Synthesis and Structural Characterization of the Phosphido Cluster $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$ and its Facile Carbonyl Substitution Reactions with a Series of Phosphines and Phosphites†

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The tetranuclear cluster $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$ **1** is formed from $[Ir_4(CO)_{11}(PPh_2H)]$ **2** by deprotonation, which yields $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ **3**, followed by protonation of the anion. It has been fully characterized by an X-ray analysis, and exhibits a tetrahedral arrangement of metal atoms with the three basal edges bridged by a phosphido, a hydrido and a carbonyl ligand. Both **1** and **3** undergo facile carbonyl substitution reactions with phosphites and phosphines L [PPh_3, $PPhMe_2$, $P(OPh)_3$ or $P(C_6H_4X\text{-}4)_3$ (X = F, Cl, Me, 4-OMe or 2-OMe)] to give $[Ir_4H(CO)_9L(\mu\text{-}PPh_2)]$ **4a–4h** and $[Ir_4(CO)_9L(\mu\text{-}PPh_2)]^-$ **5a–5h** respectively, the latter being converted into the corresponding hydride derivatives by protonation. Further substitution of a CO in **4a–4h** affords $[Ir_4H(CO)_8L_2(\mu\text{-}PPh_2)]$ **6a–6h**. An X-ray analysis of $[Ir_4H(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **4a** shows that carbonyl substitution has occurred at a basal Ir atom which is not bridged by the phosphido ligand.

The synthesis and reactivity of carbonyl clusters of the iron subgroup stabilized by the phosphido (PR_2) ligand have been the subject of numerous recent systematic studies.[1,2] These clusters have been prepared by several routes[1–3] including (*i*) the action of PR_2H on a binary carbonyl cluster under thermolytic conditions,[4] (*ii*) the thermolysis of PR_2H-containing clusters,[5] (*iii*) *via* a deprotonation/protonation sequence of co-ordinated PR_2H-containing clusters,[6] and (*iv*) by thermally induced cleavage of a P–C bond of co-ordinated $R_2PC{\equiv}CR'$ ligands,[1,7] the latter process occasionally being favoured by the action of Me_3NO.[8] Studies of the reactivities of these species have shown, as a general rule, that the PR_2 bridge is flexible, and helps to maintain the integrity of the cluster framework during chemical transformations,[1,2,8,9] although in the absence of other more favourable reaction sites the PR_2 fragment has been shown to behave as a non-innocent ligand, and undergo a series of transformations.[2,10,11]

Analogous studies of iridium tri- and tetra-nuclear clusters containing PR_2 bridges are extremely rare.[12–16] We now report that $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$ **1** is readily obtained from $[Ir_4(CO)_{11}(PPh_2H)]$ **2** *via* either route (*ii*) or (*iii*), and that it undergoes facile carbonyl substitution with a series of phosphines and phosphites. This compound provides not only a convenient entry into the chemistry of Ir_4 phosphido species,[14,15] but also an opportunity of comparing the reactivities of iridium and analogous osmium cluster compounds. A preliminary communication of part of this work has appeared,[13] and the chemistry of the analogous triphenylphosphine gold complex $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$ has been reported.[16]

Results and Discussion

Synthesis of $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$ **1**.—The light orange compound $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$ **1** was obtained in yields above 95% from the reaction of $[Ir_4(CO)_{11}(PPh_2H)]$ **2** with 1 equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) in dichloromethane under a CO or N_2 atmosphere, which gave a bright red, air-sensitive monoanionic species **3**, followed by protonation with HBF_4. Complex **1** was also produced in 90% yield from the thermolysis of **2** in toluene at 100 °C. This orange crystalline compound is soluble in common organic solvents, stable in the solid state under an atmosphere of N_2, and was formulated on the basis of microanalysis and spectroscopic measurements (Tables 1 and 2). The ^1H NMR consists of a resonance at δ −12.9 indicating a hydride–metal linkage, strongly coupled with the phosphido phosphorus, suggesting that the two nuclei were located *trans* to each other. In the ^{31}P NMR spectrum the downfield phosphorus chemical shift of δ 286.9 is within the range observed for compounds in which the phosphido ligands bridge metals involved in M–M bonds.[17] The IR spectrum in the ν_{CO} region shows the presence of one bridging carbonyl in addition to terminal carbonyls.

The reaction of compound **1** with dbu in a number of solvents, or LiBu in diethyl ether, under CO or N_2 results in the reformation of **3**, which is thus proposed to be $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ on the basis of spectroscopic data only (Tables 1 and 2). Its $[N(PPh_3)_2]^+$ salt could not be isolated, as **3** seems to react to yield a mixture of unidentified anions upon addition of $[N(PPh_3)_2]Cl$ in methanol, and the $[Hdbu]^+$ salt of **3** is air sensitive even in the solid state. The ^1H NMR spectrum of the Li^+ salt of **3** (δ −20 to +10) exhibits only resonances due to aromatic protons, and the singlet observed in the ^{31}P NMR spectrum δ 205.5, although shifted to higher field compared to that of **1**, due to the shielding effect of the cluster negative charge on the phosphorus, still suggests the presence of an Ir–Ir bond bridged by the phosphido group. In this case, however, the IR spectrum exhibits only terminal CO stretches. Compounds **1** and **3** were therefore formulated as having the structures shown. For **3**, a structure containing two terminal CO groups per Ir atom bridged by the PPh_2 ligand and three CO groups on each of the other two apexes of the Ir_4 tetrahedron is consistent with the data. The structure proposed for **1** has been confirmed by a single-crystal X-ray diffraction study; however suitable crystals of **3** have not been obtained.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Physical and analytical[a] data for the new complexes

