Two-fragment Addition of Borohydride to Iron Complexes: Synthesis of Dithioformate Iron Complexes with B–H–Fe Bond Interaction. *X*-Ray Structural Characterization of $Fe[\eta^3\text{-}HC(SMe)S \rightarrow B(H)H_2](CO)(PMe_3)_2$

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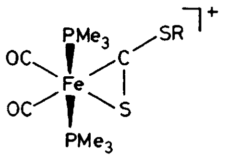
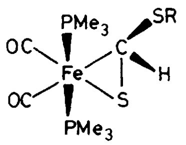
Reaction of $Fe(X)(\eta^2\text{-}CS_2R)(CO)(PR_3)_2$ (X = Cl, I) complexes with $NaBH_4$ leads to both hydride and BH_3 additions with the formation of dithioformate–iron(0) $Fe[\eta^3\text{-}HC(SR)S \rightarrow BH_3](CO)(PR_3)_2$ complexes (**4**) containing an agostic B–H–Fe interaction; the addition 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–tungsten[3] and molybdenum–phosphorus[4] systems, containing one bridging boron–hydrogen bond and derived from the addition of borane to a W≡C or a Mo=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 $M(\eta^2\text{-}CS_2R)$ has been shown to give rise to a variety of reactions. This borohydride reacts with the $Os(\eta^2\text{-}CS_2R)^+$ cation *via* hydride addition to the metal,[5] whereas with iron complexes (**1**) the reaction pathway is phosphine dependent, giving compounds derived from electron transfer[6] when L is PPh_3, or dithioformate iron derivative (**2**) when L is PMe_3. The reaction of $NaBH_4$ with neutral $Fe(X)(\eta^2\text{-}CS_2R)$ 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 (η^2-SCHSMe) ligand, arising from the addition of one hydride to the (η^2-CS_2Me) carbon of (**3a**), B–H bonds, and two non-equivalent PMe_3 groups [(**4a**): i.r. (Nujol) ν (B–H) 2480, 2400, ν(CO) 1920, ν(CS) 1160 cm^{-1}; ^1H n.m.r. (C_6D_6, 300 MHz) δ 2.21 (s, SMe), 2.04 (d, CHSMe, $^3J_{PH}$ 5.6 Hz), 1.15 (d) and 0.99 (d, PMe_3, $^2J_{PH}$ 8.5 Hz), −13.7



(**1**)



(**2**)

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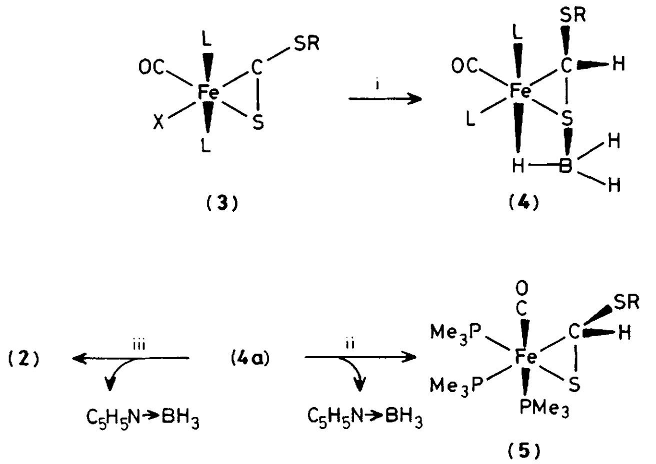
† All compounds reported have microanalytical, mass spectral, and spectroscopic data in accord with their assigned structures. Selected spectroscopic data for: (**4b**): I.r. (Nujol) ν(B–H) 2460, 2410(m), ν(CO) 1910(s), ν(CS) 1160(m) cm^{-1}; $\{^1H\}$-^{31}P n.m.r. (C_6D_6, 32.38 MHz) δ 28.84 and 14.36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

(**4c**): I.r. (Nujol) ν (B–H) 2460, 2400(m), ν(CO) 1930(s), ν (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) (=CH_2), 3.21 (AB, S–CH_2, $^2J_{HH}$ 12.9 Hz), 2.04 (d, FeCHS, $3J_{PH}$ 5.7 Hz), 1.80 (s, CH_3), 1.15 (d) and 0.99 (d) (PMe_3, $^2J_{PH}$ 8.5 Hz), −13.75 (br s, BH_3); $\{^1H\}$-^{13}C n.m.r. (C_6D_6, 75.47 MHz) δ 218.20 (t, FeCO, $^2J_{PC}$ 29.5 Hz), 141.50 (s, =C–), 113.59 (s, =CH_2), 52.10 (t, FeCHS, $^2J_{PC}$ 13.5 Hz), 48.25 (s, SCH_2), 21.16 (s, CH_3).

