Cp-Functionalized Building Blocks for Polymetallacarborane Assemblies. Multinuclear Cobaltacarborane Complexes on Fulvalene and 1,3,5-Tris(cyclopentadienyl)benzene Scaffolds[1]

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The introduction of organic and inorganic substituents onto η^5-C_5H_5 (Cp) ligands in the small cobaltacarboranes $CpCo(Et_2C_2B_4H_4)$ and *nido*-$CpCo(Et_2C_2B_3H_5)$ and their derivatives has been explored, together with metal-promoted C−C coupling to generate polycluster species featuring Cp−Cp and Cp−benzene linkages. This approach supplements alternative synthetic strategies based on functionalization of boron vertexes via metal-promoted B−C coupling, as described in a series of recent papers from our group,[4,5] and affords complexes of novel architecture as well as improved routes to previously known types. Among the new compounds are triple-sandwich trinuclear and hexanuclear benzene-centered complexes in which three cobaltacarborane units are anchored to a central 1,3,5-$(\eta^5$-$C_5H_4)_3C_6H_3$ hydrocarbon scaffold. The fulvalene-bridged dinuclear species $[(2,3$-$Et_2C_2B_4H_4)Co(\eta^5$-$C_5H_4)]_2$ (**7**) and (*closo*-2,3-$Et_2C_2B_4H_4$)(*nido*-2,3-$Et_2C_2B_3H_5$)$Co_2(\eta^5$-$C_5H_4)_2$ (**8**), previously obtained by Davis et al.[7] from the fulvalenide dianion, were prepared in this work directly from the CpCo-($Et_2C_2B_4H_4$) and *nido*-$CpCo(Et_2C_2B_3H_5)$ monomers. Apically substituted B(7)-trimethylsilylethynyl derivatives of **7** were also synthesized. New compounds were characterized via multinuclear NMR, IR, UV−visible (in some cases), and mass spectroscopy.

Introduction

Metal−boron clusters in an amazing variety of sizes, shapes, and compositions have been prepared and structurally characterized.[2] Some types, especially metallacarboranes, are sufficiently accessible and manageable to attract interest as synthons for constructing macromolecular systems via rational, controllable procedures. In the small metallacarborane area, Hosmane and co-workers have produced elegant work on complexes of the group 1, group 2, and lanthanide metals, many of which exhibit unique solid-state structural chemistry.[3] Our interest has concentrated on the development of synthetic approaches for constructing polynuclear complexes and extended systems based on *closo*-MC_2B_4 and *nido*-MC_2B_3 polyhedra where M is a transition metal such as Fe or Co.[4] These methods[4] include, inter alia, cluster linkage via metal-promoted B−B coupling, cluster "decapitation" and recapitation, metal stacking reactions to generate multidecker sandwiches, and syntheses involving radical reactions,[5] all of which have been explored in some depth. However, to this point little attention has been directed toward substitution or linkage involving metal-bound Cp (η^5-C_5H_5) ligands in metallacarborane clusters. In serendipitous findings, η^5-C_5Me_5 (Cp*) ligands were shown to exhibit reactivity under mild conditions, e.g., C−C coupling to generate dimers linked by C_5Me_4−CH_2−CH_2−C_5Me_4 chains,[6] or lowering of the hapticity from η^5-C_5Me_5 to η^4-C_5Me_5R,[5] but direct reactions of metal-bound Cp ligands in metallacarboranes have been largely unexamined.

Some years ago, workers in our laboratory prepared a series of fulvalene-bridged metallacarborane dimers[7] and higher oligomers[8] having Co(η^5-C_5H_4)−(η^5-C_5H_4)-Co linkages, and Geiger and Chin showed that these species undergo electrochemical oxidation or reduction to generate fully delocalized d^5d^6 or d^6d^7 mixed-valence systems.[9] These compounds were prepared directly from the fulvalenide dianion, an unstable species that coexists in solution with $C_5H_5^-$; in our experience this approach has been unpredictable, giving widely varying

(1) Organotransition-metal Metallacarboranes. 67. For part 66 see: Yao, H.; Grimes R. N.; Corsini, M.; Zanello, P. Submitted.

(2) The current state of the art in this field is reflected in several recent volumes, e.g.: (a) *Contemporary Boron Chemistry*, Davidson, M., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000. (b) *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1997. (c) *The Borane-Carborane-Carbocation Continuum*; Casanova, J., Ed.; Wiley-Interscience: New York, 1998. (d) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, England, 1995; Vol. 1.

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(5) Russell, J. M.; Sabat, H.; Grimes, R. N. *Organometallics* **2002**, *21*, 5613.

(6) Wang, X.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 4668.

(7) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4784.

(8) Meng, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 6143.

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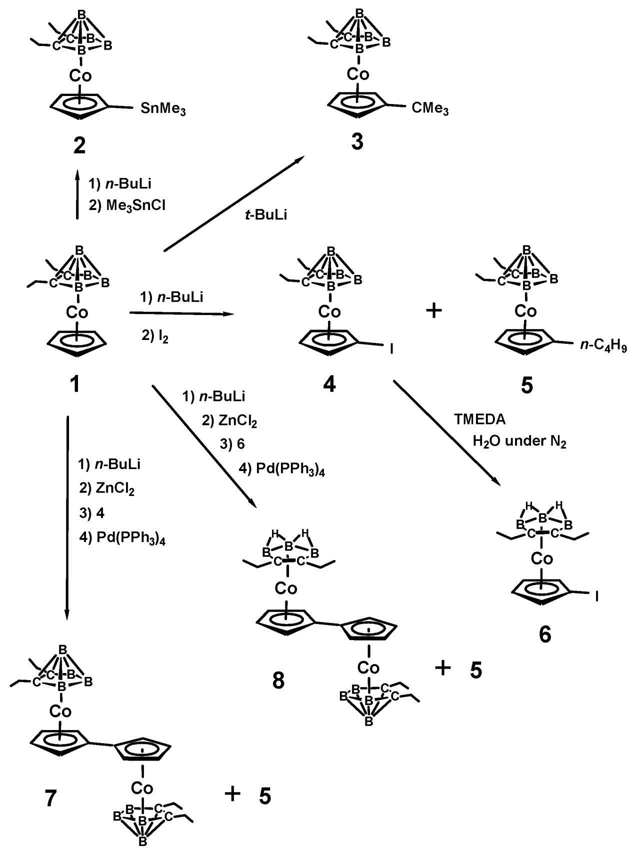
Scheme 1 [a]



[a] B = B, BH.

product yields. Although the more tractable tricyclic η^5-C_5Me_4-C_6H_4-η^5-C_5Me_4 ligand can be used as a connecting unit in place of fulvalene,[8] in these systems electron delocalization between the linked metallacarborane sandwich units is blocked by tilting of the central phenylene out of the C_5 ring plane (owing to steric interaction with the methyl groups), which prevents efficient π-conjugation with the C_5 rings.[10]

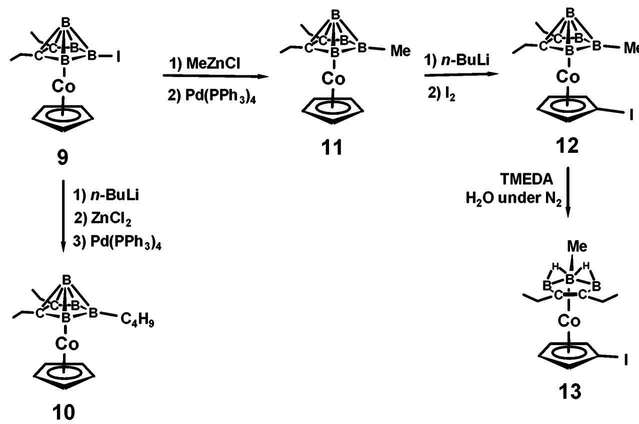
In this paper we report a direct synthetic route to fulvalene-bridged bis(cobaltacarborane) complexes from monomeric $CpCo(Et_2C_2B_4H_4)$ and related species, via substitution and metal-facilitated linkage of their Cp ligands. In related chemistry, we have employed metal-promoted C−C coupling to generate novel benzene-centered poly(multidecker sandwich) complexes connected via C_6 ring−C_5 ring linkages.