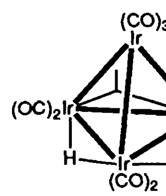
Compound[b]	Yield[c] (%)	ν(CO)[d]/cm^{-1}	Analysis (%) C	Analysis (%) H
1 $[Ir_4H(CO)_{10}(PPh_2)]$	98	2090w, 2061s, 2049vs, 2021m, 2013m, 2002vw, 1846w	21.5 (21.4)	0.9 (0.9)
3 $[Hdbu][Ir_4(CO)_{10}(PPh_2)]$	63	2052m, 2015s, 1988vs, 1921w (sh), 1785vw (br)	—	—[e]
4 $[Ir_4H(CO)_9L(PPh_2)]$				
L = PPh_3 **a**	86	2072s, 2040s (sh), 2034vs, 2007s, 1996m, 1983m, 1826w	31.8 (31.9)	1.8 (1.8)
PPh_2Me **b**	85	2071s, 2038m (sh), 2033vs, 1996m, 1981m, 1815w (br)	29.2 (29.0)	1.8 (1.7)
$P(OPh)_3$ **c**	70	2064m, 2054m, 2033vs, 1997s, 1995s (sh), 1822m	30.6 (30.9)	1.7 (1.7)
$P(C_6H_4F\text{-}4)_3$ **d**	73	2073s, 2047s (sh), 2036vs, 2010s, 1995m, 1984m 1824w	30.9 (30.7)	1.6 (1.5)
$P(C_6H_4Cl\text{-}4)_3$ **e**	70	2074s, 2045s (sh), 2036vs, 2010s, 1996m, 1984m, 1824w	29.8 (29.8)	1.7 (1.5)
$P(C_6H_4Me\text{-}4)_3$ **f**	89	2070m, 2038s (sh), 2033vs, 2005s, 1995m, 1982m, 1925w	30.5 (30.4)	2.0 (2.1)
$P(C_6H_4OMe\text{-}4)_3$ **g**	90	2069s, 2036s (sh), 2032vs, 2005s, 1993m, 1981m, 1824w	32.2 (32.2)	2.1 (2.1)
$P(C_6H_4OMe\text{-}2)_3$ **h**[f]	50	2067m, 2042s, 2027vs, 2003s, 1989w, 1985w (sh), 1973w, 1953w, 1829vw	31.9 (31.8)	2.0 (2.0)
6 $[Ir_4H(CO)_8L_2(PPh_2)]$				
L = PPh_3 **a**	86	2054s, 2045m (sh), 2026s (sh), 2023vs, 1998m, 1987m (sh), 1983s, 1978m (sh), 1806w (br)	40.0 (39.5)	2.9 (2.4)
$P(C_6H_4Cl\text{-}4)_3$ **e**	45	2057s, 2050m (sh), 2032s (sh), 2027vs, 2023s (sh), 2000m, 1992m (sh), 1987s, 1980m, 1974m (sh), 1960w (sh), 1811w (br)[g]	38.2 (37.3)	2.3 (1.9)
$P(C_6H_4Me\text{-}4)_3$ **f**	46	2052vs, 2043m (sh), 2026s (sh), 2021s, 1995m, 1986s (sh), 1982vs, 1975m (sh), 1800w (br)[g]	42.3 (41.8)	3.1 (2.6)

[a] Calculated values are given in parentheses. [b] All compounds are dark orange except **2** and **3** which are purple and light orange. [c] Based on the iridium reactant. [d] Measured in hexane unless otherwise stated. [e] Poor microanalysis data were obtained, due to sensitivity of the compounds. [f] Crystallizes with $0.4CH_2Cl_2$. [g] Measured in CH_2Cl_2.

Table 2 Proton and $^{31}P\text{-}\{^1H\}$ NMR data[a] for the new complexes

Compound	^1H (δ)	$^{31}P\text{-}\{^1H\}$ (δ)
1[b]	−12.90 [d, 1 H, μ-H, *J*(PH) 55], 7.14–7.76 (m, 10 H, Ph)	286.9 (s)[c]
3[b]		205.5 (s)
4a (L = PPh_3)[b]	−11.59 [dd, 1 H, μ-H, *J*(PH) 56, 6], 6.74–7.70 (m, 25 H, Ph)	0.42 (s, 1 P, PPh_3), 276.18 (s, 1 P, PPh_2)
4b (L = PPh_2Me)[b]	−12.00 [dd, 1 H, μ-H, *J*(PH) 57, 6], 0.41 [d, 3 H, Me *J*(PH) 10], 6.73–7.71 (m, 20 H, Ph)	
4c [L = $P(OPh)_3$][d]	−11.80 [br, d, 1 H, μ-H, *J*(PH) 54.1], 6.82–7.88 (m, 25 H, Ph)	
4d [L = $P(C_6H_4F\text{-}4)_3$][d]	−11.77 [dd, 1 H, μ-H, *J*(PH) 56, 6], 6.66–7.71 (m, 22 H, Ph and $4\text{-}FC_6H_4$)	
4e [L = $P(C_6H_4Cl\text{-}4)_3$][d]	−11.83 [dd, 1 H, μ-H, *J*(PH) 56, 6], 6.62–7.64 (m, 22 H, Ph and $4\text{-}ClC_6H_4$)	
4f [L = $P(C_6H_4Me\text{-}4)_3$][d]	−11.59 [dd, 1 H, μ-H, *J*(PH) 57, 6]; 2.40 (s, 3 H, Me), 6.75–7.48 (m, 22 H, Ph and C_6H_4)	
4g [L = $P(C_6H_4OMe\text{-}4)_3$][d]	−11.58 [dd, 1 H, μ-H, *J*(PH) 57, 6], 2.40 (s, 3 H, Me), 6.69–7.64 (m, 22 H, Ph and C_6H_4)	

[a] Chemical shifts in ppm, coupling constants in Hz. [b] Measured in CD_2Cl_2. [c] Chemical shifts positive to high frequency of 85% H_3PO_4 (external). [d] Measured in $CDCl_3$.



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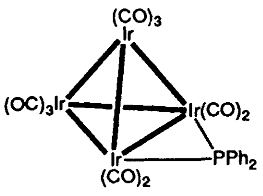


3

Crystal and Molecular Structure of Compound **1**.—The crystal consists of discrete molecular units of $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$, which are separated at normal van der Waals distances. A view of the molecule appears in Fig. 1. Relevant bond distances and angles are in Table 3.

