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Synthesis and Crystal Structure of the First Polymeric Cesium Compound of a Carborane Ligand System[†]

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Summary: The reaction between a THF solution of $(SiMe_3)_4C_4B_8H_8$ (**1**) *and excess cesium metal, in the absence of either naphthalene or aromatic solvents, produced a paramagnetic intermediate that reacted further with cesium to give the EPR-silent species* [*exo*-$Cs(TMEDA)$-1-Cs-2,4,7,9-$(SiMe_3)_4$-2,4,7,9-$C_4B_8H_8$]$_n$ (**2**). *Single-crystal X-ray analysis showed* **2** *to be a polymeric structure in which each* C_4B_8 *carborane fragment serves as a ligand to two Cs atoms and is bonded to one through an open six-membered face and to the other via upper- and lower-belt M−H−E (where E = B, C) interactions.*

There has been considerable interest in the coordination chemistry of cesium metal. The emphasis for much of this work arises from the need to be able to remove radioactive cesium metal (^{137}Cs) from nuclear wastes, in the presence of high concentrations of other group 1 cations.[1,2] Recently, the use of macrocyclic agents,[3] such as the calix[4]arene crowns,[4] or self-assembled aggregates have shown promise.[5] It has also been found that cesium, and other group 1 metals, form stable complexes with the π system of carbazoles.[6] Group 1 metal−carborane interactions have been the subject of considerable interest in our laboratories for the past several years. We have reported the structures and reactivities of half-sandwich group 1 metallacarboranes of the form 1-M(L)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (M = Na, Li; L = THF, TMEDA)[7] and *exo*-4,5-[(μ-H)$_2$M(L)]-1-M(L)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (M = Na, Li; L = THF, TMEDA)[8] and the full-sandwich lithiacarborane [Li(TMEDA)$_2$]-[*commo*-1,1′-Li{2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$}$_2$].[9] Although cesium salts of both carboranes and metallacarboranes have been synthesized, and some have been used in cesium recovery,[10] the cesium ions are not part of the cage but are present as noninteracting counterions.[11] Therefore, very little is known of the coordination of cesium with the π electrons of carboranes. These results have led us to extend our studies of the group 1 metallacarboranes to include cesium. Herein, we report the synthesis and crystal structure of a polymeric, self-assembled cesium compound of the C_4B_8 carborane cage. To our knowledge, it represents the first example of a polyhedral organometallic compound of cesium metal.

As part of our study of the electron-acceptor behavior of carbon-rich carboranes, we have demonstrated that the C-$(SiMe_3)$-substituted 2,4,7,9-tetracarba-*nido*-dodecaborane(12) (**1**)[12] acts as a restricted electron acceptor by removing only the valence electrons of a single Li or Mg metal atom, even when a large excess of the particular metal is available, thus forming the corresponding 1:1 ionic products without the loss of any

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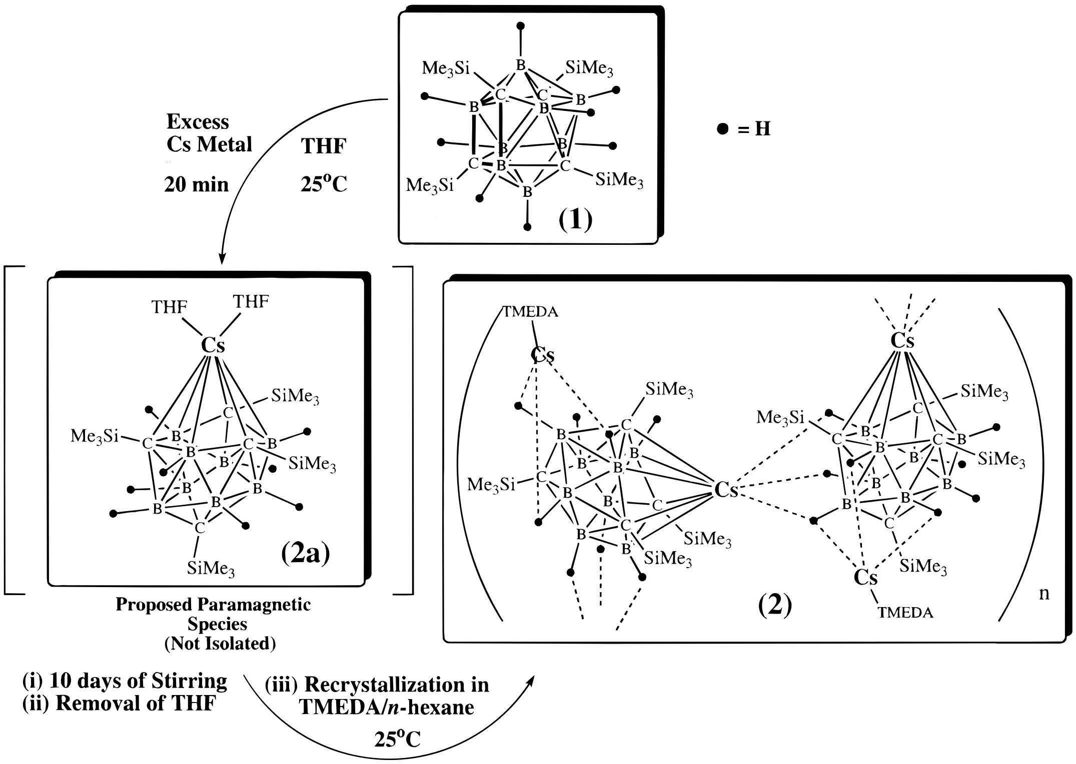
Scheme 1. Synthesis of the First Cesiacarborane Complex



