# Practical Synthesis of Aminoethyl-*o*-carboranes

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A convenient synthesis of [(*N*,*N*′-dibenzylamino)ethyl]-*o*-carboranes (**3**) is reported. Under catalytic hydrogenolysis conditions ($H_2$/Pd−C), *o*-carboranylamines with *N*-benzyl groups were selectively removed to give the corresponding secondary amines (**4**). Thus, a highly selective cleavage of one *N*-benzyl group was achieved by using Pd catalyst under mild and acidic reaction conditions. This method is efficient and compatible with other *o*-carboranyl alkyl groups such as methyl and phenyl groups present in the substrate. Alternatively, primary aminoethyl-*o*-carborane (**7**) can be prepared by monoalkylation of *o*-carborane, followed by selective deprotection of the silyl group.

## Introduction

Aminoalkyl-*o*-carboranes ($Cab^N$) have attracted interest due to their potential use in boron neutron capture therapy (BNCT).[1] Moreover, the coordination behavior of these potentially bidentate ligands has been the focus of extensive studies.[2] Furthermore, the corresponding deboronated compounds ($Dcab^N$) are the common starting materials for the preparation of new half-sandwich complexes, ($Dcab^N$)$ML_2$ (M = Ti, Zr, Hf, L = Cl;[3] M = Fe, Ru, L = Lewis base;[4] M = Ni, L = $PPh_3$[5]), with metals possessing specific structures and reactivities. Hence, there is considerable interest in the synthesis of aminoalkyl-*o*-carboranes.

The synthesis of aminoalkyl-*o*-carboranes is commonly achieved by the addition of terminal alkynes to activated boranes $B_{10}H_{12}L_2$.[6] However, despite recent modifications,[7,8] low yields of the desired aminoalkyl-*o*-carboranes are not uncommon, especially when highly functionally substituted substrates are used. In 1997, Quintana[9] reported the formation of functionalized aminoalkyl-*o*-carboranes by the reaction of lithio-*o*-carborane with *N*-(bromoalkyl)phthalimides and their application to the preparation of isocyanate-substituted *o*-carboranes. Hughes and co-workers[10] later described the successful deprotection of *N*-phthalimidoalkyl-*o*-carboranes with hydrazine hydrate; however, the purification of the resultant aminoalkyl-*o*-carboranes was unreliable, and the yields after recrystallization were consistently low as a result of the formation of deboronated coproducts.[11] Thus, we chose to explore alternative procedures for the introduction of the aminoalkyl functional group into the carboranes. With the aim of obtaining a convenient and high-yielding route to the monosubstituted aminoalkyl-*o*-carborane derivatives, *N*-(2-chloroethyl)dibenzylamine (**2**) was chosen as the starting material. The benzyl moiety is one of the most commonly employed protecting groups for amine functionality in organic synthesis[12] due to its ease of deprotection and inherent stability. Thus, the [(*N*,*N*′-dibenzylamino)ethyl]-*o*-carboranes **3** were prepared by the addition of lithio-*o*-carborane to *N*-(2-chloroethyl)-dibenzylamine (**2**). Subsequent hydrogenolysis caused *N*-debenzylation to produce the corresponding secondary amines. Alternatively, the reaction between lithio-*o*-carborane **1a** and $ClCH_2CH_2N(SiMe_3)_2$ (**5**) followed by hydrolysis of the resultant disilazane with aqueous HCl yielded the primary amine, aminoethyl-*o*-carborane (**7**), quantitatively. Therefore, an alternative and convenient synthetic methodology for the synthesis of aminoalkyl-*o*-carboranes has been developed. The carborane products were analyzed by NMR spectroscopy and X-ray crystallography where appropriate.

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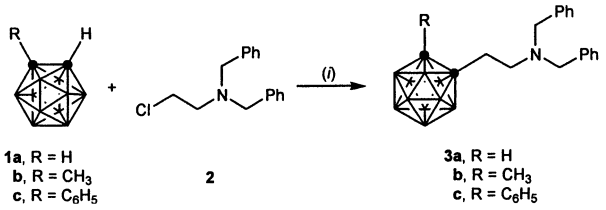
**Scheme 1. Synthesis of 3[a]**




[a] Legend: (*i*) Bu$^n$Li, benzene, 25 °C.

