# Syntheses and structural characterisation of $[Ir_4(CO)_{11}(\eta^1\text{-}L)]$ and $[Ir_4(CO)_{10}(\eta^1\text{-}L)_2]$ $\{L = [Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]\}$ and $[Ir_4(CO)_{11}\{\mu\text{-}\eta^1:\eta^1\text{-}[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]\}Ir_4(CO)_{11}]$ and its facile conversion to $[Ir_4H(CO)_{10}\{Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}P_3C(CMe_2CH_2)CBu^t]\}Ir_4(CO)_{11}]$, *via* an unusual C–H activation†

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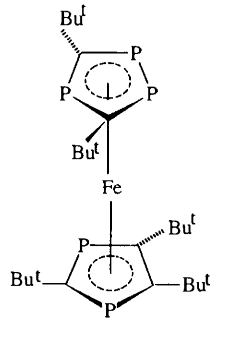
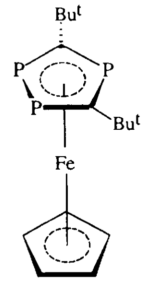
The reactions of $NBu_4[Ir_4(CO)_{11}Br]$ **1** with equivalent amounts of $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ $L^1$ or $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ $L^2$ in the presence of $AgSbF_6$ gave good yields of $[Ir_4(CO)_{11}(\eta^1\text{-}L)]$ **2a** or **2b**, besides $[Ir_4(CO)_{10}(\eta^1\text{-}L)_2]$ **3a** and **3b**, respectively, in which the ligands are bound *via* the $P_A$ atom. The solid-state structure of **2b**, established by an X-ray analysis, is that of the $T_d$-like isomer, although the low-temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum showed the presence of both $C_{3v}$- and $T_d$-like isomers in solution. Compound **2a** underwent facile conversion to $[Ir_4(CO)_{10}(\mu\text{-}\eta^2\text{-}L^1)]$ **4a** *via* CO loss and further interaction of the adjacent $P_B$ atom of $L^1$. Compound **2b** reacted with **1** in the presence of $AgSbF_6$ to yield $[Ir_4(CO)_{11}(\mu\text{-}\eta^1:\eta^1\text{-}L^2)Ir_4(CO)_{11}]$ **5b**, in which the second $Ir_4$ cluster was ligated *via* $P_C$, rather than $P_B$, according to NMR spectroscopy. This compound underwent clean conversion into $[Ir_4H(CO)_{10}\{Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}P_3C(CMe_2CH_2)CBu^t]\}Ir_4(CO)_{11}]$ **6b**, *via* CO loss and oxidative addition of a C–H bond of a *tert*-butyl substituent in the $P_3C_2Bu^t_2$ ring. The molecular structure of **6b** was determined by a single crystal X-ray diffraction analysis, which showed that C–H activation occurred on the $Ir_4$ cluster bound *via* $P_C$.

The recently reported sandwich compounds of the type $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]$,[1] $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$[2] and $[Fe(\eta^5\text{-}C_5R_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ (R = H or Me)[3,4] have the important additional potential to act as ligands[5] *via* the P lone pairs of the $\eta^5\text{-}P_3C_2Bu^t_2$ ring system, and complexes such as $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2M(CO)_n]$ [M = W, *n* = 5; M = Fe, *n* = 4],[6] $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)W(CO)_5]$,[6] $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2Bu^t_2)M(CO)_n]$ [M = Cr or W, *n* = 5; M = Fe, *n* = 4][6] and $[\{Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2Bu^t_2)Ni(CO)_2\}_2]$[7] have been described. There are only three reports involving the interaction of these ligands with carbonyl cluster compounds in the literature. Substitution of $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ for CO in $[Ru_3(CO)_{12}]$ was found to give $[Ru_3(CO)_{10}\{\mu\text{-}\eta^1:\eta^1\text{-}[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]\}]$, in which the two rings are co-ordinated to adjacent metal centres in equatorial positions,[6] while the reaction with $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ was shown first to give $[Ru_3(CO)_{11}\{\eta^1\text{-}[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2Bu^t_2)]\}]$, in which the $\eta^5\text{-}P_3C_2Bu^t_2$ ring interacts *via* one of the two adjacent phosphorus atoms, and subsequently $[Ru_3(CO)_9\{\mu_3\text{-}\eta^2\text{-}[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2Bu^t_2)]\}]$, is formed *via* further CO loss and $\mu_3\text{-}\eta^2$-ligation of a P–P and P–C multiple bonded system to the three metal centres.[8] Finally, the reaction of $[Ru_3(CO)_{12}]$ with $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ under thermolytic conditions gave $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}P_5C_5Bu^t_5)]$, albeit in minute yields among other products, as a result of the remarkable extrusion of iron and subsequent coupling of the $P_3C_2Bu^t_2$ and $P_2C_3Bu^t_3$ rings.[9]

We now describe the first examples of complexes of the $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ ($L^1$) and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ ($L^2$) systems with tetranuclear iridium carbonyl clusters and also the unprecedented attachment of a second $Ir_4$ unit *via* the unique P atom of the $\eta^5\text{-}P_3C_2Bu^t_2$ ring system. The subsequent steric crowding of one *tert*-butyl substituent in the $P_3C_2Bu^t_2$ ring leads to a novel intramolecular C–H activation at one of the iridium centres.



$L^1$



$L^2$

## Results and Discussion

### Synthesis and characterisation of $[Ir_4(CO)_{11}(\eta^1\text{-}L)]$ (L = $L^1$, 2a; L = $L^2$, 2b), $[Ir_4(CO)_{10}(\eta^1\text{-}L)_2]$ (L = $L^1$, 3a; L = $L^2$, 3b) and $[Ir_4(CO)_{10}(\mu\text{-}\eta^2\text{-}L^1)]$ 4a

Treatment of $NBu_4[Ir_4(CO)_{11}Br]$ **1** with equivalent amounts of $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ $L^1$ or $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ $L^2$, in tetrahydrofuran at −30 °C in the presence of $AgSbF_6$, gave very good yields of the respective CO monosubstituted species $[Ir_4(CO)_{11}(\eta^1\text{-}L)]$ (**2a** and **2b**). In addition, the disubstituted derivatives $[Ir_4(CO)_{10}(\eta^1\text{-}L)_2]$ (**3a**

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† Basis of the presentation given at Dalton Discussion No. 1, 3rd–5th January 1996, University of Southampton, UK.

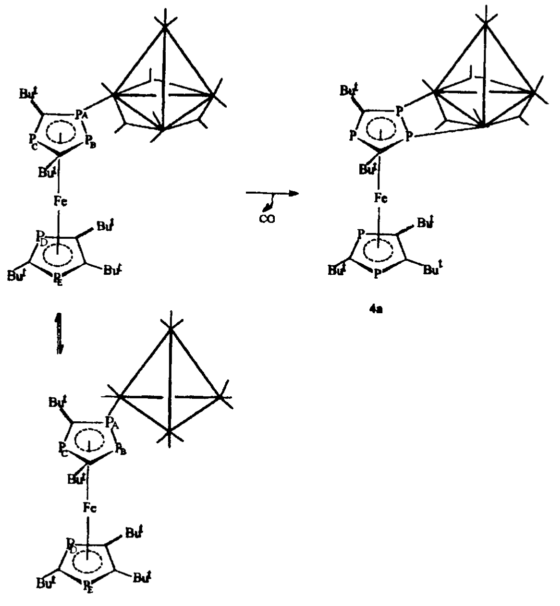
and **3b**, respectively) were also isolated in poor yields from this reaction. Furthermore, in the case of the reaction with $L^1$ a product resulting from the interaction of two of its P atoms, $[Ir_4(CO)_{10}(\mu\text{-}\eta^2\text{-}L^1)]$ **4a** was also isolated.

All these species were fully characterized by spectroscopy and, in the case of compound **2b**, also by an X-ray analysis. The compounds were formulated on the basis of their secondary-ion mass spectra which, under normal conditions, showed molecular-ion peaks, in all cases but for compound **2a**, for which saturation of the matrix with CO was necessary to avoid its conversion on the probe[10] into compound **4a**.

The observation of two doublets of doublets and a triplet resonance in the $^{31}P\text{-}\{^1H\}$ NMR spectra of the monosubstituted compounds **2a** and **2b** obtained in $CD_2Cl_2$ at 213 and 298 K, respectively, indicated that the $\eta^5\text{-}P_3C_2Bu^t_2$ rings of coordinated $L^1$ and $L^2$ were bound to these clusters by one of the two adjacent phosphorus atoms, as established for $[Ru_3(CO)_{11}(\eta^1\text{-}L^2)]$[8] and for other mononuclear systems.[6] The two other doublet resonances in the spectrum of compound **2a** and the presence of five singlets of equal intensity in the *tert*-butyl region of its $^1H$ NMR spectrum (also obtained at 213 K) indicated hindrance to $\eta^5\text{-}P_2C_3Bu^t_3$ ring rotation.

