dioactive, luminescent DNA probe in both heterogeneous and homogeneous assays.

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Synthesis and Characterization of the First Example of a Metallacarborane That Incorporates an Alkaline-Earth Metal: The Molecular Structure of *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$[1]

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The organometallic chemistry of the alkaline-earth metals has received particular attention in recent years.[2-10] In this context, high yield synthesis routes to the cyclopentadienyl[2-8] and cyclooctatetraenediyl[10] complexes of calcium, strontium, and barium have been developed and the molecular structures of $(C_5Me_5)_2Ba$,[6] $(C_5H_5)_2Ca$,[2] $[(C_5Me_5)Ca(\mu\text{-}I)(THF)_2]_2$,[9] and $[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2M(THF)$[8] (M = Ca or Sr) have been established crystallographically. The desolvated species possess polymeric structures in the solid state [for example, $(C_5Me_5)_2Ba$[6] and $(C_5H_5)_2Ca$[2]], are monomeric in the gas phase [for example, $(C_5Me_5)_2M$ (M = Ca,[3,5] Sr,[11] or Ba[11])], and the solvated species are either dimeric or monomeric in the solid state.[8,9] However, there is no previous report of a discrete metallacarborane cluster that incorporates an alkaline-earth metal. We here report the high-yield synthesis and characterization of such a metallacarborane as well as the molecular structure of the novel calcium carborane complex, *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$, the first structurally authenticated example of an alkaline-earth metallacarborane.

The addition of THF solutions of Na_2[*nido*-7,9-$C_2B_{10}H_{12}$][1,12] to THF solutions of CaI_2 at room temperature over a period of 0.5 h affords a colorless complex, which is insoluble in THF but soluble in other coordinating solvents such as MeCN or DMF. Recrystallization of this complex from $MeCN/Et_2O$ produces colorless needle-like crystals; the X-ray study showed it to have the formulation $Ca(C_2B_{10}H_{12})(MeCN)_4$ (**1**).[13] The complex **1** is extremely air- and moisture-sensitive. The presence of the [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ fragment in the complex **1** is supported by the fact that the known [*nido*-9,12-$C_2B_{10}H_{13}]^-$ (^1H and ^{11}B NMR, vide infra) is produced upon exposure to moisture/H_2O.[14-16] Complex **1** serves as a source of [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ by its reaction with $YbI_2(MeCN)_2$ in MeCN to afford the known[17] *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$YbC_2B_{10}H_{12}$ in quantitative yield.

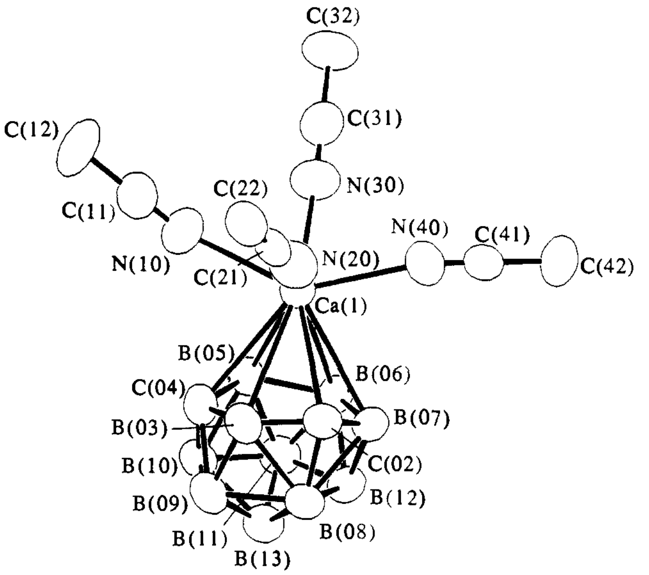

Figure 1. The molecular structure of *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$ (**1**). All hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Ca(1)–N(10), 2.471 (5); Ca(1)–N(20), 2.431 (5); Ca(1)–N(30), 2.476 (5); Ca(1)–N(40), 2.508 (5); Ca(1)–C(2), 2.701 (5); Ca(1)–B(3), 2.879 (6); Ca(1)–C(4), 2.895 (5); Ca(1)–B(5), 2.649 (6); Ca(1)–B(6), 2.828 (6); Ca(1)–B(7), 2.935 (6); C(2)–B(3), 1.518 (7); C(2)–B(7), 1.515 (7); C(2)–B(8), 1.734 (7); C(2)···B(9), 2.789 (7); C(2)···B(12), 2.814 (8); C(4)–B(3), 1.638 (8); C(4)–B(5), 1.701 (7); C(4)–B(9), 1.692 (8); C(4)–B(10), 1.691 (7); B(3)···B(8), 2.037 (9); B(3)–B(9), 1.840 (8); B(3)···B(10), 2.935 (8); B(5)–B(6), 1.739 (7).

