Synthesis, Reactions, and Crystal Structures of Carbonyl-free Hydride-bridged Mixed Organotransition Metal Derivatives of Bis(phosphine)-rhodium(III) or -iridium(III) Cations with Dihydridobis(η^5-cyclopentadienyl)-molybdenum and tungsten

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The Lewis bases [MH$_2$(η^5-C$_5$H$_5$)$_2$] (M = Mo or W) displace acetone from the labile complex [RhH$_2$(PPh$_3$)$_2$(OCMe$_2$)$_2$][PF$_6$] to give [(PPh$_3$)$_2$Rh(μ-H)$_2$M(η^5-C$_5$H$_5$)$_2$][PF$_6$] which are readily cleaved by pyridine or HCl and undergo H/D exchange at the cyclopentadienyl rings under mild conditions. The tungsten product (3b) is monoclinic, space group $P2_1/c$, a = 12.511(1), b = 9.273(1), c = 36.036(6) Å, β = 98.98(1)°, and Z = 4. 6 052 Observed reflections having $I/\sigma(I) \geqslant 3.0$ were refined to R = 0.039. The metal atoms are linked by two bridging H atoms, and have Rh-W = 2.7206(7) Å. The tungsten atom has the normal W(η^5-C$_5$H$_5$)$_2$ geometry (dihedral angle 136°) and the rhodium atom has a square-planar co-ordination. Reaction of [MH$_2$(η^5-C$_5$H$_5$)$_2$] (M = Mo or W) with [IrH$_2$(PPh$_3$)$_2$(OCMe$_2$)$_2$][PF$_6$] gives [(PPh$_3$)$_2$HIr(μ-H)$_2$(μ-σ:1—5-η-C$_5$H$_4$)M(η-C$_5$H$_5$)][PF$_6$]. Intermediate formation of [(PPh$_3$)$_2$H$_2$Ir(μ-H)$_2$M(η^5-C$_5$H$_5$)$_2$]$^+$ is observed, and kinetic parameters have been determined for the C–H insertion reaction. Hydride bridge cleavage of the product (M = W) occurs reversibly with ligands such as pyridine and acetonitrile, but dppe [1,2-bis(diphenylphosphino)ethane] also displaces PPh$_3$ to give [(PPh$_3$)(dppe)HIr(μ-H)(μ-σ:1—5-η-C$_5$H$_4$)WH(η^5-C$_5$H$_5$)][PF$_6$]. This is monoclinic, space group $P2_1/n$, a = 13.573(2), b = 19.979(3), c = 19.546(3) Å, β = 99.53(1)°, and Z = 4. 7 474 Observed reflections were refined to R = 0.035. The metal atoms each have one terminal H atom and are linked by one bridging H, with W-Ir = 3.0771(7) Å. The metallated cyclopentadienyl ring has Ir-C = 2.073(8) Å. The geometry about W is similar to that in complex (3b) (dihedral angle 142°) and that about Ir is very distorted octahedral.

THE reaction of organometallic Lewis bases with complexes containing labile ligands to give mixed-metal species is now a well established synthetic route.[1-5] In a previous communication [5] we reported carbonyl-free hydride-bridged mixed organotransition metal complexes formed by reaction of [MH$_2$(η^5-C$_5$H$_5$)$_2$] [M = Mo, (1a); W, (1b)] with [RhH$_2$(PPh$_3$)$_2$(OCMe$_2$)$_2$][PF$_6$] (2a). We have prepared a number of complexes starting from the iridium analogues (2b) which were found to be significantly different due to the presence of a μ-σ : 1—5-η-C$_5$H$_4$ ligand. Although complexes (2) are formally co-ordinatively saturated, they undergo rapid exchange with free acetone [6] in solution *via* a dissociative mechanism,[7] leading to transient species of reduced co-ordination number. We now report in full our studies of the products from the reaction of (1) with (2).

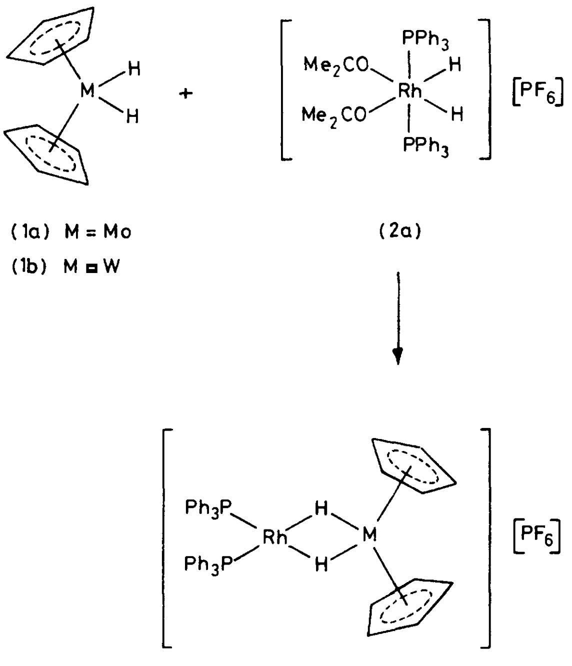
RESULTS AND DISCUSSION

Reaction of (2a) with (1) in acetone or CH$_2$Cl$_2$ at room temperature immediately gave deep brown (1a) or green (1b) solutions. Addition of ethanol and concentration under reduced pressure gave crystals of (3) in good yield. A preliminary report of the properties of (3) and *X*-ray crystal structure of (3b) has already appeared.[5] The ^{1}H n.m.r. spectra of (3) in CD$_2$Cl$_2$ at room temperature consist of a complex phenyl region (30 H), an η^5-C$_5$H$_5$ singlet (10 H), and a doublet of triplets at high field (2 H) due to coupling with Rh and two equivalent P nuclei, with W satellites for (3b). The metal–H coupling constants are comparable to those of the terminal hydrides in (2a) and (1b) [(2a), ^1J(Rh–H) 26 Hz; (1b), ^1J(W–H) 74 Hz]. As the samples are cooled to 203 K the central lines of the high-field triplets collapse, while the separation of the outer lines and the M–H couplings are maintained. The ^{1}H n.m.r. and crystal structure data (see below) are consistent with the presence of two bridging hydride ligands in positions which satisfy both square-planar co-ordination of Rh and the usual MX$_2$(η^5-C$_5$H$_5$)$_2$ geometry at M. These undergo rapid intramolecular exchange in solution at room temperature. The data do not distinguish between a dynamic process involving only the hydride ligands and a gross rotation about the Rh–M axis.

