Novel C–H activation in a bis-tetrairidium carbonyl complex of the sandwich compound $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$: crystal and molecular structures of $[Ir_4(CO)_{11}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)\}]$ and $[HIr_4(CO)_{10}\text{-}\{\mu\text{-}Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3CH_2(CMe_2)CBu^t)\}Ir_4(CO)_{11}]$

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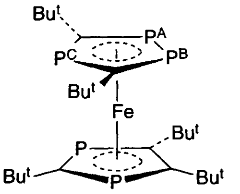
The syntheses and structural determinations of novel complexes of the type $[Ir_4(CO)_{11}L]$ $\{L = [Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ or $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]\}$ and $[HIr_4(CO)_{10}\text{-}\{\mu\text{-}Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3CH_2(CMe_2)CBu^t)\}Ir_4(CO)_{11}]$, involving an unusual C–H activation, are described.

The recently reported sandwich compounds of the type $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ **1**,[1] $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ **2**[1,2] and $[Fe(\eta^5\text{-}C_5R_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ (R = H, Me) **3**[3,4] have the important additional potential to act as ligands[5,6] *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),[7] $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2Ru_3(CO)_{10}]$,[7] $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)W(CO)_5]$,[7] $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2Bu^t_2)M(CO)_x]$ $\{[M(CO)_x] = [Cr(CO)_5]$, $[W(CO)_5]$ or $[Fe(CO)_4]\}$[8] and $[\{Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2Bu^t_2)\}Ni(CO)_2]_2$[8] have been described. To date, ligation has been observed to involve only one of the two directly bonded P atoms of the $\eta^5\text{-}P_3C_2Bu^t_2$ ring.

We now describe the first examples of complexes of $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ **2** and $[Fe(\eta^5\text{-}C_5R_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ **3** (R = H) with tetranuclear iridium carbonyl clusters and, in the case of **3**, 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 Bu^t substituent in the $P_3C_2Bu^t_2$ ring leads to a novel intramolecular C–H activation at one of the Ir centres.

Thus, treatment of $NBu_4[Ir_4(CO)_{11}Br]$[9] with an equimolar amount of **2** made directly from $[Fe(\eta^4\text{-}C_8H_8)_2]$ and Bu^tCP,[2] at −78 °C in THF in the presence of $AgSbF_6$, gave the brown complex $[Ir_4(CO)_{11}\{Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)\}]$ **4** in 60% yield. This compound was characterised by ^1H and $^{31}P\{^1H\}$ NMR and mass spectroscopy† but it proved impossible to obtain suitable crystals for X-ray diffraction analysis, since it undergoes decomposition in solution.

In a similar fashion, treatment of $NBu_4[Ir_4(CO)_{11}Br]$ with an equimolar amount of **3** (R = H) afforded a 85% yield of the stable orange complex $[Ir_4(CO)_{11}\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)\}]$ **5**. It exhibited a parent ion at *m/z* 1432 in the FAB mass spectrum and peaks corresponding to $[M - xCO]^+$ (x = 1–11). The ^1H NMR spectrum at room temperature showed the expected singlets at δ 5.3 (5 H), 1.6 (9 H) and 1.3 (9 H), while the $^{31}P\{^1H\}$ NMR spectrum exhibited an ABC pattern.‡ The IR spectrum in the ν_{CO} region,‡ both in solution and in the solid state, showed bands in both the terminal and the bridging regions, but the subsequent structure determination (see below) showed that all eleven CO ligands were terminally bonded, suggesting that isomers **5a** and **5b** are present in solution and possibly a fluxional process is operating as established for a number of $[Ir_4(CO)_{11}L]$ derivatives.[10–12]



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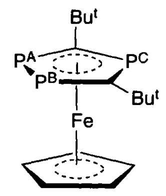

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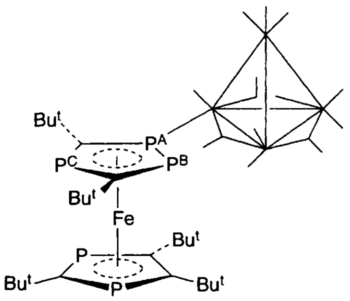