## Results and Discussion

**Synthesis of [(*N*,*N*′-Dibenzylamino)ethyl]-*o*-carborane (3).** The carborane **3** was obtained from the direct reaction of lithio-*o*-carborane with *N*-(2-chloroethyl)dibenzylamine (**2**) as described in Scheme 1.

The synthesis was initiated by the monolithiation of the *o*-carborane derivatives **1**.[13] When *o*-carborane was treated with an equimolar quantity of *n*-butyllithium in benzene followed by *N*-(2-chloroethyl)dibenzylamine (**2**), [(*N*,*N*′-dibenzylamino)ethyl]-*o*-carborane (**3**) was formed in high yield. In this case, no color change was observed and the reaction was monitored by TLC; complete disappearance of the starting material was observed after 12 h of vigorous stirring at room temperature. Compounds **3** are moderately stable in air and can be purified by low-temperature recrystallization in ethanol. The identification of all products **3** isolated was accomplished by IR and $^1$H, $^{11}$B, and $^{13}$C NMR spectroscopy. Accordingly, the compounds **3** have distinct resonances in the $^1$H NMR spectrum for each proton of the C*H*$_2$ units: $\delta$ 3.4−3.6 (s, 2H, N-C*H*$_2$-Ph), $\delta$ 2.5−2.7 (t, 2H, N-C*H*$_2$-CH$_2$), and $\delta$ 2.0−2.4 (t, 2H, Cab-C*H*$_2$). Product identification was further supported by a single-crystal X-ray diffraction analysis of **3a**. The structural parameters (Table 2) fall within the normal range for the monosubstituted *closo*-derivatives. Finally, satisfactory elemental analyses were also obtained for compounds **3**.

**Preparation of [(*N*-Benzylamino)ethyl]-*o*-carborane Hydrochloride (4).** The benzyl group is a commonly used protecting group in organic synthesis,[14] and its removal is in most cases carried out by hydrogenolysis using Pd−C catalysts with $H_2$ as the reducing agent. Although simple hydrogenolysis of the mono- and/or dibenzylamine derivatives by a conventional method, Pd−C/$H_2$, has been reported,[15] the [(*N*,*N*′-dibenzylamino)ethyl]-*o*-carborane derivatives in this study failed to undergo complete cleavage under such conditions as discussed below.[16] In 1996, Blaser and Studer reported that with catalytic amounts of HCl as a modifier, the mono- or dibenzyl derivatives can rapidly and selectively undergo debenzylation.[17] Thus, with the aid of HCl, the mono-debenzylation of **3** occurred cleanly to afford the secondary benzyl amine **4** in >80% yield after recrystallization (Scheme 2).

Compounds **4** were isolated as white, transparent crystals. These compounds are both air- and moisture-stable in the solid state. The structural identity of **4** was confirmed by a single-crystal X-ray structural analysis of **4a** (Figure 2). The reaction of **3a** in acidic ethanol with $H_2$ (60 psi) and Pd−C catalyst caused selective mono-debenzylation and produced a quantitative yield of the corresponding secondary amine **4a**. The attempted deprotection of the second *N*-benzyl group proved unsuccessful under these reaction conditions, with no evidence for the formation of primary amines even upon treatment with excess Pd catalyst and extended reaction times. Similarly, the use of the corresponding methyl- or phenyl-*o*-carborane derivative in Scheme 2 yielded the mono-debenzylated product **4b**

**Table 1. X-ray Crystallographic Data and Processing Parameters for Compounds 3a and 4a**

| | **3a** | **4a** |
|---|---|---|
| formula | $C_{18}H_{29}B_{10}N$ | $C_{11}H_{24}B_{10}ClN$ |
| fw | 367.52 | 313.86 |
| cryst class | monoclinic | orthorhombic |
| space group | $P2_1/c$ | $P2_12_12_1$ |
| $Z$ | 4 | 4 |
| cell constants | | |
| $a$, Å | 10.2077(6) | 6.8687(7) |
| $b$, Å | 15.2630(9) | 11.6255(8) |
| $c$, Å | 14.7009(12) | 23.1877(13) |
| $V$, Å$^3$ | 2263.3(3) | 1851.6(3) |
| $\beta$, deg | 98.818(6) | |
| $\mu$, mm$^{-1}$ | 0.055 | 0.196 |
| cryst size, mm | 0.4 × 0.45 × 0.45 | 0.3 × 0.35 × 0.5 |
| $D_{calcd}$, g/cm$^3$ | 1.079 | 1.126 |
| $F$(000) | 776 | 656 |
| radiation | Mo Kα ($\lambda$ = 0.7170 Å) | |
| $\theta$ range, deg | 1.94−25.97 | 1.76−25.97 |
| $h$, $k$, $l$ collected | +12,+18,±18 | +8,+14,+28 |
| no. of reflns collected/ unique | 4694/4442 | 2146/2109 |
| no. of data/restraints/ params | 4442/0/283 | 2109/0/232 |
| goodness-of-fit on $F^2$ | 0.321 | 1.106 |
| final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0389$[a] | $R_1 = 0.0594$[a] |
| | $wR_2 = 0.0886$[b] | $wR_2 = 0.1565$[b] |
| $R$ indices (all data) | $R_1 = 0.2565$[a] | $R_1 = 0.1345$[a] |
| | $wR_2 = 0.1142$[b] | $wR_2 = 0.1879$[b] |