The ^{1}H n.m.r. spectrum (CD$_2$Cl$_2$) of deuteriated (3b), generated *in situ* by reaction of (2a) with [WD$_2$(η^5-C$_5$H$_5$)$_2$] (80% D), shows resonances due to (3b), (μ-H)$_2$, and a similar, initially more intense pattern, displaced by δ 0.07 to lower field and assigned to (3b), (μ-H)(μ-D). The latter rapidly diminishes on warming, while the (μ-H)$_2$ signal of (3b) increases. The observation of a small deuterium shift but no significant change in the coupling pattern suggests that the values of J(P–H) in these complexes may be small compared with those in monomeric Rh complexes, and not comparable but of opposite sign as we originally proposed.[5]

In solution compounds (3) are readily decomposed by oxygen, but in the solid state they are moderately stable. In acetone, (3b) is immediately cleaved by excess pyridine (py) to give [Rh(py)$_2$(PPh$_3$)$_2$][PF$_6$] and (1b), and by dilute aqueous HCl to give [WH$_3$(η^5-C$_5$H$_5$)$_2$][PF$_6$] (4) and [{RhCl(PPh$_3$)$_2$}$_2$].

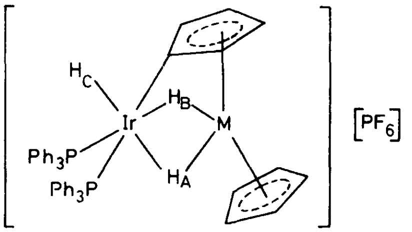
On dissolving (3b) in [^{2}H$_6$]acetone–D$_2$O, the ^{1}H n.m.r. spectrum at room temperature shows no high-field resonance, indicating rapid H/D exchange of the bridging hydride ligands. On warming, the η^5-C$_5$H$_5$ resonance decreases while the HDO resonance increases, indicating slower H/D exchange at the cyclopentadienyl ligands. After refluxing (3b) in acetone–D$_2$O (10 : 1) for 5 h, (4)



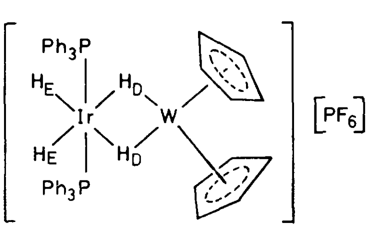
(1a) M = Mo
(1b) M = W

(2a)

(3a) M = Mo
(3b) M = W



(5a) M = Mo
(5b) M = W



(6)

was recovered by treatment with excess pyridine then dilute aqueous HCl and [NH$_4$][PF$_6$]. The ^{1}H n.m.r. spectrum of recovered (4) in [^{2}H$_6$]acetone showed 85% D incorporation on the cyclopentadienyl rings. Furthermore the system is catalytic in the presence of excess (1b). After refluxing (1b) (10 mol %) with (3b) in acetone–D$_2$O for 24 h, the ^{1}H n.m.r. spectrum of (4), isolated in 60% yield, showed 80% ring H/D exchange.

Using the convention recently described by Green and co-workers [8] to represent the bonding in hydride-bridged compounds, (3) can be regarded as complexes of Rh^{I}. In contrast the complexes [(η^5-C$_5$H$_5$)$_2$MH$_2$M'(CO)$_5$] described by Deubzer and Kaesz [1] were formulated on the basis of M–H coupling constants, as donor complexes of (1) to the metal–carbonyl moiety, with non-bridging hydrides, and only one equivalent of a ligand such as PPh$_3$ was required to displace (1) in these complexes.

Reaction of (2b) with (1) in CH$_2$Cl$_2$ or acetone at room temperature immediately gave dark green solutions from which dark green crystals of (5) were obtained in good yield by addition of ethanol and concentration under reduced pressure. An analogous complex was obtained by reaction of [IrH$_2$(PMePh$_2$)$_2$(OCMe$_2$)$_2$][PF$_6$] with (1b). An i.r. band assigned to ν(Ir–H) (Nujol mull) was observed for all complexes.

The ^{1}H n.m.r. spectra of (5) in CD$_2$Cl$_2$ at 233 K consist of a complex phenyl region (30 H), a η^5-C$_5$H$_5$ singlet (5 H), four peaks in the region δ 6.7—4.2 assigned to a μ-σ : 1—5-η-C$_5$H$_4$ ligand (each 1 H), and three high-field resonances (each 1 H). For (5b) these hydride resonances are respectively a singlet (H$_A$, δ −16.41), a doublet [H$_B$, δ −18.28, J(P–H) 50 Hz], and a doublet of doublets [H$_C$, δ −24.55, J(P–H) 17, 27 Hz], all with further poorly resolved fine structure apparent. H$_A$ and H$_B$ have W satellite peaks. On the basis of these data and by comparison with those for iridium complexes with bridging and terminal hydrides [9] we have assigned these resonances to bridging hydride ligands in *trans* positions to a hydride (H$_A$) and a phosphine (H$_B$) ligand respectively, and a terminal iridium hydride (H$_C$). Thus the Ir atom is six-co-ordinate and formally iridium(III). Above 298 K significant broadening of the hydride resonances occurs. Irradiation of any one causes the other two to saturate indicating exchange of all three hydrides. In the case of [(η-C$_5$H$_5$)W(μ-σ : C$_5$H$_4$)(μ-H)$_2$IrH(PMePh$_2$)$_2$]$^+$ broadening occurs at lower temperatures and at 323 K H$_A$ and H$_B$ have coalesced. At the same time the Me resonances of the PMePh$_2$ ligands, initially two doublets, coalesce to give one doublet. Therefore, the fluxional process or processes involve the other ligands on Ir as well as the hydrides, since interchange of the hydrides alone does not render the phosphine ligands equivalent. The observations are consistent with those for certain five-co-ordinate Ir^{I} and Rh^{I} complexes in which intramolecular rearrangements occur more readily with less hindered phosphines.[10]

The reaction of (2b) with (1b) was studied by multi-wavelength rapid scanning stopped-flow visible spectroscopy [11] at 293 K. The spectra indicated the build-up of an intermediate in a two-step reaction characterised by an isosbestic point at *ca.* 560 nm.

