Organometallics **2000,** *19,* 5447−5453

Synthesis and Structural Characterization of *closo-exo*, *exo-nido*, and *pseudocloso* Group 1 Carborane Compounds of the C_2B_{10} System

Kwoli Chui, Hung-Wing Li, and Zuowei Xie*

Department of Chemistry, The Chinese University of Hong Kong,
Shatin, New Territories, Hong Kong, China

Received June 26, 2000

Treatment of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ with excess Na or K metal in THF at room temperature gave *closo-exo*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Na_2(THF)_4$ (**1**) or [*closo-exo*-$\{(C_6H_5CH_2)_2$-$C_2B_{10}H_{10}\}K_2(THF)_2(O_2C_4H_8)_{0.5}]_n$ (**2**) in good yield after recrystallization from a THF solution or a THF/dioxane solution, respectively. Dissolution of **2** in a THF solution of 18-crown-6 ether afforded an *exo-nido*-{K(18-crown-6)}{$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$K(18-crown-6)} (**3**). An equimolar reaction between 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ and K metal or 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ and $[(C_6H_5CH_2)_2C_2B_{10}H_{10}]K_2$ in THF at room temperature in the presence of 18-crown-6 ether generated two monoanion carborane compounds, $[(THF)_2K$(18-crown-6)]-[*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{11}$] (**4**) and {(THF)K(18-crown-6)}{1-$(C_6H_5CH_2)$-2-(C_6H_5CH)-1,2-$C_2B_{10}H_{10}$} (**5**), respectively. All of these complexes have been fully characterized by various spectroscopic data, elemental analyses, and X-ray diffraction studies. Compounds **1**−**3** represent the first structurally characterized examples of group 1 salts of carborane dianions of the C_2B_{10} system.

Introduction

It has been well-documented that *o*-$C_2B_{10}H_{10}R_2$ (R = H, alkyl, aryl) can be reduced by alkali metals to form M_2[*nido*-$C_2B_{10}H_{10}R_2$], which is a very useful versatile synthon for the production of numerous metallacarboranes of s-, p-, d-, and f-elements.[1] The structure and bonding between alkali metal ion and [*nido*-$C_2B_{10}H_{10}R_2]^{2-}$ have, however, remained largely unexplored although many attempts had been made.[2,3] For a recent example, biscarborane $(C_2B_{10}H_{11})_2$ was reduced by two electrons in the hope that this reaction would result in the formation of a species that contained one carborane cage opened by the reduction and analogous to the [*nido*-$C_2B_{10}H_{12}]^{2-}$ anion, while the second *closo* cage would serve solely as an ancillary group. In fact, a biscarborane ion, $[(C_2B_{10}H_{11})_2]^{2-}$, with one negative charge on each carborane cage was isolated.[3] These problems also interest theoreticians. The molecular structures of $[C_2B_{10}H_{12}]^{2-}$ and the related species were proposed on the basis of theoretical calculations, and these results were recently reported in the literature.[4−6]

We have recently reported that *o*-$C_2B_{10}H_{10}R_2$ can be reduced to [*arachno*-$C_2B_{10}H_{10}R_2]^{4-}$ by excess alkali metal in the presence of UCl_4,[7] YCl_3,[8] or lanthanide chlorides.[8,9] In contrast, treatment of *o*-$C_2B_{10}H_{10}R_2$ with excess alkali metal gives only [*nido*-$C_2B_{10}H_{10}R_2]^{2-}$ in the absence of transition metal halides.

In view of the above-mentioned problems and rich coordination chemistry of main group metallacarboranes of C_2B_4 system,[1,10] we have become interested in exploring the chemistry of group 1 metallacarboranes of the C_2B_{10} system. We report herein the syntheses and structural characterization of several *closo-exo*, *exo-nido*, and *pseudocloso* group 1 metallacarboranes of 1,2-$(CH_2C_6H_5)_2$-1,2-$C_2B_{10}H_{10}$. Effects of coordinating solvents on the molecular structures of metallacarboranes are also discussed in this paper.

Experimental Section

General Procedures. All experiments were preformed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ was prepared according to the literature method.[11] 18-Crown-6 ether was purchased from Aldrich Chemical Co. and purified according to the

---

* To whom correspondence should be addressed. Fax: (852)-26035057. Tel: (852)26096269. E-mail: zxie@cuhk.edu.hk.

[1] For recent reviews, see: (a) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, *97*, 2421. (b) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081. (c) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. A. G., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 1, p 373.

[2] Getman, T. G.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 158.

[3] (a) Getman, T. D.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4593. (b) Getman, T. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1992**, *31*, 101.

[4] Hermansson, K.; Wójcik, M.; Sjöberg, S. *Inorg. Chem.* **1999**, *38*, 6039.

[5] McKee, M. L. *J. Am. Chem. Soc.* **1992**, *114*, 5856.

[6] McKee, M. L.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 1712.

[7] Xie, Z.; Yan, C.; Yang, Q.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 1761.

[8] Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W.-H.; Lin, Z.; Xie, Z. *J. Am. Chem. Soc.* **2000**, *122*, 5758.

[9] (a) Xie, Z.; Chui, K.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3947. (b) Chui, K.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 1391.

[10] For recent review, see: Hosmane, N. S. *J. Organomet. Chem.* **1999**, *581*, 13.

[11] Xie, Z.; Liu, Z.; Chiu, K.-y.; Xue, F.; Mak, T. C. W. *Organometallics* **1997**, *16*, 2460.

10.1021/om000547m CCC: $19.00

literature procedures.[12] All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts are reported in δ units with references to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., Brunel University, Middlesex, U.K.

