

# Alkynyl Substitution and Linkage in Cobaltacarborane Sandwich Complexes<sup>[‡]</sup>

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Linkage of Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) sandwich units by alkynyl and diethynylphenylene connectors was explored by the synthesis of two classes of complexes in which the linking groups are attached to the Cp\* ligands and to the carborane rings, respectively. Thus, the complex *nido*-( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-C≡CH)Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) (**6**) was prepared and converted in 87% yield to the novel 1,4-diethynylphenylene-linked bis(metallacarborane) 1,4-[*nido*-(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>)Co( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-C≡C)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**7**), which was characterized by multinuclear NMR and mass spectra and X-ray crystallography.

CuI-promoted coupling of **6** with (MeCN)<sub>2</sub>PdCl<sub>2</sub> in excess diethylamine was employed to prepare a palladium derivative, *nido*-(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>)Co(C<sub>5</sub>Me<sub>4</sub>)-C≡C-Pd(NHEt<sub>2</sub>)<sub>2</sub>Cl (**10**). Complexes of the second type, in which the organic linker is attached directly to the carborane ring, were obtained by synthesis of a *B*-ethynylcobaltacarborane, *nido*-Cp\*Co-[Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>(C≡CH)(C≡CSiMe<sub>3</sub>)] (**15**), which was then coupled with 1,4-diiodobenzene to generate the bis(cobaltacarborane) 1,4-[*nido*-Cp\*CoEt<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>(C≡CSiMe<sub>3</sub>)(C≡C)]<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> (**16**) in 87% yield.

## Introduction

Small metallacarborane units are versatile building blocks for the design and construction of organometallic frameworks in which metal centers are bound into stable environments;<sup>[2]</sup> typically, these are sufficiently robust to allow oxidation, reduction, and functionalization without disintegration of the system.<sup>[3]</sup> Examples include multidecker stacks,<sup>[4]</sup> arene-centered polymetallacarboranes,<sup>[5]</sup> and linked clusters.<sup>[6]</sup> Of particular interest are molecular arrays designed to promote electron delocalization between the metal centers. Such systems in general have two basic features: the presence of unpaired electrons, which can be introduced via paramagnetic metals, and connecting units that facilitate metal-to-metal electron transport. Unsaturated organic groups such as alkynes are prime candidates, and alkyne-linked organometallics are currently a subject of considerable interest as potential “molecular wires”.<sup>[7]</sup> In the boron cluster area, Hawthorne and co-workers have synthesized ethynyl-linked rigid-rod derivatives of *p*-carborane (1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>) by Pd-catalyzed coupling.<sup>[7n]</sup> Here we report the development of preparative routes to alkyne-linked bis(metallacarborane) systems and their application to the synthesis of two types of target compounds in which the connectors are attached to the Cp\* ligands and the carborane rings, respectively.

## Results and Discussion

The synthon ( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-C≡CH)Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) (**6**) was prepared in several steps, starting with lithiation of 1-tetramethylcyclopentadienyl-2-trimethylsilylacetylene (**1**)<sup>[8]</sup> to generate **2** (Scheme 1), which reacted with CoCl<sub>2</sub> to give a green solution of the presumed dimer **3**. Treatment of this solution with the Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub><sup>−</sup> ion in THF gave the red-brown complex (C<sub>5</sub>Me<sub>4</sub>-C≡CSiMe<sub>3</sub>)Co(Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>) (**4**), which was isolated in 32% yield and decapped with TMEDA and water to afford *nido*-( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-C≡C-SiMe<sub>3</sub>)Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) (**5**) as a yellow solid. Desilylation of **5** with tetrabutylammonium fluoride in THF produced yellow **6** in 82% yield. Pd/Cu-catalyzed C–C coupling<sup>[7b,7c]</sup> with 1,4-diiodobenzene was effected by reaction of **6** with bis(benzonitrile)palladium(II) chloride, copper(I) iodide, triphenylphosphane, and diethylamine, which upon workup and chromatography on silica gave the diethynyl-linked dicobalt target complex 1,4-[*nido*-(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>)Co( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-C≡C)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**7**), isolated as a yellow-brown solid in 87% yield. A minor product (4%) was tentatively identified from its proton NMR and mass spectra as the diethynyl-linked species [*nido*-(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>)Co( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-C≡C)]<sub>2</sub> (**8**).

Complex **7** was fully characterized by multinuclear NMR and mass spectra and X-ray crystallography, which established the centrosymmetric geometry depicted in Scheme 1 and Figure 1. To our knowledge, the only prior example of a structurally characterized complex in which two metallacarborane units are linked by an alkynyl-containing chain is [Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>-7-)]C<sub>2</sub>, whose C≡C group is attached to the apical boron atoms.<sup>[6a]</sup> Compound **7** is the first structurally characterized diethynylphenylene-linked metallacarborane complex, and some features are worth noting. As can be seen in Figure 1, the chain C1R1–C4–C5–C6---C6\*–C5\*–C4\*–C1R1\* forms an approximately linear ar-