To characterise the intermediate structurally, solutions of (1b) and (2b) in CD$_2$Cl$_2$ were sealed, without mixing, in an 5-mm n.m.r. tube at 77 K, and warmed to 223 K to give a deep brown solution. The high-field region

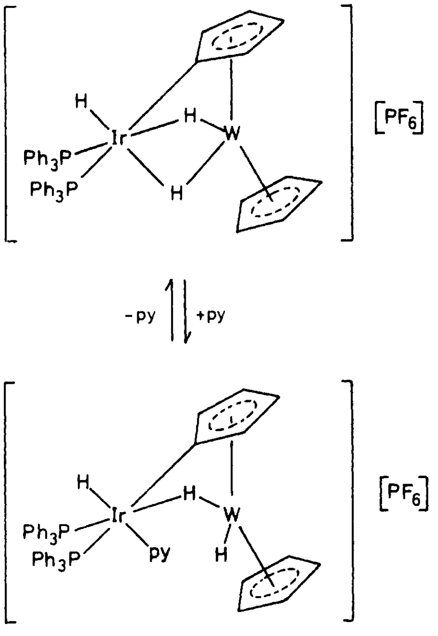
TABLE 1

Spectroscopic data

	Compound	Colour	Infrared [a]	^{1}H N.m.r.[b]
(3a)	$[(PPh_3)_2Rh(\mu\text{-}H)_2Mo(\eta^5\text{-}C_5H_5)_2][PF_6]$	Dark brown		*ca.* 7.3, *30*, m, C_6H_5; 5.27, *10*, s, C_5H_5; −16.69, *2*, dt [J(Rh–H) 29, J(P–H) 6.5], Mo–H–Rh
(3b)	$[(PPh_3)_2Rh(\mu\text{-}H)_2W(\eta^5\text{-}C_5H_5)_2][PF_6]$	Dark Green		*ca.* 7.2, *30*, m, C_6H_5; 5.23, *10*, s, C_5H_5; −18.11, *2*, dt [J(Rh–H) 29, J(P–H) 10, J(W–H) 107], W–H–Rh
(5a)	$[(PPh_3)_2HIr(\mu\text{-}H)_2(\mu\text{-}\sigma : 1\text{—}5\text{-}\eta\text{-}C_5H_4)Mo(\eta^5\text{-}C_5H_5)]$-$[PF_6]$ [c]	Green	2 195	*ca.* 7.3, *30*, m, C_6H_5; 6.29, 5.17, 4.22, *1, 1, 1*, s, 3 of C_5H_4; 4.82, *6*, s, C_5H_5 + 1 of C_5H_4; −14.33, s, 1, H_A; −16.87, *1*, d [J(P–H) 52], H_B; −21.97, *1*, m, H_C
(5b)	$[(PPh_3)_2HIr(\mu\text{-}H)_2(\mu\text{-}\sigma : 1\text{—}5\text{-}\eta\text{-}C_5H_4)W(\eta^5\text{-}C_5H_5)]$-$[PF_6]$ [c]	Green	2 210	*ca.* 7.3, *30*, m, C_6H_5; 6.72, 5.02, 4.76, 4.53, *1, 1, 1, 1*, s, C_5H_4; 4.82, *5*, s, C_5H_5; −16.41, *1*, s [J(W–H) 92], H_A; −18.28, *1*, d [J(P–H) 50, J(W–H) *ca.* 90], H_B; −24.55, *1*, dd [J(P–H) 17, 27], H_C
(7)	$[(PPh_3)(dppe)HIr(\mu\text{-}H)(\mu\text{-}\sigma : 1\text{—}5\text{-}\eta\text{-}C_5H_4)$-$WH(\eta^5\text{-}C_5H_5)][PF_6]$	Purple	2 140	7.6—6.7, *45*, m, C_6H_5; 5.51, *2*, m and 4.39, *2*, m, C_5H_4; 4.46, *5*, s, C_5H_5; −15.88, *3*, dt [J(P–H) 31, 31, 10, J(W–H) 38], M–H

[a] Nujol mull [ν(Ir–H)/cm^{-1}]. [b] In CD_2Cl_2 at 293 K. Data given as: chemical shift (δ), *relative intensity*, multiplicity [J in Hz], assignment. [c] Only major couplings reported for high-field peaks.

initially showed peaks due to unchanged (1b) and (2b), and small amounts of (5b). In addition there were two resonances of equal intensity, a singlet with W satellites [H_D, δ −15.41, J(W–H) 96 Hz], and a broad triplet with no W coupling [H_E, δ −22.61, J(P–H) 18 Hz]. On warming these resonances decreased simultaneously to be replaced by those of (5b) and the solution became green. The data indicate that the intermediate is not an analogue of (3b) but has the structure (6).



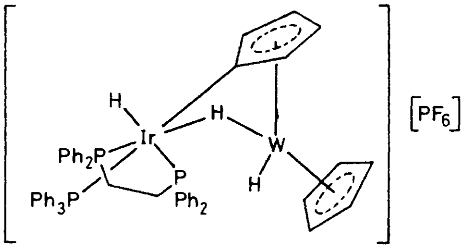
SCHEME 1

Preliminary results from single-wavelength studies in the temperature range 283—305 K under pseudo-first-order conditions [10-fold excess of (1b)] give $\Delta H^\ddagger$ = 74.0 ± 1.9 kJ mol^{-1}, $\Delta S^\ddagger$ = +4.2 ± 6.4 J K^{-1} mol^{-1}, and k_{298} = 1.12 ± 0.03 s^{-1} for the second stage of this reaction, involving insertion into the η^5-cyclopentadienyl C–H bond. The first-stage rate approaches that for dissociative exchange of ligand acetone in (2b),[7] suggesting reaction of (1b) with a co-ordinatively unsaturated species. This is also consistent with the observation that (1) does not react with $[IrH_2(PPh_3)_2(MeCN)_2][PF_6]$ under the same conditions since MeCN is more strongly bound and dissociates far less rapidly.[7]

In solution, compounds (5) are readily decomposed by oxygen but in the solid state they are moderately stable.

In contrast with (3b), the green solutions of (5b) in acetone or CH_2Cl_2 are not rapidly affected by aqueous HCl at room temperature. However, they react immediately with excess pyridine, acetonitrile, or ammonia to give purple solutions from which purple solids may be precipitated by addition of ethanol. When the purple solids were isolated they rapidly became green *in vacuo*, and gave green solutions when redissolved. Variable-temperature ^{1}H n.m.r. in CD_2Cl_2 of solutions of (5b) and pyridine suggest an equilibrium between (5b) and a pyridine complex such as that shown in Scheme 1. At low temperature (193 K) three hydride resonances are observed, a singlet (δ −14.4) a doublet of doublets [δ −23.3, J(P–H) 13, 53 Hz], and a triplet [δ −24.2, J(P–H) 17 Hz]. On warming to 293 K these shift to positions intermediate between those at low temperature and free (5b), δ −15.7, −21.5, and −24.5 respectively, with similar couplings. Although the data do not unambiguously define the structure of the adduct they do indicate that, as in the case of the complexes (3), hydride bridge cleavage is a relatively facile reaction.