[a] $R_1 = \sum||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F^2$). [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2,0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

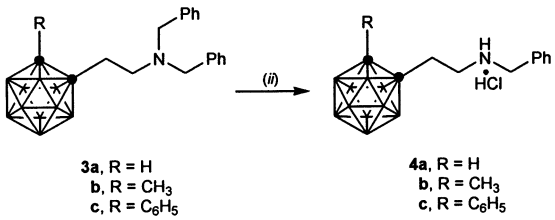
**Table 2. Selected Interatomic Distances (Å) in 3a and 4a**

| **3a** | | **4a** | |
|---|---|---|---|
| N(1)−C(5) | 1.461(3) | N(1)−C(4) | 1.483(7) |
| N(1)−C(4) | 1.464(3) | N(1)−C(5) | 1.515(7) |
| N(1)−C(12) | 1.468(3) | C(1)−C(3) | 1.531(7) |
| C(1)−C(3) | 1.532(3) | C(3)−C(4) | 1.521(7) |
| C(3)−C(4) | 1.519(3) | C(5)−C(6) | 1.479(8) |
| C(5)−C(6) | 1.502(3) | | |
| C(12)−C(13) | 1.505(3) | | |

**Table 3. Selected Interatomic Angles (deg) in 3a and 4a**

| **3a** | | **4a** | |
|---|---|---|---|
| C(5)−N(1)−C(4) | 110.4(2) | C(4)−N(1)−C(5) | 114.7(5) |
| C(5)−N(1)−C(12) | 109.8(2) | C(4)−C(3)−C(1) | 115.1(5) |
| C(4)−N(1)−C(12) | 109.9(2) | N(1)−C(4)−C(3) | 107.7(5) |
| C(4)−C(3)−C(1) | 116.6(2) | C(6)−C(5)−N(1) | 112.4(5) |
| N(1)−C(4)−C(3) | 115.1(2) | | |
| N(1)−C(5)−C(6) | 114.5(2) | | |
| N(1)−C(12)−C(13) | 111.9(2) | | |

**Scheme 2. Synthesis of 4[a]**




[a] Legend: (*i*) $H_2$, Pd/C, HCI, EtOH, 25 °C.

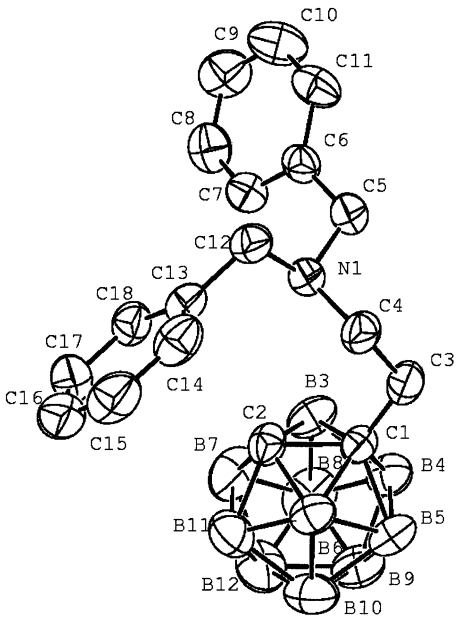



**Figure 1.** Molecular structure of 1-[(dibenzylamino)ethyl]-*o*-carborane (**3a**). The thermal ellipsoids are drawn at the 30% probability level.

