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Radical Substitution at Boron in Small Cobaltacarboranes. Conversion of η^5-C_5Me_5 to η^4-C_5Me_5R Complexes[1]

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As an alternative approach to metal-promoted cross-coupling reactions for the preparation of B-substituted organo derivatives of small cobaltacarboranes, synthesis via radical substitution reactions has been explored. Reduction of neutral Cp*Co^{III}(2,3-$Et_2C_2B_4H_3$-5-I) (**1**) and Cp*Co^{III}(2,3-$Et_2C_2B_4H_4$) (**4**) to generate the respective 19-electron anionic Co(II) complexes **1**$^-$ and **4**$^-$, followed by radical reactions with nucleophiles and electrophiles, led to substitution at boron and/or the Cp* (η^5-C_5Me_5) ligand. Reaction of **1** with Rieke Mg* in THF formed Cp*Co($Et_2C_2B_4H_3$)-5-O$(CH_2)_4$-(η^4-C_5Me_5)CoH($Et_2C_2B_4H_3$-5-I) (**2**), whose two cobaltacarborane units are linked through a tetramethyleneoxy linking group. In contrast, **1**$^-$ and **4**$^-$ reacted with $MeOSO_2CF_3$ to afford (η^4-C_5Me_6)CoH($Et_2C_2B_4H_3$-5-I) (**3**) or (η^4-C_5Me_6)CoH($Et_2C_2B_4H_3$-5-Me) (**5**) and (η^4-C_5Me_6)CoH($Et_2C_2B_4H_4$) (**6**). The somewhat reactive **1**$^-$ was stabilized with the introduction of 18-crown-6 to form the paramagnetic salt K(18-crown-6)$^+$Cp*Co^{II}($Et_2C_2B_4H_3$-5-I)$^-$ (**10**). Treatment of **1** and **10** with the nucleophile $LiNMe_2$ in the presence of K(Hg) gave respectively Cp*Co($Et_2C_2B_4H_3$-5-NMe_2) (**8**) and Cp*Co($Et_2C_2B_4H_3$-7-NMe_2) (**11**). Compound **8** was decapped on exposure to air to give Cp*Co($Et_2C_2B_3H_4$-5-NMe_2) (**9**); its apically substituted isomer **11** cannot undergo deborylation. A *tert*-butoxide group was introduced at B(5) in moderate yield by reaction of K O-*t*-Bu with **1**$^-$, affording **12**. Treatment of **12** with acidified methanol produced the B(5)−OH derivative **14**. X-ray diffraction analyses confirmed the structures of **2**, **10**, and **11**.

Introduction

The extraordinarily varied three-dimensional stereochemistry, intrinsic stability, and chemical versatility of metallacarboranes and metallo-substituted carboranes make them prime candidates for a variety of applications.[2] While research in this area has focused primarily on large (usually 12-vertex icosahedral) cage systems, a role for smaller metallacarboranes is emerging in catalysis, construction of electroactive materials, and anticancer agents.[3] Such applications, however, require the development of efficient methods for the selective introduction of functional groups at boron. As reported recently,[1,4] we have been exploring metal-facilitated cross-coupling reactions on halogenated complexes of the type LM(RR′$C_2B_4H_3$X), where L is typically Cp, Cp* (η^5-C_5Me_5), or an arene, R and R′ are usually H, alkyl, or aryl, and M is Co, Fe, Ru, or another transition metal, as a route to specified B-substituted derivatives. We have extensively studied mixed-ligand Cp′Co(RR′$C_2B_4H_4$) complexes (Cp′ = Cp, Cp*) and find them to be excellent synthons for electronically tailorable organometallic compounds in that they are soluble, are resistant to air and heat, and are easily derivatized and oligomerized.[3,5] Many of these cobaltacarboranes can be reversibly converted via chemical or electrochemical methods to highly reduced or oxidized states such as Co(I) and Co(IV).[6] The B−H bonds of the neutral complexes are in general unreactive except toward halogenating agents;[7] the metal-bound hydrocarbon ligands are inert under most reaction conditions encountered in our systems and typically (though with some exceptions[8]) are involved in the chemistry only indirectly via their electronic influence on the adjacent metal centers.[8]

In this paper we examine a different approach to small-metallacarborane derivatization. Investigation of icosahedral $CpCoC_2B_9$ clusters by Zakharkin et al.[9] showed that oxidative substitution with thallium(III) trifluoroacetate affords a trifluoroacetyl derivative that

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[1] Organotransition-metal Metallacarboranes. 62. Part 61: Yao, H.; Sabat, M.; Grimes, R. N. *Organometallics* **2002**, *21*, 2833.

[2] (a) For a broad-ranging compilation of reviews of recent work in the boron cluster field, see: *Contemporary Boron Chemistry*; Davidson, M., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000. (b) Grimes, R. N. *Coord. Chem. Rev.* **2000**, *200*, 773.

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[5] (a) Malaba, D.; Sabat, M.; Grimes, R. N. *Eur. J. Inorg. Chem.* **2001**, 2557. (b) Bluhm, M.; Pritzkow, H.; Siebert, W.; Grimes, R. N. *Angew. Chem., Int. Ed.* **2000**, *39*, 4562; *Angew. Chem.* **2000**, *112*, 4736. (c) Grimes, R. N. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1997; p 321.

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[9] Zakharkin, L. I.; Kobak, V. V.; Kovredov, A. I.; Furmanova, N. G.; Struchkov, Y. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 1097.

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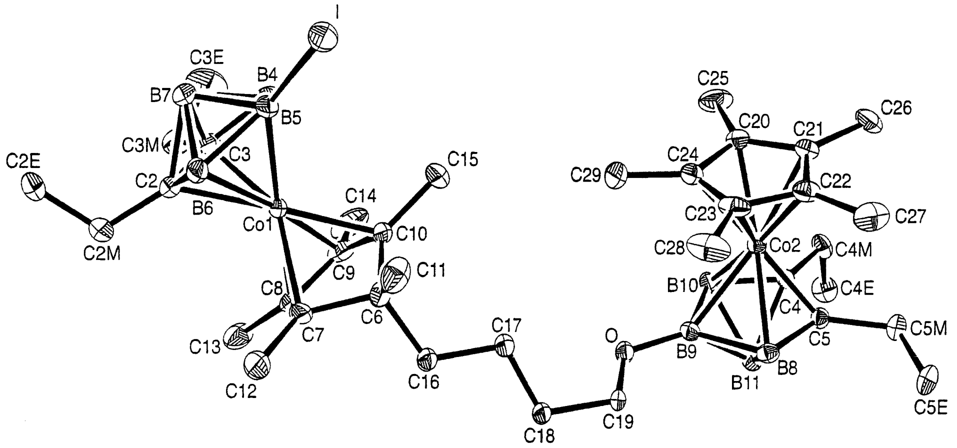


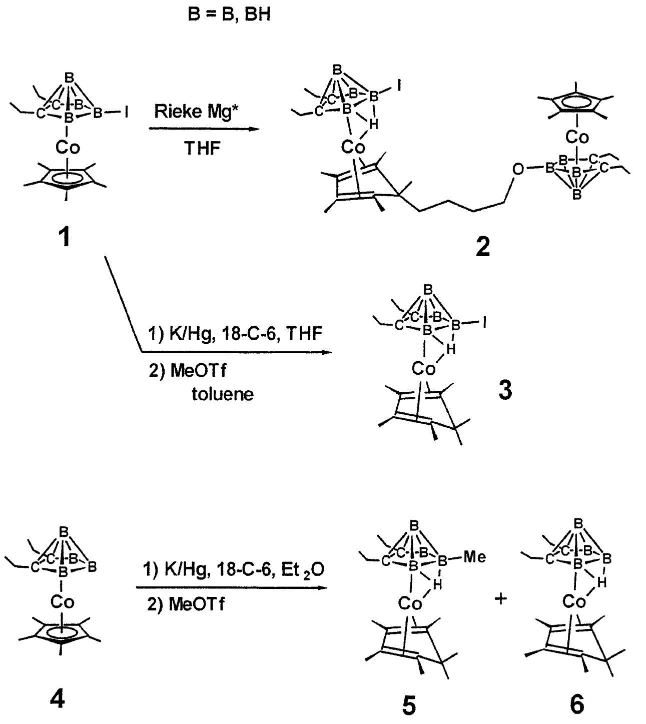
Figure 1. ORTEP representation of **2** showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

on reflux in acidic methanol yields a B-hydroxy product. Additionally, extensive work on $Co(C_2B_9H_{11})_2^-$ has shown that its electron-rich B(8) and B(8′) atoms are easily attacked by electrophiles to remove their terminal hydrogens; further reaction with nucleophiles forms either 8,8′-bridged or ring-opened derivatives.[10] In earlier work in our laboratory, Wurtz-type coupling of B(5)-halogenated cobaltacarboranes employing sodium metal in THF generated B−B-linked bis(cobaltacarboranes), while reactions of alkyllithiums with $Cp^*CoC_2B_4$ clusters afforded Cp*−Cp*-linked dimeric products.[11] Moreover, studies of the ruthenacarborane $Cp^*RuH(Et_2C_2B_4H_4)$ revealed that removal of its terminal hydride ligand followed by treatment with methyl trifluoromethanesulfonate produced $Cp^*RuH(Et_2C_2B_4H_3\text{-}5\text{-}Me)$.[12] In the present work, we undertook a systematic exploration of the reactivity of nucleophiles and electrophiles toward reduced cobaltacarboranes. As a synthetic approach, this type of reaction is capable of generating products not otherwise accessible and at the same time opens a window on some unusual metallacarborane chemistry that is interesting in its own right.