Reaction of (5b) with dppe [dppe = 1,2-bis(diphenylphosphino)ethane] in CH_2Cl_2 at room temperature immediately gave a purple solution. Addition of ethanol and concentration under reduced pressure gave purple crystals of (7) in good yield, and PPh_3 was subsequently isolated from the mother-liquor. The i.r. spectrum of (7) (Nujol mull) shows a band at 2 140 cm^{-1} assigned to ν(Ir–H). Hydrogen-1 n.m.r. in CD_2Cl_2 at 298 K showed a complex phenyl region (39 H), a η^5-C_5H_5 singlet (5 H), a broad multiplet due to CH_2 (dppe) (4 H), and two poorly resolved multiplets (each 2 H) assigned to a μ-σ : 1—5-η-C_5H_4 ligand. The high-field region consists of a doublet of triplets (δ −15.88, 3 H) with W satellites. On cooling to 183 K, the high-field region collapses to give three resonances (δ −11.2, −14.0, −22.5) which are still very broad (half-width > 100 Hz). Only the resonance at δ −11.2 shows any coupling [J(P–H) *ca.* 160 Hz]. The single-crystal *X*-ray structure of (7) (see below), together with the ^1H n.m.r. data, suggest six-co-ordinate Ir^{III} for this complex, as shown, with one bridging hydride and terminal hydrides on Ir and W. This structure is analogous to that proposed for the pyridine adduct of (5b), one bridging hydride being displaced by a unidentate ligand. Again the fluxional process appears to involve not only the hydride ligands since the σ : η-1—5-C_5H_4 protons should all be inequivalent in any structure where the WH bonds are inequivalent. In the case of (7), but not (5), this may be achieved by what is effectively a small rotation of the W moiety about the Ir–C bond accompanied by hydride interchange. This and the presence of two bridging hydrides in (5) may account for the far lower temperature required to freeze out the spectrum of (7).



(7)

The observations on the iridium systems provide a mechanism for cyclopentadienyl H/D exchange catalysed by (3b). However, it is not necessary to postulate, as we previously did,[5] that exchange of terminal Rh–H with D_2O occurs following insertion into the C–H bond. Rapid H/D exchange of bridging hydrides in (3b) occurs in acetone–D_2O, and following insertion, intramolecular exchange of bridging and terminal hydrides [as with (5)] and subsequent reductive elimination, also leads to ring H/D exchange. This is borne out by the disappearance of the resonance due to (3b), (μ-H)(μ-D), in the absence of a proton source, presumably by intramolecular exchange of D with the η^5-C_5H_5 rings. Catalysis of ring H/D exchange with excess free (1b) suggests that intermolecular exchange between (3b) and (1b) may occur, consistent with the presence of co-ordinatively unsaturated Rh^I in complexes (3).

In conclusion we note that, as has been observed with many more symmetrical hydride-bridged homonuclear metal complexes, these mixed-metal complexes and others recently reported[3] have hydride bridging ligands in positions which mutually satisfy the different co-ordination geometries of two metal centres. In complexes (3) and (5) the hydride bridges are readily cleaved by ligands such as pyridine but the Ir–C bond is not. Effectively there is an available co-ordination site in complexes (5), while a second metal is held in close proximity.

X-Ray Crystal Structures of (3b) *and* (7).—Figures 1 and 2 show the cations of (3b) and (7) respectively. In (3b), P(1), P(2), Rh, and W are coplanar (maximum deviation 0.02 Å from the best plane) with Rh–W 2.720 6(7) Å and the Rh–W axis bisecting P(1)–Rh–P(2). The dihedral angle between the rings of the W(η^5-C_5H_5)$_2$ unit is 136°. The two parts of the molecule are however, rotated about the Rh–W axis, the plane defined by the ring centroids and W making an angle of 17° with the plane normal to the P_2RhW plane. This geometry and the W-Rh distance are consistent with the presence of two bridging hydrogen atoms in or near the P_2RhW plane at distances in the range 1.7—1.9 Å from each metal and subtending angles H–M–H of the order of 75—90°. The identity of the peaks located from the difference-Fourier synthesis and refined as H(1) and H(2) is thus confirmed. The cyclopentadienyl and phenyl rings show little significant deviation from regularity.

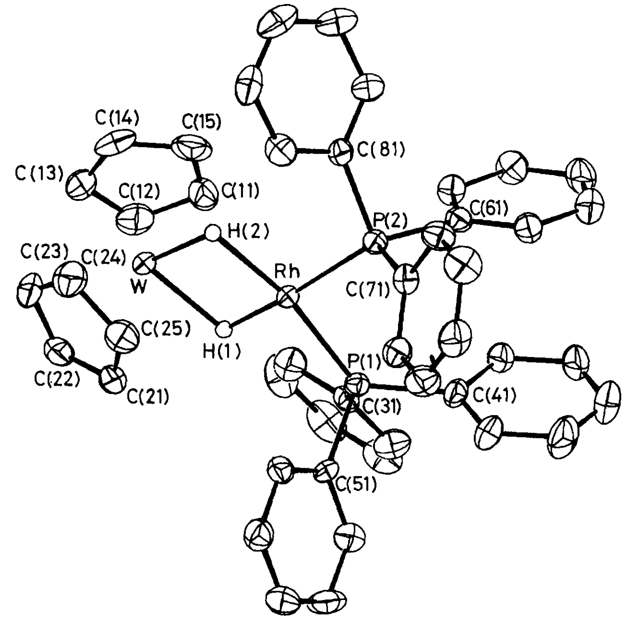


FIGURE 1 The cation of (3b), showing principal atomic numbering. Only the hydrogen atoms attached to the metal atoms are included

The structure of (7) shows a very distorted octahedral geometry about Ir, but normal (η^5-C_5H_5)$_2MX_2$ geometry about W (dihedral angle 142°). The Ir–C(11) distance [2.073(8) Å] is relatively short compared with those observed for certain σ : η-1—5-C_5H_4 systems derived from titanocene [Ti-C 2.19(2) Å] or niobocene [Nb–C 2.23(2) Å].[12,13] However, there is no evidence for any multiple bond character of the Ir–C bond since the σ : η-1—5-C_5H_4 ring shows no significant deviation from regularity. Further, and contrary to previous observations,[14] no systematic variation of bond lengths in the σ : η-1—5-C_5H_4 ring is apparent. Indeed, there is a greater variation in both W–C and C–C lengths of the η⁵-C_5H_5 ring in (7) than there is in (3b).

As would be expected, the octahedral geometry at Ir shows considerable deviations from regularity in (7). The three phosphorus atoms occupy (approximately) *fac* positions, the bite angle of dppe [P(1)–Ir–P(2)] being 83.41(8)°, with P(3)–Ir–P(1) and P(3)–Ir–P(2) having values of 100.83(9) and 98.75(8)° respectively. C(11) is in an approximately *trans* position to P(3) and *cis* to P(1) and P(2), though the distortions are obviously considerable.

