$$g_{\mathrm{eff}} = \sum_i K_i g_i \tag{6}$$

Successive application of the Wigner–Eckart theorem to the site spins and pair spins gives

$$K_1 = K_2 = \frac{\langle S_{1z}\rangle}{\langle S_z\rangle} = \frac{\alpha\gamma}{\Delta_1} \tag{7}$$

$$K_3 = \frac{\langle S_{3z}\rangle}{\langle S_z\rangle} = \frac{\delta_1\epsilon}{\Delta_2} \qquad K_4 = \frac{\langle S_{4z}\rangle}{\langle S_z\rangle} = \frac{\delta_2\epsilon}{\Delta_2} \tag{8}$$

where

$$\begin{gathered}
\alpha = [S_{12}'(S_{12}' + 1) + S_1(S_1 + 1) - S_2(S_2 + 1)]/2 \\
\gamma = [S(S + 1) + S_{12}'(S_{12}' + 1) - S_{34}'(S_{34}' + 1)]/2 \\
\Delta_1 = S_{12}'(S_{12}' + 1)S(S + 1) \\
\epsilon = [S(S + 1) + S_{34}'(S_{34}' + 1) - S_{12}'(S_{12}' + 1)]/2 \\
\delta_1 = [S_{34}'(S_{34}' + 1) + S_3(S_3 + 1) - S_4(S_4 + 1)]/2 \\
\delta_2 = [S_{34}'(S_{34}' + 1) + S_4(S_4 + 1) - S_3(S_3 + 1)]/2 \\
\Delta_2 = S_{34}'(S_{34}' + 1)S(S + 1)
\end{gathered} \tag{9}$$

Since the sites 3 and 4 form a mixed-valence pair, it is necessary to average A_3 and A_4 for these sites. (We assume $S_3 = {}^5/_2$ and $S_4 = 2$ as a convention.) Site a values for typical monomeric compounds are $a(\mathrm{Fe}^{3+}) = -20$ MHz and $a(\mathrm{Fe}^{2+}) = -22$ MHz,[4] so that for HP in the ground $|{}^9/_2\ {}^1/_2\ (4)\rangle$ state we predict $K_1 = -{}^4/_3$, $K_3 = {}^{55}/_{27}$, $K_4 = {}^{44}/_{27}$, and

$$\begin{gathered}
A_1 = A_2 = +26.7 \text{ MHz} \\
A_{3,4}^{\mathrm{av}} = -38.5 \text{ MHz}
\end{gathered} \tag{10}$$

compared with $A_1 = +20.2$ and $A_{3,4}^{\mathrm{av}} = -32.0$ MHz experimentally. For the excited substate $|{}^9/_2\ {}^1/_2\ (5)\rangle$, we predict $A_1 = A_2 = -40$ MHz and $A_{3,4}^{\mathrm{av}} = +31.3$ MHz, in contrast to experiment. For the excited $|{}^9/_2\ {}^3/_2\ (3)\rangle$ state, we find $A_1 = +12$ MHz and $A_{3,4}^{\mathrm{av}} = -23$ MHz, which can be compared with the observed hyperfine coupling only after the $S = {}^3/_2$ state is identified and its hyperfine coupling obtained by ENDOR or magnetic Mössbauer spectroscopy. This is not presently available.

If there were three local ${}^5/_2$ spins and one local $S_4 = 2$ spin with $g(\mathrm{Fe}^{3+}) = 2.002$ and $g_4(\mathrm{Fe}^{2+}) = 2.002 + \Delta g_4$, then $g_{\mathrm{eff}} = 2.002 + {}^{44}/_{27}\Delta g_4$. With a ferrous $\Delta g_4^{\mathrm{av}} = 0.05$ (see ref 7a), we calculate $g_{\mathrm{eff}}^{\mathrm{av}} = 2.08$, in good agreement with typical HP $g_{\mathrm{av}} = 2.06$. However, the S_3–S_4 pair is totally delocalized, so it is better to calculate Δg_{34} for the complete $S_{34}' = {}^9/_2$ subdimer.

Detailed quantitative calculations on HP models are under way and experiments are planned to more thoroughly explore this theoretical model.

