Transition Metal–Carbon Bonds. Part 52.[1] Large Ring and Cyclometallated Complexes formed from $Bu^t_2PCH_2CH_2CHRCH_2CH_2PBu^t_2$ (R = H or Me) and $IrCl_3$, or $[Ir_2Cl_4(\text{cyclo-octene})_4]$: Crystal Structures of the Cyclometallated Hydride, $[IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$, and the Carbene Complex $[IrCl(Bu^t_2PCH_2CH_2CCH_2CH_2PBu^t_2)]$ †

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Treatment of $Bu^t_2P(CH_2)_5PBu^t_2$ with iridium trichloride gives a mixture of the 16-atom ring dihydride $[Ir_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, a co-ordinatively saturated cyclometallated hydride, $[IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ (1b), which is non-fluxional, and an unidentified complex. A better route to the cyclometallated hydride (1b) is to treat $[Ir_2Cl_2(C_8H_{14})_4]$ (C_8H_{14} = cyclo-octene) with the diphosphine. Complex (1b) takes up carbon monoxide to give the six-co-ordinate $[IrHCl(CO)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ and loses dihydrogen on heating [*ca.* 200 °C (15 mmHg)] to give the very dark carbene/ylide complex $[IrCl(Bu^t_2PCH_2CH_2CCH_2CH_2PBu^t_2)]$ (3)/(4). This carbene/ylide complex takes up dihydrogen at 20 °C (1 atm) to give back (1b). The diphosphine $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ reacts with $IrCl_3$ to give the 16-atom ring chelate $[Ir_2H_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2]$, no cyclometallated product being detected. However, the complex $[IrHCl(Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2)]$, can be prepared from $[Ir_2Cl_2(C_8H_{14})_4]$ and the diphosphine. Hydrogen-1, ^{13}C, and ^{31}P n.m.r. and i.r. data are reported. The crystal structures of (1b) and of the carbene/ylide (3)/(4) have been determined. Cell dimensions are, for (1b), a = 1 231.8(3), b = 1 435.9(3), c = 1 485.4(3) pm, and β = 104.82(2)° and for (3)/(4), a = 1 232.6(3), b = 1 436.2(3), c = 1 480.7(3) pm, and β = 104.87(2)°. The structures are isomorphous, with space group $P2_1/c$ and Z = 4.

We have shown that steric and conformational effects can cause long-chain αω-diphosphines (i) to give stable large-ring chelates or (ii) to cyclometallate, with metal–carbon bond formation.[2,3] Thus, the diphosphine, $Bu^t_2P(CH_2)_5PBu^t_2$, with the sterically demanding end groups PBu^t_2, reacts with platinum(II) chloride to give the 16-atom ring chelate $[Pt_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, and the cyclometallated complex, $[PtCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$.[4] Similarly, with rhodium(III) chloride, this pentamethylene diphosphine gives the binuclear, 16-atom ring five-co-ordinate hydride $[Rh_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ and the cyclometallated hydride, $[RhHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$, which is fluxional.[5,6] Similar results have been obtained for other diphosphines with platinum, rhodium, and palladium.[2-7] We now describe the reactions of iridium with the diphosphines $Bu^t_2P(CH_2)_5PBu^t_2$ and $Bu_2{}^tPCH_2CH_2CHMeCH_2CH_2PBu^t_2$. Some of this work has been published as a preliminary communication.[8]

RESULTS AND DISCUSSION

A solution of hydrated iridium trichloride in propan-2-ol, when refluxed with $Bu^t_2P(CH_2)_5PBu^t_2$ for 3 days, gave a mixture of three iridium-containing products, a binuclear complex $[Ir_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, a cyclometallated hydride $[IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$, and a completely insoluble red-brown material. The red-brown material showed a strong band at 313 cm^{-1} due to ν(Ir–Cl) but we could not purify or identify it. The binuclear complex, see Table 1 for microanalytical and molecular-weight data, is deep purple and shows an electronic absorption spectrum with absorptions [$\lambda_{max.}$ (ε per Ir atom/dm^3 mol^{-1} cm^{-1})] at 429 (402), 462 (501), 525 (372), and 567 nm (412), in benzene solution: these are closely similar to those we reported for the square-pyramidal hydride, $[IrHCl_2(PBu^t_2Pr^n)_2]$.[9] This binuclear complex is non-volatile and shows a single strong band at 314 cm^{-1} due to a *trans*-Cl–Ir–Cl moiety. No i.r. absorption bands were observed in the range 1 800—2 300 cm^{-1}, presumably because the intensity of ν(Ir–H) is so weak: other five-co-ordinate iridium(III) hydrides also show bands due to ν(Ir–H) which are of very low intensity.[10-12] The ^1H n.m.r. spectrum of this binuclear hydride (in $CDCl_3$) showed a 1 : 2 : 1 triplet hydride resonance at δ −48.8, ^1J(P–H) = 11 Hz and two 1 : 2 : 1 triplet Bu^t patterns at δ 1.43 and 1.48 with $|^3J(P-H) + {}^5J(P-H)|$ = 12.1 and 12.3 Hz respectively. This binuclear complex presumably has an analogous structure to the rhodium complex, $[Rh_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$.[6] The cyclometallated, mononuclear complex is soluble in light petroleum and volatile, subliming slowly at *ca.* 200 °C (1 atm ‡) on a Kofler micro-

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† [1,5-Bis(di-t-butylphosphino)pent-3-yl-C^3PP']chlorohydridoiridium(III) and [1,5-bis(di-t-butylphosphino)pent-3-ylidene-$C^{3,3}PP'$]chloroiridium(III).

‡ Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 1

Microanalytical,[a] molecular-weight,[b] and melting-point data

Complex	M.p. (θ_c/°C)	Analysis (%) C	H	Halogen	M[b]
$[Ir_2H_2Cl_4\{Bu^t{}_2P(CH_2)_5PBu^t{}_2\}_2]$	265—290[c]	40.45 (40.4)	7.6 (7.6)	11.8 (11.35)	1 300 (1 249)
(1b) $[IrHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)]$	195—208[d]	43.25 (42.9)	7.65 (7.9)	5.85 (6.05)	595 (588)
$[IrHCl(CO)(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)]$	208—223[c]	43.05 (42.9)	7.45 (7.5)	5.65 (5.25)	630 (616)
(3) $[IrCl(Bu^t{}_2PCH_2CH_2CCH_2CH_2PBu^t{}_2)]$	208—215[c]	43.25 (43.1)	7.65 (7.55)	5.85 (6.05)	594 (586)
$[Ir_2H_2Cl_4(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)_2]$	267—284[c]	41.6 (41.4)	7.8 (7.7)	11.4 (11.1)	1 250 (1 277)

[a] Calculated values are given in parentheses. [b] Measured in chloroform solution, calculated values are given in parentheses. [c] With decomposition. [d] Sublimes with decomposition.

scope hot-stage, during which some decomposition to an almost black, volatile carbene or ylide complex also occurs (see below).

