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Unusual stability of the coordinated triethylborohydride anion in an alkaline-earth metal complex: crystallographic characterization of $[Ca(HBEt_3)\{1,2,4\text{-}C_5(SiMe_3)_3H_2\}(thf)_2]$

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The triethylborohydride anion $[HBEt_3]^-$ transfers intact from $Na[HBEt_3]$ to a calcium center to form the monomeric organocalcium complex $[Ca(HBEt_3)\{1,2,4\text{-}C_5(SiMe_3)_3H_2\}(thf)_2]$, which is stable in solution and the solid state; the $[HBEt_3]^-$ anion is coordinated in a multidentate fashion to the metal, which likely contributes to the failure of attempts to abstract the triethylborane moiety from the compound.

Owing to its exceptional nucleophilicity and selectivity, the triethylborohydride anion ($[HBEt_3]^-$) has found extensive use in organic, organometallic, and materials chemistry as a reducing agent and hydride source.[1–5] Study of the structure and bonding of the $[HBEt_3]^-$ anion itself is complicated by its high reactivity; it is usually encountered only in the form of its Group 1 (Li–K) salts, and is rarely incorporated into complexes containing other metals.[6–8] When the latter is the case, the stability of the resulting compounds may not be high; the organolanthanide species $[Sm(C_5H_4Bu^t)_2(HBEt_3)(thf)_2]$[7] and $[Nd(C_5H_4Bu^t)_2(HBEt_3)]$,[8] for example, cannot be removed from solution without decomposing. We have been interested in the $[HBEt_3]^-$ anion as a synthon for molecular main-group element hydrides, and in the course of this work discovered the unusual stability and structural features of the triethylborohydride anion in a Group 2 complex.

Parallels between the structure and reactions of the heavier Group 2 and divalent lanthanide elements[9] suggest that an alkaline-earth mono(cyclopentadienyl) halide might serve as a precursor to an organometallic hydride by metathetical reaction with an appropriate hydride source.[10,11] To examine this possibility, the iodide-bridged dimer $\{Ca(\mu\text{-}I)[1,2,4\text{-}C_5(SiMe_3)_3H_2](thf)\}_2$[12] was allowed to react in toluene with $Na[HBEt_3]$; removal of the NaI precipitate and evaporation of the filtrate left an air- and moisture-sensitive white solid that could be recrystallized from thf and was characterized as the triethylborohydride complex $[Ca(HBEt_3)\{1,2,4\text{-}C_5(SiMe_3)_3H_2\}(thf)_2]$ **1**.†

Spectroscopic evidence indicates that the $[HBEt_3]^-$ anion in **1**, which has transferred intact from Na^+, is involved in a bridging $Ca{\cdot\cdot}H{\cdot\cdot}BEt_3$ interaction. A prominent B–H stretch occurs at 1935 cm^{-1} (KBr) in the IR spectrum, in the region associated with μ-BH bonds.[13] This vicinity is where $\nu(BH)$ appears in $M[HBEt_3]$ salts [1870, 1835 and 1950 cm^{-1} for M = Li (KBr), Na (cyclohexane) and K (toluene), respectively].[14] The ^{11}B NMR resonance (δ −13.3 in C_6D_6; $J_{B\text{–}H}$ 50 Hz) of **1** is characteristic of a bridging BH contact (*cf.* 60–90 Hz for $J_{B\text{–}H_b}$ in transition metal examples),[15] and is also similar to that of $Na[HBEt_3]$ (δ −12.5; $J_{B\text{–}H}$ 50 Hz).[16]

An X-ray diffraction study of **1** provided the first details of the bonding of the triethylborohydride anion to an element other than a Group 1 metal.‡ The compound crystallizes from thf as a monomer, with the calcium center surrounded by a $[\eta^5\text{–}C_5(SiMe_3)_3H_2]^-$ ring, two thf molecules and the $[HBEt_3]^-$ ligand (Fig. 1). The average Ca–C(ring) and Ca–ring centroid distances of 2.707(9) and 2.42 Å in **1** are comparable to those in $\{Ca(C_5Pr^i{}_4H)[C\equiv CPh](thf)\}_2$ [2.713(15) and 2.43 Å, respectively],[17] which contains a formally seven-coordinate Ca^{2+} center.