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Conversion of *closo*-2,4-$C_2B_5H_7$ to [*nido*-2,4-$C_2B_4H_7$]$^-$

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The [*nido*-2,4-$C_2B_4H_7$]$^-$ ion has been previously prepared from a cage-opening reaction of *closo*-1,6-$C_2B_4H_6$ with metal hydrides or from the treatment of 5-$(CH_3)_3N$-*nido*-2,4-$C_2B_4H_6$ with a metal hydride.[1,2] Both reactions are very slow and, of course, depend upon the availability of *closo*-1,6-$C_2B_4H_6$. One of the most accessible small carboranes[3-5] is *closo*-2,4-$C_2B_5H_7$, and thus it became desirable to find a method for the removal of a boron from this C_2B_5 cage compound with the prospect of finding another route to the [*nido*-2,4-$C_2B_4H_7$]$^-$ ion.

Experimental Section

Materials and Handling of Chemicals. The parent *closo*-carborane 2,4-$C_2B_5H_7$ was obtained from R. E. Williams and used without further purification. Standard high-vacuum techniques were used in the handling of all chemicals.

Instrumentation. Proton (400- and 500-MHz) spectra were obtained by use of Bruker AM and Bruker WM instruments, respectively. All ^{11}B NMR chemical shift data are based on $\delta(BF_3\cdot OEt_2) = 0.00$ with negative values upfield.

Reaction of *closo*-2,4-$C_2B_5H_7$ with Lithium Amides. (a) With Li[N$(CH_3)_2$]. To a 3-mm NMR tube, equipped at one end with a 2.5-mL bulb, was added Li[N$(CH_3)_2$] (Aldrich, 0.19 mmol) under a nitrogen atmosphere. After the tube and its contents were attached to a high-vacuum apparatus, *closo*-2,4-$C_2B_5H_7$ (0.13 mmol) was condensed into the tube at −195 °C. The mixture was subsequently warmed to room temperature, mixed well by shaking the sample, and then allowed to stand for approximately 2 min. After the sample was cooled back to −195 °C, CH_3CN (Wilmad, 2 mmol) was added and the tube sealed and warmed to ambient temperature. The sample slowly turned to a clear yellow liquid, with no solids present. After the sample was kept at room temperature for 5.5 h, a ^{11}B NMR spectrum indicated the presence of (a) [*nido*-2,4-$C_2B_4H_7$]$^-$ (2%) (^{11}B NMR: δ(B(1)) −52.0, *J*(BH) = 158 Hz; δ(B(3)) +21.3, *J*(BH) = 121 Hz; δ(B(5,6)) +1.2, *J*(BH) = 133 Hz),[1,2] (b) starting material, *closo*-2,4-$C_2B_5H_7$[6] (97%), and traces of other compounds. After 28 h at ambient temperature the quantity of [2,4-$C_2B_4H_7$]$^-$ increased to 10% at the expense of the $C_2B_5H_7$. After 12 days at room temperature, four boron-containing cage compounds were evident: $C_2B_5H_7$ (48%), [2,4-$C_2B_4H_7$]$^-$ (29%), compound A (6%) ^{11}B NMR: δ −39.1 (d), *J*(BH) = 153 Hz; δ +7 (d); δ +21 (d); δ +49 (d)), and compound B (7%) (high-field B(1) resonance at δ −50), and approximately 10% of other boron-containing species with an assortment of resonances appearing in the regions of δ +28, +15, −5, −10 to −20, and −44. One month later the percentage of [2,4-$C_2B_4H_7$]$^-$ climbed to 76%, and after 2 months 95% of all of the boron content was attributed to this ion with the remaining ^{11}B resonances found at δ −7 and −15 to −25; no evidence of the starting material $C_2B_5H_7$, nor of compounds A and B, was found.

