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An X-ray Study of $FeH(dmpe)_2(BH_4)$: a Compound Containing a Singly-bridged BH_4 Ligand with a Bent Fe–H–B Linkage

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Recently some of us (L.D.F. and M.V.B.) reported the preparation and spectral properties (^1H, ^{31}P and IR data) of the complex $FeH(dmpe)_2(\mu\text{-}H)(BH_3)$, where dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$ [1]. It was found that, at low temperature, three hydride signals could be discerned in the proton NMR spectrum: a terminal Fe–H hydrogen, a bridging Fe–H–B hydrogen, and three equivalent terminal B–H hydrogens. At high temperature, in solution, the terminal B–H hydrogens and the bridging Fe–H–B hydrogen exchange rapidly on the NMR time scale.

Since singly-bridge BH_4 ligands are very rare [2] and since some of us (R.B. and co-workers) have had a long-standing interest in M–H–B bridges [3] as part of an extensive program on the structures of metal hydride complexes [4], it was naturally of interest to us to examine the geometry of the title compound. In this communication we confirm, via X-ray diffraction techniques, the earlier proposal [1] that the BH_4 group in $FeH(dmpe)_2(BH_4)$ is a singly-bridged (monodentate) ligand.

The title compound crystallizes in the monoclinic space group $P2_1/c$, with $a = 17.992(13)$, $b = 12.844(5)$, $c = 9.311(4)$ Å, $\beta = 105.74(4)°$, $V = 2071(2)$ Å^3, $\rho_c = 1.19$ g cm^{-3} for $Z = 4$. X-ray diffraction data were collected on a sample of dimensions 0.45 × 0.08 × 0.07 mm at room temperature using a Nicolet/Syntex $P2_1$ diffractometer with Mo Kα radiation up to a 2θ limit of 45°. The structure was solved by heavy-atom methods, with calculated hydrogen positions included for the hydrogens bonded to carbon atoms. The terminal (*ie.*, the iron-bonded) H atom, and those of the $(\mu\text{-}H)(BH_3)$ ligand were carefully located using the low-angle data method [5]. Subsequent least-squares refinement led to a final R factor of 0.055 for 1642 non-zero reflections [$I > 3\sigma(I)$]. A listing of the final atomic coordinates is given in Table I.

TABLE I. Final Atomic Positions for $HFe(dmpe)_2(BH_4)$

Atom	x	y	z
Fe	0.1767(1)	0.2030(1)	0.1052(1)
P(2)	0.3707(3)	0.1259(2)	0.1807(2)
P(3)	0.0447(3)	0.1178(2)	0.1689(2)
P(4)	−0.0197(3)	0.2678(2)	0.0233(2)
P(5)	0.3034(3)	0.2714(2)	0.0316(2)
C(6)	0.4621(12)	0.0209(10)	0.1451(7)
C(7)	0.5331(11)	0.1955(11)	0.2363(8)
C(8)	0.3124(15)	0.0616(13)	0.2576(8)
C(9)	0.1627(14)	0.0263(10)	0.2355(7)
C(10)	−0.0459(12)	0.1877(10)	0.2330(7)
C(11)	−0.1113(11)	0.0358(9)	0.1192(7)
C(12)	−0.1667(10)	0.3444(9)	0.0519(7)
C(13)	−0.1375(14)	0.1839(10)	−0.0496(8)
C(14)	0.0458(16)	0.3630(11)	−0.0379(7)
C(15)	0.1802(15)	0.3338(12)	−0.0506(8)
C(16)	0.4392(11)	0.3757(10)	0.0681(8)
C(17)	0.4097(14)	0.1900(10)	−0.0180(7)
B	0.2102(14)	0.3813(11)	0.2004(9)
H(b)	0.1800	0.3050	0.1680
H(t)	0.2067	0.4530	0.1657
H(t)	0.3188	0.3717	0.2406
H(t)	0.1245	0.3878	0.2325
H	0.1300	0.1000	0.0450

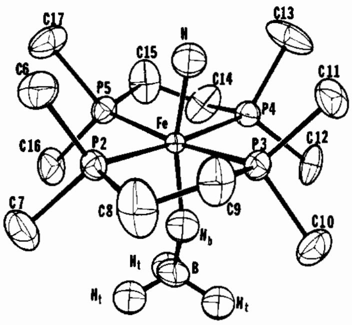

Fig. 1. Molecular structure of $FeH(dmpe)_2(BH_4)$, with H atoms on the methyl and methylene groups removed for clarity.

The structure (Fig. 1) shows an octahedrally-coordinated Fe atom with the four P atoms arranged equatorially. As mentioned earlier, the H–Fe–$(\mu\text{-}H)$–BH_3 arrangement of atoms along the central axis is fully consistent with the NMR results [1]. Selected distances and angles are: Fe–H = 1.69 Å, Fe–H(b) = 1.72 Å, B–H(b) = 1.14 Å, B–H(t) = 1.10 Å (average), Fe···B = 2.84 Å, Fe–P = 2.183 Å (average), Fe–H(b)–B = 161.7°, H–Fe–H(b) = 165.9°. The Fe–H(b)–B angle of 161.7° is substantially more obtuse than the Cu–H(b)–B angle of 121.7(4)° measured accurately by neutron dif-

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fraction on the compound $Cu(PPh_2Me)_3(BH_4)$ [3], and may, in the present case, be an artifact arising from the fact that one is observing the electron density maximum in the center of the Fe–H–B triangle, rather than the H nucleus itself. Nevertheless, the Fe–H(b)–B angle is distinctly and unambiguously bent, as has been shown in virtually all cases of M–H–M, M–H–B and B–H–B linkages studied so far [4c]. The only known exception to date is the Al–H–Al bond in the $[(CH_3)_3Al–H–Al(CH_3)_3]^-$ anion [6].

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