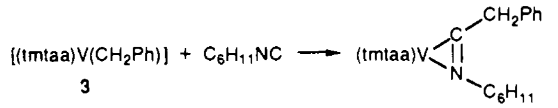
An indirect proof of the intermediacy of the acyl in the carbon monoxide reaction was obtained from the reaction of **3** with cyclohexyl isocyanide, leading to the corresponding iminoacyl, which was isolated as a crystalline solid.



3 **13** (8)

The η^2-bonding mode is confirmed by the rather low C=N stretching value, which was not observed above 1600 cm^{-1}.[31]

The structures of **1**, **4**, and **5** are shown in Figures 1–3. A selection of structural parameters in Tables V and VI allows the comparison of the structures. The ligand tmtaa maintains its usual saddle-shape conformation,[6-11] which remains almost unchanged for the three compounds. Therefore the cavity where the additional functionality (Cl, Ph, Mes) is located does not change significantly (Table VI). The four N-donor atoms define a perfect plane in **1**, and they show some significant tetrahedral distortions in **4** and **5**. The vanadium V–N4 out of plane distances are rather close. The V–N distances are not affected by the change in the axial ligand. V–Cl and V–C are close to those found in the vanadium(III)–Schiff base complexes[4] (Table V). The most significant difference between **4** and **5** consists in the orientation of the phenyl ring, which, for steric reasons, is rotated by **5** by 90° with respect to **4** (Figures 2 and 3).

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Supplementary Material Available: Listings of unrefined hydrogen coordinates (Tables SI–SIII), thermal parameters (Tables SIV–SVI), bond distances and angles (Tables SVII–SIX), complete crystallographic data (Table SX), and positional parameters and equivalent isotropic thermal parameters with esd's (Tables SXI–SXIII) (23 pages); listings of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Reduction of Biscarborane: Molecular Structures of $[(15\text{-crown-}5)_3Na_2](C_2B_{10}H_{11})_2$ and $[P(C_6H_5)_3CH_3]_2[\mu\text{-}9,10\text{-}CH\text{-}(\mu\text{-}9',10'\text{-}CH\text{-}\textit{nido}\text{-}7'\text{-}CB_{10}H_{11})\text{-}\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]$

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The synthesis, characterization, and elucidation of the structures of $[(15\text{-crown-}5)_3Na_2](C_2B_{10}H_{11})_2$ ($[(15\text{-crown-}5)_3Na_2]$(**1**)) and $[P(C_6H_5)_3CH_3]_2[\mu\text{-}9,10\text{-}CH\text{-}(\mu\text{-}9',10'\text{-}CH\text{-}\textit{nido}\text{-}7'\text{-}CB_{10}H_{11})\text{-}\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]$ ($[P(C_6H_5)_3CH_3]_2$(**2**)) are described. A comparison is made between the solid-state structures of the anion, **1**, in $[(15\text{-crown-}5)_3Na_2]$(**1**) and $[P(C_6H_5)_3CH_3]_2$(**1**). The structure of the cation $[(15\text{-crown-}5)_3Na_2]^{2+}$, described in detail, represents the first structural characterization of a 3:2 15-crown-5:Na "club sandwich" complex. $[(15\text{-crown-}5)_3Na_2](C_2B_{10}H_{11})_2$ crystallized in the triclinic space group $P\bar{1}$ with $a = 12.411$ (1), $b = 14.676$ (2), and $c = 14.988$ (2) Å, $\alpha = 101.371$ (3), $\beta = 96.222$ (3), and $\gamma = 91.549$ (4)°, $V = 2657$ Å^3, and $Z = 2$. Data were collected at 128 K on a modified Picker FACS-1 diffractometer using Mo Kα radiation, to a maximum $2\theta = 56°$, giving 12 832 unique reflections. The structure was solved by direct methods. The final discrepancy indices were $R = 0.057$ and $R_w = 0.062$ for 5012 independent reflections with $I > 3\sigma(I)$. The protonation of the species formed by the reduction of biscarborane by 4 equiv or an excess of sodium naphthalide resulted in the formation of Na_2(**2**). $[P(C_6H_5)_3CH_3]_2$(**2**) crystallized in the monoclinic space group $P2_1/n$ with $a = 11.429$ (3), $b = 15.075$ (4), and $c = 16.520$ (4) Å, $\beta = 119.648$ (8)°, $V = 2474$ Å^3, and $Z = 2$. Data were collected on a Huber diffractometer (constructed at UCLA) using Mo Kα radiation, to a maximum $2\theta = 50°$, giving 4368 unique reflections. The structure was solved by direct methods (MULTAN80). The final discrepancy indices were $R = 0.070$ and $R_w = 0.101$ for 3264 independent reflections with $I > 3\sigma(I)$.