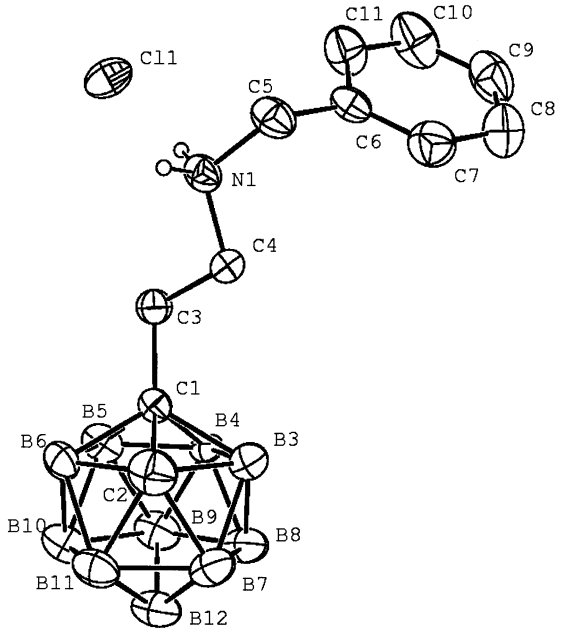
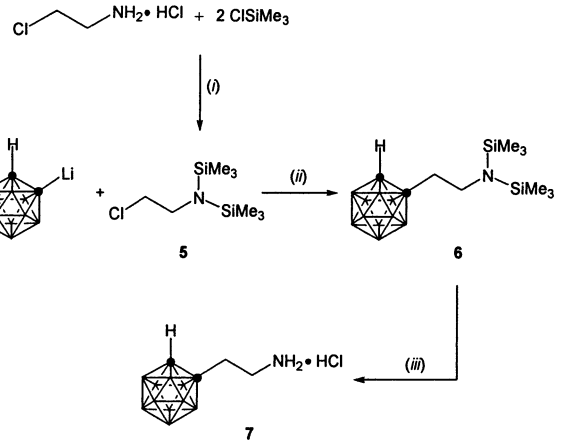



**Figure 2.** Molecular structure of 1-[(benzylamino)ethyl]-*o*-carborane·HCl (**4a**). The thermal ellipsoids are drawn at the 30% probability level.

or **4c**, in yields comparable to **4a**. Thus, the treatment of **3** with $H_2$ in acidic ethanol resulted in the monodebenzylation to exclusively afford, based on an $^1$H NMR spectroscopic analysis of the crude reaction mixture, the corresponding secondary amine [(*N*-benzylamino)ethyl]-*o*-carborane hydrochloric acid salts (**4**).

Since the debenzylation approach is not ideal for the generation of the primary aminoethyl-*o*-carborane, we felt that alternative strategies were worthy of investigation. A reported synthesis of 1-aminoethyl-*o*-carborane (**7**) consists of the treatment of Li[1,2-$C_2B_{10}H_{11}$] (**1a**) with commercially available *N*-(bromoethyl)phthalimide in glyme.[9] We believe that the synthesis of carborane **7** shown in Scheme 3 is more convenient. There was no substantial difference observed for the monoalkylation

**Scheme 3. Synthesis of 7**[a]




[a] Legend: (*i*) Methylene chloride, 25 °C; (*ii*) Bu$^n$Li, benzene, 25 °C; (iii) HCl, $Et_2O$, 25 °C.

of *o*-carborane. The HCl-promoted deprotection of silyl groups is well established and was exploited in our preparation of **7**. The disilyl group was therefore selectively cleaved to give the corresponding parent amine in high yield. In terms of selectivity and efficiency, this mild disilazane protection/deprotection protocol is superior to other conventional methods using, for example, phthalimide/hydrazine.[9] The major drawback of the latter method is the significant formation of byproducts as a result of the use of the deprotecting reagents. However, under our reaction conditions, only the desired amines were obtained in quantitative yields, with no trace of deboronated compounds.

The treatment of **1a** with 1 equiv of *n*-butyllithium followed by 1 equiv of **5** yielded the monoalkylated product **6** in high yield. Desilylation of a diethyl ether suspension of the *N*-protected product **6** with 6 N HCl at 25 °C afforded **7** directly as microcrystalline solids in high yield. Product identification was confirmed by comparison of spectroscopic properties with those reported by Quintana.[9] Thus, we have developed an efficient alternative synthetic route to primary *o*-carboranylethylamine.