TABLE 2

Crystal data

Compound	(3b)	(7)
Formula	$C_{46}H_{42}F_6P_3RhW$	$C_{54}H_{51}F_6IrP_4W$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	12.511(1)	13.573(2)
b/Å	9.273(1)	19.979(3)
c/Å	36.036(6)	19.546(3)
β/°	98.98(1)	99.53(1)
U/Å³	4 129.4(1.0)	5 227.3(1.3)
M	1 088.4	1 313.8
Z	4	4
D_c/g cm⁻³	1.75	1.67
T/°C	−120	16
λ(Mo-K_α)/Å	0.710 69	0.710 69
μ/cm⁻¹	34.10	84.98
F(000)	2 144	2 560
Reflections, total	8 138	9 772
$I/\sigma(I) \geqslant 3.0$	6 052	7 474
R	0.039	0.035
Scan range (2θ/°)	±0.75	±0.85
Minimum scan speed/ ° min⁻¹	1.0	3.0

The heavy-atom positions are consistent with the presence of one terminal hydrogen atom on each metal and a third hydrogen atom bridging the metals, all in the expected positions for normal geometry around each metal atom (see Experimental section). Idealised atoms in these positions are shown in Figure 2.

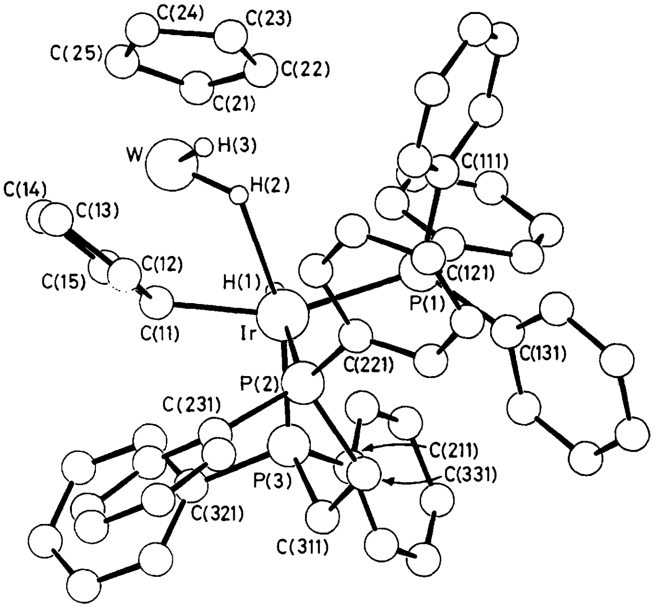


FIGURE 2 The cation of (7) (other details as for Figure 1)

EXPERIMENTAL

All reactions were carried out under dinitrogen or *in vacuo*. Hydrogen-1 n.m.r. spectra were recorded on Bruker WH90 and WH400 and Perkin-Elmer R34 instruments, and i.r. spectra as Nujol mulls on a Perkin-Elmer 580B instrument (Table 1). Microanalyses were by Butterworths Laboratories Limited. We note that though the compounds show no signs of decomposition on brief exposure to air, the analyses for C are significantly low in all cases.

The compounds [MH_2(η⁵-C_5H_5)$_2$](1; M = Mo or W)[15] and [MH_2(PPh_3)$_2$($OCMe_2$)$_2$][PF_6] (2; M = Rh or Ir)[4] were prepared as previously described.

Rapid scanning multi- and single-wavelength stopped-flow data were obtained with previously described apparatus,[11] using CH_2Cl_2 (' Specpure ', Fisons) as solvent.

Di-μ-hydrido-[bis(η⁵-cyclopentadienyl)tungsten [bis(triphenylphosphine)rhodium] Hexafluorophosphate (3b).—A pale yellow solution of (2a) was prepared *in situ* by hydrogenation of *cis,cis*-cyclo-octa-1,5-dienebis(triphenylphosphine)rhodium hexafluorophosphate (0.44 g, 0.5 mmol) in acetone for 2 h. A solution of (1b) (0.32 g, 1.0 mmol) was added with stirring at room temperature, immediately giving a deep green solution. After *ca.* 1 h the solution was filtered, ethanol added, and concentration under reduced pressure gave well formed deep green crystals (0.38 g, 70% based on Rh) (Found: C, 50.0; H, 4.1. Calc. for $C_{46}H_{42}F_6P_3RhW$: C, 50.8; H, 3.9%). The Mo analogue (3a) was prepared as deep brown crystals in similar yield by the same method.

Reaction of (3b) *with pyridine.* Addition of pyridine (py) (0.5 cm³), with stirring, to a deep green solution of (3b) (0.12 g) in acetone at room temperature immediately gave a lime-green solution, which was filtered. Addition of ethanol and concentration under reduced pressure gave yellow crystals. Hydrogen-1 n.m.r. and i.r. spectral data suggested that this compound was [Rh(py)$_2$(PPh_3)$_2$][PF_6]. The mother-liquor was taken to dryness under reduced pressure giving a yellow solid which was identified by i.r. spectroscopy as an impure sample of (1b) by comparison with the spectrum of an authentic sample.

Reaction of (3b) *with aqueous* HCl. A solution of aqueous HCl in ethanol (0.2 cm³ of 10 mol dm⁻³ HCl in 5 cm³ of ethanol) was added dropwise to a solution of (3b) (0.2 g) in acetone. The solution became red, and red-orange crystals precipitated and were isolated. The i.r. spectrum, the low solubility, and the air-sensitive nature of this compound suggests that it is [{RhCl(PPh_3)$_2$}$_2$].[16,17] The mother-liquor was taken to dryness under reduced pressure giving pale purple microcrystals which were shown by i.r. to be complex (4).