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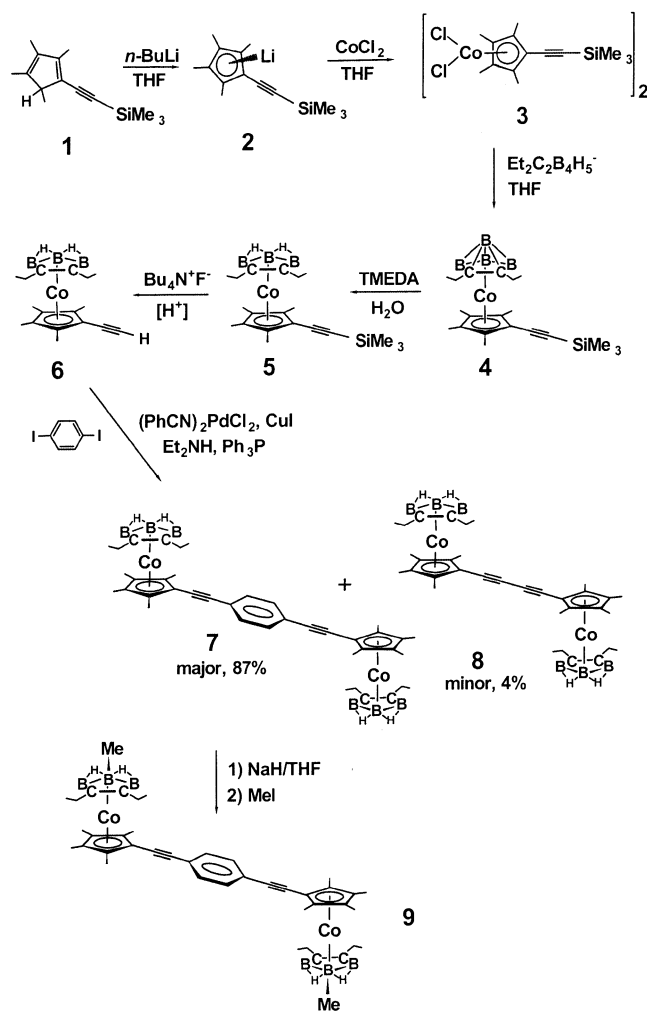
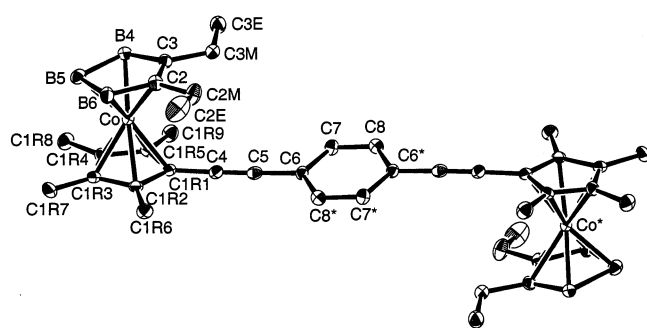
Scheme 1.  $B = BH$ ,  $B$ 

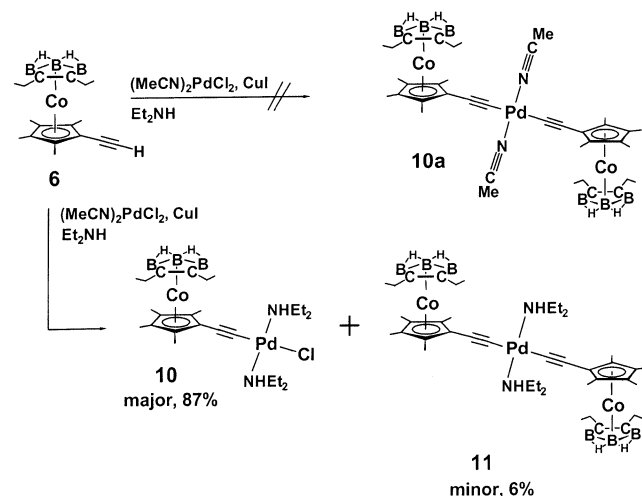
Figure 1. Molecular structure of **7** with 30% thermal ellipsoids (hydrogen atoms omitted for clarity); selected distances [Å]: C1R1–C4 1.424(7), C4–C5 1.185(7), C5–C6 1.454(7), C6–C7 1.394(7), C6–C8\* 1.401(7), Co–C<sub>5</sub> plane 1.661, Co–C<sub>2</sub>B<sub>3</sub> plane 1.508; the benzene ring subtends a dihedral angle of 13.1° with the C<sub>5</sub> ring plane

ray, but the phenylene ring is tilted 13° out of the plane defined by the C<sub>5</sub> rings. The C<sub>2</sub>B<sub>3</sub> ring is not quite parallel with the C<sub>5</sub> plane (dihedral angle 9°) and the Co atom is