Results and Discussion

Reaction of so-called Rieke Mg*[13] with the B(5)-iodo complex **1** in dry THF was anticipated to take place at the B−I bond. Instead, we unexpectedly obtained in good yield an air-stable bis(cobaltacarboranyl) complex, $Cp^*Co(Et_2C_2B_4H_3)\text{-}5\text{-}O(CH_2)_4\text{-}(\eta^4\text{-}C_5Me_5)CoH(Et_2C_2B_4H_3\text{-}5\text{-}I)$ (**2**), containing a tetramethyleneoxy linking group, as shown in Scheme 1. From ^{11}B, ^{13}C, and ^{1}H NMR data it is clear that two inequivalent cobaltacarborane moieties are present and that one of the two Cp* ligands has adopted a η^4 binding mode toward cobalt. This conclusion was confirmed via an X-ray diffraction study of **2**, whose ORTEP diagram is presented in Figure 1, with experimental details and X-ray data and bond distances and angles listed in Tables 1 and 2, respectively. A complete listing is available as Supporting Information.

Scheme 1



Both the structure of this product and the manner of its formation merit discussion. First, as the η^4-C_5Me_5 ligand supplies only four electrons to cobalt, Co(1) should be a 17-electron metal while the remaining cobalt has an 18-electron $[Co(\eta^5\text{-}C_5Me_5)]$ environment. However, this is inconsistent with the observed properties of **2**, a neutral compound that is soluble in organic solvents and exhibits normal NMR spectra with no evidence of paramagnetism. This implies the presence of an "extra" hydrogen atom in the vicinity of Co(1), probably bridging between the metal and one or more nearby boron atoms and completing an 18-electron metal configuration. Such extra hydrogens, which variably adopt M−H−B bridging (η^2), $H{-}MB_2$ face-bridging (η^3), or $M{-}H_{terminal}$ (η^1) modes, are a well-known feature in small metallaborane and metallacarborane clusters[14] (especially those of Co, Fe, and Ru) and have been located by X-ray crystallography in some instances but

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[10] (a) Sivaev, I. B.; Bregadze, V. I. *Collect. Czech. Chem. Commun.* **1999**, *64*, 783. (b) Sivaev, I. B.; Starikova, Z. A.; Sjoeberg, S.; Bregadze, V. I. *J. Organomet. Chem.* **2002**, *649*, 1

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[12] Houser, E. J.; Curtis, M. A.; Sabat, M.; Grimes, R. N. *J. Organomet. Chem.* **1997**, *536–537*, 115.

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Table 1. Experimental X-ray Diffraction Parameters and Crystal Data

	2	**10**	**11**
empirical formula	$C_{36}H_{65}B_8Co_2IO$	$C_{28}H_{52}B_4CoIKO_6$	$C_{18}H_{34}B_4NCo$
fw	845.12	752.87	366.63
crystal dimens (mm)	0.45 × 0.27 × 0.24	0.22 × 0.12 × 0.07	0.41 × 0.36 × 0.28
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	9.0890(3)	14.2941(11)	8.8292(6)
b, Å	15.8105(6)	11.4066(9)	13.9778(9)
c, Å	16.6640(6)	21.3720(16)	16.696(1)
α, deg	117.853(1)		84.742(1)
β, deg	93.755(1)	93.074(2)	78.751(1)
γ, deg	100.623(1)		89.233(1)
V, Å^3	2049.0(1)	3479.6(5)	2012.4(2)
Z	2	4	4
D(calcd), g cm^{-3}	1.370	1.437	1.210
μ(Mo Kα), mm^{-1}	1.59	1.536	0.85
temp, K	153(2)	153(2)	153(2)
$2\theta_{max}$	65	65	65
transmission factors	0.66−0.80	0.71−0.80	0.71−0.80
no. of rflns collected	28519	47333	27865
no. of obsd rflns ($I > 2\sigma(I)$)	14542	12640	14262
no. of params refined	471	578	590
R	0.0567	0.0497	0.0464
R_w	0.1411	0.0677	0.1335
largest peak in final diff map, e/Å^3	2.978	0.866	1.053
goodness of fit	0.922	0.702	0.976

Table 2. Selected Distances and Angles for 2

Distances (Å)			
Co(1)−C(2)	2.059(3)	C(2)−B(6)	1.547(5)
Co(1)−C(3)	2.090(3)	C(2)−B(7)	1.757(5)
Co(1)−B(4)	2.130(4)	C(3)−B(4)	1.542(5)
Co(1)−B(5)	2.193(3)	B(4)−B(5)	1.685(6)
Co(1)−B(6)	2.176(4)	B(4)−B(7)	1.807(5)
Co(1)−C(7)	2.057(3)	C(6)−C(10)	1.510(5)
Co(1)−C(8)	2.000(3)	C(6)−C(11)	1.530(5)
Co(1)−C(9)	1.979(3)	C(6)−C(7)	1.553(4)
Co(1)−C(10)	2.043(3)	C(6)−C(16)	1.563(4)
Co(2)−C(4)	2.009(3)	C(7)−C(8)	1.417(5)
Co(2)−C(5)	2.030(3)	C(8)−C(9)	1.395(5)
Co(2)−B(8)	2.104(3)	C(9)−C(10)	1.392(5)
Co(2)−B(9)	2.145(3)	O−C(19)	1.366(4)
Co(2)−B(10)	2.100(3)	O−B(9)	1.408(4)
⟨Co(2)−C(η^5-C_5Me_5 ring)⟩	2.042(7)	I−B(5)	2.167(4)
C(2)−C(3)	1.462(5)	C(2)−B(7)	1.757(5)

Angles (deg)			
C(3)−C(2)−B(6)	113.1(3)	C(7)−C(6)−C(16)	108.9(2)
C(2)−C(3)−B(4)	113.6(3)	C(8)−C(7)−C(6)	106.8(3)
C(3)−B(4)−B(5)	105.2(3)	C(6)−C(7)−Co(1)	91.75(18)
C(2)−B(6)−B(5)	104.1(3)	C(9)−C(8)−C(7)	107.5(3)
B(4)−B(5)−B(6)	103.7(3)	C(7)−C(8)−Co(1)	71.74(18)
B(4)−B(5)−I	127.9(2)	C(10)−C(9)−C(8)	107.4(3)
B(6)−B(5)−I	126.9(3)	C(10)−C(9)−Co(1)	72.23(19)
C(10)−C(6)−C(11)	117.2(3)	C(9)−C(10)−C(6)	109.6(3)
C(10)−C(6)−C(7)	93.9(2)	C(19)−O−B(9)	117.7(2)
C(11)−C(6)−C(7)	113.6(3)	O−B(9)−B(10)	125.5(3)
C(10)−C(6)−C(16)	114.5(3)	O−B(9)−B(8)	130.4(2)
C(11)−C(6)−C(16)	108.0(3)		

not in others.[15] In the case of **2**, we were unable to identify this hydrogen from X-ray data, but the presence of CoH groups is evident in the closely related monomeric complexes **3**−**6**, to be discussed, and by analogy in **2** as well.

The solid-state molecular structure of **2** consists of two seven-vertex cobaltacarborane clusters tethered by a tetramethyleneoxy chain, such that the original B(5)−iodo substituent on *closo*-Cp*Co($Et_2C_2B_4H_3$-5-I) has been replaced by a −O(CH_2)$_4$-(η^4-C_5Me_5)CoH($Et_2C_2B_4H_3$-5-I) moiety. The η^4 metal−C_5Me_5 binding on one cluster is clear from the nonbonded interaction between Co(1) and the tetracoordinate C(6) atom, as well as from ^{13}C and ^{1}H NMR data. The diene in **2** displays a typical envelope conformation with a dihedral angle of 35.3° and a 0.60 Å deviation of the sp^3-hybridized carbon from the C(7)−C(8)−C(9)−C(10) plane.[16] Although the reduction of metal-bound η^5-C_5Me_5 (Cp*) ligands to η^4-C_5Me_5H has been observed in metallaborane chemistry,[17] such conversions have not been reported in metallacarboranes prior to this work. Deprotonation of the Cp* methyl groups of Cp*Co($Et_2C_2B_4H_4$) by LiBu leads to C_5Me_4−(CH_2)$_2$−C_5Me_4 coupling, but with no change in hapticity of the η^5 hydrocarbon ligands.[11] In the present case, reduction of the η^5-C_5Me_5 ligand involves the addition of Me or CH_2− rather than H.