Characterizing elemental analytical and molecular-weight data for $[IrHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)]$ are given in Table 1. The ^{1}H n.m.r. spectrum (in $CDCl_3$) (Table 2) showed a hydride triplet at δ −44.7, ^2J(P–H) = 12 Hz, and two Bu^t triplets at δ 1.30 and 1.14 with $|^3J(P\text{–}H) + {}^5J(P\text{–}H)| = 12.8$ Hz, in each case. In C_6D_6 the hydride resonance consisted of a doublet of triplets at δ = −43.3, ^2J(P–H) = 12.0 and ^3J(H–H) = 5 Hz. The ^{31}P n.m.r. spectrum showed a sharp singlet resonance at 76.1 p.p.m. (in $CDCl_3$). Data from the ^{13}C-{^{1}H} n.m.r. spectrum of the hydride are given in Table 3. δ Values and values of J(P–C) are similar to those for the corresponding rhodium hydride $[RhHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)]$[6] except that the δ value (31.1) for *C*H in the iridium complex is much lower than for the rhodium complex (51.4). We cannot explain this difference. The iridium complex is not fluxional so that the δ values for two t-butyl groups are different from the other two, whereas with the rhodium complex, which is fluxional at room temperature, all four t-butyl groups are equivalent.

The i.r. spectrum of the cyclometallated hydride showed no band which we could assign to ν(Ir–H) but there was a strong band at 267 cm^{-1} characteristic of ν(Ir–Cl) with *trans* σ-bonded carbon. The electronic absorption spectrum in the visible region showed a maximum at 424 nm (ε = 601) with a shoulder at 477 nm (ε = 437 dm^3 mol^{-1} cm^{-1}) (in benzene solution).

By analogy with the cyclometallated rhodium complex $[RhHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)]$, which has the configuration (1a),[5] we might expect the iridium complex to have a similar transoid configuration (1b) rather than the alternative configuration (2) with the cisoid arrangement of H–C–Ir–H. This aspect of the stereochemistry is discussed below.

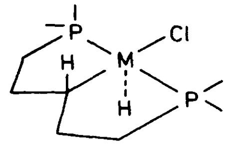
A characteristic of the highly coloured five-co-ordinate iridium hydrides, $[IrHCl_2(PR_3)_2]$, is that they rapidly take up carbon monoxide to give six-co-ordinate compounds, $[IrHCl_2(CO)(PR_3)_2]$, which are pale yellow.[13]

TABLE 2

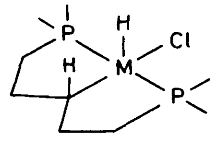
Hydrogen-1 and ^{31}P-{^{1}H} n.m.r. and i.r. data (cm^{-1})

Complex	^{1}H[a] δ(Bu^t)	Other resonances	δ(P)[b]	ν(Ir–Cl)[c]
$[Ir_2H_2Cl_4\{Bu^t{}_2P(CH_2)_5PBu^t{}_2\}_2]$	1.48 (12.3, t) 1.43 (12.1, t)	−48.8 (11.2, t) Ir–*H*		314s
(1b) $[IrHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)]$[d]	1.3 (12.8, t) 1.14 (12.8, t)	−44.7 (12.2, t) Ir–*H*	76.1	267s
$[IrHCl(CO)(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)]$[e]	1.39 (13.2, t) 1.32 (13.2, t)	−8.95 (17.2, t) Ir–*H*		
(3) $[IrCl(Bu^t{}_2PCH_2CH_2CCH_2CH_2PBu^t{}_2)]$	1.41 (12.9, t)	−2.77 (7.1, qnt) Ir=C–C*H*	83.4	279s
$[Ir_2H_2Cl_4(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)_2]$[f]		−49.75 (12, t) (Ir–*H*) 1.02 (s) CH_3–CH		313s

[a] Spectra recorded at *ca.* 35 °C and 60 MHz in $CDCl_3$ solution. δ Values ±0.02 p.p.m. J Values, shown in parentheses ±0.2 Hz; t = triplet, dt = doublet of triplets, qnt = 1 : 4 : 6 : 4 : 1 quintet, m = complex multiplet. [b] Spectra recorded at *ca.* 20 °C and 36.43 MHz in $CDCl_3$. Chemical shifts relative to 85% H_3PO_4 ± 0.1 p.p.m. All resonances were singlets. [c] In Nujol unless otherwise stated. [d] In C_6D_6. δ = −43.3 (dt), ^2J(P–H) = 12.0 Hz, ^3J(H–H) = 5 Hz. [e] ν(CO) 1 969 and 1 954 cm^{-1}, ν(Ir–H) 2 168 cm^{-1} in benzene. [f] ν(Ir–H) 2 220w cm^{-1} as KCl disc.



(1a; M = Rh)
(1b; M = Ir)

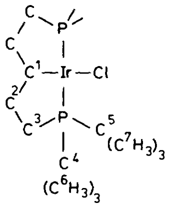


(2)

We find that the cyclometallated hydride reacts rapidly with carbon monoxide to give the pale yellow complex $[\overline{IrHCl(CO)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2})]$ (see Exmental section for further details, Table 1 for microanalytical and molecular-weight data, and Table 2 for i.r. and n.m.r. data).