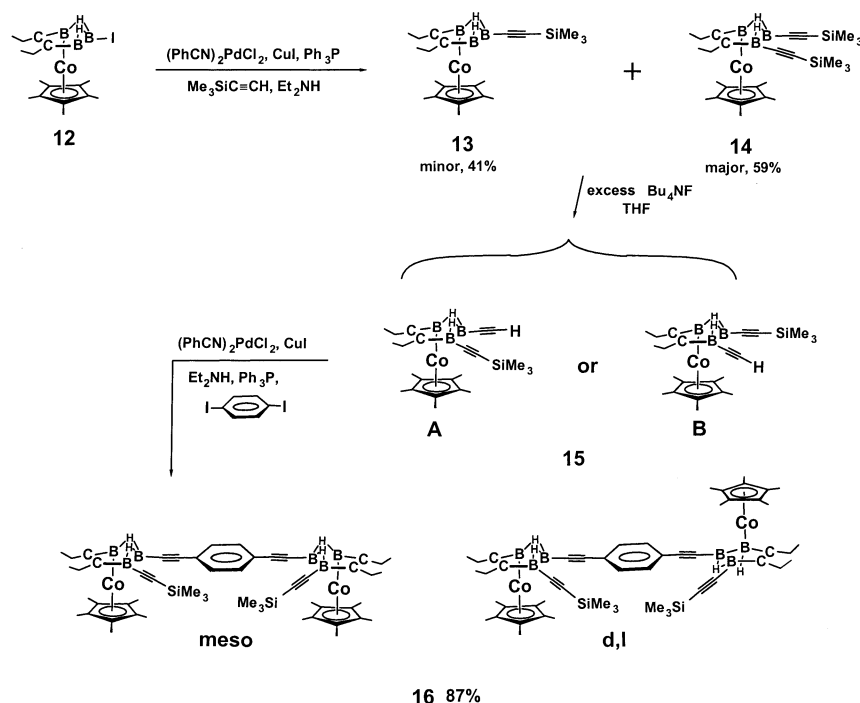
closer to the carborane ring (1.508 Å) than the C<sub>5</sub> ring (1.66 Å), both values being typical of small cobalt-acarboranes.<sup>[2–4]</sup> The short C4–C5 distance [1.185(7) Å] is within the normal range for C≡C bonds in alkynyl-linked dimetallic complexes,<sup>[9]</sup> although it is slightly shorter than that found in the previously mentioned [Cp\*Co(Et<sub>7</sub>C<sub>4</sub>B<sub>4</sub>H<sub>3</sub>–7–),C<sub>7</sub>] [1.205(12) Å].<sup>[6a]</sup>

Since **7** is a bifunctional complex having two open carborane ligands available for bridge-deprotonation and  $\eta^5$ -coordination to metal ions,<sup>[1a]</sup> it is expected to be a useful synthon for the construction of long-chain metallacarborane oligomers or polymers containing [(C<sub>5</sub>Me<sub>4</sub>)Co-(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>)<sub>2</sub>Co] tetradeccker sandwich units. This may be accomplished by removal of BHB bridging protons from both C<sub>2</sub>B<sub>3</sub> end rings and stacking with transition metal ions, as was demonstrated earlier in the synthesis of phenylene- and fulvalene-bridged “staircase” oligomers.<sup>[10]</sup> It has been found, however, that such metal stacking reactions require modification of the electron population in the C<sub>2</sub>B<sub>3</sub> end rings by introduction of methyl groups or halogen atoms.<sup>[3c,4,10]</sup> Accordingly, **7** was deprotonated and treated with methyl iodide to generate the *B,B'*-dimethyl derivative **9** (Scheme 1).

In an attempt to prepare the palladium-connected bis(cobaltacarborane) complex **10a** (Scheme 2), **6** was treated with bis(acetonitrile)palladium(II) chloride, copper(I) iodide, and diethylamine. However, the main product, isolated in 87% yield as a red-brown solid and characterized spectroscopically, was the mono(cobaltacarboranyl) species  $(\text{Et}_2\text{C}_2\text{B}_3\text{H}_5)\text{Co}(\text{C}_5\text{Me}_4)-\text{C}\equiv\text{C}-\text{Pd}(\text{NH}\text{Et}_2)_2\text{Cl}$  (**10**). An accompanying low-yield side product was tentatively identified from its mass spectrum as  $[(\text{Et}_2\text{C}_2\text{B}_3\text{H}_5)\text{Co}(\text{C}_5\text{Me}_4)-\text{C}\equiv\text{C}]_2\text{Pd}(\text{NH}\text{Et}_2)_2$  (**11**, Scheme 2).

Scheme 2.  $B = BH$ ,  $B$ 

An alternative approach to the preparation of alkynyl-linked Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>) units involves attachment of the organic chain to the carborane ring rather than the Cp\* group as in the preceding chemistry. Scheme 3 shows the



Scheme 3. B = BH, B

exploration of this idea employing as starting material the 5-iodo complex **12**,<sup>[11]</sup> which reacted with trimethylsilyl acetylene in the presence of palladium and copper reagents to produce the mono- and bis(*B*-silylethynyl) complexes **13** and **14**. The disubstituted product **14** probably formed by partial *B*-chlorination of **12** with  $(\text{PhCN})_2\text{PdCl}_2$ , a process we have observed in earlier work.<sup>[12]</sup>