## Conclusions

Large quantities of starting materials **3** and **6** are readily obtained in high yield, and the subsequent hydrogenolytic debenzylation of **3** gives the corresponding secondary aminoethyl-*o*-carboranes **4** in high purity. In addition, we have described a chemoselective method for the cleavage of nitrogen−silicon bonds to generate primary amino-*o*-carborane.[7] The main advantage of our protocol is the high yields of deprotected products obtained. Thus, our synthesis provides the first practical, unequivocal synthesis of aminoalkyl-*o*-carboranes adaptable for large-scale production.

## Experimental Section

**General Procedures.** All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques. Ether and benzene were dried and distilled from sodium/benzophenone. The $^1$H, $^{11}$B, and $^{13}$C NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1, 96.3, and 75.4 MHz, respectively. All proton and carbon chemical shifts were measured relative

to internal residual chloroform from the lock solvent (99.5% $CDCl_3$) and then referenced to $Me_4Si$ (0.00 ppm). The chemical shift values for the $^{11}B$ NMR spectra were referenced relative to external $BF_3{\cdot}OEt_2$. IR spectra were recorded on a Biorad FTS-165 spectrophotometer. The elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. All melting points are uncorrected. The carboranes and *N*-(2-chloroethyl)dibenzylamine were purchased from Katechem and Aldrich, respectively, and used without purification. Palladium on carbon catalyst was purchased from Aldrich and used without purification.

**Synthesis of 1-[(Dibenzylamino)ethyl]-*o*-carborane (3a).** To a stirred solution of *o*-carborane (**1a**; 4.3 g, 30 mmol) in benzene (600 mL) was added 2.5 M *n*-BuLi (13.2 mL, 33 mmol) via a syringe through a serum cap at 25 °C. The resulting white suspension was stirred at 25 °C for 10 min and then placed in an ice bath. When the benzene solution was cold, the *N*-(2-chloroethyl)dibenzylamine **2** (7.8 g, 30 mmol) was added to the lithio-*o*-carborane. The reaction temperature was maintained at 0 °C for 1 h. The reaction mixture was then slowly warmed to room temperature. After stirring for an additional 12 h, the reaction mixture was filtered. Diethyl ether was added, and the organic layer was washed with distilled water, dried with anhydrous $MgSO_4$, and then dried in vacuo to give a white crystalline powder. The resulting residue was taken up in a minimum of ethanol and then recrystallized from this solution by cooling it to −10 °C to afford **3a** (10.5 g, 95%) as colorless crystals. Anal. Calcd for $C_{18}H_{29}B_{10}N$: C, 58.82; H, 7.95; N, 3.81. Found: C, 58.96; H, 8.00; N, 3.85. Mp: 83 °C. IR spectrum (KBr pellet, $cm^{-1}$): 2588(s), 3031(w), 3064(w), 3086(w). $^1H$ NMR ($CDCl_3$): $\delta$ 2.36−2.41 (2H, t), 2.58−2.63 (2H, t), 3.52 (2H, s), 3.95 (1H, s), 7.27−7.39 (10H, m). $^{13}C$ NMR ($CDCl_3$): $\delta$ 34.18, 51.92, 58.72, 73.83, 138.23.

**1-[(Dibenzylamino)ethyl]-2-methyl-*o*-carborane (3b).** The same method as described for **3a** but with **1b** instead of **1a** produced **3b** (11.2 g, 98%) as white crystals. Anal. Calcd for $C_{19}H_{31}B_{10}N$: C, 59.81; H, 8.19; N, 3.67. Found: C, 59.90; H, 8.23; N, 3.73. Mp: 55 °C. IR spectrum (KBr pellet, $cm^{-1}$): 2579(s), 3029(w), 3061(w), 3085(w). $^1H$ NMR ($CDCl_3$): $\delta$ 1.71 (3H, s), 2.17−2.23 (2H, t), 2.62−2.67 (2H, t), 3.63 (2H, s), 7.27−7.38 (10H, m). $^{13}C$ NMR ($CDCl_3$): $\delta$ 22.87, 33.01, 59.26, 74.65, 76.69, 138.99.

