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Small cobaltacarborane clusters in synthesis. Peralkylation, perhalogenation, and macrocycle construction☆

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Abstract

Methods are described for achieving stepwise replacement of all BH terminal hydrogens in CoC_2B_4 clusters with halogen or alkyl groups, leading to complexes such as Cp*Co(2,3-$Et_2C_2B_4X_4$) (X = Me or I) and Cp*Co(2,3-$Et_2C_2B_4IMe_2[O_3SCF_3]$). Building on earlier work on B-functionalization of small metallacarboranes via metal-catalyzed cross-coupling, two- and three-dimensional macrocycles containing four to six metal centers have been constructed systematically from monomeric precursor complexes.

Keywords: Cobaltacarborane clusters; Peralkylation; Perhalogenation; Macrometallocycles

1. Introduction

The small carborane ligands $RR'C_2B_4H_4^{2-}$, $RR'C_2B_3H_5^{2-}$, or $RR'C_2B_3H_4^{4-}$ (where R and R′ are H or, more commonly, alkyl or other hydrocarbon groups, or $SiMe_3$) have planar C_2B_3 rings that are amenable to η^5-coordination to metal ions [1]. These ligands approximate the cyclopentadienide rings $C_5H_5^-$ (Cp) and $C_5Me_5^-$ (Cp*) in size and shape, and also electronically: all are formal six-electron donors and readily form metal π-sandwich complexes [2]. In the case of planar $RR'C_2B_3H_4^{4-}$, η^5-binding to metal ions on *both* sides of the C_2B_3 ring plane generates stable, isolable multidecker sandwiches. In contrast to many Cp and Cp* metal complexes other than ferrocenyl derivatives, most six- and seven-vertex *nido*-MC_2B_3, seven-vertex *closo*-MC_2B_4 and seven-vertex *closo*-$M_2C_2B_3$ metallacarborane clusters are chemically and thermally stable, are soluble in organic solvents, undergo reversible oxidization and reduction, and can be readily functionalized at boron and carbon cage vertices [1,2].

These favorable properties of small metallacarboranes have demonstrated applicability in several areas including catalysis [3], antitumor activity [4], and in the synthesis of electronically tailorable polycluster systems [5]. These findings have stimulated efforts to develop systematic routes for functionalizing and linking these clusters directly or via alkynyl or phenylene groups. Recent papers from this laboratory report the directed synthesis of a variety of soluble small ferracarborane and cobaltacarborane complexes including linear and branched chains [6], benzene-centered pinwheels [6,7], and other systems [8]. Here we further extend this work to include routes to poly-B-alkylation and -halogenation and the controlled assembly of some novel metallomacrocycles.

2. Perhalogenation and peralkylation

Replacement of all B–H terminal hydrogens in icosahedral C_2B_{10} carboranes has been elegantly demonstrated by Hawthorne [9], and is important as a 'camouflage' strategy for shielding boron clusters from attack by external reagents. In the small carborane/metallacarborane area, B-peralkylated clusters have been generated from alkylborane precursors; for example, the *nido*-2,4-$Et_2C_2B_4Et_4H^-$ ion reacts with $FeCl_2$ to

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☆ Organotransition-metal metallacarboranes, 65.

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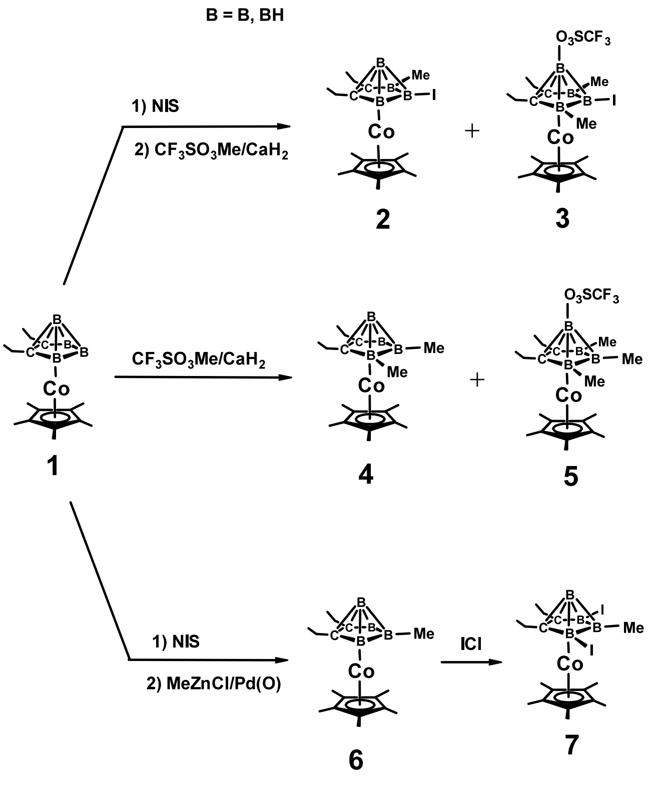
afford the B,C-perethyl sandwich $Fe(Et_2C_2B_4Et_4)_2$ [10]. There are also several examples of MC_2B_4, MC_2B_3, and $M_2C_2B_3$ clusters in which all B–H hydrogens have been replaced by alkyl or halogen substituents [11]. However, it is desirable to have systematic, efficient methods for achieving B-peralkylation and B-perhalogenation of the $R_2C_2B_4H_4^{2-}$ ligands in existing metallacarborane complexes. Such procedures have been lacking, largely because of the near-inertness of the apex hydrogen [H(7)] toward substitution; for example, in earlier work in our laboratory, treatment of $Cl_2CpTa(Et_2C_2B_4H_4)$ with excess Br_2 or methylmagnesium bromide produced $Cl_2CpTa(Et_2C_2B_4H\text{-}4,5,6\text{-}X_3)$ complexes (X = Me or Br) in which the three equatorial BH hydrogens, but not the apex H, were replaced [11d]. This presents a problem, since the introduction of substituents on the apex boron is important if one wishes to make complexes that are resistant to deboronation (decapitation) by electrophiles [1,2].

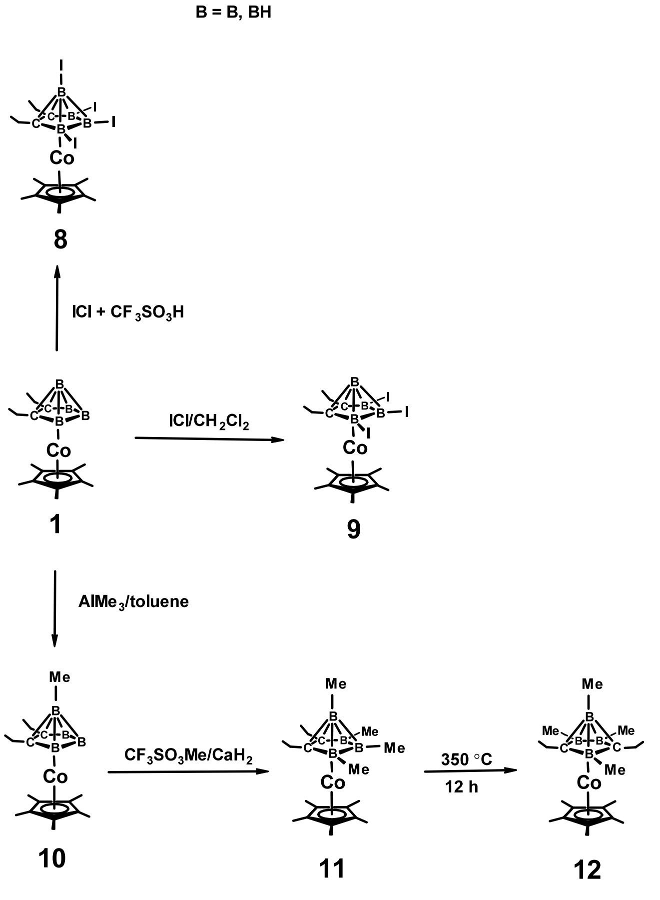
We investigated the action of methyl triflate as an agent for B-methylation on the cobaltacarborane $Cp^*Co(2,3\text{-}Et_2C_2B_4H_4)$ (**1**) and its B(5)-iodo derivative. B(5)-Iodination of **1** with *N*-iodosuccinimide [12] followed by treatment with methyl triflate and CaH_2 gave a pair of products, the orange–yellow B(4)–Me–B(5)–I derivative **2** and orange–red $Cp^*Co(2,3\text{-}Et_2C_2B_4)\text{-}4,6\text{-}Me_2\text{-}5\text{-}I\text{-}7\text{-}O_3SCF_3$ (**3**) in 39 and 26% isolated yields, respectively (Scheme 1). Reaction of unsubstituted **1** with methyl triflate afforded the orange–yellow B(4,5)-dimethyl derivative (**4**) and the B(4,5,6)-trimethyl-B(7)-triflate complex (**5**) in low yields (23 and 12%, respectively).

