Transition Metal–Carbon Bonds. Part 54.[1] Complexes of Palladium, Platinum, Rhodium, and Iridium with $\mathrm{Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2}$. Crystal Structures of $\mathrm{[PdCl(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]}$ and $\mathrm{[IrH(Cl)(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]}$ †

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The new diphosphine $\mathrm{Bu^t_2PCH_2CHMeCH_2CH_2CH_2PBu^t_2}$ (L) is shown to have ^{13}C n.m.r. shifts which can be calculated empirically from the ^{13}C n.m.r. shifts of related diphosphines. It reacts with $\mathrm{[PdCl_2(NCPh)_2]}$ to give the cyclometallated complex $\mathrm{[PdCl(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]}$ (1c), with the 2-methyl group in a pseudo-equatorial position, as shown by the crystal structure. With $\mathrm{[PtCl_2(NCBu^t)_2]}$ it gives $\mathrm{[Pt_2Cl_4L_2]}$, as a complex mixture of isomeric 16-atom ring chelates, which, on treatment with $\mathrm{CF_3COOH}$ followed by LiCl, gives $\mathrm{[PtCl(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]}$; this was not isolated pure but probably has a structure similar to (1c). Compound L also reacts with $\mathrm{[Ir_2Cl_2(C_8H_{14})_4]}$ ($\mathrm{C_8H_{14}}$ = cyclo-octene) to give the cyclometallated hydride complex $\mathrm{[IrH(Cl)(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]}$ (2c) with an equatorial methyl group. Some of the isomer with a pseudo-axial methyl group was also formed but it slowly, but completely, isomerises to (2c) in solution. Compound (2c) does not lose dihydrogen to give a carbene on heating, in contrast to $\mathrm{[IrH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]}$. Compound L reacts with $\mathrm{[Rh_2Cl_2(C_8H_{14})_4]}$ to give $\mathrm{[RhH(Cl)(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]}$ (2e), but with $\mathrm{RhCl_3\cdot 3H_2O}$ it also gives two other species, probably rhodium(I)–olefinic diphosphine complexes. Compound (2e) with sodium propan-2-oxide and CO gives $\mathrm{[Rh(CO)(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]}$. Proton, ^{13}C, and ^{31}P n.m.r. and i.r. data are given. Cell dimensions: (1c) a = 1.1907(3), b = 1.6466(4), c = 1.3537(4) nm, and β = 103.99(2)°; (2c) a = 1.1954(4), b = 1.6509(5), c = 1.3665(5) nm, and β = 104.18(3)°.

We have shown previously that ligands of the type $\mathrm{Bu^t_2PCH_2CH_2CHRCH_2CH_2PBu^t_2}$ (R = H or Me), with bulky end-groups, are capable of giving large-ring (16-atom) chelates with palladium, platinum, rhodium, or iridium and also undergo cyclometallation and dehydrogenation reactions with these metals.[2–5] Thus the large-ring chelates with platinum(II), *viz.* $\mathrm{[Pt_2Cl_4(Bu^t_2PCH_2CH_2CHRCH_2CH_2PBu^t_2)_2]}$, when treated with $\mathrm{CF_3COOH}$ give the cyclometallated complexes (1a) and (1b). Similarly, the labile cyclo-octene complex $\mathrm{[Rh_2Cl_2(C_8H_{14})_4]}$ reacts with $\mathrm{Bu^t_2P(CH_2)_5PBu^t_2}$ to give the fluxional hydride (2a). These fused five-membered ring systems are puckered and have pseudo-equatorial and pseudo-axial hydrogens, *e.g.* $\mathrm{R_e}$ = H and $\mathrm{R_a}$ = H. We set out to learn more about the stereochemistry in these cyclometallated fused-ring systems by introducing a methyl group into the 2-position of the diphosphine, *i.e.* to study $\mathrm{Bu^t_2PCH_2CHMeCH_2CH_2CH_2PBu^t_2}$. This diphosphine when cyclometallated might be expected to give isomers with pseudo-equatorial or pseudo-axial methyl substituents. These isomers might interconvert. Also we have shown that the cyclometallated iridium hydride (2b), when heated, gives the carbene (or ylide) complex (3). A feature of the ^{1}H n.m.r. spectrum of complex (3) is the occurrence of a quintet pattern at $\delta = -2.7$ p.p.m. which must be due to two hydrogens (either two $\mathrm{H_e}$ or two $\mathrm{H_a}$) on either side of the carbene carbon.[6,7] We hoped to discover whether this peculiar ^{1}H resonance pattern was due to $\mathrm{H_e}$ or $\mathrm{H_a}$ by methyl substitution.

Results and Discussion

The new ligand $\mathrm{Bu^t_2PCH_2CHMeCH_2CH_2CH_2PBu^t_2}$ was synthesised by a modification of the route we used previously to make $\mathrm{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2}$.[3] 1,5-Dibromo-2-methylpentane was converted into the 1,5-dithio-derivative and this, in turn, was treated with $\mathrm{PBu^t_2Cl}$, to give the required diphosphine (details in the Experimental section). The ^{31}P-{^{1}H} n.m.r. spectrum of the new diphosphine (in $\mathrm{C_6D_6}$) showed resonances at δ = 27.6 and 21.6 p.p.m., the ^{1}H spectrum a doublet at δ = 1.12 p.p.m. [$\mathrm{C(CH_3)_3}$], and the ^{1}H-{^{31}P} spectrum a doublet at δ = 1.25 p.p.m., ^3J(HH) = 4 Hz, due to $\mathrm{CHC}H_3$. The ^{13}C-{^{1}H} n.m.r. data for this and the two related phosphines $\mathrm{Bu^t_2PCH_2CH_2CHRCH_2CH_2PBu^t_2}$ (R = H or $\mathrm{CH_3}$) (not reported previously) are given in Table 1. It has been shown [8] that ^{13}C n.m.r. shifts in alkylphosphines can be calculated in a similar fashion to those of alkanes, since replacement of carbon by a phosphorus appears to have little influence on a ^{13}C chemical shift, *e.g.* compare the ^{13}C chemical shift of the methyl groups in $\mathrm{PMe_3}$ (14.3 p.p.m.) and $\mathrm{HCMe_3}$ (13.65 p.p.m.). Alkyl substituents in α- or β-position move the ^{13}C n.m.r. signal to high frequency (mainly an inductive effect), whilst similar γ-substituents move it to low frequency (presumed to be a steric interaction).[9] Thus, from the ^{13}C n.m.r. shifts for $\mathrm{Bu^t_2P(CH_2)_5PBu^t_2}$ (A) and $\mathrm{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2}$ (B) (Table 1), the effects of a methyl substituent on the shifts are $\Delta_\gamma = 18.7-21.7 = -3.0$, $\Delta_\beta = 38.6-30.7 = 7.9$, and $\Delta_\alpha = 36.0-33.5 = 2.5$ p.p.m. The