A possible mechanism for the formation of **2** entails reduction at the Co(III) center of **1** to generate a 19-electron species, which in turn is attacked by THF to form a ($Et_2C_2B_4H_3$-5-I)Co^{II}(η^4-C_5Me_5)−(CH_2)$_4$−O$^\bullet$ radical that combines with a second molecule of **1**, displacing its iodo substituent. A second possibility is that **1** reacts via an $S_{RN}1$ mechanism with loss of iodide and coordination of THF, followed by reaction of an electron-deficient carbon of the coordinated THF with the Cp* ligand of a second **1**$^-$ ion to give the ring-opened product. Evidence for such a process has recently been cited in Co($C_2B_9H_{11}$)$_2^-$ chemistry.[10b] In either scenario, protonation of the product by exposure to water during workup then generates neutral **2**.

To further explore the dual functionality of this system, **1** was treated with potassium amalgam in THF, generating a deep red anion which on reaction with

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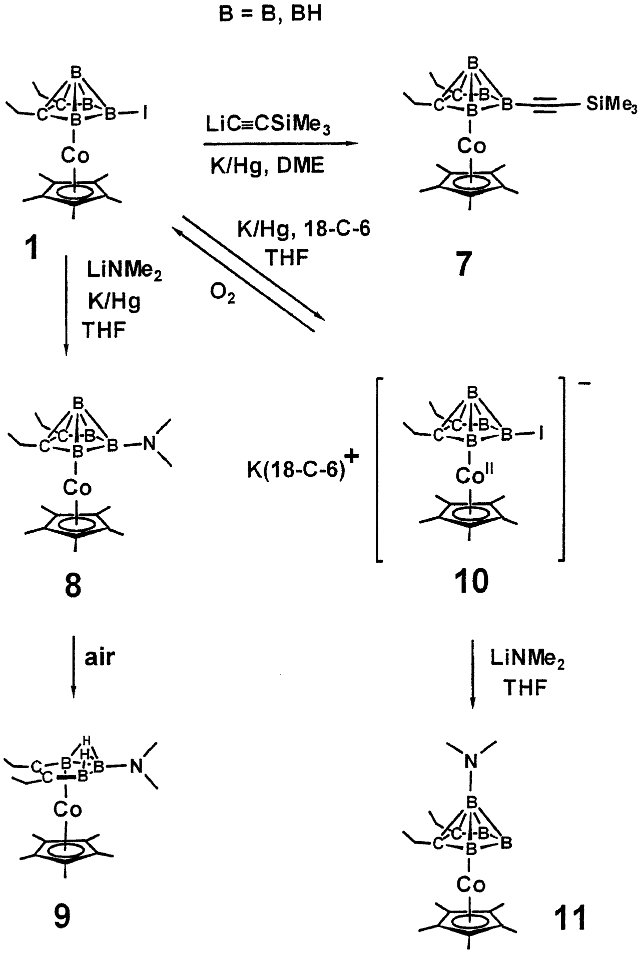
(14) (a) Grimes, R. N. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 7. (b) *Comprehensive Organometallic Chemistry II*; Abel, E., Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 1, Chapters 8 and 9.

(15) (a) For recent examples see: (a) Houser, E. J.; Curtis, M. A.; Sabat, M.; Grimes, R. N. *J. Organomet. Chem.* **1997**, *536*, 115. (b) Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 12218. (c) Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 12227.

(16) Donovan, B. T.; Hughes, R. P.; Kowalski, A. S.; Trujillo, H. A.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1038.

(17) (a) Cp*CoB$_3$H$_8$Co(η^4-C_5Me_5H): Nishihara, Y.; Deck, K. J.; Shang, M. Y.; Fehlner, T. P.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1994**, *13*, 4510; *J. Am. Chem. Soc.* **1993**, *115*, 12224. (b) (η^4-C_5Me_5H)Rh(SB_9H_9): Macias, R.; Holub, J.; Kennedy, J. D.; Stibr, B.; Thornton-Pett, Clegg, W. *J. Chem. Soc., Dalton Trans.* **1997**, 149.

Scheme 2



methyl trifluoromethanesulfonate gave the air-stable solid (η^4-C_5Me_6)CoH($Et_2C_2B_4H_3$-5-I) (**3**) in 53% yield based on **1** consumed. Characterization of **3** by multinuclear NMR and mass spectra supports the proposed structure shown in Scheme 1, and the presence of an "extra" hydrogen (CoH) is supported by the B−H$_{bridge}$ coupling that is detectable from ^{1}H NMR line broadening (the location of the Co−H signals in **2** and **3**, and their NMR spectra in general, are very closely similar). When potassium rather than magnesium was employed as an electron source, reduction of **1** generated primarily the monomer **3**, with only traces of the dimer **2** as a side product. A possible explanation for this result is provided by an earlier study[18] of ring opening and cleavage of THF by Mg* to form butanol, in which $CoCl_2$ was found to be the most active transition-metal halide catalyst for this reaction; insertion of Mg* into THF without a catalyst gave low to moderate yields of butanol. In our system, it may be that use of the less Lewis acidic potassium renders the ring-opening process less efficient.

When the latter procedure was conducted on the parent complex Cp*Co($Et_2C_2B_4H_4$) (**4**) in diethyl ether, the reaction took a different course. While reduction of the Cp* ligand (η^4-C_5Me_6) again occurred, it was accompanied by partial methylation at B(5), affording the air-stable products (η^4-C_5Me_6)CoH($Et_2C_2B_4H_3$-5-Me) (**5**) and (η^4-C_5Me_6)CoH($Et_2C_2B_4H_4$) (**6**), which on workup were isolated in 39 and 52% yields, respectively, although with low conversion rates from **4**. The ^{1}H and ^{13}C NMR spectra for **5** and **6** are very similar, but the ^{11}B patterns are different: the spectrum of **5** displays the expected 1:2:1 pattern with a singlet confirming methylation at boron, while that of **6** exhibits a 2:2 pattern with all boron atoms having terminal hydrogens. The proposed structures of the two compounds are strongly supported by their ^{13}C and boron-decoupled ^{1}H NMR spectra, which are consistent with the presence of CoHB bridges in **5** and **6** and a B(5)−Me group in **5**.

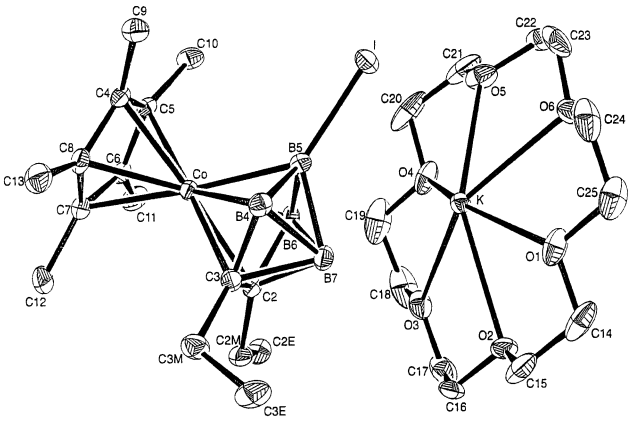


Figure 2. Molecular structure of **10** with 30% thermal ellipsoids (hydrogen atoms omitted for clarity).

Since electrophilic methyl trifluoromethanesulfonate primarily resulted in attack at the more basic Cp* ligand, it was expected that treatment of the radical anion **1**$^-$ with nucleophilic reagents would result in the replacement of the iodo group at the B(5) vertex. With lithium (trimethylsilyl)acetylenide, orange air-stable Cp*Co($Et_2C_2B_4H_3$-5-C≡$CSiMe_3$) (**7**) was isolated (Scheme 2). Substitution at B(5) was confirmed by an independent synthesis of **7** that involved Pd-promoted coupling to **1**.[19] Similarly, lithium dimethylamide reacted with **1**$^-$ to give red, air-sensitive Cp*Co($Et_2C_2B_4H_3$-5-NMe_2) (**8**) in low (13%) yield. Exposure of solid **8** to air for 7 days followed by extraction with dichloromethane afforded the decapped species *nido*-Cp*Co($Et_2C_2B_3H_4$-5-NMe_2) (**9**).

Generation of the radical anion **1**$^-$ in the presence of 18-crown-6 produced the salt K(18-crown-6)$^+$Cp*Co^{II}-($Et_2C_2B_4H_3$-5-I)$^-$ (**10**), whose structure was established by X-ray crystallography (Figure 2) from crystals obtained via diffusion of pentane into a THF solution of **10** at −20 °C. Compound **10** is significantly more stable than **1**$^-$, showing no decomposition in solution for several days at room temperature. The formation of **10** is essentially quantitative: when the synthesis was conducted in diethyl ether, within 15 min all of the starting material was completely converted to insoluble **10** with the colorless solution indicating that none of the orange starting material remained.