H/D *exchange on* (1b) *catalysed by* (3b). Complex (2a) (0.14 g, 0.15 mmol) was dissolved in acetone (20 cm³), and (1b) (0.5 g, 1.6 mmol) added, giving a deep green solution. Then D_2O (2.5 cm³, 139 mmol) was added, and the solution refluxed for 24 h. After cooling, pyridine (0.5 cm³) was added, the solution was taken to dryness under reduced pressure, the pale solid extracted with dilute HCl, and the solution filtered. Complex (4) was precipitated by addition of [NH_4][PF_6], isolated, and recrystallised from acetone–ethanol by concentration under reduced pressure. Yield

TABLE 3

Atomic co-ordinates ($\times 10^4$) for (3b), with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
W	1 506.6(2)	2 975.5(3)	1 974.1(1)
Rh	2 268.8(4)	1 430.3(5)	1 429.2(1)
P(1)	3 783(1)	142(2)	1 431.8(5)
P(2)	1 541(1)	980(2)	839.0(5)
P(3)	1 770(2)	2 424(2)	3 504.5(6)
F(1)	2 889(8)	1 836(13)	3 651(4)
F(2)	578(7)	2 979(10)	3 349(4)
F(3)	2 144(1))	3 858(10)	3 702(3)
F(4)	1 376(6)	979(8)	3 307(3)
F(5)	2 092(12)	3 070(19)	3 145(3)
F(6)	1 330(10)	1 967(15)	3 860(3)
C(11)	740(7)	701(10)	2 006(3)
C(12)	1 008(7)	1 317(10)	2 369(3)
C(13)	323(7)	2 549(11)	2 373(3)
C(14)	−304(6)	2 735(10)	2 016(3)
C(15)	−53(7)	1 547(12)	1 794(3)
C(21)	3 106(6)	4 354(8)	2 062(2)
C(22)	2 649(6)	4 330(10)	2 386(2)
C(23)	1 624(7)	5 050(10)	2 296(3)
C(24)	1 442(7)	5 410(9)	1 911(3)
C(25)	2 394(7)	4 980(9)	1 763(3)
C(31)	4 118(6)	−1 090(7)	1 834(2)
C(32)	4 938(6)	−2 096(9)	1 851(2)
C(33)	5 210(7)	−2 990(9)	2 159(2)
C(34)	4 638(8)	−2 898(9)	2 460(2)
C(35)	3 813(8)	−1 906(10)	2 443(2)
C(36)	3 550(7)	−1 008(9)	2 137(2)
C(41)	4 090(6)	−1 011(8)	1 049(2)
C(42)	4 659(7)	−504(9)	768(2)
C(43)	4 871(9)	−1 427(11)	492(3)
C(44)	4 521(9)	−2 835(12)	475(3)
C(45)	3 949(7)	−3 339(9)	745(3)
C(46)	3 734(6)	−2 442(8)	1 030(2)
C(51)	4 930(5)	1 416(8)	1 485(2)
C(52)	5 993(6)	923(9)	1 563(2)
C(52)	6 846(6)	1 924(10)	1 589(3)
C(54)	6 648(7)	3 364(9)	1 532(3)
C(55)	5 587(6)	3 866(8)	1 456(2)
C(56)	4 731(6)	2 875(8)	1 433(2)
C(61)	1 452(5)	−898(7)	686(2)
C(62)	1 105(6)	−1 900(8)	931(2)
C(63)	958(7)	−3 329(8)	828(2)
C(64)	1 182(7)	−3 799(8)	485(3)
C(65)	1 538(7)	−2 811(9)	237(3)
C(66)	1 670(6)	−1 360(8)	336(2)
C(71)	2 023(6)	1 943(7)	455(2)
C(72)	1 367(6)	2 126(9)	106(2)
C(73)	1 751(7)	2 832(10)	−185(2)
C(74)	2 798(7)	3 368(9)	−130(2)
C(75)	3 442(7)	3 217(10)	208(2)
C(76)	3 066(6)	2 511(8)	507(2)
C(81)	107(6)	1 532(8)	778(2)
C(82)	−747(6)	582(8)	711(2)
C(83)	−1 806(6)	1 055(10)	692(3)
C(84)	−2 009(7)	2 505(11)	737(3)
C(85)	−1 162(8)	3 473(9)	809(2)
C(86)	−114(6)	2 981(8)	827(2)
H(1)	2 698(74)	1 676(97)	1 868(26)
H(2)	1 093(74)	2 847(96)	1 455(26)
H(11)	1 067	−283	1 955
H(12)	1 547	821	2 554
H(13)	285	3 033	2 597
H(14)	−869	3 364	1 911
H(15)	−401	1 658	1 518
H(21)	3 793	3 850	2 059
H(22)	2 969	4 177	2 615
H(23)	1 239	5 306	2 458
H(24)	877	5 973	1 787
H(25)	2 535	5 098	1 494
H(32)	5 290	−2 141	1 678
H(33)	5 849	−3 810	2 168
H(34)	4 829	−3 523	2 670
H(35)	3 470	−1 773	2 645
H(36)	3 025	−279	2 145
H(42)	4 957	447	785
H(43)	5 338	−1 056	280
H(44)	4 561	−3 479	328
H(45)	3 648	−4 327	738
H(46)	3 331	−2 753	1 224
H(52)	6 126	−16	1 574
H(53)	7 562	1 561	1 635
H(54)	7 260	4 117	1 629
H(55)	5 412	4 830	1 417
H(56)	3 955	3 335	1 406
H(62)	1 017	−1 525	1 172
H(63)	766	−3 972	979
H(64)	1 087	−4 835	401
H(65)	1 713	−3 146	−3
H(66)	1 958	−639	156
H(72)	613	1 623	29
H(73)	1 359	2 898	−386
H(74)	3 108	3 752	−323
H(75)	4 051	3 699	283
H(76)	3 493	2 566	740
H(82)	−587	−518	672
H(83)	−2 405	298	644
H(84)	−2 777	2 960	722
H(85)	−1 262	4 494	821
H(86)	434	3 530	916

0.45 g, 62% based on W. Hydrogen-1 n.m.r. showed 80% D incorporation in the cyclopentadienyl rings; mull i.r. (Nujol) 3 100 cm^{-1}, ν(C–H); 2 330 cm^{-1}, ν(C–D); ν(C–H) : ν(C–D) = 1.33 : 1.

μ-σ : 1—5-η-*Cyclopentadienediyl)*-C^1(*Ir*)C$^{1-5}$(*W*)-*di*-μ-*hydrido*-[(η^5-*cyclopentadienyl)tungsten*][*hydridobis*(*triphenylphosphine*)*iridium*] *Hexafluorophosphate* (5b).—Complex (2b) (0.5 g, 0.51 mmol) was dissolved in acetone to give a pale yellow solution. A solution of (1b) (0.17 g, 0.53 mmol) in acetone was added with stirring at room temperature, immediately giving a deep green solution. After *ca.* 1 h the solution was filtered, ethanol added, and concentration under reduced pressure gave green microcrystals. Yield 0.51 g, 85% (Found: C, 44.9; H, 3.5. Calc. for $C_{46}H_{42}F_6IrP_3W$: C, 46.9; H, 3.6%). Compound (5a) and the $PMePh_2$ analogue of (5b) were prepared as green microcrystals in similar yield by the same method.