The molecular structure[18] of **1** is illustrated in Figure 1, along with selected interatomic distances. The calcium atom asymmetrically caps the open puckered hexagonal face of the [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligand. Four acetonitrile ligands are bonded to the calcium atom. The Ca–N bond distances range from 2.43 to 2.51 Å, and calcium–carborane distances fall in the range 2.65–2.94 Å. The Ca(1)–C(2) distance of 2.70 Å compares very well with that reported for the complexes $[C_5H_3$-1,3-

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(1) Numbers accompanying formulas refer to the positions of the heteroatoms within the *closo*-metallacarborane framework and to the location of the exopolyhedral substituents. Lowest numbers consistent with the molecular geometry are given to carbon in accordance with the inverse periodic order adhered to by the IUPAC Inorganic Nomenclature Committee (see: Adams, R. M. *Pure. Appl. Chem.* **1972**, *30*, 683). The numbering system used for the *nido*-carborane anions described herein is identical with that previously employed (see: Dustin, D. F.; Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 1109).

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(13) Data for **1**: IR (Nujol mull, NaCl) ν_{B-H} 2466 (s), 2419 (s, br), ν_{MeCN} 2302 (m), 2273 (s) cm^{-1}; ^1H NMR (CD_3CN, 20 °C, ppm) 4.12 (s, br, carboranyl C–H); ^{11}B NMR (in MeCN, 20 °C; chemical shifts referenced to external $BF_3 \cdot OEt_2$; peaks upfield of the reference are designated as negative; areas given in parentheses) 2.2 (4), $^1J_{BH}$ = 103 Hz, –6.4 (3), $^1J_{BH}$ = 147 Hz, –17.6 (3), $^1J_{BH}$ = 130 Hz. Anal. Calcd for $C_{10}H_{24}B_{10}N_4Ca$: C, 34.48; H, 6.89; N, 16.09. Found: C, 30.09; H, 7.38; N, 13.30. These values are better suited to $C_8H_{21}B_{10}N_3Ca$, which contains one less MeCN per molecule. Calcd for $C_8H_{21}B_{10}N_3Ca$: C, 31.27; H, 6.84; N, 13.68. We have not been able to obtain satisfactory elemental analyses of **1** due to facile loss of a MeCN ligand during analytical sample preparation. Loss of coordinated solvent molecules from organoalkaline-earth metal complexes is common (refs 3, 4, and 6).

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(18) Crystal data: $C_{10}H_{24}B_{10}N_4Ca$, monoclinic, $P2_1/n$, $a = 8.6985$ (7) Å, $b = 15.825$ (1) Å, and $c = 15.423$ (2) Å, $\beta = 90.106$ (3)°, $V = 2123$ Å^3, $Z = 4$, μ(Cu Kα) = 25.1 cm^{-1}, D(calcd) = 1.05 g cm^{-3}, $T = 298$ K, $\lambda = 1.5418$ Å, colorless needle specimen, 0.15 × 0.25 × 0.65 mm. A crystal obtained from $MeCN/Et_2O$ solution was sealed in a capillary on a modified Syntex $P\bar{1}$ diffractometer. Data were collected at 298 K in the θ–2θ scan mode. Of the 2177 unique reflections measured, 1676 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. The final discrepancy index was $R = 0.050$, $R_w = 0.070$, GOF = 2.55; $\Delta(\rho) = 0.2$ e Å^{-3}.

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(SiMe$_3$)$_2$]$_2$Ca(THF)[8] [average Ca–C(η^5) distance 2.68 Å] and [(C$_5$Me$_5$)Ca(μ-I)(THF)$_2$]$_2$[9] [average Ca–C(η^5) distance 2.67 Å], but is shorter than that found in the polymeric complex[2] (C$_5$H$_5$)$_2$Ca [average Ca–C(η^5) distance 2.80 Å].