(b) With Li[N$(C_2H_5)_2$]. In a manner similar to that described in section a Li[N$(C_2H_5)_2$] (Aldrich, 0.195 mmol), *closo*-2,4-$C_2B_5H_7$ (0.195 mmol), and CD_3CN (2 mmol) were mixed. After 1 day at ambient temperature the clear liquid sample was yellow with no solids present. NMR data revealed the presence of (a) [*nido*-2,4-$C_2B_4H_7$]$^-$ (39%) (^{11}B NMR: δ(B(1)) −52.9, *J*(BH) = 158 Hz; δ(B(3)) +20.7, *J*(BH) = 119 Hz; δ(B(5,6)) +0.4, *J*(BH) = 136 Hz. ^{1}H NMR: δ(H(1)) −1.59, *J*(HB) = 157 Hz; δ((Hμ)) −4.57 (broad)),[1,2] (b) starting material, *closo*-2,4-$C_2B_5H_7$[6] (45%), and small amounts of compounds A (11%) and B (5%). ^{11}B NMR data for A: δ −39.1 (area 1), *J*(BH) = 154 Hz; δ +6.7 (area 2), *J*(BH) = 131 Hz; δ +21.0 (area 1), *J*(BH) = ca. 118 Hz; δ +48.5 (area 1) (half-width ca. 260 Hz, which narrows to 170 Hz upon proton decoupling). ^{11}B NMR data for compound B: δ −48.1 (area 1), *J*(BH) = 151 Hz; δ ca. −21 (area 2), *J*(BH) = 176 Hz; δ +20.7 (doublet, area 1). After the mixture was left to stand at room temperature for an additional 6 days, the ^{11}B NMR spectrum of the sample exhibited the same resonances as observed before, but with slightly different intensities, leading to the following composition assessment: [*nido*-2,4-$C_2B_4H_7$]$^-$, 37%; *closo*-2,4-$C_2B_5H_7$, 49%; A, 7%; B, 7%. After 1 month at room temperature nearly equal amounts of the starting material, *closo*-2,4-$C_2B_5H_7$, and [*nido*-2,4-$C_2B_4H_7$]$^-$ were present, as assessed by the ^{11}B NMR pattern. No further change occurred with time.

In another experiment with $C_2B_5H_7$/Li[N$(C_2H_5)_2$] (0.25 and 0.17 mmol, respectively) dissolved in 1.5 mmol of deuteriated acetonitrile, the

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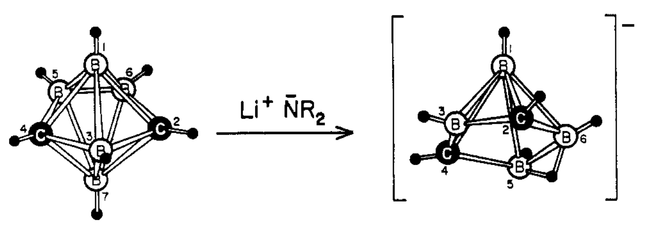

closo-2,4-$C_2B_5H_7$ nido-2,4-$C_2B_4H_7^-$

Figure 1. Conversion of *closo*-2,4-$C_2B_5H_7$ to [*nido*-2,4-$C_2B_4H_7$]$^-$.

^{11}B NMR spectrum after 12 days at room temperature exhibits the resonances of $C_2B_5H_7$[6] (19%), [*nido*-2,4-$C_2B_4H_7$]$^-$ (38%), and compound A (33%) (^{11}B NMR: $\delta(^{11}B)$ −39.1 (area 1), J(BH) = 152 Hz; δ +7 (d, area 2); δ +21.3 (d, area 1); δ +48.4 (area 1)); the remainder of the boron resonances in the NMR spectrum could not be assigned but were present as small peaks in the regions of δ +27 (broad), +29 (d), and +12. A monitoring of the ^{11}B NMR spectra over the next 3 months revealed a gradual disappearance of both $C_2B_5H_7$ and compound A coupled with a buildup of [2,4-$C_2B_4H_7$]$^-$.

(c) With Li[N(CH(CH_3)$_2$)$_2$]. In a manner similar to that described in section a, Li[N(CH(CH_3)$_2$)$_2$] (Aldrich, 0.23 mmol), *closo*-2,4-$C_2B_5H_7$ (0.15 mmol), and CH_3CN (1.5 mmol) were mixed. The sample slowly turned to a clear yellow-orange liquid, with no solids present. After the sample was kept at room temperature for 4.5 h, a ^{11}B NMR spectrum indicated the presence of (a) [*nido*-2,4-$C_2B_4H_7$]$^-$ (40%) (^{11}B NMR: δ(B(1)) −52.5, J(BH) = 157 Hz; δ(B(3)) +20.9, J(BH) = 121 Hz; δ(B(5,6)) +0.8, J(BH) = 125 Hz),[1,2] (b) starting material, *closo*-2,4-$C_2B_5H_7$[6] (51%), compound A (4%) (^{11}B NMR: δ −39.5 (d), J = 154 Hz; δ +7 (d); δ +21 (d); δ +47 (d, broad)), and an assortment of small resonances (accounting for ca. 4% of total boron) appearing in the regions of δ +27 (broad), +12, −5 to −20, −47, and −54. After 26 h at room temperature the percentages of each compound were as follows: $C_2B_5H_7$, 37%; [2,4-$C_2B_4H_7$]$^-$, 54%; compound A, 3%; an assortment of small resonances (accounting for ca. 5% of total boron) appearing in the regions of δ +27 (broad), +11, −5 to −20, and −47 (d). After 16 days at room temperature the major change observed in the ^{11}B spectrum was that the ratio [2,4-$C_2B_4H_7$]$^-$:$C_2B_5H_7$ had increased to 2.3.