TABLE 3

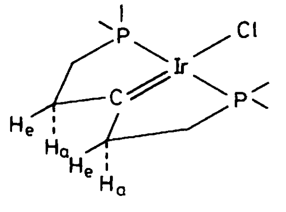
^{13}C-$\{^1H\}$ N.m.r. data[a] for $[\overline{IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2})]$ (1b) and $[\overline{IrCl(Bu^t_2PCH_2CH_2CCH_2CH_2PBu^t_2})]$ (3)



Atom	Hydride	Carbene
C^1	31.1 (s)	66.6 (t), $^2J(PC)$ = 18 Hz
C^2 [$^2J(PC) + {}^4J(PC)$]	44.4 [13] (t)	*b*
C^3 [$^1J(PC) + {}^3J(PC)$]	25.6 [25] (t)	21.1 [21] (t)
C^4 } [$^1J(PC) + {}^3J(PC)$]	36.8 [23] (t)	*b*
C^5 }	35.2 [20] (t)	
C^6	29.4 (s)	30.1 (s)
C^7	29.2 (s)	

[a] Spectra recorded at *ca.* 20 °C and 22.62 MHz in C_6D_6. Shifts relative to $SiMe_4$ as internal standard. Shifts to high frequency are positive. δ Values ±0.1 p.p.m., *J* values ±1.5 Hz; s = singlet, t = triplet. [b] No assignment made (see text).

When the cyclometallated iridium hydride compound $[\overline{IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2})]$ was heated at 200 °C (15 mmHg) in a sublimation tube a very dark brown (almost black) crystalline sublimate formed although there was some non-volatile decomposition residue. This experiment worked best on a small scale (15—20 mg); on a larger scale more decomposition to give a non-volatile residue took place. The sublimate was contaminated with much unchanged reactant $[\overline{IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2})]$ but by successive sublimations the proportion of unchanged hydride fell to a low level, as deduced from the ^{31}P-$\{^1H\}$ n.m.r. spectrum, which showed a singlet at δ = 83.4 p.p.m. due to the very dark brown component and a singlet at δ = 76.1 p.p.m. due to the cyclometallated hydride. Since each sublimation caused further decomposition to involatile residues, the amount of pure dark brown compound available to us was small and we were not able to study its chemistry in detail. Sublimations at either a lower or higher pressure were less satisfactory in producing the dark brown compound. Microanalytical and molecular-weight data (Table 1) and other evidence (see below) show that this dark brown compound is formed from the cyclometallated hydride by loss of two hydrogens. The mass spectrum of the dark brown sublimate and of $[\overline{IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2})]$ were identical, with the most intense peak of the parent molecular ion at *m/e* 586 whereas the calculated most intense peak for $[\overline{IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2})]$ is *m/e* = 588. Moreover, a benzene solution of the dark brown sublimate when stirred under dihydrogen (1 atm) at 20 °C rapidly turned red-orange (over a few minutes) and the cyclometallated hydride was isolated in essentially quantitative yield and characterized by its i.r. and ^1H n.m.r. spectra. The structure of the dark brown complex was determined by *X*-ray diffraction (see below) and has been described previously in a preliminary publication.[8] The structural determination has now been further refined including location of the hydrogens, and shows the compound to be a carbene or ylide complex, (3) or (4) respectively.



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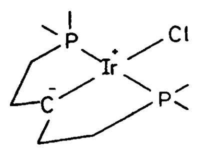


(4)

The dark brown complex showed a strong i.r. absorption at 279 cm⁻¹ due to ν(Ir–Cl). The proton n.m.r. spectrum showed no hydride resonance and one t-butyl triplet resonance at δ 1.41 p.p.m., $|^3J(P-H) + {}^5J(P-H)|$ = 12.9 Hz. The most distinctive feature of the ^1H n.m.r. spectrum was a quintet at δ = −2.77 p.p.m. of approximate relative intensities 1 : 4 : 6 : 4 : 1 with a splitting of 7.1 Hz. On decoupling the phosphorus nuclei, this quintet changed to a triplet (approximate intensity ratios of 1 : 2 : 1). The intensity of the quintet pattern corresponded to two hydrogens and we assign it to two hydrogens adjacent to the carbene carbon, either *pseudo*-axial (H_a) or *pseudo*-equatorial (H_e) as in (3). These protons are presumably abnormally shielded because they are adjacent to the unusual C=Ir or ^-C–Ir^+ moiety. It is noteworthy that a deceptively simple quintet pattern is shown for the methyl protons in *trans*-$[MX_2(PEt_3)_2]$ complexes (M = Pd or Pt; X = Cl, Br, or I).[14,15]

We did not have sufficient of the pure carbene ylide complex to record its ^{13}C-$\{^1H\}$ spectrum. However, we recorded the ^{13}C-$\{^1H\}$ spectrum of a mixture of the carbene with the cyclometallated hydride. The resonances due to the hydride were readily identified and the remainder were assigned to the carbene. In particular there was a triplet at δ = 66.6 p.p.m., $^2J(P-C)$ = 18 Hz, which we assign to *C*=Ir, a singlet at δ = 30.1 p.p.m. which we assign to CH_3, and a triplet at δ = 21.1 p.p.m. $|^1J(PC) + {}^3J(PC)|$ = 12 Hz which we tentatively assign to CH_2P. The resonances due to the other two types of carbon were obscured. There were no other resonances either at very high or at very low frequency, regions normally characteristic of carbenes[16] or ylides[17] respectively. Thus we suggest that our dark brown complex is intermediate between a carbene (3) and an ylide (4).

The transoid arrangement of the H–C–Rh–H moiety in $[\mathrm{RhHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)}]$, which is a fluxional molecule, was established by *X*-ray crystallography.[5] This transoid configuration (1a; M = Rh) is what one would expect to result from a concerted addition of C–H to Rh. We therefore assigned a similar transoid configuration (1b; M = Ir) to the iridium complex and explained the lack of fluxionality in terms of the greater inertness of iridium over rhodium. However, the addition of dihydrogen to the carbene ylide complex (3)/(4) under very mild conditions, to give the cyclometallated hydride, made us think that the configuration of the cyclometallated hydride might be cisoid, *i.e.* (2). The question has been resolved with a reasonable degree of certainty by determining the crystal structure.