The isomers of *closo*-$C_2B_{10}H_{12}$ have been reduced by sodium or sodium naphthalide solution to yield [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ species[1-3] which, in turn, have been employed in the synthesis of numerous metallacarboranes.[4-8] The oxidation of the [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ anions derived from *closo*-1,12-$C_2B_{10}H_{12}$, *closo*-1,7-$C_2B_{10}H_{12}$, and *closo*-1,2-$C_2B_{10}H_{12}$ has resulted in the formation of *closo*-1,7-$C_2B_{10}H_{12}$, *closo*-1,2-$C_2B_{10}H_{12}$, and *closo*-1,2-$C_2B_{10}H_{12}$, respectively, indicating a preference for the carbon atoms to approach one another during the oxidation process.[9] The protonation of the [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ anion prepared via the reduction of *closo*-1,2-$C_2B_{10}H_{12}$ has resulted in the formation of two isomers:[9] a kinetic product, [*nido*-7,9-$C_2B_{10}H_{13}$]$^-$, and a thermodynamic product, [(μ-9,10-CH_2)-*nido*-7-$CB_{10}H_{11}$]$^-$. However, the analogous chemistry involving the reduction of biscarborane[10] has not been investigated. Presented herein are details which concern the chemistry of the products obtained upon reduction of biscarborane, the initial results of which were reported elsewhere.[11]

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Experimental Section

Synthesis. $[P(C_6H_5)_3CH_3]_2(C_2B_{10}H_{11})_2$ ($[P(C_6H_5)_3CH_3]_2$(1)). In a drybox 0.041 g (1.8 mmol) of sodium was placed in a 100-mL Schlenk flask. A THF solution (50 mL) of biscarborane, 0.25 g (0.89 mmol), was transferred via cannula onto the sodium. The solution and sodium were stirred for 60 h until no sodium remained and a red-orange solution resulted. After the THF was removed under vacuum and acetonitrile (20 mL) was transferred by cannula onto the resulting residue, a red-orange solution resulted. Metathesis with $[P(C_6H_5)_3CH_3]Br$, 0.49 g (1.8 mmol), followed by filtration through a bed of Celite resulted in the isolation of 0.61 g (0.72 mmol, 81%) of crude $[P(C_6H_5)_3CH_3]_2$(**1**) as a tacky orange solid. The crude product was redissolved in acetonitrile, and diethyl ether was allowed to vapor-diffuse into this solution, resulting in the formation of orange crystals of $[P(C_6H_5)_3CH_3]_2$(**1**), 0.18 g (0.21 mmol, 24%), suitable for examination by X-ray diffraction. ^{11}B NMR (160.5 MHz, CH_3CN, 25 °C, $BF_3{\cdot}O(C_2H_5)_2$): −5.4 (d, J = 134 Hz), −7.4 (d, J = 141 Hz), −12.6 (d, J = 150 Hz), −13.7 (d, J = 156 Hz), −26.3 ppm (d, J = 133 Hz) in relative areas of 1:2:4:1:2, respectively. ^1H NMR (200.1 MHz, CD_3CN, 25 °C, TMS): 7.90–7.61 (mult, C_6H_5, cation), 2.81 (d, $^2J_{PH}$ = 13.9 Hz, CH_3, cation), 2.28 ppm (s, broad, carboranyl CH). IR (KBr): 2972, 2906, 2530, 2510, 2474, 1586, 1481, 1437, 1337, 1319, 1190, 1162, 1113, 1075, 1049, 1029, 995, 895, 782, 741, 717, 689, 512, 496, 483 cm^{-1}. Anal. Calcd for $B_{20}C_{42}H_{58}P_2$: C, 59.97; H, 6.96; B, 25.70; P, 7.36. Found: C, 57.44; H, 6.78; B, 25.05; P, 6.77. (Carbon analyses are frequently low in the analyses of borane derivatives which contain phosphorus.)

Alternate Method. When $[P(C_6H_5)_3CH_3]_2$(**1**) was prepared on a larger scale, 5.36 g (18.7 mmol) of biscarborane, 0.859 g (37.4 mmol) of sodium, 0.220 g (1.72 mmol) of naphthalene (functioning as an electron carrier), and 80 mL of THF were employed. The reaction was complete in 12 h, as evidenced by the consumption of the sodium. After removal of THF, metathesis with 10.2 g (36.9 mmol) of $[P(C_6H_5)_3CH_3]Br$, and filtration of the resulting acetonitrile solution through a bed of Celite, the solution was reduced to approximately 10 mL in volume and orange crystals of $[P(C_6H_5)_3CH_3]_2$(**1**) precipitated (7.71 g, 9.17 mmol, 49%). The ^1H and ^{11}B NMR spectra of the material prepared in this way were identical to those of the sample prepared via the first method.

[(15-crown-5)$_3$Na$_2$](1). A THF solution of $Na_2(C_2B_{10}H_{11})_2$ (1.21 mmol) was prepared according to the above procedure. The THF was removed under dynamic vacuum until a red oil remained. This red oil was dissolved in 20 mL of diethyl ether and 15-crown-5 ether (1.18 g, 5.37 mmol) in 15 mL of diethyl ether was added via a cannula. An orange precipitate immediately formed, and the mixture was filtered. The resulting orange solid, collected on the frit, was recrystallized from 15 mL of methylene chloride by addition of 30 mL of diethyl ether, yielding [(15-crown-5)$_3$Na$_2$](**1**) (0.903 g, 0.909 mmol, 75%). ^1H NMR (200.1 MHz, CD_2Cl_2, 25 °C, TMS): 3.68 (s, 15-crown-5 CH_2), 2.54 ppm (s, carboranyl CH). ^{11}B NMR (160.5 MHz, CD_2Cl_2, 25 °C, $BF_3{\cdot}O(C_2H_5)_2$): −6.3 (d, J = 133 Hz), −8.2 (d, J = 127 Hz), −13.5 (d, J not resolved), −14.8 (d, J = 147 Hz), −24.6 ppm (d, J = 133 Hz) in approximate relative areas of 1:2:2:3:2, respectively. IR (KBr): 2887, 2529, 1607, 1466, 1449, 1355, 1299, 1251, 1131, 1125, 1095, 1037, 946, 859, 828, 771, 699, 542, 527 cm^{-1}.