Discussion

It is well-known that alkoxide/alcohol mixtures can convert isomers of *closo*-$C_2B_{10}H_{12}$ to isomers of the [*nido*-$C_2B_9H_{12}$]$^-$ ion according to eq 1.[7-12] Unfortunately, all attempts to use alkoxide/alcohol mixtures for the $C_2B_5H_7 \rightarrow [C_2B_4H_7]^-$ conversion were unsuccessful,[13] and only cage decomposition products of the type experienced when ROH alone was utilized as the reagent[14] were generally observed (e.g. $B(OR)_3$, $CH_3B(OR)_2$, $(RO)_2BCH_2B(OR)_2$).

$$closo\text{-}C_2B_{10}H_{12} + RO^- + 2ROH \rightarrow [C_2B_9H_{12}]^- + B(OR)_3 + H_2 \quad (1)$$

The conversion of *closo*-2,4-$C_2B_5H_7$ to [*nido*-2,4-$C_2B_4H_7$]$^-$ (Figure 1) can be accomplished, however, with the use of Li[N(R)$_2$], R = CH_3, C_2H_5, CH(CH_3)$_2$, as the reagent and acetonitrile as the solvent. The stoichiometry for the reaction appears to be somewhat greater than 1:1 Li[N(R_2)]:$C_2B_5H_7$. The conversion of *closo*-2,4-$C_2B_5H_7$ to [*nido*-2,4-$C_2B_4H_7$]$^-$ is nearly quantitative at room temperature, but during the course of the reaction at least two intermediates are seen in the ^{11}B NMR spectrum. Neither of these two intermediates is normally found in high percentage at any time during the reaction. Both of these intermediates exhibit a high-field doublet in the region of δ −45 to −50, very reminiscent of an apical boron for open-face pyramidal systems.[6] In one of these intermediates (arbitrarily called compound A in the Experimental Section) two sets of ^{11}B NMR BH doublets in a ratio of 2:1 are seen in the midfield region expected for the basal-situated borons of such a pyramid; a somewhat broadened boron resonance, which sharpens to a measurable extent upon proton decoupling, is observed downfield in a region that is consistent with a "non"-cage boron but one that could well be attached, in a bridging environment,[15] to two atoms of the pentagonal base (e.g. borons 5 and 6). A definitive structure cannot be assigned at this time, but it is highly possible that compound A is [($\mu^{5,6}$-R_2NBH)-*nido*-2,4-$C_2B_4H_6$]$^-$, displayed in Figure 2. The structure of the other intermediate, never present in quantities greater than for compound A, is more difficult to assess, but from the appearance of a high-field BH doublet, assignable to a boron in an apical environment of a pyramidal-shaped compound (see above), it could well represent further progress of the reaction to eventually give [*nido*-2,4-$C_2B_4H_7$]$^-$.

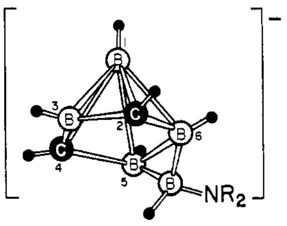

Figure 2. Plausible structure for compound A, [($\mu^{5,6}$-R_2NBH)-*nido*-2,4-$C_2B_4H_6$]$^-$.

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Registry No. A (R = CH_3), 116303-14-1; A (R = C_2H_5), 116303-15-2; A (R = CH(CH_3)$_2$), 116303-16-3; *closo*-2,4-$C_2B_5H_7$, 20693-69-0; [*nido*-2,4-$C_2B_4H_7$]$^-$, 39394-97-3; Li[N(CH_3)$_2$], 3585-33-9; Li[N(C_2H_5)$_2$], 816-43-3; Li[N(CH(CH_3)$_2$)$_2$], 4111-54-0.

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Comments on the Crystal Structure of Tetrabutylammonium Bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)nickelate(III)

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There has been considerable interest in transition-metal complexes of dithiolenes and dithiolates, which promise to add to our knowledge of low-dimensional highly conducting materials.[1-8] We, for example, have reported the synthesis of a new 1,2-dithiolene, 5,6-dihydro-1,4-dithiin-2,3-dithiolate, which when reacted with Ni(II) salts yields a complex whose structure is remarkably similar to BEDT-TTF in the rhenate salt.[9] We had undertaken a study of the effects of cations on the intermolecular contacts

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