Results and Discussion

Functionalization of Cp Ligands and Cp−Cp Linkage. Substitution at the cyclopentadienyl ring in the monomeric complex $CpCo(2,3\text{-}Et_2C_2B_4H_4)$ (**1**) was explored via several reactions, outlined in Scheme 1. Treatment with *n*-butyllithium and trimethylstannyl chloride gave air-stable orange-red $(\eta^5\text{-}C_5H_4SnMe_3)Co(2,3\text{-}Et_2C_2B_4H_4)$ (**2**) in 53% isolated yield, while the reaction of **1** and *tert*-butyllithium afforded brown $(\eta^5\text{-}C_5H_4CMe_3)Co(2,3\text{-}Et_2C_2B_4H_4)$ (**3**) (50% based on **1** consumed) together with unreacted **1** (20% recovery). The location of the *tert*-butyl substituent on the Cp ring of **3** follows from the three B−H doublets in the unde-

(10) (a) Pipal, J. R.; Grimes, R. N. *Organometallics* **1993**, *12*, 4452. (b) Pipal, J. R.; Grimes, R. N. *Organometallics* **1993**, *12*, 4559.

Scheme 2 [a]



[a] B = B, BH.

coupled ^{11}B NMR spectrum, indicating the absence of a substituent on boron, and the two triplets associated with Cp protons in the ^1H NMR spectrum, consistent with an RC_5H_4 ligand.

Iodination on the Cp ring of **1** was accomplished via reaction with *n*-butyllithium and iodine, giving orange-red $(\eta^5\text{-}C_5H_4I)Co(2,3\text{-}Et_2C_2B_4H_4)$ (**4**) in 64% yield on a ca. 2 g scale, accompanied by a minor product, orange-red $(\eta^5\text{-}C_5H_4\text{-}n\text{-}C_4H_9)Co(2,3\text{-}Et_2C_2B_4H_4)$ (**5**). The iodo complex **4** was subsequently decapped by treatment with wet TMEDA to afford orange-yellow *nido*-$(\eta^5\text{-}C_5H_4I)Co(2,3\text{-}Et_2C_2B_3H_5)$ (**6**). Clearly, nucleophilic substitution on the Cp ring of **1** proceeds more easily with *tert*-butyllithium than with *n*-butyllithium. No iodination at boron by elemental I_2 was observed at −78°; direct reaction of **1** with I_2 occurs only at higher temperatures.

An attempted synthesis of the fulvalene complex **7** via Pd-catalyzed Cp−Cp linkage of **1** and **4** was unsuccessful over a range of conditions. However, **7** was obtained from **1** and *n*-butyllithium at −78 °C followed by treatment with anhydrous $ZnCl_2$ and reaction with **4** and $Pd(PPh_3)_4$ (Scheme 1). Column chromatography afforded recovered **1** and two products, the *n*-butyl derivative **5** (12%) and the orange fulvalene-bridged target complex $[(2,3\text{-}Et_2C_2B_4H_4)Co(\eta^5\text{-}C_5H_4)]_2$ (**7**) (71% yield based on **1** consumed), which is spectroscopically identical to the compound that was originally prepared from the fulvalenide dianion and crystallographically characterized by Davis, Sinn, and Grimes.[7] The mixed-ligand fulvalene complex (*closo*-$2,3\text{-}Et_2C_2B_4H_4$)(*nido*-$2,3\text{-}Et_2C_2B_3H_5$)$Co_2(\eta^5\text{-}C_5H_4)_2$ (**8**) was similarly prepared in 34% yield from **1** and **6**; this product was previously obtained as a byproduct of the synthesis of **1**.[7] The syntheses of **1** and **8** directly from monomeric precursors, avoiding the preparation and handling of the fulvalenide dianion, represent a significant improvement over the earlier method. Since fulvalene-linked cobaltacarborane dimers[9a] and oligomers[9b] have been shown to exhibit Robin−Day class III (fully delocalized) metal−metal interaction on reduction, this synthetic advance has positive implications for future studies in this area.

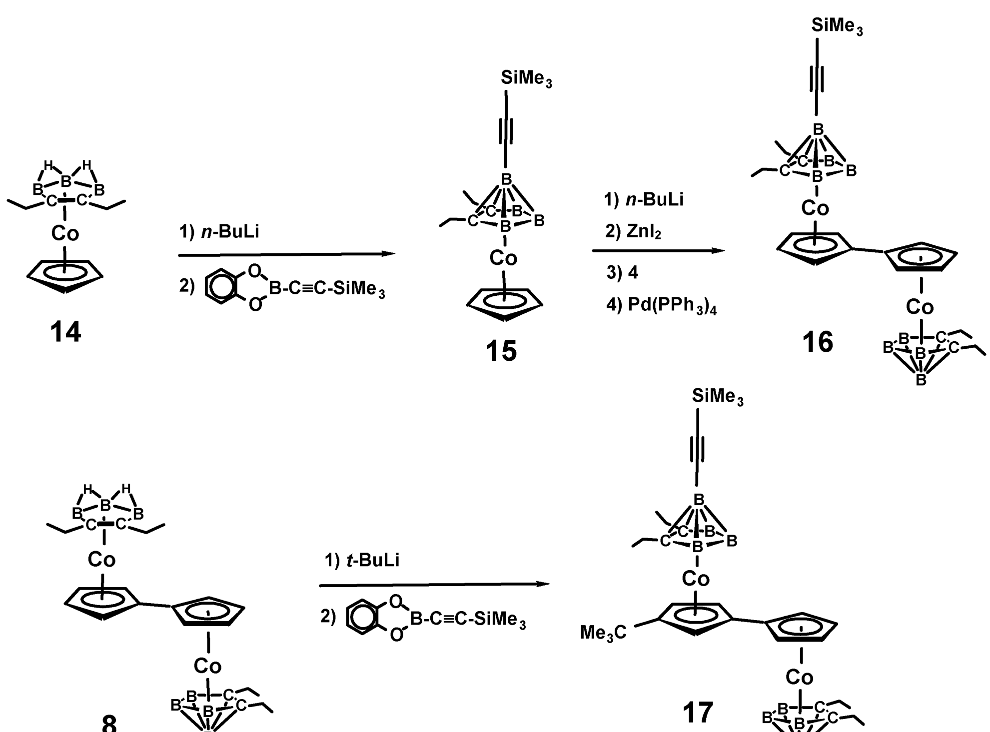
Selective, efficient introduction of substituents on the Cp and/or carborane ligands in $CpCo(C_2B_4)$ complexes can be achieved with careful control of reaction conditions. Scheme 2 shows the conversion of the B(5)-iodo derivative **9** to the corresponding B-alkyl complexes CpCo(2,3-$C_2B_4H_3$-5-R) [R = *n*-C_4H_9 (**10**) and Me (**11**)] via Pd-promoted B−C coupling (our original intent had been to generate B−C linked $[(C_5H_4)Co(2,3\text{-}C_2B_4H_3)]_n$ polymers, but only monomeric products were obtained). Iodination of the Cp ring on the B(5)-methylated species **11**, in contrast to that of **1** (vide supra), gave (η^5-C_5H_4I)-Co(2,3-$Et_2C_2B_4H_3$-5-Me) (**12**) cleanly with no significant side products; in turn, **12** was decapped to generate *nido*-(η^5-C_5H_4I)Co(2,3-$Et_2C_2B_3H_4$-5-Me) (**13**). All of these reactions afforded air-stable products in good to excellent yield.