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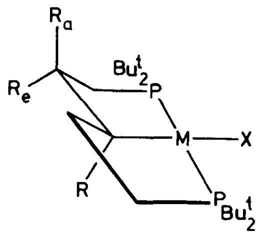
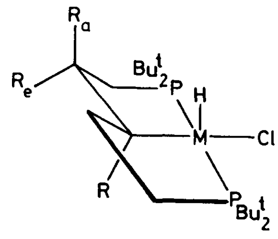
† [2-Methyl-1,5-bis(di-t-butylphosphino)pent-3-yl-C^3PP']-chloropalladium(II) and -chlorohydridoiridium(III).

Supplementary data available (No. SUP 23319, 33 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



(1a) $R = H, R_e = R_a = H, M = Pt, X = OOCCF_3$
(1b) $R = Me, R_e = R_a = H, M = Pt, X = OOCCF_3$
(1c) $R = R_a = H, R_e = Me, M = Pd, X = Cl$
(1d) $R = R_a = H, R_e = Me, M = Pt, X = Cl$
(1e) $R = R_e = H, R_a = Me, M = Pt, X = Cl$
(1f) $R = R_e = R_a = H, M = Rh, X = CO$
(1g) $R = R_a = H, R_e = Me, M = Rh, X = CO$



(2a) $R = R_e = R_a = H, M = Rh$
(2b) $R = R_e = R_a = H, M = Ir$
(2c) $R = R_a = H, R_e = Me, M = Ir$
(2d) $R = R_e = H, R_a = Me, M = Ir$
(2e) $R = R_a = H, R_e = Me, M = Rh$
(2f) $R = Me, R_e = R_a = H, M = Rh$

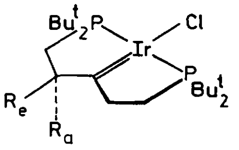


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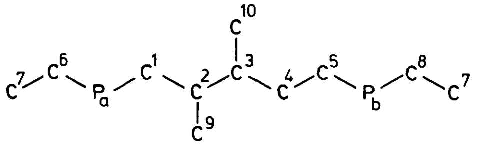
Table 1. $^{13}C-\{^1H\}$ n.m.r. data[a] for $Bu^t_2P(CH_2)_5PBu^t_2$ (A), $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ (B), and $Bu^t_2PCH_2CHMeCH_2CH_2CH_2PBu^t_2$ (C)[b]

Carbon atom	(A)	(B)	(C)
1	21.7 (d, 23)	18.7 (d, 23)	29.2 (d, 26)
2	30.7 (d, 26)	38.6 (d, 26)	33.4 (d, 21)
3	33.5 (t, 13)	36.0 (t, 13)	40.5 (dd, 13 and 9)
4			27.2 (d, 24)
5			21.4 (d, 20)
6	31.2 (d, 23)	31.1 (d, 24)	31.3 (d, 20)
7	30.0 (d, 13)	29.8 (d, 14)	29.7 (d, 13)
8			31.1 (d, 20)
9			21.1 (d, 9)
10		19.6 (s)	

[a] Recorded at 20 °C in C_6D_6. δ values (±0.1) in p.p.m. to high frequency of $SiMe_4$. Coupling constants $J(P-C)$ ±1 Hz are shown in parentheses: d = doublet, t = triplet, dd = double doublet, s = singlet. [b] The numbering scheme for carbon and phosphorus atoms is as follows:



calculated values for the ^{13}C shifts for $Bu^t_2PCH_2CHMeCH_2CH_2CH_2PBu^t_2$ (C) are thus: C^1 21.7 + 7.9 = 29.6 (obs. 29.2), C^2 30.7 + 2.5 = 33.2 (obs. 33.4), C^3 33.5 + 7.9 = 41.4 (obs. 40.5), C^4 30.7 − 3.0 = 27.7 (obs. 27.2), and C^5 calc. 21.7 (obs. 21.4).

***Palladium and Platinum Complexes of* $Bu^t_2PCH_2CHMeCH_2CH_2CH_2PBu^t_2$ (L).**—Although we made this new diphosphine primarily for work with iridium and rhodium we have made a brief study of its reactions with palladium(II) and platinum(II).

Table 2. Microanalytical and molecular-weight data, L = $Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2$

	Analysis (%)[a]			
Complex	C	H	Cl	$M^{a,b}$
(1c)	51.15 (51.25)	8.95 (9.2)	6.85 (6.9)	*c*
$[Pt_2Cl_4L_2]$	42.5 (42.25)	7.6 (7.55)	n.d.	1 247 (1 281)
(2c)	44.15 (43.9)	8.15 (8.05)	6.15 (5.9)	*c*
(2e)	51.4 (51.5)	9.25 (9.45)	6.85 (6.9)	n.d.
(1g)	54.9 (54.75)	9.2 (9.4)		504 (504)

n.d. = Not determined.
[a] Calculated values in parentheses. [b] Determined in chloroform. [c] See Discussion for mass spectrometric determination.