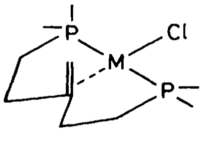
X-*Ray Diffraction Work*.—We have previously reported[5] that $[\mathrm{RhHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)}]$ (1a) occurs in two crystalline forms (α and β) and have determined the structure of each. The dimensions of the molecule do not differ significantly in the α and β forms.[5] We have now examined seven other structurally similar compounds of Rh, Pd, and Ir [complexes (5)—(9)] and each of these was found to be isomorphous with either the α or β form of (1a). The cell dimensions of these compounds are given in Table 4. As can be seen they are all remarkably similar. It is convenient to give in this Table the cell dimensions for complexes whose structures have been solved but not yet reported. We now describe the crystal structures of $[\mathrm{IrHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)}]$ (1b) and $[\mathrm{IrCl(Bu^t{}_2PCH_2CH_2CCH_2CH_2PBu^t{}_2)}]$ (3)/(4), both of which have the β structure. Details of these two crystal structures are shown in Figures 1 and 2 and selected bond lengths and angles are given in Table 5. All the hydrogens in the carbene complex and all the hydrogens in the cyclometallated hydride, except the one attached to the iridium, were located. However, as can be seen from Table 5 the angle Cl–Ir–C(3) *decreases* in

TABLE 4

Lattice parameters of compounds having the α or β structure. All are in space group $P2_1/c$ with $Z = 4$

Compd.	*a*/pm	*b*/pm	*c*/pm	β/°
(*a*) α Structures				
(1a) [a]	1 190.6(2)	1 642.7(3)	1 324.5(2)	104.13(1)
(5) [a]	1 206.0(2)	1 659.2(3)	1 305.2(3)	105.59(2)
(7) [b]	1 186.2(2)	1 634.9(3)	1 332.9(3)	104.70(2)
(8) [b]	1 190.7(3)	1 646.6(4)	1 353.7(4)	103.99(2)
(9) [b]	1 195.4(4)	1 650.9(5)	1 366.5(5)	104.18(3)
(*b*) β Structures				
(1a) [a]	1 231.6(3)	1 437.3(3)	1 484.1(2)	104.82(2)
(6) [a]	1 239.9(3)	1 423.2(3)	1 561.6(2)	107.14(2)
(3)	1 232.6(3)	1 436.2(3)	1 480.7(3)	104.87(2)
(1b)	1 231.8(3)	1 435.9(3)	1 485.4(3)	104.82(2)

[a] Ref. 5. [b] W. S. McDonald, unpublished work.



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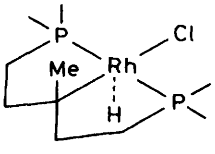

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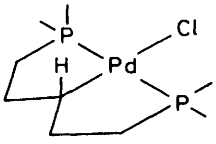

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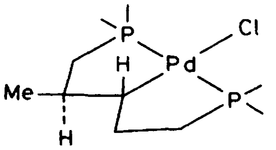

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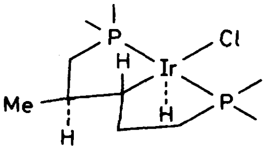

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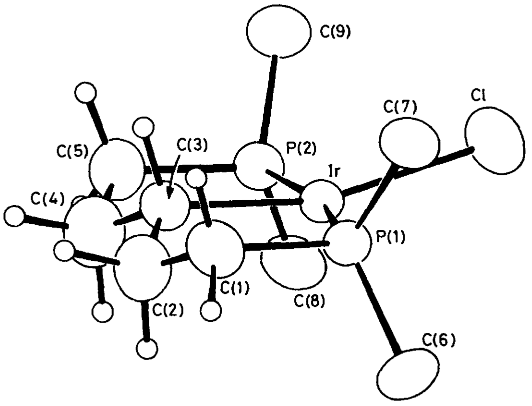

FIGURE 1 ORTEP drawing of the molecular structure of hydride (1b). Methyl groups have been omitted and hydrogen atoms given artificial thermal parameters of $B = 0.5$ Å^2

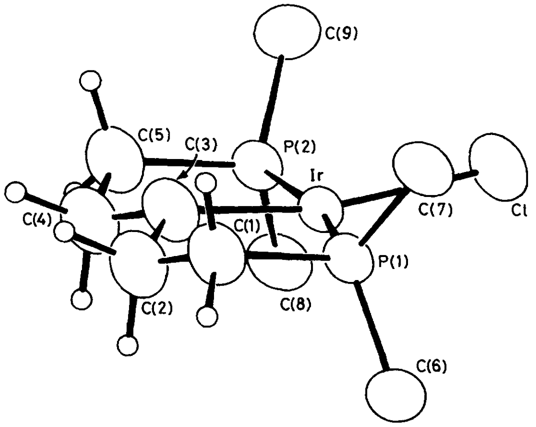

FIGURE 2 ORTEP drawing of the molecular structure of carbene (3). Methyl groups have been omitted and hydrogen atoms given artificial thermal parameters of $B = 0.5$ Å^2

going from the carbene complex, 166.7(2)°, to the cyclometallated hydride complex, 162.4(2)° [this angle being on the same side of the molecule as the C(3)–H bond] (Figure 1). It thus seems more likely that the missing hydride atom is external to this angle and that H–C(3)–Ir–H is transoid as in (1a), *i.e.* with a *ca.* 180° torsion angle rather than cisoid or eclipsed as in (2), with a torsion angle of *ca.* 0°. The rhodium complex (1a), $[\mathrm{RhHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)}]$, the crystal structure of which has been determined, also has a non-linear arrangement C(3)–Rh–Cl with a bond angle[5] of 164.3(1)° and in this case the hydrogen attached to rhodium was located and external to this angle, *i.e.* the arrangement H–C(3)–Rh–H has a torsion angle of *ca.* 180°. We are thus reasonably certain that the iridium complex also has structure (1a). We must therefore assume that the ready addition of dihydrogen to the carbene complex (3) is not simply the *cis* addition of two hydrogens to a double (*i.e.* a C=Ir) bond and involves more than one step. Possibly *cis* addition occurs first to give (2) but reductive elimination then occurs to give an eight-membered chelate ring which then oxidatively adds to give (1b).