metal- or cage-bound moieties.[13] This reduction of **1** was preceded by the work of Grimes and co-workers, who in the 1970s, showed that the carbons-adjacent $Me_4C_4B_8H_8$ carborane could be reduced by sodium metal to the corresponding mono- and dianion.[14] The X-ray crystal structure of the cobaltocenium derivative of the $[Me_4C_4B_8H_8]^{2-}$ dianion, $[(C_5H_5)Co(C_5H_4)(Me_4C_4B_8H_8)]$, showed that the carborane dianion had an arachno geometry.[14] However, the structures obtained from either the lithium or magnesium reactions were substantially different from those obtained by Grimes. Thus, it is difficult to project reasonable structures for other MC_4B_8 compounds. It was such considerations that prompted us to explore the reactivity of **1** toward excess cesium metal.[15] As depicted in Scheme 1, the initially formed compound (**2a**) was found to be EPR active. The isotropic *g* factor of 2.0030 for the partially resolved EPR spectrum is close to the free-electron value of 2.0023, indicating an ion pair situation with the spin residing predominantly in the carborane framework and not at the 5s metal.[15] When the reaction mixture was stirred over a period of 10 days followed by removal of THF and subsequent recrystallization of the resulting solid from an *n*-hexane/TMEDA solution, a novel polymeric cesium compound, identified as [*exo*-Cs(TMEDA)-1-Cs-2,4,7,9-$(SiMe_3)_4$-2,4,7,9-$C_4B_8H_8]_n$ (**2**), was produced as an EPR-silent transparent crystalline solid in 41% yield.[15]

Compound 2 was characterized by elemental analysis,[16] IR spectroscopy,[16] ^1H, ^{11}B, and ^{13}C NMR spectroscopy,[16] and X-ray crystallography.[17] The ^1H, ^{11}B, and ^{13}C NMR spectra of **2** show the presence of solvating TMEDA molecules, carborane cages, and C(cage)-bound $SiMe_3$ moieties. The ^{11}B NMR spectrum shows three doublets of 1:6:1 peak area ratio at δ −17.43, −29.03, and −42.5 ppm, which significantly differs from that

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(15) Synthetic procedure: A 1.06 mmol (0.46 g) sample of the C-$SiMe_3$-substituted 2,4,7,9-tetracarba-*nido*-dodecaborane(12), $(SiMe_3)_4C_4B_8H_8$ (**1**),[12] was reacted with a 4-fold molar excess of Cs metal in dry THF (30 mL) at room temperature, with constant stirring. The resulting colorless heterogeneous mixture turned to bright yellow-orange without any gas evolution. The EPR spectrum of this reaction mixture showed the presence of a paramagnetic species in which two equivalent boron nuclei in natural isotopic composition with $a(^{11}B)$ = 0.90 mT and one ^{133}Cs nucleus (a = 0.36 mT; $I = {}^7/_2$, 100% natural abundance) were coupled with the unpaired electron, the isotropic *g* value being 2.0030. After 30 min the reaction mixture turned to a light yellow with the formation of an off-white EPR-silent solid. After constant stirring for 10 days, the mixture was filtered in vacuo and the residue washed repeatedly with a 1:5 mixture of *n*-hexane and benzene until clear filtrate was collected. The unreacted cesium metal left on the frit (not measured) was recovered and used in subsequent experiments. After slow removal of the solvents from the filtrate, a slightly off-white residue was obtained, which when further purified by recrystallization from a 2:1 mixture of *n*-hexane and *N,N,N,N*-tetramethylethylenediamine (TMEDA) produced air-sensitive, transparent colorless crystals, identified as [*exo*-Cs(TMEDA)-1-Cs-2,4,7,9-$(SiMe_3)_4$-2,4,7,9-$C_4B_8H_8]_n$ (**2**; 0.352 g, 0.43 mmol; mp 260 °C dec) in 41% yield. The compound **2** is soluble in polar solvents but is less soluble in nonpolar organic solvents.