Treatment of $[PdCl_2(NCPh)_2]$ with L in refluxing 2-methoxyethanol for 15 min gave an orange-yellow solution and a small amount of palladium metal. Evaporation of the solution and extraction of the residue with light petroleum gave a pale yellow crystalline complex which analysed for $C_{22}H_{47}ClP_2Pd$ (see Table 2) and gave a molecular ion cluster in its mass spectrum, from *m/e* 510—521, with relative intensities in excellent agreement with this molecular formula. In the i.r. spectrum a band at 255s cm^{-1} is typical of ν(Pd–Cl) *trans* to a σ-bonded carbon.[2] The $^{31}P-\{^1H\}$ n.m.r. spectrum showed an AB pattern with δP = 66.2 and 82.4 p.p.m., $^2J(PP)$ = 337 Hz (Table 3). The $^1H-\{^{31}P\}$ pattern showed $C(CH_3)_3$ singlets at 1.38, 1.35, and 1.36 p.p.m., the last one being twice as intense as either of the other two. The ^1H n.m.r. spectrum showed a CH*Me* resonance as a doublet of doublets at δH = 1.04 (dd) p.p.m., $^4J(PH)$ = 0.9, $^3J(HH)$ = 5.9 Hz. These data are in agreement with a cyclometallated complex of formulation $[PdCl(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]$. A single-crystal *X*-ray structural determination establishes the structure to be (1c), *i.e.* with an equatorial methyl group. A small amount of

Table 3. I.r. (cm^{-1})[a] and ^{31}P-{^{1}H}[b] and ^{1}H[c] n.m.r. data

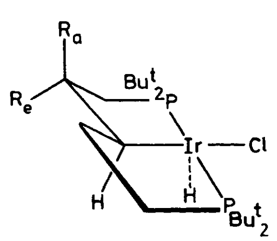
Complex	$\tilde{\nu}$(M–Cl)	$\tilde{\nu}$(M–H)	^{31}P-{^{1}H} δ(P)	^{31}P-{^{1}H} ^1J(MP)	^{31}P-{^{1}H} ^2J(PP)
(1c)	255s		66.2, 82.4		337
$[Pt_2Cl_4L_2]$	328vs		*ca.* 27, *ca.* 62	n.r.	n.r.
(1d)	261s		60.9, 76.8	3 149, 3 100	368
(2c)[d]	258s		62.2,[e] 76.5		339
(2e)[f]	261m	2 200w	80.0,[e] 84.3	122, 122	356
(1g)[g]			87.7, 103.4	155, 154	259

[a] As Nujol mulls (±2 cm^{-1}). [b] Spectra recorded at *ca.* 20 °C and 40.25 MHz in $CDCl_3$, unless stated otherwise. Chemical shifts relative to 85% H_3PO_4, ±0.1 p.p.m., shifts to high frequency being positive; J values ±1 Hz. [c] Spectra recorded at *ca.* 20 °C and 100 MHz in $CDCl_3$, unless stated otherwise. δ values ±0.01 p.p.m; J values ±0.1 Hz. Other data are in the Discussion. [d] ^{1}H N.m.r.: δ(Ir–H) = −43.0,[e] ^2J(PH) = 11.7 Hz. [e] In C_6D_6. [f] ^{1}H N.m.r.: δ(Rh–H) = −28.85,[e] ^1J(Rh–H) = 50.7, ^2J(PH) = 10.9 Hz. [g] ν(CO) at 1 923s cm^{-1}.

light petroleum-insoluble material was also obtained from the original reaction mixture but this was not characterised.

Treatment of $[PtCl_2(NCBu^t)_2]$ with $Bu^t_2PCH_2CHMeCH_2CH_2CH_2PBu^t_2$ in refluxing ethanol for 3.5 h gave a yellow solution, from which a pale yellow solid was isolated. This was shown to be *trans*-$[Pt_2Cl_4L_2]$ on the basis of microanalytical and molecular-weight data (Table 2) and its i.r. spectrum (Table 3), which showed a very strong band at 328 cm^{-1} due to ν(Pt–Cl) of a *trans* Cl–Pt–Cl moiety. The ^{31}P-{^{1}H} spectrum showed two broad, complex bands at δP *ca.* 27 and 62 p.p.m. which suggests the product is a complex mixture of isomers and rotamers (as would be expected). We have shown previously [2] that large-ring platinum(II) complexes of this type are converted by CF_3COOH into cyclometallated mononuclear complexes. We therefore heated this complex mixture of binuclear species with CF_3COOH, to give an orange solution. The ^{31}P-{^{1}H} spectrum of this solution showed at least two AB patterns with platinum satellites. A solid product could not be obtained from this solution and the crude trifluoroacetate product was converted into chloride by treatment with lithium chloride. This gave a pale yellow solid which showed a ^{31}P-{^{1}H} n.m.r. spectrum containing an AB pattern with platinum satellites as the major component, δP = 60.9 and 76.8 p.p.m., ^1J(PtP) = 3 149 and 3 100 Hz respectively, and ^2J(PP) = 368 Hz. From this spectrum another component(s) was also present which could not be completely removed by recrystallisation and an analytically pure compound was not obtained (Found: C, 42.4; H, 7.35. Calc. for $C_{22}H_{47}ClP_2Pt$: C, 43.75; H, 7.85%). The i.r. spectrum showed a band at 261s cm^{-1} typical of ν(Pt–Cl) *trans* to σ-bonded carbon. It seems likely that the major product was (1d) with an equatorial methyl group rather than (1e).

