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[21] Aliphatic hydrocarbons are usually used as the polymerization medium for industrial Ziegler–Natta polymerization in solution or slurry. Compared to toluene aliphatic hydrocarbons offer advantages in the isolation of the polymer (separation, purification, drying).
[22] The polymerization tests described in refs. [3a–x] were carried out with cationic metallocenes are usually terminated after a few minutes. To determine the activity the yield of polymer is extrapolated to a polymerization time of 1 h. Conclusions concerning the actual life time of the active catalytic species are not possible.
[23] For bulk and gas-phase polymerization homogeneous metallocene catalysts are usually used immobilized on a support (e.g., silica gel). To date there are only a few examples of supported, MAO-free metallocene catalysts with noncoordinating anions (supported metallocene catalysts; see for example, *Metalorganic Catalysts for Synthesis and Polymerisation* (Ed.: W. Kaminsky), Springer, New York, **1999**, pp. 307–431). In the polyborates of the type **Va–c** the noncoordinating anions are fixed to a "dendrimer surface". Dendrimers have various advantages over standard supports: defined molecular size, monodispersed particle-size distribution, an easily accessible surface, and a controllable number of catalytic centers.
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The First Barium–Carborate Complex: Synthesis and Structural Investigation[**]

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Of all the metallaboranes the Group 1 compounds are some of the most often encountered, in that they are common starting materials in the syntheses of higher order heteroborane clusters. Although, there is no evidence as to the role of the Group 1 metal in their reactions with other metal reagents, it has generally been assumed that they do not play an active role.[1] The Group 1 metallacarboranes are also the most common precursors in the syntheses of the p-, d-, and f-block metallacarboranes. There seems to be a more direct metal involvement with the smaller, C_2B_4 cages.[1c,d] For example, the structure of the dilithium compound shows that one [(tmeda)Li] unit (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) occupies the apical position above the C_2B_3 face of the carborane, with the other solvated Li atom being *exo*-polyhedrally bound through two B–H bridges.[2] While assignment to a *closo*-carborane is consistent with both the structure and the cage electron pair count of eight, it is not apparent that the $[(tmeda)Li]^+$ ion is in any way isolobal with a B–H group; the apical position might simply be that favored by electrostatic interactions. The compound could alternatively be described as a half-sandwich lithium complex in which the *nido*-carborane dianion is η^5-bonded to the capping Li atom. The structures of several Group 1 compounds in the C_2B_4- and C_4B_8-carborane systems have been reported.[1c,d, 3] Structural information available on the Group 2 metal complexed boranes is not plentiful, and, with several notable exceptions, seems to be limited to the two smallest members of that group, beryllium and magnesium.[4–7] In contrast to the boranes, there have been a number of reports on the Group 2 metallacarboranes,[3] one reason being that a carbon plus a Group 2 element combination is isoelectronic with two boron atoms. This isoelectronic relationship led Popp and Hawthorne to explore the syntheses and properties of the beryllacarboranes in MC_2B_9 cage systems.[8, 9] While the structures of the beryllacarboranes could not be determined, the heavier Group 2 metals form structurally known metallacarboranes with the *nido*-$[7,9\text{-}C_2B_{10}H_{12}]^{2-}$ ligand.[10, 11] The 1,1,1,1-$(CH_3CN)_4$-*closo*-1,2,4-$CaC_2B_{10}H_{12}$ was the first structurally characterized Group 2 metallacarborane. The Ca ion, which is coordinated by four CH_3CN molecules, resides above the C_2B_4 face of the carborane. A similar reaction with SrI_2 produced the novel polymeric strontium carborane, [1,1,1-$(CH_3CN)_3$-*closo*-1,2,4-$SrC_2B_{10}H_{12}]_n$, whose structure shows a cage geometry similar to that of the calcium carborane, except that one of the solvating CH_3CN molecules is replaced by a set of Sr-H-X bridge bonds to a neighboring carborane, where X can be a boron atom on the lower belt of the carborane and a carbon atom on its C_2B_4 upper ring.[11] However, the magnesacarboranes were limited to the 2,3-C_2B_4 and 2,4-C_2B_4 cage systems. The reactions of their mono- and dianions with various magnesium reagents have been studied by Hosmane and co-workers and showed that contrasting results can be obtained from slight changes in the carborane and magnesium reagents.[12, 13] Nonetheless, there have been no reports on similar carborane complexation with the heaviest Group 2 metal, barium. Here we report the first barium half-sandwich complex of any carborane and/or borane cage systems of which we are aware. The reaction of tetrakis(tetrahydrofuran)barium bis[tris(trimethylsilylmethyl)zincate][14] (**1**) with 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane in THF yields nearly quantitatively barium bis(carborate) **2** (Scheme 1). Only one of the trimethylsilylmethyl groups of

