

An Unexpected Reaction Between $B(C_6F_5)_3$ and $[Fe(\eta^5-C_5H_5)(CO)_2Me]$ Gives $\{[Fe-\sigma-C_6F_4(2-C(O)Me)](\eta^5-C_5H_5)(CO)\}$

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The reaction between $B(C_6F_5)_3$ and $[Fe(\eta^5-C_5H_5)(CO)_2Me]$ gives the unexpected product $\{[Fe-\sigma-C_6F_4(2-C(O)Me)](\eta^5-C_5H_5)(CO)\}$, which reacts with the donor molecules L, where L = PMe_3 , PPh_3 , or Bu^tNC , giving $\{[Fe-\sigma-C_6F_4(2-C(O)Me)](\eta^5-C_5H_5)(L)\}$.

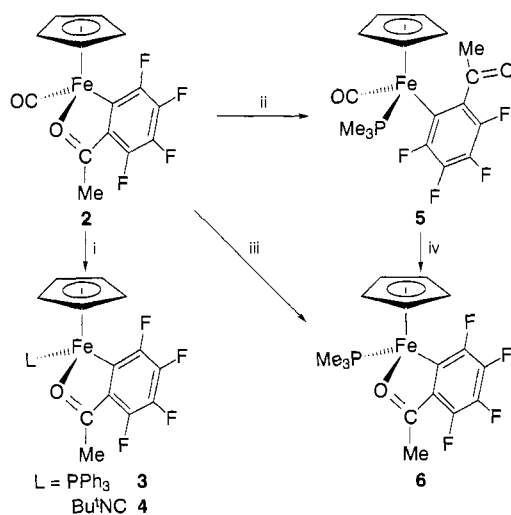
The Lewis acid $B(C_6F_5)_3$ has been shown to react with certain metal–methyl moieties to form the relatively unusual $M-\mu-Me-B(C_6F_5)_3$ grouping.^{1,2} In other reactions between metal–methyl compounds and $B(C_6F_5)_3$ the transfer of a C_6F_5 group from the boron to the metal giving a $M-C_6F_5$ fragment has been described.³ We have continued to study the reaction between the compound $B(C_6F_5)_3$ and transition metal–alkyl derivatives and found further unexpected chemistry, as described below.

Treatment of the compound $[Fe(\eta^5-C_5H_5)(CO)_2Me]$ **1** with $B(C_6F_5)_3$ in toluene at room temperature gave green crystals of the compound $\{[Fe-\sigma-C_6F_4(2-C(O)Me)](\eta^5-C_5H_5)(CO)\}$ **2** in 79% yield. The compound **2** reacts smoothly with PPh_3 or Bu^tNC resulting in the displacement of carbon monoxide and formation of the compounds $\{[Fe-\sigma-C_6F_4(2-C(O)Me)](\eta^5-C_5H_5)(PPh_3)\}$ **3** and $\{[Fe-\sigma-C_6F_4(2-C(O)Me)](\eta^5-C_5H_5)(Bu^tNC)\}$ **4**, respectively.

In contrast, treatment of **2** with PMe_3 at room temperature gives the adduct $\{[Fe-\sigma-C_6F_4(2-C(O)Me)](\eta^5-C_5H_5)(CO)(PMe_3)\}$ **5**. Refluxing a heptane solution of **5** in the presence of PMe_3 causes loss of carbon monoxide and the compound $\{[Fe-\sigma-C_6F_4(2-C(O)Me)](\eta^5-C_5H_5)(PMe_3)\}$ **6** is formed. The reactions and proposed structures of **2–6** are shown in the Scheme 1.

The crystal structures of the three compounds **3–5** have been determined. The molecular structures of **4** and **5** are shown in Figs. 1 and 2, respectively.

The structure proposed for **2** is based on the analytical and spectroscopic data. In particular, the NMR data is both consistent with the proposed structure and the bands assigned to the $[Fe-\sigma-C_6F_4(2-C(O)Me)]$ grouping are closely similar to those assigned to the identical grouping in the crystallographically characterised compounds **3–5**.



