

Two-fragment Addition of Borohydride to Iron Complexes: Synthesis of Dithioformate Iron Complexes with B–H–Fe Bond Interaction. X-Ray Structural Characterization of $\text{Fe}[\eta^3\text{-HC(SMe)S} \rightarrow \text{B(H)H}_2](\text{CO})(\text{PMe}_3)_2$

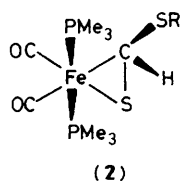
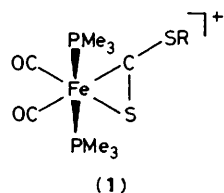
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Reaction of $\text{Fe(X)(}\eta^2\text{-CS}_2\text{R)(CO)(PR}_3)_2$ ($\text{X} = \text{Cl, I}$) complexes with NaBH_4 leads to both hydride and BH_3 additions with the formation of dithioformate–iron(0) $\text{Fe}[\eta^3\text{-HC(SR)S} \rightarrow \text{BH}_3](\text{CO})(\text{PR}_3)_2$ complexes (**4**) containing an agostic B–H–Fe interaction; the addition of pyridine to (**4**) liberates a 16 electron-iron(0) moiety by trapping of the BH_3 unit.

Boron–hydrogen–metal interactions have been shown recently to be involved in the stabilization of transition metal complexes. Among the most representative examples are the ferraborane clusters^{1,2} as well as tungsten–tungsten³ and molybdenum–phosphorus⁴ systems, containing one bridging boron–hydrogen bond and derived from the addition of borane to a $\text{W}\equiv\text{C}$ or a $\text{Mo}=\text{P}$ multiple bond respectively. We now report the synthesis and characterization of a novel class of compounds, containing a B–H–Fe interaction and resulting from the addition of borohydride to dithioester iron derivatives.

The addition of NaBH_4 to η^2 -dithioester–metal complexes $\text{M}(\eta^2\text{-CS}_2\text{R})$ has been shown to give rise to a variety of reactions. This borohydride reacts with the $\text{Os}(\eta^2\text{-CS}_2\text{R})^+$ cation *via* hydride addition to the metal,⁵ whereas with iron complexes (**1**) the reaction pathway is phosphine dependent, giving compounds derived from electron transfer⁶ when L is PPh_3 , or dithioformate iron derivative (**2**) when L is PMe_3 . The reaction of NaBH_4 with neutral $\text{Fe(X)(}\eta^2\text{-CS}_2\text{R)}$ complexes (**3**) developed in a quite unexpected way. The reaction of an excess of NaBH_4 (5 mmol) with the red complex (**3a**)⁸ (2 mmol) in tetrahydrofuran (THF) led to the formation of a yellow crystalline solid (**4a**) which was isolated from hexane in



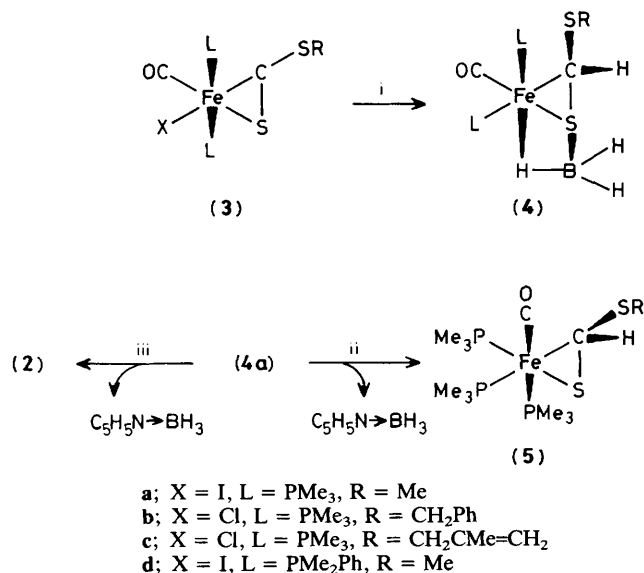
50% yield.† The spectroscopic data for (**4a**) were consistent with the presence of an $(\eta^2\text{-SCHSMe})$ ligand, arising from the addition of one hydride to the $(\eta^2\text{-CS}_2\text{Me})$ carbon of (**3a**), B–H bonds, and two non-equivalent PMe_3 groups [(**4a**): i.r. (Nujol) $\nu(\text{B-H})$ 2480, 2400, $\nu(\text{CO})$ 1920, $\nu(\text{CS})$ 1160 cm^{-1} ; ^1H n.m.r. (C_6D_6 , 300 MHz) δ 2.21 (s, SMe), 2.04 (d, CHSMe, $^3J_{\text{PH}}$ 5.6 Hz), 1.15 (d) and 0.99 (d, PMe_3 , $^2J_{\text{PH}}$ 8.5 Hz), -13.7

