of the large quadrupole doublet associated with cis-octahedral Fe(II) configurations on oxidation to Fe(III) will lead to Mössbauer resonance absorptions in the range 0–0.8 mm s^{-1} with respect to metallic iron, as observed in the data of Wei and Jean.[2]

It should be noted, however, that the present IR data pertain to spin-crossover complexes other than those examined in detail by Wei and Jean. While the present results indicate that the "particle size effect" is not a general phenomenon observable for complexes such as I and II, further detailed study by non-Mössbauer methods of the compounds discussed by Wei and Jean would appear to be appropriate.

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Department of Chemistry
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08854

D. Cower-Figg
R. H. Herber*

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Reduction of B_5H_9 by Alkali Metals. Preparation of the Dianion $(B_5H_9)^{2-}$ and a New Route to B_5H_{11}

Sir:

Although alkali-metal reductions to produce dianions have been successfully carried out with higher boron hydrides such as $B_{10}H_{14}$[1-4] and $B_{18}H_{22}$,[5] reduction of the lower boron hydrides to dianions has not been demonstrated previously. While Stock[6] reported the reduction of pentaborane(9), B_5H_9, by potassium amalgam to give a compound he formulated as $K_2B_5H_9$, later attempts to duplicate this work showed the product to contain a large amount of potassium borohydride and unidentified materials.[4] We have found that pentaborane(9) is cleanly reduced by two equivalents of sodium, potassium, rubidium, or cesium naphthalide in THF or glyme to form the nonahydropentaborate(2−) dianion, $[B_5H_9]^{2-}$ (eq 1). Protonation of this dianion

$$B_5H_9 + 2M^+(C_{10}H_8)^- \rightarrow M_2[B_5H_9] + C_{10}H_8 \qquad (1)$$

$$M = Na, K, Rb, Cs; \; C_{10}H_8 = \text{naphthalene}$$

provides a simple route from B_5H_9 to B_5H_{11} in yields up to 38%.

In a typical reaction, 4.02 mmol of B_5H_9 was condensed into a vessel containing 8.04 mmol of preformed potassium naphthalide in 10 mL of THF at −196 °C. Warming the mixture to room temperature and stirring for 30–45 min caused complete consumption of the naphthalide and produced the red-brown salt $K_2[B_5H_9]$. No hydrogen was evolved in this reaction.[7] The salt was isolated by washing it with pentane on a filter to remove naphthalene and also by pumping away the naphthalene at room temperature under high vacuum. Other alkali-metal salts were prepared similarly. The sodium salt is slightly soluble in THF and glyme while the potassium, rubidium, and cesium salts are insoluble.

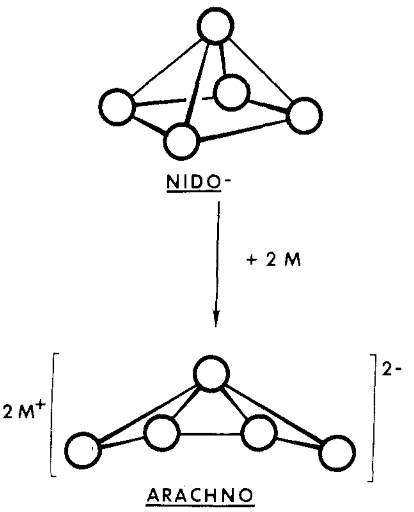

Figure 1. Expected structural change in the boron framework caused by a two-electron reduction of *nido*-B_5H_9 to *arachno*-B_5H_{11}.

In the presence of air, alkali-metal salts of $[B_5H_9]^{2-}$ fume and are quickly discolored. They appear to be quite stable under vacuum in both the solid state and in solution, showing only minimal decomposition after 1 week, as judged from physical appearance, lack of gas evolution, infrared spectra, and boron-11 NMR spectra. IR spectrum of $K_2[B_5H_9]$ (Nujol mull, $\nu_{(\text{B-H,terminal})}$, cm^{-1}): 2407 (sh), 2359 (s), 2342 (s), 2335 (s). Bands in the B–H–B bridging region were unidentifiable due to overlap of Nujol bands. Boron-11 NMR spectrum of $[K(\text{dibenzo-18-crown-6})]_2[B_5H_9]$ in THF (δ = 0.0 ppm for $BF_3 \cdot OEt_2$): −16.1 (J = 132 Hz, 4 B), −51.7 (J = 157 Hz, 1 B).