Scheme 1 Reagents and conditions: ia, PPh_3 , toluene, reflux; ib, Bu^tNC , pentane, room temp.; ii, PMe_3 , heptane, room temp.; iii, PMe_3 , heptane, reflux; iv, heptane, reflux

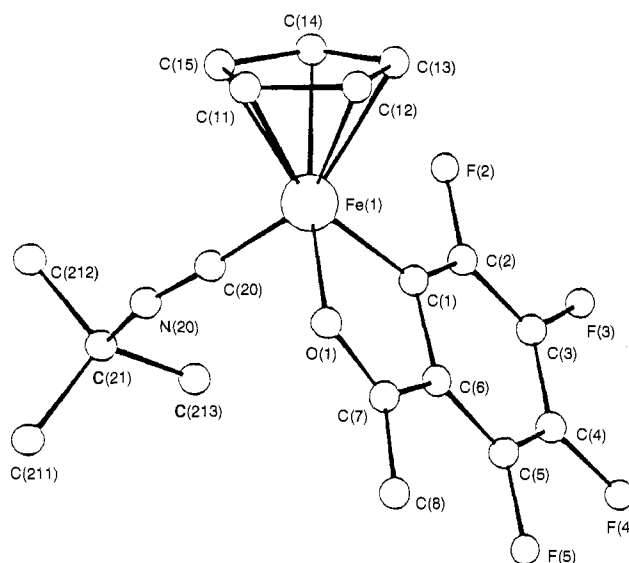


Fig. 1 Molecular structure of **4**. Selected bond distances (Å) and angles (°): Fe(1)–C(1) 1.938(2), Fe(1)–O(1) 1.964(2), Fe(1)–C(20) 1.811(2), Fe(1)–C_{pcent} 1.712, C(20)–N(20) 1.167(3), C(1)–C(6) 1.424(3), C(6)–C(7) 1.446(4), O(1)–C(7) 1.247(3), C(7)–C(8) 1.500(3); O(1)–Fe(1)–C(1) 81.05(8), O(1)–Fe(1)–C(20) 95.22(8), Fe(1)–O(1)–C(7) 117.6(2), Fe(1)–C(1)–C(6) 112.9(2), Fe(1)–C(20)–N(20) 177.4(2), C(1)–C(6)–C(7) 112.4(2), O(1)–C(7)–C(6) 115.6(2), O(1)–C(7)–C(8) 118.8(3), C_{pcent}–Fe(1)–O(1) 127.4, C_{pcent}–Fe(1)–C(1) 129.2, C_{pcent}–Fe(1)–C(20) 123.6 [C_{pcent} refers to the computed centroid for the C(11)–C(15) ring].

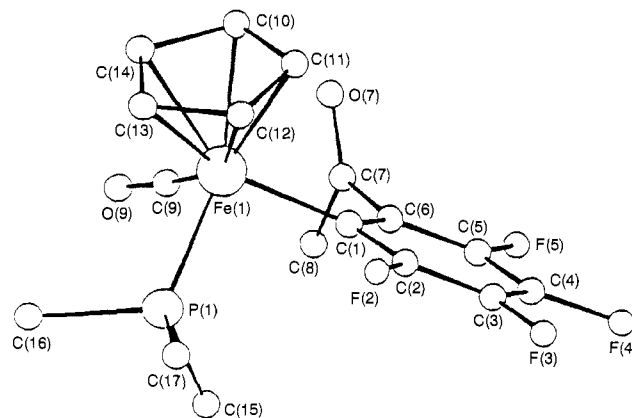
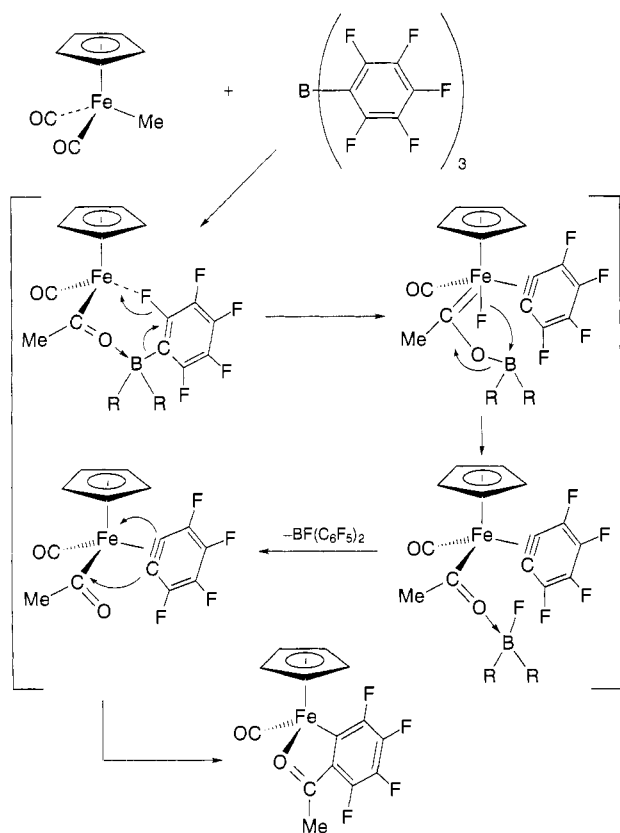