The molecular structure of the crown salt consists of a contact cation−anion pair[20] with a 3.88 Å separation between iodide and potassium and a similarly close distance of 3.41 Å between B(6) and potassium (Table 3). The coordination at the K(18-C-6)$^+$ cation is pseudo-octahedral with noncoplanar bonding to the six oxygens.

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[18] Bartmann, E. *J. Organomet. Chem.* **1985**, *284*, 149.

[19] We thank Dr. Haijun Yao in our laboratory for this finding.

[20] Chadwick, S.; Ruhlandt-Senge, K. *Chem. Eur. J.* **1998**, *4*, 1768.

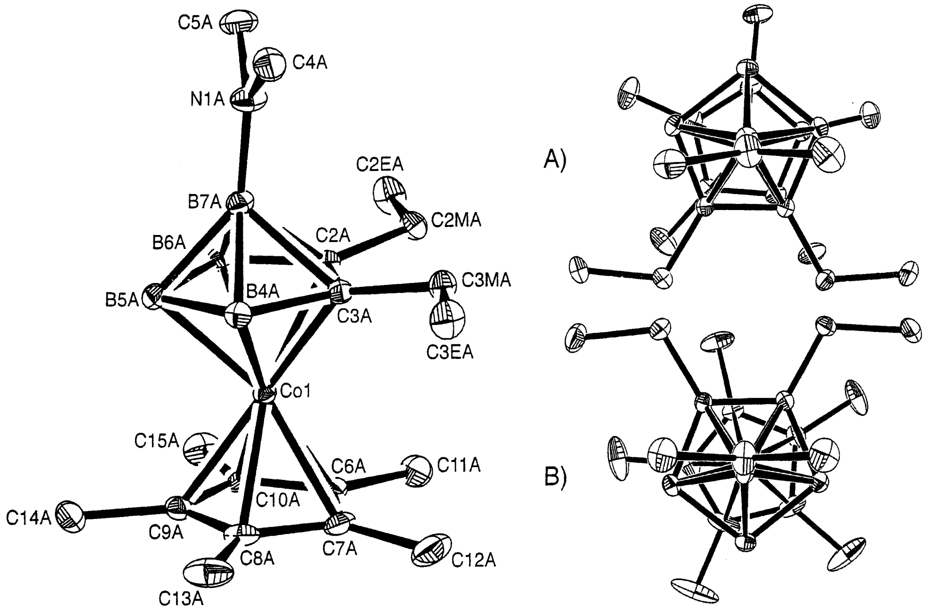

Figure 3. (left) Molecular structure of **11** with 30% thermal ellipsoids (hydrogen atoms omitted for clarity). One of the two independent molecules is depicted. (right) top-down views of the two independent molecules: (A) eclipsed; (B) staggered.

Table 3. Selected Distances and Angles for 10

Distances (Å)			
Co−C(2)	2.141(3)	B(4)−B(7)	1.814(5)
Co−C(3)	2.072(3)	B(4)−B(5)	1.634(5)
Co−B(4)	2.148(4)	B(5)−I	2.219(3)
Co−B(5)	2.123(4)	K−O(1)	2.827(2)
Co−B(6)	2.133(4)	K−O(2)	2.903(2)
⟨Co−C(C_5Me_5 ring)⟩	2.103(7)	K−O(3)	2.851(2)
C(2)−C(3)	1.484(4)	K−O(4)	2.954(2)
C(2)−B(6)	1.548(4)	K−O(5)	2.806(2)
C(2)−B(7)	1.722(5)	K−O(6)	2.847(2)
C(3)−B(4)	1.547(5)	K−I	3.878(1)
C(3)−B(7)	1.750(5)	K−B(6)	3.412(4)
B(4)−B(5)	1.634(5)	K−O(1)	2.827(2)
B(4)−B(7)	1.814(5)		
Angles (deg)			
C(3)−C(2)−B(6)	110.7(3)	B(6)−B(5)−I	125.7(2)
C(2)−C(3)−B(4)	113.8(3)	B(5)−I−K	72.2(1)
C(3)−B(4)−B(5)	102.9(3)	O(1)−K−O(4)	154.3(1)
C(2)−B(6)−B(5)	104.2(3)	O(5)−K−O(2)	147.9(1)
B(4)−B(5)−B(6)	108.2(3)	O(6)−K−O(3)	148.0(1)
B(4)−B(5)−I	125.7(2)		

The B−I bond is weaker than in **2** and the dihedral angle between the cobaltacarborane rings and the plane comprised of the oxygens is roughly 45° with the crown located on the side closest to B(6).

Attempts to record an ESR spectrum of **10** were unsuccessful, but the ^{11}B and ^{1}H NMR spectra are consistent with a paramagnetic complex. The ^{1}H NMR spectrum of **10** is dispersed over a chemical shift range of δ +30 to −46, in contrast to that of diamagnetic **1**, which has peaks in the region of δ +2.6 to +1.1. The ^{11}B NMR spectrum similarly reflects paramagnetic behavior, with resonances ranging from δ +200 to −50. Additionally, IR spectroscopy reveals an approximately 60 cm^{-1} bathochromic shift of the BH stretch in relation to **1**, which is consistent with previously reported[21] spectroelectrochemical data for $\mathbf{4}^-$.

Reaction of the salt **10** with lithium dimethylamide in THF afforded the apically substituted complex Cp*Co($Et_2C_2B_4H_3$-7-NMe_2) (**11**), which is isomeric with the 5-amino species **8** (Scheme 2). This is the first known example in which substitution has been achieved at an apex BH unit on an existing MC_2B_4 metallacarborane; heretofore, the only available route to apically functionalized derivatives was via B−R insertion into the open face of a *nido*-MC_2B_3 anionic substrate.[22] We did not investigate the mechanism of formation of **11**, but nucleophilic attack at the apical BH vertex may be favored owing to steric protection of the equatorial B(5) site by the bulky K(18-crown-6)$^+$ cation. The possibility that cluster framework rearrangement may be occurring, as has been observed in B−amino derivatives of 12-vertex ferratricarboranes in refluxing toluene,[23] is discounted as highly unlikely in our room-temperature reaction system.

The structure of **11** was established from an X-ray diffraction study that revealed the presence of two independent molecules in the unit cell, in which the C_5 and C_2B_3 rings adopt staggered and eclipsed conformations (Figure 3, with selected bond distances and angles listed in Table 4). In both cases, the plane of the NMe_2 group is roughly parallel to the carborane C−C edge. The two molecules have only minor variances in their bond length and angles. The dihedral angle between the C_2B_3 and C_5 rings is unusually large at 8°, in comparison to Cp*CoC_2B_4 clusters, whose typical values range from 2 to 4°, as in **2** and **10** reported above.

As a pair, compounds **8** and **11** supply one of the few examples of structurally characterized nonhalogenated substitution isomers in metallacarborane chemistry generally and are the only pair of equatorially and apically functionalized seven-vertex metallacarborane clusters to be reported in the literature, other than the bis(cobaltacarboranes)[11,22b] 5,5′- and 7,7′-[($Et_2C_2B_4H_3$)-CoCp*]$_2$ (however, the list is expanding, as several

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Table 4. Selected Distances and Angles for 11

Distances (Å)			
Co(1)−C(2A)	2.028(2)	N(1A)−B(7A)	1.430(3)
Co(1)−C(3A)	2.033(2)	N(1A)−C(4A)	1.437(3)
Co(1)−B(4A)	2.107(2)	N(1A)−C(5A)	1.432(3)
Co(1)−B(5A)	2.105(2)	Co(2)−C(2B)	2.036(2)
Co(1)−B(6A)	2.102(2)	Co(2)−C(3B)	2.029(2)
⟨Co(1)−C(C_5Me_5 ring)⟩	2.045(5)	Co(2)−B(4B)	2.097(2)
C(2A)−C(3A)	1.471(2)	Co(2)−B(5B)	2.093(2)
C(2A)−B(6A)	1.559(3)	Co(2)−C(6B)	2.077(2)
C(2A)−B(7A)	1.851(3)	⟨Co(2)−C(C_5Me_5 ring)⟩	2.046(5)
C(3A)−B(4A)	1.564(3)	C(2B)−B(7B)	1.858(3)
C(3A)−B(7A)	1.849(3)	C(3B)−B(4B)	1.557(3)
B(4A)−B(5A)	1.683(3)	C(3B)−B(7B)	1.859(3)
B(4A)−B(7A)	1.788(3)	B(5B)−B(7B)	1.743(3)
B(5A)−B(6A)	1.686(3)	N(1B)−B(7B)	1.429(3)
B(5A)−B(7A)	1.750(3)	N(1B)−C(4B)	1.440(3)
B(6A)−B(7A)	1.784(3)	N(1B)−C(5B)	1.428(3)
Angles (deg)			
C(3A)−C(2A)−B(6A)	112.3(2)	N(1A)−B(7A)−B(4A)	132.3(2)
C(2A)−C(3A)−B(4A)	112.3(2)	N(1A)−B(7A)−B(5A)	142.4(2)
C(3A)−B(4A)−B(5A)	105.6(2)	N(1A)−B(7A)−B(6A)	131.5(2)
C(2A)−B(6A)−B(5A)	105.7(2)	C(5A)−N(1A)−C(4A)	115.3(2)
B(4A)−B(5A)−B(6A)	104.1(2)	B(7A)−N(1A)−C(4A)	122.8(2)
N(1A)−B(7A)−C(2A)	122.2(2)	B(7A)−N(1A)−C(5A)	121.9(2)
N(1A)−B(7A)−C(3A)	122.5(2)		