Synthesis of B(7)-Alkynyl-Substituted Monomers and Dimers. The combination of direct Cp−Cp coupling with boron insertion into open C_2B_3 rings (recapitation[11]) gave fulvalene-bridged species having apically located alkynyl groups; that is, (2,3-$Et_2C_2B_4H_3$-7-C≡CSiMe$_3$)Co(η^5-C_5H_4)$_2$Co(2,3-$Et_2C_2B_4H_4$) (**16**) and (2,3-$Et_2C_2B_4H_3$-7-C≡CSiMe$_3$)Co[η^5-C_5H_3(*tert*-Bu)]-(η^5-C_5H_4)Co(2,3-$Et_2C_2B_4H_4$) (**17**) were obtained in moderate yields (Scheme 3). As shown, deprotonation and recapitation of *nido*-CpCo(2,3-$Et_2C_2B_3H_5$) (**14**) afforded CpCo-(2,3-$Et_2C_2B_4H_3$-7-C≡CSiMe$_3$) (**15**), which was easily coupled to **4** to give **16**. Deprotonation of the BHB groups in the dicobalt nido-closo complex **8** with *tert*-butyllithium led to the butylation of the fulvalene ligand of **17**, analogous to the formation of **3** from **1** discussed earlier.

Synthesis of 1,3,5-(C_5H_4)$_3C_6H_3$-Anchored Triple-Sandwich Complexes. The preparation of several varieties of benzene-centered poly(metallacarborane) complexes, a previously unreported genre, from 1,3,5-triiodobenzene has been described in recent publications.[12] In all of these compounds, the metallacarborane clusters are connected to the benzene ring (directly or with intervening organic groups) via equatorial or apical boron vertexes. In the present work, cobaltacarborane sandwich units are attached to benzene via the Cp rings with no alkynyl or other connectors. As illustrated in Scheme 4, lithiation of **1** followed by $ZnCl_2$-promoted coupling to triiodobenzene gave the triple-sandwich product 1,3,5-[(2,3-$Et_2C_2B_4H_4$)Co(η^5-C_5H_4)]$_3C_6H_3$ (**18**), isolated in 64% yield as an orange-red air-stable solid. Decapping of this complex afforded the yellow tris(*nido*-cobaltacarboranyl) species 1,3,5-[(*nido*-2,3-$Et_2C_2B_3H_5$)-Co(η^5-C_5H_4)]$_3C_6H_3$ (**19**). This complex was deprotonated with NaH and reacted with $(CpCoCl)_2$ to generate the red solid hexanuclear target compound 1,3,5-[Cp*Co-(2,3-$Et_2C_2B_3H_3$)Co(η^5-C_5H_4)]$_3C_6H_3$ (**21**) in 54% yield, together with an unexpected pentanuclear byproduct, 1,3-[Cp*Co(2,3-$Et_2C_2B_3H_3$)Co(η^5-C_5H_4)]$_2$-5-[(2,3-$Et_2C_2B_3H_5$)Co(η^5-C_5H_4)]C_6H_3 (**20**, 31%), that contains two triple-decker sandwiches and one double-decker unit.

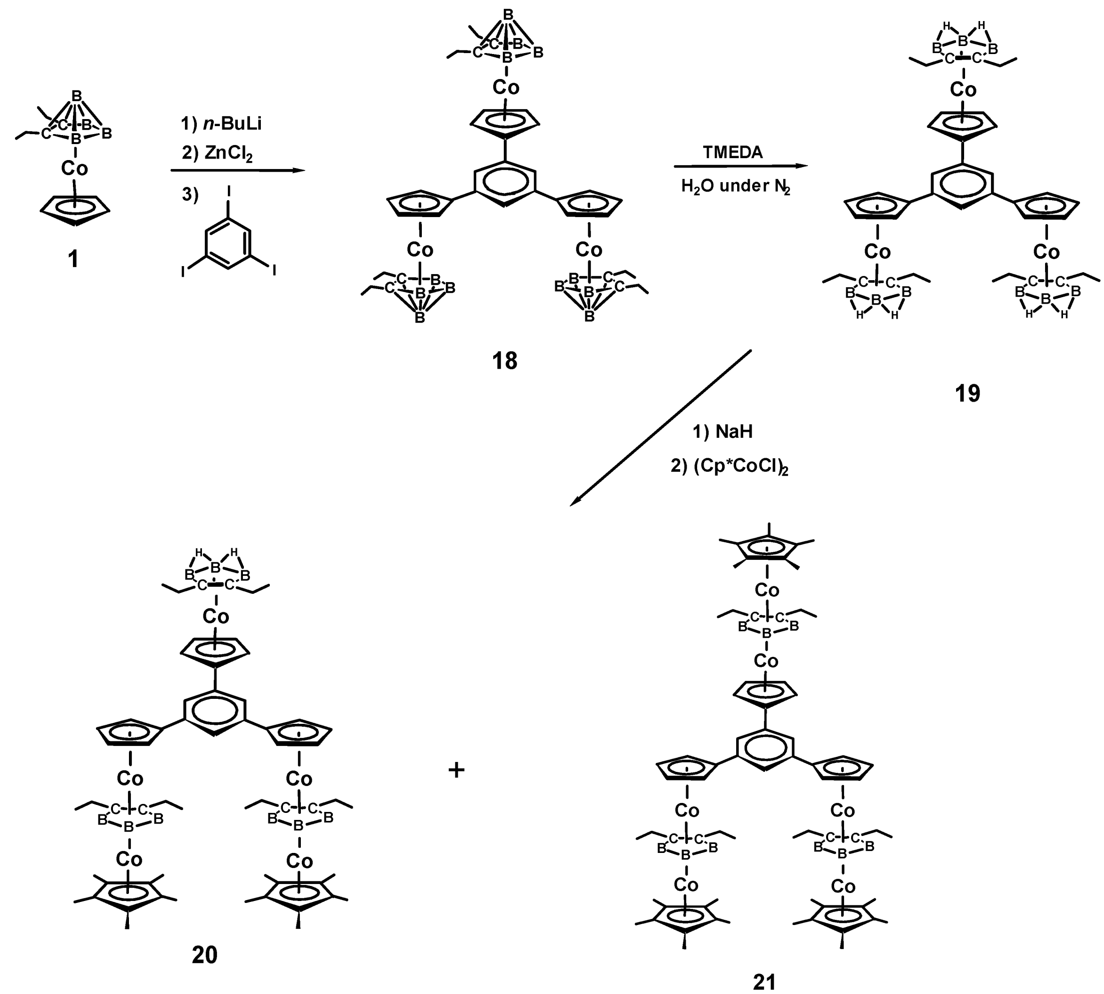
The spectroscopic and analytical characterization of **21** was augmented by X-ray data that confirmed the presence of three CpCo(2,3-$Et_2C_2B_3H_3$)Co(η^5-C_5H_4) triple-decker sandwich units directly linked to benzene with the "two-up-and-one-down" stairstep-like conformation shown in Scheme 4. The crystallographic data unfortunately could not be refined to a satisfactory level because of the appearance of persistent electron density peaks coming from a minor twin component, but the molecular conformation was established and is clearly different from that adopted by the tris(ethynyl-triple-decker)-benzene complex 1,3,5-[Cp*Co(2,3-$Et_2C_2B_3H_2$-5-C≡C)-CoCp*]$_3C_6H_3$ reported earlier.[12b] In the latter structure, the three sandwich moieties are linked to the central benzene ring via −C≡C− bridges attached to the central [B(5)] boron atoms in the C_2B_3 rings, and the molecule adopts a "flattened" orientation in which the six cobalt atoms are almost coplanar with the benzene; such a

Scheme 3 [a]



[a] B = B, BH.

Scheme 4 [a]



[a] B = B, BH.

conformation can be rationalized in terms of crystal-packing efficiency. The very different arrangement observed for **21** is similarly explained by steric considerations: in this case, intersandwich crowding is presumably less than would be experienced if all three sandwich units were lined up on the same side of the benzene plane.

On the basis of known electrochemistry of metallacarborane triple-deckers,[13] complex **21** is anticipated to show substantial electron delocalization on oxidation and/or reduction. Collaborative electrochemical studies on this compound and related species are currently in progress and will be reported elsewhere.

Conclusion

The controlled metal-promoted functionalization and C−C linkage of η^5-C_5H_5 ligands on cobaltacarborane clusters, as described here, supplies an additional tool for the directed synthesis of multinuclear organometallic systems employing metallacarborane building blocks. Together with methods allowing B−B and B−C bonding at cluster vertexes, outlined in earlier papers,[4,5] these approaches provide access to a wide range of structurally varied compound types with a reasonable level of reliability and efficiency. As advances in synthetic methodologies continue, the focus of attention in this area is shifting from issues of what stable polycluster/polysandwich architectures can be constructed, to the question of which ones represent appropriate synthetic targets. In the pursuit of compounds and materials having specific desired electronic or other properties, our own priorities are increasingly guided by this principle.