In contrast to the action of methyl triflate on $Cp^*Co(2,3\text{-}Et_2C_2B_4H_3)\text{-}5\text{-}I$, treatment of this complex with methylzinc chloride followed by $Pd(PPh_3)_4$ effected the replacement of the iodo substituent with methyl, forming the orange–red crystalline 5-Me derivative **6** in quantitative yield. Reaction of **6** with excess ICl introduced iodo groups to the B(4,6) positions, affording $Cp^*Co(2,3\text{-}Et_2C_2B_4)\text{-}4,6\text{-}I_2\text{-}5\text{-}Me$ (**7**), but left B(7)–H unaffected.

Having seen that methyl triflate attacks the apical hydrogen in $Cp^*Co(2,3\text{-}Et_2C_2B_4H_4)$ derivatives to produce **3** and **5**, we pursued this chemistry further as shown in Scheme 2. When **1** was treated with ICl and triflic acid at 70 °C for a day, the orange–yellow per-B-iodo derivative $Cp^*Co(2,3\text{-}Et_2C_2B_4I_4)$ (**8**) was obtained in 44% isolated yield, representing the first per-B-halo derivative of an MC_2B_4 cluster. However, the reaction of **1** with excess ICl in the absence of triflic acid gave only the B(4,5,6)-triiodo derivative **9**.



Scheme 1.



Scheme 2.

Full B-methylation of **1** was accomplished by a somewhat different route: reaction with $AlMe_3$ in toluene resulted in methyl substitution at B(7) exclusively, giving **10** as an orange–red solid (81%, Scheme 2); treatment of this compound with methyl triflate and calcium hydride produced the desired Cp*Co(2,3-$Et_2C_2B_4Me_4$) (**11**) in 86% yield. The expected high thermal stability of this product was demonstrated by its rearrangement at 360 °C, with no appreciable decomposition, to form the 'carbons-apart' isomer Cp*Co(2,4-$Et_2C_2B_4Me_4$) (**12**).

3. Macrocycle synthesis

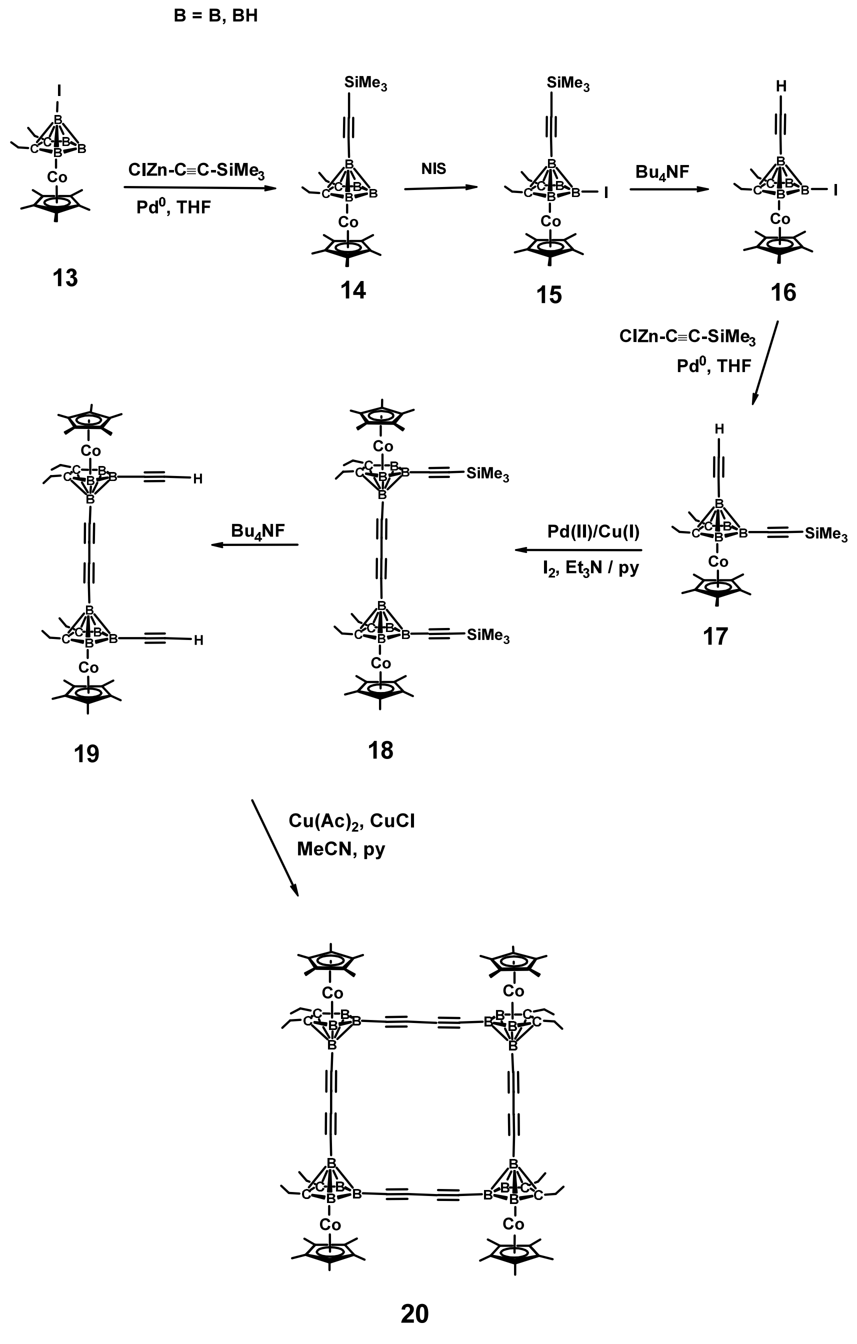
There is much current interest in metal-containing covalently bonded macrocycles, especially those exhibiting metal–metal electronic communication or other potentially useful properties [13]. Given their general stability, tailorability, and redox characteristics (vide supra), metallacarboranes would seem to be excellent candidates as modular units for such systems. Cyclic polymetallacarborane complexes have occasionally been encountered in our laboratory when serendipitously obtained products were isolated in low yields and structurally characterized; these include, inter alia, a hexametallic rectangular system consisting of two Co_3 tetradecker sandwiches cross-linked at top and bottom by phenylene rings [14], and a four-cluster octametallic $[RuCo]_4$ compound [15]. However, such examples are few and far between, and methods for efficiently assembling specific target macrocycles from metallacarboranes have not been available. This situation has changed as a result of recent work, and routes to bifunctional organosubstituted derivatives of small ferra- and cobaltacarboranes are now at hand [6–8].