Treatment of **14** with excess fluoride ion removed only one trimethylsilyl group to give a single product, formulated as  $\text{Cp}^*\text{Co}[\text{Et}_2\text{C}_2\text{B}_3\text{H}_3(\text{C}\equiv\text{CH})(\text{C}\equiv\text{CSiMe}_3)]$  (**15**), whose spectroscopic data do not distinguish between the structures **A** and **B** depicted in Scheme 3. In a procedure analogous to the synthesis of **7** and **8** described above, Pd/Cu-catalyzed alkyne linkage was carried out on **15** to produce yellow 1,4- $\{nido\text{-Cp}^*\text{Co}[\text{Et}_2\text{C}_2\text{B}_3\text{H}_3(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{C})]\}_2\text{-C}_6\text{H}_4$  (**16**), which was isolated in 87% yield together with a yellow minor product whose mass spectrum is consistent with the diethynyl-linked dimer  $\{nido\text{-Cp}^*\text{Co}[\text{Et}_2\text{C}_2\text{B}_3\text{H}_3(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{C})]\}_2$ . Although **16** is assumed to form in solution as a mixture of the nonchiral (*meso*) and chiral forms (Scheme 3),<sup>[13]</sup> the differences in proton NMR signals of these isomers are not detectable in our spectra. Compound **16** is multifunctional, having two  $\text{-C}\equiv\text{CSiMe}_3$  groups that are convertible to  $\text{-C}\equiv\text{CH}$  for use in subsequent metal-catalyzed linkage, as well as two  $\text{C}_2\text{B}_3$  end rings that are available for deprotonation and multidecker stacking (vide supra).

## Conclusion

This work combines small-metallacarborane synthetic chemistry with approaches that have been developed else-

where for preparing alkynyl-linked organometallic complexes, to generate novel alkyne-connected bis(metallacarborane) systems that are designed as building-blocks for the assembly of multimetallic extended systems. For convenience and ease of compound characterization by NMR spectroscopy, the target compounds selected in the current study are diamagnetic systems incorporating  $\text{Co}^{\text{III}}$ , which should be readily convertible by redox or electrochemistry to paramagnetic complexes; the nature and extent of electron delocalization in such systems<sup>[3]</sup> are a prime focus of interest in our laboratory. Investigations in this area are continuing and will be reported in due course.

## Experimental Section

**Materials and Procedures:** Unless otherwise stated, all reactions were performed under dry nitrogen, maintained by standard glove box and Schlenk techniques. Workup of products was generally carried out in air using benchtop techniques. Solvents were distilled from appropriate drying agents under an inert gas.  $\text{C}_5\text{Me}_4\text{H}(\text{C}\equiv\text{CSiMe}_3)$  (**1**) was prepared according to a literature method.<sup>[8]</sup> The carborane  $\text{Et}_2\text{C}_2\text{B}_4\text{H}_6$  was prepared on a multigram scale by the reaction of  $\text{B}_5\text{H}_9$  and 3-hexyne in diethyl ether solution, in a modification<sup>[14]</sup> of the literature method.<sup>[15]</sup>  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR spectra were obtained at 25 °C at 300, 115.8, and 75.5 MHz, respectively.

**$(\text{C}_5\text{Me}_4\text{-C}\equiv\text{CSiMe}_3)\text{Co}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$  (**4**):** A sample of  $\text{C}_5\text{Me}_4\text{H}(\text{C}\equiv\text{CSiMe}_3)$  (**1**; 2.20 g, 10.1 mmol) was placed in a 100-mL Schlenk flask, 50 mL of dry THF was added, and the solution was cooled to 0 °C in an ice bath. Addition of *n*-butyllithium in hexanes (6.40 mL, 1.54 M, 10.0 mmol) produced a bright yellow

solution of  $\text{Li}[\text{C}_5\text{Me}_4(\text{C}\equiv\text{CSiMe}_3)]$  (**2**), which was warmed to room temperature and stirred for 1 h, after which it was slowly added via cannula to a 250-mL Schlenk flask containing  $\text{CoCl}_2$  (1.31 g, 10.1 mmol) and 100 mL of dry THF. The reaction mixture was stirred at room temperature for 1 h, producing a dark green solution of the complex  $[\text{C}_5\text{Me}_4(\text{C}\equiv\text{CSiMe}_3)\text{CoCl}]_2$  (**3**). A solution containing 10.0 mmol of  $\text{Na}^+[\text{Et}_2\text{C}_2\text{B}_4\text{H}_5]^-$  was prepared by injecting the neutral carborane (1.32 g, 10.1 mmol) into a suspension of excess (0.40 g) dry NaH (previously washed twice with hexane) in 20 mL of dry THF. Stirring was continued until bubbling ceased, the suspension was allowed to settle for 30 min, and the solution was transferred to the stirred solution of **3** by slow cannula filtration. The reaction mixture was stirred at room temperature overnight, forming a reddish-brown solution from which the volatiles were removed, leaving a dark brown solid. The product was extracted with  $\text{CH}_2\text{Cl}_2$  and then passed through a plug (3 cm) of silica gel using  $\text{CH}_2\text{Cl}_2$  as the eluent. Solvent removal gave a reddish-brown oil which solidified on standing to yield 1.30 g (32%) of **4**. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.62 (m, 2 H,  $\text{CH}_2$ ), 2.26 (m, 2 H,  $\text{CH}_2$ ), 1.89 (s, 6 H,  $\text{C}_5\text{Me}_4$ ), 1.87 (s, 6 H,  $\text{C}_5\text{Me}_4$ ), 1.23 (t, 6 H, Et  $\text{CH}_3$ ), 0.27 (s, 9 H,  $\text{SiMe}_3$ ). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 99.2 ( $\text{C}\equiv\text{C}$ ), 97.4 ( $\text{C}\equiv\text{C}$ ), 93.7 ( $\text{C}_5\text{Me}_4$ ), 92.0 ( $\text{C}_5\text{Me}_4$ ), 77.7 ( $\text{C}_5\text{Me}_4$ ), 21.0 (Et  $\text{CH}_2$ ), 14.7 (Et  $\text{CH}_3$ ), 11.0 ( $\text{C}_5\text{Me}_4$ ), 10.4 ( $\text{C}_5\text{Me}_4$ ), –0.1 ( $\text{SiMe}_3$ ). –  $\text{CI}^+$  MS ( $\text{CH}_4$ ):  $m/z$  (%) = 407 (100) [ $\text{M} + 1$ ] $^+$ .