Raising the temperature led to a major change in the solution $^{31}P\text{-}\{^1H\}$ NMR spectrum of compound **2a**. At 298 K it exhibited two large singlets due to the $\eta^5\text{-}P_2C_3Bu^t_3$ ring phosphorus atoms [δ 42.7 ($P_E$) and 45.1 ($P_F$)], two multiplets [δ 15–22 ($P_A$) and δ −8 to −22 ($P_B$)] and a triplet [δ 15.1 ($P_C$)] due to the three P nuclei of the $\eta^5$-ligated $P_3C_2Bu^t_2$ ring. These results indicated that this compound was fluxional in solution, however the coalescence temperature could not be reached because **2a** rapidly lost CO when heated to give compound **4a**. This fluxional process most probably involves an intramolecular 1,2-shift of the Ir atom between $P_A$ and $P_B$ of the $\eta^5\text{-}P_3C_2Bu^t_2$ ring, as previously observed for $[W(CO)_5\{\eta^1\text{-}[M(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]\}]$ (M = Fe or Ru)[11] and *trans*-$[MCl(\eta^1\text{-}P_2C_3R_3)(PEt_3)_2]$ (R = $Bu^t$ or adamantyl, M = Pd or Pt) (see Scheme 1).[12]

The molecular structure of compound **2b** was established by X-ray diffraction analysis and is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The structure confirms the formulation based on spectroscopic data and the cluster attachment to the $\eta^5\text{-}P_3C_2Bu^t_2$ ring of $L^2$ by one of the two P–P bonded ring atoms. The four iridium atoms exhibit a tetrahedral $Ir_4$ core, with terminal ligands only; Ir(1), Ir(3) and Ir(4) are linked to three terminal COs while Ir(2) is in a unique environment, being joined to two terminal COs and to P(1) of $L^2$, which occupies an axial position with respect to the Ir(1)–Ir(2)–Ir(4) plane. The Ir–C and C–O bond distances are in the normal range of values found for terminal CO groups. The average Ir–Ir distance is 2.688 Å and is within the average range



Scheme 1

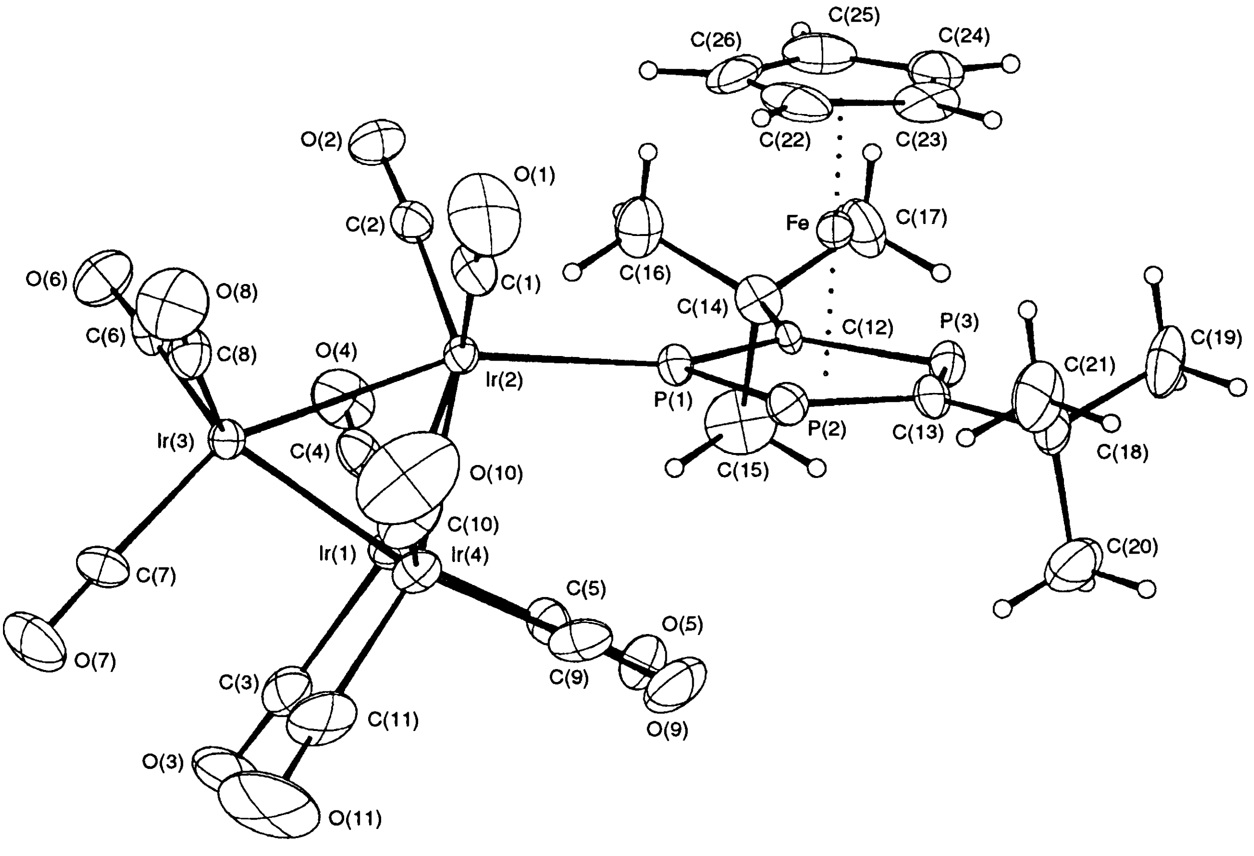
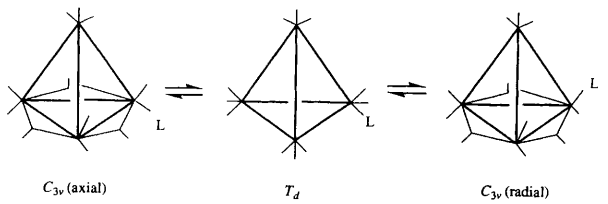


**Fig. 1** Molecular structure of $[Ir_4(CO)_{11}L^2]$ **2b** showing the atomic labelling scheme

**Table 1** Bond lengths (Å) and angles (°) for compound **2b**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ir(1)–Ir(2) | 2.6970(9) | Ir(1)–Ir(3) | 2.6861(12) | P(1)–C(12) | 1.774(14) | P(2)–C(13) | 1.75(2) |
| Ir(1)–Ir(4) | 2.6852(12) | Ir(2)–Ir(3) | 2.6761(9) | P(3)–C(12) | 1.754(13) | P(3)–C(13) | 1.77(2) |
| Ir(2)–Ir(4) | 2.7012(12) | Ir(3)–Ir(4) | 2.6840(10) | Fe–P(1) | 2.313(4) | Fe–P(2) | 2.329(5) |
| Ir(1)–C(3) | 1.92(2) | Ir(1)–C(4) | 1.89(2) | Fe–P(3) | 2.304(4) | Fe–C(12) | 2.133(13) |
| Ir(1)–C(5) | 1.91(2) | Ir(2)–C(1) | 1.88(2) | Fe–C(13) | 2.14(2) | Fe–C(22) | 2.07(2) |
| Ir(2)–C(2) | 1.90(2) | Ir(3)–C(6) | 1.95(2) | Fe–C(23) | 2.05(2) | Fe–C(24) | 2.07(2) |
| Ir(3)–C(7) | 1.92(2) | Ir(3)–C(8) | 1.89(2) | Fe–C(25) | 2.09(2) | Fe–C(26) | 2.06(2) |
| Ir(4)–C(9) | 1.91(2) | Ir(4)–C(10) | 1.90(2) | C(12)–C(14) | 1.57(2) | C(13)–C(18) | 1.54(2) |
| Ir(4)–C(11) | 1.93(2) | Ir(2)–P(1) | 2.345(4) | C(14)–C(17) | 1.51(2) | C(14)–C(16) | 1.51(2) |
| O(1)–C(1) | 1.13(2) | O(2)–C(2) | 1.12(2) | C(14)–C(15) | 1.56(2) | C(18)–C(19) | 1.52(3) |
| O(3)–C(3) | 1.13(2) | O(4)–C(4) | 1.13(2) | C(18)–C(20) | 1.52(3) | C(18)–C(21) | 1.55(3) |
| O(5)–C(5) | 1.12(2) | O(6)–C(6) | 1.11(2) | C(22)–C(26) | 1.37(3) | C(22)–C(23) | 1.43(3) |
| O(7)–C(7) | 1.10(2) | O(8)–C(8) | 1.15(2) | C(23)–C(24) | 1.38(3) | C(24)–C(25) | 1.36(3) |
| O(9)–C(9) | 1.13(2) | O(10)–C(10) | 1.13(2) | C(25)–C(26) | 1.38(3) | | |
| O(11)–C(11) | 1.12(3) | P(1)–P(2) | 2.104(5) | | | | |
| | | | | | | | |
| C(4)–Ir(1)–C(5) | 102.3(7) | C(4)–Ir(1)–C(3) | 102.3(8) | C(11)–Ir(4)–Ir(3) | 94.6(7) | C(10)–Ir(4)–Ir(1) | 154.5(7) |
| C(5)–Ir(1)–C(3) | 98.4(7) | C(4)–Ir(1)–Ir(3) | 98.2(6) | C(9)–Ir(4)–Ir(1) | 97.9(5) | C(11)–Ir(4)–Ir(1) | 95.5(7) |
| C(5)–Ir(1)–Ir(3) | 152.0(5) | C(3)–Ir(1)–Ir(3) | 95.6(5) | Ir(3)–Ir(4)–Ir(1) | 60.04(3) | C(10)–Ir(4)–Ir(2) | 98.1(7) |
| C(4)–Ir(1)–Ir(4) | 150.7(5) | C(5)–Ir(1)–Ir(4) | 93.8(5) | C(9)–Ir(4)–Ir(2) | 101.1(5) | C(11)–Ir(4)–Ir(2) | 150.3(7) |
| C(3)–Ir(1)–Ir(4) | 99.3(6) | Ir(3)–Ir(1)–Ir(4) | 59.96(3) | Ir(3)–Ir(4)–Ir(2) | 59.59(2) | Ir(1)–Ir(4)–Ir(2) | 60.09(3) |
| C(4)–Ir(1)–Ir(2) | 92.5(5) | C(5)–Ir(1)–Ir(2) | 100.3(5) | C(12)–P(1)–P(2) | 101.9(5) | C(12)–P(1)–Ir(2) | 141.4(5) |
| C(3)–Ir(1)–Ir(2) | 153.0(6) | Ir(3)–Ir(1)–Ir(2) | 59.62(3) | P(2)–P(1)–Ir(2) | 116.4(2) | Fe–P(1)–Ir(2) | 132.2(2) |
| Ir(4)–Ir(1)–Ir(2) | 60.25(3) | C(2)–Ir(2)–C(1) | 98.1(7) | C(13)–P(2)–P(1) | 97.4(5) | C(12)–P(3)–C(13) | 99.6(7) |
| C(2)–Ir(2)–P(1) | 102.5(5) | C(1)–Ir(2)–P(1) | 94.9(5) | O(1)–C(1)–Ir(2) | 177(2) | O(2)–C(2)–Ir(2) | 175(2) |
| C(2)–Ir(2)–Ir(3) | 93.1(4) | C(1)–Ir(2)–Ir(3) | 100.2(5) | O(3)–C(3)–Ir(1) | 178(2) | O(4)–C(4)–Ir(1) | 179(2) |
| P(1)–Ir(2)–Ir(3) | 156.53(9) | C(2)–Ir(2)–Ir(1) | 102.8(5) | O(5)–C(5)–Ir(1) | 177(2) | O(6)–C(6)–Ir(3) | 174(2) |
| C(1)–Ir(2)–Ir(1) | 151.6(5) | P(1)–Ir(2)–Ir(1) | 99.04(9) | O(7)–C(7)–Ir(3) | 177(2) | O(8)–C(8)–Ir(3) | 176(2) |
| Ir(3)–Ir(2)–Ir(1) | 59.99(3) | C(2)–Ir(2)–Ir(4) | 152.2(4) | O(9)–C(9)–Ir(4) | 177(2) | O(10)–C(10)–Ir(4) | 179(3) |
| C(1)–Ir(2)–Ir(4) | 93.4(5) | P(1)–Ir(2)–Ir(4) | 101.59(9) | O(11)–C(11)–Ir(4) | 178(2) | C(14)–C(12)–P(3) | 117.1(10) |
| Ir(3)–Ir(2)–Ir(4) | 59.88(2) | Ir(1)–Ir(2)–Ir(4) | 59.66(3) | C(14)–C(12)–P(1) | 124.5(9) | P(3)–C(12)–P(1) | 118.2(8) |
| C(8)–Ir(3)–C(6) | 99.5(7) | C(8)–Ir(3)–C(7) | 101.0(8) | C(18)–C(13)–P(2) | 119.9(11) | C(18)–C(13)–P(3) | 117.4(11) |
| C(6)–Ir(3)–C(7) | 98.9(7) | C(8)–Ir(3)–Ir(2) | 95.1(5) | P(2)–C(13)–P(3) | 122.5(8) | C(17)–C(14)–C(16) | 108.9(14) |
| C(6)–Ir(3)–Ir(2) | 98.4(4) | C(7)–Ir(3)–Ir(2) | 154.0(6) | C(17)–C(14)–C(12) | 111.7(12) | C(16)–C(14)–C(12) | 113.2(12) |
| C(8)–Ir(3)–Ir(4) | 96.4(5) | C(6)–Ir(3)–Ir(4) | 154.7(5) | C(17)–C(14)–C(15) | 110(2) | C(16)–C(14)–C(15) | 107.8(14) |
| C(7)–Ir(3)–Ir(4) | 97.2(6) | Ir(2)–Ir(3)–Ir(4) | 60.52(3) | C(12)–C(14)–C(15) | 105.6(12) | C(19)–C(18)–C(20) | 108(2) |
| C(8)–Ir(3)–Ir(1) | 151.5(5) | C(6)–Ir(3)–Ir(1) | 98.4(5) | C(19)–C(18)–C(13) | 113(2) | C(20)–C(18)–C(13) | 106.8(14) |
| C(7)–Ir(3)–Ir(1) | 97.9(7) | Ir(2)–Ir(3)–Ir(1) | 60.39(2) | C(19)–C(18)–C(21) | 108(2) | C(20)–C(18)–C(21) | 111(2) |
| Ir(4)–Ir(3)–Ir(1) | 60.00(3) | C(10)–Ir(4)–C(9) | 99.4(9) | C(13)–C(18)–C(21) | 110.7(13) | C(26)–C(22)–C(23) | 106(2) |
| C(10)–Ir(4)–C(11) | 100.2(11) | C(9)–Ir(4)–C(11) | 98.8(9) | C(24)–C(23)–C(22) | 107(2) | C(25)–C(24)–C(23) | 109(2) |
| C(10)–Ir(4)–Ir(3) | 98.5(7) | C(9)–Ir(4)–Ir(3) | 155.4(5) | C(24)–C(25)–C(26) | 108(2) | C(22)–C(26)–C(25) | 109(2) |