TABLE 5

Bond lengths (pm) and angles (°) with estimated standard deviations in parentheses

	Compound (1b)	Compound (3)
Ir–P(1)	230.8(2)	230.3(1)
Ir–P(2)	231.1(2)	230.2(1)
Ir–Cl	241.8(2)	241.4(1)
Ir–C(3)	210.6(7)	199.7(5)
P(1)–C(1)	184.1(6)	184.3(5)
P(1)–C(6)	189.7(6)	188.4(5)
P(1)–C(7)	188.5(7)	189.2(5)
P(2)–C(5)	185.2(8)	185.0(6)
P(2)–C(8)	186.9(7)	187.0(6)
P(2)–C(9)	189.2(7)	189.3(6)
C(1)–C(2)	149.9(9)	152.1(7)
C(2)–C(3)	149.2(10)	150.6(8)
C(3)–C(4)	151.9(10)	150.2(8)
C(4)–C(5)	153.0(11)	150.6(9)
C(6)–C(61)	154.3(10)	152.6(8)
C(6)–C(62)	152.1(11)	154.2(8)
C(6)–C(63)	151.3(11)	150.4(9)
C(7)–C(71)	152.4(11)	152.1(8)
C(7)–C(72)	157.2(11)	156.0(9)
C(7)–C(73)	154.7(11)	154.7(8)
C(8)–C(81)	155.4(10)	153.6(8)
C(8)–C(82)	152.1(11)	150.7(9)
C(8)–C(83)	157.3(11)	156.5(10)
C(9)–C(91)	153.0(9)	152.1(8)
C(9)–C(92)	151.8(10)	155.6(8)
C(9)–C(93)	152.7(11)	152.5(9)
C(3)–H(3)	85(9)	
Cl–Ir–C(3)	162.4(2)	166.7(2)
P(1)–Ir–P(2)	167.5(1)	168.1(1)
Cl–Ir–P(1)	96.3(1)	96.0(1)
Cl–Ir–P(2)	96.1(1)	95.8(1)
C(3)–Ir–P(1)	83.2(2)	84.2(1)
C(3)–Ir–P(2)	84.6(2)	84.1(1)
Ir–C(3)–C(2)	114.8(4)	119.6(3)
Ir–C(3)–C(4)	113.2(5)	119.2(4)
C(2)–C(3)–C(4)	113.0(6)	111.1(4)
Ir–P(1)–C(1)	103.5(2)	103.0(2)
Ir–P(1)–C(6)	115.8(2)	115.5(2)
Ir–P(1)–C(7)	116.2(2)	117.0(2)
Ir–P(2)–C(5)	103.1(3)	102.5(2)
Ir–P(2)–C(8)	115.5(2)	115.5(2)
Ir–P(2)–C(9)	116.5(2)	117.3(2)
P(1)–C(1)–C(2)	108.2(5)	108.4(4)
P(2)–C(5)–C(4)	108.5(5)	109.4(4)
C(1)–C(2)–C(3)	113.8(6)	113.0(4)
C(3)–C(4)–C(5)	113.4(6)	112.8(5)
Ir–C(3)–H(3)	98(6)	
C(2)–C(3)–H(3)	114(6)	
C(4)–C(3)–H(3)	102(6)	

Other features of the bond parameters for the two compounds (see Table 5) are that the iridium–chlorine bond lengths are virtually the same whereas, as would be expected, the iridium–carbon bond length in the carbene complex is much less than in the hydride, 199.7(5) and 210.6(7) pm, respectively. The Ir–C(3)–C(2) or Ir–C(3)–C(4) bond angles for the carbene complex are very close to 120° corresponding to an sp^2 carbon whereas for the hydride these angles are 114.8(4) and 113.2(5)° respectively, corresponding to more *p* character. The bond angle Ir–C(3)–H(3) in the hydride is 98(6)°.

As described above, treatment of iridium trichloride with $\mathrm{Bu^t{}_2P(CH_2)_5PBu^t{}_2}$ in refluxing propan-2-ol for several days gives a mixture of three products including $[\mathrm{IrHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)}]$ in 50—60% yield. We have not found ways of converting either of the other two products such as $[\mathrm{Ir_2H_2Cl_4\{Bu^t{}_2P(CH_2)_5PBu^t{}_2\}_2}]$ into the cyclometallated hydride by, for example, treating with base (which works well for rhodium).[6] We reasoned, however, that the readily available and labile iridium(I) complex $[\mathrm{Ir_2Cl_2(C_8H_{14})_4}]$ ($\mathrm{C_8H_{14}}$ = cyclo-octene) might react with $\mathrm{Bu^t{}_2P(CH_2)_5PBu^t{}_2}$ to give $[\mathrm{IrHCl(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)}]$. We found that treatment of $[\mathrm{Ir_2Cl_2(C_8H_{14})_4}]$ with $\mathrm{Bu^t{}_2P(CH_2)_5PBu^t{}_2}$ in benzene at room temperature rapidly gave the hoped for cyclometallated hydride complex (as evidenced from the ^{31}P-{^{1}H} n.m.r. spectrum). On a preparative scale we found it difficult to separate the cyclometallated hydride from the starting materials (even if they were present in small amounts) and found it best to heat the reactants together before isolation.

We have also treated iridium trichloride with $\mathrm{Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2}$ in refluxing propan-2-ol. A deep purple precipitate gradually formed but we could detect no mononuclear cyclometallated hydride, *e.g.* $[\mathrm{IrHCl(Bu^t{}_2PCH_2CH_2CMeCH_2CH_2PBu^t{}_2)}]$. One would anticipate that a tertiary carbon atom would be more difficult to metallate than a primary carbon atom and have for example shown that $\mathrm{Bu^t{}_2PCH_2CH_2CHRCH_2CH_2PBu^t{}_2}$ is cyclopalladated with R = H but not when R = Me.[7] The purple compound was, on the basis of microanalytical and molecular-weight data (Table 1), and i.r. and n.m.r. data (Table 2), shown to be a binuclear hydride $[\mathrm{Ir_2H_2Cl_4(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)_2}]$. The i.r. spectrum showed one intense band at 313 cm^{-1} due to ν(Cl–Ir–Cl) (*trans*) and weak bands at 2 220 and 2 000 cm^{-1} due to ν(Ir–H). The ^{1}H n.m.r. spectrum showed a complex pattern of triplets in the t-butyl region and a 1 : 2 : 1 triplet hydride resonance at $\delta = -49.7$ p.p.m., ^3J(PH) = 11.5 Hz. *X*-Ray diffraction studies show the crystals to be isomorphous with those of the palladium complex $[\mathrm{Pd_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2}]$, the crystal structure of which was determined and shows a torsion angle for $\mathrm{CH_2{-}CH{-}CHMe{-}CH_2}$ of *ca.* 60°.[7] The complex $[\mathrm{Ir_2H_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2}]$ is monoclinic with space group P_n and $a = 862.4(2)$, $b = 2\,842.5(6)$, $c = 1\,211.6(3)$ pm, and $\beta = 108.85(2)°$. The complex $[\mathrm{Pd_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2}]$ is also monoclinic, space group P_n, with $a = 861.6(2)$, $b = 2\,848.5(5)$, $c = 1\,212.7(2)$ pm, and $\beta = 109.35(2)°$.[7] The great similarity of these parameters suggests a very similar structure for both complexes.