Experimental Section

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 instruments. ^{1}H and ^{13}C shifts are referenced to residual ^{1}H and ^{13}C signals in the deuterated solvent, while ^{11}B NMR resonances are referenced 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. Ultraviolet−visible spectra were recorded on a HP 8452A diode

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array spectrophotometer or Cary 5E UV–vis–NIR spectrophotometer. Elemental analyses on end products (target compounds) were performed by Atlantic Microlabs in Norcross, GA. Slightly high carbon analyses in some cases are ascribed to occluded solvent in the isolated crystalline materials.

Materials and Procedures. All reactions were carried out in oven glassware under a nitrogen atmosphere using conventional glovebox 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. $CpCo(2,3\text{-}Et_2C_2B_4H_4)$[14] (**1**), $CpCo(2,3\text{-}Et_2C_2B_3H_5)$[14] (**14**), $CpCo(2,3\text{-}Et_2C_2B_4H_3\text{-}5\text{-}I)$[15] (**9**), $[(C_6H_4O_2)B]C{\equiv}CSiMe_3$,[12d] $C_6H_3I_3$,[16] and $(Cp^*CoCl)_2$[17] were prepared according to published procedures.

(η^5-$C_5H_4SnMe_3$)Co(2,3-$Et_2C_2B_4H_4$) (2). To 115 mg of **1** (0.45 mmol) in 5 mL of THF was added 0.45 mmol of *n*-butyllithium (0.28 mL of a 1.6 M solution in hexane) at −78 °C. After 1 h of stirring at −78 °C, 90 mg of trimethylstannyl chloride (0.45 mmol) in 2 mL of THF was added. The reaction mixture was stirred overnight, and the solvent was removed in vacuo. The red-brown residue was washed through 3 cm of silica gel with dichloromethane, and the crude material was chromatographed on TLC silica gel with 2:1 hexane–dichloromethane to afford 98 mg of **2** as an air-stable orange-red solid (53%). ^1H NMR ($CDCl_3$): δ 0.40 (s, 9H, $SnMe_3$), 1.28 (t, 6H, $J = 7.2$ Hz, ethyl CH_3), 2.44, 2.65 (sextet, 4H, $J = 7.2$ Hz, ethyl CH_2), 4.67 (t, 2H, $J = 1$ Hz, C_5H_4), 4.81 (t, 2H, $J = 1$ Hz, C_5H_4). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 15.1 (ethyl CH_3), 25.1 (ethyl CH_2), 83.5 (C_5H_4), 85.7 (C_5H_4), 97.3 (C_2B_4), 196.8 (Cp). ^{11}B NMR ($CDCl_3$): δ 2.9 (BH, 2B, $J_{BH} = 144$ Hz), 8.3 (BH, 1B, $J_{BH} = 122$ Hz), 9.1 (BH, 1B, $J_{BH} = 120$ Hz). IR (KBr pellet, cm^{-1}): ν 2968.9 (m), 2930.2 (w), 2547.5 (s, B–H), 1454.2 (m), 1380.7 (m), 1193.0 (w), 1141.4 (w), 1029.8 (m), 872.0 (w), 834.1 (m), 776.5 (m), 742.5 (w), 531.9 (m). CI$^+$-Mass: *m*/*z* (%) 416.1 ([M$^+$ − 2], 100). Anal. Calcd for $C_{14}H_{27}B_4CoSn$: C, 40.40; H, 6.54. Found: C, 41.36; H, 6.54.

(η^5-$C_5H_4CMe_3$)Co(2,3-$Et_2C_2B_4H_4$) (3). To 126 mg of **1** (0.5 mmol) in 5 mL of THF was added 0.5 mmol of *tert*-butyllithium (0.3 mL of a 1.7 M solution in hexane) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and was then warmed to room temperature and stirred overnight, after which the solvent was removed in vacuo. The remaining red-brown residue was washed through 3 cm of silica gel with dichloromethane. The crude material was chromatographed on silica gel TLC plates with a 1:5 CH_2Cl_2–hexanes solution, producing two bands. The first band afforded 60 mg of **3** as a brown oil, and the second yielded 20 mg of recovered **1** (39% yield; 50% based on **1** consumed). ^1H NMR ($CDCl_3$): δ 1.29 (t, 6H, $J = 7.5$ Hz, ethyl CH_3), 1.28 (s, 9H, *t*-Bu CH_3), 2.46, 2.68 (sextet, 4H, $J = 7.2$ Hz, ethyl CH_2), 4.57 (t, 2H, $J = 2$ Hz, C_5H_4), 4.63 (t, 2H, $J = 2$ Hz, C_5H_4). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 15.1 (ethyl CH_3), 25.1 (ethyl CH_2), 30.7 (*t*-Bu CH_3), 76.5 (C_5H_4), 78.6 (C_5H_4), 97.2 (C_2B_4), 114.4 (Cp). ^{11}B NMR ($CDCl_3$): δ 3.0 (BH, 2B, $J_{BH} = 121$ Hz), 8.1 (BH, 1B, $J_{BH} = 154$ Hz), 9.6 (BH, 1B, $J_{BH} = 137$ Hz). IR (KBr pellet, cm^{-1}): ν 2965.0 (s), 2973.1 (m), 2548.0 (vs, B–H), 1456.6 (m), 1368.8 (m), 1274.0 (w), 1151.1 (w), 1040.5 (w), 874.1 (w), 833.6 (m), 752.6 (m). CI$^+$-Mass: *m*/*z* (%) 310.2 ([M$^+$], 100).

(η^5-C_5H_4I)Co(2,3-$Et_2C_2B_4H_4$) (4) and (η^5-C_5H_4-*n*-C_4H_9)-Co(2,3-$Et_2C_2B_4H_4$) (5). To 2.03 g of **1** (8 mmol) in 40 mL of THF was added 8 mmol of *n*-butyllithium (5 mL of a 1.6 M solution in hexane) at −78 °C. After 1 h of stirring at −78 °C, 2.03 g of I_2 (8 mmol) in 15 mL of THF was added. The reaction mixture was stirred overnight, and the solvent was removed in vacuo. The remaining red-brown residue was washed through 3 cm of silica gel with dichloromethane. The crude material was column-chromatographed on silica and eluted with 1:4 CH_2Cl_2–cyclohexane, affording a yellow-brown band that was characterized as **5** (orange-red oil, 230 mg, 9% yield). Elution of the crude material with 1:2 CH_2Cl_2–cyclohexane gave a major yellow-brown band that was characterized as **4** (orange-red oil, 1.95 g, 64% yield); finally, elution with 1:1 CH_2Cl_2–cyclohexane afforded 350 mg of recovered **1**. Data for **4**: ^1H NMR ($CDCl_3$): δ 1.32 (t, 6H, $J = 7.2$ Hz, ethyl CH_3), 2.41, 2.74 (sextet, 4H, $J = 7.2$ Hz, ethyl CH_2), 4.86 (t, 2H, $J = 1.8$ Hz, C_5H_4), 4.89 (t, 2H, $J = 1.8$ Hz, C_5H_4). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 14.8 (ethyl CH_3), 23.4 (ethyl CH_2), 79.5 (C_5H_4), 79.8 (Cp), 87.1 (C_5H_4), 98.4 (C_2B_4). ^{11}B NMR ($CDCl_3$): δ 3.7 (BH, 2B, $J_{BH} = 147$ Hz), 9.4 (BH, 1B, $J_{BH} = 171$ Hz), 12.3 (BH, 1B, $J_{BH} = 181$ Hz). IR (KBr pellet, cm^{-1}): ν 2968.0 (m), 2931.5 (m), 2871.1 (w), 2556.4 (s, B–H), 1451.4 (m), 1408.2 (m), 1376.6 (m), 1343.3 (m), 1060.8 (w), 1024.2 (w), 863.3 (m), 843.1 (m), 787.3 (w), 726.6 (w), 692.0 (w). CI$^+$-Mass: *m*/*z* (%) 380 ([M$^+$], 100). Data for **5**: ^1H NMR ($CDCl_3$): δ 0.91 (t, 3H, $J = 7.5$ Hz, *n*-Bu CH_3), 1.29 (t, 6H, $J = 7.5$ Hz, ethyl CH_3), 1.46 (m, 4H, $J = 7.5$ Hz, *n*-Bu CH_2), 2.31 (t, 2H, $J = 7.5$ Hz, *n*-Bu CH_2), 2.43, 2.64 (sextet, 4H, $J = 7.2$ Hz, ethyl CH_2), 4.62 (broad, 4H, C_5H_4). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 13.8 (*n*-Bu CH_3), 15.1 (ethyl CH_3), 22.3 (*n*-Bu CH_2), 24.6 (ethyl CH_2), 27.8 (*n*-Bu CH_2), 32.3 (*n*-Bu CH_2), 78.6 (C_5H_4), 79.4 (C_5H_4), 96.9 (C_2B_4), 102.0 (Cp). ^{11}B NMR ($CDCl_3$): δ 3.1 (BH, 2B, $J_{BH} = 144$ Hz), 7.6 (BH, 1B, $J_{BH} = 183$ Hz), 9.6 (BH, 1B, $J_{BH} = 161$ Hz). IR (KBr pellet, cm^{-1}): ν 2963.2 (s), 2931.8 (m), 2870.0 (w), 2546.8 (vs, B–H), 1457.1 (m), 1380.2 (m), 1062.0 (w), 1028.9 (w), 871.0 (w), 833.5 (m), 724.8 (w). CI$^+$-Mass: *m*/*z* (%) 311 ([M$^+$] + 1, 100).