Preparation of *closo-exo*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Na_2(THF)_4$ (1). To a solution of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (0.20 g, 0.62 mmol) in 15 mL of THF was added finely cut Na metal (0.11 g, 4.78 mmol), and the mixture was stirred at room temperature overnight. After removal of excess Na, the clear pale yellow solution was concentrated to about 8 mL. *n*-Hexane vapor diffusion at room temperature gave **1** as colorless crystals (0.21 g, 51%). ^{1}H NMR (pyridine-d_5): δ 7.72 (d, $J = 7.2$ Hz, 4H, *o*-aryl H), 7.14 (t, $J = 7.2$ Hz, 4H, *m*-aryl H), 7.01 (t, $J = 7.2$ Hz, 2H, *p*-aryl H), 4.19 (s, 4H, $C_6H_5CH_2$), 3.64 (m, 16H, THF), 1.60 (m, 16H, THF). ^{13}C NMR (pyridine-d_5): δ 147.2, 129.1, 127.5, 124.3 ($C_6H_5CH_2$), 50.8 ($C_6H_5CH_2$), 67.2, 25.1 (THF); the carbon atoms of the cage were not observed. ^{11}B NMR (pyridine-d_5): δ −0.4 (4B), −6.7 (6B). IR (KBr, cm^{-1}): ν 3065 (w), 2969 (s), 2878 (s), 2506 (vs), 2422 (vs), 2350 (s), 1598 (w), 1489 (m), 1448 (m), 1243 (w), 1046 (s), 901 (m), 711 (m), 533 (w), 496 (w). Anal. Calcd for $C_{28}H_{48}B_{10}Na_2O_3$ (**1** − THF): C, 57.31; H, 8.25. Found: C, 57.55; H, 7.88.

Preparation of [*closo-exo*-$\{(C_6H_5CH_2)_2C_2B_{10}H_{10}\}K_2(THF)_2(O_2C_4H_8)_{0.5}]_n$ (2). A finely cut K metal (0.13 g, 3.33 mmol) was added to a solution of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (0.20 g, 0.62 mmol) in 15 mL of THF, and the mixture was stirred at room-temperature overnight. Removal of excess K metal, addition of a few drops of dioxane, and *n*-hexane vapor diffusion afforded **2** as colorless crystals (0.25 g, 68%). ^{1}H NMR (pyridine-d_5): δ 7.74 (d, $J = 7.2$ Hz, 4H, *o*-aryl H), 7.27 (t, $J = 6.9$ Hz, 4H, *m*-aryl H), 7.12 (t, $J = 7.2$ Hz, 2H, *p*-aryl H), 4.07 (s, 4H, $C_6H_5CH_2$), 3.66 (m, 8H, THF), 3.62 (s, 4H, dioxane), 1.62 (m, 8H, THF). ^{13}C NMR (pyridine-d_5): δ 146.7, 129.0, 128.1, 124.8 ($C_6H_5CH_2$), 67.2, 25.2 (THF), 66.5 (dioxane), 51.1 ($C_6H_5CH_2$); the carbon atoms of the cage were not observed. ^{11}B NMR (pyridine-d_5): δ −3.3 (4B), −5.4 (4B), −25.5 (2B). IR (KBr, cm^{-1}): ν 3066 (w), 2965 (m), 2915 (s), 2862 (s), 2506 (vs), 2447 (vs), 2391 (s), 1595 (w), 1487 (m), 1447 (m), 1253 (m), 1113 (s), 1049 (vs), 878 (m), 712 (m), 616 (w), 538 (w), 496 (w). Anal. Calcd for $C_{22}H_{36}B_{10}K_2O_2$ (**2** − THF): C, 50.92; H, 6.99. Found: C, 51.31; H, 6.97.

Preparation of {K(18-crown-6)}{*exo-nido*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$K(18-crown-6)} (3). To a THF solution of $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ (15 mL, 0.62 mmol) was added a THF solution (5 mL) of 18-crown-6 ether (0.17 g, 0.64 mmol) at room temperature, and the mixture was stirred for 30 min. After concentration of the resulting clear pale yellow solution to about 10 mL, toluene (about 8 mL) was added. **3** was isolated as colorless crystals after this solution stood at room temperature overnight (0.36 g, 63%).^{1}H NMR (pyridine-d_5): δ 7.96 (d, $J = 7.2$ Hz, 4H, *o*-aryl H), 7.23 (t, $J = 7.5$ Hz, 4H, *m*-aryl H), 7.08 (t, $J = 6.9$ Hz, 2H, *p*-aryl H), 4.38 (s, 4H, $C_6H_5CH_2$), 3.40 (s, 48H, $C_{12}H_{24}O_6$). ^{13}C NMR (pyridine-d_5): δ 130.2, 127.0 ($C_6H_5CH_2$), 69.9 ($C_{12}H_{24}O_6$), 51.0 ($C_6H_5CH_2$); other carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ −7.2 (4B), −18.8 (3B), −25.1 (3B). IR (KBr, cm^{-1}): ν 3050 (w), 3005 (w), 2886 (s), 2452 (s), 2393 (s), 2353 (s), 1597 (w), 1459 (m), 1350 (m), 1249 (m), 1107 (vs), 960 (s), 837 (w), 733 (w), 528 (w). Anal. Calcd for $C_{40}H_{72}B_{10}K_2O_{12}$: C, 51.59; H, 7.79. Found: C, 51.83; H, 7.55.

Alternate Method. To a THF (10 mL) solution of compound **2** (0.36 g, 0.61 mmol) was added a THF solution of 18-crown-6 ether (0.17 g, 0.64 mmol) at room temperature, followed by the procedures used above affording **3** as colorless crystals (0.38 g, 67%).