Since cyclometallation of $\mathrm{Bu^t_2P(CH_2)_5PBu^t_2}$ to give $[\mathrm{IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)}]$ using $[\mathrm{Ir_2Cl_2(C_8H_{14})_4}]$ occurs under relatively mild conditions we tried a similar treatment of $\mathrm{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2}$ which, as discussed above, was not metallated by $\mathrm{IrCl_3}$ even on prolonged treatment. When we heated the cyclo-octene complex with $\mathrm{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2}$ in benzene we obtained orange-red crystals from a deep red solution after 2 h reflux. The ^{31}P-{^{1}H} n.m.r. spectrum showed two species to be present, with $\delta(\mathrm{P}) = 75.1$ and 54.7 p.p.m., and when the t-butyl and methylene protons were selectively decoupled the peak at δ(P) at 75.1 p.p.m. showed coupling to one hydride ligand whilst the peak at δ 54.7 p.p.m. remained a singlet. The ^{1}H n.m.r. spectrum of the mixture showed a hydride resonance at $\delta(\mathrm{H}) = -38.5$ p.p.m., $^2J(\mathrm{PH}) = 11.7$ Hz, and the t-butyl resonance constituted of two 1 : 2 : 1 triplets, $\delta(\mathrm{H}) = 1.44$ and 1.24 p.p.m., $^3J(\mathrm{PH}) + {}^5J(\mathrm{PH}) = 12.9$ and 12.5 Hz respectively. The 3-methyl resonance occurred as a singlet, $\delta(\mathrm{H}) = 0.83$ p.p.m. These data are in agreement with this species being the hoped for cyclometallated complex, $[\mathrm{IrHCl(Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2)}]$. The minor (non-hydridic) component of the mixture showed a t-butyl triplet at $\delta(\mathrm{H}) = 1.34$ p.p.m., $|^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})| = 12.5$ Hz. It is possibly an olefin–iridium complex, $[\mathrm{IrCl\{Bu^t_2PCH_2CH_2C({=}CH_2)CH_2CH_2PBu^t_2\}}]$, of configuration (5; M = Ir). We have made the corresponding rhodium complex (5; M = Rh) and its structure has been established by *X*-ray diffraction.[5] We could not separate the mixture of iridium complexes.

EXPERIMENTAL

The general techniques used were the same as those described 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 FX100Q n.m.r. spectrometer using an internal deuterium lock. Except where otherwise stated, measurements were made at ambient temperature (*ca.* 296 K).

Action of $\mathrm{Bu^t_2P(CH_2)_5PBu^t_2}$ *on Hydrated Iridium Trichloride.*—A mixture of the diphosphine (2.16 g, 6.0 mmol) and hydrated iridium trichloride (1.05 g, 55.1% Ir, 3.0 mmol) in propan-2-ol (25 cm^3) was heated under reflux for 4 days. The resultant precipitate was extracted with benzene to give $[\mathrm{Ir_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2}]$ as purple plates (1.07 g, 0.85 mmol, 57%), from benzene–light petroleum (b.p. 60—80 °C), and an insoluble red-brown complex (0.47 g, *ca.* 25%) which we were unable to characterize. Evaporation of the propan-2-ol solution to dryness, and trituration with methanol gave a red solid. This gave the complex $[\mathrm{IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)}]$ (1b) as red plates (0.21 g, 0.36 mmol, 12%) from light petroleum (b.p. 60—80 °C).

$[\mathrm{Ir_2H_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2}]$.—This was prepared in a similar manner to $[\mathrm{Ir_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2}]$ (above) and formed purple prisms from dichloromethane–methanol. Yield 70%.

$[\mathrm{IrHCl(CO)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)}]$.—Carbon monoxide was bubbled through a solution of compound (1b) (0.050 g, 0.9 mmol) in benzene (3 cm^3) for 3 min. The hydrido-carbonyl compound was isolated by evaporation and formed pale yellow prisms from light petroleum (b.p. 60—80 °C). Yield 0.050 g, 0.81 mmol, 90%.

Preparation of $[\mathrm{IrHCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)}]$ (1b) *using* $[\mathrm{Ir_2Cl_2(C_8H_{14})_4}]$.—A solution of the diphosphine (0.62 g, 1.71 mmol) in benzene (8 cm^3) was added to an orange-yellow suspension of the cyclo-octeneiridium(I) complex (0.70 g, 0.78 mmol) in benzene (20 cm^3). The mixture was stirred under reflux for 30 min. n-Pentane was added to the resultant dark solution to give a brown solid. This was recrystallized from n-hexane to give (1b). Yield 0.57 g, 0.97 mmol, 62%.

Preparation of $[\mathrm{IrHCl(Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2)}]$.—A solution of $\mathrm{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2}$ (0.71 g, 1.89 mmol) in benzene (6 cm^3) was added to a suspension of $[\mathrm{Ir_2Cl_2(C_8H_{14})_4}]$ (0.68 g, 0.76 mmol) in benzene (10 cm^3) and the mixture heated under reflux for 16 h. The solvent was then evaporated under reduced pressure and the resultant oil taken up in acetone. This gave the required compound as orange prisms. Yield 0.33 g, 0.55 mmol, 36%.

Crystal Data.—(1b), $\mathrm{C_{21}H_{46}ClIrP_2}$, $M = 588.2$, Monoclinic, $a = 1\,231.8(3)$, $b = 1\,435.9(3)$, $c = 1\,485.4(3)$ pm, $\beta = 104.82(2)°$, $U = 2.540(1)$ nm^3, $Z = 4$, $D_c = 1.538$ Mg m^{-3}, $F(000) = 1\,184$, $\mu(\text{Mo-}K_\alpha) = 54.70$ cm^{-1}. (3), $\mathrm{C_{21}H_{44}ClIrP_2}$, $M = 586.2$, Monoclinic, $a = 1\,232.6(3)$, $b = 1\,436.2(3)$, $c = 1\,480.7(3)$ pm, $\beta = 104.87(2)°$, $U = 2.533(1)$ nm^3, $Z = 4$, $D_c = 1.537$ Mg m^{-3}, $F(000) = 1\,176$, $\mu(\text{Mo-}K_\alpha) = 54.85$ cm^{-1}. For both compounds the space group is $P2_1/c$ and measurement used Mo-K_α radiation, $\lambda = 71.069$ pm.

