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Synthesis of fluorophenyl derivatives of iron, molybdenum and tungsten *via* $B(C_6F_5)_3$ and unusual carbon–fluorine bond reactions†

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The reaction between $B(C_6F_5)_3$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2Me]$ gave the unexpected product $[Fe\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)]$ **1** which reacts with the donor molecules L = PMe_3, PPh_3 or Bu^tNC giving $[Fe\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)L]$.* Likewise $[\{Fe[C_6F_4C(O)Me\text{-}2](\eta\text{-}C_5H_5)\}_2(\mu\text{-dppe})]$* was formed from **1** and $Ph_2P(CH_2)_2PPh_2$ (dppe). The formation of the compound where L = PMe_3 is shown to proceed *via* initial formation of $[Fe\{C_6F_4C(O)\text{-}Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)(PMe_3)]$*. The reaction between $B(C_6F_5)_3$ and $[M(\eta\text{-}C_5H_5)(CO)_3Me]$ (M = Mo or W) gave the compounds $[M\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2]$. The compounds $[M\{C_6F_3X\text{-}5\text{-}C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2]$* (M = Mo or W) where X = H were prepared from the compounds where X = F *via* unusual C−F bond-activation reactions. The compound $[Fe\{C_6F_3H\text{-}5\text{-}C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(PMe_3)]$ was prepared by photolysis of a mixture of $[Fe\{C_6F_3H\text{-}5\text{-}C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)]$ and PMe_3. The asterisk indicates the crystal structure has been determined.

The strong Lewis acid molecule tris(pentafluorophenyl)boron, $B(C_6F_5)_3$,[1] has recently attracted considerable interest as a co-catalyst in homogeneous Ziegler–Natta catalysis.[2] It is readily available and convenient to handle. Thus, unlike BF_3 which is a volatile gas and readily hydrolyses giving HF, the compound $B(C_6F_5)_3$ is a soluble white crystalline solid which is only slowly hydrolysed. We decided to explore its reactions with organo-transition-metal compounds which might, in different ways, act as nucleophiles to the boron centre. This has led to unexpected reactions and we have recently reported that with $[Fe(\eta\text{-}C_5H_5)(CO)_2Me]$ which leads to most unusual products, namely the compound $[Fe\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)]$ **1**.[3] We have also shown that $B(C_6F_5)_3$ readily co-ordinates to the oxygen of terminal oxometal groups.[4] Here we describe further reactions of compound **1** and related studies with molybdenum and tungsten compounds.

Results and Discussion

The Lewis acid molecule $B(C_6F_5)_3$ was first prepared many years ago,[1] however the two reported syntheses have some disadvantages. The first method employed was to treat a pentane solution of pentafluorophenyl bromide with *n*-butyllithium at low temperatures to generate $Li(C_6F_5)$. The latter is thermally highly sensitive and detonates at *ca.* −20 °C. The resulting suspension of the lithium salt was treated with boron trichloride to form LiCl and $B(C_6F_5)_3$. The reported yield of the crude product was between 30 and 50%, but in our hands, when working on a several gram scale, the overall yield after purification was much lower at *ca.* 20%. The compound can also be prepared[1] using the thermally stable Grignard reagent $Mg(C_6F_5)Cl$ in Et_2O and $BF_3{\cdot}Et_2O$. The yield of the compound $Et_2O{\cdot}B(C_6F_5)_3$ was 88%. This preparation is unsatisfactory due to the difficulty of removal of co-ordinated diethyl ether to give the desired solvent-free molecule $B(C_6F_5)_3$.

It was decided to seek a modified procedure and improved preparation for solvent-free $B(C_6F_5)_3$. The reaction vessel shown in the Experimental section was designed to enable the addition of the thermally sensitive suspension of $Li(C_6F_5)$ to a solution of BBr_3 at −78 °C. Maintaining the entire reaction vessel at −78 °C is an *essential* feature of this synthesis.[2] This method, which is described in detail in the Experimental section, gave pure $B(C_6F_5)_3$ in ≈50% yield on a 20 g scale.

Table 1 Selected bond lengths (Å) and angles (°) for the compounds **2**, **3**, **7** and **13**

	2	**3**	**7**	**13**
M−C(6)	1.949(4)	1.957(12)	1.950(4)	1.900(14)
M−C(7)	2.003(4)	2.003(11)	2.005(4)	
M−C(8)	2.172(3)	2.171(10)	2.162(4)	2.107(13)
M−O(3)	2.141(2)	2.141(7)	2.145(2)	2.078(9)
C(14)−O(3)	1.258(4)	1.283(14)	1.236(4)	1.254(12)
C(10)−F(4)	1.347(4)	1.355(12)	1.353(4)	
C(11)−F(3)	1.353(4)	1.392(12)	1.344(5)	
C(12)−F(2)	1.340(4)	1.366(13)	—	
C(13)−F(1)	1.357(4)	1.335(12)	1.364(4)	
M−$Cp_{centroid}$	1.999	2.003	1.990	
W−P(1)				2.480(3)
W−C(1)				2.390(13)
O(3)−W−P(1)				77.4(2)
C(6)−M−O(3)	120.0(1)	120.9(4)	119.24(12)	118.34
C(8)−M−O(3)	73.2(1)	73.1(3)	72.00(11)	71.8(4)
M−O(3)−C(14)	121.4(2)	120.8(7)	122.1(2)	125.3(9)
O(3)−C(14)−C(9)	117.1(10)	116.3(3)	116.3(3)	114.1(11)
C(14)−C(9)−C(8)	113.5(3)	112.6(10)	112.6(3)	109.7(11)
C(9)−C(8)−M	115.5(2)	116.1(7)	116.0(3)	118.9(9)
C(6)−M−C(7)	77.0(1)	76.9(4)	76.9(2)	—
C(6)−M−C(8)	78.0(1)	78.3(4)	77.82(14)	77.4(5)

The reactions between the compound $B(C_6F_5)_3$ and the methyl derivatives $[Fe(\eta\text{-}C_5H_5)(CO)_2Me]$, $[Mo(\eta\text{-}C_5H_5)(CO)_3Me]$ and $[W(\eta\text{-}C_5H_5)(CO)_3Me]$ have been studied. Treatment of a toluene solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2Me]$ with 1 equivalent of $B(C_6F_5)_3$ gave air-sensitive black-green crystals of the compound $[Fe\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)]$ **1** in 79% yield. Similarly, treatment of $[Mo(\eta\text{-}C_5H_5)(CO)_3Me]$ with $B(C_6F_5)_3$ gives moderately air-sensitive red crystals of $[Mo\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2]$ **2**. The reaction between $[W(\eta\text{-}C_5H_5)(CO)_3Me]$ and $B(C_6F_5)_3$ gave purple crystals of $[W\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2]$ **3**. The crystal structures of **2** and **3** have been determined and they are closely similar. The molecular structure of **3** is shown in Fig. 1 and selected distances and angles for **2** and **3** are given in Table 1. A discussion of these structures will be given later in the text.

The analytical and spectroscopic data for **1**–**3** and all the other new compounds described in this work are given in Table

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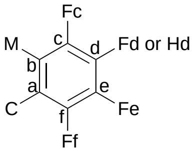
† *Non-SI units employed*: Torr ≈ 133 Pa, eV ≈ 1.60 × 10^{-19} J.