**1-[(Dibenzylamino)ethyl]-2-phenyl-*o*-carborane (3c).** The procedure was analogous to that described for **3a** but using **1c** instead of **1a** to give **3c** (13.0 g, 98%) as white crystals. Anal. Calcd for $C_{24}H_{33}B_{10}N$: C, 64.98; H, 7.50; N, 3.16. Found: C, 65.06; H, 7.60; N, 3.24. Mp: 67 °C. IR spectrum (KBr pellet, $cm^{-1}$): 2588(s), 3030(w), 3064(w), 3084(w). $^1H$ NMR ($CDCl_3$): $\delta$ 2.00−2.06 (2H, t), 2.56−2.61 (2H, t), 3.46 (2H, s), 7.27−7.38 (15H, m). $^{13}C$ NMR ($CDCl_3$): $\delta$ 31.85, 58.37, 80.74, 83.64, 138.78.

**Preparation of 1-[(Benzylamino)ethyl]-*o*-carborane·HCl (4a).** The Pd−C catalyst (1.5 g, 20 wt %) was introduced into a reactor together with an equimolar quantity of concentrated HCl, ethanol (60 mL), and the starting material **3a** (7.35 g, 20 mmol) under a hydrogen atmosphere (60 psi) at room temperature. The reaction mixture was shaken for 5 h at room temperature. The suspended solid was then collected by filtration, and the solvent was removed under vacuum. The resulting residue was taken up in a minimum of ethanol and then recrystallized from this solution by cooling it to −10 °C to afford **4a** (4.6 g, 74%) as colorless crystals. Anal. Calcd for $C_{11}H_{24}B_{10}NCl$: C, 42.09; H, 7.71; N, 4.46. Found: C, 42.60; H, 7.83; N, 4.54. Mp: 250−251 °C. IR spectrum (KBr pellet, $cm^{-1}$): 2602(s), 3340(w), 3422(w). $^1H$ NMR (DMSO-$d_6$): $\delta$ 2.77−2.83 (2H, t), 3.01−3.07 (2H, t), 4.13 (2H, s), 5.42 (1H, s), 7.41−7.56 (5H, m), 9.69 (1H, s). $^{13}C$ NMR (DMSO-$d_6$): $\delta$ 44.84, 49.88, 63.13, 72.51, 131.86.

**1-[(Benzylamino)ethyl]-2-methyl-*o*-carborane·HCl (4b).** The method was similar to that described for **4a** but using **3b** instead of **3a** to yield **4b** (5.8 g, 89%) as a white powder. Anal. Calcd for $C_{12}H_{26}B_{10}NCl$: C, 43.96; H, 7.99; N, 4.27. Found: C, 44.40; H, 8.08; N, 4.37. Mp: 230−231 °C. IR spectrum (KBr pellet, $cm^{-1}$): 2592(s), 3344(w), 3440(w). $^1H$ NMR (DMSO-$d_6$): $\delta$ 2.13 (3H, s), 2.83−2.89 (2H, t), 3.10−3.13 (2H, t), 4.17 (2H, s), 7.41−7.58 (5H, m), 9.69 (2H, s). $^{13}C$ NMR (DMSO-$d_6$): $\delta$ 22.89, 30.87, 49.85, 75.60, 76.68, 132.04.

**1-[(Benzylamino)ethyl]-2-phenyl-*o*-carborane·HCl (4c).** The procedure was analogous to that described for **4a** but using **3c** instead of **3a** to give **4c** (6.3 g, 81%) as a white powder. Anal. Calcd for $C_{17}H_{28}B_{10}NCl$: C, 52.36; H, 7.24; N, 3.59. Found: C, 52.47; H, 7.32; N, 3.64. Mp: 215−216 °C. IR spectrum (KBr pellet, $cm^{-1}$): 2588(s), 3327(w), 3451(w). $^1H$ NMR (DMSO-$d_6$): $\delta$ 1.95−2.00 (2H, t), 2.66−2.71 (2H, t), 3.61 (2H, s), 7.41−7.61 (10H, m), 9.69 (2H, s). $^{13}C$ NMR (DMSO-$d_6$): $\delta$ 31.59, 51.24, 75.98, 77.59, 132.05, 134.24.