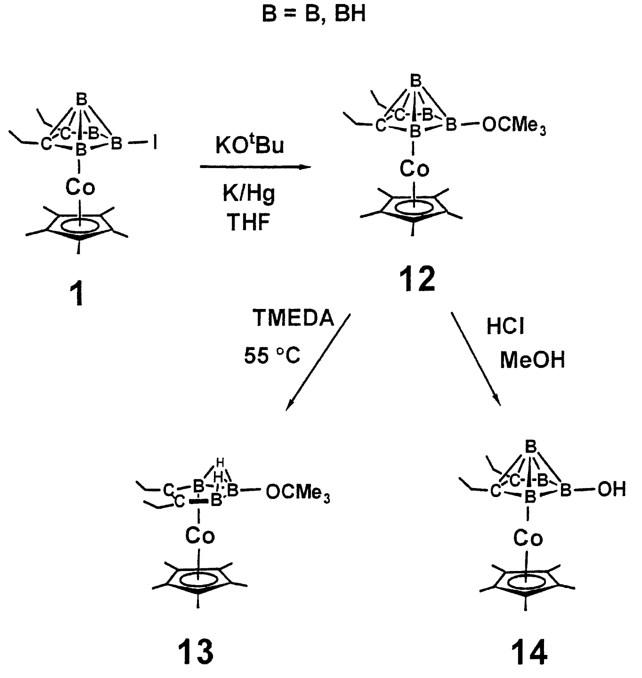
isomeric B(5/7)−alkynyl ferracarboranes[4] and cobaltacarboranes[24] have been prepared recently). A comparison of their properties is therefore of interest, and they are strikingly different: the apically substituted **11** is an air-stable yellow solid that dissolves easily in hexane, while **8** is an air-sensitive dark red solid that can be purified only on deactivated silica gel, owing to its polarity.

The proton NMR spectra for **8** and **11** reveal a large (0.9 ppm) increase in shielding of the dimethylamino resonance when the NMe_2 group is moved from an equatorial to the apical vertex; similar shielding is observed in the boron NMR spectra, which exhibit a 13 ppm upfield shift in the substituted boron of **11** compared to **8**.

We ascribe the greater stability of **11** in part to decreased cluster polarity and in part to the steric protection of the apex boron from cage degradation (decapitation). In **8**, the placement of the amino group at B(5) has the opposite effect, increasing the cluster polarity and promoting reactivity toward oxidants. The remarkable change in properties that is effected on changing from equatorial to apical substitution has implications for tailoring metallacarboranes to specific purposes, a point to be further addressed in forthcoming publications.

The radical anion $\mathbf{1}^-$ reacted with the nucleophilic *tert*-butoxide ion to give the B(5)−*tert*-butoxy derivative **12** (Scheme 3) in 70% yield as a waxy red solid. Although **12** was resistant to decapping, treatment with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) at 55 °C for 7 days gave *nido*-Cp*Co($Et_2C_2B_3H_4$-5-O-*t*-Bu) (**13**) in a yield of 90% based on **12** consumed, with most of the starting material recovered. Acidification of **12** with HCl in methanol produced the B(5)−hydroxy derivative **14**, a moderately air-stable orange solid, in 58% isolated yield (91% based on **12** consumed). Structural characterization of **12**−**14** is based on their mass spectra and ^1H, ^{11}B, and ^{13}C NMR spectroscopy, which show mirror symmetry in each case. The fact that **12** can be decapped locates its substituent (and hence that of **14** as well) at B(5) rather than B(7). In the NMR spectra of each of the compounds reported here, the apical B(7) nucleus is shielded by ca. 13 ppm relative to B(5) (see above); replacement of hydrogen by amino, butoxy, or hydroxy groups produces significant deshielding at the boron directly affected. In **14**, the ^1H signal at δ 2.09 is assigned to the B−hydroxy group.

Scheme 3



Summary

The reduction of the species **1** and **4** with group 1 and 2 metals in the presence of an array of nucleophiles or electrophiles sheds light on a relatively unexplored facet of metallacarborane chemistry. Treatment of **1** with Mg* or the reduced cobaltacarboranes, $\mathbf{1}^-$ or $\mathbf{4}^-$, with methyl trifluoromethanesulfonate afforded the first reported η^4-cyclopentadiene seven-vertex cobaltacarboranes. Two distinct dimethylamino-substituted isomers were synthesized, with the substitution affected by the presence of a crown ether. The use of potassium *tert*-butoxide under relatively mild conditions allowed the introduction of a butoxide group, which was easily converted into the potentially useful B−OH derivative without the use of more toxic reagents such as thallium. Radical-substitution reactions furnish a useful alternative approach to the controlled introduction of functional groups into small cobaltacarboranes, complementing previously employed metal-catalyzed cross-coupling reactions and allowing the synthesis of some novel types of products.

Experimental Section

Instrumentation. ^1H (500 MHz (where noted), 300 MHz), ^{11}B (160.4 MHz (where noted), 96.4 MHz), and ^{13}C (125.8 MHz (where noted), 75.4 MHz) NMR spectra were recorded on GE GN-300/44 and Varian Unity/Inova 500/51 and 300/51 instruments. ^1H and ^{13}C shifts are referenced to residual ^1H and ^{13}C signals in the deuterated solvent. ^{11}B NMR resonances are referenced to the external standard $BF_3 \cdot OEt_2$. Unit resolution

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(24) Yao, H.; Sabat, M.; Grimes, R. N. Manuscripts in preparation.

mass spectra were acquired on a Finnigan (Model LCQ Classic) quadrupole ion trap mass spectrometer using an atmospheric pressure chemical ionization interface. Infrared spectra were obtained on a Nicolet Impact-400 spectrophotometer either as thin films or as pressed pellets. Ultraviolet−visible spectra were recorded on a HP 8452A diode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab in Norcross, GA. Owing to incomplete combustion (not uncommon in polyhedral boron clusters), the carbon analyses for **2**, **7**, and **13** were slightly outside normal limits. For all new compounds, compound purity and identity was established from multinuclear NMR spectra supplemented by mass spectrometry, showing the expected isotopic envelopes. X-ray crystallography provided unambiguous structural assignments for **2**, **10**, and **11**.

Materials and Procedures. All reactions were carried out in oven-dried glassware under a dinitrogen atmosphere using conventional glovebox or Schlenk techniques, and the products were worked up in air unless otherwise noted. All commercial reagents (Aldrich) were used as received without further purification. Clean mercury was prepared by washing the metal with dilute nitric acid, distilled water (until pH 7), and then acetone and dried in vacuo at 100 °C for 12 h. THF, diethyl ether, 1,2-dimethoxyethane, and toluene were distilled from sodium benzophenone ketyl prior to use. Lithium naphthalenide[25] and Cp*Co($Et_2C_2B_4H_3$-5-I) (**1**)[7] were prepared according to the published procedures. Periodically the organolithium reagents were titrated with 2,2-diphenylacetic acid to determine the active organometallic content.

