80 °C) (0.22 g, 0.36 mmol, 93%).

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}phenylethynylnickel*.—The chloro-complex (0.18 g, 0.37 mmol) was added to a mixture of n-butyl-lithium (0.55 mmol in 0.2 ml hexane solution) and phenylacetylene (0.06 g, 0.55 mmol) in dry tetrahydrofuran (2 ml). The resultant mixture was stirred at 20 °C for 45 min, cooled to −78 °C, and then hydrolysed by the cautious addition of wet tetrahydrofuran (5 ml, 10% v/v). The product was isolated by addition of benzene and water. The product formed yellow prisms (0.22 g, 0.37 mmol, *ca.* 100%) from light petroleum (b.p. 60—80 °C).

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}carbonylnickel*(II) *Tetraphenylborate*.—Carbon monoxide was bubbled briskly through a solution of {2,6-bis[(di-t-butylphosphino)-methyl]phenyl}chloronickel(II) (0.15 g, 0.31 mmol) in ethanol (10 ml) for 5 min. Treatment of the subsequent clear yellow solution with a solution of sodium tetraphenylborate (0.32 g, 0.92 mmol) in ethanol (2 ml) yielded the product (0.22 g, 0.27 mmol, 86%) as light yellow needles.

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}chloro(hydrido)rhodium*.—The diphosphine (3.10 g, 7.85 mmol) was added to a solution of rhodium trichloride trihydrate (1.39 g, 5.24 mmol) in a mixture of water (3 ml) and propan-2-ol (20 ml). The resultant mixture was heated under reflux for 20 h, then cooled to −5 °C. The product separated and formed orange needles (1.93 g, 3.59 mmol, 69%).

{2,6-*Bis[(di-t-butylphosphino)methyl]phenyl}carbonylrhodium*.—A vigorous stream of carbon monoxide was bubbled through a solution of the above-mentioned hydride (0.43 g, 0.80 mmol) in ethanol (15 ml) for 10 min. An ethanolic solution of sodium ethoxide (0.5 ml, 0.94M, 470 mmol) was then added. The slow addition of water

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[8] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 1887.

(30 ml) then caused the required product to crystallize out as yellow needles (0.38 g, 0.72 mmol, 91%). A sample was purified for analysis by sublimation (140—145 °C/0.01 mmHg).

{2,6-*Bis*[(*di-t-butylphosphino*)*methyl*]*phenyl*}*chlorohydridoiridium*.—A mixture of the diphosphine (1.44 g, 3.63 mmol), hydrated iridium trichloride (0.65 g, 1.82 mmol) in water (2 ml), and propan-2-ol (15 ml) was heated under reflux for 20 h. The mixture was then cooled to −5 °C, when the product separated. It formed dark-brown needles (0.84 g, 1.34 mmol, 74%) from light petroleum (b.p. 60—80 °C).

{2,6-*Bis*[(*di-t-butylphosphino*)*methyl*]*phenyl*}*carbonyl*(*chloro*)*hydridoiridium*.—A stream of carbon monoxide was bubbled briskly through a solution of the above-mentioned chloro(hydrido)-complex (0.057 g, 0.087 mmol) in benzene (0.3 ml) for 2 min. The product was isolated by evaporation under reduced pressure and formed white prisms (yield 0.058 mmol, 68%).

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