Table 2 Analytical and spectroscopic data



	Compound^{a}	NMR data^{b}
1	[Fe{C$_6$F$_4$C(O)Me-2}(η-C$_5$H$_5$)(CO)] Black-green C, 49.8 (49.45); H, 2.45 (2.4) Mass (EI): 340, M^+; 312, $[M - \mathrm{CO}]^+$ (base peak); 297, $[M - \mathrm{CO} - \mathrm{CH_3}]^+$; 247, $[M - \mathrm{CO} - \mathrm{C_5H_5}]^+$ IR (Nujol): 1968vs, 1630m, 1581m	
2	[Mo{C$_6$F$_4$C(O)Me-2}(η-C$_5$H$_5$)(CO)$_2$] Red C, 44.35 (44.1); H, 2.0 (2.0); Mo, 23.2 (23.5) Mass (EI): 413 (410), M^+; 385 (382), $[M - \mathrm{CO}]^+$; 357 (354), $[M - 2\mathrm{CO}]^+$ IR (KBr): 1975vs, 1877vs, 1632s, 1573s, 1504s	^{1}H:^{c} 2.13 (d, 3 H, J_{FH} = 4.2, COCH$_3$), 4.80 (s, 5 H, C$_5$H$_5$) ^{13}C-{^{1}H}:^{c} 27.7 (d, J_{FC} = 8.5, CO*C*H$_3$), 93.5 (s, C$_5$H$_5$), 123.7 (m, C$_{\mathrm{b}}$), 136.2 (dm, $^{1}J_{\mathrm{FC}}$ = 242, C$_{\mathrm{e}}$), 137.6 (dm, $^{1}J_{\mathrm{FC}}$ = 252, C$_{\mathrm{d}}$), 139.2 (dm, $^{1}J_{\mathrm{FC}}$ = 248, C$_{\mathrm{f}}$), 150.5 (dm, $^{1}J_{\mathrm{FC}}$ = 243, C$_{\mathrm{c}}$), 183.2 (dm, J_{FC} = 45, C$_{\mathrm{a}}$), 203.4 (m, *C*OCH$_3$), 246.8 (d, J = 5.0, CO), 253.2 (s, CO) ^{19}F:^{c} −164.9 (m, 1 F, F$_{\mathrm{e}}$), −156.8 (m, 1 F, F$_{\mathrm{d}}$), −138.4 (m, 1 F, F$_{\mathrm{f}}$), −115.7 (m, 1 F, F$_{\mathrm{c}}$)
3	[W{C$_6$F$_4$C(O)Me-2}(η-C$_5$H$_5$)(CO)$_2$] Purple C, 36.2 (36.3); H, 1.6 (1.6); W, 38.9 (37.1) Mass (EI): 502 (496), M^+ IR (KBr): 1966vs, 1864vs, 1636s, 1567s, 1505s	^{1}H:^{c} 2.80 (d, 3 H, J_{FH} = 3.8, COCH$_3$), 5.07 (s, 5 H, C$_5$H$_5$) ^{13}C-{^{1}H}:^{c} 26.7 (d, J_{FC} = 8.4, CO*C*H$_3$), 92.1 (s, C$_5$H$_5$), 124.3 (m, C$_{\mathrm{b}}$), 136.0 (dm, $^{1}J_{\mathrm{FC}}$ = 246, C$_{\mathrm{e}}$), 140.2 (dm, $^{1}J_{\mathrm{FC}}$ = 266, C$_{\mathrm{d}}$), 150.0 (dm, $^{1}J_{\mathrm{FC}}$ = 263, C$_{\mathrm{f}}$), 152.2 (dm, $^{1}J_{\mathrm{FC}}$ = 233, C$_{\mathrm{c}}$), 178.1 (dm, J_{FC} = 40, C$_{\mathrm{a}}$), 202.7 (pseudo-t, J_{FC} = 6.1, COCH$_3$), 236.6 (d, J = 4.7, CO), 245.6 (s, CO) ^{19}F:^{c} −165.3 (m, 1 F, F$_{\mathrm{c}}$), −157.1 (m, 1 F, F$_{\mathrm{d}}$), −140.0 (m, 1 F, F$_{\mathrm{f}}$), −116.0 (m, 1 F, F$_{\mathrm{c}}$)
4	[Fe{C$_6$F$_4$C(O)Me-2}(η-C$_5$H$_5$)(Bu$^{\mathrm{t}}$NC)] Dark purple C, 54.7 (54.7); H, 4.45 (4.3); Fe, 14.2 (14.1); N, 3.5 (3.5) Mass (FAB$^+$): 395, M^+ (base peak) IR (Nujol): 2044s, 1629m, 1560w, 1530m	
5	[Fe{C$_6$F$_4$C(O)Me-2}(η-C$_5$H$_5$)(CO)(PMe$_3$)] Black-purple C, 49.3 (49.1); H, 4.2 (4.1); Fe, 13.95 (13.4); P, 7.7 (7.4) IR (Nujol): 1968s, 1627s, 1547m, 1504s	
6	[Fe{C$_6$F$_4$C(O)Me-2}(η-C$_5$H$_5$)(PMe$_3$)] Purple Mass (FAB$^+$): 388, M^+ (base peak); 323, $[M - \mathrm{C_5H_5}]^+$; 312, $[M - \mathrm{PMe_3}]^+$; 247 IR (Nujol): 1626s, 1553m, 1502s	^{1}H:^{d} 1.02 (m, 9 H, PCH$_3$), 2.54 (m, 3 H, COCH$_3$), 4.28 (s, 5 H, C$_5$H$_5$) ^{13}C-{^{1}H}:^{d} 17.2 (d, J_{PC} = 24.4, PCH$_3$), 27.6 (s, CO*C*H$_3$), 76.1 (s, C$_5$H$_5$), 130.9 (m, C$_{\mathrm{b}}$), 133.0 (m, C$_{\mathrm{e}}$), 140.7 (m, C$_{\mathrm{d}}$), 149.6 (m, C$_{\mathrm{f}}$), 156.1 (m, C$_{\mathrm{e}}$), 195.6 (m, C$_{\mathrm{a}}$), 206.7 (s, COCH$_3$) ^{19}F:^{d} −170.6 (m, 1 F, F$_{\mathrm{e}}$), −159.1 (m, 1 F, F$_{\mathrm{d}}$), −140.2 (m, 1 F, F$_{\mathrm{f}}$), −120.5 (m, 1 F, F$_{\mathrm{c}}$) ^{31}P-{^{1}H}:^{d} 31.9 (s, 1 P)
7	[Mo{C$_6$F$_3$H-5-C(O)Me-2}(η-C$_5$H$_5$)(CO)$_2$] Dark red^{e} Mass (EI): M^+, $[M - \mathrm{CO}]^+$ IR (KBr): 1975vs, 1876vs, 1624vs, 1564vs, 1519s	^{1}H:^{c} 2.81 (d, 3 H, J_{FH} = 4.2, COCH$_3$), 5.44 (s, 5 H, C$_5$H$_5$), 6.89 (m, 1 H, H$_{\mathrm{d}}$) ^{13}C-{^{1}H}:^{c} 28.9 (d, J_{FC} = 9.2, CO*C*H$_3$), 94.7 (s, C$_5$H$_5$), 104.5 (dd, J_{FC} = 21 and 37, C$_{\mathrm{d}}$), 129.7 (dm, J_{FC} = 18, C$_{\mathrm{b}}$), 146.0 (dm, $^{1}J_{\mathrm{FC}}$ = 256, C$_{\mathrm{e}}$), 150.9 (dm, $^{1}J_{\mathrm{FC}}$ = 255, C$_{\mathrm{f}}$), 164.2 (dm, $^{1}J_{\mathrm{FC}}$ = 260, C$_{\mathrm{c}}$), 183.1 (dm, J_{FC} = 49, C$_{\mathrm{a}}$), 205.0 (s, *C*OCH$_3$), 247.9 (s, CO), 253.6 (s, CO) ^{19}F:^{c} −146.9 (m, 1 F, F$_{\mathrm{e}}$ or F$_{\mathrm{f}}$), −144.9 (m, 1 F, F$_{\mathrm{f}}$ or F$_{\mathrm{e}}$), −92.3 (m, 1 F, F$_{\mathrm{c}}$)
8	[W{C$_6$F$_3$H-5-C(O)Me-2}(η-C$_5$H$_5$)(CO)$_2$] Green^{e} IR (KBr): 1965vs, 1864vs, 1726s, 1559s	^{1}H:^{c} 2.92 (d, 3 H, J_{FH} = 4.0, COCH$_3$), 5.58 (s, 5 H, C$_5$H$_5$), 6.85 (m, 1 H, H$_{\mathrm{d}}$) ^{13}C-{^{1}H}:^{c} 27.8 (d, CO*C*H$_3$), 92.9 (s, C$_5$H$_5$), 104.3 (m, C$_{\mathrm{d}}$), 130.3 (m, C$_{\mathrm{b}}$), 145.5 (dm, $^{1}J_{\mathrm{FC}}$ = 243, C$_{\mathrm{e}}$), 150.3 (dm, $^{1}J_{\mathrm{FC}}$ = 271, C$_{\mathrm{f}}$), 164.1 (dm, $^{1}J_{\mathrm{FC}}$ = 237, C$_{\mathrm{c}}$), 178.4 (dm, J_{FC} = 64, C$_{\mathrm{a}}$), 204.3 (m, COCH$_3$), 238.3 (s, CO), 246.5 (s, CO) ^{19}F:^{c} −147.5 (m, 1 F, F$_{\mathrm{e}}$), −146.5 (m, 1 F, F$_{\mathrm{f}}$), −92.0 (m, 1 F, F$_{\mathrm{c}}$)
9	[W{C$_6$F$_3$H-5-C(O)Me-2}(η-C$_5$H$_5$)(CO)(PMe$_3$)] Blue violet C, 38.5 (38.8); H, 3.0 (3.45); P, 5.7 (5.9) Mass (FAB): 526, M^+ IR (KBr): 1802vs, 1632s, 1586m, 1540m	^{1}H:^{c} 1.54 [d, J_{PH} = 9.0, 9 H, P(CH$_3$)], 2.99 (d, 3 H, J_{FH} = 3.0, COCH$_3$), 5.17 (s, 5 H, C$_5$H$_5$), 6.44 (m, 1 H, H$_{\mathrm{d}}$) ^{13}C-{^{1}H}:^{c} 19.2 [d, J_{PC} = 29.0, P(CH$_3$)], 26.7 (d, J_{FC} = 7.7, CO*C*H$_3$), 91.3 (s, C$_5$H$_5$), 100.0 (m, C$_{\mathrm{d}}$), 128.9 (m, C$_{\mathrm{b}}$), 144.2 (dm, $^{1}J_{\mathrm{FC}}$ = 236, C$_{\mathrm{e}}$), 150.2 (dm, $^{1}J_{\mathrm{FC}}$ = 249, C$_{\mathrm{f}}$), 165.4 (dm, $^{1}J_{\mathrm{FC}}$ = 250, C$_{\mathrm{c}}$), 190.4 (m, *C*OCH$_3$), 193.2 (dm, C$_{\mathrm{a}}$), 240.6 (d, J_{PC} = 10.7, CO) ^{19}F:^{c} −151.1 (m, 1 F, F$_{\mathrm{e}}$ or F$_{\mathrm{f}}$), −149.7 (m, 1 F, F$_{\mathrm{f}}$ or F$_{\mathrm{e}}$), −91.3 (m, 1 F, F$_{\mathrm{c}}$) ^{31}P-{^{1}H}:^{c} 11.3 (s)
10	[Fe{C$_6$F$_3$H-5-C(O)Me-2}(η-C$_5$H$_5$)(PMe$_3$)] Black purple C, 51.4 (51.9); H, 4.8 (4.9); Fe, 15.1 (15.1); P, 8.3 (8.4) Mass (FAB$^+$): 370, M^+ (base peak) IR (KBr): 1619s, 1547s, 1505s	^{1}H:^{d} 1.00 [m, 9 H, P(CH$_3$)], 2.56 (m, 3 H, COCH$_3$), 4.28 (s, 5 H, C$_5$H$_5$), 6.78 (m, 1 H, H$_{\mathrm{d}}$) ^{13}C-{^{1}H}:^{d} 17.1 [d, J_{PC} = 25.6, P(CH$_3$)], 27.6 (s, COCH$_3$), 76.1 (s, C$_5$H$_5$), 103.5 (m, C$_{\mathrm{d}}$), 137.1 (m, C$_{\mathrm{b}}$), 143.1 (m, C$_{\mathrm{e}}$), 149.6 (m, C$_{\mathrm{f}}$), 169.8 (m, C$_{\mathrm{c}}$), 196.4 (m, C$_{\mathrm{a}}$), 207.4 (s, COCH$_3$) ^{19}F:^{d} −153.0 (m, 1 F, F$_{\mathrm{e}}$), −146.6 (m, 1 F, F$_{\mathrm{f}}$), −96.4 (m, 1 F, F$_{\mathrm{c}}$) ^{31}P-{^{1}H}:^{d} 32.3 (s)

Table 2 (*Continued*)