$[P(C_6H_5)_3CH_3]_2[\mu$-9,10-CH-(μ-9′,10′-*nido*-7′-$CB_{10}H_{11}$)-*nido*-7-$CB_{10}H_{11}]$ ($[P(C_6H_5)_3CH_3]_2$(2)). To 1.78 g (13.9 mmol) of naphthalene in a 100-mL Schlenk flask was added 0.60 g (26 mmol) of sodium. The flask was stoppered with a rubber septum and placed under an atmosphere of N_2; 60–70 mL of dry THF was then cannulated onto the naphthalene and sodium. Immediately a green solution of sodium naphthalide began to form, and stirring was continued for 24 h. The sodium naphthalide solution was cannulated onto 0.992 g (3.46 mmol) of biscarborane, and a deep red solution resulted. To this red solution, under a stream of N_2, was added the excess sodium from the naphthalide preparation. The solution turned dark green over a period of 1 h, indicating that all the biscarborane had been completely reduced. The solution was added to 50 mL of degassed water, and a yellow solution resulted which was allowed to stir for 30 min. The resulting solution was filtered through a bed of Celite and placed on a rotary evaporator to remove the THF. The resulting aqueous solution was filtered to remove the naphthalene and added to 200 mL of benzene. The water was removed as an azeotrope using a Dean–Starke apparatus. The benzene was decanted from the resulting white solid. The solid was dissolved in acetonitrile, and the solution was filtered. The acetonitrile was removed on a rotary evaporator, the resulting oil was dissolved in water, and an aqueous solution containing 2.47 g (6.92 mmol) of $[P(C_6H_5)_3CH_3]Br$ was added. The precipitate which immediately formed was collected by filtration, dissolved in a minimum of acetonitrile, and recrystallized by addition of diethyl ether, yielding 0.71 g (0.84 mmol, 24%) of $[P(C_6H_5)_3CH_3]_2$(**2**). Another recrystallization yielded an additional 0.44 g (0.52 mmol, 15%) of $[P(C_6H_5)_3CH_3]_2$(**2**) (total yield 39%). ^{11}B NMR (160.5 MHz, $(CD_3)_2CO$, 25 °C, $BF_3{\cdot}O(C_2H_5)_2$: 15.3 (d, J = 126 Hz), 7.7 (d, J = 135 Hz), −2.5 (d, J = 133 Hz), −9.4 (d, J = 145 Hz), −13.5 (d, J = 133), −20.5 ppm (d, J = 135 Hz) in approximate relative areas of 2:1:1:2:2:2, respectively. ^1H NMR (200.1 MHz, CD_3CN, 25 °C, TMS): 7.85 (mult, C_6H_5, cation), 7.68 (mult, C_6H_5, cation), 3.43 (s, carboranyl CH), 2.82 (d, $^2J_{PH}$ = 13.8 Hz, CH_3, cation), 2.51 ppm (s, carboranyl CH). IR (KBr): 3054, 2990, 2972, 2917, 2540, 2514, 1439, 1116, 896, 743, 720, 689, 510 cm^{-1}.

Table I. Crystallographic Data for [(15-crown-5)$_3$Na$_2$](**1**) and $[P(C_6H_5)_3CH_3]_2$(**2**)

	[(15-crown-5)$_3$Na$_2$](**1**)	$[P(C_6H_5)_3CH_3]_2$(**2**)
formula	$C_{34}H_{82}B_{20}Na_2O_{15}$	$C_{42}H_{58}B_{20}P_2$
fw	993.34	841.14
space group	$P\bar{1}$	$P2_1/n$
λ/Å	0.7107	0.7107
a/Å	12.411 (1)	11.429 (3)
b/Å	14.676 (2)	15.075 (4)
c/Å	14.988 (2)	16.520 (4)
α/deg	101.371 (3)	
β/deg	96.222 (3)	119.648 (8)
γ/deg	91.549 (4)	
V/Å^3	2657	2474
Z	2	2
T/K	128	298
ρ(calcd)/g cm^{-3}	1.24	1.13
μ/cm^{-1}	1.0	1.0
R, R_w, GOF[a]	0.057, 0.062, 1.60	0.070, 0.101, 3.39

[a] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Crystallography. [(15-crown-5)$_3$Na$_2$](1). A yellow crystal obtained from a $CH_2Cl_2/(C_2H_5)_2O$ solution was sealed in a capillary on a modified Picker FACS-1 diffractometer equipped with a graphite-monochromatized Mo source and a gas-stream low-temperature device. Unit cell parameters were determined from a least-squares fit of 26 accurately centered reflections (9.6 < 2θ < 20.4°). These dimensions and other parameters, including conditions of data collection, are summarized in Table I. Data were collected at 128 K in the θ–2θ scan mode. Three intense reflections (050, 1$\bar{2}$3, 21$\bar{3}$) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (124.9 h). Of the 12 832 unique reflections measured, 5012 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects but not for absorption or extinction. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; SHELX76 (Sheldrick) crystal structure package, SHELX86 (Sheldrick) structure solution package, and ORTEP (Johnson).