Preparation of $[(THF)_2K(18\text{-crown-}6)]$[*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{11}$] (4) and {(THF)K(18-crown-6)}{1-$(C_6H_5CH_2)$-2-(C_6H_5CH)-1,2-$C_2B_{10}H_{10}$} (5). To a solution of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (0.20 g, 0.62 mmol) in 15 mL of THF was added finely cut K metal (0.024 g, 0.62 mmol), and the mixture was then stirred at room temperature for 24 h until no K metal remained and a bright yellow solution resulted. No any gas evolution was detected. After addition of a toluene solution (20 mL) of 18-crown-6 ether (0.16 g, 0.61 mmol), the resulting solution was allowed to stand at 10 °C for 2 days, giving **4** as colorless crystals (0.14 g, 29%). ^{1}H NMR (pyridine-d_5): δ 7.59 (d, $J = 7.2$ Hz, 4H, *o*-aryl H), 7.28 (t, $J = 7.5$ Hz, 4H, *m*-aryl H), 7.17 (t, $J = 7.2$ Hz, 2H, *p*-aryl H), 4.26 (s, 4H, $C_6H_5CH_2$), 3.64 (m, 8H, THF), 3.41 (s, 24H, $C_{12}H_{24}O_6$), 1.59 (m, 8H, THF). ^{13}C NMR (pyridine-d_5): δ 144.8, 129.0, 127.6, 124.8 ($C_6H_5CH_2$), 69.7 ($C_{12}H_{24}O_6$), 50.5 ($C_6H_5CH_2$), 67.1, 25.1 (THF); the carbon atoms of the cage were not observed. ^{11}B NMR (pyridine-d_5): δ 12.3 (1B), 4.5 (2B), −0.8 (1B), −8.4 (2B), −16.0 (2B), −19.6 (2B). IR (KBr, cm^{-1}): ν 3066 (w), 3019 (w), 2956 (m), 2903 (s), 2521 (s), 2462 (m), 1601 (w), 1455 (m), 1350 (m), 1254 (m), 1106 (vs), 1056 (m), 959 (m), 902 (w), 803 (m), 729 (w), 516 (m). Anal. Calcd for $C_{30}H_{53}B_{10}KO_{6.5}$ (**4** − 1.5THF): C, 54.27; H, 7.89. Found: C, 54.04; H, 8.25.

After removal of **4**, the mother liquor was then concentrated to about 10 mL. **5** was isolated as bright yellow crystals after this solution stood at room temperature for days (0.16 g, 37%). ^{1}H NMR (pyridine-d_5): δ 7.96 (d, $J = 7.5$ Hz, 2H, *o*-aryl H), 7.37 (d, $J = 6.9$ Hz, 2H, *o*-aryl H), 7.29 (t, $J = 7.5$ Hz, 2H, *m*-aryl H), 7.18 (m, 3H, *p*,*m*-aryl H), 7.05 (s, 1H, C_6H_5CH), 7.01 (t, $J = 7.5$ Hz, 1H, *p*-aryl H), 3.64 (m, 4H, THF), 3.56 (s, 2H, $C_6H_5CH_2$), 3.40 (s, 24H, $C_{12}H_{24}O_6$), 1.60 (m, 4H, THF). ^{13}C NMR (pyridine-d_5): δ 142.4, 141.5, 130.3, 128.0, 127.5, 125.5, 125.0, 123.3 (C_6H_5), 118.9 (C_6H_5CH), 70.0 ($C_{12}H_{24}O_6$), 43.4 (CH_2), 67.5, 25.4 (THF); the carbon atoms of the cage were not observed. ^{11}B NMR (pyridine-d_5): δ −1.6 (2B), −5.3 (2B), −11.0 (1B), −11.9 (1B), −13.5 (1B), −16.0 (1B), −23.0 (1B), −26.2 (1B). IR (KBr, cm^{-1}): ν 3019 (w), 2899 (m), 2533 (s), 1590 (w), 1522 (m), 1450 (m), 1348 (m), 1246 (w), 1107 (vs), 1039 (m), 960 (m), 838 (w), 699 (w), 527 (w). Anal. Calcd for $C_{28}H_{47}B_{10}KO_6$ (**5** − THF): C, 53.65; H, 7.56. Found: C, 53.86; H, 7.67.

Alternate Method. Finely cut K metal (0.13 g, 3.33 mmol) was added to a THF solution (10 mL) of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (0.10 g, 0.31 mmol), and the mixture was stirred at room-temperature overnight. Removal of excess K metal gave a pale yellow solution to which was then added a THF solution of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (0.10 g, 0.31 mmol) at room temperature. The color of the resulting solution was immediately turned to bright yellow, and this solution was then stirred at room temperature overnight. A toluene solution (20 mL) of 18-crown-6 ether (0.17 g, 0.64 mmol) was added. The resulting clear solution was stirred for 0.5 h, followed by the procedures used before affording **4** as colorless crystals (0.15 g, 32%) and **5** as bright yellow crystals (0.15 g, 35%), respectively.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS-IIC imaging plate using Mo Kα radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program.[13] All structures were solved by direct methods and

---

[12] Perrin, D. D.; Armarego, W. L. F. In *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U.K., 1993; p 129.

[13] Higashi, T. *ABSCOR-An Empirical Absorption Correction Based on Fourier Coefficient Fitting*; Rigaku Corp.: Tokyo, 1995.

Table 1. Crystal Data and Summary of Data Collection and Refinement for 1−5

	1	2	3	4	5
formula	$C_{32}H_{56}B_{10}Na_2O_4$	$C_{26}H_{44}B_{10}K_2O_3$	$C_{40}H_{72}B_{10}K_2O_{12}$	$C_{36}H_{65}B_{10}KO_8$	$C_{32}H_{55}B_{10}KO_7$
cryst size (mm)	0.44 × 0.38 × 0.22	0.42 × 0.36 × 0.32	0.40 × 0.40 × 0.05	0.52 × 0.25 × 0.11	0.49 × 0.26 × 0.15
fw	658.8	590.9	931.2	773.1	699.0
cryst system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$C2/c$	$P2_1/n$	$Pmc2_1$	$Pca2_1$
a, Å	14.196(1)	25.860(5)	19.117(4)	23.793(2)	21.524(2)
b, Å	16.141(1)	10.350(2)	10.776(2)	10.368(1)	11.046(1)
c, Å	17.469(1)	26.976(5)	24.694(5)	18.307(1)	16.746(2)
β, deg	93.74(1)	110.30(3)	95.19(3)	90.00	90.00
V, Å^3	3994(1)	6772(2)	5066(2)	4516(1)	3981(1)
Z	4	8	4	4	4
D_{calcd}, Mg/m^3	1.096	1.159	1.221	1.137	1.166
radiation (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2θ range, deg	3.4−50.0	4.2−50.0	4.1−50.0	1.7−50.0	3.6−50.0
μ, mm^{-1}	0.083	0.306	0.242	0.162	0.175
F(000)	1408	2496	1984	1656	1488
no. of indep reflcns	7029	3732	5086	7897	6842
no. of obsd reflcns	7029	3732	5086	7897	6842
no. of params refnd	432	446	589	552	460
goodness of fit	0.795	1.077	1.132	0.856	0.840
R1	0.067	0.084	0.100	0.061	0.056
wR2	0.189	0.225	0.256	0.143	0.128