Macrocycles connected by alkynyl or polyalkynyl chains (carbon wires) are likely to exhibit some degree of metal–metal electron delocalization [16], and accordingly we are exploring the possibilities in this area. Scheme 3 depicts a seven-step sequence by which the iodo derivative Cp*Co(2,3-$Et_2C_2B_4H_3$-7-I) (**13**) [17] was converted into a B(5,7)-dialkynyl species that was then dimerized and subsequently cyclized to obtain a novel tetrametallic species **20**; this complex contains a novel planar octagonal (tetratruncated square) B_8C_{16} ring, as reported in a recent Communication [8]. Each of the species **14**–**20** was isolated and spectroscopically characterized, the individual yields varying from 78 to 99%. The structure of the target molecule [Cp*Co(2,3-$Et_2C_2B_4H_3$-5-C≡C-7-C≡C)]$_4$ (**20**), a red crystalline air-stable solid, was confirmed via X-ray diffraction [8]. The diethynyl linkages and cobaltacarborane cluster units have bond distances and angles within normal limits, and the molecule has nanostructural dimensions with a maximum separation of ca. 24 Å measured diagonally between the Cp* methyl hydrogens. Cyclic and Osteryoung square wave voltammetry on **20** revealed a significant degree of electron delocalization between the four cobalt centers, with two one-electron reductions followed by a two-electron reduction in a total separation of ca. 300 mV [8]. Detailed electrochemical studies of **20** and related compounds are under way in collaboration with Prof. Zanello and Dr Fabrizi di Biani and will be reported in full in a later publication.

The preparation of the two-dimensional cycle **20** led us to attempt the construction of a hexanuclear three-dimensional macrocycle via a three-way diethynyl linkage of two tris(metallacarboranylalkynyl)benzene 'pinwheel' complexes, a genre of which several examples have recently been prepared in our laboratory [6b,6e,7]. The synthetic approach, outlined in Scheme 4, entailed first preparing the tris(trimethylsilylethynylcobaltacarboranyl-ethynyl)benzene species (**23**), which was accomplished via two different methods. In one procedure, the tricobalt complex **21** [6e] was selectively iodinated or brominated to give the tri-B-halo compounds **22a** and **22b**, respectively; treatment of **22b** with (ethynyltrimethylsilyl)zinc chloride, prepared in situ, in the presence of a Pd(0) catalyst, gave red–orange solid **23** in 90% isolated yield. Alternatively, we obtained **23** in one step (83% yield) from the B(5,7)-dialkynyl complex **17** via Pd-catalyzed cross-coupling with 1,3,5-triiodobenzene (Scheme 4).

Desilylation of **23** afforded the tris(ethynylcobaltacarboranyl-ethynyl)benzene complex **24** quantitatively, and this product was allowed to react with acetonitrile and pyridine in the presence of copper(II) acetate and copper(I) chloride to afford the target complex {[Cp*Co(2,3-$Et_2C_2B_4H_3$-5-C≡C-7-C≡C)]$_3C_6H_3$}$_2$ (**25**) as an air-stable red–orange crystalline solid in 44% isolated yield. The structure proposed for this compound in Scheme 4 has not been confirmed crystallographically, owing to severe loss of solvent from crystals before satisfactory X-ray data could be obtained. However, the highly symmetrical structure shown is supported by (1) a parent envelope at *m*/*z* 2368 in the FAB-mass spectrum; (2) unique C_5Me_5, ethyl CH_3, ethyl CH_2, and C_6H_3 signals in the 500 MHz ^{1}H-NMR spectrum; and (3) unique C_5Me_5, $C_5\mathit{Me}_5$, ethyl CH_3, ethyl CH_2, and carborane signals as well as two benzene lines, in the 125.75 MHz ^{13}C-NMR spectrum. The ^{11}B-NMR spectrum consists of extremely broad, uninformative bands (not uncommon in very large, bulky molecules). The complex was further characterized from its UV–Vis and IR spectra.

Macrocycles such as **20** and **25** are envisioned as prototypes for construction modules that can be assembled into supramolecular or polymeric metallacarborane-based organometallic systems whose bulk elec-



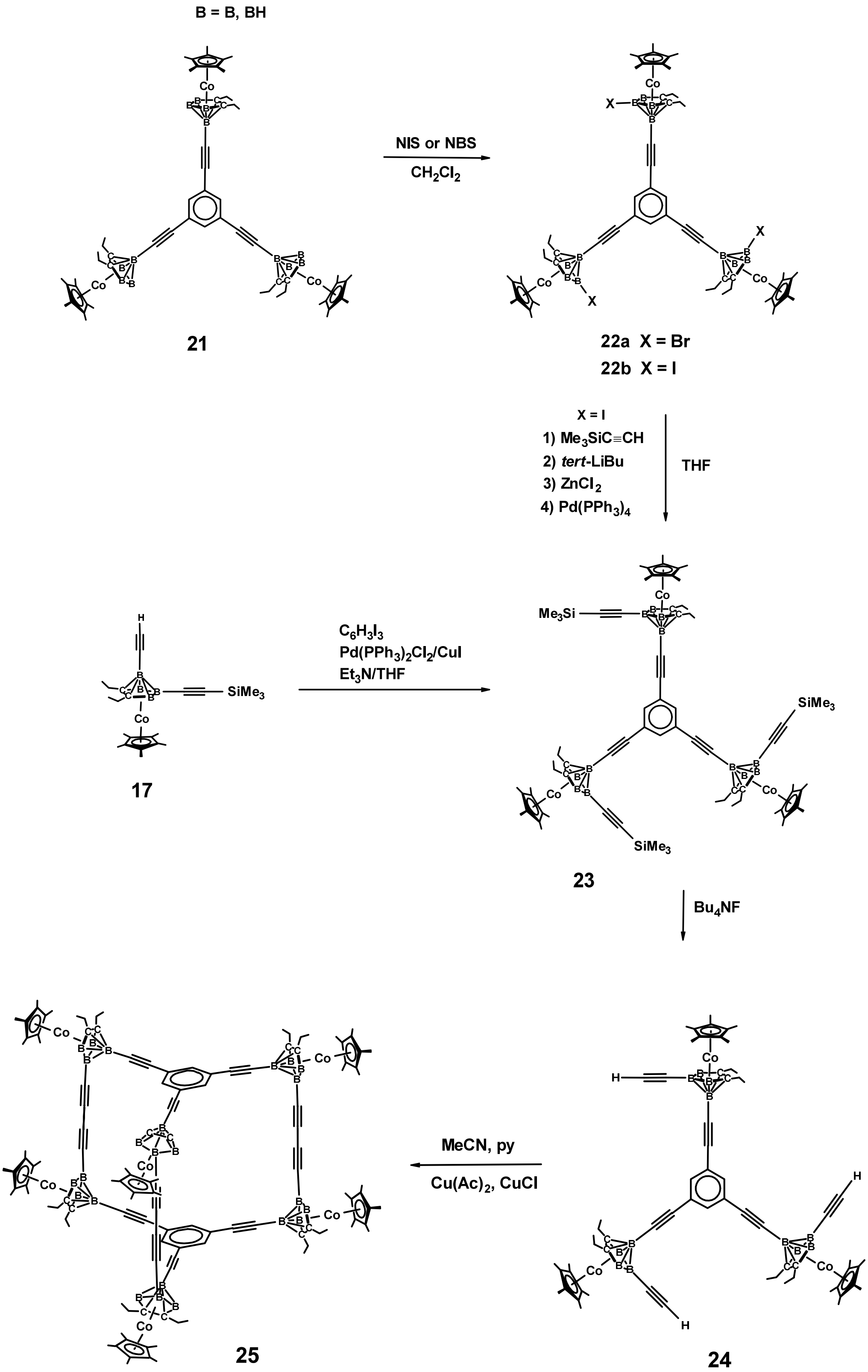
Scheme 3.

tronic properties can be tailored by appropriate introduction of electron-attracting or -withdrawing functional groups to the carborane ligands. However, of perhaps broader significance than the particular species described here, is the demonstrated viability of the synthetic approaches we have employed in this and earlier work for effecting substitution and linkage at specific boron cage locations, since these methods are applicable to a wide range of metallacarborane systems. Studies in this area are continuing.