The four iridium atoms define a distorted tetrahedron with Ir–Ir edge lengths in the range 2.677(2)–2.797(2) Å, which is comparable to values reported in di- and tri-substituted Ir_4 clusters with the general formula $[Ir_4(CO)_{12-n}(PPh_3)_n]$ ($n = 2$ or 3).[18] The average Ir–Ir distance in **1** of 2.737 Å is somewhat longer than the Ir–Ir distance of 2.693 Å in the parent binary carbonyl $[Ir_4(CO)_{12}]$.[19] The three basal edges of the tetrahedron are bridged by a carbonyl [Ir(2)–Ir(3) 2.735(2) Å],

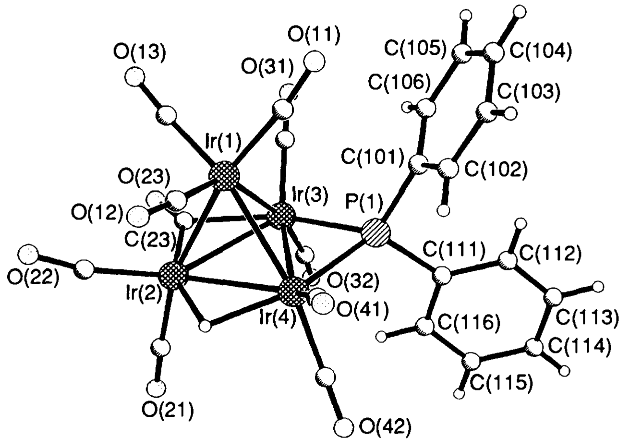


Fig. 1 The molecular structure of compound **1** showing the atom labelling scheme

Table 3 Selected bond lengths (Å) and angles (°) for compound **1**

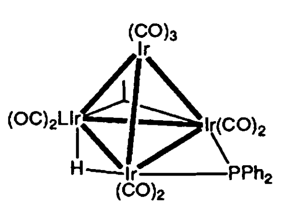
Ir(1)–Ir(2)	2.677(2)	Ir(1)–Ir(3)	2.734(2)
Ir(1)–Ir(4)	2.712(2)	Ir(2)–Ir(3)	2.735(2)
Ir(2)–Ir(4)	2.769(3)	Ir(3)–Ir(4)	2.797(2)
Ir(3)–P	2.342(11)	Ir(4)–P	2.292(10)
Ir(2)–C(23)	1.92(4)	Ir(3)–C(23)	2.14(4)
Ir(2)–Ir(1)–Ir(3)	60.7(1)	Ir(2)–Ir(1)–Ir(4)	61.8(1)
Ir(3)–Ir(1)–Ir(4)	61.8(1)	Ir(1)–Ir(2)–Ir(3)	60.7(1)
Ir(1)–Ir(2)–Ir(4)	59.7(1)	Ir(3)–Ir(2)–Ir(4)	61.1(1)
Ir(3)–Ir(2)–C(23)	51.2(12)	Ir(4)–Ir(2)–C(23)	112.2(12)
Ir(1)–Ir(3)–Ir(2)	58.6(1)	Ir(1)–Ir(3)–Ir(4)	58.7(1)
Ir(2)–Ir(3)–Ir(4)	60.1(1)	Ir(1)–Ir(3)–P	84.2(2)
Ir(2)–Ir(3)–P	112.1(2)	Ir(4)–Ir(3)–P	52.1(2)
Ir(1)–Ir(3)–C(23)	79.3(11)	Ir(2)–Ir(3)–C(23)	44.4(11)
Ir(4)–Ir(3)–C(23)	104.4(11)	P(1)–Ir(3)–C(23)	156.3(12)
Ir(1)–Ir(4)–Ir(2)	58.5(1)	Ir(1)–Ir(4)–Ir(3)	59.5(1)
Ir(2)–Ir(4)–Ir(3)	58.9(1)	Ir(1)–Ir(4)–P	85.6(2)
Ir(2)–Ir(4)–P	112.5(3)	Ir(3)–Ir(4)–P	53.7(3)
Ir(3)–P–Ir(4)	74.2(3)	Ir(2)–C(23)–Ir(3)	84.4(15)

a hydride [Ir(2)–Ir(4) 2.769(3) Å] and a PPh_2 group [Ir(3)–Ir(4) 2.797(2) Å], respectively. These three distances are all longer than the three unbridged apex to base edges (average 2.708 Å). In particular, it is interesting that, as in other Ir_4 clusters,[20] instead of the expected shortening of an Ir–Ir edge associated with a bridging carbonyl ligand, in **1** the Ir(2)–Ir(3) edge is marginally longer than the unbridged edges. The Ir–Ir distances in **1** follow the same trends as in the isolobal cluster $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$.[16] There are, however, small differences between the metal cores between the two structures. The Ir–Ir edge bridged by the $AuPPh_3$ group is *ca.* 0.03 Å shorter than the equivalent hydride-bridged edge in **1**, and the phosphine- and carbonyl-bridged edges in the gold derivative are *ca.* 0.03 and 0.04 Å longer, respectively, than the equivalent edges in **1**. In both complexes the shortest Ir–Ir distance is between the apical Ir atom and the basal Ir atom that is not bonded to the bridging PPh_2 group.

The ligand distribution in compound **1** is also similar to that in $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$.[16] In both clusters nine of the carbonyl ligands are terminal and essentially linear, with three co-ordinated to the apical Ir atom and two to each of the basal Ir atoms. Apparently, the bridging carbonyl in **1** shows a greater asymmetry [Ir(2)–C(23) 1.92(4) Å and Ir(3)–C(23) 2.14(4) Å] than in the gold analogue [both Ir–C distances are 2.01(3) Å], but the high estimated standard deviations make a detailed assessment of the bonding meaningless. However, both clusters show an asymmetry in the Ir–P distances of the bridging PPh_2 group [Ir–P 2.29(1) and 2.34(1) in **1**, and 2.29(1) and 2.36(1) Å in the gold cluster]. In both complexes the longer of the Ir–P distances involves the Ir atom which is also bonded to the bridging carbonyl. The Ir–P–Ir angles are essentially equivalent in the two clusters. The phosphorus atom of the PPh_2 group adopts a distorted-tetrahedral geometry and is virtually coplanar with the basal Ir_3 triangle [the Ir(3)–Ir(4)–P(1) plane makes an angle of 1.8° with the Ir(2)–Ir(3)–Ir(4) plane] and with the bridging ligand [the Ir(3)–Ir(4)–P(1) plane makes an angle of 3.5° with the Ir(2)–Ir(3)–C(23) plane]. The hydride ligand was not located directly, but potential-energy calculations[21] suggest that it bridges the Ir(2)–Ir(4) edge.