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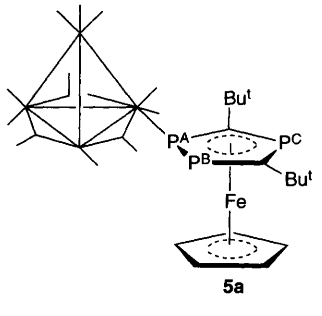
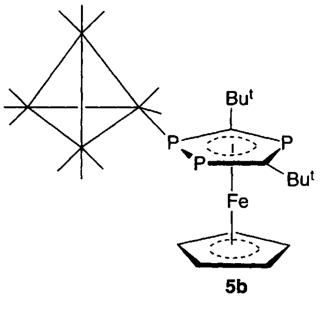
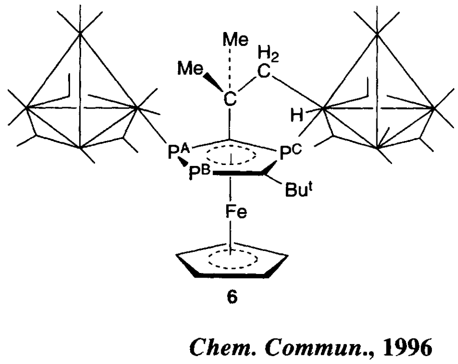


5a



5b



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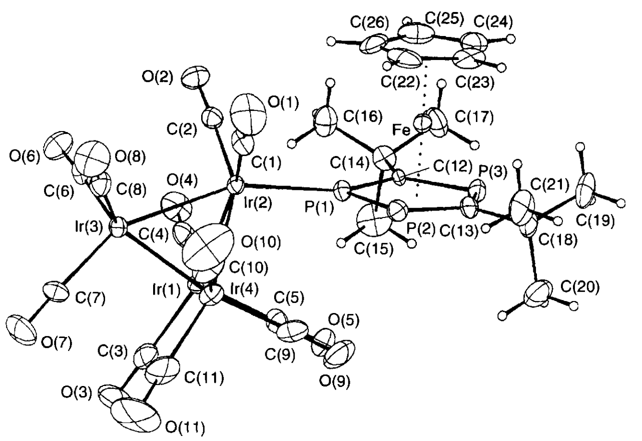
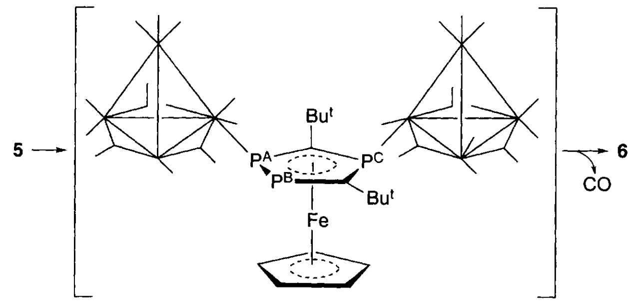


Fig. 1 Molecular structure of **5**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–Ir(2) 2.6970(9), Ir(1)–Ir(3) 2.6861(12), Ir(1)–Ir(4) 2.6852(12), Ir(2)–Ir(3) 2.6761(9), Ir(2)–Ir(4) 2.7012(12), Ir(3)–Ir(4) 2.6840(10), Ir(2)–P(1) 2.345(4), P(1)–P(2) 2.104(5), P(1)–C(12) 1.774(14), P(2)–C(13) 1.75(2), P(3)–C(12) 1.754(13), P(3)–C(13) 1.77(2), P(1)–Ir(2)–Ir(4) 101.59(9), P(2)–P(1)–Ir(2) 116.4(2), C(12)–P(1)–P(2) 101.9(5), C(12)–P(1)–Ir(2) 141.4(5), C(13)–P(2)–P(1) 97.4(5), P(3)–C(12)–P(1) 118.(8), P(2)–C(13)–P(3) 122.5(8).