of Ir–Ir bond distances observed in other $[Ir_4(CO)_{11}L]$ clusters with the same ligand arrangement [L = CO, 2.693;[13] SCN, 2.684;[14] CNBu$^t$, 2.685[15] or $P(OCH_2)_3CEt$, 2691(1) Å[16]]. The Ir(2)–P(1) bond length [2.345(4) Å] is within the values observed for Ir–P bond lengths in other tetranuclear iridium clusters, *e.g.* $[Ir_4(CO)_{11}\{AuPPh_2(PPh_3)\}]$ 2.36[17] and $[Ir_4(CO)_9(PPh_3)(nbd)]$ (nbd = norbornadiene) 2.344(7) Å.[18] The $P_3C_2Bu^t_2$ and $C_5H_5$ rings are parallel and eclipsed, and the bond lengths and angles of $L^2$ agree well with those of closely related complexes.[6–8] There are no unusual intermolecular interactions in the crystal structure of **2b**.

Compounds **2b** and $[Ir_4(CO)_{11}\{P(OCH_2)_3CEt\}]$[16] are the only monosubstiuted $Ir_4$ clusters having phosphorus-containing ligands, whose structures, in the solid state, are devoid of bridging COs. In solution, the cluster compounds $[Ir_4(CO)_{11}L]$ have a ground-state geometry either with all ligands terminal ($T_d$-like geometry), or with three edge bridging COs defining the basal plane of the metal tetrahedron ($C_{3v}$-like geometry). In the latter case, L is usually located in the axial position, although an isomer with L in a radial position has been observed for ligands L with small cone angles.[19,20] A correlation has been found between the preference for a given ground state cluster geometry and the electronic[16] and steric properties of the phosphorus ligand. Thus, clusters containing tertiary phosphines, in particular the most basic ones, exhibit the $C_{3v}$-like geometry, since bridging COs are better π acceptors than terminal COs, while clusters containing good π acceptors like trialkyl phosphites have $T_d$-type geometry. Furthermore, large ligands tend to favour $C_{3v}$-like geometry, while with small ligands the $T_d$-type geometry is preferred. These structures are configurationally non-rigid and undergo interconversion at relatively low temperatures.[19–22]

Even though the solid-state structure of compound **2b** exhibited only terminally bound CO ligands, its IR spectra, both in the solid state and in solution, showed the presence of both terminal and bridging CO ligands, implying that this compound existed as a mixture of the $T_d$-and $C_{3v}$-like isomers. A variable-temperature $^{31}P-\{^1H\}$ NMR study of compound **2b** was then undertaken. The limiting spectrum in $CD_2Cl_2$–$CFCl_3$ at 172 K presented two sets of three resonances at δ −17.6 (dd, $P_A$), 17.7 (dd, $P_B$), 16.7 [t, $P_C$, $^1J(P_AP_B)$ 449, $^2J(P_AP_C)$ 54, $^2J(P_BP_C)$ 36] and −47.1 (dd, $P_A$), 20.7 (dd, $P_B$), 14.8 [t, $P_C$, $^1J(P_AP_B)$ 425, $^2J(P_AP_C)$ 50, $^2J(P_BP_C)$ 37 Hz], with approximate relative intensities 1 : 0.15 and with Δδ (δ co-ordinated − δ free L) of −55.5 and −85.0 ppm, respectively. In previous studies[22] more negative Δδ have been observed for P-donor atoms in an axial position of the $C_{3v}$-like isomer than for P-donor atoms in the $T_d$-like isomer. Our results seemed therefore to indicate the predominance of the $T_d$-like isomer in solution.

The $^{31}P-\{^1H\}$ NMR spectrum of compound **2a**, obtained at 183 K, only showed one set of five resonances, indicating that only one of the isomers is present in solution in high enough concentration to be detected. The solution IR spectrum of this species also suggested that, also in this case, it is the $T_d$-like isomer that was present in highest concentration, as the ν(μ-CO) were as weak as those observed in the spectrum of $[Ir_4(CO)_{11}(PPhH_2)]$, for which a ratio of 1:0.016:0.012 [$T_d$:$C_{3v}$(radial):$C_{3v}$(axial)] was established by variable-temperature $^{13}C-\{^1H\}$ NMR studies.[19] The fluxional behaviour of both **2a** and **2b** are under study and will be reported shortly.[23]

No comparative theoretical studies on the bonding capabilities of $L^1$ and $L^2$ have been reported to date, however the above results tend to indicate that $L^1$ is a poorer σ donor/better π acceptor than $L^2$. This suggestion agrees well with the results of UV absorption and magnetic circular dichroism studies of phosphabenzene that have established that the P atom is, in a π-electron sense, more electronegative than carbon.[24] Related studies on the photoelectron spectroscopy of transition-metal complexes containing the $\eta^5$-$P_2C_3Bu^t_3$ ring gave similar results.[25] Thus, just as with the benzene–phosphabenzene system, the $\eta^5$-$P_2C_3Bu^t_3$ ring in $L^1$ (relative to the $\eta^5$-$C_5H_5$ ring in $L^2$) must have comparable π donor but higher π acceptor strength, and, as a result, the central Fe atom in $L^1$ must carry a more positive partial charge than that in $L^2$. This would account for the apparent poorer σ donor/better π acceptor capability of $L^1$ compared to $L^2$ towards '$Ir_4(CO)_{11}$'.

In solution, compound **2a** undergoes CO dissociation and further interaction with $L^1$ to give compound **4a** (see Scheme 1).