	Compound[a]	NMR data[b]
11	$[\mathrm{Fe\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(PPh_3)}]$ Black-purple C, 65.2 (64.8); H, 3.7 (4.0); Fe, 9.2 (9.7); P, 5.2 (5.3) Mass ($\mathrm{FAB^+}$): 574, M^+ (base peak); 509, $[M - \mathrm{C_5H_5}]^+$; 383 IR (Nujol): 1734m, 1628m, 1562w	^{1}H:[c] 1.75 (m, 3 H, $\mathrm{COCH_3}$), 4.32 (s, 5 H, $\mathrm{C_5H_5}$), 6.94 [m, 9 H, $\mathrm{P(C_6H_5)}$], 7.35 [m, 6 H, $\mathrm{P(C_6H_5)}$] ^{13}C-{^{1}H}:[c] 27.1 (s, $\mathrm{COCH_3}$), 77.2 (s, $\mathrm{C_5H_5}$), 127.8, 129.4 [m, $\mathrm{P(C_6H_5)}$], 134.2 (m, $\mathrm{C_e}$), 141.1 (m, $\mathrm{C_d}$), 149.8 (m, $\mathrm{C_f}$), 156.3 (m, $\mathrm{C_c}$), 193.7 (m, $\mathrm{C_a}$), 207.2 (s, $C\mathrm{OCH_3}$), $\mathrm{C_b}$ not observed ^{19}F:[c] −167.1 (m, 1 F, $\mathrm{F_e}$), −154.3 (m, 1 F, $\mathrm{F_d}$), −136.4 (m, 1 F, $\mathrm{F_f}$), −115.4 (m, 1 F, $\mathrm{F_c}$) ^{31}P-{^{1}H}:[c] 76.0 (s)
12	$[\mathrm{\{Fe[C_6F_4C(O)Me\text{-}2](\eta\text{-}C_5H_5)\}_2(\mu\text{-}dppe)}]$ Purple C, 61.5 (61.1); H, 4.2 (3.9); Fe, 10.6 (10.9) Mass ($\mathrm{FAB^+}$): 1022, M^+	^{1}H:[d] 1.28 [m, 4 H, $\mathrm{P(CH_2)_2P}$], 2.06 (s, 3 H, $\mathrm{COCH_3}$), 4.09 (s, 5 H, $\mathrm{C_5H_5}$), 6.93, 7.21, 7.39 [m, 20 H, $\mathrm{P(C_6H_5)}$] ^{13}C-{^{1}H}:[d] 21.6 [s, $\mathrm{P(CH_2)_2P}$], 27.6 (s, $\mathrm{CO}C\mathrm{H_3}$), 76.5 (s, $\mathrm{C_5H_5}$), 128.4, 129.7 [m, $\mathrm{P(C_6H_5)}$], 131.3 (m, $\mathrm{C_b}$), 132.6 [br m, $\mathrm{P(C_6H_5)}$], 134.0 (m, $\mathrm{C_e}$), 140.8 (m, $\mathrm{C_d}$), 149.5 (m, $\mathrm{C_f}$), 155.5 (m, $\mathrm{C_c}$), 194.0 (m, $\mathrm{C_a}$), 207.3 (s, $\mathrm{COCH_3}$), $\mathrm{C_b}$ not observed ^{19}F:[d] −170.1 (m, 1 F, $\mathrm{F_e}$), −158.2 (m, 1 F, $\mathrm{F_d}$), −139.4 (m, 1 F, $\mathrm{F_f}$), −120.1 (m, 1 F, $\mathrm{F_c}$) ^{31}P-{^{1}H}:[d] 69.2 (s)

[a] Analytical data given as found (calculated) in %. Mass spectral data given as: *m*/*z* (assignment), IR data ($\mathrm{cm^{-1}}$) as KBr discs or Nujol mulls, as indicated. [b] At probe temperature. Data given as: chemical shift (δ) (multiplicity, relative intensity, *J* in Hz, assignment). The data for compounds **1**, **4** and **5** are given in ref. 3. [c] In $\mathrm{C_6D_6}$. [d] In $\mathrm{CD_2Cl_2}$. [e] Analysis not made; characterised by spectroscopic data only.

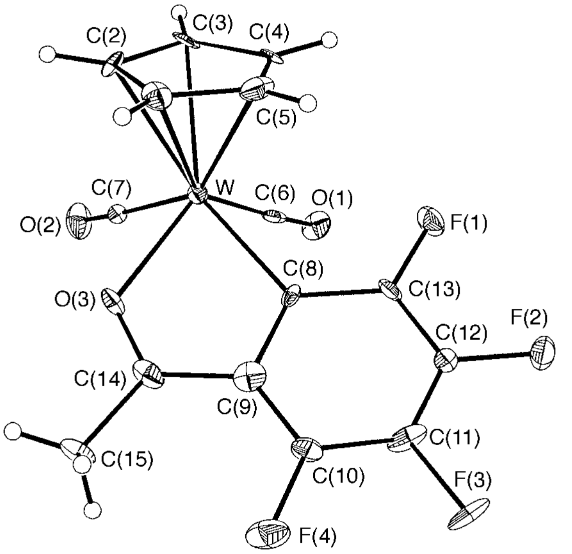
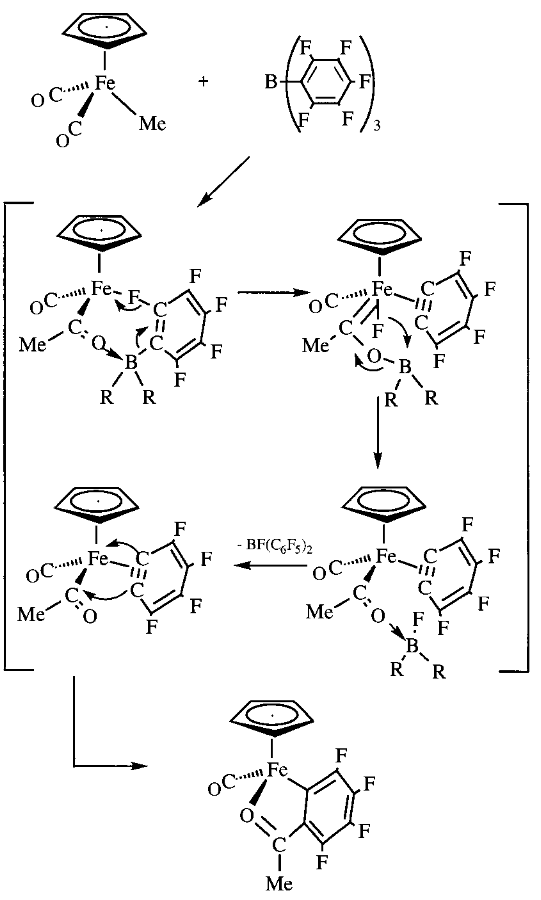


Fig. 1 Molecular structure of $[\mathrm{W\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2}]$ **3**; that of **2** is almost superimposable

2. For many of the compounds the complete assignment of the ^{13}C and ^{19}F NMR spectra was assisted by two-dimensional NMR experiments, including F–F COSY (correlation spectroscopy), C–F heteronuclear single-quantum correlation (HSQC) and heteronuclear multiple-bond coherence (HMBC) experiments. The close similarities between the NMR and IR spectra of **1** and those of **2** and **3** strongly suggest **1** has the same five-membered $\mathrm{MC_2CO}$ ring that is found in **2** and **3**. This is further supported by the crystal structures of several derivatives of **1**, as described below.

The formation of compounds **1**–**3** appears to involve a formal insertion of a tetrafluorobenzyne $\mathrm{C_6F_4}$ fragment, arising from $\mathrm{B(C_6F_5)_3}$, into the M–C bond of a acetylmetal group. To help to elucidate the reaction mechanism, boron-containing products of the reaction were isolated and characterised. Thus, the preparation of **1** was repeated under the same conditions, but the highly volatile products of the reaction mixture were collected in a cold trap and then treated with 4-methylpyridine. After removal of solvent a white powder was recovered. The ^{1}H and ^{11}B-{^{1}H} NMR spectra of this residue showed the formation of the 4-methylpyridine adducts $\mathrm{C_6H_7N{\cdot}BF_2(C_6F_5)}$ and $\mathrm{C_6H_7N{\cdot}BF_3}$. The observed chemical shifts were identical with the values quoted in the literature (see the Experimental section).[5] Owing to the lower volatility of $\mathrm{BF(C_6F_5)_2}$ it was not possible selectively to evaporate it from the initial reaction mixture. However, this mixture was monitored by ^{11}B-{^{1}H} NMR spectroscopy which showed the formation of bands assignable to $\mathrm{BF(C_6F_5)_2}$. The reaction between the compound $[\mathrm{Mo(\eta\text{-}C_5H_5)(CO)_3Me}]$ and $\mathrm{B(C_6F_5)_3}$ was monitored by ^{11}B NMR spectroscopy and the data also showed the formation of $\mathrm{BF(C_6F_5)_2}$, $\mathrm{BF_2(C_6F_5)}$ and $\mathrm{BF_3}$. In light of the observation of these boron-containing products, the reaction of the compound $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2Me}]$ was repeated using only 1/3 equivalent of $\mathrm{B(C_6F_5)_3}$. The yield of **1** under these conditions was essentially the same as before but it was necessary to double the reaction time. We infer that during the formation of **1**–**3** the $\mathrm{B(C_6F_5)_3}$ successively loses $\mathrm{C_6F_4}$ fragments to the metal centre with formation of the compounds $\mathrm{BF(C_6F_5)_2}$, $\mathrm{BF_2(C_6F_5)}$ and, finally, $\mathrm{BF_3}$. On the basis of these preliminary observations, we tentatively propose a mechanism for the formation of **1**, as shown in Scheme 1. The first step is the co-ordination of the Lewis acid $\mathrm{B(C_6F_5)_3}$ to the oxygen atom of a CO ligand thereby promoting migration of the methyl group. In related systems other Lewis acids such as $\mathrm{(AlBr_3)_2}$ have been shown to promote the migration of a methyl group to give an acyl ligand.[6] It is envisaged that the resulting vacant co-ordination site on the Fe is then occupied by a fluorine atom of a weakly co-ordinating η^2-$\mathrm{C_6F_5}$ group of $\mathrm{B(C_6F_5)_3}$. Similar co-ordination of $\mathrm{B(C_6F_5)_3}$ to metal centres has been reported.[7–10] The next proposed step involves fragmentation of the $\mathrm{B(C_6F_5)_3}$ ligand by cleavage of a C–F bond and a B–C bond leading to the elimination of $\mathrm{BF(C_6F_5)_2}$, as shown in Scheme 1. Finally, the co-ordinated benzyne $\mathrm{C_6F_4}$ fragment inserts into the metal–acyl group giving the neutral compound **1**.

The five-membered rings formed by the atoms $\mathrm{MC_3O}$ in compounds **1**–**3** are unusual and the reactions of these compounds with potential donor ligands were studied with a view to displacing the acyl oxygen from the metal. Treatment of the compound $[\mathrm{Fe\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)}]$ **1** with *tert*-butyl isocyanide gave air-sensitive dark purple crystals of $[\mathrm{Fe\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(Bu^tNC)}]$ **4** in 45% yield. This compound is thermally stable, sublimes at 75 °C under vacuum (10^{-1} Torr) and melts without decomposition in a sealed capillary at 85 °C. It is moderately soluble in pentane and very soluble in $\mathrm{Et_2O}$, benzene, $\mathrm{CH_2Cl_2}$ and tetrahydrofuran (thf). Its crystal structure has been determined and the molecular structure is shown in Fig. 2(*a*). Selected distances and angles are given in Table 3. The structure shows that the *tert*-butyl isocyanide group has replaced the terminal carbonyl in **1** and a five-membered $\mathrm{FeC_3O}$ ring is still present. Attempts to cleave the Fe–O bond in **1** by treatment with an excess of *tert*-butyl isocyanide gave only **4**. In contrast to the formation of **4**, treat-



1

Scheme 1 A possible mechanism for the formation of compound **1**

ment of **1** with 1 equivalent of trimethylphosphine gives air-sensitive purple crystals of the compound [Fe{$C_6F_4C(O)$-Me-2}(η-C_5H_5)(CO)(PMe_3)] **5** which it appears is formed by a simple addition of a trimethylphosphine ligand and displacement of the co-ordinating acyl oxygen. Compound **5** melts without decomposition at 95 °C and is soluble in all common organic solvents. Its crystal structure has been determined and the molecular structure is shown in Fig. 2(*b*). Selected distances and angles are given in Table 3. The structure shows that both the PMe_3 and CO ligands are bound to the iron centre and the oxygen atom of the acyl group is no longer co-ordinated to the metal.