Atoms were located by use of direct methods (SHELX86). All calculations were performed on the VAX 3100 computer in the J. D. McCullough Crystallography Laboratory. All cation H atoms were included in calculated positions as members of rigid groups, C–H distances were 1.0 Å, and H–C–H angles were 109.5°. Most carboranyl H atoms were kept in located positions. Positional parameters for H(7) through H(11) and H(7′) through H(11′), the hydrogen atoms of the bonding faces, were refined. H atoms were assigned u values of 0.04 Å^2. Scattering factors for H atoms were obtained from Stewart et al.,[12] and those for other atoms were taken from ref 13. Anomalous dispersion terms were applied to the scattering of sodium. The largest peak on a final difference electron density map was 0.4 e Å^{-3}. Final positional and thermal parameters for non-hydrogen atoms are given in Table II.

$[P(C_6H_5)_3CH_3]_2$(2). A colorless crystal, obtained from an $CH_3CN/(C_2H_5)_2O$ solution, was mounted on a fiber on a Huber diffractometer constructed at UCLA and equipped with a graphite-monochromatized Mo source. Systematic absences were found for 0k0 reflections for which $k = 2n$ and for $h0l$ reflections for which $h + l = 2n$. Unit cell parameters were determined from a least-squares fit of 53 accurately centered re-

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Table II. Final Non-Hydrogen Positional and Thermal Parameters for [(15-crown-5)$_3$Na$_2$](**1**)[a]

atom	*x*	*y*	*z*	$\langle u^2\rangle/\text{Å}^2$
Na(1)	0.7323 (1)	0.0934 (1)	0.7754 (1)	0.025
O(1A)	0.6725 (2)	−0.0691 (2)	0.7451 (2)	0.026
C(2A)	0.5808 (3)	−0.0856 (3)	0.7910 (3)	0.026
C(3A)	0.6167 (4)	−0.0650 (3)	0.8916 (3)	0.030
O(4A)	0.6555 (2)	0.0308 (2)	0.9186 (2)	0.028
C(5A)	0.7381 (4)	0.0479 (3)	0.9954 (3)	0.031
C(6A)	0.8491 (4)	0.0304 (3)	0.9658 (3)	0.030
O(7A)	0.8666 (2)	0.0876 (2)	0.9018 (2)	0.028
C(8A)	0.9754 (3)	0.0874 (3)	0.8792 (3)	0.033
C(9A)	0.9844 (4)	0.1521 (3)	0.8140 (3)	0.036
O(10A)	0.9125 (2)	0.1224 (2)	0.7309 (2)	0.033
C(11A)	0.9540 (4)	0.0524 (3)	0.6655 (3)	0.038
C(12A)	0.8690 (4)	0.0271 (3)	0.5841 (3)	0.036
O(13A)	0.7689 (2)	−0.0054 (2)	0.6089 (2)	0.033
C(14A)	0.7675 (4)	−0.1017 (3)	0.6152 (3)	0.033
C(15A)	0.6658 (4)	−0.1224 (3)	0.6539 (3)	0.030
Na(2)	0.3544 (1)	0.3229 (1)	0.7109 (1)	0.025
O(1B)	0.4733 (2)	0.3788 (2)	0.6073 (2)	0.029
C(2B)	0.5109 (4)	0.4747 (3)	0.6296 (3)	0.032
C(3B)	0.5276 (3)	0.5037 (3)	0.7315 (3)	0.030
O(4B)	0.4296 (2)	0.4859 (2)	0.7646 (2)	0.034
C(5B)	0.4348 (4)	0.5109 (3)	0.8614 (3)	0.037
C(6B)	0.3214 (4)	0.4977 (3)	0.8848 (3)	0.038
O(7B)	0.2880 (2)	0.4033 (2)	0.8476 (2)	0.033
C(8B)	0.1772 (4)	0.3782 (3)	0.8583 (3)	0.037
C(9B)	0.1038 (4)	0.3738 (3)	0.7722 (3)	0.040
O(10B)	0.1375 (2)	0.3016 (2)	0.7042 (2)	0.034
C(11B)	0.0817 (4)	0.3010 (3)	0.6145 (3)	0.039
C(12B)	0.1385 (3)	0.3659 (3)	0.5653 (3)	0.034
O(13B)	0.2473 (2)	0.3370 (2)	0.5627 (2)	0.030
C(14B)	0.3066 (4)	0.3863 (3)	0.5089 (3)	0.032
C(15B)	0.4202 (4)	0.3526 (3)	0.5155 (3)	0.032
O(1C)	0.3925 (2)	0.1638 (2)	0.6213 (2)	0.029
C(2C)	0.4728 (4)	0.0989 (3)	0.5922 (3)	0.033
C(3C)	0.5765 (4)	0.1510 (3)	0.5884 (3)	0.037
O(4C)	0.6237 (2)	0.1853 (2)	0.6805 (2)	0.028
C(5C)	0.6973 (4)	0.2651 (3)	0.6906 (3)	0.034
C(6C)	0.7018 (4)	0.3163 (3)	0.7873 (3)	0.037
O(7C)	0.7435 (2)	0.2562 (2)	0.8457 (2)	0.035
C(8C)	0.7332 (4)	0.2926 (3)	0.9408 (3)	0.042
C(9C)	0.6273 (4)	0.2603 (3)	0.9681 (3)	0.040
O(10C)	0.5382 (3)	0.3078 (2)	0.9340 (2)	0.036
C(11C)	0.4367 (4)	0.2746 (3)	0.9564 (3)	0.030
C(12C)	0.3933 (4)	0.1845 (3)	0.8963 (3)	0.033
O(13C)	0.3615 (2)	0.1949 (2)	0.8058 (2)	0.029
C(14C)	0.3257 (4)	0.1068 (3)	0.7472 (3)	0.030
C(15C)	0.3037 (4)	0.1205 (3)	0.6514 (3)	0.031
B(1)	0.2028 (4)	0.3859 (3)	0.1238 (3)	0.025
B(2)	0.2404 (4)	0.3027 (3)	0.1907 (3)	0.026
B(3)	0.1605 (4)	0.2675 (3)	0.0837 (3)	0.027
B(4)	0.0666 (4)	0.3526 (4)	0.0714 (3)	0.027
B(5)	0.0940 (4)	0.4480 (3)	0.1667 (3)	0.027
B(6)	0.1955 (4)	0.4109 (3)	0.2453 (3)	0.022
C(7)	0.1361 (4)	0.2278 (3)	0.1763 (3)	0.028
B(8)	0.0225 (4)	0.2556 (3)	0.1199 (3)	0.025
B(9)	−0.0237 (4)	0.3736 (3)	0.1555 (3)	0.022
B(10)	0.0579 (4)	0.4110 (3)	0.2665 (3)	0.024
B(11)	0.1361 (4)	0.3062 (3)	0.2712 (3)	0.023
C(12)	−0.0121 (3)	0.3122 (3)	0.2358 (2)	0.017
B(1′)	−0.3159 (4)	0.1898 (3)	0.3712 (3)	0.024
B(2′)	−0.3473 (4)	0.2644 (3)	0.2924 (3)	0.027
B(3′)	−0.2917 (4)	0.3113 (3)	0.4074 (3)	0.026
B(4′)	−0.1889 (4)	0.2370 (3)	0.4375 (3)	0.023
B(5′)	−0.1933 (4)	0.1364 (3)	0.3477 (3)	0.021
B(6′)	−0.2869 (4)	0.1579 (3)	0.2546 (3)	0.021
C(7′)	−0.2517 (3)	0.3477 (3)	0.3177 (3)	0.027
B(8′)	−0.1488 (4)	0.3341 (3)	0.3910 (4)	0.027
B(9′)	−0.0833 (4)	0.2219 (3)	0.3650 (3)	0.021
B(10′)	−0.1447 (4)	0.1659 (3)	0.2499 (3)	0.023
B(11′)	−0.2284 (4)	0.2636 (3)	0.2275 (3)	0.023
C(12′)	−0.0896 (3)	0.2707 (2)	0.2752 (2)	0.015