Reactions of Complex **1** *with Phosphites and Phosphines.*—Substitution of a CO in compound **1** is easily and selectively achieved with a range of phosphites and phosphines L, to generate complexes with the general formula $[Ir_4H(CO)_9L(\mu\text{-}PPh_2)]$ [L = PPh_3 **4a**, $PPhMe_2$ **4b**, $P(OPh)_3$ **4c** or $P(C_6H_4\text{-}X\text{-}4)_3$ (X = F **4d**, Cl **4e**, Me **4f**, 4-OMe **4g** or 2-OMe **4h**] in acetonitrile, tetrahydrofuran, dichloromethane, or hexane at room temperature. The dark orange monosubstituted derivatives **4a**–**4h**, the formation of which is conveniently monitored by IR spectroscopy, are produced in yields of between 60 and 90% (after purification by thin-layer chromatography and crystallization), depending on the nucleophile and the reaction conditions. Kinetic studies of these reactions have shown that they proceed *via* an associative mechanism, and will be reported elsewhere.[22] Studies have been reported[23] in which the reaction of **1** with PPh_3 under various conditions was followed on a FAB mass spectrometry probe in an attempt to detect a possible intermediate resulting from addition of PPh_3, but besides **1** only **4a** was detected. However, further substitution of CO has been achieved by using higher concentrations of the nucleophile, longer reaction times, and by increasing the reaction temperature to 40 °C, to give compounds $[Ir_4H(CO)_8L_2(\mu\text{-}PPh_2)]$ [L = PPh_3 **6a**, $PPhMe_2$ **6b**, $P(OPh)_3$ **6c** or $P(C_6H_4X\text{-}4)_3$ (X = F **6d**, Cl **6e**, Me **6f**, 4-OMe **6g** or 2-OMe **6h**], in yields not higher than 40%, after purification and crystallization, and these results suggest that the reaction conditions in the FAB matrix are milder than those described above. The best yields of compounds **6a**, **6e** and **6f** were obtained by reaction of **4a**, **4e** and **4f** with the respective phosphines in the presence of Me_3NO, and these species were formulated on the basis of microanalysis and spectroscopic measurements only (Tables 1 and 2).

Complexes **4a**–**4h** are orange crystalline solids, which are air stable and soluble in common organic solvents. The data discussed below suggest that they all exhibit similar structures. The FAB mass spectra of compounds **4b**–**4h** display a $[MH]^+$ ion as well as ions resulting from stepwise loss of five CO ligands and from a complicated fragmentation of PPh_2 and PR_3 groups, as has been previously reported for **4a**.[23] The IR spectra of the $P(C_6H_4X\text{-}4)_3$ derivatives exhibit identical patterns, but show an expected small wavenumber shift towards lower frequencies with the increase in the basicity of the PR_3 ligand. Variation in the Tolman cone angle of the phosphorus donor ligand $[P(OPh)_3 < P(C_6H_4X\text{-}4)_3]$ results only in slight changes in the IR patterns of the derivatives. The room-temperature ^1H NMR spectra of compounds **4a**–**4h** are very similar, and establish that these species contain $\mu\text{-}HIr_2$ groups, with the protons coupled to the two inequivalent phosphorus atoms of the PR_2 ligand (*ca.* 56.4 Hz) and of the PR_3 group (*ca.* 5.9 Hz). The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4a** consists of two uncoupled resonances, at δ −0.4 and 276.2, which indicate first that the two ligands are not bonded to the same Ir atom and secondly that the PPh_2 bridging group spans an Ir–Ir bond. Compounds **4a**–**4h** were thus proposed to have one of the structures shown, with a PR_3 ligand substituting either the axial CO on the basal Ir atom that does not support the PPh_2 ligand (**I**), or one of the CO ligands on the apical Ir atom (**II**). In order to establish unequivocally their structures a single X-ray diffraction study of derivative **4a** was undertaken, which confirmed structure I.



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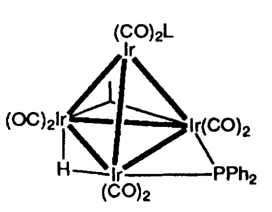


II

Crystal and Molecular Structure of Compound **4a**.—The molecular structure of compound **4a** is shown in Fig. 2. Relevant bond distances and angles are in Table 4. The Ir–Ir distances in the Ir_4 tetrahedron in **4a** follow the same trends as in the structure of **1**. The three basal edges which are bridged by a carbonyl [Ir(1)–Ir(3) 2.771(2) Å], a hydride [Ir(1)–Ir(4) 2.785(2) Å], and a PPh_2 group [Ir(3)–Ir(4) 2.802(2) Å], respectively, all are longer than the three unbridged apex-to-base edges (average 2.716 Å). The largest difference between the basal Ir–Ir distances in **1** and **4a** is an increase in the carbonyl-bridged edge length of *ca.* 0.04 Å in the phosphine-substituted derivative. The overall

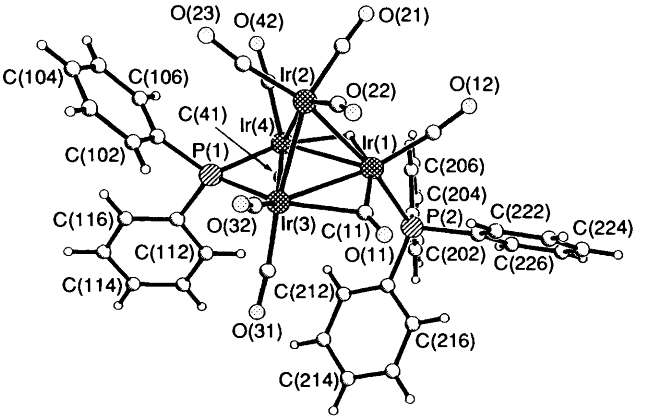


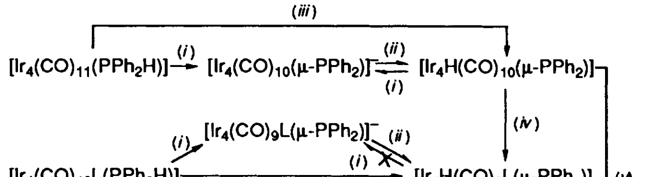
Fig. 2 The molecular structure of compound **4a** showing the atom labelling scheme