Reactions of $Bu^t_2PCH_2CHMeCH_2CH_2CH_2PBu^t_2$ (L) *with Iridium*.—We reasoned that treatment of iridium trichloride with this diphosphine would give a complex mixture of products and have therefore confined our study to the labile iridium(I) cyclo-octene complex $[Ir_2Cl_2(C_8H_{14})_4]$. Treatment of this olefin complex with the diphosphine, L, in hot toluene readily gave the hoped for cyclometallated hydrido-complex $[IrH(Cl)(Bu^t_2PCH_2CHMeCHCH_2CH_2PBu^t_2)]$ in *ca.* 50% yield. Microanalytical data are in Table 2. The ^{31}P-{^{1}H} n.m.r. spectrum (Table 3) showed an AB pattern, δP = 76.5 and 62.2 p.p.m., ^2J(PP) = 339 Hz. The ^{1}H n.m.r. spectrum showed a hydride resonance of δH = −43.0 p.p.m. as a 1 : 2 : 1 triplet, ^2J(PH) = 11.7 Hz. The ^{1}H-{^{31}P} n.m.r. spectrum showed four non-equivalent Bu^t resonances as singlets, δH = 1.24, 1.25, 1.34, and 1.36 p.p.m. A single-crystal X-ray structural determination showed the methyl group to be equatorial, *i.e.* the structure is almost certainly (2c) for the reasons discussed below. The mass spectrum of the complex showed a molecular ion cluster for $C_{22}H_{46}ClIrP_2$, *i.e.* two hydrogens fewer than in (2c). Loss of two hydrogens in the mass spectrometer is common for such iridium complexes, *e.g.* with $[IrH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$.[7] In one treatment of $[Ir_2Cl_2(C_8H_{14})_4]$ with L the product was worked up rapidly and showed in the ^{31}P-{^{1}H} n.m.r. spectrum the AB pattern described above and a second (minor) AB pattern with very similar parameters to those of (2c), *viz.* δP = 60.5 and 74.3 p.p.m. and ^2J(PP) = 334 Hz. In solution (C_6D_6) this minor pattern gradually disappeared over a few hours and after 1 day it had completely disappeared, leaving only the pattern due to (2c). We suggest therefore that this minor, unstable, product is the isomer with an axial methyl group, *i.e.* (2d), and that isomerisation of (2d) to (2c) occurs *via* reductive elimination to give an eight-membered ring chelate followed by oxidative addition, to give (2c). Such a process occurs rapidly with the fluxional rhodium complex (2a).[4,5]



(4a) $R_e = R_a = H$
(4b) $R_e = Me$, $R_a = H$
(4c) $R_e = H$, $R_a = Me$

We have shown that the cyclometallated hydride (2b) when either heated *in vacuo* or in refluxing decalin dehydrogenates to give the carbene/ylide complex (3).[6,7] However, on heating (2c) *in vacuo* it sublimed unchanged and no carbene could be detected. Moreover, on heating its solution in refluxing decalin a complex mixture of products was obtained, which could not be separated and showed no resonances at *ca.* δ −3 p.p.m. in the ^{1}H n.m.r. spectrum, *i.e.* no carbene/ylide analogous to (3) appeared to be formed. A possible explanation for this difference in behaviour between (2c) and (2d) is that carbene/ylide (3; $R_e = R_a = H$) readily takes up dihydrogen to give (2b). We suggested [7] that this goes *via* the *cis* hydride (4a) (in which the torsion angle H–C–Ir–H is 0°); reductive elimination then gives the eight-membered ring complex $[IrCl\{Bu^t_2P(CH_2)_5PBu^t_2\}]$ which, in turn, undergoes internal oxidative addition to give (2b) (in which the torsion angle H–C–Ir–H is 180°). It is possible that the carbene (3) is formed from (2b) by the reverse sequence of steps. However, the 2-methyl-substituted diphosphine, $Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2$, would give an eight-membered ring chelate, $[IrCl\{Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2\}]$, in which the 2-methyl group would sterically interfere with the formation of a hydride (4b) or (4c) by a concerted *cis* addition of C–H to iridium but would not interfere substantially with metallation to give (2c) [or even (2d)], which is also thought to go *via* a

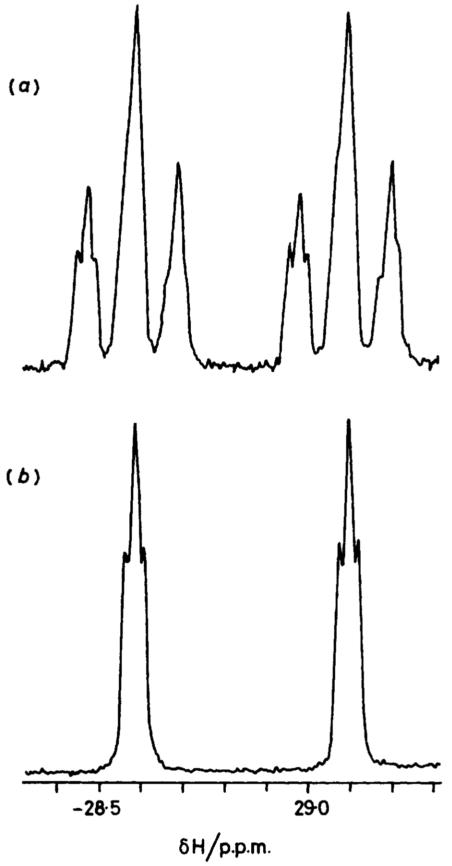
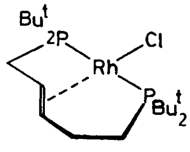


Figure 1. The ^{1}H n.m.r. spectrum (*a*) and the ^{1}H-{^{31}P} n.m.r. spectrum (*b*) of [RhH(Cl)(Bu$^t_2$PCH$_2$CHMeCHCH$_2$CH$_2$PBu$^t_2$)] (2e) in the hydride region, measured at 100 MHz in C_6D_6–C_6H_6

concerted *cis* addition of C–H to iridium. We tentatively suggest that the complex mixture formed by heating (2c) in decalin contains olefinic diphosphines co-ordinated to iridium(I) since such dehydrogenations of polymethylene diphosphines to give olefin complexes have been shown to occur with rhodium (see also below).[5]