Table 2. Key Structural Parameters for 1−5[a]

	1	2	3	4	5
M	Na	K	K	K	K
av M−cage atom	2.776(2)	3.174(2)			
C(cage)−C(benzyl)	1.562(3)	1.559(2)	1.540(5)	1.531(4)	1.540(3)
	1.536(2)	1.508(2)	1.492(5)	1.525(4)	1.365(3)
av M···B(B3)	2.850(2)	3.253(2)	3.323(3)		
av M−O(THF or dioxane)	2.273(1)	2.632(1)		2.840(5)	2.702(5)
av K−O(crown)			2.861(3)	2.783(5)	2.783(1)
displacement[b]	+0.15	+0.29	+0.29	+0.34	
	−0.07	−0.22	−0.20	−0.27	
C(cage)−C−C(phenyl)	114.5(1)	113.2(1)	115.9(3)	115.4(3)	129.9(2)
	111.6(1)	108.2(1)	114.5(3)	112.2(2)	116.5(2)

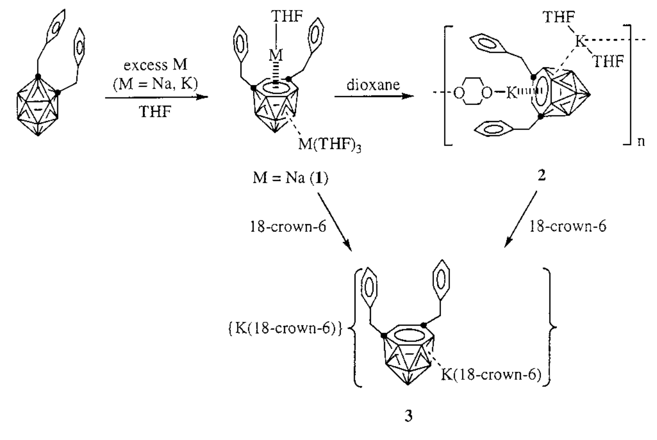
[a] Distances are in Å and angles are in deg. [b] Distance from the cage carbon atom to the mean plane of the four boron atoms in the hexagonal C_2B_4 face; "+" and "−" indicate above and below this mean plane, respectively.

subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the Siemens SHELXTL program package (PC version).[14a] For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[14b] Most of the carborane hydrogen atoms were located from different Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinement are given in Table 1. Selected bond distances are listed in Table 2. Further details are included in the Supporting Information.

Results

Dianion Compounds. Treatment of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ with excess finely cut Na metal in THF at room temperature gave, after recrystallization from a n-hexane/THF solution, a *closo-exo*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$-$Na_2(THF)_4$ (**1**) as colorless crystals in 51% isolated yield. Its potassium analogue, under the same reaction condition, was isolated as a white powder. Recrystallization of this potassium salt from a mixed solvent of THF/dioxane/n-hexane afforded [*closo-exo*-$\{(C_6H_5CH_2)_2C_2B_{10}H_{10}\}K_2(THF)_2(O_2C_4H_8)_{0.5}]_n$ (**2**) as colorless crystals. Dissolution of **2** or the above powdered potassium salt in a THF solution of 18-crown-6 ether generated, after workup, {K(18-crown-6)}{*exo-nido*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$-K(18-crown-6)} (**3**) as colorless crystals in 63% yield. All these transformations are summarized in Scheme 1.

Scheme 1



Compounds **1**−**3** are extremely air- and moisture-sensitive but remain stable for months at room temperature under an inert atmosphere. They are quite soluble in polar organic solvents such as THF and pyridine, sparingly soluble in toluene, and insoluble in n-hexane.

The ^{1}H NMR spectra show that two benzyl groups on the carborane cage in all three compounds are equivalent in the solution and support the ratio of four THF

---

(14) (a) *SHELXTL V 5.03 Program Package*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1995. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

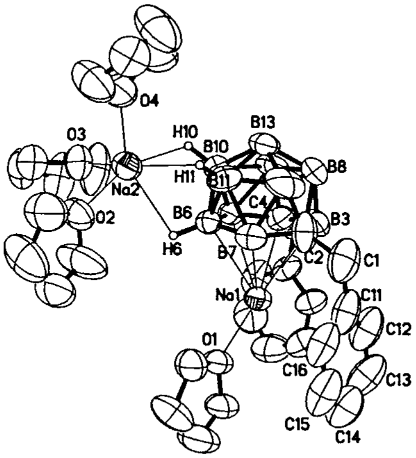


Figure 1. Molecular structure of *closo*-*exo*-[$(C_6H_5CH_2)_2$-$C_2B_{10}H_{10}$]$Na_2(THF)_4$ (**1**). (Thermal ellipsoids are drawn at the 35% probability level.)

molecules per carboranyl ligand for **1**, two THF and a half dioxane molecules per ligand for **2**, and two 18-crown-6 ether molecules per ligand for **3**, respectively. The ^{13}C NMR spectra are consistent with the results derived from the ^{1}H NMR spectra. The ^{11}B NMR spectra exhibit 2:3, 2:2:1, and 4:3:3 splitting patterns for **1**−**3**, respectively, perhaps implying different structures for these compounds. Their solid-state IR spectra display both a characteristic doublet centered around 2460 cm^{-1} and a shoulder at about 2360 cm^{-1} attributable to a M−H−B stretching mode.[9,15,16]

The molecular structures of all three compounds have been confirmed by single-crystal X-ray analyses. As shown in Figure 1, compound **1** has a monomeric structure in which one sodium is bonded to the open six-membered C_2B_4 face in η^6 fashion and the other is bonded to a trigonal B_3 face through three B−H bonds forming a 13-vertex *closo*-*exo*-metallacarborane. The coordination sphere around the sodium atoms is then completed by four THF molecules.