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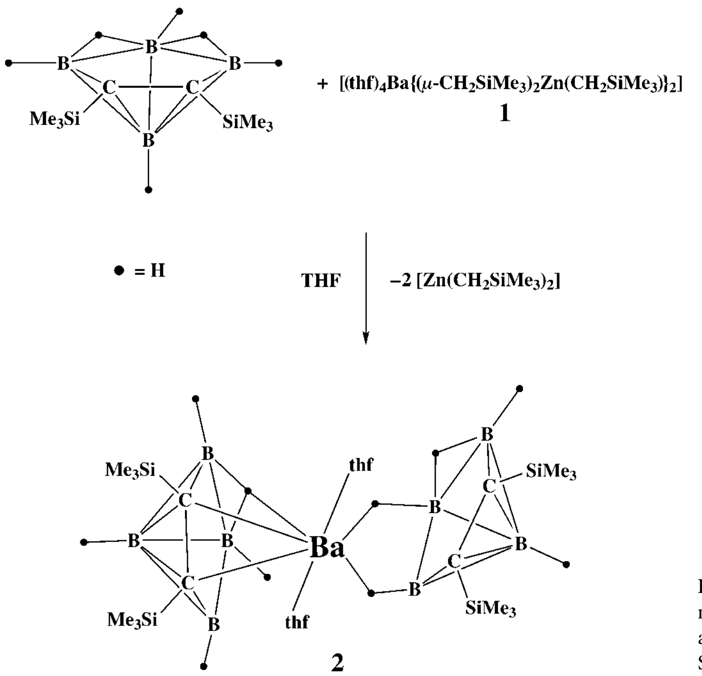
1433-7851/01/4010-1902 $ 17.50+.50/0



Scheme 1. Synthesis of barium bis(carborate) **2** by metalation of **1** with barium bis[tris(trimethylsilylmethyl)zincate] in THF.

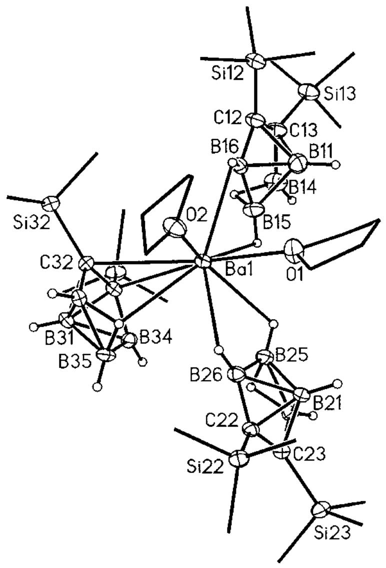


Figure 2. The coordination sphere of the barium center in **2**. The numbering of the H atoms corresponds to that of the respective boron atoms (H356 deontes the H atom that bridges the B atoms B35 and B36). Selected bond lengths [pm]: Ba1-O1 276.7(4), Ba1-O2 273.7(3), Ba1-C32 318.8(5), Ba1-C33 311.3(5), Ba1-H15 287(4), Ba1-H16 282(4), Ba1-H25 279(4), Ba1-H26 288(4), Ba1-H356 290(4).

the zincate is active in this metalation reaction. The resulting bis(trimethylsilylmethyl)zinc neither reacts with the carborane nor with **2**.