μ-σ : 1—5-η-*Cyclopentadienediyl*-C^1(*Ir*)C$^{1-5}$(*W*)-μ-*hydrido*-{[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*triphenylphosphine*)*iridium*}[(η^5-*cyclopentadienyl*)*hydridotungsten*] *Hexafluorophosphate* (7).—To a deep green solution of (5b) (0.3 g, 0.25 mmol) in CH_2Cl_2 at room temperature was added dppe (0.1 g, 0.25 mmol), immediately giving a deep purple solution. Ethanol was added and the solution concentrated under reduced pressure giving purple crystals of (7) (0.28 g, 83%). The mother-liquor was taken to dryness under reduced pressure and extracted with toluene. The extract was concentrated and ethanol added, giving white crystals which were shown by i.r. to be PPh_3 by comparison of the spectrum with that of an authentic sample (Found: C, 48.2; H, 3.9. Calc. for $C_{54}H_{51}F_6IrP_4W$: C, 49.4; H, 3.9%).

Crystal Structure Determinations of (3b) *and* (7).—Crystals for both structures were grown by adding warm ethanol to acetone solutions of the complexes and leaving to cool and stand for 24—48 h at room temperature. For crystal data, see Table 2.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50° with scan speed up to 29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 25% of the scan time. Three standard reflections were monitored every 200 reflections, and showed no changes during

TABLE 4

Atomic co-ordinates (× 10^4) for (7), with estimated standard deviations in parentheses

Atom	X	Y	Z
Ir	2 911.9(2)	2 279.6(2)	655.8(2)
W	1 006.1(3)	1 466.6(2)	146.1(2)
P(1)	2 508(2)	3 436(1)	578(1)
P(2)	3 354(2)	2 192(1)	1 892(1)
P(3)	4 609(2)	2 320(1)	697(1)
P(4)	7 684(2)	3 531(2)	2 684(2)
F(1)	7 822	2 979	2 135
F(2)	6 936	2 931	2 813
F(21)	6 498	3 442	2 743
F(3)	7 565	4 103	3 191
F(4)	8 839	3 632	2 707
F(41)	8 426	4 069	2 414
F(5)	6 867	3 884	2 155
F(51)	7 466	3 889	1 950
F(6)	7 843	3 180	3 423
F(61)	8 524	3 100	3 130
F(7)	9 374	670	1 357
C(11)	2 656(7)	1 262(4)	521(5)
C(12)	2 086(8)	906(4)	967(5)
C(13)	1 441(9)	428(5)	555(6)
C(14)	1 648(9)	465(5)	−135(6)
C(15)	2 388(7)	978(5)	−156(5)
C(21)	439(8)	1 901(6)	−944(6)
C(22)	105(8)	2 337(5)	−476(6)
C(23)	−522(8)	2 008(6)	−93(6)
C(24)	−625(8)	1 323(6)	−324(6)
C(25)	−31(9)	1 263(6)	−846(6)
C(111)	1 208(6)	3 595(4)	681(5)
C(112)	599(8)	4 041(5)	280(6)
C(113)	−366(8)	4 148(6)	409(6)
C(114)	−722(8)	3 828(6)	923(6)
C(115)	−135(8)	3 385(5)	1 325(5)
C(116)	828(7)	3 261(5)	1 204(5)
C(121)	2 516(7)	3 836(5)	−264(5)
C(122)	2 140(8)	3 497(6)	−860(5)
C(123)	2 031(10)	3 806(7)	−1 501(6)
C(124)	2 316(11)	4 461(7)	−1 554(7)
C(125)	2 707(11)	4 797(6)	−966(8)
C(126)	2 798(9)	4 504(5)	−330(6)
C(131)	3 183(7)	4 028(5)	1 196(5)
C(132)	2 743(9)	4 330(6)	1 706(7)
C(133)	3 294(13)	4 723(9)	2 216(8)
C(134)	4 279(14)	4 847(8)	2 202(8)
C(135)	4 735(10)	4 566(6)	1 698(8)
C(136)	4 196(8)	4 160(5)	1 195(6)
C(211)	4 537(7)	2 654(5)	2 082(5)
C(221)	2 574(8)	2 507(5)	2 494(5)
C(222)	1 666(9)	2 178(6)	2 500(6)
C(223)	1 024(11)	2 393(9)	2 932(8)
C(224)	1 306(13)	2 930(11)	3 355(8)
C(225)	2 183(14)	3 251(10)	3 356(9)
C(226)	2 825(9)	3 038(7)	2 916(6)
C(231)	3 779(7)	1 383(5)	2 285(5)
C(232)	3 779(9)	1 268(6)	2 990(6)
C(233)	4 187(12)	700(7)	3 306(6)
C(234)	4 610(11)	228(6)	2 929(7)
C(235)	4 638(10)	338(6)	2 244(7)
C(236)	4 209(9)	911(5)	1 929(5)
C(311)	5 241(7)	2 411(6)	1 602(5)
C(321)	5 151(7)	1 575(5)	370(5)
C(322)	4 768(7)	1 373(5)	−305(5)
C(323)	5 159(9)	850(6)	−620(6)
C(324)	5 954(11)	499(7)	−258(8)
C(325)	6 335(11)	679(7)	407(8)
C(326)	5 945(9)	1 209(7)	725(7)
C(331)	5 154(7)	2 936(5)	183(5)
C(332)	4 626(8)	3 158(6)	−436(5)
C(333)	5 031(10)	3 599(6)	−847(6)
C(334)	5 997(12)	3 818(7)	−645(8)
C(335)	6 541(10)	3 583(8)	−58(8)
C(336)	6 141(9)	3 149(7)	365(6)
H(1)	2 889	2 377	−120
H(2)	1 296	1 922	635
H(3)	531	1 576	898
H(12)	2 093	997	1 540
H(13)	1 033	147	812
H(14)	1 311	195	−588
H(15)	2 659	1 127	−600
H(21)	995	1 998	−1 372
H(22)	322	2 792	−485
H(23)	−838	2 115	300
H(24)	−1 062	974	−95
H(25)	41	886	−1 180
H(112)	731	4 311	−158
H(113)	−597	4 475	247
H(114)	−1 300	3 930	1 161
H(115)	−445	3 165	1 692
H(116)	1 267	2 903	1 511
H(122)	1 962	3 054	−853
H(123)	1 757	3 536	−1 927
H(124)	2 218	4 690	−2 037
H(125)	2 985	5 199	−1 037
H(126)	3 089	4 729	6
H(132)	2 066	4 256	1 782
H(133)	2 921	4 929	2 575
H(134)	4 620	5 130	2 655
H(135)	5 445	4 686	1 653
H(136)	4 462	4 013	807
H(211)	4 387	3 099	2 065
H(212)	4 842	2 614	2 599
H(222)	1 515	1 679	2 113
H(223)	367	2 084	2 916
H(224)	964	3 109	3 732
H(225)	2 332	3 633	3 587
H(226)	3 443	3 269	2 848
H(232)	3 491	1 614	3 271
H(233)	4 205	657	3 750
H(234)	4 915	−127	3 188
H(235)	4 964	98	1 937
H(236)	4 255	966	1 586
H(311)	5 578	1 884	1 833
H(312)	5 745	2 688	1 583
H(322)	4 307	1 615	−487
H(323)	4 895	739	−1 050
H(324)	6 164	143	−480
H(325)	6 966	493	807
H(326)	6 190	1 241	1 307
H(332)	3 944	3 018	−582
H(333)	4 559	3 779	−1 248
H(334)	6 311	4 133	−897
H(335)	7 090	3 708	49
H(336)	6 452	2 889	747