† All compounds reported have microanalytical, mass spectral, and spectroscopic data in accord with their assigned structures. Selected spectroscopic data for: (**4b**): I.r. (Nujol) $\nu(\text{B-H})$ 2460, 2410(m), $\nu(\text{CO})$ 1910(s), $\nu(\text{CS})$ 1160(m) cm^{-1} ; $\{^1\text{H}\}$ - ^{31}P n.m.r. (C_6D_6 , 32.38 MHz) δ 28.84 and 14.36 p.p.m. (s, PMe_3); $\{^1\text{H}\}$ - ^{13}C n.m.r. (C_6D_6 , 75.47 MHz) δ 218.44 (t, FeCO , $^2J_{\text{PC}}$ 27 Hz), 51.97 (t, FeCHS , $^3J_{\text{PC}}$ 13.5 Hz), 45.22 (s, SCH_2), 21.17 (d, PMe_3 , $^1J_{\text{PC}}$ 28 Hz), 19.62 (d, PMe_3 , $^1J_{\text{PC}}$ 24 Hz).

(**4c**): I.r. (Nujol) $\nu(\text{B-H})$ 2460, 2400(m), $\nu(\text{CO})$ 1930(s), $\nu(\text{CS})$ 1160(m) cm^{-1} ; ^{31}P n.m.r. (C_6D_6 , 32.38 MHz) δ 28.92 and 14.29 p.p.m. (s, PMe_3); ^1H n.m.r. (C_6D_6 , 300 MHz) δ 4.95 (s), 4.86 (s) ($=\text{CH}_2$), 3.21 (AB, S-CH_2 , $^2J_{\text{HH}}$ 12.9 Hz), 2.04 (d, FeCHS , $^3J_{\text{PH}}$ 5.7 Hz), 1.80 (s, CH_3), 1.15 (d) and 0.99 (d) (PMe_3 , $^2J_{\text{PH}}$ 8.5 Hz), -13.75 (br s, BH_3); $\{^1\text{H}\}$ - ^{13}C n.m.r. (C_6D_6 , 75.47 MHz) δ 218.20 (t, FeCO , $^2J_{\text{PC}}$ 29.5 Hz), 141.50 (s, $=\text{C}$), 113.59 (s, $=\text{CH}_2$), 52.10 (t, FeCHS , $^2J_{\text{PC}}$ 13.5 Hz), 48.25 (s, SCH_2), 21.16 (s, CH_3).

(**4d**): I.r. (Nujol) $\nu(\text{B-H})$ 2475, 2400(m), $\nu(\text{CO})$ 1930(s), $\nu(\text{CS})$ 1160(m) cm^{-1} ; ^{31}P n.m.r. (C_6D_6 , 32.38 MHz) δ 38.94 and 22.94 p.p.m. (s), ^1H n.m.r. (C_6D_6 , 300 MHz) δ 2.17 (s, SMe), 2.07 (d, FeCHS , $^3J_{\text{PH}}$ 6.1 Hz), -13.5 (br s BH_3); $\{^1\text{H}\}$ - ^{13}C n.m.r. (C_6D_6 , 75.47 MHz) δ 218.53 (t, FeCO , $^2J_{\text{PC}}$ 26.5 Hz), 57.43 (t, FeCHS , $^3J_{\text{PC}}$ 13.5 Hz), 24.45 (s, SMe).