The $^{31}P-\{^1H\}$ NMR spectrum of compound **4a** is extremely simple, in that it shows the equivalence of the two adjacent P nuclei of the $P_3C_2Bu^t_2$ ring, $P_A$ and $P_B$, which appear as doublets at relatively low frequency, thus indicating that $L^1$ is co-ordinated to this cluster *via* the two P atoms. Both the mass spectral and IR data confirm such a formulation for this brown compound whose proposed structure is illustrated in Scheme 1. This behaviour is analogous to that previously observed for $[Ru_3(CO)_{11}(\eta^1-L^2)]$, except that this compound undergoes further dissociation of two COs to give $[Ru_3(CO)_9(\mu_3-\eta^2-L^2)]$, in which the $P_3C_2Bu^t_2$ ring interacts further *via* the P=P bond.[8]

The lability of compound **2a** was markedly higher than that of **2b**. In solution, at room temperature, it lost either CO to give **4a** or $L^1$ to give $[Ir_4(CO)_{12}]$ and unidentified decomposition product(s). On the other hand compound **2b** was inert towards loss of $L^2$, and heating at 60 °C for 48 h did not lead to its conversion into a compound analogous to **4a**. In the light of the relative bonding properties proposed above for $L^1$ and $L^2$, this is an unexpected result. Indeed, kinetic studies of the CO substitution reactions of a series of $[Ir_4(CO)_{11}L]$ compounds with L′ = phosphine, *etc.* have established that the process is mostly dissociative and that the ligand L shows a relatively large labilisation of CO, the better σ donor and poorer π acceptor it is. The source of kinetic acceleration was ascribed to the stabilisation of the resulting transition state, the other possible source being ground-state destabilisation.[26] Thus, it might be possible that $L^1$ in compound **2a** is more efficient in destabilising the ground state than $L^2$ in compound **2b**.

### Synthesis of $[Ir_4(CO)_{11}(\mu-\eta^1:\eta^1-L^2)Ir_4(CO)_{11}]$ 5b and its transformation into $[Ir_4H(CO)_{10}\{Fe(\eta^5-C_5H_5)[\eta^5-P_3C(CMe_2CH_2)CBu^t]\}Ir_4(CO)_{11}]$ 6b

We have investigated further the bonding possibilities of co-ordinated $L^2$ in **2b**, since both $P_B$ and $P_C$ have lone pairs available for co-ordination. Compound **2b** was chosen rather than **2a** because, as mentioned above, it is less labile. In addition to compounds **2a** and **2b**, other compounds in which both $P_A$ and $P_B$ atoms are ligated are known.[7] However, prior to this work, $P_C$ was never found to utilize its lone pair, and this was believed to be due to the protection of the two adjacent *tert*-butyl groups.

Thus, treatment of compound **2b** with $NBu_4[Ir_4(CO)_{11}Br]$ in the presence of $AgSbF_6$ gave high yields of the dark orange species $[Ir_4(CO)_{11}(\mu-\eta^1:\eta^1-L^1)Ir_4(CO)_{11}]$ **5b**, which was fully characterised by $^{31}P-\{^1H\}$ and $^1H$ NMR spectroscopy. The room temperature $^{31}P-\{^1H\}$ NMR spectrum of **5b** is of AMX type, which proved that $P_B$ was not involved in the second ligation step and the significant downfield chemical shift of $P_C$ showed unequivocally that the second $Ir_4$ cluster was ligated *via* $P_C$, rather than $P_B$. This is no doubt a direct consequence of the steric size of the first ligated $Ir_4$ undecacarbonyl cluster, restricting $P_B$ from further interaction, thereby facilitating the involvement of $P_C$.

Compound **5b** could not be further characterised because it was extremely labile and underwent an unprecedented rearrangement involving both loss of CO and oxidative addition of a C–H bond of a $Bu^t$ substituent in the $P_3C_2Bu^t_2$ ring to give the brown compound $[Ir_4H(CO)_{10}\{Fe(\eta^5-C_5H_5)[\eta^5-P_3C(CMe_2CH_2)CBu^t]\}Ir_4(CO)_{11}]$ **6b** as the only product. The room temperature $^{31}P-\{^1H\}$ NMR of **6b** showed only minor shifts in the P frequencies, compared to those of **5b**. The $^1H$ NMR spectrum indicated that oxidative addition of a $Bu^t$ group C–H bond had also occurred, by the observation of both the methylene resonance at δ 1.6 [*J*(HH) 12.0 Hz] and the characteristic hydride which appeared as a doublet at δ −22.1 [$^2J$(PH) 7.0 Hz]. In order to establish the nature of this process a single-crystal structure determination was carried out on **6b**.

The molecular structure of compound **6b**, is shown in Fig. 2. Selected bond lengths and angles are shown in Table 2. The structure confirms the mode of attachment of the two $Ir_4$ clusters to the $P_3C_2Bu^t_2$ ring and indicated that the CO displacement occurred from the second $Ir_4$ carbonyl cluster by an intramolecular oxidative addition reaction, to afford the novel hydridocarbonyl complex (see Scheme 2).

The structure consists of two $Ir_4$ tetrahedra linked by $[Fe(\eta^5-C_5H_5)\{\eta^5-P_3C(CMe_2CH_2)CBu^t\}]$ *via* P(1) to Ir(1) and both P(2), that is not adjacent to P(1), and the $CH_2$ group to Ir(6). It is interesting that the '$Ir_4(CO)_{11}$' unit bonded to P(1) exhibits the $C_{3v}$-type structure with three edge bridging COs defining the basal plane of the metal polyhedron and P(1) in the axial position with respect to the Ir(1)–Ir(3)–Ir(4) plane, in contrast to the $T_d$-like structure of **2b**. The metal–metal bond distances in the $Ir_4(CO)_{11}$ unit range from 2.698(2) to 2.7486 Å, average 2.719 Å, longer than the mean value observed in compound **2b**, in agreement with the general trend shown by most CO bridged $Ir_4$ species.[27] The Ir–C and C–O bond distances are in the normal range of values found for terminal and bridging CO groups. The other $Ir_4$ unit exhibits a similar CO distribution. Apical Ir(5) is bonded to three terminal COs, basal Ir(7) and Ir(8) are bonded to two terminal and two bridging COs each, however, in addition to the two bridging COs, Ir(6) also bears P(2) and an alkyl group bonded *via* C(26) in place of a terminal CO. Two COs bridge asymmetrically the Ir(6)–Ir(7) and Ir(6)–Ir(8) edges [Ir(6)–C(12) 2.00(3), C(12)–Ir(7) 2.28(3) and Ir(6)–C(13) 2.03(3), C(13)–Ir(8) 2.24(3) Å], both being closest to Ir(6) which bears the most electron-withdrawing ligands. The Ir(6)–P(2) distance of 2.230(7) Å is shorter than Ir(1)–P(1) [2.318(7) Å] possibly as the result of further ligation of the $\eta^5$-$P_3C(CMe_2CH_2)CBu^t$ ring *via* C(26). The Ir(6)–C(26) bond distance [2.13(3) Å] is very close to the value encountered in the only other neutral $Ir_4$ alkyl containing cluster $[Ir_4Me(CO)_8(\mu_4-\eta^3-Ph_2PCCPh)(\mu-PPh_2)]$ [2.14(1) Å][28] and similar to the values found in the other two $Ir_4$ alkyl clusters $[Ir_4(CO)_{11}(CH_2CO_2Me)]^-$ [two independent molecules, 2.15(5) and 2.22(3) Å] and $[Ir_4(CO)_{10}(CH_2CO_2Me)_2]^{2-}$ [2.19(8) and 2.181(10) Å].[29]

The hydride ligand was not located. It could bridge the Ir(5)–Ir(6) edge of the tetrahedron because the Ir(5)–Ir(6) distance [2.890(2) Å] is significantly longer than the others in this unit [mean 2.720(2) Å], as observed in other bridging systems.[30,31] However the expected deviations from linearity are not noted in the apical carbonyls on Ir(5), as were

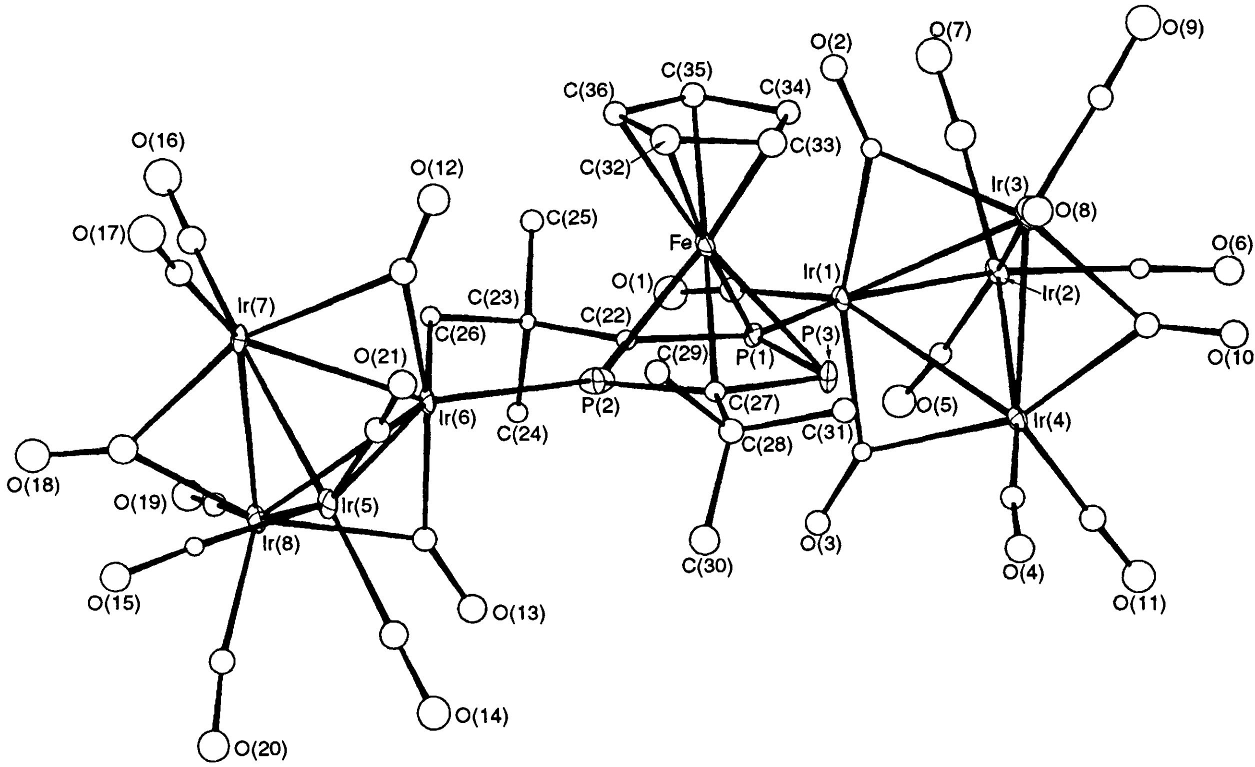
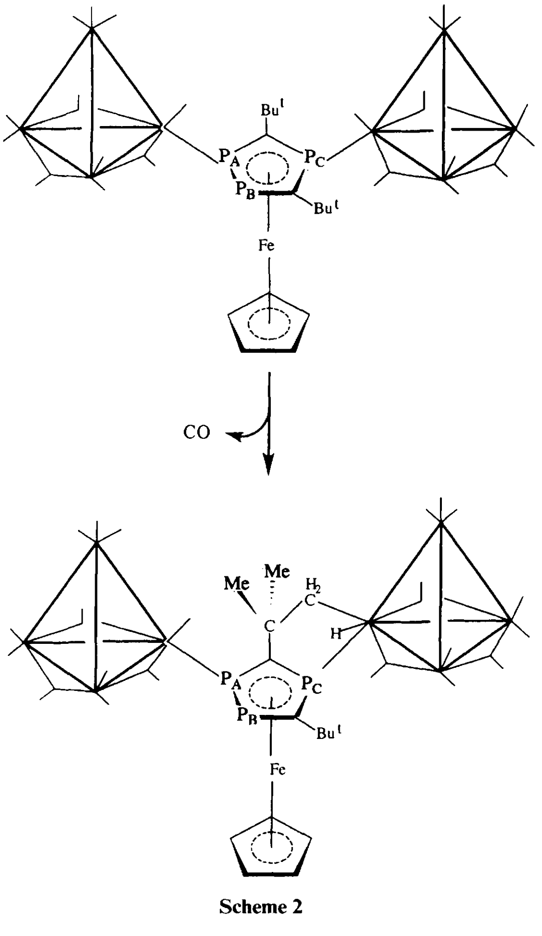