Reactions of Bu$^t_2$PCH$_2$CHMeCH$_2$CH$_2$CH$_2$PBu$^t_2$ (L) *with Rhodium*.—Treatment of $RhCl_3 \cdot 3H_2O$ with this diphosphine in refluxing propan-2-ol gave a yellow-brown precipitate, which gradually dissolved over a period of 4 h to give an orange-yellow solution and a small amount of metallic rhodium. A pentane-soluble product, isolated from the orange-yellow solution, showed in its ^{31}P-{^{1}H} n.m.r. spectrum one ABX and two AMX patterns (X = rhodium-103). The ABX pattern was established as being due to the complex [RhH(Cl)(Bu$^t_2$PCH$_2$CHMeCHCH$_2$CH$_2$PBu$^t_2$)] (2e) (see below). The two AMX patterns showed the following ^{31}P parameters: AMX(1) $\delta P_A = 66.2$ p.p.m., $^1J(RhP_A) = 136$ Hz, $\delta P_B = -34.5$ p.p.m., $^1J(RhP_B) = 95$ Hz, $^2J(P_AP_B) = 376$ Hz, and AMX(2) $\delta P_A = 54.9$ p.p.m., $^1J(RhP_A) = 129$ Hz, $\delta P_B = -55.3$ p.p.m., $^1J(RhP_B) = 95$ Hz, $^2J(P_AP_B) = 352$ Hz. A ^{31}P n.m.r. spectrum, with t-butyl methylene, methine, and methyl protons selectively decoupled, established that the ABX pattern was that of a monohydride, *i.e.* each peak gave a doublet, whilst the AMX patterns were unaffected. These AMX patterns are probably due to olefin complexes: we have shown[5] that Bu$^t_2$P(CH$_2$)$_5$PBu$^t_2$ is dehydrogenated by $RhCl_3 \cdot 3H_2O$ to give what is almost certainly the olefin complex (5).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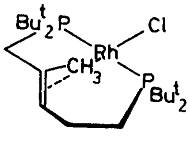
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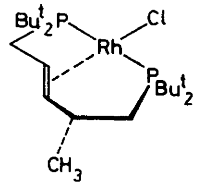
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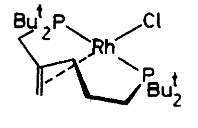
(8)

The ^{1}H n.m.r. spectrum of our three-component mixture showed a broad resonance at 4.1 p.p.m., probably due to olefinic hydrogens; a similar resonance was observed in the ^{1}H n.m.r. spectrum of (5).[5] The pure hydrido-complex was prepared by treating [$Rh_2Cl_2(C_8H_{14})_4$] with L and had identical ^{31}P n.m.r. parameters to the species giving the ABX pattern. Microanalytical data (Table 2) were in agreement with a molecular formula of $C_{22}H_{48}ClP_2Rh$, although the molecular ion pattern in the mass spectrum, *m/e* 510—514, corresponded to loss of two hydrogens in the mass spectrometer (a common phenomenon in compounds such as these, see the iridium complexes discussed above). The ^{1}H-{^{31}P} n.m.r. spectrum showed four t-butyl resonances, at δ = 1.37, 1.35, 1.26, and 1.25 p.p.m., and a doublet at 1.11 p.p.m., $^3J(CH_3CH) = 5.7$ Hz, due to the 2-methyl group. The hydride resonance at δ = −28.85 p.p.m. consisted of a doublet of complex 1 : 2 : 1 triplets without decoupling from phosphorus-31, $^1J(RhH) = 50.7$ and $^2J(PH) = 10.9$ Hz. With phosphorus decoupling this resonance consisted of a doublet of triplets, see Figure 1: the triplet pattern must arise from second-order coupling to two protons on the alkyl chain, *i.e.* in the phosphorus-31 decoupled spectrum the hydride resonance forms the ' M ' part of an ABMX pattern (X = rhodium-103). This hydride is not fluxional, probably because such a process, observed with the fluxional hydride (2a), would involve a movement of the 2-methyl group between equatorial and axial positions. In the i.r. spectrum a peak at 2 200 cm^{-1} was assigned to ν(Rh–H). Since the stable cyclometallated complexes formed from L and palladium or iridium have the 2-methyl substituent in the equatorial position it seems likely that the cyclometallated rhodium hydride complex has configuration (2e), with the 2-methyl group similarly equatorial. The olefinic rhodium complexes, formed along with (2e) when rhodium trichloride was heated with L, are possibly two of the three complexes (6)—(8), the phosphorus-31 resonance at very low frequency (*i.e.* negative δ value) (Table 3) being due to $RhP{-}C{-}C{=}C$: other complexes containing this moiety, where the double bond is similarly co-ordinated to rhodium in a small ring, have similar negative δP values.[5]

We have shown previously that the cyclometallated complex

Table 4. Selected bond lengths (pm) and angles (°) with estimated standard deviations in parentheses

