

A Facile and Practical Synthetic Route to 1,1'-Bis(*o*-carborane)

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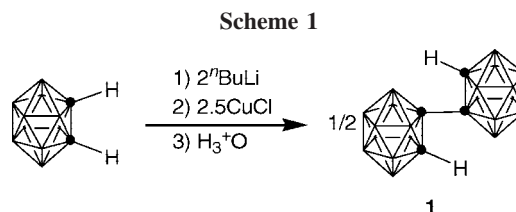
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Summary: Reaction of dilithiocarborane ($1,2\text{-Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$) with CuCl in toluene affords a single product, $1,1':2,2'\text{-[Cu(toluene)]}_2(\text{C}_2\text{B}_{10}\text{H}_{10})_2$, which gives 1,1'-bis(*o*-carborane) after hydrolysis. This serves as the most efficient method for the preparation of 1,1'-bis(*o*-carborane).

1,1'-Bis(*o*-carborane) has been found to act as a unique bidentate ligand for transition metals, forming a class of remarkably stable complexes $[\text{M}\{(\text{C}_2\text{B}_{10}\text{H}_{10})_2\}]^{n-}$,¹ and as a building block for the construction of rigid-rod molecules.² It is usually prepared by the reaction of $\text{B}_{10}\text{H}_{12} \cdot 2\text{L}$ ($\text{L} = \text{SEt}_2, \text{CH}_3\text{CN}$) with $\text{HC}\equiv\text{CC}\equiv\text{CH}$.³ CuCl_2 -mediated coupling reactions of the monolithium⁴ or dilithium salts of *o*-carborane are also reported to give 1,1'-bis(*o*-carborane), but in low yields, since the C–B and B–B coupling products are generated in the same reaction.⁵ The separation of $1,1\text{-}(\text{C}_2\text{B}_{10}\text{H}_{11})_2$ from its isomers is a tedious process. We were interested in the properties of 1,1'-bis(*o*-carborane) as potential multidentate π ligands⁶ after reduction.⁷ We then revisited the copper-mediated coupling reactions and report here a facile and practical synthesis of 1,1'-bis(*o*-carborane).

Results and Discussion

Treatment of $1,2\text{-Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ with 2.5 equiv of CuCl in toluene at room temperature gave, after hydrolysis with a dilute HCl solution, the C–C coupling product 1,1'-bis(*o*-carborane) (**1**) in 83% isolated yield (Scheme 1). It is noteworthy that the coupling efficiency is highly dependent on the reaction conditions. Donor solvents such as THF, diethyl ether, and DME offer poor yields. On the other hand, the copper salts play a crucial role in the reaction. Both CuCN and CuI are much less active than CuCl , and CuCl_2 leads to a mixture of isomers containing C–C, C–B, and B–B coupling products.⁵ The use of cuprous salt is essential to avoid C–B and B–B couplings. When the monolithium salt



$\text{LiC}_2\text{B}_{10}\text{H}_{11}$ is used instead of $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$, the yield of 1,1'-bis(*o*-carborane) is dramatically decreased to 30% with a recovery of *o*-carborane. The coupling efficiency also drops if <2 equiv of CuCl is used. No coupling product is observed when 1-Li-2-Me- $1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ is employed as starting material.

The molecular structure of 1,1'-bis(*o*-carborane) is shown in Figure 1. The C(1)–C(1A) distance of 1.530(3) Å is significantly shorter than the C(1)–C(2) distance of 1.690(3) Å but is very close to the corresponding values (1.512(13)–1.539(12) Å) found in $[\text{M}\{(\text{C}_2\text{B}_{10}\text{H}_{10})_2\}]^{n-}$.¹

To gain some insight into the aforementioned C–C coupling reaction, we have isolated the intermediate $1,1':2,2'\text{-[Cu(toluene)]}_2(\text{C}_2\text{B}_{10}\text{H}_{10})_2$ (**2**) from the reaction system before hydrolysis. Single-crystal X-ray analyses reveal that **2** adopts a centrosymmetrical structure with an inversion center at the midpoint of the C(1)–C(1A) bond (Figure 2). Each Cu atom is σ -bound to the cage carbon atom and η^3 -bound to a toluene molecule in a linear geometry. The C(1)–C(1A)/C(1)–C(2) distances of 1.533(4)/1.679(3) Å are very close to those observed in **1**. The Cu(1)–C(2) distance of 1.920(2) Å is slightly shorter than the corresponding values (2.005(6)–2.031(6) Å) found in $[\text{Cu}\{(\text{C}_2\text{B}_{10}\text{H}_{10})_2\}]^{n-}$ ($n = 1, 2$),¹ probably due to steric reasons.

A possible reaction pathway is proposed in Scheme 2 on the basis of the above results and the formation of copper mirror during the reaction. Transmetalation between $1,2\text{-Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ and CuCl gives dicuprous carborane.⁸ Coupling of $1,2\text{-Cu}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ affords **2** and eliminates copper metal. Hydrolysis of **2** produces **1**.

In summary, CuCl -mediated C–C coupling of $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ in toluene is a facile and practical method for the preparation of 1,1'-bis(*o*-carborane).