Fig. 2 Molecular structure of **5**. Selected bond distances (Å) and angles (°): Fe(1)–C(1) 2.017(4), Fe(1)–C(9) 1.744(4), Fe(1)–P(1) 2.195(1), Fe(1)–C_{pcent} 1.722, C(1)–C(6) 1.414(6), C(6)–C(7) 1.514(6), O(7)–C(7) 1.207(5), C(7)–C(8) 1.501(6); P(1)–Fe(1)–C(1) 93.0(1), P(1)–Fe(1)–C(9) 86.4(1), C(1)–Fe(1)–C(9) 99.4(2), Fe(1)–C(1)–C(6) 124.9(3), C(1)–C(6)–C(7) 122.5(3), C(6)–C(7)–O(7) 121.5(4), C_{pcent}–Fe(1)–P(1) 125.8, C_{pcent}–Fe(1)–C(1) 120.7, C_{pcent}–Fe(1)–C(9) 123.0 [C_{pcent} refers to the computed centroid for the C(10)–C(14) ring].



Scheme 2 Proposed mechanism for the formation of 2

The formation of the compound **2** must involve the insertion of a C_6F_4 fragment from $B(C_6F_5)_3$ into the metal acetyl bond.

The reaction between **1** and $B(C_6F_5)_3$ has been monitored by ^{11}B NMR spectroscopy. This shows the formation of $BF(C_6F_5)_2$, $BF_2(C_6F_5)$ and BF_3 during the reaction. An examination of boron-containing products from the reaction between **1** and $B(C_6F_5)_3$ shows that there is a substantial yield of $BF_2(C_6F_5)$ and BF_3 (characterised as the γ -picoline adduct⁴). Thus, it appears that the transfer of C_6F_5 groups occurs more rapidly from $BF_n(C_6F_5)_{3-n}$ when n increases from 0 to 2.

In conclusion, the formation of **2** from **1** is unexpected and the mechanism is not self-evident. On the basis of the preliminary observations described above we propose a mechanism for the formation of **2** along the lines shown in the Scheme 2.

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Footnote

† Satisfactory analyses have been obtained for the new compounds **2–6**. The NMR, IR and crystal structure data have been provided for the referees.