In **1**, the calcium–carbon distances reflect the multidentate ligation of the triethylborohydride anion to the metal. The hydrogen atom on B(1) was located from difference maps and successfully refined, with B(1)–H(1) and Ca(1)–H(1) distances of 1.13(4) and 2.21(4) Å, respectively, and a Ca(1)–H(1)–B(1) angle of 110(2)°. These values are similar to those observed for the $[HBEt_3]^-$ anion in, for example, the dimeric complex $[Nb_2(\text{hexahydropyrimido}\{1,2\text{-}a\}\text{pyrimidinate})_4{\bullet}NaHBEt_3]$ (B–H 1.24, Na···H(B) 2.17 Å; Na–H–B 108°).[18] In **1**, the niobium dimer, and in related compounds such as $[Pd_2(dippp)_2H_2]{\bullet}[(Li,Na)(BEt_4)]$ [dippp = 1,3-bis(diisopropylphosphino)propane][19] and $[TaH_5(dmpe)_2]{\bullet}[LiBEt_4]$,[20] there is a close contact between the metal center and a methylene hydrogen on one or more ethyl groups. In **1**, the methylene hydrogen positions are calculated from the carbon atom locations, so the $Ca{\cdot\cdot}H(\alpha\text{-}C)$ distance is not as reliable as is the $Ca{\cdot\cdot}H(B)$ separation. Even so, the $Ca{\cdot\cdot}H(25a)$ contact in **1** (2.41 Å)

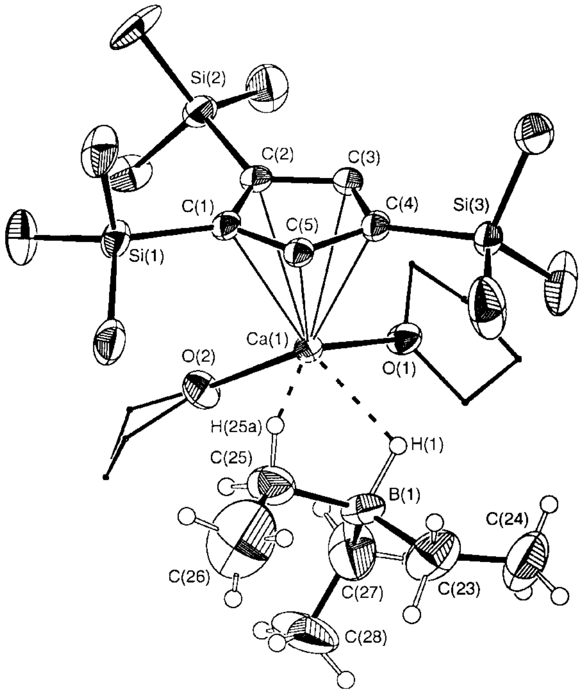

Fig. 1 ORTEP diagram of $[Ca(HBEt_3)\{1,2,4\text{-}C_5(SiMe_3)_3H_2\}(thf)_2]$ **1**. The trimethylsilyl groups on C(1) and C(2) were found to be disordered; for clarity, only one conformation for each is shown. Selected bond distances (Å) and angles (°): Ca(1)–C(1) 2.733(4), Ca(1)–C(2) 2.764(4), Ca(1)–C(3) 2.685(4), Ca(1)–C(4) 2.676(4), Ca(1)–C(5) 2.679(4), Ca(1)–C(19) 2.84(2), Ca(1)–O(1) 2.386(3), Ca(1)–O(2) 2.367(3), B(1)–C(23) 1.629(9), B(1)–C(25) 1.629(8), B(1)–C(27) 1.610(8), B(1)–H(1) 1.13(4); O(1)–Ca(1)–O(2) 86.3(1), Ca(1)–H(1)–B(1), 110(2).

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appears to be structurally significant, and the triethylborohydride group should be regarded as binding through both H(1) and H(25a).

The triethylborohydride anion in **1** proves to be remarkably robust, and several approaches to removing the BEt_3 moiety from **1** have been unsuccessful. For example, no reaction is observed with the competing base PMe_3 in toluene, and refluxing a solution of **1** in toluene leads to decomposition and the formation of the metallocene $[Ca\{\eta^5\text{-}1,2,4\text{-}C_5(SiMe_3)_3H_2\}]$.[21] The bidentate bonding of the $[HBEt_3]^-$ anion to the calcium evidently strengthens the attachment of the BEt_3 fragment.