data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Reflections were corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR.[18] Both structures were solved by Patterson and heavy-atom methods, followed by difference-Fourier location of all non-hydrogen atoms except for the PF_6 fluorine atoms. In each case several fluorines were located, then (i) for (3b), the rest were calculated using BONDAT; (ii) for (7), half fluorines in some positions (deduced from a ΔF map) gave better results. Hydrogen atoms attached to carbon were loaded in calculated positions, though many were evident in the ΔF maps before inclusion. They were not refined.

For (3b) the metal hydrogens were placed from a ΔF map, and were refined. For (7), assuming M–H distances of the order of 1.9 Å and H–M–H angles at Ir and W of the order of 90° and 75° respectively, positions were calculated for two hydrogen atoms at each metal centre. Those on W were placed symmetrically about the plane defined by the tungsten atom and the ring centroids and those on Ir were *trans* to P(1) and P(2) on Ir. The position of the hydrogen atom in a *trans* position to P(1) at Ir is then very close to the calculated position of one hydrogen atom attached to W. A single bridging hydrogen atom in this position therefore

TABLE 5

Selected bond lengths (Å) and angles (°) for (3b)

W–Rh	2.720 6(7)	W–C(22)	2.271(8)
W–C(11)	2.328(9)	W–C(23)	2.240(10)
W–C(12)	2.249(10)	W–C(24)	2.270(9)
W–C(13)	2.254(10)	W–C(25)	2.352(9)
W–C(14)	2.305(8)	W–H(1)	2.00(9)
W–C(15)	2.364(9)	W–H(2)	1.86(9)
W–C(21)	2.354(8)	C–C (C_5H_5 ring)	1.415 (mean)
H(1)–W–H(2)	84(3)	H(1)–Rh–H(2)	89(3)
Rh–P(1)	2.238(2)	P(1)–Rh–P(2)	97.13(7)
Rh–P(2)	2.219(2)	P(1)–Rh–W	132.05(5)
Rh–H(1)	1.60(9)	P(2)–Rh–W	130.79(5)
Rh–H(2)	2.05(9)	P(2)–Rh–H(1)	85(3)
P(1)–C(31)	1.843(7)	P(2)–Rh–H(2)	89(2)
P(1)–C(41)	1.834(8)		
P(1)–C(51)	1.846(7)		
P(2)–C(61)	1.825(7)		
P(2)–C(71)	1.827(7)		
P(2)–C(81)	1.845(7)		
P(3)–F	1.548 (mean)		

TABLE 6

Selected bond lengths (Å) and angles (°) for (7)

W–Ir	3.0771(7)	W–C(21)	2.311(11)
W–C(11)	2.275(9)	W–C(22)	2.347(10)
W–C(12)	2.281(9)	W–C(23)	2.318(11)
W–C(13)	2.268(10)	W–C(24)	2.270(10)
W–C(15)	2.278(10)	W–C(25)	2.237(10)
W–C(14)	2.286(10)	W–H(2)	1.33
C(11)–C(12)	1.445(14)	W–H(3)	1.71
C(12)–C(13)	1.448(14)	C(21)–C(22)	1.392(16)
C(13)–C(14)	1.425(17)	C(22)–C(23)	1.388(17)
C(14)–C(15)	1.441(15)	C(23)–C(24)	1.442(16)
C(15)–C(11)	1.430(13)	C(24)–C(25)	1.406(17)
H(2)–W–H(3)	54	C(25)–C(21)	1.452(17)
		P(1)–Ir–P(2)	98.75(8)
Ir–P(1)	2.374(2)	P(1)–Ir–P(3)	100.83(9)
Ir–P(2)	2.397(2)	P(1)–Ir–H(1)	81
Ir–P(3)	2.293(2)	P(1)–Ir–H(2)	95
Ir–C(11)	2.073(8)	P(2)–Ir–P(3)	83.41(8)
Ir–H(1)	1.52	P(2)–Ir–C(11)	93.7(2)
Ir–H(2)	2.30	P(2)–Ir–H(2)	94
		P(3)–Ir–C(11)	100.7(3)
P(1)–C(111)	1.837(9)	P(3)–Ir–H(1)	83
P(1)–C(121)	1.831(10)	C(11)–Ir–H(1)	91
P(1)–C(131)	1.825(10)	C(11)–Ir–H(2)	63
P(2)–C(211)	1.836(10)	H(1)–Ir–H(2)	99
P(2)–C(221)	1.820(11)		
P(2)–C(231)	1.842(10)		
P(3)–C(311)	1.843(9)		
P(3)–C(231)	1.822(10)		
P(3)–C(331)	1.822(10)		
C(211)–C(311)	1.524(15)		

satisfies the normal co-ordination geometries of both metal centres. The other hydrogen atoms are beyond reasonable bonding distance from any atoms other than the metals themselves. Inspection of the final difference-Fourier maps in these regions revealed peaks of similar intensity to residual electron density in the positions of the terminal hydrides, but not the bridging hydride. Hydrogen atoms were placed in these three positions but could not be refined successfully. Final refinement was by least-squares methods, in large blocks, including an extinction parameter. One amorphous and broad area of electron density still remained on the final ΔF maps for (7) but was not recognisable or refinable as any particular small molecule. It may be due to a small amount of disordered solvent in the unit cell. A weighting scheme of the form $w = X \times Y$ was used, where $X = 1.0$ or $100/F$ for $F > 100$ and $Y = 1.0$ or $(\sin\theta/\lambda)/0.1$ for $(\sin\theta/\lambda) < 0.1$. This was shown to be satisfactory by a weight analysis. Computing was with the *X*-RAY 72 and 76 systems,[19] on Burroughs B6700 and a CDC7600 computers. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 20. Final atomic co-ordinates are given in Tables 2 and 3, and selected bond lengths and angles in Tables 4 and 5. Anisotropic and isotropic temperature factors and observed and calculated structure factors are listed in Supplementary Publication No. SUP 23207 (80 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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