(5) I.r. (Nujol) $\nu(\text{CO})$ 1870 cm^{-1} ; ^1H n.m.r. (C_6D_6 , 80 MHz) δ 4.18 (m, FeCHS), 2.59 (s, SMe), 1.33 (6.8 Hz), 1.29 (7.3 Hz), 1.02 (6.8 Hz) (each d, PMe_3); ^{31}P n.m.r. (C_6D_6 , 32.38 MHz) δ 25.15 (dd), 13.76 (d), 10.97 p.p.m. (d, $^2J_{\text{PP}}$ 39.0 Hz, $^2J_{\text{PP}}$ 48.8 Hz).



Scheme 1. Reagents and conditions: i, NaBH_4 , THF; ii, pyridine, PMe_3 ; iii, pyridine, CO.

(br s, BH_3); $\{^1\text{H}\}$ - ^{13}C n.m.r. (C_6D_6 , 75.47 MHz) δ 218.29 (t, FeCO , $^2J_{\text{PC}}$ 27 Hz), 56.43 (t, FeCHSMe , $^2J_{\text{PC}}$ 13.5 Hz), 24.60 (s, SMe), 21.33 (d, PMe_3 , $^1J_{\text{PC}}$ 28 Hz); ^{31}P n.m.r. (C_6D_6 , 32.38 MHz) δ 29.22 and 13.99 p.p.m. (s, PMe_3). Under similar conditions (**3b**), (**3c**), and (**3d**) led to the formation of (**4b**) (53%), (**4c**) (55%), and (**4d**) (30%), respectively and gave spectroscopic data† analogous to those of (**4a**) (Scheme 1). Analytical data† for complexes (**4**) indicated the absence of halide and suggested a 16-electron configuration for the iron atom. As no information could be obtained on the location of the BH_3 fragment a single-crystal X-ray structural analysis was carried out on complex (**4a**).‡ An ORTEP plot of the structure is shown in Figure 1. The molecule has a dithioformate ligand η^2 -co-ordinated to iron. The sulphur atom S(1) attached to iron is involved in a donor-acceptor bond with the BH_3 unit. One B-H bond of the latter occupies a site *trans* to the CO group on the iron atom and therefore allows the metal atom to attain an 18 electron configuration. The Fe-H_A distance [1.55(4) Å] is in the range of Fe-H distances found in $\text{HFe}_4(\text{CO})_{12}\text{BH}_2$ [1.55(5) and 1.58(5) Å].¹ The Fe-H_A interaction effects a lengthening of the corresponding B-H_A bond [1.28(4) Å] as compared to the other two B-H bonds [1.16(4) and 1.11(4) Å]. Thus, the reaction of (**3**) with borohydride results in a net two-fragment addition of BH_4^- to the complex, with hydride adding to carbon and a BH_3 unit to the co-ordinated sulphur atom. The elimination of halide is compensated by the co-ordination of one B-H bond to iron. The halide ligand in (**3**) is essential for the formation of (**4**),

‡ Crystal data for (**4a**): $\text{C}_8\text{H}_{25}\text{BOP}_2\text{S}_2\text{Fe}$, $M_r = 342.03$, orthorhombic, space group $Pna2_1$, $a = 15.946(5)$, $b = 13.444(2)$, $c = 8.232(2)$ Å, $Z = 4$, $\mu = 12.43 \text{ cm}^{-1}$. 2163 reflections of which 1578 had $I > 3\sigma(I)$; Enraf-Nonius CAD-4 diffractometer, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $2\theta_{\text{max}} = 54^\circ$; scan $\omega-2\theta = I$, $t_{\text{max}} = 60$ s, no absorption corrections. The structure was solved by Patterson and Fourier techniques. After isotropic and anisotropic refinement, the hydrogen atoms were located on a difference Fourier map (between 0.38 and 0.19 e Å⁻³). Final full-matrix least-squares refinement of positional parameters with anisotropic thermal parameters for non-hydrogen atoms led to $R = 0.025$ and $R_w = 0.022$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