Fig. 2 Molecular structure of $[Ir_4H(CO)_{10}\{Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}P_3C(CMe_2CH_2)CBu^t]\}Ir_4(CO)_{11}]$ **6b** showing the atomic labelling scheme



**Scheme 2**

encountered in the structure of $[Ir_4H(CO)_{11}]^-$, in which the bridging position of the hydride was established by a neutron diffraction study.[30] In addition, the Ir(5)–Ir(6)–P(2) angle of 127.7(2)° indicates that there is enough room for a terminal hydride and indeed, a free co-ordination site seems to be available on Ir(6) in the space-filling diagram of **6b** shown in Fig. 3.

A comparison of the hydride chemical shift in **6b** ($\delta$ −22.1) with those of terminal and bridging hydride ligands in the few $Ir_4$ hydrido clusters reported to date was inconclusive. For example, the terminal hydride-containing clusters $[Ir_4H(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)]$[32] and $[Ir_4H_2(CO)_{10}]^{2-}$[33] exhibit resonances at $\delta$ −11.8 and −16.2, respectively, whereas the bridging-hydride clusters $[Ir_4H(CO)_{11}]^-$,[30] $[Ir_4H(CO)_7(Ph_2PCH{=}CHPPh_2)(PhC_6H_4PCH{=}CHPPh_2)]$[31] and $[Ir_4H(CO)_{10}(\mu\text{-}PPh_2)]$[34] show resonances at $\delta$ −15.2, −12.9 and −22.2, respectively.

The only other known $Ir_8$ cluster that consists of two $Ir_4$ tetrahedra joined together by a bridging ligand is $[Ir_4(CO)_{11}(\mu_4\text{-}\eta^2\text{-}PhPPPh)Ir_4(CO)_9\{Au(PEt_3)\}_2]$, which also contains an $Ir_4$ unit with the $C_{3v}$-type structure bonded to the bridging ligand *via* one of the P lone pairs.[35]

Complex **6b** represents the first example of C–H activation at an unsaturated carbon by an $Ir_4$ cluster, although a product from orthometallation in co-ordinated $Ph_2PCH{=}CHPPh_2$, $[Ir_4H(CO)_7(Ph_2PCH{=}CHPPh_2)(PhC_6H_4PCH{=}CHPPh_2)]$[31] has been described. The generality and possible reversibility of the C–H oxidative addition process in our systems are currently being explored.

## Experimental

### Materials and methods

All manipulations and reactions were performed under an atmosphere of dry argon, unless otherwise specified, by using Schlenk-type glassware. Solvents were dried as described previously[32] and distilled under argon before use. Thin layer chromatography was carried out in air using *ca.* 1 mm thick, glass-backed silica gel plates (20 × 20 cm) prepared from silica gel GF 254 (type 60, Fluka). Infrared spectra were recorded on a JASCO FT-IR 1720 instrument scanning between 2200 and 1600 cm$^{-1}$. Proton and $^{31}P$ NMR data were obtained on