(**4d**): I.r. (Nujol) ν(B–H) 2475, 2400(m), ν(CO) 1930(s), ν(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, $^3J_{PH}$ 6.1 Hz), −13.5 (br s BH_3); $\{^1H\}$-^{13}C n.m.r. (C_6D_6, 75.47 MHz) δ 218.53 (t, FeCO, $^2J_{PC}$ 26.5 Hz), 57.43 (t, FeCHS, $^3J_{PC}$ 13.5 Hz), 24.45 (s, SMe).

(**5**) I.r. (Nujol) ν(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, $^2J_{PP}$ 39.0 Hz, $^2J_{PP}$ 48.8 Hz).



a; X = I, L = PMe_3, R = Me
b; X = Cl, L = PMe_3, R = CH_2Ph
c; X = Cl, L = PMe_3, R = $CH_2CMe{=}CH_2$
d; X = I, L = PMe_2Ph, R = Me

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

(br s, BH_3); $\{^1H\}$-^{13}C n.m.r. (C_6D_6, 75.47 MHz) δ 218.29 (t, FeCO, $^2J_{PC}$ 27 Hz), 56.43 (t, Fe*C*HSMe, $^2J_{PC}$ 13.5 Hz), 24.60 (s, SMe), 21.33 (d, PMe_3, $^1J_{PC}$ 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 $HFe_4(CO)_{12}BH_2$ [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**), since the reaction of complex (**2**) with $BH_3{\cdot}THF$ 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.

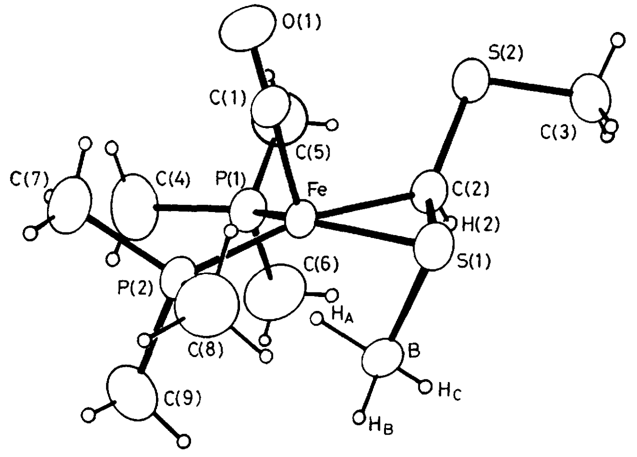


Figure 1. Molecular structure of Fe[η^3-HC(SMe)SBH_3](CO)$(PMe_3)_2$ (**4a**) (ORTEP view). Bond distances (Å) and angles (°): Fe–S(1) 2.220(1), Fe–C(2) 2.026(4), Fe–C(1) 1.769(3), Fe–P(1) 2.178(1), Fe–P(2) 2.245(1), Fe–H_A 1.55(4), B–H_A 1.28(4), B–H_B 1.16(4), B–H_C 1.11(4), C(2)–H(2) 0.87(4), C(2)–S(1) 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).

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.

Received, 9th September 1986; Com. 1296

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[‡] *Crystal data* for (**4a**): $C_8H_{25}BOP_2S_2Fe$, M_r = 342.03, orthorhombic, space group $Pna\,2_1$, a = 15.946(5), b = 13.444(2), c = 8.232(2) Å, Z = 4, μ = 12.43 cm^{-1}. 2163 reflections of which 1578 had $I > 3\sigma(I)$; Enraf–Nonius CAD-4 diffractometer, λ(Mo-K_α) = 0.71069 Å, $2\theta_{max.}$ = 54°; scan ω–2θ = I, t_{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.