On heating a heptane solution of the compound [Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(CO)(PMe_3)] **5** carbon monoxide was evolved and [Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(PMe_3)] **6** was formed in 74% yield. The black-purple crystals are sensitive to air and melt without decomposition at 92 °C in a sealed capillary. The crystal structure of **6** has been determined and the molecular structure is shown in Fig. 2(*c*). Selected distances and angles are given in Table 3. The structure is closely similar to those of compounds **2**–**4** and includes the by now familiar five-membered MC_3O ring system. Thus it appears that compound **5** is an intermediate in the formation of **6**. Indeed, refluxing a heptane solution of **1** with an excess of PMe_3 leads directly to the formation of **6**, as shown by monitoring the infrared spectra of the reaction mixture.

Compound **2** was treated with trimethylphosphine in the expectation that the co-ordinated acyl oxygen or a CO ligand would be displaced. However instead an unexpected and specific activation of a C−F bond occurs giving purple crystals of [Mo{C_6F_3H-5-C(O)Me-2}(η-C_5H_5)$(CO)_2$] **7**. Its crystal structure has been determined; the molecular structure is shown in Fig. 3 and selected distances and angles are given in Table 1. The molecular structure is closely similar to that of **2** except that the F atom attached to the C(12) carbon has been replaced by a hydrogen atom. The anisotropic thermal parameters of all fluorine atoms are unexceptional. The spectroscopic properties of **7** are closely similar to those of **2**. For example, the IR spectra of **2** and **7** were almost identical and the carbonyl region for both is consistent with the presence of an $Mo(CO)_2$ fragment. Further, the ^{19}F NMR spectrum of **7** confirms the presence of only three fluorine atoms and in the ^1H NMR spectrum there is a multiplet at δ 6.89 which may be assigned to a hydrogen attached to the C(12) carbon of the aryl ring. The conversion of **2** into **7** requires the presence of the PMe_3 since refluxing **2** in

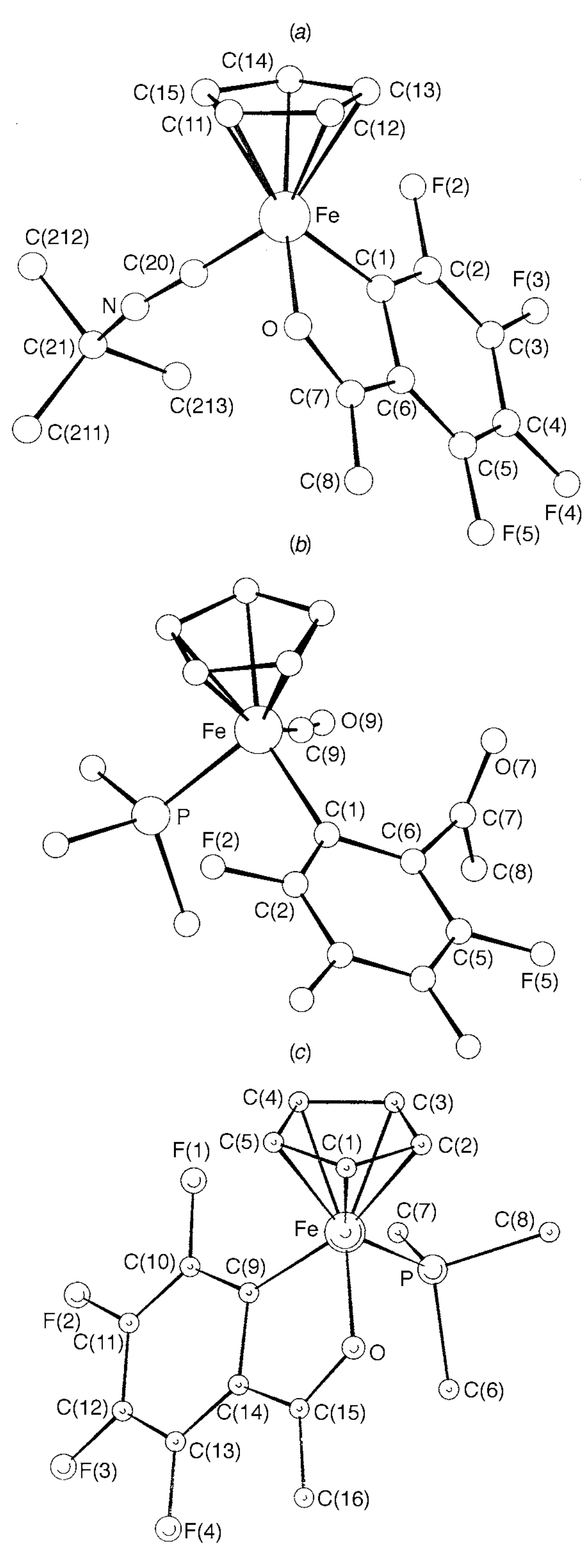


Fig. 2 Molecular structures of (*a*) [Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)-(Bu^tNC)] **4**, (*b*) [Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(CO)(PMe_3)] **5** and (*c*) [Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(PMe_3)] **6**

Table 3 Selected interatomic distances (Å) and angles (°) for compounds **4**–**6**, **11** and **12**

Compound				
4	Fe–O	1.964(2)	O–Fe–C(1)	81.05(8)
	Fe–C(1)	1.938(2)	O–Fe–C(20)	95.22(8)
	Fe–C(20)	1.811(2)	C(1)–Fe–C(20)	87.30(9)
	Fe–Cp_{cen}	1.712	Fe–O–C(7)	117.6(2)
	O–C(7)	1.247(3)	Fe–C(1)–C(6)	112.9(2)
	C(1)–C(2)	1.378(4)	O–C(7)–C(6)	115.6(2)
	C(1)–C(6)	1.424(3)	Fe–C(20)–N	117.4(2)
	C(21)–N	1.453(3)	C(1)–C(6)–C(7)	112.4(2)
5	Fe–P	2.195(1)	P–Fe–C(1)	93.0(1)
	Fe–C(1)	2.017(4)	P–Fe–C(9)	86.4(1)
	Fe–C(9)	1.744(4)	C(1)–Fe–C(9)	99.4(2)
	Fe–Cp_{cen}	1.722	C(1)–C(6)–C(7)	122.5(3)
	O(7)–C(7)	1.207(5)	Fe–C(1)–C(6)	124.9(3)
	C(1)–C(2)	1.377(6)	O(7)–C(7)–C(6)	121.5(4)
	C(1)–C(6)	1.414(6)	Fe–C(9)–O(9)	172.2(4)
	C(9)–O(9)	1.158(5)	C(6)–C(7)–O(7)	121.5(4)
6	Fe–P	2.188(1)	P–Fe–C(9)	88.2(1)
	Fe–C(9)	1.929(3)	C(9)–Fe–O	81.7(1)
	Fe–O	1.946(3)	P–Fe–O	95.30(9)
	Fe–Cp_{cen}	1.701	C(9)–C(14)–C(15)	112.3(3)
	O–C(15)	1.262(5)	Fe–C(9)–C(14)	112.0(3)
	C(9)–C(14)	1.436(5)	O–C(15)–C(14)	115.8(3)
	C(14)–C(15)	1.433(6)	Fe–O–C(15)	117.4(2)
	P–C(6)	1.816(5)	C(10)–C(9)–C(14)	114.1(3)
11	Fe–P	2.220(1)	P–Fe–C(1)	93.7(1)
	Fe–C(1)	1.939(5)	C(1)–Fe–O	81.6(2)
	Fe–O	1.980(3)	P–Fe–O	88.8(1)
	Fe–Cp_{cen}	1.717	C(1)–C(6)–C(7)	112.9(4)
	O–C(7)	1.256(5)	Fe–C(1)–C(6)	112.5(3)
	C(1)–C(6)	1.442(6)	O–C(7)–C(6)	115.9(4)
	C(6)–C(7)	1.440(7)	Fe–O–C(7)	116.9(3)
	P–C(111)	1.844(4)	C(2)–C(1)–C(6)	115.0(4)
12	Fe(1)–P(1)	2.186(2)	P(1)–Fe(1)–C(6)	93.1(2)
	Fe(1)–C(6)	1.921(6)	C(6)–Fe(1)–O(1)	81.3(2)
	Fe(1)–O(1)	1.956(4)	P(1)–Fe(1)–O(1)	92.9(1)
	Fe(1)–Cp_{cen}	1.692	C(6)–C(11)–C(12)	112.3(6)
	O(1)–C(12)	1.264(7)	Fe–C(6)–C(11)	113.4(6)
	C(6)–C(11)	1.429(9)	O(1)–C(12)–C(11)	116.0(6)
	C(11)–C(12)	1.42(1)	Fe–O(1)–C(12)	117.0(5)
	P(1)–C(14)	1.822(6)	C(7)–C(6)–O(11)	115.3(7)

Cp_{cen} denotes the centroid of the C_5H_5 ring.

toluene for 48 h in the absence of PMe_3 showed no evidence for the formation of **7**. Under similar conditions, no reaction occurred between **2** and triphenylphosphine. This suggests the trimethylphosphine is directly responsible for the removal of the fluorine during the formation of **7**. The reactions of **2** and **3** are given in Scheme 2. The reaction between $[W\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2]$ **3** and PMe_3 gave the green tungsten compound $[W\{C_6F_3H\text{-}5\text{-}C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2]$ **8** and the similarity of the spectroscopic data showed that **8** and **7** were very closely similar and therefore we propose they are isostructural. Photolysis of **3** in the presence of an excess of trimethylphosphine causes displacement of a carbonyl ligand giving the blue-violet compound $[W\{C_6F_3H\text{-}5\text{-}C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)(PMe_3)]$ **9**, together with some **8**; these may be separated by column chromatography on alumina. It seems likely that the formation of **9** from **3** proceeds *via* **8** as an intermediate.

Following the discovery of C–F bond-activation reactions which lead to the formation of compounds **7** and **8**, the photolysis of a refluxing toluene solution of **1** and trimethylphosphine was investigated. Chromatography of the reaction mixture allowed the separation of the purple-black crystalline compound $[Fe\{C_6F_3H\text{-}5\text{-}C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(PMe_3)]$ **10** in 26% yield. The air-sensitive crystals of **10** are soluble in common organic solvents and melt without decomposition at 90 °C.