**Table 2** Bond lengths (Å) and angles (°) for compound **6b**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ir(1)–Ir(2) | 2.708(2) | Ir(5)–Ir(6) | 2.890(2) | O(9)–C(9) | 1.15(4) | O(10)–C(10) | 1.15(3) |
| Ir(1)–Ir(3) | 2.737(2) | Ir(5)–Ir(7) | 2.736(2) | O(11)–C(11) | 1.09(4) | O(12)–C(12) | 1.16(3) |
| Ir(1)–Ir(4) | 2.7486(14) | Ir(5)–Ir(8) | 2.721(2) | O(13)–C(13) | 1.16(3) | O(14)–C(14) | 1.13(4) |
| Ir(2)–Ir(3) | 2.698(2) | Ir(6)–Ir(7) | 2.721(2) | O(15)–C(15) | 1.16(3) | O(16)–C(16) | 1.12(4) |
| Ir(2)–Ir(4) | 2.7034(14) | Ir(7)–Ir(8) | 2.709(2) | O(17)–C(17) | 1.13(4) | O(18)–C(18) | 1.14(4) |
| Ir(3)–Ir(4) | 2.7203(14) | Ir(6)–Ir(8) | 2.716(2) | O(19)–C(19) | 1.16(3) | O(20)–C(20) | 1.11(3) |
| Ir(1)–C(1) | 1.87(3) | Ir(1)–C(2) | 2.04(2) | O(21)–C(21) | 1.08(3) | Fe–C(22) | 2.14(3) |
| Ir(1)–C(3) | 2.06(2) | Ir(2)–C(5) | 1.90(3) | Fe–C(27) | 2.12(3) | Fe–C(32) | 2.12(3) |
| Ir(2)–C(6) | 1.90(3) | Ir(2)–C(7) | 1.93(3) | Fe–C(33) | 2.05(3) | Fe–C(34) | 2.04(3) |
| Ir(3)–C(2) | 2.21(3) | Ir(3)–C(8) | 1.92(3) | Fe–C(35) | 2.07(3) | Fe–C(36) | 2.09(3) |
| Ir(3)–C(9) | 1.85(3) | Ir(3)–C(10) | 2.11(3) | Fe–P(1) | 2.304(7) | Fe–P(2) | 2.269(8) |
| Ir(4)–C(3) | 2.13(3) | Ir(4)–C(4) | 1.89(3) | Fe–P(3) | 2.329(8) | P(1)–C(22) | 1.72(3) |
| Ir(4)–C(10) | 2.14(3) | Ir(4)–C(11) | 1.90(3) | P(2)–C(22) | 1.74(3) | P(2)–C(27) | 1.71(3) |
| Ir(5)–C(14) | 1.93(3) | Ir(5)–C(15) | 1.88(3) | P(3)–C(27) | 1.78(3) | P(3)–P(1) | 2.115(9) |
| Ir(5)–C(21) | 1.97(3) | Ir(6)–C(12) | 2.00(3) | C(22)–C(23) | 1.53(3) | C(23)–C(25) | 1.55(3) |
| Ir(6)–C(13) | 2.02(3) | Ir(6)–C(26) | 2.13(3) | C(23)–C(24) | 1.56(3) | C(23)–C(26) | 1.57(4) |
| Ir(7)–C(12) | 2.28(3) | Ir(7)–C(16) | 1.88(3) | C(27)–C(28) | 1.57(4) | C(28)–C(30) | 1.47(4) |
| Ir(7)–C(17) | 1.90(3) | Ir(7)–C(18) | 2.15(4) | C(28)–C(29) | 1.54(4) | C(28)–C(31) | 1.56(4) |
| Ir(8)–C(13) | 2.24(3) | Ir(8)–C(18) | 2.10(4) | C(32)–C(33) | 1.40(5) | C(32)–C(36) | 1.43(4) |
| Ir(8)–C(19) | 1.90(3) | Ir(8)–C(20) | 1.92(3) | C(33)–C(34) | 1.41(4) | C(34)–C(35) | 1.39(4) |
| Ir(1)–P(1) | 2.318(7) | Ir(6)–P(2) | 2.230(7) | C(35)–C(36) | 1.43(4) | C(37)–C(38) | 1.25(5) |
| O(1)–C(1) | 1.19(3) | O(2)–C(2) | 1.15(3) | C(37)–C(42) | 1.40(5) | C(38)–C(39) | 1.39(5) |
| O(3)–C(3) | 1.16(3) | O(4)–C(4) | 1.16(3) | C(42)–C(41) | 1.39(6) | C(40)–C(41) | 1.37(6) |
| O(5)–C(5) | 1.15(3) | O(6)–C(6) | 1.16(3) | C(40)–C(39) | 1.44(5) | | |
| O(7)–C(7) | 1.13(4) | O(8)–C(8) | 1.09(3) | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(1)–Ir(1)–C(2) | 102.3(11) | C(1)–Ir(1)–C(3) | 90.8(11) | Ir(8)–Ir(6)–Ir(5) | 57.98(4) | Ir(7)–Ir(6)–Ir(5) | 58.27(4) |
| C(2)–Ir(1)–C(3) | 161.5(11) | C(1)–Ir(1)–P(1) | 101.4(10) | C(16)–Ir(7)–C(17) | 93.9(13) | C(16)–Ir(7)–C(18) | 94.7(12) |
| C(2)–Ir(1)–P(1) | 96.8(8) | C(3)–Ir(1)–P(1) | 93.2(8) | C(17)–Ir(7)–C(18) | 102.2(14) | C(16)–Ir(7)–C(12) | 93.3(12) |
| C(1)–Ir(1)–Ir(2) | 97.1(10) | C(2)–Ir(1)–Ir(2) | 82.0(8) | C(17)–Ir(7)–C(12) | 99.9(12) | C(18)–Ir(7)–C(12) | 155.9(12) |
| C(3)–Ir(1)–Ir(2) | 83.4(8) | P(1)–Ir(1)–Ir(2) | 161.2(2) | C(16)–Ir(7)–Ir(8) | 108.3(9) | C(17)–Ir(7)–Ir(8) | 144.2(9) |
| C(1)–Ir(1)–Ir(3) | 145.3(9) | C(2)–Ir(1)–Ir(3) | 52.8(7) | C(18)–Ir(7)–Ir(8) | 49.7(10) | C(12)–Ir(7)–Ir(8) | 106.2(7) |
| C(3)–Ir(1)–Ir(3) | 109.5(7) | P(1)–Ir(1)–Ir(3) | 105.0(2) | C(16)–Ir(7)–Ir(6) | 105.4(10) | C(17)–Ir(7)–Ir(6) | 140.7(9) |
| Ir(2)–Ir(1)–Ir(3) | 59.41(4) | C(1)–Ir(1)–Ir(4) | 133.3(9) | C(18)–Ir(7)–Ir(6) | 109.7(10) | C(12)–Ir(7)–Ir(6) | 46.2(7) |
| C(2)–Ir(1)–Ir(4) | 112.1(7) | C(3)–Ir(1)–Ir(4) | 50.1(7) | Ir(8)–Ir(7)–Ir(6) | 60.03(4) | C(16)–Ir(7)–Ir(5) | 166.7(10) |
| P(1)–Ir(1)–Ir(4) | 104.6(2) | Ir(2)–Ir(1)–Ir(4) | 59.39(4) | C(17)–Ir(7)–Ir(5) | 99.4(9) | C(18)–Ir(7)–Ir(5) | 82.3(8) |
| Ir(3)–Ir(1)–Ir(4) | 59.46(4) | C(6)–Ir(2)–C(5) | 102.2(11) | C(12)–Ir(7)–Ir(5) | 84.7(7) | Ir(8)–Ir(7)–Ir(5) | 59.98(4) |
| C(6)–Ir(2)–C(7) | 98.0(14) | C(5)–Ir(2)–C(7) | 101.1(13) | Ir(6)–Ir(7)–Ir(5) | 63.96(4) | C(19)–Ir(8)–C(20) | 95.9(12) |
| C(6)–Ir(2)–Ir(3) | 95.2(7) | C(5)–Ir(2)–Ir(3) | 154.1(9) | C(19)–Ir(8)–C(18) | 95.1(12) | C(20)–Ir(8)–C(18) | 101.9(13) |
| C(7)–Ir(2)–Ir(3) | 95.3(10) | C(6)–Ir(2)–Ir(4) | 95.5(7) | C(19)–Ir(8)–C(13) | 93.3(12) | C(20)–Ir(8)–C(13) | 97.2(12) |
| C(5)–Ir(2)–Ir(4) | 98.5(8) | C(7)–Ir(2)–Ir(4) | 153.3(11) | C(18)–Ir(8)–C(13) | 158.2(12) | C(19)–Ir(8)–Ir(7) | 110.6(8) |
| Ir(3)–Ir(2)–Ir(4) | 60.48(4) | C(6)–Ir(2)–Ir(1) | 152.0(7) | C(20)–Ir(8)–Ir(7) | 142.3(9) | C(18)–Ir(8)–Ir(7) | 51.1(9) |
| C(5)–Ir(2)–Ir(1) | 96.7(9) | C(7)–Ir(2)–Ir(1) | 98.5(11) | C(13)–Ir(8)–Ir(7) | 107.1(7) | C(19)–Ir(8)–Ir(6) | 107.1(9) |
| Ir(3)–Ir(2)–Ir(1) | 60.82(4) | Ir(4)–Ir(2)–Ir(1) | 61.05(4) | C(20)–Ir(8)–Ir(6) | 137.0(9) | C(18)–Ir(8)–Ir(6) | 111.3(9) |
| C(9)–Ir(3)–C(8) | 96.0(12) | C(9)–Ir(3)–C(10) | 99.1(13) | C(13)–Ir(8)–Ir(6) | 46.9(7) | Ir(7)–Ir(8)–Ir(6) | 60.20(4) |
| C(8)–Ir(3)–C(10) | 95.7(11) | C(9)–Ir(3)–C(2) | 96.6(11) | C(19)–Ir(8)–Ir(5) | 169.5(8) | C(20)–Ir(8)–Ir(5) | 94.5(8) |
| C(8)–Ir(3)–C(2) | 99.6(11) | C(10)–Ir(3)–C(2) | 156.8(10) | C(18)–Ir(8)–Ir(5) | 83.4(9) | C(13)–Ir(8)–Ir(5) | 84.7(7) |
| C(9)–Ir(3)–Ir(2) | 97.9(9) | C(8)–Ir(3)–Ir(2) | 166.1(9) | Ir(7)–Ir(8)–Ir(5) | 60.51(4) | Ir(6)–Ir(8)–Ir(5) | 64.21(4) |
| C(10)–Ir(3)–Ir(2) | 81.7(8) | C(2)–Ir(3)–Ir(2) | 79.3(6) | C(27)–P(2)–C(22) | 102.7(14) | C(27)–P(2)–Ir(6) | 144.1(10) |
| C(9)–Ir(3)–Ir(4) | 142.1(9) | C(8)–Ir(3)–Ir(4) | 108.0(8) | C(22)–P(2)–Ir(6) | 113.2(10) | C(22)–P(1)–P(3) | 101.2(9) |
| C(10)–Ir(3)–Ir(4) | 50.7(8) | C(2)–Ir(3)–Ir(4) | 107.5(6) | C(22)–P(1)–Ir(1) | 135.5(9) | P(3)–P(1)–Ir(1) | 123.3(4) |
| Ir(2)–Ir(3)–Ir(4) | 59.85(4) | C(9)–Ir(3)–Ir(1) | 137.7(8) | O(1)–C(1)–Ir(1) | 171(3) | O(2)–C(2)–Ir(1) | 143(2) |
| C(8)–Ir(3)–Ir(1) | 109.3(9) | C(10)–Ir(3)–Ir(1) | 111.0(8) | O(2)–C(2)–Ir(3) | 137(2) | Ir(1)–C(2)–Ir(3) | 80.0(8) |
| C(2)–Ir(3)–Ir(1) | 47.2(6) | Ir(2)–Ir(3)–Ir(1) | 59.77(4) | O(3)–C(3)–Ir(1) | 142(2) | O(3)–C(3)–Ir(4) | 136(2) |
| Ir(4)–Ir(3)–Ir(1) | 60.49(4) | C(11)–Ir(4)–C(4) | 94.3(12) | Ir(1)–C(3)–Ir(4) | 82.0(9) | O(4)–C(4)–Ir(4) | 174(3) |
| C(11)–Ir(4)–C(3) | 101.6(11) | C(4)–Ir(4)–C(3) | 95.2(11) | O(5)–C(5)–Ir(2) | 175(3) | O(6)–C(6)–Ir(2) | 175(2) |
| C(11)–Ir(4)–C(10) | 96.6(12) | C(4)–Ir(4)–C(10) | 97.1(11) | O(7)–C(7)–Ir(2) | 176(4) | O(8)–C(8)–Ir(3) | 173(3) |
| C(3)–Ir(4)–C(10) | 157.1(10) | C(11)–Ir(4)–Ir(2) | 99.9(9) | O(9)–C(9)–Ir(3) | 176(3) | O(10)–C(10)–Ir(3) | 141(2) |
| C(4)–Ir(4)–Ir(2) | 165.8(8) | C(3)–Ir(4)–Ir(2) | 82.4(7) | O(10)–C(10)–Ir(4) | 139(2) | Ir(3)–C(10)–Ir(4) | 79.7(11) |
| C(10)–Ir(4)–Ir(2) | 81.0(8) | C(11)–Ir(4)–Ir(3) | 140.3(10) | O(11)–C(11)–Ir(4) | 178(3) | O(12)–C(12)–Ir(6) | 151(3) |
| C(4)–Ir(4)–Ir(3) | 108.5(8) | C(3)–Ir(4)–Ir(3) | 108.0(6) | O(12)–C(12)–Ir(7) | 130(3) | Ir(6)–C(12)–Ir(7) | 78.6(10) |
| C(10)–Ir(4)–Ir(3) | 49.6(8) | Ir(2)–Ir(4)–Ir(3) | 59.67(4) | O(13)–C(13)–Ir(6) | 147(3) | O(13)–C(13)–Ir(8) | 132(2) |
| C(11)–Ir(4)–Ir(1) | 142.1(9) | C(4)–Ir(4)–Ir(1) | 108.6(9) | Ir(6)–C(13)–Ir(8) | 79.2(10) | O(14)–C(14)–Ir(5) | 179(3) |
| C(3)–Ir(4)–Ir(1) | 48.0(6) | C(10)–Ir(4)–Ir(1) | 109.5(8) | O(15)–C(15)–Ir(5) | 176(2) | O(16)–C(16)–Ir(7) | 176(3) |
| Ir(2)–Ir(4)–Ir(1) | 59.56(4) | Ir(3)–Ir(4)–Ir(1) | 60.05(4) | O(17)–C(17)–Ir(7) | 177(3) | O(18)–C(18)–Ir(8) | 141(3) |
| C(15)–Ir(5)–C(14) | 97.1(13) | C(15)–Ir(5)–C(21) | 101.6(12) | O(18)–C(18)–Ir(7) | 139(3) | Ir(8)–C(18)–Ir(7) | 79.2(13) |
| C(14)–Ir(5)–C(21) | 105.8(12) | C(15)–Ir(5)–Ir(8) | 87.4(7) | O(19)–C(19)–Ir(8) | 179(3) | O(20)–C(20)–Ir(8) | 171(3) |
| C(14)–Ir(5)–Ir(8) | 96.2(9) | C(21)–Ir(5)–Ir(8) | 154.7(8) | O(21)–C(21)–Ir(5) | 176(3) | C(23)–C(22)–P(1) | 131(2) |
| C(15)–Ir(5)–Ir(7) | 89.9(7) | C(14)–Ir(5)–Ir(7) | 154.5(9) | C(23)–C(22)–P(2) | 111(2) | P(1)–C(22)–P(2) | 119(2) |
| C(21)–Ir(5)–Ir(7) | 96.6(8) | Ir(8)–Ir(5)–Ir(7) | 59.52(4) | C(22)–C(23)–C(25) | 112(2) | C(22)–C(23)–C(24) | 107(2) |
| C(15)–Ir(5)–Ir(6) | 140.5(7) | C(14)–Ir(5)–Ir(6) | 104.2(10) | C(25)–C(23)–C(24) | 109(2) | C(22)–C(23)–C(26) | 111(2) |
| C(21)–Ir(5)–Ir(6) | 103.9(9) | Ir(8)–Ir(5)–Ir(6) | 57.81(4) | C(25)–C(23)–C(26) | 108(2) | C(24)–C(23)–C(26) | 111(2) |
| Ir(7)–Ir(5)–Ir(6) | 57.77(4) | C(12)–Ir(6)–C(13) | 168.3(14) | C(23)–C(26)–Ir(6) | 120(2) | C(28)–C(27)–P(2) | 123(2) |
| C(12)–Ir(6)–C(26) | 90.7(11) | C(13)–Ir(6)–C(26) | 95.3(11) | C(28)–C(27)–P(3) | 118(2) | P(2)–C(27)–P(3) | 119(2) |
| C(12)–Ir(6)–P(2) | 97.6(10) | C(13)–Ir(6)–P(2) | 93.5(9) | C(30)–C(28)–C(29) | 110(3) | C(30)–C(28)–C(31) | 113(2) |
| C(26)–Ir(6)–P(2) | 77.9(7) | C(12)–Ir(6)–Ir(8) | 115.0(10) | C(29)–C(28)–C(31) | 109(2) | C(30)–C(28)–C(27) | 107(2) |
| C(13)–Ir(6)–Ir(8) | 53.9(9) | C(26)–Ir(6)–Ir(8) | 101.5(7) | C(29)–C(28)–C(27) | 109(2) | C(31)–C(28)–C(27) | 110(3) |
| P(2)–Ir(6)–Ir(8) | 147.4(2) | C(12)–Ir(6)–Ir(7) | 55.3(10) | C(33)–C(32)–C(36) | 108(3) | C(32)–C(33)–C(34) | 108(3) |
| C(13)–Ir(6)–Ir(7) | 113.7(9) | C(26)–Ir(6)–Ir(7) | 99.4(7) | C(35)–C(34)–C(33) | 110(3) | C(34)–C(35)–C(36) | 107(3) |
| P(2)–Ir(6)–Ir(7) | 152.9(2) | Ir(8)–Ir(6)–Ir(7) | 59.76(4) | C(35)–C(36)–C(32) | 108(3) | C(38)–C(37)–C(42) | 125(4) |
| C(12)–Ir(6)–Ir(5) | 85.9(10) | C(13)–Ir(6)–Ir(5) | 84.4(9) | C(37)–C(38)–C(39) | 121(4) | C(37)–C(42)–C(41) | 116(4) |
| C(26)–Ir(6)–Ir(5) | 154.5(7) | P(2)–Ir(6)–Ir(5) | 127.7(2) | C(41)–C(40)–C(39) | 118(4) | C(38)–C(39)–C(40) | 118(4) |