(η^5-Cp*)Co($Et_2C_2B_4H_3$)-5-O(CH_2)$_4$-(η^4-C_5Me_5)CoH($Et_2C_2B_4H_3$-5-I) (2). In a 50 mL Schlenk flask equipped with a glass-coated stirring bar, a fine suspension of Mg* was made by dropwise addition of 608 μL of a 2.04 M lithium naphthalenide solution (1.24 mmol) to 114 mg of anhydrous $MgBr_2$ (0.619 mmol) in 15 mL of THF. When the addition was complete, the Mg* was allowed to settle and the supernatant liquid was removed. The remaining Mg* was washed with three 10 mL portions of fresh THF or until the washings were clear. THF (15 mL) was added, followed by 100 mg (0.222 mmol) of Cp*Co($Et_2C_2B_4H_3$-5-I) (**1**), producing an immediate dark red color formation. After 30 min 1.0 mL of degassed water and then 1.0 mL of 2 M HCl were added with a color change to the original orange of the starting material. The solvent was removed in vacuo, and the remaining residue was placed atop 3 cm of silica gel and eluted with CH_2Cl_2 to give 33 mg of recovered **1** and then with ethyl acetate to afford 44 mg of **2** as a red oil. X-ray-quality crystals were obtained by slow cooling of a hot methanol solution (yield 47%, 70% based on **1** consumed). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.67 (t, 2H, J = 7 Hz, CH_2O), 2.43, 2.34, 2.27, 2.17 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.99 (s, 6H, η^4-C_5Me_5), 1.77 (s, 15H, η^5-C_5Me_5), 1.59 (s, 3H, η^4-C_5Me_5), 1.35 (t, 2H, J = 7 Hz, CH_2CH_2O), 1.15, 1.08 (t, 6H, J = 7 Hz, ethyl CH_3), 0.90 (s, 6H, η^4-C_5Me_5), 0.76 (m, 2H, η^4-$C_5Me_5CH_2$), 0.68 (m, 2H, $CH_2CH_2CH_2O$). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 99.2 (C_2B_4), 95.8 (η^4-C_5Me_5), 91.6 (C_2B_4), 90.4 (η^5-C_5Me_5), 75.2 (η^4-C_5Me_5), 72.4 (CH_2O), 59.2 (η^4-C_5Me_5), 41.9 (η^4-$C_5Me_5CH_2$), 32.4 (CH_2CH_2O), 24.3 (η^4-C_5Me_5), 22.1 (ethyl CH_2), 22.0 ($CH_2CH_2CH_2O$), 21.9 (ethyl CH_2), 15.1 (ethyl CH_3), 15.0 (ethyl CH_3), 12.2 (η^4-C_5Me_5), 11.0 (η^4-C_5Me_5), 9.7 (η^5-C_5Me_5). ^{11}B NMR (160.4 MHz, $CDCl_3$): δ 29.6 (s, 1B, B−O(CH_2)$_4$), 2.1 (1B, unresolved), −4.5 (4B, unresolved), −9.9 (1B, unresolved), −15.2 (s, 1B, B−I). IR (KBr pellet, cm^{-1}): 2969 (s), 2932 (s), 2910 (s), 2872 (s), 2843 (m), 2568 (s), 2541 (s), 1452 (s), 1377 (s), 1231 (s), 1077 (m), 1024 (s), 857 (m). UV−vis (CH_2Cl_2, nm (%)): 230 (72), 291 (100), 368 (8) ϵ_{max} = 22 100 cm^{-1} M^{-1}. CI$^+$-MS: m/z (%) 846 ([M$^+$], 100). Anal. Calcd for $C_{36}H_{65}B_8Co_2IO$: C, 51.16; H, 7.75. Found: C, 50.27; H, 7.56.

(η^4-C_5Me_6)CoH($Et_2C_2B_4H_3$-5-I) (3). In a 50 mL Schlenk flask under dinitrogen, 17 mg of potassium metal (0.43 mmol) was dissolved in 0.5 mL of clean mercury. A 10 mL portion of THF followed by 59 mg of 18-crown-6 (0.22 mmol) and 100 mg (0.222 mmol) of **1** were added, producing a deep red color. After 3 h, the solvent was removed in vacuo and the residue was redissolved in 10 mL of dry, degassed toluene. A 1.0 mL portion of methyl trifluoromethanesulfonate was added, and after 30 min the solvent was removed in vacuo. The remaining residue was placed atop 3 cm of silica gel and eluted with CH_2Cl_2. The crude material was chromatographed on silica gel TLC plates with a 1:3 CH_2Cl_2−hexanes solution, affording 12 mg of **3** and 78 mg of recovered **1** (12% yield, 53% based on **1** consumed). ^{1}H{^{11}B} NMR (500 MHz, C_6D_6): δ 3.31 (s, 2H, B(4,6)−H), 2.03, 1.81 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.65 (s, 6H, C_5Me_6), 1.51 (s, 1H, B(7)−H), 1.49 (s, 3H, C_5Me_6), 0.96 (t, 6H, J = 7 Hz, ethyl CH_3), 0.83 (s, 1H, CoHB), 0.81 (s, 6H, C_5Me_6), 0.15 (s, 3H, C_5Me_6). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 99.2 (C_2B_4), 95.5 (C_5Me_6), 76.4 (C_5Me_6), 55.5 (C_5Me_6), 29.8 (C_5Me_6), 23.8 (C_5Me_6), 22.1 (ethyl CH_2), 15.1 (ethyl CH_3), 11.3 (C_5Me_6), 11.3 (C_5Me_6). ^{11}B NMR ($CDCl_3$): δ −4.7 (d, 2B, J = 151 Hz), −9.3 (d, 1B, J = 161 Hz), −14.7 (s, 1B, B−I). IR (KBr pellet, cm^{-1}): 2970 (s), 2931 (s), 2576 (s), 2546 (s), 1454 (s), 1377 (s), 1350 (m), 1077 (m), 1023 (s), 912 (w), 878 (w), 843 (m), 747 (w), 615 (m), 508 (w), 459 (w). CI$^+$-MS: m/z (%) 466 ([M$^+$], 20), 451 ([M$^+$ − CH_3], 100). Anal. Calcd for $C_{17}H_{32}B_4CoI$: C, 43.86; H, 6.93. Found: C, 44.32; H, 6.68.

(η^4-C_5Me_6)CoH($Et_2C_2B_4H_3$-5-Me) (5) and (η^4-C_5Me_6)CoH($Et_2C_2B_4H_4$) (6). In a 50 mL Schlenk flask under dinitrogen, 17 mg of potassium metal (0.43 mmol) was dissolved in 0.5 mL of clean mercury. A 10 mL portion of diethyl ether followed by 59 mg of 18-crown-6 (0.22 mmol) and 100 mg (0.222 mmol) of Cp*Co($Et_2C_2B_4H_4$) (**4**) were added, producing a deep red color. After 3 h all of the cobaltacarborane had precipitated. The solvent was removed in vacuo, and the residue was dissolved in 1.0 mL of methyl trifluoromethanesulfonate. After 30 min the solvent was removed in vacuo and the remaining residue was placed atop 3 cm of silica gel and eluted with CH_2Cl_2. The crude material was chromatographed on silica gel TLC plates with a 1:7 CH_2Cl_2−hexanes solution, affording 7 mg of **5** (39% based on **4** consumed), 9 mg of **6** (52% based on **4** consumed), and 77 mg of recovered **4**. Data for **5**: ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$) δ 2.57 (s, 2H, B(4,6)−H), 2.34, 2.15 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.98 (s, 6H, C_5Me_6), 1.44 (s, 3H, C_5Me_6), 1.07 (t, 6H, J = 7 Hz, ethyl CH_3), 0.92 (s, 6H, C_5Me_6), 0.81 (s, 1H, B(7)−H), 0.64 (s, 3H, BMe), 0.28 (s, 3H, C_5Me_6), −1.25 (s, 1H, CoHB); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) 98.1 (C_2B_4), 93.1 (C_5Me_6), 72.4 (C_5Me_6), 54.5 (C_5Me_6), 28.6 (C_5Me_6), 24.1 C_5Me_6), 22.3 (ethyl CH_2), 15.3 (ethyl CH_3), 11.5 (C_5Me_6), 11.3 (C_5Me_6); ^{11}B NMR ($CDCl_3$) δ 0.7 (s, 1B, B−Me), −7.1 (d, 2B, J = 144 Hz), −10.7 (d, 1B, J = 166 Hz); IR (KBr pellet, cm^{-1}) 2967 (s), 2931 (s), 2901 (s), 2563 (s), 2519 (s), 1456 (m), 1376 (s), 1349 (w), 1303 (w), 1078 (w), 1025 (m); CI$^+$-MS: m/z (%) 354 ([M$^+$], 100). Data for **6**: ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$) δ 2.82 (s, 1H, B(5)−H), 2.76 (s, 2H, B(4,6)−H), 2.39, 2.17 (sextet, 2H, J = 7 Hz, ethyl CH_2), 1.99 (s, 6H, C_5Me_6), 1.44 (s, 3H, C_5Me_6), 1.10 (t, 6H, J = 7 Hz, ethyl CH_3), 0.94 (s, 6H, C_5Me_6), 0.72 (s, 1H, B(7)−H), 0.28 (s, 3H, C_5Me_6), −1.64 (s, 1H, CoHB); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) δ 98.4 (C_2B_4), 93.7 (C_5Me_6), 73.2 (C_5Me_6), 54.7 (C_5Me_6), 28.9 (C_5Me_6), 24.0 (C_5Me_6), 22.4 (ethyl CH_2), 15.2 (ethyl CH_3), 12.0 (C_5Me_6), 11.3 (C_5Me_6); ^{11}B NMR ($CDCl_3$) δ −6.1 (d, 2B, J = 144 Hz), −11.4 (d, 2B, J = 149 Hz); IR (KBr pellet, cm^{-1}) 2965 (s), 2931 (s), 2871 (m), 2556 (s), 1453 (m), 1376 (s), 1350 (m), 1079 (w), 1025 (m), 910 (w), 885 (w); CI$^+$-MS: m/z (%) 339 ([M$^+$], 40), 323 ([M$^+$ − CH_3], 100).