***nido*-(η^5-C_5H_4I)Co(2,3-$Et_2C_2B_3H_5$) (6).** A 700 mg sample of **4** (1.85 mmol) was placed in a flask under nitrogen, and 4 mL of tetra-*N*-methylethylenediamine (TMEDA) and ca. 10 drops of water were added. The mixture was stirred for 1 h at 0 °C, the TMEDA was removed in vacuo, and the residue was taken up in hexane and flash-chromatographed through 5 cm of silica gel in hexane to give one orange-yellow band. Removal of solvent gave 598 mg of **6** as an orange-yellow oil (88%). ^1H NMR (500 MHz, $CDCl_3$): δ −5.77 (s, 2H, B–H–B), 1.16 (t, 6H, $J = 7.5$ Hz, ethyl CH_3), 2.14, 2.20 (sextet, 4H, $J = 7$ Hz, ethyl CH_2), 4.79 (t, 2H, $J = 2.4$ Hz, C_5H_4), 4.93 (t, 2H, $J = 2.4$ Hz, C_5H_4). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 16.1 (ethyl CH_3), 25.0 (ethyl CH_2), 82.8 (C_5H_4), 89.3 (C_5H_4). ^{11}B NMR ($CDCl_3$): δ 3.4 (BH, 2B, $J_{BH} = 143$ Hz), 5.3 (BH, 1B, $J_{BH} = 169$ Hz). IR (KBr pellet, cm−1): ν 2960.8 (s), 2925.4 (m), 2867.9 (w), 2535.3 (vs, B–H), 1867.5 (m, B–H–B), 1634.2 (w), 1563.5 (m), 1451.6 (w), 1413.6 (w), 1380.4 (w), 1022.7 (w), 930.5 (m), 826.1 (m), 781.0 (m), 741.4 (w). CI$^+$-Mass: *m*/*z* (%) 370.0 ([M$^+$], 100).

[(2,3-$Et_2C_2B_4H_4$)Co(η^5-C_5H_4)]$_2$ (7). A solution of 126 mg of **1** (0.5 mmol) in 3 mL of THF at −78 °C was treated dropwise with 0.31 mL of a 1.6 M *n*-butyllithium solution in hexanes (0.5 mmol). After 1 h of stirring at −78 °C, 68 mg of anhydrous $ZnCl_2$ (0.5 mmol) in 1 mL of THF was added. The reaction mixture was warmed to room temperature with stirring for 40 min. After an additional 0.5 h of stirring, 189 mg of **4** (0.5 mmol) and 29 mg of $Pd(PPh_3)_4$ (0.025 mmol) were added and the contents were stirred overnight. The THF was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 1:1 CH_2Cl_2–hexanes solution, producing three bands. The first band afforded 18 mg of **5** (12%), the second yielded 75 mg of recovered **1**, and the last band afforded 72 mg of **7** (29% yield; 71% based on **1** consumed).

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(*closo*-2,3-$Et_2C_2B_4H_4$)(*nido*-2,3-$Et_2C_2B_3H_5$)Co_2(η^5-C_5H_4)$_2$ (8). A solution of 412 mg of **1** (1.6 mmol) in 10 mL of THF at −78 °C was treated dropwise with 1 mL of a 1.6 M *n*-butyllithium solution in hexanes (1.6 mmol). After 1 h of stirring at −78 °C, 218 mg of anhydrous $ZnCl_2$ (1.6 mmol) in 3 mL of THF was added. The reaction mixture was warmed to room temperature with stirring for 40 min. After an additional 0.5 h of stirring, 480 mg of **6** (1.3 mmol) and 75 mg of $Pd(PPh_3)_4$ (0.065 mmol) were added and the contents were stirred overnight. The THF was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then column-chromatographed on silica and eluted with 1:2 CH_2Cl_2−hexane, affording two yellow-brown bands, the first band afforded 45 mg of **5** (9%), and the major band yielded 220 mg of **8** (34%).

CpCo(2,3-$C_2B_4H_3$-5-*n*-C_4H_9) (10). A solution of 204 mg of CpCo(2,3-$Et_2C_2B_4H_3$-5-I) (**9**, 0.54 mmol) in 5 mL of THF at −78 °C was treated dropwise with 0.34 mL of a 1.6 M *n*-butyllithium solution in hexanes (0.54 mmol). After 1 h of stirring at −78 °C, 74 mg of anhydrous $ZnCl_2$ (0.54 mmol) in 2 mL of THF was added. The reaction mixture was warmed to room temperature with stirring for 40 min. After an additional 0.5 h of stirring, 31 mg of $Pd(PPh_3)_4$ (0.03 mmol) was added and the contents were stirred overnight. The THF was removed in vacuo, and the residue was washed through 3 cm of silica gel with 1:1 hexane−dichloromethane to afford 152 mg of **10** as an orange-red oil (91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.68 (t, 3H, J = 7.5 Hz, *n*-Bu CH_3), 0.75 (m, 2H, J = 7.8 Hz, *n*-Bu CH_2), 0.99 (m, 2H, J = 7.8 Hz, *n*-Bu CH_2), 1.29 (t, 2H, J = 7.5 Hz, *n*-Bu CH_2), 1.39 (t, 6H, J = 7.8 Hz, ethyl CH_3), 2.24, 2.52 (sextet, 4H, J = 7.5 Hz, ethyl CH_2), 4.73 (s, 5H, C_5H_5). ^{13}C-{^{1}H} NMR (125.75 MHz, $CDCl_3$): δ 13.7 (*n*-Bu CH_3), 14.9 (ethyl CH_3), 24.5 (ethyl CH_2), 24.7 (*n*-Bu CH_2), 27.5 (*n*-Bu CH_2), 32.4 (*n*-Bu CH_2), 79.6 (C_5H_5), 99.8 (C_2B_4). ^{11}B NMR ($CDCl_3$): δ 3.0 (BH, 2B, J_{BH} = 137 Hz), 9.3 (BH, 1B, J_{BH} = 139 Hz), 20.3 (s, 1B). IR (KBr pellet, cm^{-1}): ν 2963.9 (s), 2932.2 (m), 2870.2 (w), 2549.0 (vs, B−H), 1457.1 (m), 1379.0 (m), 1028.2 (w), 871.4 (w), 833.5 (m), 725.0 (w). CI$^+$-Mass: *m*/*z* (%) 311 ([M$^+$] + 1, 100). Anal. Calcd for $C_{15}H_{27}B_4Co$: C, 58.20; H, 8.79. Found: C, 58.12; H, 8.82.