[a] Esd's for the least significant digits are given in parentheses.

Table III. Final Non-Hydrogen Positional and Thermal Parameters for [P(C$_6$H$_5$)$_3$CH$_3$]$_2$(**2**)[a]

atom	*x*	*y*	*z*	$\langle u^2\rangle/\text{Å}^2$
P(1)	0.7286 (1)	0.0554 (1)	0.1899 (1)	0.039
B(1)	0.7049 (5)	−0.2623 (3)	0.1873 (3)	0.050
B(2)	0.5321 (5)	−0.2469 (3)	0.1512 (4)	0.054
B(3)	0.6287 (5)	−0.3187 (3)	0.2436 (3)	0.051
B(4)	0.7422 (4)	−0.3761 (3)	0.2185 (3)	0.045
B(5)	0.7223 (4)	−0.3342 (3)	0.1099 (3)	0.044
B(6)	0.5803 (5)	−0.2590 (3)	0.0654 (3)	0.050
C(7)	0.4786 (4)	−0.3493 (2)	0.1562 (3)	0.047
B(8)	0.5897 (5)	−0.4282 (3)	0.1910 (3)	0.045
B(9)	0.6642 (4)	−0.4444 (3)	0.1140 (3)	0.041
B(10)	0.5613 (4)	−0.3686 (3)	0.0163 (3)	0.042
B(11)	0.4420 (4)	−0.3202 (3)	0.0510 (3)	0.047
C(12)	0.5061 (3)	−0.4644 (2)	0.0342 (3)	0.040
C(12P)	0.7567 (2)	−0.0469 (2)	0.3373 (2)	0.057
C(13P)	0.8288 (2)	−0.0987 (2)	0.4168 (2)	0.074
C(14P)	0.9637 (2)	−0.1181 (2)	0.4483 (2)	0.079
C(15P)	1.0266 (2)	−0.0858 (2)	0.4003 (2)	0.072
C(16P)	0.9544 (2)	−0.0340 (2)	0.3209 (2)	0.055
C(11P)	0.8195 (2)	−0.0146 (2)	0.2894 (2)	0.043
C(22P)	0.6629 (2)	0.2315 (2)	0.2019 (2)	0.052
C(23P)	0.6960 (2)	0.3202 (2)	0.2262 (2)	0.063
C(24P)	0.8303 (2)	0.3468 (2)	0.2712 (2)	0.060
C(25P)	0.9316 (2)	0.2846 (2)	0.2919 (2)	0.082
C(26P)	0.8985 (2)	0.1958 (2)	0.2676 (2)	0.075
C(21P)	0.7641 (2)	0.1693 (2)	0.2226 (2)	0.042
C(32P)	0.7868 (3)	−0.0562 (1)	0.0827 (2)	0.051
C(33P)	0.8115 (3)	−0.0757 (1)	0.0100 (2)	0.062
C(34P)	0.8244 (3)	−0.0071 (1)	−0.0417 (2)	0.072
C(35P)	0.8126 (3)	0.0809 (1)	−0.0207 (2)	0.086
C(36P)	0.7880 (3)	0.1003 (1)	0.0520 (2)	0.068
C(31P)	0.7751 (3)	0.0318 (1)	0.1037 (2)	0.042
C(41M)	0.5519 (4)	0.0330 (3)	0.1381 (3)	0.055

