Preparation, Isolation, and Structure of $[NBu_4]^+[\mu\text{-}Fe(CO)_4\text{-}B_7H_{12}]^-$; Preparation and Isolation of $Fe(CO)_4B_7H_{11}$: Electrophilic Stabilization of a Heptaborane Species

By ORIN HOLLANDER, WILLIAM R. CLAYTON, and SHELDON G. SHORE*
(*Department of Chemistry, Ohio State University, Columbus, Ohio* 43210)

Summary The crystalline solids $[NBu_4]^+[\mu\text{-}Fe(CO)_4\text{-}B_7H_{12}]^-$ and $Fe(CO)_4B_7H_{11}$ have been isolated and the structure of the $[\mu\text{-}Fe(CO)_4\text{-}B_7H_{12}]^-$ ion has been determined.

THE existence of heptaboranes has been inferred from studies of boron hydride pyrolysis products.[1] However, the validity of some of this work has been questioned.[2] Indeed, a neutral heptaborane or a heptaborane anion has yet to be isolated and well characterized as a binary hydride species. The $B_7H_{12}^-$ ion was prepared in solution;[3] it decomposed above −70° in solution and the isolated tetra-n-butylammonium salt rapidly decomposed upon warming from −78° to room temperature. An attempt to convert $B_7H_{12}^-$ into a neutral boron hydride failed.[4]

We report here the preparation and structure of $[\mu\text{-}Fe(CO)_4\text{-}B_7H_{12}]^-$ and the preparation of $Fe(CO)_4B_7H_{11}$. The ion (Figure) is a B_6 pentagonal pyramid with a BH_3 group and an $Fe(CO)_4$ group inserted into bridging positions between and beneath basal borons. Boron–boron and boron-hydrogen distances fall within observed values for boron hydride structures.[5] The average B–Fe distance is 2·20 ± 0·02 Å. The position of the $Fe(CO)_4$ group is as yet undetermined in $Fe(CO)_4B_7H_{11}$, but is most likely in a bridge site. Both $[Bu_4N]^+[\mu\text{-}Fe(CO)_4\text{-}B_7H_{12}]^-$ and $Fe(CO)_4\text{-}B_7H_{11}$ appear to be stable at room temperature for at least an hour; the latter compound melts at about 20°. These appear to be the first examples of stabilization of boron hydride species by an electron-withdrawing group. Stabilization of boron hydrides such as BH_3 by electron donors is well-known.[5]

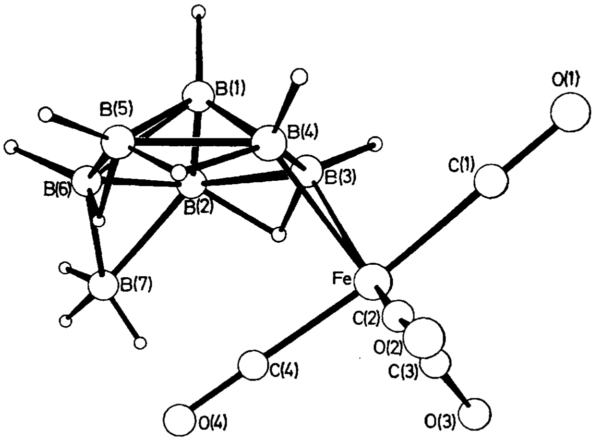

FIGURE. The structure of $\mu\text{-}Fe(CO)_4\text{-}B_7H_{12}^-$

$\mu\text{-}Fe(CO)_4\text{-}B_6H_{10}$[6] is smoothly and rapidly deprotonated at a bridging site [equation (1)] as in the case of B_6H_{10}.[7]

$$\mu\text{-Fe(CO)}_4\text{-B}_6\text{H}_{10} + \text{KH} \longrightarrow \text{K}^+ [\mu\text{-Fe(CO)}_4\text{-B}_6\text{H}_9]^- + \text{H}_2 \quad (1)$$

Proton competition reactions procedurally similar to previously described studies[8] showed that μ-Fe(CO)$_4$-B$_6$H$_{10}$ is a stronger Brønsted acid than B$_6$H$_{10}$.

