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$(C_5Me_5)Co(Et_2C_2B_3H_4\text{–}R)$ Metallacarborane Sandwich Complexes as Versatile Synthons. Introduction of Organomethyl Functional Groups at Boron[1]

Kent W. Piepgrass and Russell N. Grimes*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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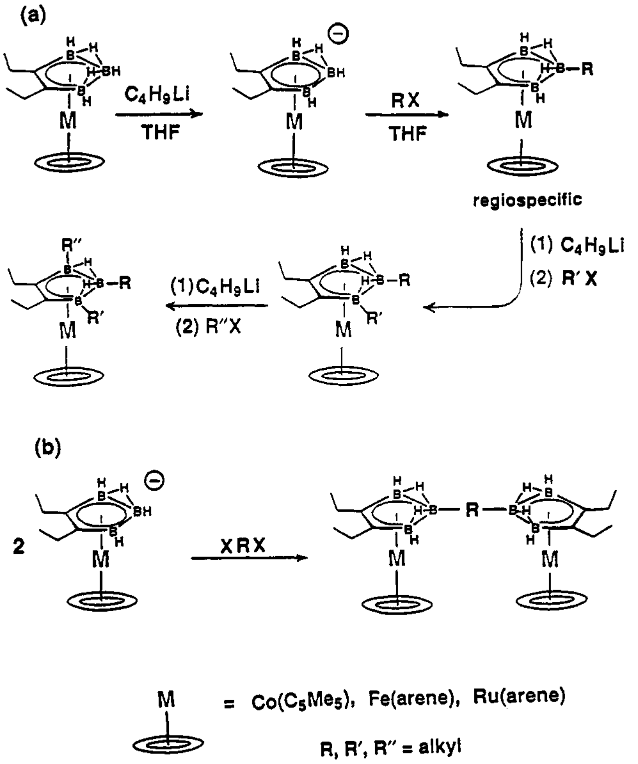
The air-stable complex $(C_5Me_5)Co(Et_2C_2B_3H_5)$ (1), a synthon of demonstrated utility in the construction of multidecker sandwiches and organometallic polymers, was derivatized at B(5) (the middle boron on the C_2B_3 ring) via bridge-deprotonation and reaction of the 1^- ion with organomethyl halides. This approach, previously developed in our laboratory for B-alkylation of *nido*-$LM(R_2C_2B_3H_5)$ metallacarboranes (L = aromatic hydrocarbon; M = Fe, Ru, or Co; R = alkyl), was employed in the present work to prepare a series of $(C_5Me_5)Co(Et_2C_2B_3H_4\text{-}5\text{-}CH_2\text{-}R')$ complexes in which R′ is an aryl, cyano, alkoxy, acyl, alkenyl, alkynyl, ester, fluoroalkyl, or fluoroaryl group. Organic transformations of several of these compounds afforded carboxylic acid, amino, amide, and hydroxy derivatives. These species, characterized via ^1H, ^{13}C, and ^{11}B NMR, IR, UV–visible, and mass spectra, represent the first organic derivatization of small metallacarboranes beyond alkyl or arylalkyl substitution and demonstrate that the cluster framework of 1 remains intact under a wide range of organic reaction conditions.

Introduction

Sandwich complexes of the type $LM(RR'C_2B_3H_5)$, in which L is a hydrocarbon ligand and M is a transition metal (typically Fe, Co, Ru, or Rh), are in many respects ideal building blocks for assembling stable organometallic oligomers and polymers and tailoring them for specific properties.[2] Among the attributes of these complexes, particularly those of cobalt, are (1) high structural integrity and resistance to degradation, (2) wide-ranging chemical versatility, (3) controllable reaction chemistry, and (4) the ability to stabilize unusual organometallic species. As reported in a number of earlier papers, these versatile synthons have been employed in several ways. In the $(C_5H_5)Co$ and $(C_5Me_5)Co$ complexes, the C_2B_3 open faces (following removal of one or both B–H–B bridge protons) are amenable to metal stacking reactions, forming triple- and quadruple-decker sandwiches.[3] Coordination of the metals to bicyclic or polycyclic arenes allows the construction of arene-bridged oligomers and polymers,[4] and linked-cage systems can be created via reactions of functional groups attached to boron or carbon atoms in the C_2B_3 ring.[4b,5]

Scheme I



In developing the last-mentioned strategy in our laboratory, we sought methods for introducing organic substituents to the carborane ligand. It was demonstrated in earlier work[6] that regioselective attachment of alkyl or haloalkyl groups at B(5) (the middle boron) an be accomplished efficiently via treatment of $LM(Et_2C_2B_3H_4)^-$ anions with alkyl or arylalkyl halides (RX), as shown in Scheme Ia. Further deprotonation/alkyl halide sequences effect substitution at the remaining boron positions, B(4) and B(6).[6] From all indications, these reactions proceed via electrophilic attack of R^+ on the electron-rich deprotonated B–B edge to form alkyl-bridged intermediates in which the alkyl subsequently exchanges with a terminal B–H proton (usually that on B(5)), forming the observed B–R product.[7] When organic dihalides that can bond to two such metallacarborane units are employed, this reaction has been

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[6] Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171.