(16) Characterization of **2**: ^1H NMR (C_6D_6, relative to external Me_4Si) δ 2.39 (s, 4H, CH_2, TMEDA), 2.21 (s, 12H, Me, TMEDA), 0.31 (s, 9H, $SiMe_3$), 0.13 (s, 9H, $SiMe_3$), 0.01 (s, 18H, $SiMe_3$); ^{11}B NMR (C_6D_6, relative to external $BF_3{\cdot}OEt_2$) δ −17.43 (d, 1B, $^1J(BH)$ = 141 Hz, cage BH), −29.03 (d, v br, 6B, $^1J(BH)$ = unresolved, cage BH), −42.51 (d, 1B, $^1J(BH)$ = 125 Hz, cage BH); ^{13}C NMR (C_6D_6, relative to external Me_4Si) δ 57.71 (t, CH_2, TMEDA, $^1J(^{13}C-^1H)$ = 132 Hz), 45.82 (q, Me, TMEDA, $^1J(^{13}C-^1H)$ = 133 Hz), 2.19 (s, 2C, cage carbons (SiCB)), 1.89 (q(br, overlapping), $SiMe_3$, $^1J(^{13}C-^1H)$ = 120 Hz), 1.42 (q(br, overlapping), $SiMe_3$, $^1J(^{13}C-^1H)$ = 122 Hz), 0.55 (q(br, overlapping), $SiMe_3$, $^1J(^{13}C-^1H)$ = 119 Hz), −0.14 (s, 2C, cage carbons (SiCB)); IR (cm^{-1}, THF vs THF): 3013 (br, s), 2818 (br, m), 2692 (ms), 2556 (w), 2375 (w), 2294 (ms), 2227 (m), 2145 (w), 2095 (w), 1973 (vs), 1475 (vs), 1373 (ms), 1297 (ms), 1196 (vs), 1060 (br, s), 925 (br, s), 655 (vs), 528 (w), and 477 (m). Anal. Calcd for $C_{22}H_{60}B_8Si_4N_2Cs_2$: C, 32.33; H, 7.40, N, 3.43. Found: C, 32.58; H, 7.58; N, 3.51.

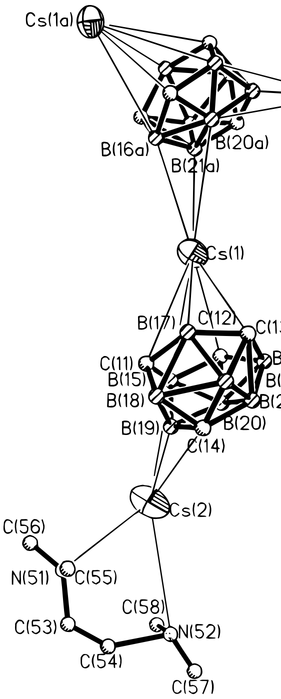

Figure 1. Perspective view of **2** with Cs atoms drawn at the 40% probability level. Pertinent distances (Å) and angles (deg): Cs(1)−C(11), 3.585(36); Cs(1)−C(12), 2.954(43); Cs(1)−C(13), 3.506(50); Cs(1)−B(15), 3.526(48); Cs(1)−B(16), 3.561(52); Cs(1)−B(17), 3.318(59); Cs(1)−C(33), 3.475(44); Cs(1)−C(36), 3.454(46); Cs(1)−C(39), 3.641(58); Cs(1)−B(16A), 3.441(52); Cs(1)−B(20A), 3.729(45); Cs(1)−B(21A), 3.751(52); Cs(1)−C(35A), 3.574(60); Cs(2)−B(15), 3.703(48); Cs(2)−B(19), 3.528(47); Cs(2)−B(20), 3.754(43); Cs(2)−C(34), 3.637(38); Cs(2)−N(51,52), 3.175(55), 3.639(72); Cs(2)−C(32A), 3.906(40), (see the Supporting Information, Tables S-2 and S-3, for detailed bond lengths and angles). For clarity, C(cage)−$SiMe_3$ groups are omitted. The Cs-bound TMEDA molecules and carborane cage atoms are drawn with circles of arbitrary radii.