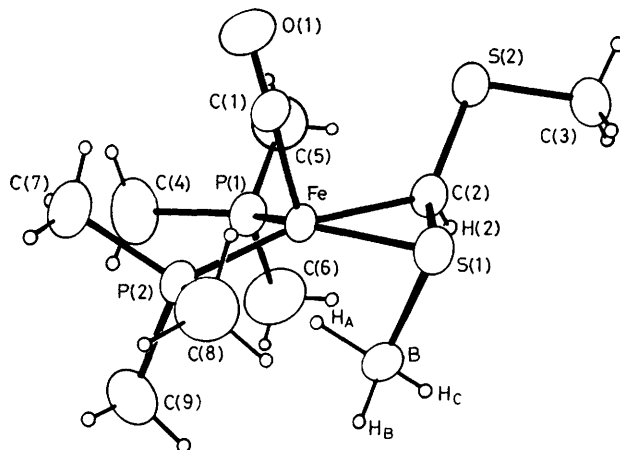


Figure 1. Molecular structure of $\text{Fe}[\eta^3\text{-HC(SMe)SBH}_3](\text{CO})(\text{PMe}_3)_2$ (**4a**) (ORTEP view). Bond distances (Å) and angles ($^\circ$): Fe-S(1) 2.220(1), Fe-C(2) 2.026(4), Fe-C(1) 1.769(3), Fe-P(1) 2.178(1), Fe-P(2) 2.245(1), Fe-H_A 1.55(4), B-H_A 1.28(4), B-H_B 1.16(4), B-H_C 1.11(4), C(2)-H(2) 0.87(4), C(2)-S(1) 1.782(4), C(2)-S(2) 1.824(4), S(1)-B 1.941(5), Fe-B 2.389(2), P(1)-Fe-P(2) 104.58(4), C(2)-Fe-S(1) 49.4(1), Fe-S(1)-B 69.7(1), C(2)-S(1)-B 91.7(2), P(1)-Fe-H(1) 86(1), P(2)-Fe-H_A 84(1), C(1)-Fe-H_A 175(1), S(1)-B-H_A 96(2), S(1)-B-H_B 114(2), S(1)-B-H_C 116(2).

since the reaction of complex (**2**) with $\text{BH}_3 \cdot \text{THF}$ does not lead to the formation of (**4**) by displacement of a carbonyl ligand on addition of BH_3 to the co-ordinated sulphur atom.

An appropriate description of complexes (**4**) appears to be that of a BH_3 adduct of a square pyramidal 16 electron dithioformate iron complex. As pyridine is known to give a stable donor-acceptor adduct with BH_3 , attempts were made to trap the BH_3 moiety of complexes (**4**) with pyridine. Complex (**4a**) was treated, at room temperature in pentane, with an excess of pyridine (3 equiv.); after 4 h complex (**2**)⁷ was obtained in 43% yield without observation of a pyridine-iron complex. When the same reaction was carried out under a CO atmosphere, complex (**2**) was obtained in 95% yield. Complex (**4a**) in pentane with PMe_3 (3 equiv.) is stable at room temperature, but the addition of an excess of pyridine led progressively to the formation at 25 °C of the yellow complex (**5**) which was isolated in 95% yield (Scheme 1).

These preliminary reactions show the potential of the unusual BH_3 adducts (**4**), with agostic B-H-Fe interaction, for the liberation of 16 electron iron(0) species, under mild conditions.

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