[a] Esd's for the least significant digits are given in parentheses.

flections ($9.5 < 2\theta < 20.3°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table I. Data were collected at 25 °C in the θ–2θ scan mode. Three intense reflections ($311, 30\bar{8}, 14\bar{2}$) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (90.2 h). Of the 4368 unique reflections measured, 3264 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement, MULTAN80 (Main et al.), statistical methods, and ORTEP (Johnson).

Atoms were located by use of direct methods (MULTAN80). All calculations were performed on the VAX 3100 computer in the J. D. McCullough Crystallography Laboratory. All methyl and phenyl H atoms were included in calculated positions as members of rigid groups, C–H distances were 1.0 Å, H–C–H angles were 109.5°, or phenyl group angles were 120°. Carboranyl H atoms were kept in located positions. The methyl, phenyl, and carboranyl H atoms were assigned *u* values of 0.08, 0.08, and 0.06 Å^2, respectively. Scattering factors for H atoms were obtained from Stewart et al.,[12] and those for other atoms were taken from ref 13. Anomalous dispersion terms were applied to the scattering of P. The larger peaks on a final difference electron density map were ±0.5 e Å^{-3}. Final positional and thermal parameters for non-hydrogen atoms are given in Table III.

Results

When a THF solution of biscarborane reacted with 2 equiv of sodium metal or sodium naphthalide solution, the intensely orange disodium salt Na$_2$(**1**) was formed. Metathesis of Na$_2$(**1**) with [P(C$_6$H$_5$)$_3$CH$_3$]Br resulted in the formation and isolation of [P(C$_6$H$_5$)$_3$CH$_3$]$_2$(**1**). The interaction of Na$_2$(**1**) with 15-crown-5 ether in diethyl ether resulted in the formation and isolation of [(15-crown-5)$_3$Na$_2$](**1**). Biscarborane was further reduced by the addition of a total of 4 equiv of sodium metal or sodium naphthalide. Protonation of the species formed by reduction of biscarborane with 4 equiv (or an excess) of sodium naphthalide resulted in the formation of Na$_2$(**2**). Metathesis of Na$_2$(**2**) with [P(C$_6$H$_5$)$_3$CH$_3$]Br resulted in the formation and isolation of [P(C$_6$H$_5$)$_3$CH$_3$]$_2$(**2**). The molecular structures of [(15-crown-5)$_3$Na$_2$](**1**) and [P(C$_6$H$_5$)$_3$CH$_3$]$_2$(**2**) were determined by single-

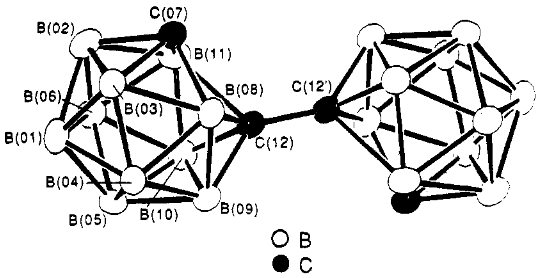

Figure 1. Solid-state molecular structure of **1** in $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$ with thermal ellipsoids drawn at 50% probability. The terminal hydrogen atoms have been omitted for clarity. The distance 1.95 Å was arbitrarily chosen as the cutoff point for the representation of connectivity between boron and carbon. The anion, **1**, is centrosymmetric.

Table IV

C(12)–B Interatomic Distances (Å) in $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$ and $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$

	$[P(C_6H_5)_3CH_3]_2(\mathbf{1})$	$[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ unprimed	$[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ primed
C(12)–B(8)	1.838 (4)	1.869 (6)	2.024 (6)
C(12)–B(9)	1.628 (4)	1.634 (7)	1.641 (7)
C(12)–B(10)	1.643 (4)	1.626 (6)	1.626 (6)
C(12)–B(11)	1.925 (4)	1.867 (6)	1.786 (6)
C(12)···C(7)	2.414 (4)	2.400 (6)	2.418 (6)

Selected Interatomic Distances (Å) and Angles (deg) in $[P(C_6H_5)_3CH_3]_2(\mathbf{2})$

C(12)–C(12′)	1.515 (5)	C(12′)–C(12)–B(9)	112.7 (3)
C(12)–B(9)	1.656 (5)	C(12′)–C(12)–B(10)	112.7 (3)
C(12)–B(10)	1.661 (5)	C(12)–B(9)–B(8)	83.2 (3)
		C(12)–B(10)–B(11)	83.4 (3)
C(12)···C(7)	2.794 (5)		
C(12)···B(11)	2.355 (5)		
C(12)···B(8)	2.343 (8)		

crystal X-ray diffraction methods.