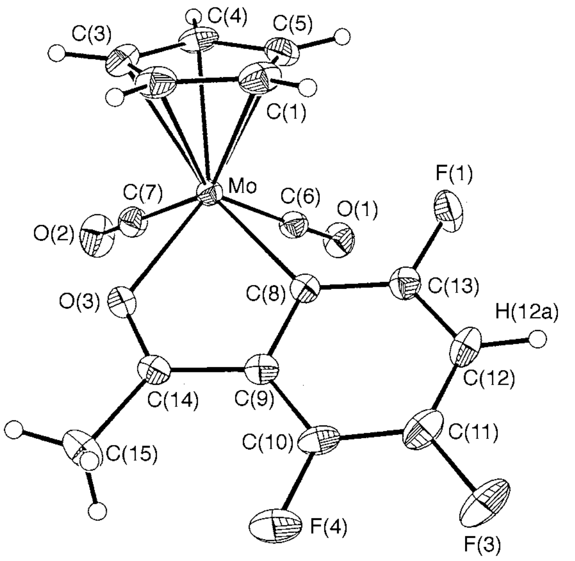
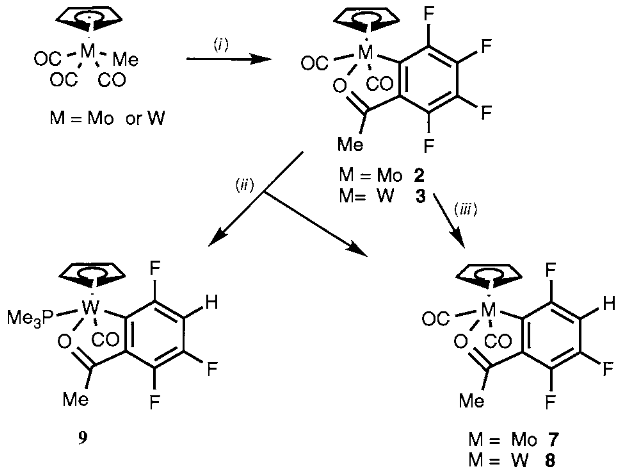


Fig. 3 Molecular structure $[Mo\{C_6F_3H\text{-}5\text{-}C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2]$ **7**

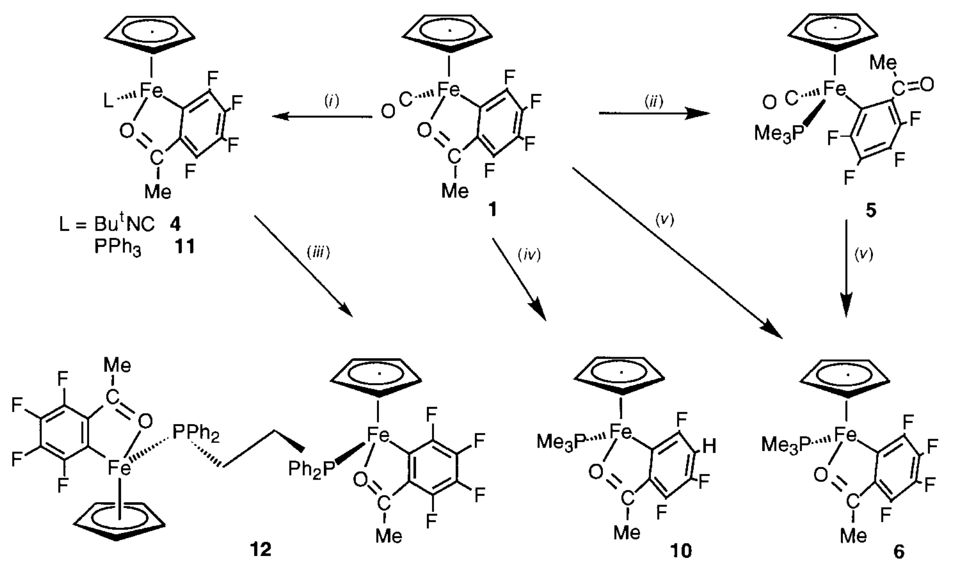


Scheme 2 (*i*) M = Mo, $B(C_6F_5)_3$ in toluene for 42 h, yield 25%; M = W, same except 48 h, 75%; (*ii*) excess of PMe_3 in toluene, photolysis for 7.5 h then room temperature (r.t.) for 16.5 h, chromatography on alumina, *ca.* 25% **8** and 25% **9**; (*iii*) excess of PMe_3 in toluene, reflux for 3 h, stir at r.t. for 15 h, 25%

The spectroscopic data show that, as for **7** and **8**, there is a hydrogen attached to the C_d carbon atom of the aromatic C_6 ring. The reactions of **1** described above are shown in Scheme 3.

Analogous photolysis reactions on mixtures of compound **1** with PPh_3 or dppe ($Ph_2PCH_2CH_2PPh_2$) did not result in the substitution of fluorine F_d by hydrogen. Instead, displacement of the terminal carbonyl occurred. A toluene solution of a mixture of **1** and triphenylphosphine was refluxed for 18 h, until the ν(CO) absorption of the carbonyl ligand of **1** had disappeared, to give black-purple crystals of $[Fe\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(PPh_3)]$ **11**, in 42% yield. Similarly, when a mixture of **1** and dppe in toluene at 60 °C was photolysed for 15 h dark purple crystals of $[\{Fe[C_6F_4C(O)Me\text{-}2](\eta\text{-}C_5H_5)\}_2(\mu\text{-dppe})]$ **12** were prepared in 34% yield. The crystals of **11** and **12** are moderately stable in air and only show signs of decomposition after several hours. They dissolve sparingly in pentane and heptane and are very soluble in benzene, CH_2Cl_2 and thf. Compound **11** sublimes at 105 °C under vacuum (10^{-1} Torr) and melts without decomposition at 172 °C. The crystal structures of **11** and **12** have been determined and the molecular structures are shown in Fig. 4(*a*) and 4(*b*), respectively. Selected distances and angles are given in Table 3. In the light of the crystal structure data an explanation for the preference for fluorine substitution at the C(12) (or C_d) position of **4**, **6**, **11** and **12** is offered below.

The compound $[W\{C_6F_4C(O)Me\text{-}2\}(\eta\text{-}C_5H_5)(CO)_2]$ **3** was



Scheme 3 (*i*) L = Bu^{t}NC, in pentane at r.t. for 18 h, yield 45%; L = PPh$_3$, in toluene, reflux for 18 h, 42%; (*ii*) PMe$_3$ in heptane at r.t. for 15 h, 45%; (*iii*) dppe (0.5 equivalent) in toluene under photolysis for 15 h at 60 °C, 34%; (*iv*) excess of PMe$_3$ in toluene at reflux under photolysis for 3 d, 26%; (*v*) excess of PMe$_3$ in heptane under reflux for 15 h, 74%

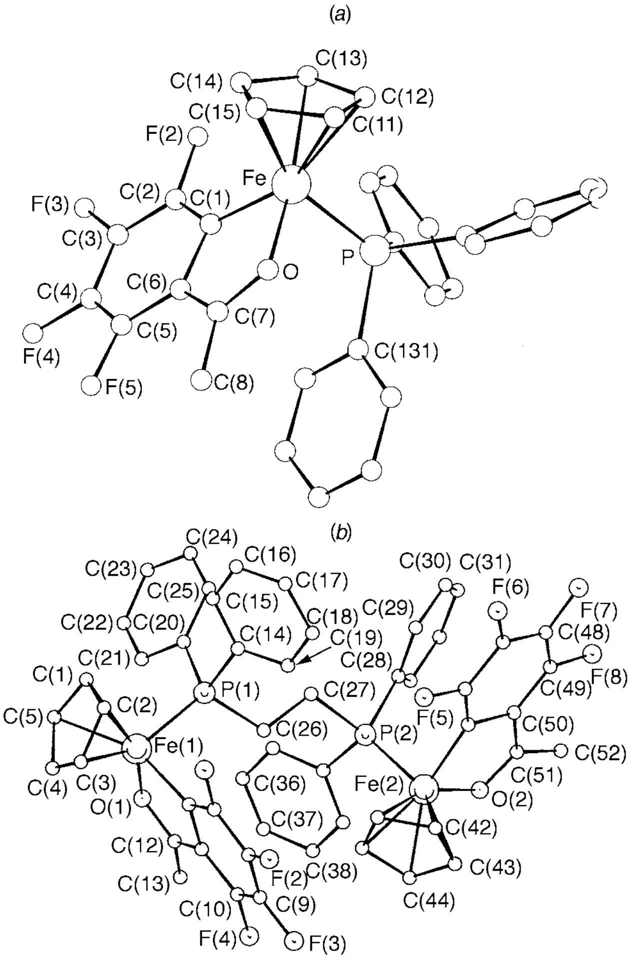


Fig. 4 Molecular structures of (*a*) [Fe{C$_6$F$_4$C(O)Me-2}(η-C$_5$H$_5$)(PPh$_3$)] **11** and (*b*) [{Fe[C$_6$F$_4$C(O)Me-2](η-C$_5$H$_5$)}$_2$(μ-dppe)] **12**. The H atoms are omitted for clarity

treated with dppe and then the product was subsequently photolysed in the presence of PMe$_3$. After chromatography a few crystals of a blue-violet compound were obtained and the crystal structure was determined. The molecular structure of **13** is shown in Fig. 5 and selected interatomic distances and angles are given in Table 1. The structure shows that the dppe ligand has replaced one of the terminal carbonyl ligands and is bonded to the metal centre in a monodentate fashion *via* one phosphorus atom. The usual bidentate co-ordination of dppe may be prevented by steric constraints. In addition to dppe co-ordination, the aromatic fluorine atom *meta* to the metal centre has been substituted by hydrogen. This substitution is presumed to arise from the presence of PMe$_3$. The bond lengths and angles in compound **13** compare favourably with those obtained for [Fe{C$_6$F$_4$C(O)Me-2}(η-C$_5$H$_5$)(PPh$_3$)] **11**. For example, the acyl C=O bond length is found to be 1.254(12) Å as compared with 1.256(5) Å in **11**. The acyl O–metal bond in **13** is 2.078(9) Å compared to 1.980(3) Å in **11**. Since only a few crystals of **13** were available further characterisation was not made.