**nido-( $\eta^5$ - $\text{C}_5\text{Me}_4$ - $\text{C}\equiv\text{C}$ - $\text{SiMe}_3$ )Co( $\text{Et}_2\text{C}_2\text{B}_3\text{H}_5$ ) (**5**) and ( $\eta^5$ - $\text{C}_5\text{Me}_4$ - $\text{C}\equiv\text{CH}$ )Co( $\text{Et}_2\text{C}_2\text{B}_3\text{H}_5$ ) (**6**):** To a solution of 0.900 g (2.22 mmol) of **4** in 15 mL of TMEDA were added a few drops of water, and the mixture was stirred at room temperature for 3 h in air. The solvent was removed in vacuo and the product was taken up in hexane and purified by flashing through a 12-cm column of silica gel with hexane as the eluent. Removal of the solvent gave a yellowish-brown oil which on standing gave 0.755 g (86%) of yellow solid **5**. –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 99.2 ( $\text{C}\equiv\text{C}$ ), 98.2 ( $\text{C}\equiv\text{C}$ ), 96.1 ( $\text{C}_5\text{Me}_4$ ), 93.8 ( $\text{C}_5\text{Me}_4$ ), 80.3 ( $\text{C}_5\text{Me}_4$ ), 22.1 (Et  $\text{CH}_2$ ), 17.1 (Et  $\text{CH}_3$ ), 11.3 ( $\text{C}_5\text{Me}_4$ ), 11.0 ( $\text{C}_5\text{Me}_4$ ), 0.6 ( $\text{SiMe}_3$ ). – Compound **5** (0.755 g, 1.91 mmol) was dissolved in 30 mL of dry THF and the resulting solution was cooled to 0 °C. A solution of  $\text{Bu}_4\text{NF}$  (1.0 mL, 1.0 M in THF) was added dropwise and the reaction mixture was stirred at 0 °C for 1 h in air, warmed to room temperature, and stirred for 30 min. The solvent was removed using a rotary evaporator and the product was subsequently taken up in  $\text{CH}_2\text{Cl}_2$  and placed on a 12-cm column of silica gel and eluted with hexanes, giving a yellow solution. The solvent was removed in vacuo leaving a yellowish-brown oil which solidified on standing to afford 0.504 g (82%) of yellow **6**. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.05 (s, 1 H,  $\text{C}\equiv\text{CH}$ ), 2.12 (m, 2 H,  $\text{CH}_2$ ), 1.98 (m, 2 H,  $\text{CH}_2$ ), 1.87 (s, 6 H,  $\text{C}_5\text{Me}_4$ ), 1.85 (s, 6 H,  $\text{C}_5\text{Me}_4$ ), 1.11 (t, 6 H, Et  $\text{CH}_3$ ), –5.86 (broad s, 2 H, BHB). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 96.2 ( $\text{C}\equiv\text{C}$ ), 94.0 ( $\text{C}\equiv\text{C}$ ), 80.6 ( $\text{C}_5\text{Me}_4$ ), 79.1 ( $\text{C}_5\text{Me}_4$ ), 22.4 (Et  $\text{CH}_2$ ), 17.2 (Et  $\text{CH}_3$ ), 11.1 ( $\text{C}_5\text{Me}_4$ ), 11.0 ( $\text{C}_5\text{Me}_4$ ). –  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 3.9 (d, 2 B,  $J_{\text{BH}}$  = 158 Hz), 6.8 (d, 1 B,  $J_{\text{BH}}$  = 98 Hz). –  $\text{CI}^+$  MS ( $\text{CH}_4$ ):  $m/z$  (%) = 324 (100) [ $\text{M}^+$ ].