The interatomic distance B(3)···B(8) in **1** is 2.037 (9) Å and is somewhat shorter than the distance 2.166 Å found in the complex 1,1-(PPh$_3$)$_2$-1-H-1,2,4-RhC$_2$B$_{10}$H$_{12}$,[19] but is more comparable to the distance 2.082 Å found in the complex 1-(η-C$_5$H$_5$)-1,2,4-CoC$_2$B$_{10}$H$_{12}$.[20] The B(9)···C(2) distance is 2.789 (7) Å and is somewhat longer than the distance 2.720 Å found in the complex 1,1-(PPh$_3$)$_2$-1-H-1,2,4-RhC$_2$B$_{10}$H$_{12}$.[19] The C(2)···B(12) distance is 2.814 (8) Å and is nearly the same (2.841 Å) as found in the complex 1,1-(PPh$_3$)$_2$-1-H-1,2,4-RhC$_2$B$_{10}$H$_{12}$.[19] The B(3)···B(10) distance is 2.935 (8) Å, nearly identical with the distance 2.938 Å found in the complex 1,1-(PPh$_3$)$_2$-1-H-1,2,4-RhC$_2$B$_{10}$H$_{12}$.[19] The four boron atoms in the top belt (bonding face) of **1** are essentially coplanar (within 0.03 Å) with C(2) lying above (0.277 Å) and C(4) lying below (0.227 Å) this plane. The five boron atoms of the lower belt are coplanar (within 0.07 Å). The planes defined by the top and the bottom belt are nearly parallel (3.4° between their normals).

The molecular structure of **1** raises a number of questions concerning the nature of the interaction of the calcium atom and the carborane unit. The IR spectrum of **1** in the solid state exhibits two broad B–H stretching bands (split pattern), one centered at 2466 cm^{-1} and another at 2419 cm^{-1}. This pattern has previously been observed in lanthanacarborane complexes, viz., *closo*-1,1,1,1-(THF)$_4$-1,2,3-LnC$_2$B$_9$H$_{11}$ and *closo*-1,1,1,1-(THF)$_4$-1,2,4-LnC$_2$B$_{10}$H$_{12}$ (Ln = Sm or Yb), in which the bonding of the metal atom to the carborane fragment is believed to be largely ionic in nature.[17,21] The origin of IR band "splitting" in *closo*-1,1,1,1-(THF)$_4$-1,2,3-LnC$_2$B$_9$H$_{11}$ (Ln = Sm or Yb) was elucidated by selective deuteration of the carborane cage, and the corresponding deuterated lanthanacarboranes, *closo*-1,1,1,1-(THF)$_4$-1,2,3-LnC$_2$B$_9$H$_9$D$_2$ [Ln = Sm (**2**) or Yb (**3**)], were prepared.[17,22] In these deuterated complexes the two nonadjacent borons [B(4) and B(6)] in the upper belt are bound to deuterium and should exhibit a characteristic low-frequency B–D stretch in the IR spectrum. The solid-state IR spectra of both **2** and **3** indeed exhibited an absorption at ca. 1839 cm^{-1} due to a terminal B–D stretch,[17] and there is a concomitant decrease in the intensity of the low-frequency branch of the terminal B–H absorption.[17] The ratio of ν(BH) to ν(BD) (using the low-frequency branch of the BH absorption) is 1.32 for both **2** and **3**. Given the consistency of ν(BH)/ν(BD) ratios[24] using the low-frequency absorption along with the observed decrease in intensity of this stretch due to deuteration, one may assign the low-frequency absorption to the B–H vertices of the top belt and the high-frequency absorption to the B–H vertices of the bottom belt and an apical B–H vertex.[17] Similar arguments can be used to assign the IR spectrum of **1** arising from B–H vertices of the lower belt combined with an apical B–H vertex at 2466 cm^{-1} and another at 2419 cm^{-1} due to B–H vertices of the top belt. It may be concluded from these IR correlations that in complexes **1**, **2**, and **3** strong ionic interactions exist between the cationic metal center and the anionic carborane unit.[26] However, with the data in hand it is impossible to ascertain the relative degree of covalent bonding present. We are currently exploring the chemistry of the alkaline-earth metals with other anionic carborane derivatives.

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Supplementary Material Available: Tables of crystallographic data collection, atom coordinates, bond distances and angles, and anisotropic thermal parameters for **1** (6 pages); table of observed and calculated structure factors for **1** (8 pages). Ordering information is given on any current masthead page.

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Determination of the Torsional Potential of Allene from Highly Excited Torsional Vibrations Observed by Ultraviolet Resonance Raman Spectroscopy: The Torsional Barrier of Cumulenes

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Resonance Raman spectra of ethylene obtained with excitation in the region of the $\pi\pi^*$ N → V transition exhibit considerable intensity in high-level overtone transitions of the torsional mode.[1-3] The frequencies of these transitions follow a remarkably simple pattern, and thus from data of this type it is possible to determine the parameters of a potential energy function representing the torsional motion.[1,4] This is of interest because of the intrinsic importance of the prototypical π-bond, the relevance of this potential to the isomerization reaction of ethylene,[5] and because of the challenge that these data present to quantum chemical theory.

We have now applied the ultraviolet resonance Raman technique[6-8] to allene, H$_2$C=C=CH$_2$. We also observe highly excited torsional excitations. The experimental methods used are described elsewhere.[2,6] The results to be presented here demonstrate the general utility of this technique for observing highly excited torsional excitations of alkenes.

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