The Na(1)−cage atom distances range from 2.683(3) to 2.851(2) Å with an average value of 2.776(2) Å. This measured value compares to the 2.726(18) Å in [*closo*-*exo*-{$(Me_3Si)_2C_2B_4H_4$}$Na_2(THF)_4$]$_2$[17] and the value of 2.795 Å that would be expected by subtracting the difference, 0.12 Å, between Shannon's ionic radii[18] of 7-coordinate and 9-coordinate sodium ions from the average Na−cage atom distance of 2.915(6) Å in *closo*-*exo*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]$_4Sm_2Na_3$.[19] The average Na(2)···B (B_3 face) distance of 2.850(2) Å is close to the 2.845(19) Å in [*closo*-*exo*-{$(Me_3Si)_2C_2B_4H_4$}$Na_2(THF)_4$]$_2$[17] and the 2.892 Å derived from the subtraction of the difference in the ionic radii,[18] 0.12 Å, from the average Na···B (B_3 face) distance, 3.012(6) Å, in *closo*-*exo*-[$(C_6H_5$-$CH_2)_2C_2B_{10}H_{10}$]$_4Sm_2Na_3$[19] and is also comparable to the corresponding values found in the literature.[1,20] The distances between the benzyl substituents and Na(1) range from 2.998(2) to 4.383(2) Å with the closest approach being through C(22), implying that the Na(1) ion has certain interactions with the aromatic rings.[19,21]

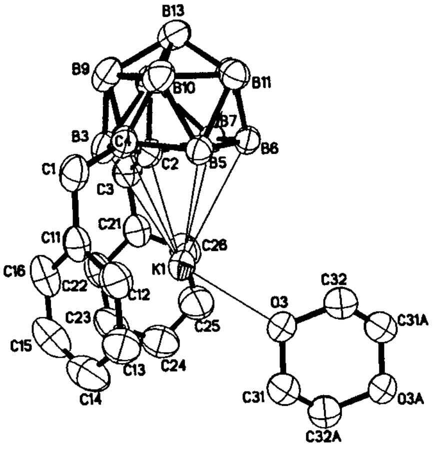


Figure 2. Perspective view of the coordinating sphere around the K(1) atom in **2**. (Thermal ellipsoids are drawn at the 35% probability level.)

In contrast to compound **1**, **2** adopts a polymeric structure in which the dioxane and the potassium ion serve as alternating bridging groups to give a zigzag metallacarborane−K−metallacarborane−dioxane−metallacarborane chain that is maintained in one-dimension throughout the lattice. As far as we are aware, **2** represents the first structurally characterized example of a metallacarborane of potassium element.

As shown in Figure 2, the K(1) ion is η^6-bound to the hexagonal C_2B_4 face of the C_2B_{10} cage forming a 13-vertex metallacarborane structural motif and coordinated to one oxygen atom of the bridging dioxane molecule, a coordination environment that is similar to that of Na(1) in **1**. The distances from K(1) to the two phenyl rings of the benzyl substituents fall in a relatively large range (3.181(2)−3.657(2) Å), indicating a somewhat asymmetric K−arene interactions.[22] The average K(1)−cage atom distance of 3.174(2) Å is close to the value of 3.116 Å that is expected by adding the difference, 0.34 Å, between Shannon's ionic radii[18] of K^+ and Na^+ ions from the average Na−cage atom distance of 2.776(2) Å in **1** and the value of 3.18 Å derived from the subtraction of the difference in the ionic radii,[18] 0.23 Å, from the average Cs−cage atom distance, 3.41(4) Å in [*closo*-*exo*-{$(Me_2Si)_4C_4B_8H_8$}Cs_2-(TMEDA)]$_n$.[23] Another potassium ion K(2) in the solid-state structure of **2** is bonded to two trigonal B_3 faces

---

(15) (a) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *29*, 2191. (b) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962.

(16) (a) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Xue, F.; Mak, T. C. W. *Organometallics* **1998**, *17*, 489. (b) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907. (c) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1641. (d) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 2420. (e) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 1578. (f) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 334.

(17) Hosmane, N. S.; Jia, L.; Zhang, H.; Bausch, J. W.; Prakash, G. K. S.; Williams, R. E.; Onak, T. P. *Inorg. Chem.* **1991**, *30*, 3793.

(18) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(19) Xie, Z.; Liu, Z.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3603.

(20) Hosmane, N. S.; Saxena, A. K.; Barreto, R. D.; Zhang, H.; Maguire, J. A.; Jia, L.; Wang, Y.; Oki, A. R.; Grover, K. V.; Whitten, S. J.; Dawson, K.; Tolle, M. A.; Siriwardane, U.; Demissie, T.; Fagner, J. S. *Organometallics* **1993**, *12*, 3001.

(21) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501 and references therein.

(22) (a) Clark, D. L.; Watkin, J. G.; Huffman, J. C. *Inorg. Chem.* **1992**, *31*, 1554. (b) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent-Hollis, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 5903. (c) Evans, W. J.; Anwander, R.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5. (d) Evans, W. J.; Ansari, M. A. *Organometallics* **1995**, *14*, 558.