Structure Determinations.—Cell dimensions for each compound were determined by least-squares treatment of the diffractometer-centred angles of 15 reflections with $35 < 2\theta < 40°$. Intensities of independent reflections to $2\theta = 40°$ were measured in the ω—2θ scan mode using scan speeds from 0.5 to 29.3° min^{-1} and were corrected for Lorentz, polarisation, and absorption factors. The structure analyses used those reflections with $I > 2\sigma(I)$; 2 288 for (1b) and 2 259 for (3), with a further 87 for (1b) and 109 for (3) rejected as ' unobserved '. The structure of (3) was solved from Patterson and difference syntheses, and the coordinates for (3) were used as initial values for (1b). Full-matrix least-squares refinement, using the SHELX program,[18] gave *R* values of 0.041 and 0.033 respectively, with allowance for anisotropic vibrations (H atoms excluded). For (3) all hydrogens appeared on a difference map. They were included as idealised methyl or methylene groups

TABLE 6

Atomic co-ordinates with estimated standard deviations in parentheses: upper values are for hydride (1b), lower values for carbene (3)

Atom	*x*	*y*	*z*
Ir	0.272 77(2)	0.034 71(2)	0.281 62(2)
	0.274 69(2)	0.034 72(1)	0.283 90(1)
Cl	0.306 56(17)	0.181 34(12)	0.213 53(14)
	0.306 13(13)	0.180 25(9)	0.213 14(11)
P(1)	0.406 43(16)	−0.049 33(12)	0.232 14(13)
	0.407 94(12)	−0.048 78(9)	0.234 02(10)
P(2)	0.135 90(14)	0.089 91(12)	0.349 11(12)
	0.137 10(11)	0.090 12(9)	0.349 58(9)
C(1)	0.430 4(6)	−0.151 7(4)	0.309 3(4)
	0.431 4(4)	−0.151 0(3)	0.311 8(3)
H(11)	0.502 9(6)	−0.140 1(4)	0.366 9(4)
	0.504 0(4)	−0.139 3(3)	0.369 5(3)
H(12)	0.444 0(6)	−0.212 6(4)	0.270 9(4)
	0.444 9(4)	−0.212 0(3)	0.273 5(3)
C(2)	0.328 3(6)	−0.165 7(4)	0.345 2(4)
	0.327 9(4)	−0.164 8(3)	0.348 3(3)
H(21)	0.349 9(6)	−0.212 2(4)	0.404 2(4)
	0.351 9(4)	−0.204 1(3)	0.412 5(3)
H(22)	0.263 2(6)	−0.196 8(4)	0.290 7(4)
	0.266 3(4)	−0.203 5(3)	0.297 1(3)
C(3)	0.283 1(6)	−0.077 5(4)	0.374 8(4)
	0.276 0(4)	−0.074 5(3)	0.367 7(3)
H(3)	0.327 2(73)	−0.052 1(51)	0.421 9(63)
	—	—	—
C(4)	0.175 7(7)	−0.092 2(6)	0.405 6(6)
	0.176 2(6)	−0.091 7(3)	0.406 2(4)
H(41)	0.193 2(7)	−0.139 4(6)	0.464 2(6)
	0.112 4(6)	−0.126 7(3)	0.353 4(4)
H(42)	0.113 5(7)	−0.122 7(6)	0.348 5(6)
	0.201 8(6)	−0.135 8(3)	0.467 0(4)
C(5)	0.128 0(7)	−0.001 9(6)	0.434 8(6)
	0.127 1(6)	−0.003 0(4)	0.433 4(4)
H(51)	0.041 5(7)	−0.012 6(6)	0.436 0(6)
	0.040 1(6)	−0.014 2(4)	0.432 4(4)
H(52)	0.176 4(7)	0.018 9(6)	0.503 2(6)
	0.173 4(6)	0.017 3(4)	0.502 8(4)
C(6)	0.360 9(7)	−0.096 4(4)	0.108 9(4)
	0.361 4(4)	−0.096 0(3)	0.111 4(3)
C(7)	0.550 3(6)	0.004 6(6)	0.255 4(4)
	0.552 7(4)	0.004 7(3)	0.255 8(3)
C(8)	−0.007 5(6)	0.101 9(4)	0.268 9(4)
	−0.006 1(4)	0.100 6(3)	0.268 2(3)
C(9)	0.173 0(6)	0.196 4(4)	0.425 6(4)
	0.171 5(4)	0.197 1(3)	0.426 4(3)
C(61)	0.457 5(6)	−0.146 2(6)	0.079 9(6)
	0.453 5(6)	−0.148 0(4)	0.080 1(4)
H(611)	0.531 1(6)	−0.104 2(6)	0.082 9(6)
	0.519 9(6)	−0.101 5(4)	0.073 6(4)
H(612)	0.426 9(6)	−0.174 2(6)	0.010 5(6)
	0.418 1(6)	−0.181 5(4)	0.013 8(4)
H(613)	0.479 0(6)	−0.202 6(6)	0.129 3(6)
	0.486 9(6)	−0.200 2(4)	0.132 4(4)
C(62)	0.266 8(7)	−0.165 7(6)	0.104 7(6)
	0.266 4(6)	−0.166 4(4)	0.110 0(4)
H(621)	0.294 6(7)	−0.226 6(6)	0.147 1(6)
	0.301 6(6)	−0.226 6(4)	0.150 8(4)
H(622)	0.236 9(7)	−0.186 3(6)	0.032 7(6)
	0.234 4(6)	−0.186 4(4)	0.037 7(4)
H(623)	0.199 6(7)	−0.132 3(6)	0.127 1(6)
	0.198 9(6)	−0.138 5(4)	0.136 1(4)
C(63)	0.315 0(8)	−0.017 7(6)	0.042 6(6)
	0.314 1(6)	−0.018 9(4)	0.044 5(4)
H(631)	0.386 7(8)	0.026 7(6)	0.045 9(6)
	0.383 1(6)	0.025 3(4)	0.039 0(4)
H(632)	0.249 4(8)	0.021 9(6)	0.061 2(6)
	0.250 1(6)	0.022 8(4)	0.063 0(4)
H(633)	0.284 5(8)	−0.044 4(6)	−0.027 3(6)
	0.279 2(6)	−0.052 6(4)	−0.021 8(4)
C(71)	0.645 3(6)	−0.065 6(6)	0.264 9(6)
	0.647 5(4)	−0.065 5(4)	0.264 9(4)