Table 4 Selected bond lengths (Å) and angles (°) for compound **4a**

Ir(1)–Ir(2)	2.706(2)	Ir(1)–Ir(3)	2.771(2)
Ir(1)–Ir(4)	2.785(2)	Ir(1)–P(2)	2.342(10)
Ir(1)–C(11)	1.95(5)	Ir(2)–Ir(3)	2.724(2)
Ir(2)–Ir(4)	2.719(2)	Ir(3)–Ir(4)	2.802(2)
Ir(3)–P(1)	2.289(9)	Ir(3)–C(11)	2.27(4)
Ir(4)–P(1)	2.311(11)		
Ir(2)–Ir(1)–Ir(3)	59.6(1)	Ir(2)–Ir(1)–Ir(4)	59.3(1)
Ir(3)–Ir(1)–Ir(4)	60.6(1)	Ir(2)–Ir(1)–P(2)	168.9(3)
Ir(3)–Ir(1)–P(2)	112.8(3)	Ir(4)–Ir(1)–P(2)	110.3(2)
Ir(2)–Ir(1)–C(11)	88.3(12)	Ir(3)–Ir(1)–C(11)	54.3(12)
Ir(4)–Ir(1)–C(11)	114.8(12)	P(2)–Ir(1)–C(11)	93.3(13)
Ir(1)–Ir(2)–Ir(3)	61.4(1)	Ir(1)–Ir(2)–Ir(4)	61.8(1)
Ir(3)–Ir(2)–Ir(4)	62.0(1)	Ir(1)–Ir(3)–Ir(2)	59.0(1)
Ir(1)–Ir(3)–Ir(4)	60.0(1)	Ir(2)–Ir(3)–Ir(4)	58.9(1)
Ir(1)–Ir(3)–P(1)	112.8(3)	Ir(2)–Ir(3)–P(1)	85.7(3)
Ir(4)–Ir(3)–P(1)	52.8(3)	Ir(1)–Ir(3)–C(11)	44.1(12)
Ir(2)–Ir(3)–C(11)	81.7(12)	Ir(4)–Ir(3)–C(11)	104.1(12)
P(1)–Ir(3)–C(11)	156.9(13)	Ir(1)–Ir(4)–Ir(2)	58.9(1)
Ir(1)–Ir(4)–Ir(3)	59.5(1)	Ir(2)–Ir(4)–Ir(3)	59.1(1)
Ir(1)–Ir(4)–P(1)	111.6(3)	Ir(2)–Ir(4)–P(1)	85.4(3)
Ir(3)–Ir(4)–P(1)	52.1(2)	Ir(3)–P(1)–Ir(4)	75.0(3)
Ir(1)–C(11)–Ir(3)	81.6(13)		

average Ir–Ir distance in **4a** (2.751 Å) is *ca.* 0.01 Å longer than in **1**, which may reflect the increase in electron density on the metal core induced by the introduction of the terminal phosphine ligand co-ordinated to Ir(1). The phosphine ligand occupies an axial site and is pseudo-*trans* to the Ir(1)–Ir(2) edge [Ir(2)–Ir(1)–P(2) 168.9(3)°]. The ligand arrangement involving the phosphine is comparable to that in the clusters $[Ir_4(CO)_{11}L]$ (L = PPh_3, PPh_2Me or $PPhMe_2$)[24] and $[Ir_4(CO)_9(2,3\text{-}\eta:5,6\text{-}\eta\text{-nbd})(PPh_3)]$ (nbd = norbornadiene).[25] The Ir(1)–Ir(2) length, as in **1** and the gold analogue $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$,[16] remains the shortest metal–metal contact in the structure, but is lengthened by *ca.* 0.03 Å compared to the value in **1**.

The bridging carbonyl in compound **4a** shows a greater asymmetry than in **1**. The shorter Ir–C(carbonyl) distance is associated with Ir(1) which is co-ordinated to the terminal phosphine ligand. The remaining eight carbonyl ligands are terminally co-ordinated and are essentially linear. The bridging PPh_2 group in **4a** shows less asymmetry than in **1**, and at the 3σ level the two Ir–P distances are not significantly different. The average Ir–P distance of 2.30 Å is *ca.* 0.04 Å shorter than the terminal Ir(1)–P(2) distance. As in **1**, the hydride was not located directly but its position along the Ir(1)–Ir(4) edge is confirmed by potential-energy calculations.[21]



Scheme 1 (*i*) dbu (1 equivalent) in CH_2Cl_2, or LiBu in thf; (*ii*) HBF_4 in CH_2Cl_2; (*iii*) toluene, 100 °C, 1.5 h; (*iv*) L = PPh_3, PPh_2Me, $P(OPh)_3$ or $P(C_6H_4X\text{-}4)_3$ (X = F, Cl, Me or OMe) (1.5 equivalents), CH_2Cl_2, 25 °C; (*v*) L = PPh_3 or $P(C_6H_4X\text{-}4)_3$ (X = Cl or Me) (6 equivalents), thf, 40 °C; (*vi*) L = PPh_3 (1 equivalent), Me_3NO (1 equivalent), CH_2Cl_2; (*vii*) L = PPh_3 (**7a**), toluene, 100 °C, 0.25 h

Other Synthetic Routes to $[Ir_4H(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **4a**.—Deprotonation of compound **1** with an excess of LiBu in tetrahydrofuran (thf), followed by addition of equivalent amounts of PPh_3 to the bright red solution of the anion **3**, resulted in its instantaneous darkening, with the formation of an unstable brown anionic species, which could not be isolated and was characterized only by IR spectroscopy. This compound was formulated as $[Ir_4(CO)_9(PPh_3)(PPh_2)]^-$ **5a**, as its protonation gave **4a** in 90% yield. Interestingly, when the deprotonation of **1** was achieved with 1 equivalent of dbu, **4a** was formed immediately, which indicated that the basicity of the anion **5a** initially formed is higher than that of dbu, as it deprotonated $[Hdbu]^+$ to give the hydride **4a** (Scheme 1). When an excess of PPh_3 was added to the monoanion **3**, followed by protonation, the disubstituted derivative **6a** was also produced in yields up to 40%. The enhancement in the substitution lability found for the anion **3**, when compared to that of the hydrido compound **1**, is not unique. Indeed the anions $[Ru_3(CO)_{11}]^-$ and $[Ru_3(CO)_{11}(CO_2Me)]^-$ have been found to be many orders of magnitude more substitutionally labile than are either $[Ru_3(CO)_{12}]$ or $[Ru_3H(CO)_{11}(CO_2Me)]$,[26] and kinetic studies, to establish whether in the case of compounds **1** and **3** this enhanced lability can also be attributed to an increase in the dissociative component, are in progress.