Several features of the complex are worth noting. (i) The similarity of the bonding arrangement of the triethylborohydride anion in **1** to complexes of the alkali metals may indicate that this is its typical ligation geometry to highly electropositive metals. The structure of **1** may thus serve as a model for the triethylborohydride complexes of the lanthanide elements, which have yet to be structurally characterized.[6–8]

(ii) The resistance of the BEt_3 moiety to removal from **1** may stem from several factors. Heavy organoalkaline-earth complexes containing the bulky 1,2,4-tris(trimethylsilyl)cyclopentadienyl ligand are kinetically stabilized against ligand redistribution,[12] and the presence of the thf ligands enables **1** to remain coordinately saturated without having to oligomerise. These structural features combined with the bidentate ligation of the $[HBEt_3]^-$ ion probably leave it without a facile pathway for decomposition. Knowledge of these bonding requirements may help in the use of the triethylborohydride anion with other metals.

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Notes and references

† To a flask with $\{Ca(\mu\text{-}I)[1,2,4\text{-}C_5(SiMe_3)_3H_2](thf)\}_2$ (0.331 g, 0.64 mmol) dissolved in 50 mL of toluene was added a solution of $Na[HBEt_3]$ (0.64 mL of a 1.0 M solution in toluene, 0.64 mmol) at room temperature. The reaction mixture was stirred for 30 min before filtration, and the filtrate evaporated to dryness. Recrystallisation of the crude product from thf led to $[Ca(HBEt_3)\{1,2,4\text{-}C_5(SiMe_3)_3H_2\}(thf)_2]$ as air-sensitive, colorless crystals (0.285 g, 79%), mp 152 °C. Anal. Calc. for $C_{28}H_{61}BCaO_2Si_3$: C, 59.53; H, 10.88. Found: C, 58.18; H, 10.61%. The low value for carbon probably reflects the high air-sensitivity of the compound and/or partial loss of coordinated thf. Note for $[Ca(HBEt_3)\{1,2,4\text{-}C_5(SiMe_3)_3H_2\}(thf)]$: C, 58.49; H, 10.84%. ^1H NMR (300 MHz, thf-d_8, 20 °C): δ −0.03 (br, 6H, CH_2CH_3), 0.20 [s, 9H, $Si(CH_3)_3$], 0.27 [s, 18H, $Si(CH_3)_3$], 0.79 (t, ^3J 7.5 Hz, 9H, CH_2CH_3), 6.85 (s, 2H, ring-C*H*). ^{13}C NMR (75.5 MHz, thf-d_8, 20 °C): δ 1.0 [s, 1C, $Si(CH_3)_3$], 2.5 [s, 2C, $Si(CH_3)_3$], 12.7 (s, 3C, CH_2CH_3), 122.7 [s, 1C, ring-*C*$Si(CH_3)_3$], 127.8 [s, 2C, ring-*C*$Si(CH_3)_3$], 132.4 (s, 2C, ring-CH). No signal was observed from the carbon atoms on the boron. Principal IR bands (KBr, cm^{-1}): 2952 vs, br, 2898s, 1935m, br, 1456m, 1427m, 1407m, 1250vs (sh), 1089ms, 1062ms 1024ms, 979m, 831vs, br, 753s sh, 688m.

‡ *Crystal data* for $C_{28}H_{61}BCaO_2Si_3$ **1**: $M = 564.93$, orthorhombic, $a = 22.306(2)$, $b = 19.9944(9)$, $c = 16.009(2)$ Å, $U = 3568.9(6)$ Å^3, $T = 173 \pm 2$ K, space group $Pna2_1$ (no. 33), $Z = 4$, μ(Mo-Kα) = 0.297 mm^{-1}, 24468 reflections measured, 6321 unique ($R_{int} = 0.055$) which were used in all calculations. The final $wR(F^2)$ was 0.1316 (all data) and 0.1175 [for 4440 reflections with $I > 2.0\sigma(I)$]. Single crystals of **1** were grown from toluene, attached to the tip of a 0.1 mm diameter glass capillary and transferred to the cold gas stream of a diffractometer at the University of Minnesota. The structure was solved using a combination of direct methods and Fourier difference maps, and refined by full-matrix least squares on F^2. CCDC 182/1544. See http://www.rsc.org/suppdata/cc/a9/a908674i/ for crystallographic files in .cif format.

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