**1,4-[nido-( $\text{Et}_2\text{C}_2\text{B}_3\text{H}_5$ )Co( $\eta^5$ - $\text{C}_5\text{Me}_4$ - $\text{C}\equiv\text{C}$ )] $_2\text{C}_6\text{H}_4$  (**7**) and [nido-( $\text{Et}_2\text{C}_2\text{B}_3\text{H}_5$ )Co( $\text{C}_5\text{Me}_4$ - $\text{C}\equiv\text{C}$ )] $_2$  (**8**):** Compound **6** (0.445 g, 1.37 mmol), diiodobenzene (0.277 g, 0.687 mmol), bis(benzonitrile)palladium (II) chloride (0.0132 g, 0.0344 mmol), copper(I) iodide (0.0131 g, 0.0687 mmol), and triphenylphosphane (0.018 g, 0.0687 mmol) were placed in a Schlenk flask, vacuum-degassed and placed under  $\text{N}_2$ . Ca. 50 mL of dry diethylamine (freshly distilled from  $\text{CaH}_2$ ) was added via cannula and the reaction mixture was stirred at room temperature for 36 h. The solvent was removed under vacuum and the resulting crude product was chromatographed

on silica gel with  $\text{CH}_2\text{Cl}_2$ /hexane (1:5). The first product to elute was **7**, which was obtained as a yellow-brown solid (0.43 g, 87%) upon solvent removal. Recrystallization of **7** from  $\text{CH}_2\text{Cl}_2$ /hexane gave crystals suitable for X-ray analysis. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.46 (s, 4 H,  $\text{C}_6\text{H}_4$ ), 2.14 (m, 4 H, Et  $\text{CH}_2$ ), 2.03 (m, 4 H, Et  $\text{CH}_2$ ), 1.95 (s, 12 H,  $\text{C}_5\text{Me}_4$ ), 1.87 (s, 12 H,  $\text{C}_5\text{Me}_4$ ), 1.12 (t, 12 H, Et  $\text{CH}_3$ ), –5.86 (broad s, 4 H, BHB). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 131.0 ( $\text{C}_6\text{H}_4$ ), 122.8 ( $\text{C}_6\text{H}_4$ ), 95.0 ( $\text{C}_5\text{Me}_4$ ), 93.3 ( $\text{C}_5\text{Me}_4$ ), 91.8 ( $\text{C}_5\text{Me}_4$ ), 84.7 ( $\text{C}\equiv\text{C}$ ), 79.2 ( $\text{C}\equiv\text{C}$ ), 21.8 (Et  $\text{CH}_2$ ), 16.4 (Et  $\text{CH}_3$ ), 10.5 ( $\text{C}_5\text{Me}_4$ ). –  $^{11}\text{B}$  { $^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 4.0 (s, 2 B), 6.8 (s, 1 B). –  $\text{CI}^+$  MS ( $\text{CH}_4$ ):  $m/z$  (%) = 722 (100) [ $\text{M}^+$ ]. – The second compound eluted was **8**, which was isolated as a yellow-brown solid (ca. 20 mg, 4%) upon solvent removal. Attempts to recrystallize **8** were unsuccessful and resulted in decomposition of the product. –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.15 (m, 4 H, Et  $\text{CH}_2$ ), 2.05 (m, 4 H, Et  $\text{CH}_2$ ), 1.92 (s, 12 H,  $\text{C}_5\text{Me}_4$ ), 1.87 (s, 12 H,  $\text{C}_5\text{Me}_4$ ), 1.15 (t, 12 H, Et  $\text{CH}_3$ ), –5.85 (broad s, 4 H, BHB). –  $\text{CI}^+$  MS ( $\text{CH}_4$ ):  $m/z$  (%) = 647 (100) [ $\text{M} + 1$ ] $^+$ .

**X-ray Crystallographic Study of 7:**  $\text{C}_{40}\text{H}_{58}\text{B}_6\text{Co}_2$  (721.62); monoclinic space group  $P2_1/n$  (no. 14);  $a$  = 9.139(3),  $b$  = 16.423(5),  $c$  = 12.841(5) Å,  $\beta$  = 93.78(3)°,  $V$  = 1923(1) Å $^3$ ,  $Z$  = 2,  $d_{\text{calcd.}}$  = 1.246 g/cm $^3$ ;  $\mu(\text{Mo-K}\alpha)$  = 8.90 cm $^{-1}$ . Data were collected with a Rigaku AFC6S diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71069 Å) at –120 °C, employing an orange needle crystal having approximate dimensions of 0.28 × 0.24 × 0.48 mm mounted on a glass fiber. The  $\omega$ -2 $\theta$  scan technique was employed to a maximum 2 $\theta$  value of 46°. Of 2978 measured reflections, 2782 were independent ( $R_{\text{int}}$  = 0.041,  $R_w$  = 0.065), 217 parameters,  $R$  = 0.047 [for reflections with  $I > 3\sigma(I)$ ], max./min residual electron density 1.10/–0.049 e $\cdot$ Å $^{-3}$ . The data were corrected for absorption, with transmission factors ranging from 0.93 to 1.00. The structure was solved by direct methods.<sup>[16]</sup> The final cycle of full-matrix least-squares refinement was based on 1875 observed reflections [ $I > 3\sigma(I)$ ]. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.<sup>[17]</sup> All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.<sup>[18]</sup> Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160497. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