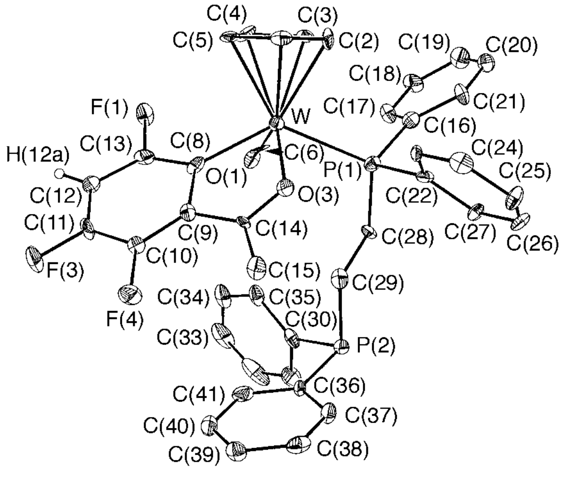


Fig. 5 Molecular structure of [W{C$_6$F$_3$H-5-C(O)Me-2}(η-C$_5$H$_5$)(CO){P(Ph)$_2$CH$_2$CH$_2$PPh$_2$}] **13**

Spectroscopic studies

The labelling of the C$_6$F$_4$ atoms used in the assignments of the NMR spectra are shown in Table 2. For the most part the assignments are straightforward. However it is interesting that the ^{1}H NMR spectra showed that the resonances due to the methyl hydrogens of the acyl group occur either as doublets (**1**, **4**, **2**, **3**, **7**) or multiplets (**5**, **6**, **10**, **11**) between δ 1.85 and 2.56. The four fluorine atoms F$_{c-f}$ of compound **11** were irradiated in turn whilst the ^{1}H NMR spectrum of the acyl methyl group was monitored. It was found that irradiation of the fluorine at δ −136.4 led to the collapse of the methyl multiplet. This selective ^{1}H-{^{19}F} irradiation experiment suggests that the splitting of the methyl signals is the result of through-space coupling. The ^{1}H-{^{19}F} difference nuclear Overhauser effect (NOE) spectrum of **3** also indicates that the coupling arises from a through-space interaction with a ^{19}F nucleus. A ^{19}F–^{19}F COSY experiment on **3** gave the order of δ(^{19}F) −140.0, −165.3, −157.1 and −116.0 for the C_6F_4 fluorines and ^{1}H-{^{19}F} selective-irritation experiments identified the ^{19}F signal at δ −140.0 as due to F_f (J_{FH} = 3.8 Hz). A ^{19}F–^{13}C multiple-bond correlation (^{19}F–^{13}C HMBC) experiment further indicates the F_f atom is the one adjacent to the carbon atom bearing the acetyl group (C_a), and the ^{19}F signal at δ −116.0 is due to the F_c atom. Also, a ^{19}F–^{13}C single-bond correlation (^{19}F–^{13}C HSQC) experiment for **3** also indicates the same assignment of the four C_6F_4 fluorines, as shown in Table 2. Independent support for this assignment comes from a similar NMR study of **7**, which also indicated a close spatial proximity of the F_f fluorine atom as giving rise to the splitting of the ^{1}H NMR signal of the acyl methyl group.

The assignments of the carbon resonances of the C_6F_4 fragment of compound **1** were achieved by ^{19}F–^{13}C single-bond correlation experiments. The signals of atoms C_c–C_f were assigned with the help of the cross-peaks of the related fluorine resonances. The remaining signals of atoms C_a and C_b of the C_6F_4 fragment could be assigned on the basis of their chemical shifts. Thus C_a bound to the acyl group is expected to be less shielded than C_b which is bound to the metal atom.

Comparison of the chemical shifts of the C_dF carbon of compounds **1**–**3** and **6** with those of the C_dH carbons of **7**–**9** show that, as expected, the latter are shifted upfield, by 33, 36 and 37 ppm, respectively.

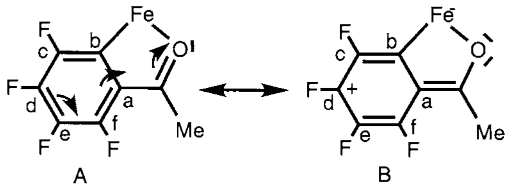
The resonances of the carbon atoms of the acyl groups in compounds **1**–**12** were observed between δ 206 and 211. For **5**, where the acyl group is not co-ordinated to the iron centre, the acyl carbon signal was observed in the same range indicating that the co-ordination of the oxygen atom to the metal has little influence on the shielding of the acyl carbons.

The IR spectra of compounds **1**–**12** reveal strong bands between 1581 and 1547 cm^{-1} characteristic of ν(CO) of acyl groups. The absorption of the non-co-ordinating acyl group in **5** occurs at 1547 cm^{-1} compared to 1581 cm^{-1} for [Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(CO)] **1**.

Structural aspects

In compounds **2**–**4**, **6**, **7** and **11**–**13** the atoms of the five-membered MC_3O ring are essentially coplanar and deviations from planarity do not exceed 0.5 Å; the MC_3O rings lie essentially coplanar with the condensed benzene ring. For example, the angle between the FeC_3O ring and the C_6 rings for **6** and **12** are 2.4 and 1.3°, respectively. The bond lengths of the C=O groups in **4**, **6**, **11** and **12** are 1.247(3), 1.262(5), 1.256(5) and 1.264(7) Å respectively, and these are longer than in the compound **5** [1.207(5) Å]. The latter distance is typical for related non-co-ordinating C=O groups, values for which occur in the range 1.19–1.22 Å.[11]

The carbon–carbon bond distance between the C_6 ring and the carbon of the acyl C=O group [C_a–C (acyl)] in compounds **4**, **6**, **11** and **12** are unusually short with the values 1.446(4), 1.433(6), 1.440(7) and 1.42(1) Å, respectively. The C_a–C (acyl) bond length in **5** is longer at 1.514(6) Å which is characteristic of a single bond[11] between an aromatic ring and a sp^2-hybridised carbon atom. These shorter bond distances can be understood in terms of a contribution of the resonance form **B** shown in Scheme 4. This would develop a positive charge on the C_d carbon which may account for its susceptibility to nucleophilic substitution of the F_d fluorine as observed in the formation of **7**, **8** and **10**. We note that the substitution of fluorine atoms by hydrogen on aryl rings using organic and organometallic nucleophiles is known[12] but, to our knowledge, there is no previous report of the use of tertiary phosphines for this transformation.[13]



Scheme 4 Resonance structures suggested from the interatomic distances, showing the development of a positive charge on C_d in **B**

In conclusion, we have identified surprising reactions, namely the formation of the metallacycle MC_3O group in a high-yield reaction which incorporates a benzenoid C_6F_4 moiety derived from $B(C_6F_5)_3$, and a high-yield and selective substitution of a fluorine of the aromatic C_6F_4 group by a hydrogen atom.

Experimental

All manipulations of air- and moisture-sensitive materials were carried out under dinitrogen using either standard Schlenk techniques, or in an inert-atmosphere dry-box containing dinitrogen. The dinitrogen was purified by passing over 4 Å molecular sieves, and either BASF catalyst or MnO. Solvents were predried by standing over 4 Å molecular sieves and then refluxed and distilled under an atmosphere of dinitrogen from sodium–potassium alloy [pentane, light petroleum (b.p. 40–60 °C), toluene, benzene], and stored over freshly activated molecular sieves (4 Å). Deuteriated solvents for NMR studies were refluxed and condensed from potassium (C_6D_6, [$^{2}H_8$]-toluene) or CaH_2 (CD_2Cl_2), then stored in Young ampoules. The NMR data were recorded using a Bruker AM 200 or 300 (^{1}H, ^{13}C) and Varian Unity Plus 500 spectrometer (^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{31}P, variable-temperature and two-dimensional experiments). Most two-dimensional experiments were performed using z gradients with a version of the pulse sequences. An unambiguous assignment of all ^{19}F and ^{13}C NMR signals was carried out for compounds **3** and **8** (see text). The signals of **2**, **7** and **5** were assigned by analogy. Standards: $SiMe_4$ (^{1}H, ^{13}C); internal solvents as secondary standards, δ(^{1}H)($CHCl_3$) 7.24, (C_6D_5H) 7.15, δ(^{13}C)($CDCl_3$) 77.0, (C_6D_6) 128.0; $CFCl_3$ (^{19}F, fluorobenzene as a secondary standard, δ −116.0); external BF_3·OEt_2 (^{11}B). Chemical shifts (δ) in ppm; a positive sign indicates a downfield shift relative to the standard. Coupling constants are given as absolute values. The IR spectra were recorded as Nujol mulls on NaCl plates or KBr discs, using a Perkin-Elmer 1510 Fourier-transform interferometer. Mass spectra were measured using electron-impact (EI, 70 eV, the calibration of the instrument is unreliable and varies ±1%) and fast atom bombardment techniques. Elemental analyses were performed by the analytical department of this laboratory.

The compounds [Fe(η-C_5H_5)$(CO)_2$Me] and [M(η-C_5H_5)$(CO)_3$Me] (M = Mo or W) were prepared as previously described.[14]

Preparations

$B(C_6F_5)_3$. A modification of a previously published method[1] was used. **CAUTION:** extreme precautions were exercised due to the explosive nature of the intermediate lithium salt Li(C_6F_5) which detonates above *ca.* −20 °C. It is essential to maintain the reaction mixture at −78 °C until the reaction with BBr_3 has been completed. The use of safety screens is advised. The apparatus used is shown in Fig. 6.

A solution of bromopentafluorobenzene (53.5 g, 0.217 mol) in light petroleum (b.p. 40–60 °C) (1 l) was treated with a solution of *n*-butyllithium in hexane (86.8 cm^3, 2.5 mol dm^{-3}, 0.217 mol) at −78 °C. The resulting white suspension was stirred for 1 h and then added to a solution of boron tribromide (72.0 cm^3, 1 mol dm^{-3}, 0.072 mol) in light petroleum (0.3 l) at −78 °C. After additional stirring for 15 h at room temperature the mix-

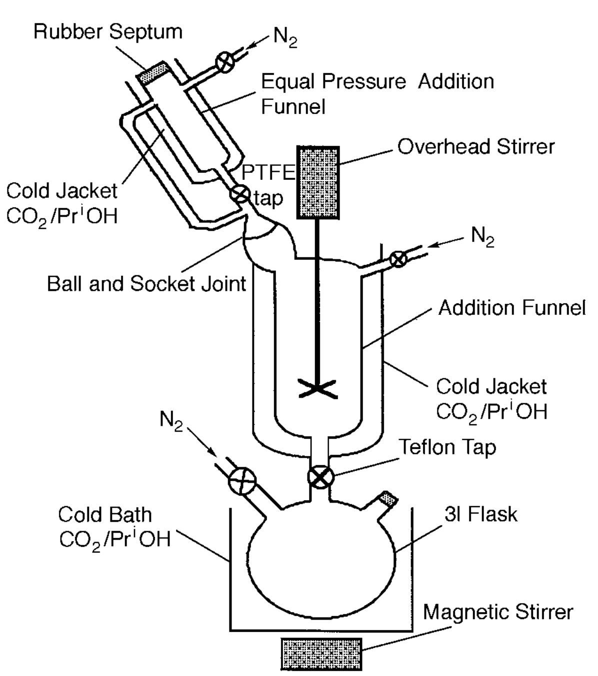


Fig. 6 Apparatus used for the preparation of solvent-free $B(C_6F_5)_3$

ture was filtered through a bed of Celite to give a clear colourless solution. A white microcrystalline solid was obtained after the volume of the filtrate was concentrated to 30 cm^3. The supernatant was decanted off and the resulting white solid dried *in vacuo*. Further purification by vacuum sublimation (140 °C, 10^{-1} Torr) gave white crystals. Yield: 18 g (48%).

[Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(CO)] 1. A red solution of [Fe(η-C_5H_5)$(CO)_2$Me] (4.34 g, 22.6 mmol) in toluene (30 cm^3) was treated with $B(C_6F_5)_3$ (11.57 g, 22.6 mmol) in toluene (120 cm^3) and was stirred for 15 h at room temperature. Completion of the reaction was revealed by IR spectroscopy [replacement of the ν(CO) absorptions of the starting material at 2009 and 1952 cm^{-1} by that of the product at 1957 cm^{-1}]. The resulting orange-green mixture was evaporated to dryness, and purified by alumina column chromatography at −25 °C. Elution with Et_2O–pentane (1:10) gave a green-brown fraction, from which compound **1** was isolated as a microcrystalline solid after removal of the volatiles *in vacuo*. Extraction into pentane and crystallisation at −80 °C yielded green-brown crystals. Yield: 6.03 g (79%).

The volatiles of the reaction mixture were isolated in a cold trap (77 K) and were treated with an excess of 4-methylpyridine to form Lewis acid–base adducts with the boron-containing by-products. The clear solution was warmed to room temperature and the volatiles were evaporated under reduced pressure to give a white residue. The components of the residue were identified as $BF_3{\cdot}NC_6H_7$ and $BF_2(C_6F_5){\cdot}NC_6H_7$ by ^1H and ^{11}B NMR spectroscopy. $BF_3{\cdot}NC_6H_7$: ^1H NMR (C_6D_6) δ 1.46 (s, 3 H, $\mathrm{NC_5H_4C}H_3$), 6.18 (d, 2 H, $^3J = 6.0$, $\mathrm{NC_5}H_{4\alpha}\mathrm{CH_3}$) and 8.14 (d, 2 H, $^3J = 6.0$, $\mathrm{NC_5}H_{4\beta}\mathrm{CH_3}$); ^{11}B NMR (C_6D_6) δ 1.0 (q, 1 B, $J = 11.0$ Hz, BF_3). $BF_2(C_6F_5){\cdot}NC_6H_7$: ^1H NMR (C_6D_6) δ 1.50 (s, 3 H, $\mathrm{NC_5H_4C}H_3$), 6.28 (d, 2 H, $^3J = 6.3$, $\mathrm{NC_5}H_{4\alpha}\mathrm{CH_3}$) and 8.22 (d, 2 H, $^3J = 6.3$, $\mathrm{NC_5}H_{4\beta}\mathrm{CH_3}$); ^{11}B NMR (C_6D_6) δ 3.9 (t, 1 B, $J = 47.9$ Hz, $BF_2C_6F_5$).

[Mo{$C_6F_4C(O)Me$-2}(η-C_5H_5)$(CO)_2$] 2. A solution of $B(C_6F_5)_3$ (1.57 g, 3.08 mmol) in toluene (25 cm^3) was added to a stirred solution of [Mo(η-C_5H_5)$(CO)_3$Me] (0.8 g, 3.08 mmol) in toluene (30 cm^3). The solution rapidly changed from golden yellow to dark red. It was left to stir for 42 h. The reaction mixture was blood-red and the IR spectrum indicated that all the starting material had reacted. The solvent was removed under reduced pressure to give a dark red solid which was then placed on alumina (*ca.* 3 g). The coated alumina was added to a low-temperature (−25 °C) chromatography column which had been filled with light petroleum and alumina (25 cm). The product was washed with light petroleum (3 × 100 cm^3) and slow elution with light petroleum–Et_2O (10:1) facilitated collection of a red band. The solvent was removed from the eluate under reduced pressure and the solid obtained recrystallised from warm heptane to give red crystals of compound **2**. Yield: 25%.

[W{$C_6F_4C(O)Me$-2}(η-C_5H_5)$(CO)_2$] 3. A solution of $B(C_6F_5)_3$ (1.47 g, 2.87 mmol) in toluene (25 cm^3) was added to a stirred solution of [W(η-C_5H_5)$(CO)_3$Me] (1 g, 2.87 mmol) in toluene (30 cm^3). The solution immediately turned from yellow-orange to dark red. It was left to stir and the reaction progress was monitored by solution IR spectroscopy. After stirring for 48 h the solution was dark purple and the IR spectrum indicated that the starting material had reacted. The solvent was removed under reduced pressure to give a dark purple solid which was then placed on alumina. The coated alumina was added to a low-temperature (−25 °C) chromatography column which had previously been filled with pentane and 25 cm of alumina. The product was washed with pentane (3 × 100 cm^3) and elution with pentane–Et_2O (1:1) developed a deep purple band which was collected. The solvent was removed under reduced pressure and the residue recrystallised from hot heptane to give purple crystals (m.p. 175–176 °C; sublimation point 95 °C, 0.1 Torr) of compound **3**. Yield: 75%.

[Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(Bu^tNC)] 4. An orange-brown solution of [Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(CO)] **1** (230 mg, 0.68 mmol) in pentane (100 cm^3) was treated with *tert*-butyl isocyanide (56.5 mg, 0.68 mmol) and stirred for 18 h at room temperature. Completion of the reaction was monitored by IR spectroscopy [replacement of the ν(CO) absorption of the starting material at 1957 cm^{-1} by the ν(C≡NBu^t) absorption at 2038 cm^{-1}]. The resulting purple mixture was evaporated to dryness and purified by column chromatography on alumina at −25 °C. Compound **4** was eluted with Et_2O–pentane (1:4) and the volatiles of the purple eluate were removed *in vacuo*. Extraction into pentane and crystallisation at −80 °C yielded dark purple crystals. Yield: 120 mg (45%).

[Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(CO)(PMe_3)] 5. An orange-brown solution of compound **1** (410 mg, 1.21 mmol) in heptane (50 cm^3) was treated with trimethylphosphine (96 mg, 1.21 mmol) and stirred for 15 h at room temperature. The resulting purple solution was evaporated to dryness and vacuum sublimation (70 °C, 10^{-1} Torr) gave a microcrystalline solid. Extraction into heptane and crystallisation at −80 °C yielded purple crystals. Yield: 120 mg (45%). Compound **5** melts without decomposition at 100 °C in a sealed capillary and sublimes at 85 °C under vacuum (10^{-1} Torr). It is soluble in common organic solvents.

[Fe{$C_6F_4C(O)Me$-2}(η-C_5H_5)(PMe_3)] 6. *Method A*. A purple solution of compound **5** (110 mg, 0.26 mmol) in heptane (30 cm^3) was refluxed for 15 h. The elimination of CO from the compound was revealed by IR spectroscopy, as in the synthesis of compound **4**. The solvent was evaporated under reduced pressure, and extraction of the residue into heptane and crystallisation at −80 °C yielded purple crystals of **6**. Yield: 75 mg (74%).

Method B. A solution of compound **1** (550 mg, 1.62 mmol) and trimethylphosphine (1 cm^3; 735 mg, 9.6 mmol) in heptane (50 cm^3) was refluxed for 15 h until the reaction was complete (IR monitoring). The volatile materials were removed under reduced pressure and the purple residue was purified by column chromatography on alumina at −25 °C. Elution with Et_2O–pentane (1:20) gave a purple fraction, from which the compound **6** was isolated as a microcrystalline solid after removal of the solvent *in vacuo*. Yield: 200 mg (32%).

[Mo{C_6F_3H-5-C(O)Me-2}(η-C_5H_5)$(CO)_2$] 7. A blood-red solution of [Mo{C_6F_4C(O)Me-2}(η-C_5H_5)$(CO)_2$] (0.06 g, 1.47 mmol) in toluene (40 cm^3) was treated with PMe_3 (1.22 cm^3, 11.79 mmol) and the mixture was left to stir at r.t. for 5 h. It became purple and the solution IR spectrum showed little change in the CO region. The mixture was refluxed for 3 h and then left to stir at r.t. for 16 h. The solvent was removed under reduced pressure and the dark purple residue chromatographed on alumina at −25 °C. Elution with light petroleum gave a purple band. Further elution with light petroleum–Et_2O (10:1) developed this band further and also initiated a slow-moving blue band towards the top of the column. The purple band was collected, the solvent was removed under reduced pressure and the residue recrystallised from hot heptane to yield dark red crystals of compound **7**. Yield: 65%.

[W{C_6F_3H-5-C(O)Me-2}(η-C_5H_5)$(CO)_2$] 8 and [W{C_6F_3H-5-C(O)Me-2}(η-C_5H_5)(CO)(PMe_3)] 9. A claret-purple solution of [W{C_6F_4C(O)Me-2}(η-C_5H_5)$(CO)_2$] **3** (0.4 g, 0.81 mmol) in toluene (60 cm^3) was treated with PMe_3 (1.03 cm^3, 9.95 mmol). The mixture was photolysed under reflux using an ultraviolet lamp (500 W) for 7.5 h. The solution was then allowed to stir for 16.5 h, giving a violet-purple solution with a black deposit. The solvent was removed under reduced pressure and the dark violet-black residue chromatographed at −25 °C. Elution with light petroleum (3 × 100 cm^3) and then with light petroleum–Et_2O (2:1) developed a claret-purple band. Increasing the solvent ratio to 1:1 also developed a second blue band. The two bands were neatly separated by very slow elution and collected separately. The solvent in each case was removed under reduced pressure to yield green and blue-violet solids. The green solid was recrystallised from hot heptane to give green crystals of compound **8**. The blue-violet solid was also recrystallised from hot heptane to give a blue-violet microcrystalline powder of **9**.

[Fe{C_6F_3H-5-C(O)Me-2}(η-C_5H_5)(PMe_3)] 10. An orange-brown solution of [Fe{C_6F_4C(O)Me-2}(η-C_5H_5)(CO)] **1** (490 mg, 1.44 mmol) and an excess of trimethylphosphine (≈3 cm^3) in toluene (50 cm^3) were refluxed and photolysed using a ultraviolet lamp (500 W) for 3 d. The volatile materials of the blue-purple reaction mixture were removed under reduced pressure and the residue was purified by column chromatography on alumina at −25 °C. Elution with Et_2O–pentane (1:1) gave a purple fraction and after removal of the solvent *in vacuo* the compound [Fe{C_6F_3H-5-C(O)Me-2}(η-C_5H_5)(PMe_3)] **10** was isolated as a microcrystalline solid. The residue was extracted into boiling heptane and cooling of the solution to −80 °C gave black-purple crystals. Yield: 140 mg (26%). Compound **10** can also be prepared in the same manner starting from **6**, in 74% yield.

[Fe{C_6F_4C(O)Me-2}(η-C_5H_5)(PPh_3)] 11. Compound **1** (700 mg, 2.06 mmol) and triphenylphosphine (540 mg, 2.06 mmol) were refluxed in toluene (50 cm^3) for 18 h until the reaction was complete. It was monitored by IR spectroscopy [disappearance of the ν(CO) absorption of the starting material at 1957 cm^{-1}]. The volatiles of the resulting purple solution were removed under reduced pressure and the residue was purified by column chromatography on alumina at −25 °C. Elution with Et_2O–pentane (1:2) gave a purple fraction which was evaporated to dryness *in vacuo* and crystallisation from a solution of pentane at −80 °C gave dark purple crystals. Yield: 500 mg (42%).