The crown ether (dibenzo-18-crown-6) complexes of the potassium, rubidium, and cesium salts of $[B_5H_9]^{2-}$ are soluble in THF and glyme and thus could be used to obtain NMR spectra. These complexes were prepared by stirring equimolar quantities of alkali-metal and crown ether along with a small amount of naphthalene (*ca.* 5 mol %) in THF or glyme to form a yellow complex. This complex was then used to reduce B_5H_9 to the dianion $[B_5H_9]^{2-}$. The boron-11 NMR spectra of the $[K(\text{dibenzo-18-crown-6})]_2[B_5H_9]$ complex and $Na_2[B_5H_9]$ are nearly identical. Boron-11 NMR spectra of $[B_5H_9]^{2-}$ salts were clean and showed no other boron-containing species to be present. A two-electron reduction of *nido*-B_5H_9 to the *arachno*-$[B_5H_9]^{2-}$ dianion is expected[8] to open the B_5H_9 square pyramid to give a boron framework like that of B_5H_{11} (a pentagonal pyramid with one basal vertex site absent) as illustrated in Figure 1. The fact that only two NMR signals are observed indicates that the $[B_5H_9]^{2-}$ molecule is highly fluxional at room temperature. Low-temperature (−70 °C) ^{11}B NMR spectra showed broadening of the signals; however, additional signals were not observed. Boron-11 NMR spectra of other pentaborane anions, $[B_5H_8]^-$, $[B_5H_{10}]^-$, and $[B_5H_{12}]^-$, also show two doublets in a relative ratio of 4:1.[9-12] Although the ^{11}B NMR spectrum for $[B_5H_9]^{2-}$ is very similar to that obtained for the $[B_5H_8]^-$ anion, the stabilities, solubilities, and IR spectra of $[B_5H_9]^{2-}$ salts are very different from those of $[B_5H_8]^-$ salts. In addition, protonation of $[B_5H_9]^{2-}$ produces B_5H_{11} in good yield. No B_5H_9 is obtained from this protonation.

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Protonation of $[B_5H_8]^-$ gives nearly quantative yields of B_5H_9.[13]

Protonation of $K_2[B_5H_9]$ or $Cs_2[B_5H_9]$ with hydrogen chloride or hydrogen bromide provides a convenient route to pentaborane(11), B_5H_{11} (eq 2). The protonation of $K_2[B_5H_9]$ with

$$M_2[B_5H_9] + 2HX \rightarrow B_5H_{11} + 2MX \tag{2}$$

$$M = K, Cs; X = Cl, Br$$

HCl in butane at −78 °C has provided B_5H_{11} in 38% yield based upon the B_5H_9 starting material. The product was isolated by trap to trap fractionation on the vacuum line through traps held at −111 and −196 °C. Pentaborane(11) was collected in the −111 °C trap and identified by its characteristic IR and ^{11}B NMR spectra[14,15] and by its vapor pressure at 0 °C of 52 mm.[16] This represents the simplist, most convenient, and safest preparative method to date for B_5H_{11}.[11,17–22] The starting material is commercially available.[23] Butane was chosen because it is chemically inert toward the boron hydrides and because its low boiling point allows easy separation of the B_5H_{11} product on the vacuum line fractionation train.