Compound **4a** was also produced from $[Ir_4(CO)_{10}(PPh_3)(PPh_2H)]$ **7a** *via* deprotonation with LiBu followed by protonation, as described for the synthesis of **1**, with formation of the intermediate **5a**. Furthermore, thermolysis of compound **7a** gives **4a** in quantitative yields. A comparison of the conditions for the decarbonylation of **2** and **7a** (at 100 °C, 1.5 and 0.25 h, respectively) shows that compound **7a** is the more labile. Recent ^{13}C NMR studies have established that **2** exists predominantly as the non-bridged isomer,[27] while **7a** exhibits the same structure as those of other disubstituted Ir_4 derivatives, with three bridging CO ligands.[24] The same argument is proposed to explain the increase in lability observed in the reactions of $[Ir_4(CO)_{12-n}L_n]$ + L (L = PPh_3, PBu_3 or $AsPh_3$; $n = 0 < 1 < 2 < 3$),[28,29] *i.e.* change from a non-bridged to a bridged systems[28] can therefore also be invoked to explain the increasing lability observed in the decarbonylations of **2** and **7a**.

At this stage a comparison between the analogous hydrido-phosphido compounds $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$ **1** and $[Os_3H(CO)_{10}(\mu\text{-}PPh_2)]$ is pertinent. Both have been produced *via* the decarbonylation, and the base/acid sequential reactions of $[Ir_4(CO)_{11}(PPh_2H)]$ **2** and $[Os_3(CO)_{11}(PPh_2H)]$,[11] respectively, and exhibit a rich carbonyl substitution chemistry, which in the case of the iridium derivative is only at its infancy.[13,15] Differences in their behaviour have been noted, though the osmium derivative can be activated reversibly under thermolytic conditions to yield $[Os_3H_2(CO)_9\{\mu_3\text{-}PPh(C_6H_4)\}]$, the cyclometallation of **1** has not been observed. Also, while compound **1** undergoes extremely facile carbonyl substitution with phosphorus-donor ligands *via* an associative mechanism,

Table 5 Crystal data and details of measurements for compounds **1** and **4a** *

	1	**4a**
Formula	$C_{22}H_{11}Ir_4O_{10}P$	$C_{39}H_{26}Ir_4O_9P_2$ + disordered solvent
M_r	1235.1	1469.3
Crystal size (mm)	0.057 × 0.120 × 0.236	0.15 × 0.19 × 0.39
Colour, habit	Orange tablet	Orange block
Space group	$P2_1/c$	$P2_1/n$
a/Å	8.796(2)	20.605(2)
b/Å	17.168(4)	10.293(1)
c/Å	18.021(2)	20.937(2)
β/°	91.12(2)	104.34(1)
U/Å^3	2720.8(9)	4302.1(7)
D_c/g cm^{-3}	3.015	2.269
μ/cm^{-1}	196.11	124.57
F(000)	2184	2680
Scan speed (s per step)	1.0–4.0	0.75–3.0
Index ranges	$-9 \leqslant h \leqslant 9, 0 \leqslant k \leqslant 17, 0 \leqslant l \leqslant 18$	$-21 \leqslant h \leqslant 20, 0 \leqslant k \leqslant 10, 0 \leqslant l \leqslant 21$
Reflections collected	3514	5463
Independent reflections (R_{int})	3119 (0.0304)	4937 (0.0560)
Observed reflections	2128 [$F > 4\sigma(F)$]	3196 [$F > 6\sigma(F)$]
Transmission factors	0.152–0.486	0.099–0.694
g in weighting scheme $w^{-1} = \sigma^2(F) + gF^2$	0.0010	0.0025
Number of parameters refined	203	248
Final R, R'	0.0655, 0.0771	0.0902, 0.1119
Goodness of fit	1.53	1.81
Largest and mean Δ/σ	0.006, 0.001	0.15, 0.001
Data-to-parameter ratio	10.5:1	12.9:1
Largest difference peak, hole/e Å^{-3}	2.79, −2.24	6.34, −4.87

* Details in common: monoclinic: $Z = 4$; 2θ data collection range $5 \leqslant 2\theta \leqslant 43°$; scan type ω–θ; step width 0.04°; number of steps 24; profile fitted, numerical absorption correction; quantity minimized $\Sigma w(F_o - F_c)^2$.

in the osmium species a carbonyl dissociation component seems to be operative under the conditions reported,[11,30] although kinetic studies are necessary for further discussion.

Experimental

Iridium trichloride (Johnson and Matthey), triphenylphosphine, methyldiphenylphosphine, triphenyl phosphite, tetraalkylammonium halides, silver hexafluoroantimonate and the tetrafluoroboric acid–diethyl ether complex (Aldrich), and tris(4-fluoro-, 4-chloro-, 4-methyl- and 4-methoxy-phenyl)phosphines (Strem Chemicals) were used as purchased; trimethylamine *N*-oxide (Aldrich) was sublimed and 1,8-diazabicyclo[5.4.0]undec-7-ene was distilled before use. The compounds $[Ir_4(CO)_{12}]$[31] and $[Ir_4(CO)_{11}Br]^-$[32] were prepared by literature methods, $[Ir_4(CO)_{11}L]$ (L = PPh_3, PPh_2Me or PPh_2H) by displacement of bromide from $[NBu_4][Ir_4(CO)_{11}Br]$ by 1 molar equivalent of $AgSbF_6$ and L,[13,24,27] and $[Ir_4(CO)_{10}(PPh_3)(PPh_2H)]$ by reaction of $[Ir_4(CO)_{11}(PPh_3)]$ with $[NBu_4]Br$, followed by $AgSbF_6$ and PPh_2H.[33] Manipulations were performed in a Schlenk tube, under an atmosphere of dry nitrogen. Tetrahydrofuran was dried over sodium and benzophenone, dichloromethane over CaH_2, hexane over sodium, and acetonitrile over phosphorus pentaoxide. Solvents were freshly distilled under nitrogen and freed from dissolved oxygen, where compatible by freeze degassing before use. The progress of the reactions was monitored by analytical TLC (precoated plates, silica gel F 254, 0.25 mm thick; E. Merck). Preparative TLC was carried out in air by using *ca.* 2 mm thick glass-backed silica gel plates (20 × 20 cm) prepared from silica GF 254 (type 60, E. Merck). All substituted Ir_4 cluster compounds were stored under an inert atmosphere for they were found to be slightly air sensitive in the solid state.