Discussion

Molecular Structure of 1. When a THF solution of biscarborane reacts with 2 equiv of sodium metal or sodium naphthalide solution, the intensely orange disodium salt $Na_2(C_2B_{10}H_{11})_2$, $(Na_2(\mathbf{1}))$ is formed.[11] The salt $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$, the synthesis and molecular structure (Figure 1) of which have been previously reported,[11] has been isolated via the metathesis reaction of $Na_2(\mathbf{1})$ with $[P(C_6H_5)_3CH_3]Br$. The anion, **1**, in $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$ consists of two carborane polyhedra connected via a carbon–carbon bond (C(12)–C(12′) = 1.377 (4) Å), which exhibits substantial double-bond character. It has been postulated that the asymmetry in the two long (C(12)–B(8) and C(12)–B(11)) and two short (C(12)–B(9) and C(12)–B(10)) C(12)–B distances (Table IV) in $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$ is due to packing forces. In an effort to prove this postulation, a species consisting of the anion **1** combined with a different countercation has been synthesized.

When an excess of 15-crown-5 in diethyl ether is added to a diethyl ether solution of $Na_2(\mathbf{1})$, an orange solid immediately forms. Dissolution of this solid in methylene chloride, followed by precipitation with diethyl ether, leads to the isolation of $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ in 75% yield. The solution-state ^{11}B NMR spectra of $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ and $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$ in acetonitrile are identical, as are the solution-state ^{11}B NMR spectra of $Na_2(\mathbf{1})$ and $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ in methylene chloride. These spectra indicate that in solution the structure of **1** is the same in all three salts: $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$, $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$, and $Na_2(\mathbf{1})$. However, although they are similar, differences are observed between the solid-state structures of **1** in $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ and $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$.

Crystals of $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$, suitable for X-ray diffraction study, have been obtained by vapor diffusion of diethyl ether into a methylene chloride solution. The molecular structure of **1** in $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ consists of two carborane polyhedra connected via a carbon–carbon bond (C(12)–C(12′) = 1.370 (5) Å) (Figure 2). The major differences between **1** in $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ and **1** in $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$ are summarized in Table IV. From Table IV, Figure 1, and Figure 2, it is clear that there is asymmetry in the C(12)–B(8)/C(12)–B(11) and C(12)–B(9)/C(12)–B(10) pairs of interatomic distances in $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$, even greater asymmetry in the primed carborane cage of $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$, and no asymmetry (within experimental error) in the unprimed carborane cage of $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$. These three distinct geometries of the carborane cages in the solid-state structure of **1** demonstrate that the interaction between C(12) (C(12′)) and the open face of the carborane cage is the only flexible link in an otherwise rigid molecule, and in addition, the asymmetry of the C(12)–B distances initially found in $[P(C_6H_5)_3CH_3](\mathbf{1})$ is not due to bonding requirements but simply to crystal packing forces.

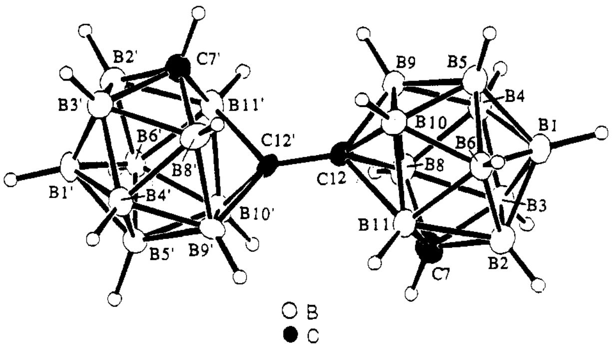

Figure 2. Solid-state molecular structure of **1** in $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ with thermal ellipsoids drawn at 50% probability. The distance 1.95 Å was arbitrarily chosen as the cutoff point for the representation of connectivity between boron and carbon. The anion, **1**, is not centrosymmetric.

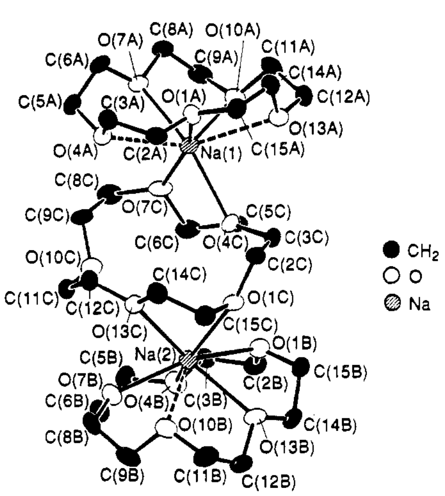

Figure 3. Solid-state molecular structure of $[(15\text{-crown-}5)_3Na_2]^{2+}$ in $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ with thermal ellipsoids drawn at 50% probability. The hydrogen atoms have been omitted for clarity.

Structure of $[(15\text{-crown-}5)_3Na_2]^{2+}$. To our knowledge, the determination of the molecular structure of the complex cation in $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ (Figure 3) represents the first structural characterization of such a species. Crown ether complexes have been shown to exhibit the following stoichiometries with alkali-metal cations: 1:1, 2:1 ("sandwich"), and 3:2 ("club sandwich") crown ether:metal cation complexes.[14] The "sandwich" structures are typically formed with potassium, rubidium, and cesium cations, while sodium forms both 1:1 and "sandwich" complexes.[15] However, the "club sandwich" structural motif initially proposed for 3:2 crown ether:metal complexes[14] has typically been limited to complexes involving the cesium cation.