Selected data for 2: 1H in $[^2H_6]$ -benzene: δ 1.850 (s, 3 H, CO-CH₃), 4.329 (s, 5 H, C₅H₅). ^{13}C : δ 27.65 (q, 1 C, CO-CH₃), 81.07 (s, 5 C, C₅H₅), 129.71 (dm, 1 C, C₆), 135.46 (dddd, 1 C, C₇), 142.29 (dddd, 1 C, C₈), 149.30 (dm, 1 C, C₄), 154.74 (dm, 1 C, C₂), 174.91 (ddm, 1 C, C₃), 211.82 (m, 1 C, CO-CH₃), 216.52 (s, 1 C, CO). ^{19}F : δ -163.044 (m, 1 F, F₁), -149.077 (m, 1 F, F₂), -134.123 (m, 1 F, F₃), -117.809 (m, 1 F, F₄). IR (Nujol): 1968vs, 1630m, 1581m, 1544m cm^{-1} . **Selected data for 4:** 1H in $[^2H_6]$ -benzene: δ 0.886 [s, 9 H, CNC(CH₃)₃], 2.101 (s, 3 H, CO-CH₃), 4.504 (s, 5 H, C₅H₅). ^{13}C { 1H }: δ 27.58 (s, 1 C, CO-CH₃), 30.91 [s, 3 C, CNC(CH₃)₃], 57.12 [s, 1 C, CNC(CH₃)₃], 78.26 (s, 5 C, C₅H₅), 134.17 (m, 1 C, C₇), 141.82 (m, 1 C, C₆), 150.77 (m, 1 C, C₄), 154.15 (m, 1 C, C₂), 177.33 [s, 1 C, CNC(CH₃)₃], 188.41 (m, 1 C, C_{3a}), 208.78 (m, 1 C, CO-CH₃). ^{19}F : δ -165.651 (t, 1 F, F₁), -153.163 (m, 1 F, F₂), -136.139 (m, 1 F, F₃), -117.734 (m, 1 F, F₄). IR (Nujol): 2044s, 1629m, 1560w, 1530m cm^{-1} .

Crystal data for 4: Dark-purple crystal, C₁₈H₁₇F₄FeNO, $M = 395.2$, triclinic, $a = 8.4663(7)$, $b = 10.5039(7)$, $c = 10.9915(8)$ Å, $U = 881.2$ Å³, space group $P\bar{1}$, $Z = 2$, Mo-K α ($\lambda = 0.71069$ Å), $D_c = 1.49$ g cm^{-3} , $F(000) = 404$, $T = 293$ K. Of the 4372 reflections measured, 3838 were unique with $I > 3\sigma(I)$. Data were corrected for Lorentz, polarisation effects and absorption (Diffabs.) The structure was solved by the Patterson method, to yield final $R = 3.25$, $R_w = 3.10\%$ for 226 least-squares parameters.

Selected data for 5: 1H in $[^2H_6]$ -benzene: δ 0.562 [d, 9 H, $^2J_{(PH)}$ 8.6 Hz, P(CH₃)₃], 2.202 (s, 3 H, CO-CH₃), 4.238 (s, 5 H, C₅H₅). ^{13}C { 1H }: δ 16.69 [d, 3 C, $^1J_{(PC)}$ 24.7 Hz, P(CH₃)₃], 27.04 (s, 1 C, CO-CH₃), 76.09 (s, 5 C, C₅H₅), 132.98 (dm, 1 C, C₇), 140.63 (dm, 1 C, C₆), 149.48 (dm, 1 C, C₄), 156.21 (dm, 1 C, C₂), 196.34 (m, 1 C, C₃), 206.23 (s, 1 C, CO-CH₃), 213.82 (s, 1 C, CO). ^{19}F : δ -166.422 (t, 1 F, F₁), -154.856 (m, 1 F, F₂), -136.700 (t, 1 F, F₃), -116.601 (m, 1 F, F₄). ^{31}P : δ 32.199 (s, 1 P). IR (Nujol): 2043w, 1998w, 1968vs, 1627s, 1547m, 1504s.

Crystal data for 5: Dark-purple crystal, C₁₇H₁₇F₄FeO₂P, $M = 416.14$, monoclinic, $a = 8.586(2)$, $b = 13.215(2)$, $c = 15.712(3)$ Å, $U = 1724.39$ Å³, space group $P2_1/c$, $Z = 4$, Mo-K α ($\lambda = 0.71069$ Å), $D_c = 1.60$ g cm^{-3} , $F(000) = 848$, $T = 293$ K. Of the 6712 reflections measured, 2597 were unique with $I > 2\sigma(I)$. Data were corrected for Lorentz, polarisation effects and absorption (Diffabs.) The structure was solved by the Patterson method, to yield final $R = 4.27$, $R_w = 4.84\%$ for 226 least-squares parameters.

For both structures, 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.

Structure **3** has also been determined. Crystal data have been submitted and supplementary data have been deposited at the Cambridge Crystallographic Data Centre. Because of the similarity of the structure with that of **4**, details are not provided here.

References

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