H(711)	0.633 6(6)	−0.093 7(6)	0.195 7(6)
	0.648 0(4)	−0.117 2(4)	0.318 0(4)
H(712)	0.645 5(6)	−0.121 7(6)	0.313 4(6)
	0.725 3(4)	−0.027 0(4)	0.283 0(4)
H(713)	0.724 3(6)	−0.028 8(6)	0.284 8(6)
	0.638 7(4)	−0.099 5(4)	0.198 4(4)
C(72)	0.565 0(7)	0.059 3(6)	0.349 2(6)
	0.568 7(6)	0.058 8(4)	0.349 6(4)
H(721)	0.563 4(7)	0.010 0(6)	0.403 7(6)
	0.567 4(6)	0.005 5(4)	0.400 8(4)
H(722)	0.509 0(7)	0.116 5(6)	0.352 2(6)
	0.506 3(6)	0.111 0(4)	0.351 6(4)
H(723)	0.649 3(7)	0.085 5(6)	0.358 5(6)
	0.650 7(6)	0.090 8(4)	0.365 1(4)
C(73)	0.554 0(6)	0.077 1(6)	0.178 9(6)
	0.555 9(4)	0.077 0(3)	0.179 3(4)
H(731)	0.544 4(6)	0.041 2(6)	0.113 4(6)
	0.547 1(4)	0.046 3(3)	0.111 2(4)
H(732)	0.632 1(6)	0.115 3(6)	0.195 5(6)
	0.636 2(4)	0.111 6(3)	0.201 2(4)
H(733)	0.484 9(6)	0.124 9(6)	0.173 4(6)
	0.489 5(4)	0.126 9(3)	0.175 8(4)
C(81)	−0.094 0(6)	0.142 4(6)	0.318 2(6)
	−0.095 3(4)	0.138 3(4)	0.314 4(4)
H(811)	−0.070 4(6)	0.214 9(6)	0.328 0(6)
	−0.070 4(4)	0.209 6(4)	0.331 6(4)
H(812)	−0.098 2(6)	0.112 7(6)	0.384 0(6)
	−0.101 7(4)	0.102 1(4)	0.376 8(4)
H(813)	−0.175 1(6)	0.136 8(6)	0.268 9(6)
	−0.175 7(4)	0.137 2(4)	0.263 6(4)
C(82)	−0.001 3(6)	0.160 4(6)	0.185 5(6)
	−0.001 1(4)	0.159 0(6)	0.185 0(4)
H(821)	0.018 1(6)	0.230 3(6)	0.211 4(6)
	0.022 6(4)	0.231 2(6)	0.197 6(4)
H(822)	−0.085 6(6)	0.158 4(6)	0.140 8(6)
	−0.085 1(4)	0.154 9(6)	0.140 1(4)
H(823)	0.057 4(6)	0.139 5(6)	0.146 3(6)
	0.056 6(4)	0.124 9(6)	0.151 8(4)
C(83)	−0.047 5(7)	0.001 0(6)	0.235 0(7)
	−0.042 4(6)	−0.000 4(6)	0.233 9(6)
H(831)	−0.056 7(7)	−0.041 2(6)	0.292 7(7)
	−0.050 1(6)	−0.042 1(6)	0.292 7(6)
H(832)	0.009 0(7)	−0.033 1(6)	0.200 6(7)
	0.022 5(6)	−0.029 2(6)	0.205 2(6)
H(833)	−0.128 4(7)	0.010 1(6)	0.186 2(7)
	−0.121 3(6)	−0.000 7(6)	0.181 1(6)
C(91)	0.112 1(7)	0.202 2(6)	0.503 4(6)
	0.108 9(6)	0.203 8(6)	0.502 3(4)
H(911)	0.023 1(7)	0.208 6(6)	0.472 0(6)
	0.121 5(6)	0.140 2(6)	0.542 5(4)
H(912)	0.140 9(7)	0.261 8(6)	0.547 3(6)
	0.020 5(6)	0.212 9(6)	0.469 8(4)
H(913)	0.127 9(7)	0.139 4(6)	0.544 8(6)
	0.139 2(6)	0.262 1(6)	0.547 9(4)
C(92)	0.298 2(6)	0.187 2(6)	0.470 3(4)
	0.299 7(4)	0.188 8(4)	0.472 9(4)
H(921)	0.321 7(6)	0.120 3(6)	0.502 8(4)
	0.313 3(4)	0.123 4(4)	0.510 1(4)
H(922)	0.330 8(6)	0.241 9(6)	0.519 7(4)
	0.325 7(4)	0.245 4(4)	0.521 7(4)
H(923)	0.332 5(6)	0.194 3(6)	0.410 6(4)
	0.348 0(4)	0.190 2(4)	0.421 6(4)
C(93)	0.153 9(7)	0.285 9(4)	0.368 8(6)
	0.153 7(6)	0.286 5(3)	0.369 0(4)
H(931)	0.064 3(7)	0.288 3(4)	0.339 2(6)
	0.064 9(6)	0.295 5(3)	0.338 2(4)
H(932)	0.196 0(7)	0.278 1(4)	0.313 8(6)
	0.197 3(6)	0.283 6(3)	0.314 4(4)
H(933)	0.181 1(7)	0.349 6(4)	0.406 4(6)
	0.184 9(6)	0.344 5(3)	0.414 7(4)

(C–H = 108 pm, H–C–H = 109.5°) and these were refined as rigid groups to give a final R of 0.024, $R' = 0.033$. For (1b) the corresponding hydrogens also appeared in a difference map. Of the two additional hydrogens, that attached to C(3) also showed clearly in the difference map, but that attached to iridium was less clear, and when included in the refinement would not refine satisfactorily. The methyl and methylene hydrogens were therefore refined as part of rigid groups as for (3), while the co-ordinates of H(3) were allowed to refine, and H(0) attached to iridium was held fixed at its difference-map position. This gave a final R of 0.032, $R' = 0.043$. Weights were derived from the expression $w^{-1} = \sigma_c^2(F) + 0.0004\, F^2$, where σ_c^2 is the variance from counting statistics. The atomic co-ordinates and their standard deviations are given in Table 6. Observed and calculated structure factors and anisotropic thermal parameters are in Supplementary Publication No. SUP 23256 (46 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc. Dalton Trans.*, 1981, Index issue.

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