Fast atom bombardment (FAB) mass spectra were obtained by S. Naylor on a Kratos MS 902 instrument using *p*-nitrobenzyl alcohol as a matrix, IR spectra on Perkin Elmer 983 or 1700 Fourier-transform spectrophotometers between 2200 and 1600 cm^{-1}, and ^1H and ^{31}P NMR spectra on Bruker WM-250 or WH-400 spectrometers using deuteriated solvents as lock and reference [^1H, $SiMe_4$; ^{31}P, 85% H_3PO_4 (external)]. Microanalyses were performed in the Chemical Laboratory, University of Cambridge.

Preparation of $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$ **1**.—A yellow solution of compound **2** (123.5 mg, 0.1 mmol) in CH_2Cl_2 (20 cm^3) was treated with dbu (15 μl, 0.1 mmol) at room temperature and left stirring for 10 min to give the monoanion $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ **3**. Addition of HBF_4 (30 μl, 0.185 mmol) resulted in a drastic colour change from red to orange. After reduction of the solvent to 5 cm^3, compound **1** was purified by TLC with CH_2Cl_2–hexane (1:4), recrystallized from CH_2Cl_2–hexane, and obtained as orange microcrystals (121.0 mg, 98%).

Thermolysis of $[Ir_4(CO)_{11}(PPh_2H)]$ **2**.—A solution of compound **2** (30 mg, 0.024 mmol) in toluene (10 cm^3) was heated at 100 °C for 1.5 h. The solvent was evaporated, and the mixture purified by TLC as described above to yield $[Ir_4H(CO)_{11}(\mu\text{-}PPh_2)]$ **1** (21 mg, 70%) and decomposition products.

Preparation of $[Ir_4H(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **4a**.—To a solution of compound **1** (49.4 mg, 0.04 mmol) in CH_2Cl_2 (10 cm^3), PPh_3 (15.7 mg, 0.06 mmol) was added as a solid, and the mixture was allowed to react for 2 h at room temperature. The solvent was evaporated and the mixture separated by TLC with CH_2Cl_2–hexane (3:7) to yield unreacted **1** (3.5 mg), **4a**, which was recrystallized from CH_2Cl_2–hexane by slow evaporation as dark red crystals (50.5 mg, 86%), and traces of **6a**.

Preparation of $[Ir_4H(CO)_9L(\mu\text{-}PPh_2)]$ **4b**–**4h** [L = PPh_2Me, $P(OPh)_3$ *or* $P(C_6H_4X\text{-}4)_3$, X = F, Cl, Me, 4-OMe *or* 2-OMe].—A similar procedure to that described for the synthesis of **4a** was followed to obtain compounds **4b**–**4h**, except that the reactions were scaled down by 50% and were left stirring for only 0.5 h in the case of the nucleophiles $P(OPh)_3$

and $P(C_6H_4X\text{-}4)_3$ (X = Me or OMe) in order to avoid formation of the disubstituted species. The mixtures were purified as described for **4a**, and the compounds obtained in variable yields, **4b** (23.9, 85), **4c** (21.3, 70), **4d** (22.3, 73), **4e** (22.0, 70), **4f** (27.0, 89) and **4g** (28.0, 90%), besides traces of unreacted **1** and of the disubstituted derivatives **6b**–**6g**.

Preparation of $[Ir_4H(CO)_8(PR_3)_2(\mu\text{-}PPh_2)]$ $[PR_3 = PPh_3$ **6a**, $P(C_6H_4X\text{-}4)_3$ (X = Cl **6e** *or* Me **6f**)].—To solutions of compound **1** (12.4 mg, 0.1 mmol) in thf (5 cm^3) was added a six-fold excess of the desired phosphine, and the mixtures were allowed to react for 6 h at 40 °C. The solvent was evaporated, the compounds were purified by TLC with CH_2Cl_2–hexane (3:7), and obtained as red oils, **6a** (7.7, 51), **6e** (8.6, 45) and **6f** (8.3 mg, 46%), together with the respective monosubstituted compounds and some decomposition products.

Alternative Preparation $[Ir_4H(CO)_8(PPh_3)_2(\mu\text{-}PPh_2)]$ **6a**.—To a solution of compound **4a** (29.4 mg, 0.02 mmol) in CH_2Cl_2 (8 cm^3) cooled to −40 °C were added in sequence PPh_3 (5.3 mg, 0.02 mmol) as a solid and a freshly made 0.1 mol dm^{-3} solution of Me_3NO (0.2 cm^3, 0.02 mmol). The mixture was allowed to warm to room temperature and left stirring for 1 h, after which time it was separated by TLC as described above to yield **6a** (25 mg, 85%) and some decomposition products.

Alternative Preparation of $[Ir_4H(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **4a**.—To a solution of compound **1** (24.7 mg, 0.02 mmol) in thf (5 cm^3) were added a solution of LiBu in hexane (62.5 µl, 0.1 mmol) and PPh_3 (5.2 mg, 0.02 mmol) as a solid. An excess of HBF_4 (1 drop) was added after 5 min. The mixture was purified as described previously, to yield **4a** (25.0 mg, 85%), besides decomposition products.