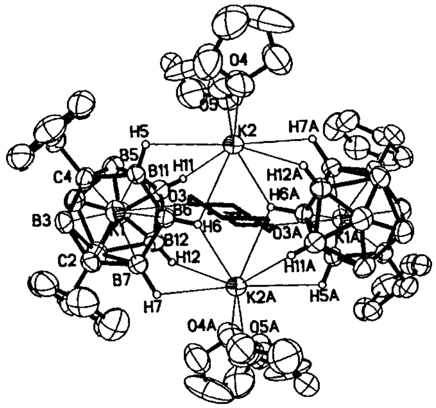


Figure 3. Perspective view of the coordinating sphere around the K(2) atom in **2** showing the interactions of the K(2) ions with two carborane cages. (Thermal ellipsoids are drawn at the 35% probability level.)

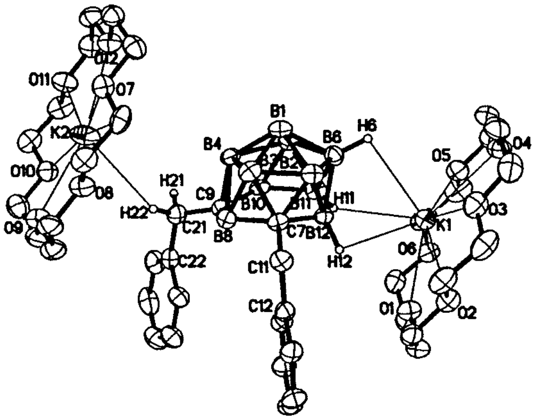
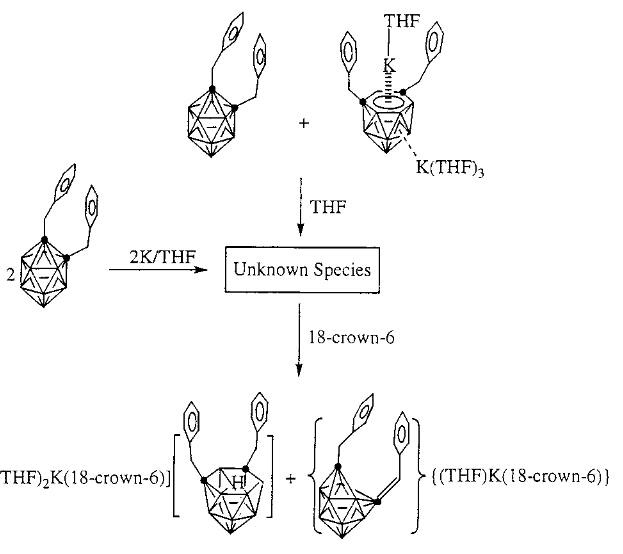


Figure 4. Molecular structure of {K(18-crown-6)}{*exo*-*nido*-[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$]K(18-crown-6)} (**3**). (Thermal ellipsoids are drawn at the 35% probability level.)

through two sets of three unequal K−H−B bonds from two neighboring carborane cages, and its coordinating sphere is completed by two THF molecules, as shown in Figure 3. The average K(2)···B distance of 3.253(2) Å is slightly longer than that of the K(1)−cage atom distance but is comparable to the 2.850(2) Å in **1** and the 3.64(4) Å in [*closo*-*exo*-{$(Me_2Si)_4C_4B_8H_8$}Cs_2-(TMEDA)]$_n$[23] if the differences in Shannon's ionic radii[18] are taken into account.

Unlike the molecular structures of **1** and **2**, **3** consists of a *nido*-C_2B_{10} cage and two K(18-crown-6) moieties, and they are linked to each other through a set of three unequal K(1)−H−B bonds and a K(2)−H−C bond, respectively, as shown in Figure 4. The average K(1)···B distance of 3.313(3) Å is close to the corresponding value of 3.253(2) Å in **2**. Such interactions pull the K(1) atom out of the mean plane of six oxygen atoms of the crown ether molecule by 0.861 Å. In contrast, the K(2)···H(22)−C(21) interaction (3.00 Å) is relatively weak leading to a relatively small (0.338 Å) out of plane displacement for K(2). The average K(1)−O distance of 2.913(3) Å is longer than the 2.810(3) Å average K(2)−O distance due to the differences in coordination number and out of plane displacement of K^+ ions. These measured values can be compared with those normally observed in the complexes containing the [K(18-crown-6)] moiety.[24]

Scheme 2



4 **5**

Monoanion Compounds. Reaction of 1,2-(C_6H_5-$CH_2)_2$-1,2-$C_2B_{10}H_{10}$ with 1 equiv of finely cut potassium metal in THF at room temperature gave, after addition of 18-crown-6 ether, [$(THF)_2$K(18-crown-6)][*nido*-$(C_6H_5$-$CH_2)_2C_2B_{10}H_{11}$] (**4**) as colorless crystals in 29% yield and {(THF)K(18-crown-6)}{1-($C_6H_5CH_2$)-2-(C_6H_5CH)-1,2-$C_2B_{10}H_{10}$} (**5**) as bright yellow crystals in 37% yield, respectively. Compounds **4** and **5** could also be prepared by mixing K_2[$(C_6H_5CH_2)_2C_2B_{10}H_{10}$] and 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ in a molar ratio of 1:1 in a THF solution of 18-crown-6 ether. These reactions are outlined in Scheme 2. Both compounds **4** and **5** are EPR-silent. **4** is air-stable, while **5** is air-sensitive. Traces of air convert **5** from bright yellow crystals to a colorless powder. They are soluble in THF and pyridine, sparingly soluble in toluene, and insoluble in *n*-hexane.

The IR spectrum of **4** exhibits a strong B−H absorption at 2521 cm^{-1} and a medium strong peak at 2462 cm^{-1}, while that of **5** displays a strong sharp B−H absorption at 2533 cm^{-1}. The ^{11}B NMR spectra show 1:2:1:2:2:2 and 2:2:1:1:1:1:1:1 splitting patterns for **4** and **5**, respectively. The ^1H NMR spectrum of **4** shows one set of benzyl protons and supports the ratio of two THF and one 18-crown-6 ether molecules per carboranyl ligand, which is consistent with its ^{13}C NMR results. The ^1H NMR spectrum of **5**, however, clearly exhibits two sets of aromatic protons and a singlet at $\delta = 7.05$ ppm attributable to the vinyl proton, which is also reflected in the ^{13}C NMR spectrum showing two sets of aromatic carbons and a unique resonance at $\delta = 118.9$ ppm assignable to the vinyl carbon. The above-mentioned spectroscopic data suggest that **4** and **5** have different structures.