**nido-[( $\text{Et}_2\text{C}_2\text{B}_3\text{H}_4\text{Me}$ )Co( $\text{C}_5\text{Me}_4$ - $\text{C}\equiv\text{C}$ )] $_2\text{C}_6\text{H}_4$  (**9**):** Compound **7** (0.549 g, 0.761 mmol) was dissolved in 50 mL of dry THF and the solution was cooled to –78 °C using a dry ice/acetone bath. A solution of ( $\text{Me}_3\text{Si}$ ) $_2\text{NLi}$  (1.70 mL, 2.2 mmol, 1.0 M in THF) was added dropwise producing a yellowish-brown precipitate. Upon warming to room temperature the precipitate dissolved and the resulting solution was stirred at room temperature for 1 h. Methyl iodide (0.216 g, 1.522 mmol) was added dropwise via a syringe and stirred at room temperature for 3 h. The solvent was removed in vacuo and the product was extracted with a small amount of  $\text{CH}_2\text{Cl}_2$  which was then passed through a plug of silica gel. Removal of solvent gave yellow solid **9** (0.450 g, 80%). –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.46 (s, 4 H,  $\text{C}_6\text{H}_4$ ), 2.20 (m, 4 H, Et  $\text{CH}_2$ ), 2.00 (m, 4 H, Et  $\text{CH}_2$ ), 1.95 (s, 12 H,  $\text{C}_5\text{Me}_4$ ), 1.81 (s, 12 H,  $\text{C}_5\text{Me}_4$ ), 1.26 (s, 6 H, B-Me), 1.10 (t, 12 H, Et  $\text{CH}_3$ ), –5.13 (broad s, 4 H, BHB). –  $\text{CI}^+$  MS ( $\text{CH}_4$ ):  $m/z$  (%) = 750 (100) [ $\text{M}^+$ ].

**nido-( $\text{Et}_2\text{C}_2\text{B}_3\text{H}_5$ )Co( $\text{C}_5\text{Me}_4$ )- $\text{C}\equiv\text{C}$ -Pd( $\text{Et}_2\text{NH}$ ) $_2\text{Cl}$  (**10**) and [nido-( $\text{Et}_2\text{C}_2\text{B}_3\text{H}_5$ )Co( $\text{C}_5\text{Me}_4$ - $\text{C}\equiv\text{C}$ )] $_2\text{Pd}(\text{Et}_2\text{NH})_2$  (**11**):** Com-



pound **6** (0.292 g, 0.902 mmol), bis(acetonitrile)palladium (II) chloride (0.122 g, 0.902 mmol), and copper(I) iodide (8 mg, 0.025 mmol) were placed in a Schlenk flask and an excess of Et<sub>2</sub>NH was added. The reaction mixture was stirred at room temperature for 17 h, following which the solvent was removed in a rotary evaporator, and the crude product was flash-chromatographed on silica gel and eluted with hexanes. The first product eluted was **10**, isolated as a red-brown solid (0.480 g, 87%) upon solvent removal. The second product, eluted with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1), was red-brown solid **11** (ca. 30 mg, 6%). – **10**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.32 (broad s, 2 H, NH), 3.17 (m, 4 H, amine CH<sub>2</sub>), 2.66 (m, 4 H, amine CH<sub>2</sub>), 2.13 (m, 2 H, carborane CH<sub>2</sub>), 2.00 (m, 2 H, carborane CH<sub>2</sub>), 1.81 (s, 6 H, C<sub>5</sub>Me<sub>4</sub>), 1.80 (s, 6 H, C<sub>5</sub>Me<sub>4</sub>), 1.60 (t, 12 H, amine CH<sub>3</sub>), 1.24 (t, 6 H, carborane CH<sub>3</sub>), –6.00 (broad s, 2 H, BHB). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 95.8 (C<sub>5</sub>Me<sub>4</sub>), 94.2 (C<sub>5</sub>Me<sub>4</sub>), 91.9 (C<sub>5</sub>Me<sub>4</sub>), 86.5 (C≡C), 84.9 (C≡C), 49.6 (NCH<sub>2</sub>), 21.8 (Et CH<sub>2</sub>), 16.9 (Et CH<sub>3</sub>), 15.5 (NCH<sub>3</sub>), 10.9 (C<sub>5</sub>Me<sub>4</sub>), 10.6 (C<sub>5</sub>Me<sub>4</sub>). – <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>): δ = –6.0 (broad s, 3 B). – <sup>1</sup>Cl<sup>+</sup> MS (CH<sub>4</sub>): *m/z* (%) = 611 (100) [M<sup>+</sup>]. – **11**: <sup>1</sup>Cl<sup>+</sup> MS (CH<sub>4</sub>): *m/z* (%) = 899 (100) [M + 1]<sup>+</sup>.