The molecular structure of dimeric **2** is shown in Figure 1. Each barium atom shows a coordination number of nine (Figure 2). The Ba–O bond lengths of approximately 274 pm lie in the expected region. Furthermore, two carborate ligands are bonded through hydride bridges with Ba–H distances of approximately 290 pm; these bridges were refined isotropically and can be interpreted as three-center Ba-H-B. A third carborate ligand is coordinated with Ba–C distances of 316 pm and the bridging hydrogen atom (Ba1–H356 293(4) pm). This situation corresponds to a four-center $BaHB_2$ bond. In the highly ionic solvated $Ba(BH_4)_2$ the boranate anions coordinate through three H atoms to the alkaline earth metal thus forming three-center Ba-H-B bonds.[15] The Ba–C distances are similar to those of the barium bis[tris(trimethylsilylmethyl)-zincates][14] (**1**), in which bridging trimethylsilylmethyl moieties between barium and zinc were found. The Ba–C distances of substituted barocenes vary between 290 and 300 pm.[16] This coordination of the carborate to the barium center is quite different to that observed for the carborate complexes of magnesium and calcium.[10–13] In the magnesacarborane complex the metal center bonds to the hydride substituents but not to the carbon atoms. With the doubly deprotonated carborane ligands the metal centers show shorter contacts to the boron than to the carbon atoms. In **2** very long Ba–B bonds are observed due to the coordination geometry about the metal center. Nevertheless, the baracarborane **2** is the first metallacarborane of the heaviest Group 2 metal.

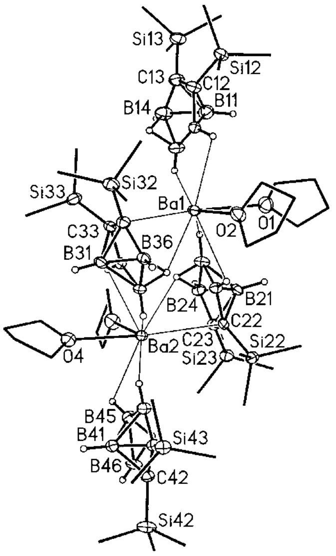


Figure 1. Molecular structure of barium bis(carborate) **2**. The ellipsoids of heavier atoms represent a probability of 40 %. The boron-bonded hydrogen atoms are drawn with arbitrary radii.

Experimental Section

All manipulations were carried out in an anhydrous argon atmosphere. The solvents were thoroughly dried and distilled under argon.