An X-ray diffraction study reveals that **4** has an ionic structure consisting of well-separated, alternating layers

---

[23] (a) Hosmane, N. S.; Demissie, T.; Zhang, H.; Maguire, J. A.; Lipscomb, W. N.; Baumann, F.; Kaim, W. *Organometallics* **1998**, *17*, 293. (b) Hosmane, N. S.; Zhang, H.; Maguire, J. A.; Wang, Y.; Demissie, T.; Colacot, T. J.; Ezhova, M. B.; Lu, K.-J.; Zhu, D.; Gray, T. G.; Helfert, S. C.; Helfert, S. C.; Hosmane, S. N.; Collins, J. D.; Baumann, F.; Kaim, W.; Lipscomb, W. N. *Organometallics* **2000**, *19*, 497.

[24] (a) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1996**, 1987. (b) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F.; Laschi, F. *Organometallics* **1999**, *18*, 5539.

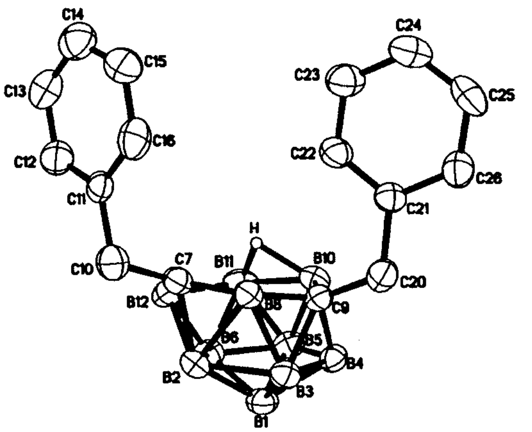


Figure 5. Perspective view of the monoanion [*nido*-$(C_6H_5\text{-}CH_2)_2C_2B_{10}H_{11}$] in **4**. (Thermal ellipsoids are drawn at the 35% probability level.)

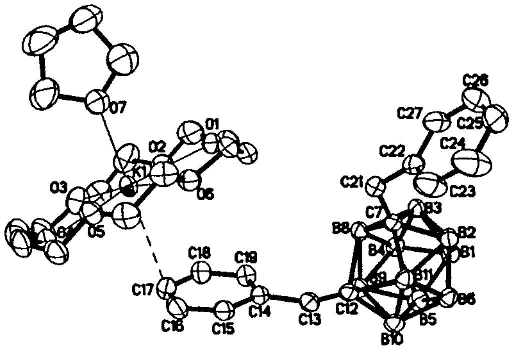


Figure 6. Molecular structure of {(THF)K(18-crown-6)}-{1-$(C_6H_5CH_2)$-2-(C_6H_5CH)-1,2-$C_2B_{10}H_{10}$} (**5**). (Thermal ellipsoids are drawn at the 35% probability level.)

of discrete cations $[(THF)_2K(18\text{-crown-}6)]^+$ and carborane monoanion [*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{11}]^-$. As shown in Figure 5, this monoanion contains a hexagonal face in which the four boron atoms are coplanar and the two carbon atoms are staggered, one above and one below this plane, a geometry that is similar to the kinetic product of [*nido*-$(CH_3)_2C_2B_{10}H_{11}]^-$ [2] or the dianion [*nido*-$(C_6H_5CH_2)_2C_2B_{10}H_{10}]^{2-}$ in **3** with the bridging proton removed. The less connected C(7) atom is 0.34 Å above the plane, and the more connected C(9) atom is 0.27 Å below the plane. The cation $[(THF)_2K(18\text{-crown-}6)]^+$ has crystallographically imposed C_2 symmetry and adopts a hexagonal-bipyramidal geometry with two THF molecules occupying the axial positions. The potassium ions are assigned half site occupancy and sit in the mean plane formed by six oxygen atoms of the 18-crown-6 ether molecule.

The solid-state structure of **5** consists of a monoanion [1-$(C_6H_5CH_2)$-2-(C_6H_5CH)-1,2-$C_2B_{10}H_{10}]^-$ and a cation $[(THF)K(18\text{-crown-}6)]^+$, which are associated with each other through a weak K···C(17) interaction at a distance of 3.211(3) Å that is very close to an average K···C interatomic distance of 3.210(7) Å observed in [K(18-crown-6)][{η^5-$(Me_3Si)_2C_5H_3\}_2La(C_6H_6)$],[24] as shown in Figure 6. The carborane monoanion adopts a *pseudocloso* geometry[25] in which the C(7)···C(12) connectivity is broken and an approximately square C(7)B(8)C(12)B(11) face is generated. Such geometry was also observed in the dianion $[(C_2B_{10}H_{11})_2]^{2-}$.[3]

The two long (C(12)−B(8,11) = 2.010(4), 1.847(3) Å) and two short (C(12)−B(9,10) = 1.617(3), 1.630(4) Å) C−B distances are observed in **5**, which can be explained as being due to crystal packing forces.[3] The C(12)−C(13) distance of 1.365(3) Å exhibits substantial double-bond character, which is very close to the C(cage)−C(cage) distance of 1.377(4) Å in $[(C_2B_{10}H_{11})_2]^{2-}$.[3] It is further noted that the eight atoms of C(12) and C(13) to C(19) are coplanar, indicating that the negative charge is delocalized over the cage and one of the two benzyl groups, which can stabilize the monoanion, and on the other hand can explain the interaction between K(1) and C(17). Close examinations show that the cage geometry in the present compound is very similar to that in $[(C_2B_{10}H_{11})_2]^{2-}$, which suggests that the function of the benzyl group in **5** resembles that of the carborane cage in $[(C_2B_{10}H_{11})_2]^{2-}$.