	Palladium complex (1c)	Iridium complex (2c)		Palladium complex (1c)	Iridium complex (2c)
M-Cl	242.8(3)	242.8(4)	C(4)-C(5)	155.3(14)	152.5(21)
M-P(1)	230.2(3)	229.9(3)	C(5)-P(2)	185.8(10)	183.8(13)
M-P(2)	232.0(2)	231.5(3)	P(1)-C(6)	191.8(12)	189.8(15)
M-C(3)	210.2(9)	207.3(14)	P(1)-C(7)	186.3(11)	185.6(14)
P(1)-C(1)	184.5(11)	181.8(15)	P(2)-C(8)	188.1(10)	187.0(14)
C(1)-C(3)	151.9(14)	153.0(20)	P(3)-C(9)	188.2(11)	186.8(14)
C(2)-C(3)	150.0(14)	148.4(19)	C(2)-C(21)	157.0(14)	152.7(20)
C(3)-C(4)	149.7(14)	151.1(22)			
Cl-M-P(1)	96.4(1)	96.5(1)	P(1)-C(1)-C(2)-C(21)	−169.6	−172.1
Cl-M-P(2)	96.2(1)	95.9(1)	M-C(3)-C(2)-C(21)	172.7	173.6
Cl-M-C(3)	175.9(3)	176.7(4)	C(4)-C(3)-C(2)-C(21)	−56.8	−40.9
P(1)-M-C(3)	83.8(3)	84.0(4)	C(1)-P(1)-M-Cl	177.5	177.3
P(2)-M-C(3)	83.3(3)	83.5(4)	C(6)-P(1)-M-Cl	−66.5	−66.1
P(1)-M-P(2)	166.8(1)	167.4(1)	C(7)-P(1)-M-Cl	65.3	65.5
M-P(1)-C(1)	103.0(4)	103.7(4)	C(5)-P(2)-M-Cl	−178.8	−177.6
M-P(2)-C(5)	103.6(3)	103.7(4)	C(8)-P(2)-M-Cl	67.2	67.3
P(1)-C(1)-C(2)	108.8(7)	110.6(11)	C(9)-P(2)-M-Cl	−66.8	−66.7
C(1)-C(2)-C(3)	112.1(9)	114.2(14)	C(1)-P(1)-M-C(3)	1.6	0.6
C(2)-C(3)-C(4)	111.3(9)	113.7(13)	C(6)-P(1)-M-C(3)	117.6	117.2
C(3)-C(4)-C(5)	112.2(9)	113.0(14)	C(7)-P(1)-M-C(3)	−110.6	−111.3
C(4)-C(5)-P(2)	107.3(7)	111.5(10)	C(5)-P(2)-M-C(3)	−2.8	−0.8
C(1)-C(2)-C(21)	110.3(9)	114.1(13)	C(8)-P(2)-M-C(3)	−116.9	−115.9
C(3)-C(2)-C(21)	111.9(9)	117.5(13)	C(9)-P(2)-M-C(3)	109.2	110.0

(2a) when treated with carbon monoxide and sodium propan-2-oxide gives a rhodium(I) carbonyl complex (1f).[5] Similar treatment of (2e) gives (1g) in 47% yield. This complex was characterised by microanalytical (Table 2) and mass spectral data (*m/e* = 504 for the molecular ion). The i.r. spectrum showed a very strong band at 1 923 cm^{-1} due to ν(CO) and the ^{31}P-{^{1}H} n.m.r. spectrum showed an ABX pattern with δP_A = 103.4 p.p.m., $^{1}J(\mathrm{RhP_A})$ = 155 Hz, δP_B = 87.7 p.p.m., $^{1}J(\mathrm{RhP_B})$ = 154 Hz, and $^{2}J(\mathrm{P_AP_B})$ = 259 Hz. These values of ^{1}J(RhP) are very similar to those of the complex (1f).[5]

X-Ray Diffraction Work.—The molecular structures of (1c) and (2c) are shown in Figure 2 and selected bond lengths, bond angles, and torsion angles are in Table 4. As can be seen from the Figure, the 2-methyl groups are equatorial in both complexes. There is a very close correspondence in the dimensions of the two molecules, although in (1c) the metal is four-co-ordinate, whilst in (2c) the metal is five-co-ordinate. The stereochemical effect of the metal–hydride bond appears to be small. As noted in a previous paper,[7] (1c) and (2c) are members of isomorphous series of closely related compounds, all of which crystallise in either the α- or β-structures: the present compounds both have α-structures. The angle C(3)–M–Cl is smaller in the β- than in the α-structures, *e.g.* for the three β-structures (2a), (2f), and (2b) this angle is 164.3(1), 160.2(2), and 162.4(2)°, respectively,[6,10] whilst for the α-structures (2a), (1c), and (2c) it is 169.0(2), 175.9(3), and 176.7(4)°, respectively. Thus packing forces are important. The hydride ligand was located by *X*-ray crystallography in the case of the three rhodium structures [10] and the hydride shown to be external to the C(3)–Rh–Cl angles quoted above. We have previously presented an argument [7] that the iridium complex $[\mathrm{IrH(Cl)(Bu^{t}{}_2PCH_2CHRCHCH_2CH_2PBu^{t}{}_2)}]$, with R = H, has a similar arrangement, *i.e.* (2b). Although we did not locate the hydride ligand in the iridium complex discussed in the present paper (with R = CH_3), we think it very likely that it has an analogous structure, *i.e.* (2c), since one would expect a transoid arrangement of H–C(3)–Ir–H to be formed much

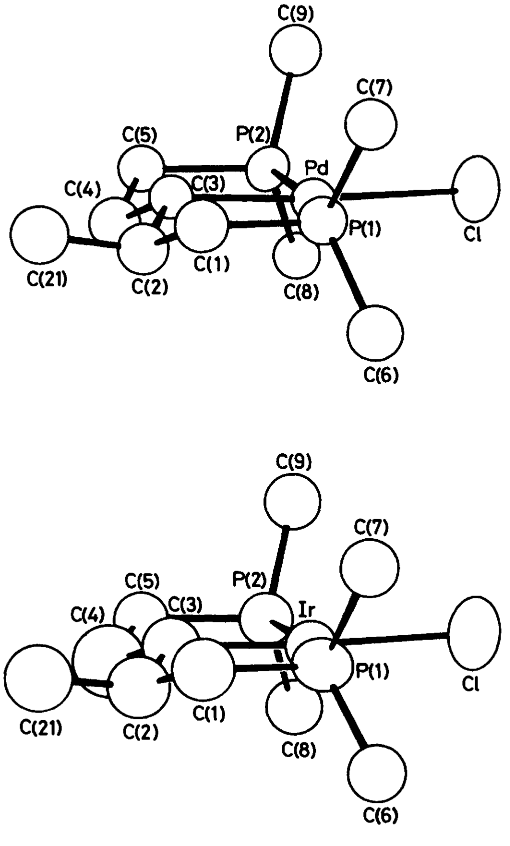

Figure 2. ORTEP drawings of the molecular structures of the palladium complex (1c) and of the iridium complex (2c). 50% Probability thermal ellipsoids are shown. For clarity the methyls of the t-butyl groups are not shown

Table 5. Atomic co-ordinates with estimated standard deviations in parentheses for the palladium (upper values) and for the iridium compound (lower values)