2: Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane (1.29 g, 5.88 mmol) was added dropwise to a solution of **1** (2.64 g, 2.44 mmol) in THF (15 mL). The solution was stirred at room temperature for several hours. Then all volatile materials were removed at room temperature under reduced pressure. The colorless residue was dissolved in toluene (10 mL). Cooling to −20 °C afforded the precipitation of colorless crystalline **2** (0.73 g, 1.78 mmol; 73 %); m.p. 185 °C (decomp). ^1H NMR ($[D_8]THF$): $\delta = 0.19$ (s, 18 H; $SiMe_3$), 1.78 (4 H; THF), 3.63 (4 H; THF); $^{13}C\{^1H\}$ NMR ($[D_8]THF$): $\delta =$ 2.52 (s; $SiMe_3$), 25.47(s; THF), 67.43(s; THF), 111.15 (br.s; SiCB); ^{11}B NMR ($[D_8]THF$): $\delta = -50.26$ (s, br., 1 B, $^1J(^{11}B,^1H)$ unresolved; BH_{apical}), −1.28 (br.s, 1 B, $^1J(^{11}B,^1H)$ unresolved; BH_{basal}); 14.62 (br.s, 2 B, $^1J(^{11}B,^1H)$ unresolved; BH_{basal}); $^{29}Si\{^1H\}$ NMR ($[D_8]THF$): $\delta = -7.20$; IR (Nujol, KBr): $\tilde{\nu} = 2589$ sh, 2579 s, 2556 sh, 2545 sh, 2535 sh, 2501 m, 2445 s, 2424 s, 2378 m, 1944 m, 1927 m, 1872 m, 1496 m, 1472 m, 1459 m, 1447 m, 1404 s, 1369 m, 1343 m, 1250 s, 1205 m, 1182 s, 1162 sh, 1073 m, 1035 s, 998 m, 987 m, 961 m, 931 s, 858 s, 841 sh, 834 vs, 753 s, 683 s, 664 sh, 626 m, 590 m, 524 m, 479 m, 413 s, 386 s, 373 m cm^{-1}; elemental analysis (%) calcd for $C_{24}H_{63}B_8BaO_2Si_4$ (718.912): C 40.10, H 8.69; found: C 38.04, H 8.47. X-ray structure determination:[17] Siemens P4 diffractometer with CCD imaging plate, 193 K, monoclinic, $P2_1/n$, $a = 2100.8(5)$, $b = 1886.5(5)$, $c =$ 2188.2(6) pm, $\beta = 111.893(5)^\circ$, $Z = 4$, 12938 symmetry-independent reflections, 783 parameters, $wR2(F^2) = 0.081$, $R1$ (7545 data with $I > 2\sigma(I)$) = 0.039. All non-hydrogen atoms were refined anisotropically, the B-bonded hydrogen atoms isotropically. All other H atoms were considered with the riding model.

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[17] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154161. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

$NSCl_2^-$: Thiazyl Dichloride—An Aza Analogue of Thionyl Dichloride**

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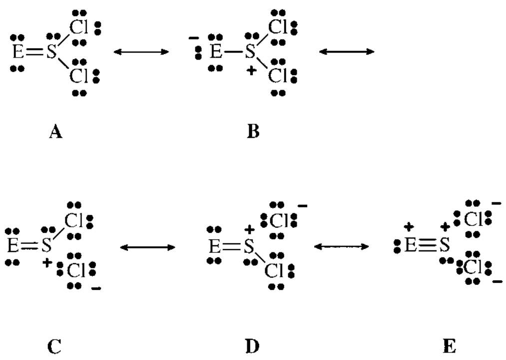
Formally, the $NSCl_2^-$ ion can be regarded as the isoelectronic aza analogue of thionyl dichloride ($OSCl_2$) with sulfur in the oxidation state +IV. $OSCl_2$ represents a highly polarized electron-rich species with a strong S–O bond and two labile S–Cl bonds (Scheme 1). Exchanging the oxygen atom for an N^- ion should result in S–Cl bonds which are further destabilized, and a strong N–S bond with a large amount of π character (bond order between 2 and 3).



Scheme 1. VB representation of $OSCl_2$ and $NSCl_2^-$ ($E = O, N^-$).

The $NSCl_2^-$ ion belongs to a new class of very labile ternary anions NSX_2^- (X = halogen) of which, to the best of our knowledge, no representative containing the "naked" anion has been structurally characterized[1] or synthesized in high yield. Most compounds containing the NSX_2 unit are stabilized by covalent interaction of the N atom with either a metal center, for example, $[Hg(NSF_2)_2]$[2–4] or organic groups as in $RNSCl_2$ ($R = R'C, R''SO_2, C_6F_5$, etc.).[5]

First we undertook a theoretical study of the acceptor properties of the Cl^- ion and the thermodynamics of NSCl. Ab initio (CCSD(T)) and density functional (B3LYP) calculations indicate a barrier-free attack of the Cl^- ion at the NSCl molecule resulting in the formation of the highly polarized $NSCl_2^-$ ion. This reaction represents an exothermic Lewis acid Lewis base reaction with an estimated molar enthalpy ΔH_{298} of $-124.6\ \mathrm{kJ\,mol^{-1}}$ and a charge transfer Q_{CT} of 0.385 e

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