Discussion

Structural studies on compounds **1**−**3** reveal that the bonding between Na^+ or K^+ ion and carborane dianion is ionic in nature, and the capping alkali netal ion can be easily removed by strong chelating ligands such as 18-crown-6 ether or replaced by other main group and transition metal ions.[1] These properties ensure $M_2[C_2B_{10}H_{10}R_2]$ to be useful synthons for the preparation of a variety of metallacarboranes. Since the interactions between M^+ and carborane dianion are weak and the negative charge is localized on the cage, unlike transition metal analogues,[7−9,26] group 1 metallacarboranes cannot be further reduced by group 1 metals although they have similar half-sandwich structures. Compounds **1**−**3** represent the first structurally characterized examples of group 1 metallacarboranes of the C_2B_{10} system, which offer theoreticians experimental data for comparison.

The formation of compounds **4** and **5** is very interesting. To gain some insight into the reduction reaction, alternate methods were approached, and ^{11}B NMR was employed to follow these reactions. Since compounds **4** and **5** can be isolated from either treatment of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ with 1 equiv of K metal or reaction of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ with $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ in a molar ratio of 1:1 in the presence of 18-crown-6 ether, one-electron reduction of carborane cage could then be ruled out. In the former reaction, a half amount of the carborane cage is reduced by K metal to give $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ that then reacts with the remaining half amount of carborane to form an unknown species. The ^{11}B NMR spectrum of this species exhibits only two resonances at 9.6 and 3.9 ppm in a ratio of 3:7, a splitting pattern which differs from that of neutral carborane, carborane dianion, and compounds **4** and **5**. Many attempts were made without success to isolate this species. Upon addition of 18-crown-6 ether, many resonances appeared in the ^{11}B NMR which are attributable to both **4** and **5**. From this solution, **4** and **5** were isolated as final products in reasonable yields.

---

(25) (a) Brain, P. T.; Bühl, M.; Cowie, J.; Lewis, Z. G.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1996**, 231. (b) Thomas, R. L.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, 631.

(26) (a) Evans, W. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 38. (b) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 6. (c) Maxwell, W. M.; Weiss, R.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 4016.

It has been known that $[nido\text{-}C_2B_{10}H_{10}R_2]^{2-}$ is a Lewis base (6e$^-$ donor) and the methylene proton of the benzyl group in 1-CH_3-2-$(C_6H_5CH_2)$-1,2-$C_2B_{10}H_{10}$ is a weak Brønsted acid with $pK_a = 19.5$.[27] An acid−base adduct may be formed in a THF solution upon mixing $[(C_6H_5CH_2)_2C_2B_{10}H_{10}]K_2$ with 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$. Addition of 18-crown-6 ether will remove the capping K^+ ion leaving a "naked" open hexagonal C_2B_4 face bearing three pairs of electrons, which could enhance the Lewis basicity of the carborane dianion; this anion may then attack the acidic proton of the benzyl group of neutral carborane molecule resulting in the formation of the monoanions **4** and **5** (Scheme 2). **4** is a kinetic product of the monoprotonated dianion and will slowly isomerize to a more stable thermodynamic species at room temperature over a period of 1 week as evidenced by the ^{11}B NMR.[28] The above hypothesis for the formation of **5** is further supported by the following experiment. Treatment of 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ with 1 equiv of *n*-BuLi in THF in the presence of 18-crown-6 ether gave a species that has a ^{11}B NMR spectrum identical with that of **5**. It is proposed that *n*-BuLi deprotonates one of the methylene hydrogens of a benzyl group in 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ to generate a carbanionic center immediately adjacent to the carborane icosahedron, and the anionic charge delocalizes into the electron-deficient cage by forming an *exo* double bond. A similar phenomenon was observed in the anions $[1\text{-X-2-}C_6H_5\text{-1,2-}C_2B_{10}H_{10}]^-$ (X = O, S, NR).[29]

Conclusion

Group 1 metallacarboranes of C_2B_{10} system have been structurally characterized for the first time. Their structures are very diverse, ranging from monomeric to polymeric and from *closo* through *psedocloso* to *nido* structures depending on the chelating solvents and negative charge on the carborane cage.

The bonding interactions between group 1 metal ion and carborane dianion are relatively weak and ionic in nature, so that the capping metal ion in 13-vertex metallacarboranes can be easily removed by strong chelating ligands such as 18-crown-6 ether or replaced by transition metal ions, which ensures group 1 metallacarboranes to be very useful synthons for the production of various metallacarboranes. Such weak interactions lead to the localization of the negative charge on the carborane cage, which prevents further reduction of 13-vertex group 1 metallacarboranes by alkali metals. In contrast, 13-vertex metallacarboranes of transition metals can be further reduced by alkali metals to form a new type of metallacarborane.[7−9,26]

An unprecedented proton-transfer reaction between the dianion $[nido\text{-}(C_6H_5CH_2)_2C_2B_{10}H_{10}]^{2-}$ and neutral carborane 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ is discovered, which leads to the isolation and structurally characterization of two monoanion carborane compounds. The possible pathways for the formation of these compounds are also proposed.

Acknowledgment. The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administration Region (Project No. CUHK 4210/99P).

Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates, figures giving atom-numbering schemes for compounds **1**−**5**, and X-ray CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000547M

---

[27] Zakharkin, L. I.; Ol'shevskaya, V. A. *Izv. Akad. Nauk, Ser. Khim.* **1992**, *2*, 431.

[28] For examples of the thermodynamic products, see: (a) Tolpin, E. I.; Lipscomb, W. N. *Inorg. Chem.* **1973**, *12*, 2257. (b) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1973**, *12*, 2674.

[29] (a) Brown, D. A.; Clegg, W.; Colquhoun, H. M.; Daniels, J. A.; Stephenson, I. R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1987**, 889. (b) Coult, R.; Fox, M. A.; Gill, W. R.; Wade, K. *Polyhedron* **1992**, *11*, 2717.