Scheme 1

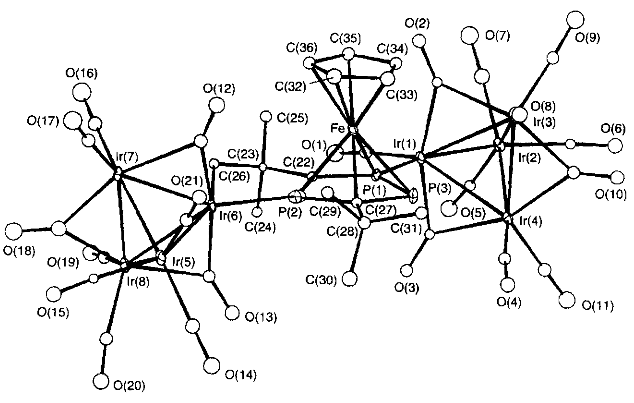


Fig. 2 Molecular structure of **6**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–Ir(2) 2.708(2), Ir(1)–Ir(3) 2.737(2), Ir(1)–Ir(4) 2.743(14), Ir(2)–Ir(3) 2.698(4), Ir(2)–Ir(4) 2.7034(14), Ir(3)–Ir(4) 2.7203(14), Ir(5)–Ir(6) 2.890(2), Ir(5)–Ir(7) 2.736(2), Ir(5)–Ir(8) 2.721(2), Ir(6)–Ir(7) 2.721(2), Ir(6)–Ir(8) 2.716(2), Ir(6)–Ir(8) 2.716(2), Ir(7)–Ir(8) 2.709(2), Ir(1)–P(1) 2.318(7), Ir(6)–P(2) 2.230(7), Ir(6)–C(26) 2.13(3), P(1)–P(3) 2.115(9), C(26)–Ir(6)–P(2) 77.9(7).

The molecular structure of **5**,§ shown in Fig. 1 together with important bond distances and angles, confirms the formulation based on spectroscopic data and, as expected, the cluster attachment to the η^5-$P_3C_2Bu^t_2$ ring of **3** is by one of the two directly bonded P ring atoms. The four iridium atoms in **5** exhibit a nearly tetrahedral core, and the average Ir–Ir distance is 2.688 Å which lies within the range of Ir–Ir distances observed in other $[Ir_4(CO)_{11}L]$ clusters with the same ligand arrangement, *e.g*. L = CO, 2.693 Å;[13] SCN, 2.684 Å;[14] CNBu^t, 2.685 Å.[15] The bond lengths and angles in the coordinated $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ unit are similar to those of closely related complexes.[8]

Interestingly, complex **5** readily reacts further with $NBu_4[Ir_4(CO)_{11}Br]$ in THF, at −78 °C in the presence of $AgSbF_6$ to give the dark orange compound $[HIr_4(CO)_{10}\{\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3CH_2(CMe_2)CBu^t)\}Ir_4(CO)_{11}]$ **6** in 60% yield, (Scheme 1). The room-temperature $^{31}P\{^1H\}$ NMR of **6** is of [AMX] type,¶ which showed unequivocally that the second Ir_4 cluster was ligated *via* P^C, rather than P^B. Such behaviour is unprecedented but no doubt is a direct consequence of the steric size of the first ligated $[Ir_4(CO)_{11}]$ cluster which makes it difficult for P^B to interact further, thereby facilitating the involvement of P^C. The ^1H NMR¶ spectrum of **6** indicated that oxidative addition by a C–H bond of one of the methyls of a Bu^t group had also occurred, and in order to establish the nature of this process a single-crystal X-ray structure determination was carried out on **6**.

The molecular structure of **6**, § shown in Fig. 2 together with selected bond lengths and angles, confirms the mode of attachment of the two Ir_4 clusters to the η^5-ligated $P_3C_2Bu^t_2$ ring and clearly indicates that a further CO displacement occurred from the second Ir_4 carbonyl cluster by an intramolecular oxidative addition reaction, to afford the novel hydridocarbonyl complex. The structure consists of two Ir_4 tetrahedra linked by the bridging $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3CH_2(CMe_2)CBu^t)]$ unit, and the P(1) and P(2) atoms of the ring of the triphosphaferrocene are each attached to one of the tetrairidium clusters. Owing to the proximity of Ir(6) to one methyl group of the tertiary butyl group attached to the ring carbon C(22) lying between P(1) and P(2), C–H activation leads to Ir(6)–H bond formation and an Ir–CH_2 linkage at C(26). The latter Ir–C bond length [2.13(3) Å] is comparable with the Ir–C_{Me} bond distance in $[MeIr_4(CO)_8(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)\text{-}(\mu\text{-}PPh_2)]$ [2.09(1) Å].[16] The literature contains two reports of Ir_8 carbonyl clusters whose structures consist of two linked tetrahedra, namely $[Ir_4(CO)_{11}(PhPPPh)Ir_4(CO)_9(AuPEt_3)_2]$[17] and $[Ir_8(CO)_{22}]^{2-}$,[18] but linkage involving C–H activation has not been previously described.

C–H activation is unusual in carbonyl clusters and a further structural feature of interest in **6** is the lack of any terminal CO ligands on the eight-coordinate Ir(6) atom carrying the CH_2 and H groups. We are currently studying the reactivity of this unusual type of cluster hydride towards a variety of unsaturated ligands.

We thank the EPSRC for support of phosphaalkyne chemistry at Sussex and the EEC and CNPq (Brazil) for financial support through grants awarded to J. F. N. and M. D. V. and M. D. V. and M. H. A. B. respectively.