4. Experimental

4.1. Instrumentation

^{1}H (500 MHz [where noted], 300 MHz), ^{13}C (125.8 MHz [where noted], 75.4 MHz), and ^{11}B (96.4 MHz)-NMR spectra were recorded on GN-300/44 and Varian Unity/Inova 500/51 and 300/51 instruments. ^{1}H and ^{13}C shifts are referenced to residual ^{1}H and ^{13}C signals in the deuterated solvent. ^{11}B-NMR resonances are referenced



Scheme 4.

to the external standard $BF_3 \cdot OEt_2$. Unit resolution mass spectra were acquired on a Finnigan (Model LCQ Classic) quadruple ion trap mass spectrometer using an atmospheric pressure chemical ionization interface. Infrared spectra were obtained on a Nicolet Impact-400 spectrophotometer. UV–Vis spectra were recorded on a

HP 8452A diode array spectrophotometer or a Cary 5E UV–Vis–NIR Spectrophotometer. Elemental analyses were performed by Atlantic Microlabs in Norcross, GA.

4.2. Materials and procedures

All reactions were carried out in oven glassware under a dinitrogen atmosphere using conventional glove box or Schlenk techniques, and the products were worked up in air. All commercial reagents were used as received without further purification. THF, diethyl ether, and toluene were distilled from sodium benzophenone ketyl prior to use. Triethylamine was distilled from CaH_2 under an inert atmosphere. When anhydrous dichloromethane was required, the solvent was distilled from P_2O_5 under N_2. Cp*Co(2,3-$Et_2C_2B_4H_3$-7-I) (**13**) [17], **21** [6e] and Cp*Co(2,3-$Et_2C_2B_4H_4$) (**1**) [18] were prepared according to published procedures. Full details on the synthesis and characterization of compounds **14**–**20** have been published [8].

4.3. Cp*Co(2,3-$Et_2C_2B_4H_2$-4-Me-5-I) (2) and Cp*Co(2,3-$Et_2C_2B_4$-4,6-Me_2-5-I-7-CF_3SO_3) (3)

Cp*Co(2,3-$Et_2C_2B_4H_3$-5-I) (**1**) (45 mg, 0.1 mmol), 21 mg of CaH_2 (0.5 mmol) and 1 ml of methyl triflate were heated at 70 °C for 2 days. The mixture was cooled to room temperature, 2 ml of water and 5 ml of dichloromethane were added, and the organic phase was separated and washed twice with 2 ml of water and dried over anhydrous sodium sulfate. The mixture was washed through 2 cm of silica gel with dichloromethane, after which the crude material was chromatographed on silica gel TLC plates in 1:1 hexane–dichloromethane, yielding two major orange–red bands. The first band afforded 18 mg (39%) of **2** as an air-stable orange–yellow solid, and the second band gave 16 mg (26%) of **3** as an air-stable orange–red solid. Data for **2**: ^{1}H-{^{11}B}-NMR (500 MHz, $CDCl_3$): $\delta = 0.49$ (s, 3H, Me), 0.94, 1.21 (t, 3H, $J = 7.8$ Hz, ethyl CH_3), 1.36 (s, 1H, BH), 3.31 (s, 1H, BH), 1.73 (s, 15H, C_5Me_5), 2.29, – 2.61 (m, 4H, $J = 7$ Hz, ethyl CH_2); ^{13}C-NMR ($CDCl_3$): $\delta = 9.2$ (C_5Me_5), 13.1, 15.4 (ethyl CH_3), 19.1, 21.6 (ethyl CH_2), 91.1 (C_5Me_5), 93.8 (C_2B_4); ^{11}B-NMR ($CDCl_3$): $\delta = 1.9$ (BH, 1B, unresolved), 4.1 (BH, 2B, unresolved), 10.0 (s, 1B); IR (KBr pellet, cm^{-1}): $\nu = 2966.6$ (vs), 2932.6 (s), 2870.6 (m), 2566.3 (vs, B–H), 2529.9 (vs, B–H), 1472.5 (m), 1451.7 (s), 1378.6 (s), 1307.1 (m), 1190.7 (w), 1066.7 (m), 1027.4 (s), 881.8 (m), 814.2 (m), 762.3 (w), 671.7 (w), 622.7 (w), 449.0 (w); CI^+-MS: m/z (%) = 464.4 ([M^+], 100). Anal. Calc. for $B_4C_{17}CoH_{30}I$: C, 44.05; H, 6.52%. Found: C, 44.18; H, 6.67%.

Data for **3**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.56$ (s, 6H, Me), 1.14 (t, 6H, $J = 7.5$ Hz, ethyl CH_3), 1.69 (s, 15H, C_5Me_5), 2.48, 2.62 (sextet, 4H, $J = 7.5$ Hz, ethyl CH_2); ^{13}C-NMR ($CDCl_3$): $\delta = 8.9$ (C_5Me_5), 12.7 (ethyl CH_3), 20.3 (ethyl CH_2), 92.3 (C_5Me_5), 87.3 (C_2B_4); ^{11}B-NMR ($CDCl_3$): $\delta = 8.9$ (s, 2B),0.9 (s, 1B), 8.8 (s, 1B); IR (KBr pellet, cm^{-1}): $\nu = 2980.1$ (m), 2942.0 (m), 2907.8 (w), 1471.2 (w), 1395.9 (s), 1385.0 (m), 1310.3 (m), 1253.4 (w), 1206.1 (vs), 1149.8 (s), 1101.3 (m), 1082.8 (m), 1062.4 (m), 1022.3 (m), 917.2 (vs), 663.2 (w), 620.9 (m), 507.1 (w), 461.1 (w); CI^+-MS: m/z (%) = 626.3 ([$M^+ +$ 1], 100). Anal. Calc. for $B_4C_{19}CoF_3H_{31}ISO_3$: C, 36.48; H, 5.00%. Found: C, 36.22; H, 5.00%.

4.4. Cp*Co(2,3-$Et_2C_2B_4H_2$-4,5-Me_2) (4) and Cp*Co(2,3-$Et_2C_2B_4$-4,5,6-Me_3-7-CF_3SO_3) (5)

Compound **1** (33 mg, 0.1 mmol), 34 mg of CaH_2 (0.8 mmol) and 1 ml of methyl triflate were heated at 108 °C for 4 days. The mixture was cooled to room temperature, two drops of water were added, and the solvent was removed under vacuum. The mixture was washed through 2 cm of silica gel with dichloromethane, and the crude material was chromatographed on silica gel TLC plates in 1:1 hexane–dichloromethane, yielding two major orange–red bands. The first band afforded 8 mg (23%) of **4** as an air-stable orange–yellow solid. The second band gave 6 mg (12%) of **5** as an air-stable orange–red solid.