CpCo(2,3-$C_2B_4H_3$-5-Me) (11). A 12.9 mL sample of methyllithium in 1.4 M of ether (18 mmol) was placed in 20 mL of THF, 2.45 g of anhydrous zinc chloride in 10 mL of THF was added at −78 °C, and the mixture was warmed to room temperature and stirred for 2 h. Following this, 2.36 g of (2,3-$Et_2C_2B_4H_3$-5-I)CoCp (**9**, 6 mmol) and 347 mg of $Pd(PPh_3)_4$ (0.3 mmol) were added, and the mixture was stirred at 70 °C for 16 h. The solvent was removed by vacuum, and the mixture was washed through 5 cm of silica gel with 50% of hexane−dichloromethane, yielding 1.42 g of **11** as an air-stable orange-red solid (89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.67 (s, 3H, Me), 1.28 (t, 6H, J = 7 Hz, ethyl CH_3), 2.42, 2.63 (sextet, 4H, J = 7 Hz, ethyl CH_2), 4.68 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.1 (ethyl CH_3), 24.7 (ethyl CH_2), 79.9 (C_5H_5), 97.7 (C_2B_4). ^{11}B NMR ($CDCl_3$): δ 1.4 (BH, 2B, J_{BH} = 156 Hz), 9.2 (BH, 1B, J_{BH} = 154 Hz), 22.1 (s, 1B). IR (KBr pellet, cm^{-1}): ν 2972.6 (s), 2931.8 (m), 2892.6 (w), 2537.7 (vs, B−H), 1450.1 (w), 1416.2 (w), 1376.6 (w), 1295.5 (w), 1158.1 (w), 1004.0 (w), 833.4 (m), 779.1 (m), 417.9 (w). CI$^+$-Mass: *m*/*z* (%) 268 ([M$^+$], 100).

(η^5-C_5H_4I)Co(2,3-$Et_2C_2B_4H_3$-5-Me) (12). To 1.42 g of **11** (5.31 mmol) in 10 mL of THF was added 5.31 mmol of *n*-butyllithium (3.3 mL of a 1.6 M solution in hexane) at −78 °C. After 1 h of stirring at −78 °C, 1.35 g of I_2 (5.31 mmol) in 5 mL of THF was added. The reaction mixture was stirred overnight, the solvent was removed in vacuo, and the remaining red-brown residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then column-chromatographed on silica and eluted with 1:1 CH_2Cl_2−hexane, affording a major yellow-brown band that was characterized as **12** (orange-red oil, 1.49 g, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.67 (s, 3H, Me), 1.29 (t, 6H, J = 7 Hz, ethyl CH_3), 2.38, 2.70 (sextet, 4H, J = 7.5 Hz, ethyl CH_2), 4.75 (t, 2H, J = 2 Hz, C_5H_4), 4.80 (t, 2H, J = 2 Hz, C_5H_4). ^{13}C{^{1}H} NMR (125.75 MHz, $CDCl_3$): δ 14.8 (ethyl CH_3), 23.2 (ethyl CH_2), 80.4 (C_5H_4), 87.1 (C_5H_4), 98.2 (C_2B_4). ^{11}B NMR ($CDCl_3$): δ 2.3 (BH, 2B, J_{BH} = 146 Hz), 9.9 (BH, 1B, J_{BH} = 156 Hz), 24.1 (s, 1B). IR (KBr pellet, cm^{-1}): ν 2967.4 (m), 2929.6 (m), 2893.2 (w), 2545.7 (vs, B−H), 1451.9 (m), 1413.0 (w, 1381.2 (w), 1298.6 (w), 1159.8 (m), 1023.1 (w), 829.4 (m), 784.9 (w), 427.8 (w). CI$^+$-Mass: *m*/*z* (%) 394 ([M$^+$], 100).

***nido*-(η^5-C_5H_4I)Co(2,3-$Et_2C_2B_3H_4$-5-Me) (13).** A 1.2 g sample of **12** (3.05 mmol) was placed in a flask under nitrogen, and 6 mL of tetra-*N*-methylethylenediamine (TMEDA) and ca. 10 drops of water were added. The mixture was stirred for 1 h at 0 °C. The TMEDA was removed in vacuo, and residue was taken up in hexane and flash-chromatographed through 5 cm of silica gel in hexane to give one orange-yellow band. Removal of solvent gave 1.1 g of **13** as an orange-yellow oil (94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ −5.0 (s, 2H, B−H−B), 1.15 (t, 6H, J = 7.0 Hz, ethyl CH_3), 2.12, 2.20 (sextet, 4H, J = 7.5 Hz, ethyl CH_2), 4.72 (m, 4H, J = 1 Hz, C_5H_4). ^{13}C{^{1}H} NMR (125.75 MHz, $CDCl_3$): δ −0.4 (CH_3), 16.2 (ethyl CH_3), 24.8 (ethyl CH_2), 82.3 (Cp), 83.9 (C_5H_4), 90.1 (C_5H_4), 112.9 (C_2B_3). ^{11}B NMR ($CDCl_3$): δ 1.1 (BH, 2B, J_{BH} = 129 Hz), 19.2 (s, 1B). IR (KBr pellet, cm^{-1}): ν 2959.9 (vs), 2926.8 (s), 2866.8 (m), 2518.6 (vs, B−H), 1931.9 (m, B−H−B), 1547.6 (m), 1449.2 (m), 1427.4 (w), 1346.4 (m), 1307.9 (m), 1075.2 (m), 1005.9 (m), 895.3 (m), 822.5 (s), 772.7 (s), 427.8 (w). CI$^+$-Mass: *m*/*z* (%) 383.0 ([M$^+$], 25), 225 ([M$^+$ − I, 100).

CpCo(2,3-$Et_2C_2B_4H_3$-7-C≡CSiMe$_3$) (15). To a solution of 752 mg of 2,3-$Et_2C_2B_3H_5$CoCp (**14**, 3.1 mmol) in 20 mL of dry, degassed toluene at −78 °C was added dropwise 3.9 mL of a 1.6 M *n*-butyllithium solution in hexane (6.2 mmol). The mixture was stirred for 2 h, allowed to warm to room temperature, and stirred for an additional 6 h. The now dark brown solution was cooled to 0 °C, and 2 g of [($C_6H_4O_2$)B]C≡CSiMe$_3$ (9.3 mmol) dissolved in 3 mL of toluene was added. The mixture was allowed to warm to room temperature and was stirred overnight. The solvent was removed in vacuo, and the residue was placed atop 3 cm of silica gel and washed first with hexane to recover 345 mg of **14** and then with dichloromethane. The dichloromethane wash was column-chromatographed on silica gel and eluted with a 50% CH_2Cl_2−hexanes solution to afford 364 mg of pure **15** as an orange-red, air-stable crystalline solid (27% yield; 60% based on **14** consumed). ^{1}H NMR (500 MHz, $CDCl_3$): δ −0.03 (s, 9H, SiMe$_3$), 1.41 (t, 6H, J = 7.5 Hz, ethyl CH_3), 2.41, 2.60 (sextet, 4H, J = 7.5 Hz, ethyl CH_2), 4.77 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR (125.75 MHz, $CDCl_3$): δ −0.4 (SiMe$_3$), 14.7 (ethyl CH_3), 24.6 (ethyl CH_2), 79.9 (C_5H_5), 96.1 (C_2B_4), 100.0 (C≡C). ^{11}B NMR ($CDCl_3$): δ 2.3 (BH, 3B, unresolved), 9.1 (BH, 1B, J_{BH} = 85 Hz). IR (KBr pellet, cm^{-1}): ν 2967.9 (m), 2545.5 (s, B−H), 2360.6 (m), 1455.1 (w), 1416.1 (w), 1380.2 (w), 1250.0 (m), 1141.8 (m), 1005.4 (w), 856.6 (vs), 805.7 (s), 761.6 (w), 700.0 (w). CI$^+$-Mass: *m*/*z* (%) 350 ([M$^+$], 85), 278 ([M$^+$ − SiMe$_3$], 100).