Atom	x	y	z	Atom	x	y	z
Pd	0.126 66(6)	0.152 06(5)	0.233 03(5)	C(21)	0.201 9(9)	0.078 2(6)	0.560 4(8)
Ir	0.127 54(4)	0.150 91(3)	0.235 72(4)		0.206 8(13)	0.070 9(9)	0.558 5(12)
Cl	0.145 5(2)	0.191 3(2)	0.064 9(2)	C(61)	0.540 7(12)	0.071 2(8)	0.325 4(11)
	0.144 2(2)	0.194 7(2)	0.070 2(2)		0.540 0(18)	0.067 7(12)	0.324 6(17)
P(1)	0.321 5(2)	0.152 3(2)	0.310 0(2)	C(62)	0.352 0(12)	−0.009 2(9)	0.278 4(11)
	0.322 1(2)	0.147 8(2)	0.309 9(2)		0.358 1(19)	−0.013 8(16)	0.278 1(16)
P(2)	−0.074 1(2)	0.152 8(2)	0.193 9(2)	C(63)	0.405 4(12)	0.079 2(7)	0.152 1(9)
	−0.072 1(2)	0.151 2(2)	0.197 1(2)		0.405 0(16)	0.081 3(11)	0.155 5(13)
C(1)	0.324 9(9)	0.127 7(6)	0.443 6(7)	C(71)	0.508 0(11)	0.262 9(7)	0.406 3(9)
	0.329 2(12)	0.120 2(8)	0.440 1(11)		0.504 7(18)	0.254 5(12)	0.405 5(14)
C(2)	0.212 4(8)	0.085 7(6)	0.447 3(7)	C(72)	0.295 2(11)	0.315 7(7)	0.334 1(8)
	0.214 0(13)	0.085 0(9)	0.449 8(12)		0.294 7(17)	0.308 8(12)	0.339 0(13)
C(3)	0.109 0(7)	0.126 9(6)	0.380 8(6)	C(73)	0.426 9(9)	0.274 8(6)	0.216 6(7)
	0.111 4(12)	0.120 4(8)	0.378 8(9)		0.423 6(12)	0.273 6(8)	0.224 0(11)
C(4)	−0.000 7(8)	0.083 6(6)	0.383 6(7)	C(81)	−0.285 2(9)	0.069 2(6)	0.090 4(8)
	−0.001 9(16)	0.086 6(11)	0.390 8(13)		−0.281 0(13)	0.072 0(9)	0.090 8(12)
C(5)	−0.109 1(8)	0.125 8(6)	0.316 3(7)	C(82)	−0.095 2(9)	−0.009 1(7)	0.149 0(8)
	−0.106 2(11)	0.123 3(7)	0.316 8(9)		−0.101 1(17)	−0.010 8(12)	0.148 4(13)
C(6)	0.413 4(9)	0.071 4(7)	0.264 5(7)	C(83)	−0.122 1(11)	0.081 9(7)	−0.003 6(8)
	0.410 2(12)	0.069 3(8)	0.260 2(11)		−0.125 0(16)	0.084 4(11)	0.002 2(12)
C(7)	0.393 0(8)	0.253 5(6)	0.318 0(7)	C(91)	−0.266 1(11)	0.262 8(7)	0.181 0(8)
	0.395 2(12)	0.247 8(8)	0.321 9(11)		−0.261 5(16)	0.261 8(11)	0.187 1(12)
C(8)	−0.149 1(7)	0.072 9(6)	0.102 0(6)	C(92)	−0.055 3(12)	0.316 8(8)	0.235 7(9)
	−0.148 4(12)	0.074 2(7)	0.103 9(9)		−0.056 2(18)	0.312 3(13)	0.239 7(14)
C(9)	−0.141 5(8)	0.256 1(6)	0.163 9(7)	C(93)	−0.150 7(11)	0.277 7(7)	0.050 9(8)
	−0.137 6(12)	0.254 1(7)	0.171 7(9)		−0.146 6(17)	0.277 2(12)	0.057 0(14)

more easily by the concerted *cis* addition of HC–H to iridium than a cisoid arrangement.

Experimental

The general techniques used were the same as in other recent papers from this laboratory.[11] The ^{1}H, ^{1}H-{^{31}P}, ^{31}P-{^{1}H}, and ^{13}C-{^{1}H} n.m.r. spectra were recorded with a JEOL FX 1000 n.m.r. spectrometer using an internal deuterium lock. Except where otherwise stated, measurements were made at ambient temperatures (*ca.* 296 K). Reactions were conducted under a nitrogen or argon atmosphere.

$Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2$ (L).—A solution of 1,5-dibromo-2-methylpentane (37.0 g, 0.15 mol) in dry diethyl ether (60 cm^3) was added dropwise, with rapid stirring, to lithium foil (6.32 g, 0.91 mol) in dry ether (250 cm^3) at −15 °C. The resultant solution of the dilithio-reagent was filtered and estimated to contain 0.18 mol lithium by titration. It was added dropwise to a solution of PBu^t_2Cl (30.25 g, 0.17 mol) in dry ether (50 cm^3) over a period of 70 min. The mixture was then hydrolysed with water (100 cm^3) and the product isolated by distillation. It was obtained as a viscous oil, b.p. 140 °C ($\approx$1.34 Pa). Yield 17.6 g, 56%.

Treatment of $[PdCl_2(NCPh)_2]$ *with* L.—A solution of the diphosphine (L) (0.24 g, 0.64 mmol) in 2-methoxyethanol (10 cm^3) was added to a solution of $[PdCl_2(NCPh)_2]$ (0.24 g, 0.61 mmol) in 2-methoxyethanol (7 cm^3) and the resultant mixture was heated under reflux for 15 min, filtered, and the filtrate evaporated to dryness. The residue was extracted exhaustively with n-pentane to give a pale yellow extract and an insoluble residue. Isolation of the extract gave (1c) as pale yellow needles, from n-pentane. Yield 0.11 g, 36%.