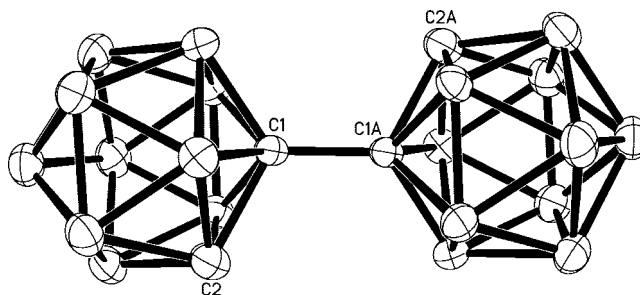


Figure 1. Molecular structure of 1,1'-bis(*o*-carborane) (**1**) (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å): C(1)–C(1A) = 1.530(3), C(1)–C(2) = 1.690(3).

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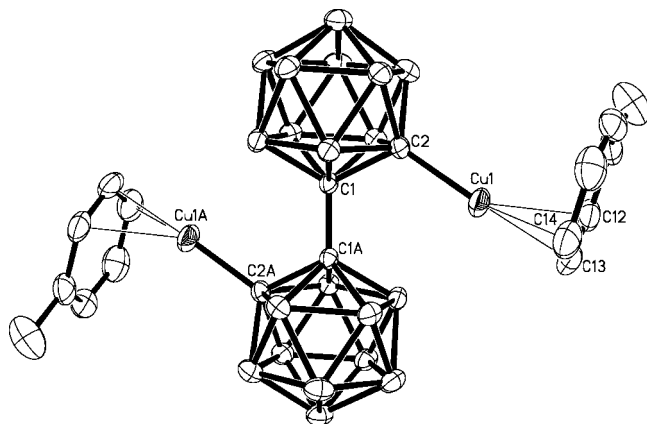
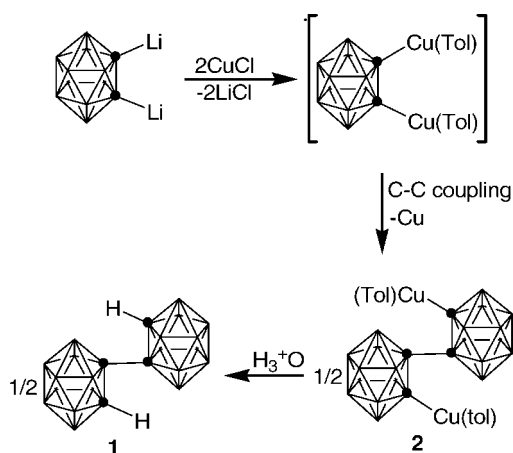


Figure 2. Molecular structure of 1,1':2,2'-[Cu(toluene)]₂(C₂B₁₀H₁₀)₂ (**2**) (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å): Cu(1)–C(2) = 1.920(2), Cu(1)–C(13) = 2.078(3), Cu(1)–C(12) = 2.261(3), Cu(1)–C(14) = 2.424(4), C(1)–C(1A) = 1.533(4), C(1)–C(2) = 1.679(3).

Scheme 2



Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen, 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. All chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.0 and 75.5 MHz, respectively. ¹¹B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.3 MHz. All chemical shifts were reported in δ units with reference to the residual protons and carbons of the deuterated solvents for proton and carbon chemical shifts and to external BF₃·OEt₂ (0.00 ppm) for boron chemical shifts.

Preparation of 1,1'-Bis(*o*-carborane) (1**).** To a toluene solution (20 mL) of *o*-carborane (432 mg, 3.0 mmol) was slowly added ⁿBuLi (3.75 mL, 6.0 mmol, 1.6 M in hexane), and the mixture was stirred at room temperature overnight. CuCl powder (750 mg, 7.5 mmol) was added to the above suspension, and the reaction mixture was stirred at room temperature for 2 days. The resulting dark red suspension was then quenched by 3 M HCl. The organic layer was separated, and the aqueous solution was extracted with ethyl ether (30 mL × 2). The organic portions were combined and concentrated to dryness. The crude product was purified by flash column

Table 1. Crystal Data and Summary of Data Collection and Refinement Details for **1** and **2**

	1	2
formula	C ₄ H ₂₂ B ₂₀	C ₁₈ H ₃₆ B ₂₀ Cu ₂
cryst size, mm	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.30
fw	286.42	595.75
cryst syst	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> , Å	7.017(1)	7.036(3)
<i>b</i> , Å	9.885(2)	9.412(3)
<i>c</i> , Å	12.375(2)	11.529(4)
α, deg	90	92.36(1)
β, deg	90.44(1)	95.14(1)
γ, deg	90	105.41(1)
<i>V</i> , Å ³	858.3(2)	731.4(5)
<i>Z</i>	2	1
<i>D</i> _{calcd} , Mg/m ³	1.108	1.353
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2θ range, deg	5.3–56.0	3.6–56.0
μ, mm ⁻¹	0.045	1.466
<i>F</i> (000)	292	302
no. of obsd rflns	2055	3441
no. of params refined	109	181
goodness of fit	1.114	1.080
R1	0.069	0.044
wR2	0.210	0.121

chromatography on silica gel using hexane as eluent to give **1** as a white solid (355 mg, 83%). X-ray-quality crystals were grown from hexane/ether (1/1, v/v) solution. ¹H NMR (acetone-*d*₆, ppm): δ 5.51 (s, cage CH). ¹³C NMR (acetone-*d*₆, ppm): δ 65.2, 73.5 (cage C). ¹¹B{¹H} NMR (acetone-*d*₆, ppm): δ -1.56 (2B), -2.05 (2B), -8.72 (6B), -9.16 (6B), -11.65 (4B). These data are identical with those reported in the literature.⁵

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.⁹ Both structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on *F*² using the SHELXTL program package.¹⁰ All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1. Further details are included in the Supporting Information.

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Supporting Information Available: CIF files giving crystallographic data for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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