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Department of Chemistry
The Ohio State University
Columbus, Ohio 43210

Joseph R. Wermer
Sheldon G. Shore*

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Superconductivity at 91 K in the Magnetic Oxide $HoBa_2Cu_3O_{6+x}$

Sir:

A remarkable increase in T_c (superconducting transition temperature) to temperatures near 90 K has been reported[1,2] recently for a phase of the Y–Ba–Cu–O system, variously identified as $YBa_2Cu_3O_{9-\delta}$ ($\delta = 2.1$),[3] $YBa_2Cu_3O_{6+x}$ ($x = 0.5$),[4] and $YBa_2Cu_3O_{6.81}$.[5] Relatively sharp superconducting transitions occur for this material with onset T_c's at 93–98 K, with zero resistance at 80–94 K, and with substantial Meissner effects measured at temperatures not far below zero resistance. This superconducting oxide is a compound similar in metal stoichiometry to $Y_2Cu_2O_5$[6] on the basis of the total noncopper metal-to-copper atomic ratios. It is well documented that, in addition to Y, the lanthanide ions, Ln^{3+}, with more than seven 4f electrons form similar compounds, $Ln_2Cu_2O_5$.[6,7] Consequently, one speculates that superconducting oxides with T_c's near 90 K might also occur for compositions $LnBa_2Cu_3O_{6+x}$, where Ln^{3+} is any one of the heavier lanthanide ions. An interesting question in this case is the effect of the magnetic moment on superconductivity. Normally, the presence of the moment decreases T_c through exchange interactions and, if magnetic ordering occurs, may lead to the coexistence of superconductivity and magnetism, or reentrant superconductivity (reentrant means return to the normal state). We have chosen to explore the synthesis and superconducting properties of $HoBa_2Cu_3O_{6+x}$ because Ho^{3+} has the same radius as nonmagnetic Y^{3+} (0.89 Å)[8] and, along with Dy^{3+}, has the largest magnetic moment (10.4 μ_B)[9] of the Ln^{3+} ions. In the course of this work, conflicting reports have appeared which indicate that an uncharacterized phase (or phases) of the Ho–Ba–Cu–O system is superconducting with T_c's of ~46,[10] 70,[11] or 93 K.[12,13] In this communication we report on bulk superconductivity near 91 K without reentrant behavior down to 0.55 K for $HoBa_2Cu_3O_{6+x}$.

Synthesis. Ceramic oxides of both the Y and Ho compounds of initial composition $MBa_2Cu_3O_{6+y}$ (M = Y or Ho) were prepared to provide a comparison of the properties of the Ho-based material with the superconducting properties of the Y-based material. These were synthesized by adding stoichiometric amounts of Y_2O_3 or Ho_2O_3 to CuO and $BaCO_3$ (all dry, reagent grade powders). The components were intimately mixed and ground by the use of a ball mill, placed in a Pt crucible, and calcined in air at 950 °C in a muffle furnace. After 24 h, the samples were removed and allowed to cool to room temperature in air. The calcined products were reground with a mortar and pestle and pressed into pellets. The pellets, contained in a Pt boat, were placed in a fused silica tube, which was heated in a tube furnace. Under an atmosphere of pure O_2 at a flow rate of 85 mL/m, the pellets were sintered at 950 °C for 16 h and then cooled to 200 °C over a period of 1 h. After this sintering, the pellets were removed from the furnace and further cooled in air.

Analysis. X-ray powder diffraction patterns of the Y-based ceramic pellet indicated the existence of two phases. These could be identified as the superconducting phase $YBa_2Cu_3O_{6+x}$ and the semiconducting[3] phase Y_2BaCuO_5.[14] Chemical analysis of the metal constituents gave ~70% for the molar concentration of the superconducting phase. The Ho-based ceramic also showed the existence of two phases by X-ray powder diffraction analysis. The major phase could be indexed by use of an orthorhombic unit cell with a = 12.178 (3) Å, b = 5.660 (2) Å, and c = 7.127 (2) Å, in excellent agreement with the parameters reported for Ho_2BaCuO_5.[14] The second phase was indexed by use of an orthorhombic unit cell with a = 3.825 (3) Å, b = 3.894 (4) Å, and c = 11.682 (11) Å. These dimensions are close to those reported for the $YBa_2Cu_3O_{6+x}$ superconducting phase,[3–5] and since Ho^{3+} and Y^{3+} have essentially identical radii, we conclude that the second phase is $HoBa_2Cu_3O_{6+x}$.

Measurements of the atomic ratios of metal constituents in the ceramic pellets were carried out by the method of inductively coupled plasma/atomic emission spectroscopy. Since the X-ray diffraction patterns indicate the presence of only two phases,

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