Data for **4**: ^{1}H-{^{11}B}-NMR (500 MHz, $CDCl_3$): $\delta =$ 0.36, 0.45 (s, 3H, Me), 0.93 1.21 (t, 3H, $J = 7.5$ Hz, ethyl CH_3), 1.21 (s, 1H, BH), 2.93 (s, 1H, BH), 1.72 (s, 15H, C_5Me_5), 2.38, 2.53 (sextet, 4H, $J = 7.5$ Hz, ethyl CH_2); ^{13}C-NMR ($CDCl_3$): $\delta = 9.4$ (C_5Me_5), 13.0, 15.5 (ethyl CH_3), 19.2, 21.9 (ethyl CH_2), 89.8 (C_5Me_5); ^{11}B-NMR ($CDCl_3$): $\delta = 1.2$ (BH, 1B, $J = 183$ Hz), 3.6 (BH, 1B, $J = 186$ Hz), 8.0 (s, 1B), 19.2 (s, 1B); IR (KBr pellet, cm^{-1}): $\nu = 2967.7$ (vs), 2924.3 (s), 2889.8 (m), 2870.2 (m), 2822.3 (w), 2538.2 (vs, B–H), 2501.9 (s, B–H), 1467.6 (w), 1449.7 (w), 1377.2 (s), 1305.3 (m), 1187.2 (w), 1143.5 (w), 1065.0 (m), 1028.0 (m), 909.6 (w), 880.5 (w) 447.8 (w); CI^+-MS: m/z (%) = 353.2 ([$M^+ + 1$], 100). Anal. Calc. for $B_4C_{18}CoH_{33}$: C, 61.48; H, 9.46%. Found: C, 61.42; H, 9.49%.

Data for **5**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.34$ (s, Me), 0.44 (s, 6H, Me), 1.11 (t, 6H, $J = 7.8$ Hz, ethyl CH_3), 1.69 (s, 15H, C_5Me_5), 2.45, 2.59 (sextet, 4H, $J = 7.5$ Hz, ethyl CH_2); ^{13}C-NMR ($CDCl_3$): $\delta = 9.1$ (C_5Me_5), 12.8 (ethyl CH_3), 20.2 (ethyl CH_2), 91.1 (C_5Me_5), 87.2 (C_2B_4); ^{11}B-NMR ($CDCl_3$): $\delta = 7.6$ (s, 1B), 6.7 (s, 2B), 15.0 (s, 1B); IR (KBr pellet, cm^{-1}): $\nu = 2979.6$ (m), 2925.6 (m), 2900.5 (m), 2829.8 (w), 1468.8 (w), 1454.1 (w), 1400.1 (s), 1381.0 (m), 1307.4 (m), 1251.8 (m), 1214.6 (vs), 1198.4 (vs), 1149.7 (s), 1068.5 (m), 1038.7 (s), 932.1 (vs), 873.9 (w), 622.4 (s), 589.8 (w), 563.5 (w), 510.2 (m), 466.5 (w); CI^+-MS: m/z (%) = 515.2 ([$M^+ + 1$], 100). Anal. Calc. for $B_4C_{20}CoF_3H_{34}SO_3$: C, 46.76; H, 6.67%. Found: C, 46.89; H, 6.72%.

4.5. *Cp*Co(2,3-Et$_2$C$_2$B$_4$H$_3$-5-Me)* (**6**)

Methyllithium (2.14 ml in 1.4 M of ether (3 mmol) in 12 ml of THF) was added to 409 mg of anhydrous zinc chloride and 5 ml of THF was added at −78 °C. The mixture was warmed to room temperature and stirred for 2 h, after which 541 mg (1.2 mmol) of Cp*Co(2,3-Et$_2$C$_2$B$_4$H$_3$-5-I), and 69 mg (0.06 mmol) of Pd(PPh$_3$)$_4$ were added, the solution was stirred at 70 °C for 16 h, and the solvent was removed under vacuum. The residue was washed through 5 cm of silica gel in 1:1 hexane–dichloromethane yielding 394 mg of **6** (97%) as an air-stable orange–red solid. ^{1}H-{^{11}B}-NMR (500 MHz, CDCl$_3$): $\delta = 0.55$ (s, 3H, Me), 1.17 (t, 6H, $J = 7$ Hz, ethyl CH$_3$), 1.18 (s, 1H, BH), 3.01 (s, 2H, BH), 1.77 (s, 15H, C$_5$Me$_5$), 2.32, 2.49 (m, 4H, $J = 7.5$ Hz, ethyl CH$_2$); ^{13}C-NMR (CDCl$_3$): $\delta = 1.0$ (CH$_3$), 9.6 (C$_5$Me$_5$), 15.1 (ethyl CH$_3$), 21.8 (ethyl CH$_2$), 90.2 (C$_5$Me$_5$), 93.0 (C$_2$B$_4$); ^{11}B-NMR (CDCl$_3$): $\delta = 2.5$ (BH, 3B, $J = 120$ Hz), 20.7 (s, 1B); IR (KBr pellet, cm^{-1}): $\nu = 2967.3$ (s), 2923.7 (s), 2872.2 (m), 2825.3 (w), 2532.5 (vs, B–H), 1476.6 (m), 1450.0 (m), 1376.5 (s), 1294.0 (m), 1261.4 (m), 1159.7 (w), 1095.8 (m), 1066.8 (s), 1026.2 (s), 901.3 (w), 882.6 (w), 801.8 (m); CI$^+$-MS: m/z (%) = 338.2 ([M$^+$], 100).

4.6. *Cp*Co(2,3-Et$_2$C$_2$B$_4$H-4,6-I$_2$-5-Me)* (7)

Compound **6** (290 mg, 0.86 mmol) was dissolved in 30 ml of dry CH$_2$Cl$_2$ at 0 °C. To this solution was added dropwise 1.89 ml of iodine monochloride in 1 M dichloromethane (1.89 mmol). The reaction mixture was stirred at 0 °C for 2 h, and then for 20 h at room temperature, after which the solvent was removed and the residue was taken up in hexane and flash chromatographed, first through 3 cm of silica gel in hexane to remove iodine, and then through CH$_2$Cl$_2$, to give 440 mg (87%) of **7** as an air-stable orange–red solid. ^{1}H-NMR (CDCl$_3$): $\delta = 0.41$ (s, 3H, Me), 1.10 (t, 6H, $J = 7.8$ Hz, ethyl CH$_3$), 1.70 (s, 15H, C$_5$Me$_5$), 2.55, 2.79 (m, 4H, $J = 7.2$ Hz, ethyl CH$_2$); ^{13}C-NMR (CDCl$_3$): $\delta = 8.7$ (C$_5$Me$_5$), 13.8 (ethyl CH$_3$), 22.1 (ethyl CH$_2$), 91.9 (C$_5$Me$_5$), 91.1 (C$_2$B$_4$); ^{11}B-NMR (CDCl$_3$): $\delta = 1.6$ (s, 2B), 3.2 (d, 1B, $J = 137$ Hz), 18.4 (s, 1B); IR (KBr pellet, cm^{-1}): $\nu = 2969.7$ (s), 2931.3 (m), 2912.5 (m), 2870.2 (w), 2597.0 (m, B–H), 1465.1 (m), 1377.8 (s), 1296.3 (m), 1261.2 (w), 1171.3 (w), 1117.2 (m), 1026.8 (s), 831.0 (m), 793.5 (m), 650.0 (w), 593.5 (w), 448.1 (w); CI$^+$-MS: m/z (%) = 591.1 ([M$^+$ + 1], 100). Anal. Calc. for B$_4$C$_{17}$CoH$_{29}$I$_2$: C, 34.64; H, 4.96%. Found: C, 35.30; H, 5.12%.