Crystalline [NBu$_4$]$^+$[μ-Fe(CO)$_4$-B$_7$H$_{12}$]$^-$ was isolated as in equations (2) and (3).

$$\text{K}^+[\mu\text{-Fe(CO)}_4\text{-B}_6\text{H}_9]^- + [\text{NBu}_4]^+\text{I}^- \longrightarrow [\text{NBu}_4]^+[\mu\text{-Fe(CO)}_4\text{-B}_6\text{H}_9]^- + \text{KI} \quad (2)$$

$$[\text{NBu}_4]^+[\mu\text{-Fe(CO)}_4\text{-B}_6\text{H}_9]^- + 1/2\ \text{B}_2\text{H}_6 \longrightarrow [\text{NBu}_4]^+[\mu\text{-Fe(CO)}_4\text{-B}_7\text{H}_{12}]^- \quad (3)$$

Crystals of [NBu$_4$]$^+$[μ-Fe(CO)$_4$-B$_7$H$_{12}$]$^-$ are of the monoclinic space group $P2_1/c$: $a = 10{\cdot}891(5)$, $b = 11{\cdot}656(6)$, $c = 23{\cdot}803(9)$ Å, $\beta = 90{\cdot}34(1)°$, $Z = 4$. At −50°, the intensities of 5770 unique reflections were measured using Mo-K_α scintillation counter data of which 2283 were greater than $3\sigma(I)$ and were regarded as observed. Positions of non-hydrogen atoms were located by a combination of direct methods and a Fourier map. There is unresolved partial disorder in the cation. Hydrogen atoms were located by a difference Fourier and a conventional R of 0·11 was obtained.

Liquid, anhydrous HCl was added at −196° to a known quantity of isolated K$^+$[μ-Fe(CO)$_4$-B$_7$H$_{12}$]$^-$. At −110° reaction (4) occurred; one equivalent of H$_2$ was quantitatively recovered, and no B$_2$H$_6$ or μ-Fe(CO)$_4$-B$_6$H$_{10}$ was formed.

$$\text{K}^+[\mu\text{-Fe(CO)}_4\text{-B}_7\text{H}_{12}]^- + \text{HCl} \longrightarrow \text{Fe(CO)}_4\text{B}_7\text{H}_{11} + \text{H}_2 + \text{KCl} \quad (4)$$

The ^{11}B n.m.r. spectrum of Fe(CO)$_4$B$_7$H$_{11}$ in CH$_2$Cl$_2$ (^{1}H decoupled) consists of three broad low-field resonances ($\delta = -10{\cdot}7\ -5{\cdot}3,\ 0$ p.p.m.) and a high-field resonance ($\delta = 53{\cdot}2$ p.p.m.). The m.s. of Fe(CO)$_4$B$_7$H$_{11}$ at 55 °C included a parent ion group of peaks followed by successive loss of three CO groups. A similar fragmentation behaviour has been reported for Fe(CO)$_4$B$_6$H$_{10}$.[6]

We acknowledge support of this work by the National Science Foundation.

(*Received*, 28*th November* 1973; *Com.* 1629.)

[1] S. J. Steck, G. A. Pressley, Jr., F. E. Stafford, J. Dobson, and R. Schaeffer, *Inorg. Chem.*, 1970, **9**, 2452; A. B. Baylis, G. A. Pressley, Jr., M. E. Jordan, and F. E. Stafford, *J. Amer. Chem. Soc.*, 1966, **88**, 929. T. P. Fehlner and W. S. Koski, *ibid.*, 1964, **86**, 1012. R. W. Schaeffer, K. H. Ludlum, and S. E. Wiberly, *ibid.*, 1959, **81**, 3157.

[2] J. F. Ditter, J. R. Spielman, and R. E. Williams, *Inorg. Chem.*, 1966, **5**, 118.

[3] H. D. Johnson, II and S. G. Shore, *J. Amer. Chem. Soc.*, 1971, **93**, 3798.

[4] H. D. Johnson, II and R. J. Remmel, unpublished results from this laboratory.

[5] W. N. Lipscomb, 'Boron Hydrides,' W. A. Benjamin, New York, 1961.

[6] A. Davison, D. D. Traficante, and S. S. Wreford, *Chem. Comm.*, 1972, 1155.

[7] H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 1970, **9**, 908.

[8] H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Amer. Chem. Soc.*, 1969, **91**, 2131.