Preparation of $[Pt_2Cl_4\{Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2\}_2]$.—A suspension of $[PtCl_2(NCBu^t)_2]$ (0.30 g, 0.69 mmol) in ethanol (10 cm^3) was treated with a solution of L (0.29 g, 0.76 mmol) in ethanol (5 cm^3) and the mixture refluxed for 3.5 h, to give a yellow solution. The solvent was removed under reduced pressure and the residual oil triturated with n-hexane to give the required product, as a pale yellow solid. Yield 0.45 g.

Conversion of $[Pt_2Cl_4\{Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2\}_2]$ *into* (1d) + (1e).—A solution of $[Pt_2Cl_4\{Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2\}_2]$ (0.20 g, 0.32 mmol) in CF_3COOH (10 cm^3) was heated under reflux for 2.75 h; the solvent was then evaporated to give an orange oil. Lithium chloride (0.13 g, 3.17 mmol) and acetone (4 cm^3) were then added and the resultant mixture refluxed for 15 min. The solution was filtered, evaporated to dryness, and the product isolated with n-pentane, as pale yellow microcrystals. Yield 0.090 g, 46%.

Treatment of $[Ir_2Cl_2(C_8H_{14})_4]$ *with* L.—A suspension of $[Ir_2Cl_2(C_8H_{14})_4]$ (0.68 g, 0.76 mmol) in benzene (10 cm^3) was treated with a solution of $Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2$ (0.71 g, 1.89 mmol) in benzene (6 cm^3) and the mixture was refluxed for 16 h. The resultant solution was filtered and evaporated to an oil which was taken up in acetone. Orange prisms of the cyclometallated complex (2c) separated. Yield 0.33 g.

Treatment of $RhCl_3 \cdot 3H_2O$ *with* L.—A solution of the diphosphine (L) (0.58 g, 1.55 mmol) in propan-2-ol (10 cm^3) was added to a solution of $RhCl_3 \cdot 3H_2O$ (41.5% Rh, 0.31 g, 1.24 g atom of Rh) in propan-2-ol. A chocolate brown precipitate was formed rapidly but this gradually dissolved on heating. After reflux for 4 h the mixture was filtered and the resultant orange-yellow solution evaporated to dryness. Extraction with n-pentane gave a yellow-brown residue (0.26 g) and a yellow solid (0.20 g) was isolated from the n-pentane extract and shown, by ^{31}P-{^{1}H} n.m.r. spectroscopy, to be a three-component mixture (see Discussion).

Preparation of $[RhH(Cl)\{Bu^t_2PCH_2CHMeCH(CH_2)_2PBu^t_2\}]$ (2e).—A solution of L (0.44 g, 1.16 mmol) in benzene

(8 cm^3) was added to a suspension of [$Rh_2Cl_2(C_8H_{14})_4$] (0.38 g, 0.53 mmol) in benzene (6 cm^3). The resultant mixture was refluxed for 2.5 h and the hot solution filtered and evaporated to dryness. The product was extracted into hot hexane which was then removed under reduced pressure. The product formed orange-yellow microcrystals from n-pentane. Yield 0.28 g, 51%.

Preparation of [$\mathrm{Rh(CO)\{Bu^t_2PCH_2CHMeCH(CH_2)_2PBu^t_2\}}$] (1g).—A solution of sodium propan-2-oxide in propan-2-ol (0.8 cm^3, 0.113 mol dm^{-3}) was added to a solution of (2e) (0.040 g, 0.08 mmol) in acetone (2 cm^3). Carbon monoxide was bubbled briskly through the resultant solution for *ca.* 5 min. The volume of the solution was reduced at the pump and water (2.5 cm^3) added. The resultant yellow solid was extracted into benzene and isolated. It formed yellow microcrystals from benzene–methanol. Yield 0.02 g, 50%.

Crystal Data.—(1c), $C_{22}H_{47}ClP_2Pd$, $M = 515.4$, Monoclinic, $a = 1.1907(3)$, $b = 1.6466(4)$, $c = 1.3537(4)$ nm, $\beta = 103.99(2)°$, $U = 2.5754(10)$ nm^3, $Z = 4$, $D_c = 1.329$ Mg m^{-3}, $F(000) = 1\,088$, space group $P2_1/c$, Mo-K_α radiation, $\lambda = 71.069$ pm, μ(Mo-K_α) = 943 m^{-1}.

(2c), $C_{22}H_{48}ClIrP_2$, $M = 874.25$, Monoclinic, $a = 1.1954(4)$, $b = 1.6509(5)$, $c = 1.3665(5)$ nm, $\beta = 104.18(3)°$, $U = 2.6146(15)$ nm^3, $Z = 4$, $D_c = 2.221$ Mg m^{-3}, $F(000) = 1\,216$, space group $P2_1/c$, Mo-K_α radiation, $\lambda = 71.069$ pm, μ(Mo-K_α) = 5 315 m^{-1}.

Structure Determination.—Measurements were made on a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations for each compound were determined by least-squares treatment of the setting angles of 15 reflections with $35 < 2\theta < 40°$. Intensities of all independent reflections with $4 < 2\theta < 45°$ were measured in the ω—2θ scan mode. The data were corrected for Lorentz, polarisation, and transmission factors and the structure analyses used the 2 557 reflections for (1c) and the 2 550 reflections for (2c) having $I > 3\sigma(I)$. The compounds (1c) and (2c) are isomorphous with the α form of [$\mathrm{RhH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)}$] (see Table 4 in ref. 7). The structure of (1c) was determined by using the co-ordinates of the rhodium complex as starting point, and locating the 2-methyl carbon atom from a subsequent difference map. The structure of (2c) used the co-ordinates of (1c) as starting point. Both (1c) and (2c) were refined by full-matrix least squares with allowance for anisotropic vibrations for the metal, phosphorus, and chlorine atoms, and isotropic vibrations for carbon atoms. Hydrogen atoms were not included, and the final R values were 0.061 for (1c) and 0.048 for (2c). The atomic co-ordinates and their estimated standard deviations are listed in Table 5.

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