4.7. *Cp*Co(2,3-Et$_2$C$_2$B$_4$I$_4$)* (**8**)

Complex **1** (37 mg, 0.11 mmol) was dissolved in 1 ml of triflic acid and the solution was cooled to −78 °C. To this mixture was added 186 mg (1.1 mmol) of iodine monochloride. The reaction mixture was warmed to room temperature, stirred for 1 h, and heated at 70 °C for 1 day. A saturated aqueous solution of sodium thiosulfate (4 ml) was added to remove residual halogen, and the aqueous layer was separated and washed with dichloromethane. The combined organic materials were washed with a concentrated aqueous NaCl solution and dried over anhydrous magnesium sulfate. The crude material was chromatographed on silica gel TLC plates in 1:2 hexane–dichloromethane yielding a major orange–yellow band, which afforded 42 mg (46%) of **8** as an air-stable orange–yellow solid. ^{1}H-NMR (CDCl$_3$): $\delta = 1.35$ (t, 6H, $J = 7.8$ Hz, ethyl CH$_3$), 1.68 (s, 15H, C$_5$Me$_5$), 2.78, 2.98 (m, 4H, $J = 7.5$ Hz, ethyl CH$_2$); ^{13}C-NMR (CDCl$_3$): $\delta = 8.7$ (C$_5$Me$_5$), 12.5 (ethyl CH$_3$), 24.2 (ethyl CH$_2$), 93.8 (C$_5$Me$_5$); ^{11}B-NMR (CDCl$_3$): $\delta = 19.0$ (s, 1B), 0.8 (s, 2B), 7.7 (s, 1B); IR (KBr pellet, cm^{-1}): $\nu = 2975.6$ (s), 2931.5 (m), 2908.5 (m), 2869.0 (w), 1464.6 (m), 1446.8 (s), 1425.7 (m), 1376.9 (s), 1132.3 (m), 1114.5 (s), 1067.0 (s), 1021.0 (vs), 979.1 (m), 905.0 (m), 875.4 (s), 798.9 (m), 643.7 (w), 562.8 (m), 450.9 (m), 433.9 (m); CI$^+$-MS: m/z (%) = 828.0 ([M$^+$ + 1], 100); Anal. Calc. for B$_4$C$_{16}$CoH$_{25}$I$_4$: C, 23.23; H, 3.05%. Found: C, 23.42; H, 3.00%.

4.8. *Cp*Co(2,3-Et$_2$C$_2$B$_4$HI$_3$)* (**9**)

Compound **1** (71 mg, 0.22 mmol) was dissolved in 8 ml of dry CH$_2$Cl$_2$ at 0 °C and 1 ml of iodine monochloride in 1 M dichloromethane (1 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 2 h, and then 4 h at room temperature, after which a saturated aqueous solution of sodium thiosulfate (4 ml) was added to remove residual halogen, and the aqueous layer was separated and washed with dichloromethane. The combined organic materials were washed with a concentrated aqueous solution of sodium chloride and dried over anhydrous magnesium sulfate. Removal of the solvent afforded 145 mg (94%) of **9** as an air-stable orange–yellow solid. ^{1}H-NMR (CDCl$_3$): $\delta = 1.11$ (t, 6H, $J = 7.2$ Hz, ethyl CH$_3$), 1.69 (s, 15H, C$_5$Me$_5$), 2.57, 2.81 (m, 4H, $J = 7.2$ Hz, ethyl CH$_2$); ^{13}C-NMR (CDCl$_3$): $\delta = 8.5$ (C$_5$Me$_5$), 13.8 (ethyl CH$_3$), 22.4 (ethyl CH$_2$), 91.7 (C$_2$B$_4$), 93.1 (C$_5$Me$_5$); ^{11}B-NMR (CDCl$_3$): $\delta = 0.2$ (s, 3B), 4.8 (s, 1B); IR (Kerr pellet, cm^{-1}): $\nu =$ 2969.2 (s), 2932.5 (m), 2905.6 (m), 2869.4 (w), 2590.9 (s, BH), 1462.6 (s), 1448.7 (m), 1424.8 (w), 1131.6 (w), 1116.8 (s), 1057.5 (s), 1025.9 (vs), 869.0 (s), 827.2 (m), 791.8 (m), 630.9 (m), 656.9 (m), 449.3 (w); CI$^+$-MS: m/z (%) = 702.0 ([M$^+$], 100); Anal. Calc. for B$_4$C$_{16}$CoH$_{26}$I$_3$: C, 27.40; H, 3.74%. Found: C, 27.54; H, 3.65%.

*4.9. Cp*Co(2,3-$Et_2C_2B_4H_3$-7-Me) (**10**)*

Complex **1** (300 mg, 0.93 mmol) was dissolved in 5 ml of trimethylaluminum in 2 M toluene in a dry box. The reaction vessel was closed, removed from the dry box, and heated at 110 °C with stirring for 5 days. The solvent was removed under vacuum, and the residue was taken up in hexane, washed through 5 cm of silica gel in 1:1 hexane–dichloromethane to afford 253 mg (81%) of **10** as an air-stable orange–red solid. ^{1}H-{^{11}B}-NMR (500.05 MHz, $CDCl_3$): $\delta = 0.91$ (s, 3H, Me), 1.29 (t, 6H, $J = 7.5$ Hz, ethyl CH_3), 1.78 (s, 15H, C_5Me_5), 2.11, 2.42 (m, 4H, $J = 7.5$ Hz, ethyl CH_2), 3.29 (s, 2H, BH), 3.47 (s, 1H, BH); ^{13}C-NMR ($CDCl_3$): $\delta = 5.1$ (CH_3), 10.0 (C_5Me_5), 14.5 (ethyl CH_3), 21.8 (ethyl CH_2), 90.3 (C_5Me_5), 92.6 (C_2B_4); ^{11}B-NMR ($CDCl_3$): $\delta = 4.3$ (BH, 2B, $J = 139$ Hz), 12.3 (s, 2B); IR (KBr pellet, cm^{-1}): $\nu =$ 2964.8 (s), 2931.8 (s), 2905.1 (s), 2829.7 (w), 2539.5 (vs, B–H), 2511.1 (vs, B–H), 1476.7 (m), 1452.1 (m), 1378.0 (s), 1307.6 (m), 1136.8 (w), 1073.6 (w), 1026.0 (m), 809.5 (vs), 448.2 (w); CI$^+$-MS: *m*/*z* (%) = 339.3 ([M$^+$ + 1], 100).

*4.10. Cp*Co(2,3-$Et_2C_2B_4Me_4$) (**11**)*

Compound **10** (101 mg, 0.3 mmol), 252 mg of CaH_2 (6 mmol) and 2 ml of methyl triflate were heated at 80 °C for 3 days. The solvent was removed under vacuum, the residue was taken up in 5 ml of hexane and filtered to remove the solid, yielding 98 mg (86%) of **11** as an air-stable orange–red solid. ^{1}H-NMR ($CDCl_3$): $\delta = 0.85$ (s, 3H, 7-Me), 0.28 (s, 3H, 5-Me), 0.32 (s, 6H, 4,6-Me), 1.08 (t, 6H, $J = 7.8$ Hz, ethyl CH_3), 1.67 (s, 15H, C_5Me_5), 2.50, 2.62 (m, 4H, $J = 7.2$ Hz, ethyl CH_2); ^{13}C-NMR ($CDCl_3$): $\delta = 5.8$ (CH_3), 9.1 (C_5Me_5), 13.1 (ethyl CH_3), 21.0 (ethyl CH_2), 89.1 (C_5Me_5); ^{11}B-NMR ($CDCl_3$): $\delta =$ 8.2 (s, 2B), 17.2 (s, 1B), 18.7 (s, 1B); IR (KBr pellet, cm^{-1}): $\nu = 2973.4$ (m), 2919.4 (s), 2820.4 (w), 1466.9 (m), 1452.1 (m), 1357.9 (m), 1306.4 (s), 1258.5 (w), 1229.1 (w), 1175.1 (w), 1097.4 (w), 1055.2 (m), 1021.0 (w), 876.2 (s), 581.4 (w), 438.5 (w); CI$^+$-MS: *m*/*z* (%) = 381.2 ([M$^+$ + 1], 100). Anal. Calc. for $B_4C_{20}CoH_{37}$: C, 63.27; H, 9.82%. Found: C, 63.10; H, 9.75%.