[{Fe[C_6F_4C(O)Me-2](η-C_5H_5)}$_2$(μ-dppe)] 12. An orange-brown solution of compound **1** (295 mg, 0.87 mmol) and 1,2-bis(diphenylphosphino)ethane (173 mg, 0.43 mmol) in toluene (50 cm^3) was photolysed using an ultraviolet lamp (500 W) for 15 h at 60 °C until the reaction was complete (IR monitoring). An important feature is that exactly half an equivalent of dppe must be used to avoid bidentate co-ordination of the phosphine ligand. The solvent was removed under reduced pressure and the residue was extracted into pentane–Et_2O (1:1) and filtered through a bed of alumina. The volatiles of the filtrate were evaporated under reduced pressure and the residue was extracted into boiling heptane. Crystallisation at −80 °C yielded purple crystals of compound **12**. Yield 150 mg (34%).

[W{C_6F_3H-5-C(O)Me-2}(η-C_5H_5)(CO){P(Ph)$_2CH_2CH_2$-PPh_2}] 13. The compound [W{C_6F_4C(O)Me-2}(η-C_5H_5)$(CO)_2$] (1.14 g, 2.30 mmol) was dissolved in toluene (50 cm^3) and $Ph_2PCH_2CH_2PPh_2$ (dppe) (0.916 g, 2.30 mmol) was added. The mixture was refluxed for 5.5 h after which time the solution IR spectrum showed no change in the carbonyl region. The mixture was left to stir at room temperature for 7 d. No reaction was obvious so the solvent was removed under reduced pressure and the solid obtained was placed on alumina (*ca.* 5 g). The coated alumina was added to a low-temperature (−25 °C) chromatography column filled with light petroleum and 20 cm of alumina. The column was washed with light petroleum (3 × 100 cm^3) and elution with light petroleum–Et_2O (1:1) gave a purple band. The solvent was removed under reduced pressure and recrystallisation from boiling heptane gave claret-purple crystals.

Trimethylphosphine (1.03 cm^3, 9.95 mmol) was added to a stirred solution of the above crystals in toluene (40 cm^3) and the mixture photolysed for 7 h using a medium-pressure ultraviolet lamp (500 W). After this time the solution had turned to dark blue-violet and the carbonyl region of the IR spectrum showed the formation of a new product. The solvent was removed under reduced pressure and the solid obtained was suspended on alumina. The coated alumina was added to a low-temperature (−25 °C) chromatography column which had been filled with light petroleum and 20 cm of alumina. The product was washed with light petroleum (2 × 100 cm^3) and eluted with light petroleum–Et_2O (10:1). This developed a blue-violet band which was collected by gradually increasing the solvent ratio to 1:1. The solvent was removed under reduced pressure and recrystallisation from boiling heptane gave blue-violet crystals of the compound [W{C_6F_3H-5-C(O)Me-2}(η-C_5H_5)(CO)-{P(Ph)$_2CH_2CH_2PPh_2$}] **13**. Only a few crystals were obtained (yield *ca.* 4%) and their characterisation was by X-ray crystallography only.

Crystallography

X-Ray-quality crystals were obtained by slow cooling of hot saturated solutions of the compounds in pentane (**4**, **6**, **11**) and heptane (**2**, **3**, **5**, **7**, **12**, **13**) to −80 °C. They were sealed in a Lindemann capillary (0.5–0.7 mm) under dinitrogen. For **2**, **5**–**7** and **12** the data collection was carried out on an Enraf-Nonius CAD4 diffractometer. The unit-cell parameters were calculated from the setting angles of 25 strong high-angle carefully centred reflections. Three reflections were chosen as intensity standards and measured every 3600 s of X-ray exposure time and three orientation controls were measured every 147–200 reflections. The data were measured using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) with an ω–2θ scan mode. The ratio of the scanning rates was ω:θ = 1:2. Data were corrected for Lorentz-polarisation effects. For **3**, **4** and **13** the data collection was carried out on a Delft Instruments FAST TV area-detector diffractometer, equipped with a rotating-anode FR 591 generator (50 kV, 10 mA); further details are described in ref. 15.

For compound **6** a correction for crystal decay (*ca.* 13%) was applied during processing the data set. For **6** and **12** data were also corrected using an empirical absorption correction.[16] In **12**

Table 4 Crystallographic details for compounds **2**, **3**, **7** and **13**

	2	**3**	**7**	**13**
Formula	$C_{15}H_8F_4MoO_3$	$C_{15}H_8F_4O_3W$	$C_{15}H_9F_3MoO_3$	$C_{40}H_{33}F_3O_2P_2W$
Colour	Red	Red	Purple	Blue-violet
Formula weight	408.16	496.06	390.16	848.49
Crystal size/mm	0.33 × 0.36 × 0.24	0.28 × 0.14 × 0.14	0.5 × 0.25 × 0.15	0.14 × 0.14 × 0.07
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	8.3420(4)	8.206(8)	8.285(2)	11.577(2)
b/Å	8.9687(7)	8.905(4)	8.933(1)	19.525(4)
c/Å	11.1874(9)	11.104(9)	11.176(2)	15.389(3)
α/°	69.126(6)	68.44(8)	68.79(1)	90.00
β/°	75.691(5)	75.48(8)	74.55(2)	97.20(3)
γ/°	63.515(5)	63.83(4)	63.78(2)	90.00
U/Å^3	698.47	673.5(9)	683.3(2)	3451.1(1)
Z	2	2	2	4
D_c/g cm^{-3}	1.94	2.446	1.896	1.633
F(000)	400	464	384	1680
μ/cm^{-1}	9.47	8.636	10.04	3.491
T/K	293(2)	120	293(2)	150
Lattice segment	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, +l$	$\pm h, \pm k, \pm l$
θ_{max}/° for data	25.0	29.9	29	25.0
No. reflections:				
total	2836	1913 (after red.)	2144 (after red.)	8529
unique	2437	1913	2144	5015 (R_{int} = 0.0784)
in refinement	2072 [$I > 3\sigma(I)$]	1810 [$F > 4\sigma(F)$]	1882 [$F > 4\sigma(F)$]	2404 [$F > 4\sigma(F)$]
R_{merge}	0.013	0.0	0.0	0.078
Parameters	240	198	200	434
Data: parameter ratio	9 : 1 [$F > 3\sigma(F)$]	9.7 : 1; 9.1 : 1 [$F > 4\sigma(F)$]	10.7 : 1; 9.4 : 1 [$F > 4\sigma(F)$]	11.6 : 19; 5.5 : 1 [$F > 4\sigma(F)$]
Minimum, maximum transmission	0.88, 1.14	0.616, 1,0	0.575, 1.0	0.72, 1.0
R[a]/R'[b]	0.0272/0.0325	—	—	—
$R1$ [$F > 4\sigma(F)$]	—	0.0467	0.0315	0.0494
$wR2$ (all data)	—	0.1325	0.0706	0.1028
Goodness of fit	—	1.098	1.072	0.645
Maximum, minimum peaks in difference maps/e Å^{-3}	0.70, −0.40	1.794, −1.355	0.832, −0.669	1.020, −0.835

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o$. [b] $R' = [w\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 5 Crystal data and experimental details for compounds **4**–**6**, **11** and **12**

	4	**5**	**6**	**11**	**12**
Formula	$C_{18}H_{17}F_4FeNO$	$C_{17}H_{17}F_4FeO_2P$	$C_{16}H_{17}F_4FeOP$	$C_{31}H_{23}F_4FeOP$	$C_{52}H_{40}F_8Fe_2O_2P_2$
M	395.18	416.14	388.12	574.34	1022.52
Crystal size/mm	0.19 × 0.22 × 0.40	0.07 × 0.22 × 0.18	0.31 × 0.40 × 0.74	0.13 × 0.18 × 0.25	0.34 × 0.42 × 0.43
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	8.4663(7)	8.586(2)	8.577(2)	9.391(3)	10.667(4)
b/Å	10.5039(7)	13.215(2)	9.222(3)	10.195(6)	22.408(3)
c/Å	10.9915(8)	15.712(3)	20.916(7)	13.26(1)	19.185(5)
α/°	98.927(6)			95.23(4)	
β/°	106.067(6)	104.70(1)	92.53(2)	103.13(4)	93.92(2)
γ/°	104.746(6)			93.49(3)	
U/Å^3	881.2	1724.39	1652.9(8)	1226.9	4575(2)
Z	2	4	4	2	4
D_c/g cm^{-3}	1.49	1.60	1.56	1.56	1.48
F(000)	404	848	792	588	2088
μ/cm^{-1}	8.97	10.10	10.45	7.29	7.74
T/K	293	120	293	120	293
Total data collected	4372	6712	3826	4014	7970
Total unique data	3838	2597	3585	2629	7525
Total observed data	2322 [$I > 3\sigma(I)$]	1795 [$I > 2\sigma(I)$]	2053 [$I > 3\sigma(I)$]	2018 [$I > 2\sigma(I)$]	4499 [$I > 3\sigma(I)$]
R Merge	0.020	0.061	0.061	0.068	0.030
No. parameters	226	226	208	253	595
Observations/ parameters	10.3	7.9	9.9	8.0	7.6
Chebychev weighting scheme parameters	6.64, −3.52, 5.57	15.1, −9.4, 11.6	21.90, −5.94, 18.70	6.06, 0.60, 3.51	10.90, −17.70, 8.19, −7.70
Minimum, maximum residual peak/e Å^{-3}	−0.23, 0.22	−0.36, 0.83	−0.39, 0.39	−0.41, 0.67	−0.67, 0.54
R	0.033	0.043	0.043	0.047	0.055
R'[b]	0.031	0.048	0.051	0.049	0.051

all hydrogens were located in the difference maps whilst for **6** only H atoms of the Me were located (positions of the H atoms of the C_5 ring were calculated). All hydrogens of **6** and **12** were included in the final refinement with fixed positional and thermal parameters. Neutral atom scattering factors were taken from the usual sources.[17]

For compounds **2**, **3**, **7** and **13** the non-hydrogen atoms were located by Patterson (**2**, **13**) and direct methods (**3**, **7**) and Fourier-difference syntheses. A DIFABS[18] absorption correction was carried out on all three data sets. The hydrogen atoms were placed in calculated positions in the final cycles of refinement. The structures were refined using full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. All crystallographic calculations were carried out using the CRYSTALS[19] program package on a MicroVax 3800 computer (**2**, refinement against F) or with the SHELXL 93[20] software on a personal computer (**3** and **7**, refinement against F^2). The crystallographic data are given in Tables 4 and 5. For **2**, a Chebychev weighting scheme was applied (parameters: 8.89, −5.46, 6.92);[21] for **3** ($n = 0.0779$) and **7** ($n = 0.0403$) the weighting scheme was $w^{-1} = \sigma^2 F_o^2 + (nP)^2 + 0.0P$, where $P = (F_o^2 + 2F_c^2)/3$. Only the relevant R values are given in Table 4. Atomic scattering factors were taken from the usual sources.[17]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/518.

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