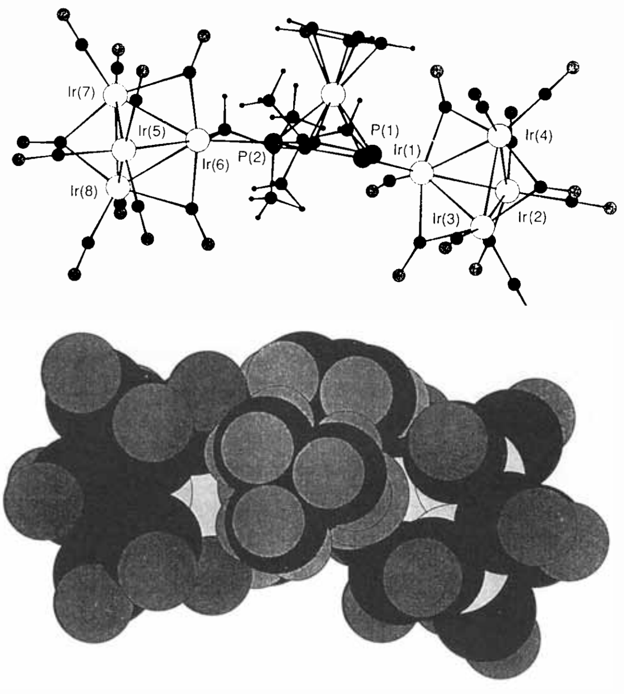


**Fig. 3** Space-filling diagram of $[Ir_4H(CO)_{10}\{Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}P_3C(CMe_2CH_2)CBu^t]\}Ir_4(CO)_{11}]$ **6b** showing the free co-ordination site on Ir(6)

Bruker AMX 500 or AC 250 instruments, using deuteriated solvents as lock and reference [$^1H$, $SiMe_4$ (δ 0); $^{31}P$, $H_3PO_4$, 85% (δ 0); high frequency positive]. Secondary-ionisation mass spectra (SIMS) were obtained on a VG Autospec-Fisons instrument operating between 25 and 30 kV and a current of 40 μA; *p*-nitrobenzyl alcohol was used as a matrix and was treated by bubbling CO or Ar through it for 0.5 h prior to use. All *m*/*z* values are referred to $^{193}Ir$. Compounds $[Ir_4(CO)_{12}]$ (Strem), $NBu_4Br$ and $AgSbF_6$ (Aldrich) were used as supplied. Compounds $NBu_4[Ir_4(CO)_{11}Br]$ **1**,[36] $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)]$ $L^1$ [12] and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t{}_2)]$ $L^2$ [3] were prepared according to published procedures.

### Syntheses of the $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)]$ ($L^1$) derivatives 2a and 3a

Silver hexafluoroantimonate (54 mg, 0.156 mmol) was added as a solid to a solution of $NBu_4[Ir_4(CO)_{11}Br]$ **1** (180 mg, 0.13 mmol) and $L^1$ (73 mg, 0.13 mmol) in tetrahydrofuran (20 $cm^3$) at −78 °C. The reaction mixture was allowed to warm slowly to −30 °C and was stirred at this temperature for 0.5 h. The solvent was removed under vacuum between −30 and −15 °C, and the brown residue dissolved in dichloromethane (2 $cm^3$) and separated by TLC, using dichloromethane–cyclohexane (1 : 9) as eluent. The following compounds were obtained. $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)]$ $L^1$, $R_f$ 0.93 (2 mg, 2%). $[Ir_4(CO)_{11}L^1]$ **2a**, brown, $R_f$ 0.46 (148 mg, 70%); $\tilde{\nu}_{max}/cm^{-1}$ (hexane) (CO) 2088s, 2070w, 2055s, 2032vs, 2012w, 2003w, 1991m, 1978m, 1854w and 1830w; NMR ($CD_2Cl_2$, −60 °C) $^1H$, δ 1.8 (s, 9 H, $Bu^t$), 1.6 (s, 9 H, $Bu^t$), 1.5 (s, 9 H, $Bu^t$), 1.2 (s, 9 H, $Bu^t$) and 1.1 (s, 9 H, $Bu^t$); $^{31}P$, δ −13.5 (dd, $P_A$), 12.2 (dd, $P_B$), 11.4 (t, $P_C$), 41.0 (d, $P_D$), 42.2 (d, $P_E$), [$^1J(P_AP_B)$ 444, $^2J(P_AP_C)$ 47, $^2J(P_BP_C)$ 36, $^2J(P_DP_E)$ 34 Hz]; mass spectrum *m*/*z* 1636 (18, $M^+$), 1608 (10, *M* − CO), 1552 (26, *M* − 3CO), 1524 (21, *M* − 4CO), 1496 (36, *M* − 5CO), 1468 (39, *M* − 6CO), 1440 (28, *M* − 7CO), 1412 (26, *M* − 8CO), 1384 (31, *M* − 9CO), 1356 (28, *M* − 10CO), 1328 (34, *M* − 11CO), 556 (100, $L^1$). $[Ir_4(CO)_{10}L^1{}_2]$ **3a**, brown, $R_f$ 0.35 (14 mg, 5%); $\tilde{\nu}_{max}/cm^{-1}$ (hexane) (CO) 2089, 2056vs, 2027vs, 2019s (sh), 1887w, 1854s and 1830s. $[Ir_4(CO)_{10}L^1]$ **4a**, brown, $R_f$ 0.65 (20 mg, 15%); $\tilde{\nu}_{max}/cm^{-1}$ (hexane) (CO) 2086s, 2054vs, 2028vs, 1971w (br), 1843w (br) and 1824w (br); NMR ($CD_2Cl_2$, −60 °C) $^1H$, δ 1.6 (s, 18 H, 2 $Bu^t$), 1.5 (s, 18 H, 2 $Bu^t$) and 1.3 (s, 9 H, $Bu^t$); $^{31}P$, δ −136.4 (d, $P_A$), 38.7 (t, $P_B$) and 42.8 (1 s, $P_C$) [$^2J(P_AP_B)$ 41 Hz]; mass spectrum *m*/*z* 1608 (10, $M^+$), 1580 (14, *M* − CO), 1524 (7, *M* − 3CO), 1496 (19, *M* − 4CO), 1468 (22, *M* − 5CO), 1440 (30, *M* − 6CO), 1412 (24, *M* − 7CO), 1384 (17, *M* − 8CO), 1356 (29, *M* − 9CO), 1328 (39, *M* − 10CO), 1298 (79, *M* − 7CO − $2CMe_3$), 1269 (100, *M* − 6CO − $3CMe_3$), 556 (100, $L^1$).