**Preparation of *N*,*N*′-Bis(trimethylsilylamino)ethylene Chloride (5).** A 500 mL flask was charged with 2-chloroethylamine hydrochloride (11.6 g, 100 mmol), $NEt_3$ (46.4 mL, 330 mmol), and freshly distilled methylene chloride (300 mL). A solution of chlorotrimethylsilane (28.0 mL, 220 mmol) in methylene chloride (50 mL) was added to the vigorously stirred slurry of chloroethylamine slowly over 1 h via a cannula. The reaction mixture was stirred overnight, and the precipitate of $NEt_3{\cdot}HCl$ was filtered off. The methylene chloride solution was evaporated, and the residue was extracted with hexane. The extracts were combined, and the solvent was removed in vacuo. The residue was dried in vacuo to give the product as a slightly yellow liquid (18.1 g, 81%). $^1H$ NMR ($CDCl_3$): $\delta$ 0.12 (18H, s), 3.04−3.09 (2H, t), 3.23−3.29 (2H, t). $^{13}C$ NMR ($CDCl_3$): $\delta$ 3.02, 44.52, 45.61.

**Synthesis of 1-[Bis(trimethylsilyl)aminoethyl]-*o*-carborane (6).** To a stirred solution of *o*-carborane (**1a**; 4.3 g, 30 mmol) in benzene (600 mL) was added 2.5 M *n*-BuLi (13.2 mL, 33 mmol) via a syringe through a serum cap at 25 °C. The resulting white suspension was stirred at 25 °C for 10 min and then placed in an ice bath. When the benzene solution was cold, $ClCH_2CH_2N(SiMe_3)_2$ (6.7 g, 30 mmol) was added to the lithio-*o*-carborane. The reaction mixture was maintained at 0 °C for 1 h and then slowly warmed to room temperature. After stirring for an additional 12 h, the reaction mixture was filtered. The filtrate volume was reduced under vacuum, and the resulting residue was taken up in a minimum of hexane and then recrystallized from this solution by cooling it to −10 °C to afford **6** (7.7 g, 78%) as a white powder. Anal. Calcd for $C_{10}H_{33}B_{10}NSi_2$: C, 36.22; H, 10.03; N, 4.22. Found: C, 36.62; H, 10.18; N, 4.33. Mp: 53 °C. IR spectrum (KBr pellet, $cm^{-1}$): 2598(s), 2957(m), 3069(w). $^1H$ NMR ($CDCl_3$): $\delta$ 0.24 (18H, s), 2.43−2.50 (2H, t), 2.96−3.04 (2H, t), 3.34 (1H, br s). $^{13}C$ NMR ($CDCl_3$): $\delta$ 0.20, 33.81, 37.98, 54.56.

**Preparation of 1-[(Amino)ethyl]-*o*-carborane·HCl (7).** A 100 mL flask was charged with 1-[bis(trimethylsilyl)-aminoethyl]-*o*-carborane (1.66 g, 5.0 mmol) and diethyl ether (50 mL). The reaction flask was cooled in an ice bath, and 6 N HCl (15 mL) was slowly added to the ethereal solution. After 12 h, the ether and water layer were separated, and the latter was washed with ether (330 mL). The water was removed on a rotary evaporator to give a yellowish-white powder. This residue was taken up in a minimum of acetone and then recrystallized from this solution by cooling it to −10 °C to afford **7** (0.94 g, 84%) as a white crystalline powder. Anal. Calcd for $C_4H_{18}B_{10}NCl$: C, 21.47; H, 8.11; N, 6.26. Found: C, 21.73; H, 8.25; N, 6.42. Mp: 121−122 °C. IR spectrum (KBr pellet, $cm^{-1}$): 2578(s), 2909(w), 2958(w), 3070(s). $^1H$ NMR (DMSO-$d_6$): $\delta$ 2.57−2.63 (2H, t), 2.83−2.89 (2H, t), 5.38 (1H, br s), 8.04 (3H, br s). $^{13}C$ NMR (DMSO-$d_6$): $\delta$ 35.74, 37.50, 63.13.

**X-ray Crystallography.** Details of the crystal data and a summary of the intensity data collection parameters for **3a** and **4a** are given Table 1 in the Supporting Information. The crystals of **3a** and **4a** were grown from ethanol solutions stored

at −10 °C. The crystals of **3a** and **4a** were mounted in thin-walled glass capillaries and sealed under argon. The data sets of **3a** and **4a** were collected using an Enraf CAD4 automated diffractometer. Mo Kα radiation ($\lambda = 0.7107$ Å) was used for all the structures. Each structure was solved by the application of direct methods using the SHELXS-96 program[18a] and least-squares refinement using SHELXL-97.[18b] The absolute configuration of **4a** was confirmed by the refinement of the Flack parameter.

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**Supporting Information Available:** Tables of bond distances and angles, atomic coordinates, and thermal parameters for compounds **3a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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