Cp*Co($Et_2C_2B_4H_3$-5-C≡CSiMe$_3$) (7). In a 50 mL Schlenk flask under dinitrogen, a solution of 250 μL of (trimethylsilyl)acetylene (1.80 mmol) in 10 mL of dry, degassed THF at 0 °C was treated with 1.0 mL of a 1.57 M n-butyllithium solution in hexanes (1.6 mmol). After 30 min the solution was warmed to room temperature and stirred for an additional 30 min. The solvent was removed in vacuo, and the residue was redissolved

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[25] Wu, X.; Chen, T.; Rieke, R. D. *Macromolecules* **1996**, *29*, 7671.

in 25 mL of 1,2-dimethoxyethane. A 235 mg portion of **1** (0.523 mmol) and then an amalgam of 41 mg of potassium (1.0 mmol) in 1.0 mL of mercury were added, and the mixture was stirred for 16 h. A 1.0 mL portion of an aqueous saturated ammonium chloride solution was added, and after 10 min the solvent was removed in vacuo. The remaining residue was placed atop 3 cm of silica gel and eluted with CH$_2$Cl$_2$. The crude material was chromatographed on silica gel TLC plates to yield three bands. The last band afforded 54 mg of **7** as an orange air-stable solid (25% yield). ^{1}H NMR (CDCl$_3$): δ 2.49, 2.27 (sextet, 2H, J = 7 Hz, ethyl C*H*$_2$), 1.81 (s, 15H, C$_5$*Me*$_5$), 1.16 (t, 6H, J = 7 Hz, ethyl C*H*$_3$), 0.22 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$): δ 116.1 (BC≡*C*SiMe$_3$), 93.0 (*C*$_2$B$_4$), 91.0 (*C*$_5$Me$_5$), 21.6 (ethyl *C*H$_2$), 14.9 (ethyl *C*H$_3$), 9.3 (C$_5$*Me*$_5$), 0.5 (Si*Me*$_3$). ^{11}B NMR (CDCl$_3$): δ 7.7 (s, 1B, *B*C≡CSiMe$_3$), 4.3 (d, 2B, J = 149 Hz), 2.1 (d, 1B, J = 198 Hz). IR (KBr pellet, cm^{-1}): 2971 (s), 2934 (m), 2909 (m), 2874 (m), 2552 (s), 2105 (m), 1476 (m), 1451 (m), 1381 (m), 1245 (s), 1178 (w), 1028 (m), 897 (m), 841 (s), 804 (w), 758 (m), 695 (m). CI$^+$-MS: m/z (%) 420 ([M$^+$], 100), 348 ([M$^+$ − SiMe$_3$], 23). Anal. Calcd for C$_{21}$H$_{37}$B$_4$CoSi: C, 60.09; H, 8.88. Found: C, 59.47; H, 8.89.

Cp*Co(Et$_2$C$_2$B$_4$H$_3$-5-NMe$_2$) (8) and *nido*-Cp*Co(Et$_2$C$_2$B$_3$H$_4$-5-NMe$_2$) (9). In a 50 mL Schlenk flask under dinitrogen, 17 mg of potassium metal (0.43 mmol) was dissolved in 0.5 mL of clean mercury. A 10 mL portion of THF and then 22 mg of LiNMe$_2$ (0.43 mmol) and 100 mg of **1** (0.222 mmol) were added, with the appearance of a deep red color. After 18 h, 1.0 mL of an aqueous saturated ammonium chloride solution was added, and after 10 min the solvent was removed in vacuo. The remaining residue was placed atop 3 cm of silica gel and washed first with CH$_2$Cl$_2$ to recover 15 mg of **1** and then with a 95% ethyl acetate−5% triethylamine solution to give the crude product. Chromatography of this material on a silica gel TLC plate with 1:4 ethyl acetate−hexanes solution containing 5% triethylamine afforded 9 mg of **8** as a red air-sensitive solid (11% yield, 13% yield based on **1** consumed). Upon exposure to air for 1 week, **8** decomposed; extraction of the remaining solid with dichloromethane gave 5 mg of **9**, as a pale yellow solid (57% yield). Data for **8**: ^{1}H NMR (CDCl$_3$) δ 2.94 (s, 6H, N*Me*$_2$), 2.46, 2.28 (sextet, 2H, J = 7 Hz, ethyl C*H*$_2$), 1.76 (s, 15H, C$_5$*Me*$_5$), 1.16 (t, 6H, J = 7 Hz, ethyl C*H*$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 93.1 (*C*$_2$B$_4$), 90.4 (*C*$_5$Me$_5$), 46.0 (N*Me*$_2$), 21.9 (ethyl *C*H$_2$), 15.0 (ethyl *C*H$_3$), 9.8 (C$_5$*Me*$_5$); ^{11}B NMR (CDCl$_3$) δ 23.1 (s, 1B, *B*−NMe$_2$), 2.7 (d, 1B, J = 132 Hz), −4.1 (d, 2B, J = 127 Hz); IR (KBr pellet, cm^{-1}) 2964 (s), 2930 (s), 2870 (s), 2822 (m), 2774 (m), 2545 (s), 2498 (s), 1449 (m), 1384 (s), 1374 (s), 1358 (s), 1210 (w), 1143 (s), 1124 (m), 1065 (m), 1028 (m), 954 (w), 855 (w), 552 (w); CI$^+$-MS m/z (%) 367 ([M$^+$], 100). Data for **9**: ^{1}H NMR (CDCl$_3$) δ 2.51 (s, 6H, N*Me*$_2$), 2.13, 1.80 (sextet, 2H, J = 7 Hz, ethyl C*H*$_2$), 1.72 (s, 15H, C$_5$*Me*$_5$), 1.07 (t, 6H, J = 7 Hz, ethyl C*H*$_3$), −3.70 (br s, 2H, B*H*B); ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$) δ 92.2 (*C*$_5$Me$_5$), 42.3 (BN*Me*$_2$), 23.1 (ethyl *C*H$_2$), 17.5 (ethyl *C*H$_3$), 9.3 (C$_5$*Me*$_5$); ^{11}B NMR (CDCl$_3$) δ 26.9 (s, 1B, *B*−NMe$_2$), −12.7 (d, 2B, J = 112 Hz); IR (KBr pellet, cm^{-1}) 2960 (s), 2925 (s), 2906 (s), 2864 (s), 2832 (m), 2783 (m), 2479 (s), 2024 (w), 1479 (m), 1449 (m), 1378 (s), 1331 (s), 1195 (m), 1167 (w), 1123 (m), 1105 (s), 1072 (w), 1050 (m), 1029 (m), 982 (w), 929 (m), 864 (w), 751 (m), 565 (w), 448 (m); CI$^+$-MS m/z (%) 356 ([M$^+$], 100). Anal. Calcd for C$_{18}$H$_{35}$B$_3$CoN: C, 60.59; H, 9.89. Found: C, 60.73; H, 9.97.

K(18-crown-6)$^+$Cp*Co$^{\mathrm{II}}$(Et$_2$C$_2$B$_4$H$_3$-5-I)$^-$ (10). In a 50 mL Schlenk flask under dinitrogen, 47 mg of **1** (0.10 mmol) and 28 mg of 18-crown-6 (0.11 mmol) were dissolved in 10 mL of dry, degassed THF. An amalgam of 5.0 mg of potassium (0.13 mmol) in 0.25 mL of mercury was added and stirred for 2 h. The now dark red solution was cooled to −20 °C, and a layer of pentane was added. After this mixture stood undisturbed overnight, X-ray-quality crystals of **10** formed and were subjected to X-ray diffraction analysis. The above procedure was also repeated in dry, degassed diethyl ether, in which **10** proved to be insoluble and precipitated as a dark brown solid in quantitative yield. IR (KBr pellet, cm^{-1}): 2958 (m), 2901 (s), 2515 (m, B−H), 2493 (m, B−H), 2471 (w, B−H), 1473 (m), 1453 (w), 1377 (w), 1352 (m), 1284 (w), 1251 (w), 1107 (vs), 962 (s), 835 (w). For comparison the previously unreported IR spectrum of **1** was run (KBr pellet, cm^{-1}): 2968 (s), 2930 (s), 2869 (m), 2551 (s, B−H), 1474 (s), 1447 (s), 1426 (m), 1378 (s), 1114 (w), 1067 (s), 1046 (m), 1030 (s), 995 (m), 962 (w), 882 (w), 860 (m), 832 (s), 786 (w), 744 (m), 724 (w), 670 (w), 612 (m), 590 (m), 498 (w), 450 (m).