Footnotes

† *Spectroscopic data* for **4**: IR, ν_{CO} (hexane), 2088s, 2070w, 2055s, 2032vs, 2012w, 2003w, 1991m, 1978m, 1854w, 1830w cm^{-1}; FAB MS (*p*-nitrobenzylalcohol matrix, saturated with CO), *m/z* 1636 (M$^+$) $[M-x\text{CO}]^+$ (x = 1–11); ^1H NMR (CD_2Cl_2, −60 °C) δ 1.8(s), 1.6(s), 1.5(s), 1.2(s), 1.1(s) (5 × Bu^t); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ −13.5 (dd, P^A), 12.2 (dd, P^B), 11.4 (t, P^C) ($^1J_{P^AP^B}$ 446 Hz, $^2J_{P^AP^C}$ 47 Hz, $^2J_{P^BP^C}$ 36 Hz), 42.2 (d, P^D), 41.0 (d, P^E) ($^2J_{P^DP^E}$ 34 Hz).

‡ *Spectroscopic data* for **5**: IR, ν_{CO} (hexane), 2091s, 2058vs, 2035s, 2024s, 1970w, 1888w, 1854m, 1830m cm^{-1}; ν_{CO} (KBr), 2091s, 2053s (br), 2028s (br), 2016s (br), 1996s (br), 1991s (br), 1958m, 1889w, 1845m (br), 1823m (br) cm^{-1}; FAB MS (*p*-nitrobenzylalcohol matrix,) *m/z* 1432 (M$^+$), $[M-x\text{CO}]^+$ (x = 1–11), $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ −24.5 (dd, P^A), 15.2 (dd, P^B), 18.1 (t, P^C) ($^1J_{P^AP^B}$ 449 Hz, $^2J_{P^AP^C}$ 54 Hz, $^2J_{P^BP^C}$ 35 Hz).

§ *Crystal data*: for **5**. $C_{26}H_{23}FeIr_4O_{11}P_3$, M = 1429.0, monoclinic, space group $P2_1/c$ (no. 14), a = 8.638(2), b = 13.319(3), c = 30.366(12) Å, β = 94.22(3)°, U = 3484(2) Å^3, Z = 4. Data were obtained with an Enraf-Nonius CAD 4 diffractometer using monochromated Mo-Kα radiation; λ = 0.71069 Å, μ = 15.82 mm^{-1} on a crystal of dimensions *ca*. 0.35 × 0.35 × 0.30 mm. A total of 8383 unique reflections were recorded and 5794 with $F^2 > 2\sigma(F^2)$ were used for solution and refinement. The structure was solved by direct methods (SHELX-86) and refined by full-matrix least-squares using SHELX-93, non H-anisotropic; $R1$ = 0.093, $wR2$ = 0.160.

For **6**. $C_{42}H_{28}FeIr_8O_{21}P_3$, M = 2555.0, monoclinic, space group Cc (no. 9), a = 16.060(4), b = 30.425(6), c = 11.247(3) Å, β = 97.36(3)°, U = 5450(2) Å^3, Z = 4, Data were obtained as for **5** at −100(2) °C. A total of 4799 independent reflections were recorded (λ = 0.71069 Å, μ = 19.87 mm^{-1}) for a crystal of dimensions *ca.* 0.40 × 0.35 × 0.10 mm, and 4347 with $F^2 > 2\sigma(F^2)$ were used for solution and refinement. The structure was solved by direct methods and refined by full-matrix least-squares, Ir, Fe and P atoms anisotropic; $R1$ = 0.050, $wR2$ = 0.099.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ *Spectroscopic data* for **6**: IR, ν_{CO} (hexane), 2103 m, 2095s, 2070vs, 2059vs, 2038vs, 2019vs, 1986w (sh), 1970w, 1866m, 1830 cm^{-1}; ^{1}H NMR ($CDCl_3$, 25 °C) δ 5.3 (5 H, C_5H_5), 1.6 (d, 2 H, CH_2, J_{H-H} 11.5 Hz), 1.3 (s, 9 H CMe_3), 1.28 (3 H, CH_3), 1.2 (3 H, CH_3), −22.1 (d, $^2J_{P-H}$ 7.0 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ −63.0 (dd, P^A), −8.0 (dd, P^B), 95.0 (dd, P^C ($^1J_{P^AP^B}$ 463 Hz, $^2J_{P^AP^C}$ 43 Hz, $^2J_{P^BP^C}$ 5 Hz).

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Received, 22nd August 1995; Com. 5/05581D