Thermolysis of $[Ir_4(CO)_{10}(PPh_3)(PPh_2H)]$ **7a**.—A solution of compound **7a** (15 mg, 0.01 mmol) in toluene (5 cm^3) was heated at 70 °C for 2.5 h, and at 100 °C for 0.25 h. The solvent

Table 6 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Ir(1)	3539(2)	3003(1)	−992(1)
Ir(2)	2653(2)	3776(1)	215(1)
Ir(3)	3195(2)	2211(1)	311(1)
Ir(4)	5614(2)	3244(1)	117(1)
P	5773(12)	1913(5)	180(5)
C(101)	6338	1319	−580
C(102)	7642(29)	1534(12)	−958(14)
C(103)	8142	1084	−1549
C(104)	7337	418	−1764
C(105)	6033	203	−1386
C(106)	5533	653	−795
C(111)	6869	1483	951
C(112)	8001(37)	928(17)	843(12)
C(113)	8879	663	1445
C(114)	8625	954	2155
C(115)	7492	1509	2263
C(116)	6614	1774	1661
C(11)	4425(39)	2323(16)	−1673(15)
O(11)	4829(37)	1909(16)	−2138(12)
C(12)	4149(48)	3931(13)	−1445(19)
O(12)	4430(36)	4522(11)	−1723(15)
C(13)	1561(18)	2859(21)	−1374(19)
O(13)	355(18)	2724(20)	−1612(16)
C(21)	2425(61)	4186(26)	1171(11)
O(21)	2278(65)	4393(23)	1778(10)
C(22)	1711(47)	4602(17)	−296(20)
O(22)	1037(33)	5014(15)	−692(14)
C(23)	1220(46)	2940(25)	314(22)
O(23)	−79(45)	2828(21)	343(18)
C(31)	2019(43)	1404(17)	−104(21)
O(31)	1338(34)	899(15)	−379(17)
C(32)	2934(52)	1887(23)	1294(9)
O(32)	2622(43)	1738(23)	1900(9)
C(41)	7209(31)	3571(21)	−483(17)
O(41)	8055(24)	3861(16)	−884(11)
C(42)	6688(38)	3509(20)	990(12)
O(42)	7304(36)	3654(19)	1548(10)

Table 7 Atomic coordinates (× 10^4) for compound **4a**

Atom	*x*	*y*	*z*
Ir(1)	−42(1)	4692(2)	2086(1)
Ir(2)	627(1)	6342(2)	3027(1)
Ir(3)	1340(1)	4899(2)	2348(1)
Ir(4)	743(1)	3748(2)	3273(1)
P(1)	1872(5)	4055(10)	3352(5)
C(101)	2403	5012	4003
C(102)	2815(13)	5983(25)	3857(10)
C(103)	3203	6740	4363
C(104)	3178	6525	5014
C(105)	2765	5554	5160
C(106)	2377	4797	4655
C(111)	2380	2589	3378
C(112)	2123(11)	1603(27)	2929(12)
C(113)	2491	468	2921
C(114)	3115	318	3363
C(115)	3373	1303	3812
C(116)	3005	2438	3819
P(2)	−467(6)	2969(10)	1373(5)
C(201)	−816	1604	1752
C(202)	−827(12)	371(25)	1473(11)
C(203)	−1114	−668	1731
C(204)	−1391	−475	2268
C(205)	−1381	758	2547
C(206)	−1094	1798	2289
C(211)	112	2190	985
C(212)	600(14)	1366(26)	1356(10)
C(213)	1056	753	1063
C(214)	1025	964	398
C(215)	538	1787	26
C(216)	81	2401	320
C(221)	−1145	3501	688
C(222)	−1121(13)	4733(25)	417(15)
C(223)	−1627	5128	−123
C(224)	−2157	4291	−392
C(225)	−2181	3060	−121
C(226)	−1675	2665	419
C(11)	460(25)	5415(45)	1492(17)
O(11)	467(14)	5977(31)	1014(14)
C(12)	−892(14)	5469(56)	1901(33)
O(12)	−1376(11)	6089(26)	1819(19)
C(21)	−128(12)	6569(38)	3365(17)
O(21)	−612(12)	6682(37)	3549(20)
C(22)	517(23)	7755(32)	2444(19)
O(22)	549(22)	8572(27)	2071(15)
C(23)	1260(16)	7105(35)	3727(15)
O(23)	1599(17)	7620(34)	4182(15)
C(31)	1727(16)	3795(32)	1831(15)
O(31)	2014(14)	3159(29)	1535(13)
C(32)	1835(19)	6341(29)	2190(22)
O(32)	2097(15)	7299(19)	2102(16)
C(41)	715(18)	1926(10)	3239(19)
O(41)	675(20)	804(11)	3190(15)
C(42)	567(16)	4010(34)	4101(9)
O(42)	508(20)	4254(37)	4625(9)
C(100)	5002(33)	4558(67)	5733(33)
C(101)	4656(37)	3639(71)	5063(39)
C(102)	4802(36)	3988(74)	4408(37)

was evaporated, and the mixtures were purified by TLC as described previously to yield **4a** (13, 90; and 10 mg, 70%, respectively), and, in the latter case decomposition products.

Crystal Structure Determinations for Compounds **1** *and* **4a**.—Crystal data and details of data collection and structure solution are summarized in Table 5. Crystals of the two compounds were mounted on glass fibres with epoxy resin, and transferred to a Stoe four-circle diffractometer. Intensity data were recorded at room temperature using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The unit-cell parameters were refined by a least-squares procedure. Three check reflections were monitored at regular intervals throughout the data collection and showed no significant variations. All intensity data were corrected for Lorentz polarization effects, and for absorption using numerical methods. The structures were solved by a combination of direct methods and Fourier-difference techniques, and refined on F by full-matrix least squares (using the SHELXTL PC™ program[34]). The phenyl rings were refined as rigid groups, and phenyl hydrogen atoms were placed in idealized positions (C–H 0.96 Å) and allowed to ride on the relevant C atom; the phenyl H atoms were assigned a common isotropic thermal parameter. The metal hydride positions were estimated by potential-energy calculations,[21] but these atoms were not included in the refinement. Both crystals were weakly diffracting, and in particular the quality of the data for **4a** was poor and the refinement unstable. The refinements were improved by imposing additional positional constraints on the Ir–C(carbonyl) [1.88(3) Å] and the C–O [1.160(1) Å] distances. During the final cycles of refinement weighting schemes were applied, and analysis of the variation of the sum of $w\Delta^2$ ($\Delta = F_o - |F_c|$) according to $|F_o|$ and sin θ indicated that they were appropriate. The final positional coordinates for the non-hydrogen atoms for **1** and **4a** are listed in Tables 6 and 7, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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