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(14) Pedersen, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 386.
(15) Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1980**, 1066.

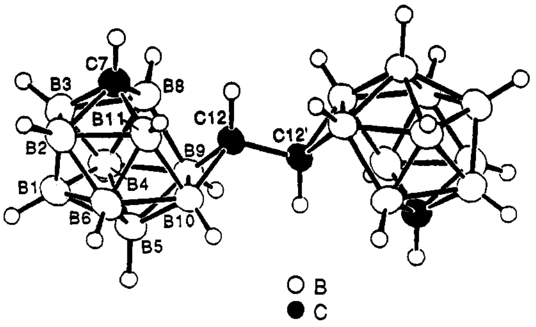

Figure 4. Solid-state molecular structure of **2** in $[P(C_6H_5)_3CH_3]_2(\mathbf{2})$ with thermal ellipsoids drawn at 50% probability. The anion, **2**, is centrosymmetric.

The cation $[(15\text{-crown-}5)_3Na_2]^{2+}$ is composed of two sodium ions sandwiched in a stack of three 15-crown-5 ether ligands (Figure 3). Each sodium ion is coordinated to seven oxygen atoms, two of the central 15-crown-5 ether and all five of the adjacent outer 15-crown-5 ether. Sodium 1 is complexed to the five oxygen atoms of crown ether A and to two oxygen atoms (O(4C) and O(7C)) of the central crown ether, C, while sodium 2 is complexed to the five oxygen atoms of crown ether B and to two different oxygen atoms (O(1C) and O(13C)) of crown ether C. The sodium to crown ether C coordinating oxygen distances range from 2.407 (3) to 2.568 (3) Å, while the sodium to A and B coordinating oxygen distances range from 2.400 (3) to 2.743 (3) Å (see supplementary material). Oxygen 10C is not within the coordination sphere of either sodium. Sodium 1 is located 1.062 (2) Å and sodium 2 is located 1.035 (2) Å from the least-squares plane through the oxygen atoms of A and B, respectively, in the direction of C (see supplementary material). The angles between the least-squares planes defined by the five oxygen atoms of each of the crown ethers are 11.4, 31.4, and 20.1° between A and B, A and C, and B and C, respectively.

The formation of this unique 3:2 "club sandwich" complex in $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ can be attributed to two factors: one, the low coordinating ability of the anion, **1**, and two, the low coordinating ability of diethyl ether, the only coordinating solvent with which the crystals of $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ have come in contact.

Four-Electron Reduction of Biscarborane. When 4 equiv of sodium or sodium naphthalide is added to biscarborane, a light yellow solution results, from which the expected anion, $(C_2B_{10}H_{11})_2^{4-}$, has not been isolated. However, upon protonation of these solutions and subsequent workup, $[P(C_6H_5)_3CH_3]_2(\mathbf{2})$ has been isolated in 39% yield. The formation of the anion, **2**, is most likely the result of the protonation of an anion, $(C_2B_{10}H_{11})_2^{4-}$, analogous to the protonation of $(nido\text{-}C_2B_{10}H_{11})^{2-}$, which yields $(\mu\text{-}9,10\text{-}CH_2\text{-}nido\text{-}CB_{10}H_{11})^-$.[9]

Crystals of $[P(C_6H_5)_3CH_3]_2(\mathbf{2})$, suitable for X-ray diffraction studies, have been obtained by slow diffusion of diethyl ether into an acetonitrile solution. The structure of **2** (Figure 4) consists of two carborane polyhedra connected via a carbon–carbon bond (C(12)–C(12′) = 1.515 (5) Å). Comparing the structure of **2** with those of **1**, it is apparent that the long contacts C(12)–B(8) and C(12)–B(11) which exist in **1** no longer exist in **2** and the C(12)–C(12′) distance in **2** (1.515 (5) Å) has increased with respect to the C(12)–C(12′) bond in **1** (1.377 (4) or 1.370 (5) Å) but is quite close to the corresponding carbon–carbon bond found in biscarborane (1.522 (2) Å[16]). Selected interatomic distances and angles for **2** are given in Table IV.

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Registry No. $[P(C_6H_5)_3CH_3]_2(\mathbf{1})$, 127229-15-6; $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$, 137541-66-3; $[P(C_6H_5)_3CH_3]_2(\mathbf{2})$, 137541-64-1; $[P(C_6H_5)_3CH_3]Br$, 1779-49-3; biscarborane, 12075-02-4.

Supplementary Material Available: Listings of crystallographic data, positional and thermal parameters, and interatomic distances, angles, and torsion angles for $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ and listings of crystallographic data, positional and thermal parameters, and interatomic distances and angles for $[P(C_6H_5)_3CH_3]_2(\mathbf{2})$ (27 pages); listings of calculated and observed structure factors for $[(15\text{-crown-}5)_3Na_2](\mathbf{1})$ and $[P(C_6H_5)_3CH_3]_2(\mathbf{2})$ (48 pages). Ordering information is given on any current masthead page.

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(16) Hall, L. H.; Perloff, A.; Mauer, F. A.; Block, S. *J. Chem. Phys.* **1965**, *43*, 3911.