### Synthesis of $[Ir_4(CO)_{10}L^1]$ 4a

A solution of compound **2a** (45 mg, 0.027 mmol) in dichloromethane (10 $cm^3$) was heated under reflux for 48 h. The solvent was evaporated under vacuum and **4a** obtained in good yield (30 mg, 70%), together with $L^1$ and decomposition products, after TLC using dichoromethane–hexane (1 : 9) as eluent.

### Syntheses of the $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t{}_2)]$ ($L^2$) derivatives 2b and 3b

A solution of $NBu_4[Ir_4(CO)_{11}Br]$ **1** (50 mg, 0.045 mmol) and $L^2$ (16 mg, 0.045 mmol) in dichloromethane (10 $cm^3$) was stirred at room temperature for 24 h. The solvent was concentrated under vacuum to 1 $cm^3$ and the mixture separated by TLC using dichloromethane–hexane (3 : 7) as eluent to afford the following. $[Ir_4(CO)_{11}L^2]$ **2b**, orange, $R_f$ 0.67 (38 mg, 60%); $\tilde{\nu}_{max}/cm^{-1}$ (hexane) (CO) 2091s, 2058vs, 2035s, 2024s, 1970w, 1888w, 1854m and 1830m; (KBr) 2091s, 2053s (br), 2028s (br), 2016s (br), 1996s (br), 1991s (br) 1958m, 1889w, 1845m (br) and 1823m (br); NMR ($CDCl_3$, 25 °C) $^1H$, δ 5.3 (s, 5 H, $C_5H_5$), 1.6 (s, 9 H, $Bu^t$) and 1.3 (s, 9 H, $Bu^t$); $^{31}P$, δ −24.5 (dd, $P_A$), 15.2 (dd, $P_B$) and 18.1 (t, $P_C$) [$^1J(P_AP_B)$ 449, $^2J(P_AP_C)$ 54, $^2J(P_BP_C)$ 36 Hz]; mass spectrum *m*/*z* 1432 (34, $M^+$), 1404 (30, *M* − CO), 1376 (13, *M* − 2CO), 1348 (17, *M* − 3CO), 1320 (31, *M* − 4CO), 1292 (23, *M* − 5CO), 1264 (18, *M* − 6CO), 1236 (100, *M* − 7CO), 1208 (34, *M* − 8CO), 1180 (9, *M* − 9CO), 1152 (12, *M* − 10CO) and 1124 (8, *M* − 11CO). $[Ir_4(CO)_{10}L^2{}_2]$ **3b**, orange, $R_f$ 0.41 (4 mg, 4%); $\tilde{\nu}_{max}/cm^{-1}$ (hexane) (CO) 2074vs, 2049vs, 2015vs, 2005s, 1990m, 1850w, 1831s and 1809s; mass spectrum *m*/*z* 1672 (11, *M* − 3CO), 1644 (41, *M* − 4CO), 1616 (14, *M* − 5CO), 1588 (96, *M* − 6CO), 1560 (100, *M* − 7CO), 1532 (70, *M* − 8CO), 1504 (26, *M* − 9CO) and 1476 (16, *M* − 10CO).

Alternatively, the reaction of compound **1** (50 mg, 0.045 mmol) with $L^2$ (16 mg, 0.045 mmol) was carried out under the conditions described for the reaction with $L^1$ and the resulting mixture separated as described above to give compounds **2b** (55 mg, 85%) and **3b** (8 mg, 10%).

### Synthesis of $[Ir_4(CO)_{11}L^2Ir_4(CO)_{11}]$ 5b

Silver hexafluoroantimonate was added as a solid to an orange solution of $NBu_4[Ir_4(CO)_{11}Br]$ **1** (126 mg, 0.09 mmol) and $[Ir_4(CO)_{11}L^2]$ **2b** (128 mg, 0.09 mmol) in tetrahydrofuran (30 $cm^3$) at −78 °C. The reaction mixture was allowed to warm slowly to −30 °C and was left stirring at this temperature for 0.5 h, after which time pronounced darkening was noted. The solvent was removed under vacuum between −30 and −15 °C, the brown residue was dissolved in dichloromethane (1 $cm^3$) and the mixture separated by TLC using dichloromethane–hexane (1 : 4) as eluent to yield **5b** and decomposition products. $[Ir_4(CO)_{11}L^2Ir_4(CO)_{11}]$ **5b**, dark orange, $R_f$ 0.77 (130 mg, 60%); $\tilde{\nu}_{max}/cm^{-1}$ (hexane) (CO) 2103m, 2070vs, 2059vs, 2038vs, 2019vs, 1986w (sh), 1970w, 1866m and 1830m; $^1H$ NMR ($CDCl_3$, 25 °C) δ 5.3 (s, 5 H, $C_5H_5$), 1.6 (s, 9 H, $Bu^t$) and 1.3 (s, 9 H, $Bu^t$).

### Synthesis of $[Ir_4H(CO)_{10}\{Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}P_3C(CMe_2CH_2)\text{-}CBu^t]\}Ir_4(CO)_{11}]$ 6b

A solution of dark orange **5b** (50 mg, 0.02 mmol) in benzene (5 $cm^3$) was left stirring for 12 h, after which time the volume of the solvent was reduced to 2 $cm^3$ and the brown solution left at room temperature to crystallise. Compound **6b** was obtained as the only product (32 mg, 65%) as brown crystals. $[Ir_4H(CO)_{10}\{Fe(\eta^5-C_5H_5)[\eta^5-P_3C(CMe_2CH_2)CBu^t]\}Ir_4(CO)_{11}]$ **6b** brown, $\tilde{\nu}_{max}/cm^{-1}$(hexane) (CO) 2092m, 2068vs, 2030s, 1901m, 1848m and 1824m; NMR ($CDCl_3$, 25 °C) $^1H$, δ 5.3 (s, 5 H, $C_5H_5$), 1.6 (d, 2 H, $CH_2$) [$^2J(HH)$ 12], 1.4 (s, 9 H, $Bu^t$), 1.3 (s, 3 H, Me), 1.2 (s, 3 H, Me) and −22.1 (d, 1 H, IrH) ($J_{PH}$ 7 Hz); $^{31}P$, δ −63.0 (dd, $P_A$), −8.2 (dd, $P_B$), 95.0 [dd, $P_C$, $^1J(P_AP_B)$ 463, $^2J(P_AP_C)$ 43, $^2J(P_BP_C)$ 5 Hz].

### Crystal-structure determinations

X-Ray diffraction studies were performed on an Enraf-Nonius CAD4 diffractometer.[37] The crystal structures were solved using SHELXS 86[38] and refined using SHELXL 93.[39] Graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) was employed.

**Complex 2b.** Orange crystals were grown at +10 °C from a dichloromethane–hexane (1 : 3) solution. Data were collected at 20(2) °C.

*Crystal data.* $C_{26}H_{23}FeIr_4O_{11}P_3$, $M = 1429.0$, monoclinic, space group $P2_1/c$ (no. 14), $a = 8.638(2)$, $b = 13.319(3)$, $c = 30.366(12)$ Å, $\beta = 94.22(3)°$, $U = 3484(2)$ Å$^3$, $Z = 4$, $D_c = 2.72$ Mg $m^{-3}$, $\mu = 15.82$ $mm^{-1}$, $F(000) = 2584$. A total of 8383 unique reflections were recorded for a crystal *ca.* 0.35 × 0.35 × 0.30 mm in the range $2 \leqslant \theta \leqslant 30°$ of which 5794 with $I > 2\sigma(I)$ were used for solution and refinement. The structure was solved by routine direct methods and refined by full-matrix least squares on all $F^2$. All non-H atoms were allowed to vibrate anisotropically. Hydrogen atoms were included in calculated positions and refined in riding mode with $U_{iso}(H)$ equal to 1.2 $U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. The final agreement factors were $R1 = 0.093$, $wR2 = 0.160$, goodness-of-fit = 1.006.

**Complex 6b.** Brown crystals were grown at 25 °C from a benzene solution of the compound. Data were collected at −100(2) °C.

*Crystal data.* $C_{42}H_{28}FeIr_8O_{21}P_3$, $M = 2555.0$, monoclinic, space group $Cc$ (no. 9), $a = 16.060(4)$, $b = 30.425(6)$, $c = 11.247(3)$ Å, $\beta = 97.36(3)°$, $U = 5450(2)$ Å$^3$, $Z = 4$, $D_c = 3.11$ Mg $m^{-3}$, $\mu = 19.87$ $mm^{-1}$, $F(000) = 4540$. A total of 4799 independent reflections were recorded for a crystal *ca.* 0.40 × 0.35 × 0.10 mm in the range $2 \leqslant \theta \leqslant 25°$ of which 4347 with $I > 2\sigma(I)$ were used for solution and refinement. The structure was solved by routine direct methods and refined by full-matrix least squares on all $F^2$. The Ir, Fe and P atoms were anisotropic, hydrogen atoms were included in calculated positions and refined in riding mode with $U_{iso}(H)$ equal to 1.2 $U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. The final agreement factors were $R1 = 0.050$, $wR2 = 0.099$, goodness-of-fit = 1.024.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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