**nido-Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>–C≡CSiMe<sub>3</sub>) (13) and nido-Cp\*Co[Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>(C≡CSiMe<sub>3</sub>)<sub>2</sub>] (14)**: Compound **12** (0.900 g, 2.05 mmol), bis(benzonitrile)palladium(II) chloride (0.039 g, 0.102 mmol), copper(I) iodide (0.019 g, 0.102 mmol), and triphenylphosphane (0.054 g, 0.205 mmol) were placed in a Schlenk flask, vacuum-degassed and placed under an inert gas. About 100 mL of dry diethylamine was added via cannula. Excess trimethylsilylacetylene (0.50 g, 5.09 mmol, 1.1 mmol.) was added via a syringe and the reaction mixture was stirred at room temperature for 36 h. The solvent was removed under vacuum and the resulting crude product was subjected to column chromatography on silica gel [elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5)] The first product to elute was **13**, which was obtained as a yellow solid (0.34 g, 41%) upon solvent removal. Yield. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.14 (m, 2 H, Et CH<sub>2</sub>), 1.91 (m, 2 H, Et CH<sub>2</sub>), 1.77 (s, 15 H, Cp\* Me), 1.08 (t, 6 H, Et CH<sub>3</sub>), 0.20 (s, 9 H, SiMe<sub>3</sub>), –5.16 (br, 2 H, B-H-B). – <sup>1</sup>Cl<sup>+</sup> MS (CH<sub>4</sub>): *m/z* (%) = 410 (100) [M<sup>+</sup>]. – The second compound to elute was yellow solid **14** (0.60 g, 58%). – <sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.11 (m, 2 H, Et CH<sub>2</sub>), 1.90 (m, 2 H, Et CH<sub>2</sub>), 1.76 (s, 15 H, Cp\* Me), 1.10 (t, 6 H, Et CH<sub>3</sub>), 0.23 (s, 9 H, SiMe<sub>3</sub>), 0.16 (s, 9 H, SiMe<sub>3</sub>), –4.70 (br, 2 H, B-H-B). – <sup>1</sup>Cl<sup>+</sup> MS (CH<sub>4</sub>): *m/z* (%) = 507 (100) [M + 1]<sup>+</sup>.

**nido-Cp\*Co[Et<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>(C≡CH)(C≡CSiMe<sub>3</sub>)] (15)**: Compound **14** (0.300 g, 0.593 mmol) was dissolved in 10 mL of dry THF and the solution was cooled to 0 °C. A solution of Bu<sub>4</sub>NF (1.0 mL, 1.0 M in THF) was added dropwise and the reaction mixture was stirred at 0 °C in air for 1 h. The mixture was warmed to room temperature and stirred for 30 min. The solvent was removed using a rotary evaporator and the product was subsequently taken up in CH<sub>2</sub>Cl<sub>2</sub>, placed on a 12-cm column of silica gel, and eluted with hexanes affording a yellow solution. The solvent was removed in vacuo, leaving yellow solid **15** (0.206 g, 80%). – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.45 (s, 1 H, C≡CH) 2.10 (m, 2 H, Et CH<sub>2</sub>), 1.91 (m, 2 H, Et CH<sub>2</sub>), 1.71 (s, 15 H, Cp\* Me), 1.10 (t, 6 H, Et CH<sub>3</sub>), 0.18 (s, 9 H, SiMe<sub>3</sub>), –4.70 (br, 2 H, B-H-B). – <sup>1</sup>Cl<sup>+</sup> MS (CH<sub>4</sub>): *m/z* (%) = 435 (100) [M + 1]<sup>+</sup>.

**1,4-[nido-Cp\*CoEt<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>(C≡CSiMe<sub>3</sub>)(C≡C)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (16)**: Compound **15** (0.200 g, 0.461 mmol), diiodobenzene (0.076 g, 0.231 mmol), bis(benzonitrile)palladium(II) chloride (0.009 g, 0.023 mmol), copper(I) iodide (0.0044 g, 0.023 mmol), and triphenylphosphane (0.012 g, 0.0461 mmol) were placed in a Schlenk flask,

vacuum-degassed and placed under an inert gas. About 50 mL of dry diethylamine (freshly distilled from CaH<sub>2</sub>) was added via cannula and the reaction mixture was stirred at room temperature for 36 h. The solvent was removed under vacuum and the resulting crude product was column chromatographed on silica gel [elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5)]. The first product to elute was **16**, obtained as a yellow solid (0.19 g, 87%) upon solvent removal. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.49 (s, 4 H, C<sub>6</sub>H<sub>4</sub>), 2.14 (m, 4 H, Et CH<sub>2</sub>), 1.93 (m, 4 H, Et CH<sub>2</sub>), 1.72 (s, 30 H, Cp\*), 1.13 (t, 12 H, Et CH<sub>3</sub>), 0.23 (s, 18 H, SiMe<sub>3</sub>), –4.62 (br, 2 H, B-H-B). – <sup>1</sup>Cl<sup>+</sup> MS (CH<sub>4</sub>): *m/z* (%) = 946 (100), [M + 4]<sup>+</sup>. – The second compound to elute was tentatively identified from its mass spectrum as *nido*-[(C<sub>5</sub>Me<sub>5</sub>)CoEt<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>3</sub>–(C≡CSiMe<sub>3</sub>)(C≡C)]<sub>2</sub>. – <sup>1</sup>Cl<sup>+</sup> MS (CH<sub>4</sub>): *m/z* (%) = 870 (100) [M + 4]<sup>+</sup>.

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