(2,3-$Et_2C_2B_4H_3$-7-C≡CSiMe$_3$)Co(η^5-C_5H_4)$_2$Co(2,3-$Et_2C_2B_4H_4$) (16). A solution of 291 mg of **15** (0.83 mmol) in 6 mL of THF at −78 °C was treated dropwise with 0.52 mL of a 1.6 M *n*-butyllithium solution in hexanes (0.83 mmol). After 1 h of stirring at −78 °C, 265 mg of anhydrous ZnI_2 (0.83 mmol) in 3 mL of THF was added. The reaction mixture was warmed to room temperature with stirring for 40 min. After an additional 0.5 h of stirring at room temperature, 303 mg of **4** (0.8 mmol) and 46 mg of $Pd(PPh_3)_4$ (0.04 mmol) were added, and the contents were stirred overnight. The THF was removed in vacuo, and the residue was washed through 3 cm of silica gel with dichloromethane. The dichloromethane wash was column-chromatographed on silica gel in 50% CH_2Cl_2−hexanes, affording a major orange band that was characterized as **16** (orange-yellow solid, 187 mg, 39% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ −0.06 (s, 9H, SiMe$_3$), 1.14 (t, 6H, J = 7.5 Hz, ethyl CH_3), 1.25 (t, 6H, $J = 7.5$ Hz, ethyl CH_3), 2.15−2.19 (m, 4H, $J = 6$ Hz, ethyl CH_2), 2.25−2.34 (m, 4H, $J = 7$ Hz, ethyl CH_2), 4.90, 4.91 (br, 4H, $J = 2$ Hz, C_5H_4), 4.94 (t, 4H, $J = 2$ Hz, C_5H_4). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ −0.5 ($SiMe_3$), 14.4 (ethyl CH_3), 14.8 (ethyl CH_3), 23.7 (ethyl CH_2), 24.0 (ethyl CH_2), 77.5 (Cp), 79.9 (Cp), 83.9 (Cp), 97.6 (Cp), 99.7 (C_2B_4), 111.8 (C≡C). ^{11}B NMR ($CDCl_3$): δ 2.7 (BH, 6B, unresolved), 9.3 (BH, 2B, unresolved). IR (KBr pellet, cm^{-1}): ν 2965.3 (m), 2930.5 (w), 2872.4 (w), 2542.1 (vs, B−H), 1454.0 (m), 1425.4 (w), 1380.6 (w), 1248.9 (m), 1139.0 (m), 1064.2 (m), 843.6 (s), 807.9 (m), 758.4 (w), 600.1 (w). UV−vis (CH_2Cl_2, nm (%)): 295 (100), 361 (23), 435 (4) ϵ_{max} = 37 888 cm^{-1} M^{-1}. CI^+-Mass: *m*/*z* (%) 602.4 ([M^+], 100).

(2,3-$Et_2C_2B_4H_3$-7-C≡CSiMe$_3$)Co[η^5-C_5H_3(*tert*-Bu)]-(η^5-C_5H_4)Co(2,3-$Et_2C_2B_4H_4$) (17). A solution of 320 mg of **8** (0.65 mmol) in 8 mL of dry, degassed toluene at −78 °C was treated dropwise with 0.76 mL of a 1.7 M *tert*-butyllithium solution in pentane (1.3 mmol). After 2 h of stirring at −78 °C, the mixture was warmed to room temperature and stirred for an additional 6 h. The now dark brown solution was cooled to 0 °C, and 281 mg of [($C_6H_4O_2$)B]C≡CSiMe$_3$ (1.3 mmol) dissolved in 2 mL of toluene was added. The mixture was allowed to warm to room temperature, and its contents were stirred overnight. The solvent was removed in vacuo, and the remaining residue was placed atop 3 cm of silica gel and washed with dichloromethane. The dichloromethane wash was column-chromatographed on silica gel in 50% CH_2Cl_2−hexanes, affording a major orange band that was characterized as **17** (orange-red solid, 110 mg, 28% yield). ^1H NMR ($CDCl_3$): δ −0.06 (s, 9H, $SiMe_3$), 1.05−1.12 (m, 6H, $J = 7.2$ Hz, ethyl CH_3), 1.24 (t, 6H, $J = 6$ Hz, ethyl CH_3), 1.36 (s, 9H, ^{t}Bu CH_3), 1.98−3.34 (m, 8H, $J = 7.5$ Hz, ethyl CH_2), 4.71 (t, 1H, $J = 2$ Hz, C_5H_4), 4.75 (t, 1H, $J = 2$ Hz, C_5H_4), 4.81 (t, 1H, $J = 2$ Hz, C_5H_4), 4.89 (t, 2H, $J = 2$ Hz, C_5H_4), 4.98 (t, 2H, $J = 2$ Hz, C_5H_4). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ −0.5 ($SiMe_3$), 14.4 (ethyl CH_3), 14.8 (ethyl CH_3), 23.6 (ethyl CH_2), 24.9 (ethyl CH_2), 30.7 (^{t}Bu CH_3), 74.2 (Cp), 75.8 (Cp), 76.2 (Cp), 77.5 (Cp), 77.6 (Cp), 79.6 (Cp), 79.8 (Cp), 89.4 (Cp), 92.3 (Cp), 99.7 (C_2B_4), 115.1 (C≡C). ^{11}B NMR ($CDCl_3$): δ 3.0 (BH, 6B, unresolved), 10.2 (BH, 2B, unresolved). IR (KBr pellet, cm^{-1}): ν 2965.1 (m), 2934.4 (w), 2875.7 (w), 2552.3 (vs, B−H), 2360.8 (m), 1455.9 (w), 1412.0 (w), 1378.0 (w), 1250.2 (m), 1141.5 (m), 1061.5 (w), 854.1 (vs), 807.1 (s), 759.6 (w), 452.9 (w). UV−vis (CH_2Cl_2, nm (%)): 298 (100), 362 (28), 443 (4) ϵ_{max} = 46 701 cm^{-1} M^{-1}. CI^+-Mass: *m*/*z* (%) 657.5 ([M^+ − 1], 100). Anal. Calcd for $B_8C_{31}Co_2H_{52}Si$: C, 56.66; H, 7.98. Found: C, 57.10; H, 7.99.

1,3,5-[(2,3-$Et_2C_2B_4H_4$)Co(η^5-C_5H_4)]$_3$$C_6H_3$ (18). A solution of 887 mg of **1** (3.5 mmol) in 10 mL of THF at −78 °C was treated dropwise with 2.2 mL of a 1.6 M *n*-butyllithium solution in hexanes (3.5 mmol). After 1 h of stirring at −78 °C, 477 mg of anhydrous $ZnCl_2$ (3.5 mmol) in 4 mL of THF was added. The reaction mixture was warmed to room temperature with stirring for 40 min. After an additional 0.5 h of stirring, 410 mg of $C_6H_3I_3$ (0.9 mmol) and 156 mg of $Pd(PPh_3)_4$ (0.135 mmol) were added, and the contents were stirred overnight. The THF was removed in vacuo, the residue was washed through 3 cm of silica gel with dichloromethane, and the wash solution was column-chromatographed on silica gel in 50% CH_2Cl_2−hexanes, affording a major orange band that was characterized as **18** (air-stable orange-red solid, 483 mg, 64% yield). ^1H NMR ($CDCl_3$): δ 1.23 (t, 18H, $J = 7.5$ Hz, ethyl CH_3), 2.35, 2.52 (sextet, 12H, $J = 7.2$ Hz, ethyl CH_2), 5.01 (t, 6H, $J = 2$ Hz, C_5H_4), 5.24 (t, 6H, $J = 2$ Hz, C_5H_4), 7.61 (s, 3H, C_6H_3). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 15.0 (ethyl CH_3), 24.2 (ethyl CH_2), 77.5 (C_5H_4), 80.1 (C_5H_4), 97.6 (C_2B_4), 98.3 (Cp), 125.6 (C_6H_3), 133.7 (C_6H_3). ^{11}B NMR ($CDCl_3$): δ 3.8 (BH, 6B, unresolved), 10.0 (BH, 6B, unresolved). IR (KBr pellet, cm^{-1}): ν 3106.5 (w), 2967.5 (m), 2931.1 (m), 2872.0 (w), 2545.9 (vs, B−H), 1601.5 (w), 1436.8 (m), 1383.6 (m), 1096.3 (w), 1043.6 (w), 870.5 (m), 835.1 (m), 725.1 (w), 467.3 (w). UV−vis (CH_2Cl_2, nm (%)): 281 (100), 231 (78), 406 (4) ϵ_{max} = 77 590 cm^{-1} M^{-1}. CI^+-Mass: *m*/*z* (%) 833.5 ([M^+ − 1], 100). Anal. Calcd for $B_{12}C_{39}Co_3H_{57}$: C, 56.27; H, 6.90. Found: C, 56.92; H, 6.87.