found for the precursor **1** (a single resonance at δ −5.57 ppm)[12] and from those for the products of either the Li or the Mg reactions.[13] The uniqueness of the cesium compound was confirmed by its single-crystal X-ray analysis.[17] The X-ray diffraction study shows a polymeric structure of **2** in which a cesium is bonded to the open six-membered face of a C_4B_8 cage (Cs(1)−C(11,12,13) = 3.59(4), 2.95(4), 3.51(5) Å; Cs(1)−B(15,16,17) = 3.53(5), 3.56(5), 3.32(6) Å) and to a B_3 face of a neighboring carborane through a set of three unequal Cs−H−B bonds (Cs(1)−B(16a,20a,21a) = 3.44(5), 3.73(4), 3.75(5) Å) (Figure 1). The net effect is a staggered −C_4B_8−Cs−C_4B_8−Cs− polymeric structure (see Figure 2). In addition, there is a TMEDA-solvated Cs that is not part of the polymeric structure but is attached to each cage via upper- and lower-belt M−H−E interactions (where E = B, C) (Cs(2)−B(15,19,20) = 3.70(5), 3.53(5), 3.75(4) Å; Cs(2)−C(34) = 3.64(4) Å] (Figure 1).[17] The primary six-membered C_3B_3 faces of the carboranes are not planar but show that one carbon (C(12)) and one boron (B(17)) are displaced toward the capping Cs (see Figure 1). However, the other Cs−C_3B_3 distances indicate considerable metal interactions with all of the facial atoms. These interatomic distances are comparable to the Cs−arene interactions reported for *N*-cesiocarbazole−PMDTA (Cs−C = 3.343(5)−3.511(6) Å),[6] calixarene-cupped cesium (Cs−Centroid(phenyl) = 3.57 Å),[18] and the cesium picrate complex of 1,3-alternate calix[4]arene-crown-6 conformers (3.431(10)− 3.864(7) Å).[4] A polymeric structure, similar to that shown in Figures 1 and 2, has been observed for a Sr complex of the $[C_2B_{10}H_{12}]^{2-}$ ligand, reported by Hawthorne and coworkers.[19] However, the interatomic distances of Cs to the carborane cages are such that **2** could be regarded as a cesium−carborane complex in which some degree of interaction exists between the metal and the π-electron density on the carborane cage. Since **2** can also be prepared by an ion-exchange reaction directly from lithium, sodium, and potassium salts of **1**, further study of this compound and its potential application is in order.

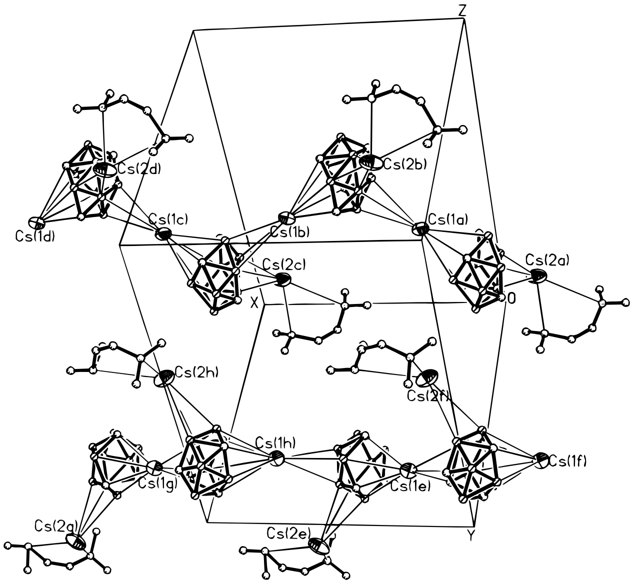

Figure 2. Packing diagram showing the polymeric structure of **2**. For clarity, C(cage)−$SiMe_3$ groups are omitted.

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Supporting Information Available: Tables of positional and thermal parameters and bond distances and angles for **2** (8 pages). Ordering information is given on any current masthead page.

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(17) X-ray data for **2** ($C_{22}H_{60}N_2B_8Si_4Cs_2$; fw 817.4; $P2_12_12_1$): data were collected at 228 K on a Siemens R3m/V diffractometer with a = 13.517(3) Å, b = 15.902(4) Å, c = 18.927(4) Å, V = 4068(2) Å^3, Z = 4, D(calcd) = 1.334 Mg/m^3. Of the 2775 reflections collected (2θ = 3.5−44.0°), 1423 reflections were considered as observed ($F > 6.0\sigma(F)$). Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods, and full-matrix least-squares refinements were performed by using SHELXTL-PLUS (Sheldrick, G. M. Structure Determination Software Programs; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990). All non-H atoms, except for borons and carbons, were refined anisotropically. The methyl, methylene and cage H's were placed in calculated positions with fixed isotropic thermal parameters. The final refinements converged at R = 0.096, R_w = 0.121, and GOF = 2.46.

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