Cp*Co(Et$_2$C$_2$B$_4$H$_3$-7-NMe$_2$) (11). In a 50 mL Schlenk flask under dinitrogen, 59 mg of 18-crown-6 (0.22 mmol) and 11 mg of LiNMe$_2$ (0.22 mmol) were slurried in 10 mL of dry, degassed THF. After 15 min of stirring, 100 mg of **1** (0.222 mmol) was added followed by an amalgam of 9.0 mg of potassium (0.23 mmol) in 0.25 mL of mercury, and the reaction mixture was stirred for 21 h. To the now dark red-brown mixture was added 1.0 mL of an aqueous saturated ammonium chloride solution, and after 10 min the solvent was removed in vacuo. The remaining residue was placed atop 3 cm of silica gel and washed first with CH$_2$Cl$_2$ to recover 81 mg of **1** and then with a 95% ethyl acetate−5% triethylamine solution to give crude product. Chromatography on a silica gel TLC plate with a 1:4 ethyl acetate−hexanes solution that contained 5% triethylamine afforded 12 mg of **11** as a yellow crystalline solid (77% yield based on **1** consumed). X-ray-quality crystals were obtained by slow evaporation of a hexanes solution. ^{1}H NMR (CDCl$_3$): δ 2.39, 2.23 (sextet, 2H, J = 7 Hz, ethyl C*H*$_2$), 2.03 (s, 6H, N*Me*$_2$), 1.78 (s, 15H, C$_5$*Me*$_5$), 1.25 (t, 6H, J = 7 Hz, ethyl C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 101.8 (*C*$_2$B$_4$), 90.6 (*C*$_5$Me$_5$), 38.9 (N*Me*$_2$), 22.2 (ethyl *C*H$_2$), 14.6 (ethyl *C*H$_3$), 10.2 (C$_5$*Me*$_5$). ^{11}B NMR (CDCl$_3$): δ 16.1 (d, 1B, J = 115 Hz), 13.1 (s, 1B, *B*−NMe$_2$), −2.1 (d, 2B, J = 124 Hz). IR (KBr pellet, cm^{-1}): 2966 (s), 2889 (s), 2856 (s), 2832 (s), 2784 (s), 2521 (s), 1489 (s), 1447 (s), 1374 (s), 1202 (m), 1134 (s), 1071 (m), 1026 (s), 960 (w), 925 (m), 812 (s), 789 (s). CI$^+$-MS: m/z (%) 367 ([M$^+$], 100). Anal. Calcd for C$_{18}$H$_{34}$B$_4$CoN: C, 58.97; H, 9.35. Found: C, 59.12; H, 9.33.

Cp*Co(Et$_2$C$_2$B$_4$H$_3$-5-O-*t*-Bu) (12). In a 50 mL Schlenk flask under dinitrogen, 17 mg of potassium metal (0.43 mmol) was dissolved in 0.5 mL of clean mercury. A 10 mL portion of THF and then 50 mg potassium *tert*-butoxide (0.45 mmol) and 100 mg of **1** (0.222 mmol) were added, producing a deep red color. After 16 h, 1.0 mL of an aqueous saturated ammonium chloride solution was added, and after 10 min the solvent was removed in vacuo. The remaining residue was placed atop 3 cm of silica gel and washed first with CH$_2$Cl$_2$ to remove impurities and then with ethyl acetate to afford 62 mg (70% yield) of **12** as an air-stable red solid. ^{1}H NMR (CDCl$_3$): δ 2.43, 2.27 (sextet, 2H, J = 7 Hz, ethyl C*H*$_2$), 1.77 (s, 15H, C$_5$*Me*$_5$), 1.35 (s, 9H, C*Me*$_3$), 1.16 (t, 6H, J = 7 Hz, ethyl C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 92.1 (*C*$_2$B$_4$), 90.1 (*C*$_5$Me$_5$), 72.9 (*C*Me$_3$), 30.4 (C*Me*$_3$), 21.9 (ethyl *C*H$_2$), 15.0 (ethyl *C*H$_3$), 9.6 (C$_5$*Me*$_5$). ^{11}B NMR (CDCl$_3$): δ 27.3 (s, 1B, *B*−OCMe$_3$), 2.7 (d, 1B, J = 144 Hz), −3.1 (d, 2B, J = 117 Hz). IR (KBr pellet, cm^{-1}): 2966 (s), 2929 (s), 2869 (m), 2535 (s), 1472 (w), 1454 (m), 1382 (s), 1356 (m), 1247 (s), 1190 (s), 1130 (w), 1026 (w), 944 (m), 856 (m). CI$^+$-MS: m/z (%) 396 ([M$^+$], 6), 340 ([M$^+$ − CMe$_3$], 100). Anal. Calcd for C$_{20}$H$_{37}$B$_4$CoO: C, 60.71; H, 9.43. Found: C, 60.48; H, 9.40.

***nido*-Cp*Co(Et$_2$C$_2$B$_3$H$_4$-5-O-*t*-Bu) (13).** A 50 mg portion of **12** was transferred to a Pyrex tube equipped with a Teflon stopcock and a stir bar. A 2 mL portion of TMEDA and 10 drops of water were added, and the reaction mixture was stirred for 1 week at 55 °C. The solvent was removed in vacuo, and the residue was placed atop 3 cm of silica gel. Elution with hexanes gave 7 mg of **13** (14%, 90% based on **12** consumed), and subsequent elution with CH$_2$Cl$_2$ afforded 41 mg of recovered **12**. Data for **13**: ^{1}H NMR (CDCl$_3$) δ 2.15, 1.81 (sextet, 2H, J = 7 Hz, ethyl C*H*$_2$), 1.74 (s, 15H, C$_5$*Me*$_5$), 1.23 (s, 9H, C*Me*$_3$), 1.08 (t, 6H, J = 7 Hz, ethyl C*H*$_3$), −3.46 (br s, 2H, B*H*B); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 92.3 (*C*$_5$Me$_5$), 28.9 (C*Me*$_3$), 22.5 (ethyl CH_2), 17.4 (ethyl CH_3), 9.0 (C_5Me_5); ^{11}B NMR ($CDCl_3$) δ 23.1 (s, 1B, $B-OCMe_3$), -6.2 (d, 2B, $J = 100$ Hz); IR (KBr pellet, cm^{-1}) 2971 (s), 2958 (s), 2924 (s), 2867 (m), 2498 (s), 2487 (s), 2036 (vw), 1458 (m), 1383 (m), 1363 (s), 1258 (s), 1188 (s), 1075 (w), 1034 (m), 919 (m), 867 (w), 774 (m), 582 (w), 479 (w), 458 (w); CI^+-MS: m/z (%) 386 ($[M^+]$, 32), 329 ($[M^+ - CMe_3]$, 100). Anal. Calcd for $C_{20}H_{38}B_3CoO$: C, 62.25; H, 9.93. Found: C, 62.54; H, 9.35.

Cp*Co($Et_2C_2B_4H_3$-5-OH) (14). In a 25 mL flask in air, 14 mg of **12** (0.035 mmol) was dissolved in 11 mL of a 1:10 concentrated HCl−MeOH solution. After 1 h at room temperature the solvent was removed in vacuo. The crude material was chromatographed on a silica gel TLC plate with a 1:5 ethyl acetate−hexanes solution, affording 5 mg of recovered **12** and 7 mg of **14** as a moderately air-sensitive orange solid (58% yield, 91% based on **12** consumed). ^1H NMR ($CDCl_3$): δ 2.44, 2.29 (sextet, 2H, $J = 7$ Hz, ethyl CH_2), 2.09 (s, 1H, OH), 1.81 (s, 15H, C_5Me_5), 1.15 (t, 6H, $J = 7$ Hz, ethyl CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 90.4 (C_5Me_5), 21.9 (ethyl CH_2), 15.1 (ethyl CH_3), 9.6 (C_5Me_5). ^{11}B NMR ($CDCl_3$): δ 30.1 (s, 1B, $B-OH$), 2.8 (d, 1B, $J = 147$ Hz), -3.3 (d, 2B, $J = 129$ Hz). IR (KBr pellet, cm^{-1}): 3288 (s), 2965 (s), 2923 (s), 2868 (m), 2537 (s), 1476 (m), 1451 (m), 1384 (s), 1249 (m), 1180 (s), 1130 (m), 1065 (m), 1030 (m), 900 (w), 861 (m), 790 (w), 587 (w), 559 (w), 502 (w).

X-ray Structure Determinations on 2, 10, and 11. Diffraction data were collected on a Bruker SMART APEX CCD diffractometer at −120 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). A hemisphere of frame data was collected using ω and ϕ scans, and empirical absorption corrections were applied. Structures were solved by direct methods using the SHELXTL-97 suite of programs,[26] and the refinement was by full-matrix least squares on F^2 with all measured reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters for all three structures. All hydrogens were located in the final difference map and refined isotropically for **10**. For **11** all boron-bound hydrogens were located and refined isotropically; the remaining were placed in idealized positions based on geometry. For **2** all hydrogen positions were calculated. All ORTEP representations were created with ORTEP-III.[27] Crystallographic data for all structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 176287 (**2**), 176286 (**10**), and 176288 (**11**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Figures giving ^1H and $^{13}C\{^1H\}$ NMR spectra for **2** and ^1H and $^1H\{^{11}B\}$ NMR spectra for **3**, **5**, and **6** and tables of atomic coordinates, bond distances, angles, anisotropic thermal parameters, and calculated mean planes for **2**, **10**, and **11**; X-ray data for **2**, **10**, and **11** in CIF format are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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