1,3,5-[(*nido*-2,3-$Et_2C_2B_3H_5$)Co(η^5-C_5H_4)]$_3$$C_6H_3$ (19). A 350 mg sample of **18** (0.42 mmol) was placed in a flask under nitrogen, to which was added 8 mL of tetra-*N*-methylethylenediamine (TMEDA) and ca. 5 drops of water. The mixture was stirred for 1 h at 0 °C, after which the TMEDA was removed in vacuo and the residue was taken up in hexane and flash-chromatographed through 3 cm of silica gel in hexane to give one orange-yellow band. Removal of solvent gave 300 mg of **19** as an orange-yellow solid (89%). ^1H NMR (500 MHz, $CDCl_3$): δ −5.97 (s, B−H−B), 1.10 (t, 18H, $J = 7.5$ Hz, ethyl CH_3), 1.93, 2.05 (sextet, 12H, $J = 7.5$ Hz, ethyl CH_2), 4.95 (t, 6H, $J = 2$ Hz, C_5H_4), 5.24 (t, 6H, $J = 2$ Hz, C_5H_4), 7.44 (s, 3H, C_6H_3). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 16.2 (ethyl CH_3), 25.2 (ethyl CH_2), 79.8 (C_5H_4), 82.7 (C_5H_4), 100.6 (Cp), 113.8 (C_2B_3), 124.2 (C_6H_3), 133.9 (C_6H_3). ^{11}B NMR ($CDCl_3$): δ 2.7 (BH, 6B, unresolved), 4.3 (BH, 3B, unresolved). IR (KBr pellet, cm^{-1}): ν 3109.1 (w), 2960.5 (s), 2925.1 (m), 2866.7 (m), 2534.3 (vs, B−H), 1866.2 (m, B−H−B), 1600.8 (m), 1555.7 (m), 1448.0 (m), 1383.1 (w), 1041.9 (w), 927.3 (m), 828.0 (m), 778.9 (s), 464.0 (w). UV−vis (CH_2Cl_2, nm (%)): 229 (100), 278 (95), 322 (37), 372 (8), 431 (3) ϵ_{max} = 45 200 cm^{-1} M^{-1}. CI^+-Mass: *m*/*z* (%) 803.2 ([M^+ − 1], 100).

1,3-[Cp*Co(2,3-$Et_2C_2B_3H_3$)Co(η^5-C_5H_4)]$_2$-5-[(2,3-$Et_2C_2B_3H_5$)Co(η^5-C_5H_4)]C_6H_3 (20) and 1,3,5-[Cp*Co(2,3-$Et_2C_2B_3H_3$)Co(η^5-C_5H_4)]$_3$$C_6H_3$ (21). Compound **19** (169 mg, 0.21 mmol) in 3 mL of THF was treated with 30 mg of NaH (1.3 mmol) at room temperature. This solution was stirred for 2 h, unreactive NaH was removed by filtration, and 145 mg of $(Cp*CoCl)_2$ (0.32 mmol) in 2 mL of THF was added. The mixture was stirred overnight, and the solvent was removed in vacuo. The remaining dark red residue was washed through 3 cm of silica gel with dichloromethane. The crude material was then chromatographed on silica gel TLC plates with a 2:1 CH_2Cl_2−hexanes solution, producing two bands. The first band afforded 77 mg of red solid **20** (31%), while the second band yielded 157 mg of **21**, also a red solid (54%). Data for **20**: ^1H NMR (500 MHz, $CDCl_3$): δ −5.98 (s, 2H, B−H−B), 1.09 (t, 6H, $J = 7.5$ Hz, ethyl CH_3), 1.37 (t, 12H, $J = 7.5$ Hz, ethyl CH_3), 1.52 (s, 30H, C_5Me_5), 1.94, 2.05 (sextet, 4H, $J = 7.5$ Hz, ethyl CH_2), 2.39, 2.47 (sextet, 8H, $J = 7.5$ Hz, ethyl CH_2), 4.69 (t, 4H, $J = 2$ Hz, C_5H_4), 4.78 (t, 4H, $J = 2$ Hz, C_5H_4), 4.94 (t, 2H, $J = 2$ Hz, C_5H_4), 5.26 (t, 2H, $J = 2$ Hz, C_5H_4), 7.21 (s, 1H, C_6H_3), 7.33 (br, 2H, $J = 2$ Hz, C_6H_3). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 9.5 (C_5Me_5), 15.9 (ethyl CH_3), 16.2 (ethyl CH_3), 24.9 (ethyl CH_2), 25.2 (ethyl CH_2), 75.2 (C_5H_4), 78.0 (C_5H_4), 79.8 (C_5H_4), 82.5 (C_5H_4), 87.7(C_5Me_5), 89.0 (C_2B_4), 95.4 (Cp), 101.0 (Cp), 123.8 (C_6H_3), 124.0 (C_6H_3), 133.6 (C_6H_3), 133.7 (C_6H_3). ^{11}B NMR ($CDCl_3$): δ 4.0 (BH, 6B, unresolved), 7.9 (BH, 1B, unresolved), 55.0 (BH, 2B, unresolved). IR (KBr pellet, cm^{-1}): ν 2961.4 (m), 2904.1 (m), 2481.3 (vs, B−H), 1866.1 (w, B−H−B), 1599.1 (m), 1559.1 (w), 1448.6 (m), 1377.9 (m), 1030.3 (w), 925.6 (w), 806.6 (vs), 730.4 (w), 461.9 (w). UV−vis (CH_2Cl_2, nm (%): 355 (100), 274 (61), 430 (13), 539 (3) ϵ_{max} = 74 454 cm^{-1} M^{-1}. CI^+-Mass: *m*/*z* (%) 1187.3 ([M^+ − 1], 100). Anal. Calcd for $B_9C_{59}Co_5H_{86}$: C, 59.69; H, 7.30. Found: C, 61.04; H, 7.29. Data for **21**: ^1H NMR (500 MHz, $CDCl_3$): δ 1.37 (t, 18H, $J = 7.5$ Hz, ethyl CH_3), 1.52 (s, 45H, C_5Me_5), 2.40, 2.47 (sextet, 12H, $J = 7.5$ Hz, ethyl CH_2), 4.72 (t, 6H, $J = 2$ Hz, C_5H_4), 4.81 (t, 6H, $J = 2$ Hz, C_5H_4), 7.19 (s, 3H, C_6H_3). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$): δ 9.5 (C_5Me_5), 15.9 (ethyl CH_3), 24.8 (ethyl CH_2), 75.1 (C_5H_4), 77.9 (C_5H_4), 87.6 (C_5Me_5), 88.9 (C_2B_4), 95.6 (Cp), 123.6 (C_6H_3), 133.5 (C_6H_3). ^{11}B NMR ($CDCl_3$): δ 9.7 (BH, 6B, unresolved), 54.0 (BH, 3B, unresolved). IR (KBr pellet, cm^{-1}): ν 2962.1 (m), 2902.9 (m), 2480.3 (vs, B−H), 1598.1 (w), 1448.6 (w), 1378.0 (m), 1236.1 (w), 1030.3 (w), 807.0 (vs), 462.7 (w). UV−vis (CH_2Cl_2, nm (%)): 357 (100), 280 (41), 431 (13), 548 (4) ϵ_{max} = 115 380 cm^{-1} M^{-1}. CI^+-Mass: *m*/*z* (%) 1379.0 ([M^+ − 1], 100). Anal. Calcd for $B_9C_{69}Co_6H_{99}$: C, 60.08; H, 7.23. Found: C, 61.14; H, 7.30.

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