*4.11. Cp*Co(2,4-$Et_2C_2B_4Me_4$) (**12**)*

Compound **11** (100 mg, 0.26 mmol) was sealed in a Pyrex tube and heated at 360 °C for 12 h. The residue was taken up in 3 ml of hexane and washed through 2 cm of silica gel in hexane, yielding 89 mg (89%) of **12** as an air-stable orange–red solid. ^{1}H-NMR ($CDCl_3$): $\delta =$ 0.90 (s, 3H, Me), 0.38 (s, 6H), 0.73 (s, 3H, Me), 0.78 (t, 6H, $J = 7.8$ Hz, ethyl CH_3), 1.66 (s, 15H, C_5Me_5), 1.88, 2.15 (m, 4H, $J = 7.8$ Hz, ethyl CH_2); ^{13}C-NMR ($CDCl_3$): $\delta = 6.2$ (CH_3), 9.1 (C_5Me_5), 13.6 (ethyl CH_3), 21.4 (ethyl CH_2), 89.1 (C_5Me_5); ^{11}B-NMR ($CDCl_3$): $\delta =$ 9.5 (s, 1B), 11.2 (s, 3B); IR (KBr pellet, cm^{-1}): $\nu =$ 2960.0 (s), 2932.2 (vs), 2912.0 (s), 2858.4 (s), 2822.1 (w), 1451.5 (m), 1425.1 (m), 1382.3 (m), 1375.6 (s), 1325.6 (s), 1229.1 (m), 1178.7 (w), 1080.3 (w), 1056.6 (w), 1028.0 (m), 897.6 (m), 883.3 (m); CI$^+$-MS: *m*/*z* (%) = 380.3 ([M$^+$], 100).

*4.12. {Cp*Co(2,3-$Et_2C_2B_4H_2$-5-Br-7-CC)}$_3C_6H_3$ (**22a**)*

Complex **21** (22 mg, 0.02 mmol) was dissolved in 2 ml of dry CH_2Cl_2 at 0 °C, and a solution of 11.7 mg (0.066 mmol) of *N*-bromosuccinimide in 2 ml of dry CH_2Cl_2 was added dropwise. The reaction mixture was stirred at 0 °C for 1 h, and then for 1 h at room temperature, after which the solvent was removed and flash chromatographed through 3 cm of silica gel in CH_2Cl_2 to give one orange band. Removal of solvent gave 21 mg (78%) of **22a** as an orange–red solid. ^{1}H-NMR ($CDCl_3$): $\delta = 1.30$ (t, 18H, $J = 7.5$ Hz, ethyl CH_3), 1.79 (s, 45H, C_5Me_5), 2.27, 2.42 (sextet, 12H, $J = 7$ Hz, ethyl CH_2), 6.96 (s, 3H, C_6H_4); ^{13}C-NMR ($CDCl_3$): $\delta = 9.5$ (C_5Me_5), 14.6 (ethyl CH_3), 21.8 (ethyl CH_2), 87.6 (C≡C), 91.8 (C_5Me_5), 92.5 (C_2B_4), 95.8 (C≡C), 123.3 (C_6H_4), 134.3 (C_6H_4); ^{11}B-NMR (At 50 °C, $CDCl_3$): $\delta = 18.1$ (s, 3B, B–Br), 2.8 (BH, 6B, unresolved), 3.1(s, 3B, BC≡C); IR (KBr pellet, cm^{-1}): $\nu = 2970.6$ (s), 2932.8 (m), 2911.4 (m), 2873.6 (w), 2547.3 (s, B–H), 2174.0 (w, C≡C), 1715.1 (m), 1575.2 (vs), 1452.3 (m), 1409.7 (m), 1382.2 (vs), 1218.3 (s), 1031.3 (s), 879.8 (m), 802.7 (s), 630.0 (w); CI$^+$-MS: *m*/*z* (%) = 1352.6 ([M$^+$], 100).

*4.13. {Cp*Co(2,3-$Et_2C_2B_4H_2$-5-I-7-CC)}$_3C_6H_3$ (**22b**)*

Compound **21** (128 mg, 0.115 mmol) was dissolved in 5 ml of dry CH_2Cl_2 at 0 °C, and a solution of 85 mg of *N*-bromosuccinimide (0.38 mmol) in 10 ml of dry CH_2Cl_2 was added dropwise. The reaction mixture was stirred for 1 h at 0 °C, and then for 1 h at room temperature, after which the solvent was removed and flash chromatographed through 3 cm of silica gel in CH_2Cl_2 to give one orange–red band. Removal of solvent gave **22b** as an orange–red solid (162 mg, 94.4%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.31$ (t, 18H, $J = 7.8$ Hz, ethyl CH_3), 1.77 (s, 45H, C_5Me_5), 2.29, 2.46 (sextet, 12H, $J = 7.2$ Hz, ethyl CH_2), 6.97 (s, 3H, C_6H_4); ^{13}C-NMR ($CDCl_3$): $\delta = 9.6$ (C_5Me_5), 14.6 (ethyl CH_3), 21.6 (ethyl CH_2), 87.5 (C≡C), 91.8 (C_5Me_5), 92.0 (C_2B_4), 95.5 (C≡C), 123.3 (C_6H_4), 134.1 (C_6H_4); ^{11}B-NMR (At 50 °C, $CDCl_3$): $\delta = 4.2$ (BH, 6B, unresolved), −1.8 (s, 3B, BC≡C), −4.5 (s, 3B, B–I); IR (KBr pellet, cm^{-1}): $\nu = 2969.7$ (s), 2931.8 (m), 2910.5 (m), 2872.9 (w), 2545.3 (s, B–H), 2175.0 (w, C≡C), 1713.9 (m), 1574.6 (vs), 1452.0 (m), 1410.1 (m), 1382.1 (vs), 1218.4 (s), 1026.8 (s), 879.7 (m), 801.9 (s), 628.6 (w); UV–Vis (CH_2Cl_2, nm

(%)): 313 (100) $\varepsilon_{max} = 153\,593$ cm^{-1} M^{-1}; CI$^+$-MS: *m*/*z* (%) = 1494.3 ([M$^+$], 100).

4.14. *{Cp*Co(2,3-$Et_2C_2B_4H_3$-5-CCTMS-7-CC)}$_3C_6H_3$}* (**23**)

4.14.1. *Method 1*

To a mixture of **17** (83 mg, 0.19 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), CuI (4 mg, 0.02 mmol), $C_6H_3I_3$ (27 mg, 0.06 mmol) were added 5 ml of THF and 1 ml of Et_3N. The mixture was stirred for 2.5 days, after which the solvent was removed in vacuo. The residue was taken up in CH_2Cl_2 and flash chromatographed through 3 cm of silica gel in CH_2Cl_2, following which solvents were removed and the solid remaining was chromatographed on TLC plates in 1:2 hexane/CH_2Cl_2, giving **23** as a major orange–red band (70 mg, 83% based on $C_6H_3I_3$, the limiting reagent).

4.14.2. *Method 2*

To a solution of TMSCCH (90 mg, 0.9 mmol) in 5 ml of THF was added 0.6 ml of 1.51 M *n*-BuLi (0.90 mmol) in hexane at 0 °C. The mixture was stirred at 0 °C for 30 min, anhydrous $ZnCl_2$ (123 mg, 0.9 mmol) in 5 ml of THF was added at 0 °C, and the mixture was stirred at room temperature for 2 h, following which **22b** (150 mg, 0.1 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) were added. The residue was taken up in CH_2Cl_2 and flash-chromatographed through 3 cm of silica gel in 1:2 hexane:CH_2Cl_2 to give **23** as an orange–red solid (126 mg, 90%). ^{1}H-NMR ($CDCl_3$): $\delta = 0.22$ (s, 27H, $Si(CH_3)_3$), 1.30 (t, 18H, $J = 7.5$ Hz, ethyl CH_3), 1.80 (s, 45H, C_5Me_5), 2.27, 2.42 (sextet, 12H, $J = 7.5$ Hz, ethyl CH_2), 6.91 (s, 3H, C_6H_4); ^{13}C-NMR ($CDCl_3$): $\delta =$ 0.5 ($Si(CH_3)_3$), 9.4 (C_5Me_5), 14.6 (ethyl CH_3), 21.9 (ethyl CH_2), 87.1 ($C{\equiv}C$), 91.2 (C_5Me_5), 95.0 (C_2B_4), 116.1 ($C{\equiv}C$), 123.4 (C_6H_4), 133.9 (C_6H_4); ^{11}B-NMR (At 50 °C, $CDCl_3$): $\delta = 7.5$ (BH, 6B, unresolved), 4.4 (s, 3B, $BC{\equiv}C$), −3.1 (s, 3B, $BC{\equiv}CSi(CH_3)_3$), IR (KBr pellet, cm^{-1}): $\nu = 2968.1$ (s), 2933.7 (m), 2910.4 (m), 2547.3 (s, B–H), 2175.6 (w, $C{\equiv}C$), 2108.2 (m, $C{\equiv}C$), 1576.6 (s), 1574.4 (s), 1457.0 (m), 1452.2 (m), 1383.6 (m), 1245.2 (s), 1029.2 (w), 854.8 (vs), 838.9 (vs), 757.7 (m); UV–Vis (CH_2Cl_2, nm (%)): 314 (100), 255 (26) $\varepsilon_{max} = 170\,038$ cm^{-1} M^{-1}; CI$^+$-MS: *m*/*z* (%) = 1404.7 [M$^+$]-CH_3, 70), 1260.8 ([M$^+$]-2Si(CH_3), 100), 1187.8 ([M$^+$]-3Si(CH_3, 60).

4.15. *{Cp*Co(2,3-$Et_2C_2B_4H_2$-5-CCH-7-CC)}$_3C_6H_3$}* (**24**)

Complex **23** (92 mg, 0.066 mmol) was desilylated with 0.2 ml of 1.0M TBAF solution (0.2 mmol) in 10 ml of THF. The reaction mixture was stirred at 0 °C for 1 h, after which the THF was removed and flash chromatographed through 3 cm of silica gel in CH_2Cl_2 to give one orange band. Removal of solvent gave 78 mg (99%) of orange–red solid **24**. ^{1}H-NMR ($CDCl_3$): $\delta = 1.31$ (t, 18H, $J = 8$ Hz, ethyl CH_3), 1.80 (s, 45H, C_5Me_5), 2.27, 2.43 (sextet, 12H, $J = 7.5$ Hz, ethyl CH_2), 3,22 (s, 3H, $C{\equiv}CH$), 6.91 (s, 3H, C_6H_4); ^{13}C-NMR ($CDCl_3$): $\delta = 9.5$ (C_5Me_5), 14.5 (ethyl CH_3), 21.8 (ethyl CH_2), 87.1 ($C{\equiv}C$), 91.3 (C_5Me_5), 94.9 (C_2B_4), 96.5 ($C{\equiv}C$), 123.4 (C_6H_4), 134.0 (C_6H_4); ^{11}B-NMR (At 50 °C, $CDCl_3$): $\delta = 6.2$ (BH, 6B, unresolved), −3.5 (s, 6B, $BC{\equiv}C$, $BC{\equiv}CH$), IR (KBr pellet, cm^{-1}): $\nu = 3291.1$ ($C{\equiv}CH$), 2970.1 (s), 2932.3 (m), 2910.7 (m), 2873.8 (w), 2545.3 (s, B–H), 2177.4 (m, $C{\equiv}C$), 2045.3 (w, $C{\equiv}C$), 1713.8 (vs), 1576.1 (vs), 1573.7 (m), 1456.9 (m), 1409.8 (m), 1383.1 (s), 1219.6 (vs), 1090.8 (m), 1068.9 (m), 1027.6 (m), 879.1 (s), 805.8 (s), 644.5 (m); UV–Vis (CH_2Cl_2, nm (%)): 312 (100), 252 (27), 454 (0.3) $\varepsilon_{max} = 156\,418$ cm^{-1} M^{-1}; CI$^+$-MS: *m*/*z* (%) = 1188.7 ([M$^+$], 100); Anal. Calc. for $C_{66}H_{87}B_{12}Co_3$: C, 66.79; H, 7.39%. Found: C, 66.73; H, 7.39%.

4.16. *{[Cp*Co(2,3-$Et_2C_2B_4H_3$-5-CC-7-CC)]$_3C_6H_3$}$_2$* (**25**)

To a mixture of $Cu(OAc)_2$ (81 mg, 0.45 mmol), CuCl (45 mg, 0.45 mmol), and **24** (53 mg, 0.045 mmol) in 20 ml of CH_3CN was added 20 ml of pyridine, and the mixture was stirred at 60 °C for 40 h. The solution was cooled to room temperature, 60 ml of H_2O was added, and the precipitate was filtered off, washed with H_2O, and dried under vacuum. The crude material was chromatographed on silica gel TLC plates in dichloromethane, yielding a major orange–red band which afforded 20 mg (37%) of **25** as an air-stable orange–red solid. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.31$ (t, 36H, $J = 8$ Hz, ethyl CH_3), 1.82 (s, 90H, C_5Me_5), 2.22, 2.40 (sextet, 6H, $J = 7.5$ Hz, ethyl CH_2), 6.90 (s, 3H, C_6H_4); ^{13}C-NMR (125.75 MHz, CD_2Cl_2): $\delta = 9.9$ (C_5Me_5), 14.8 (ethyl CH_3), 22.3 (ethyl CH_2), 91.8 (C_5Me_5), 95.2 (C_2B_4), 123.7 (C_6H_4), 134.7 (C_6H_4); IR (KBr pellet, cm^{-1}): $\nu = 2968.4$ (m), 2922.5 (s), 2546.2 (s, B–H), 2169.8 (m, $C{\equiv}C$), 2075.8 (w, $C{\equiv}C$), 1723.5 (w), 1575.1 (m), 1454.8 (m), 1380.9 (m), 1212.9 (s), 1101.9 (vs), 879.7 (w), 801.5 (m), 632.9 (w), 468.7(m); UV–Vis (CH_2Cl_2, nm (%)): 310 (100), 248 (63), 484 (2) $\varepsilon_{max} = 144\,831$ cm^{-1} M^{-1}; FAB-MS: *m*/*z* (%) = 2367.6 ([M$^+$]-3, 100).

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