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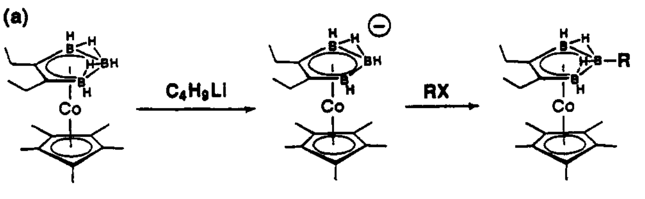
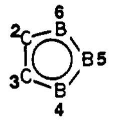
Scheme II



1 1⁻

Ring numbering:



Compound	R	Isolated Yield (%)
3	CH_2-C_6H_5	80
4	CH_2-CF_3[a]	4
5	CH_2-C_6F_5	66
6	CH_2-C_2H_5	81
7	$CH(CH_3)_2$	44
8	CH_2-CN	18
9[b]	CH_2-CH_2NH_2	50
11	CH_2-OCH_3	65
12	CH_2-C(O)CH_3	24
13	CH_2-C≡C-H	80
14	CH_2-C≡C-CH_3	87
15	CH_2-C≡C-CH_2Cl	48
17	CH_2-CH=CH_2	87
18	CH_2-C(O)-OCH_3	56
20[c]	CH_2-C(O)OH	68
22[c]	CH_2-C(O)NH_2	77
23	CH_2-O-C(O)-CH_3	25
26[d]	CH_2-OH	77

[a] Mixture of B(4)-R and B(5)-R isomers. [b] Prepared from 8. [c] Prepared from 18. [d] Prepared from 23.

exploited to prepare hydrocarbon-linked oligomers (Scheme Ib).[4b,5]

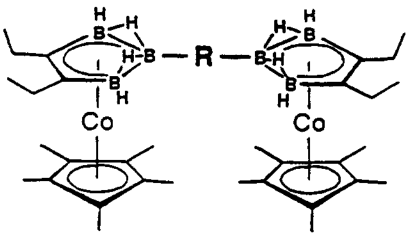
Further development of this approach clearly required the introduction of a wider range of organic functional groups, particularly those that are amenable to modification via standard organic methods. In this paper we report the application of the RX-type reaction in the synthesis of a variety of B(5)-organosubstituted derivatives of $(C_5Me_5)Co(Et_2C_2B_3H_5)$ (1), a yellow crystalline air-stable complex that is easily prepared in multigram quantities;[3a] several of these were, in turn, converted to other B(5)–R complexes. The family of products so generated represents the first derivatization of a small metallacarborane system beyond simple alkylation or halogenation. Moreover, some of the organic moieties introduced are novel to metallacarborane chemistry generally.

During this investigation it became apparent that the addition of electron-withdrawing substituents, such as halogens, cyano, and acetyl, frequently involves processes that take a different course from the alkyl halide reactions, generating products other than (or in addition to) the simple B(5)–R species; this chemistry is treated separately in an accompanying article.[8]

Results and Discussion

Alkyl Halide Reactions. The general approach shown in Scheme I was employed in the present work with a variety of organomethyl halides to generate the corresponding $(C_5Me_5)Co(Et_2C_2B_3H_4$-5-R) species (Scheme II). The reactions were conducted in THF solutions which were initially cooled in dry ice and allowed to warm to room temperature following addition of the R–CH_2–X reagent. Although a 3:1 ratio of R–CH_2–X to 1^- was usually employed, in most cases only 1 equiv reacted, forming the B(5)-monosubstituted target complex. However, in the preparation of the methyl acetate derivative 18, the 4,6-bis(methyl acetate)-5-bromo derivative 19 was obtained as a minor side product, evidently forming via further reaction of 18. The structure of 19 was assigned from its NMR spectra and confirmed by X-ray diffraction data, which was processed only to the point necessary to establish the atom connectivities.

Scheme III



16 R = CH_2–C≡C–CH_2
24 R = CH_2-O-CH_2
25 R = CH_2-O-CH_2-O-CH_2

Individual compounds were isolated and purified, usually as air-stable, yellow crystalline solids, via chromatography in air on silica gel columns or preparative-scale plates (see Experimental Section). A competing process in the alkyl halide reactions is the reprotonation of 1^- (in the reaction vessel and/or during subsequent workup in air) to generate the starting material 1, which is recoverable by chromatography. Despite this problem, isolated yields of most of the B(5)–CH_2–R products (based on 1 employed) were fair to excellent, as indicated in Scheme II (yields calculated on the basis of 1 *consumed* are, of course, higher). The least efficient of the syntheses shown were those of the trifluoroethyl and cyanomethyl species 4 and 8, whose formation was inhibited by extensive regeneration of starting material 1. Attempted reactions of hindered alkyl halides, including 1- and 2-bromoadamantane and *tert*-butyl bromide, gave no detectable metallacarborane products, and over 80% of the starting material 1 was recovered. A trace material which was isolated in several cases (see Experimental Section) and accumulated in sufficient quantity to permit its characterization, was identified as an isomer of $(C_5Me_5)Co(Et_2C_2B_3H_3)$–$OC_4H_8$ (27) which is *formally* generated by replacing two terminal hydrogen atoms with a molecule of THF solvent. The proton and carbon-13 NMR spectra of this compound show that the THF ring is intact and suggest that it is bonded to the C_2B_3 ring via both C and O; beyond this the structure is unclear. Efforts to develop a controlled synthesis of 27 were unsuccessful.

An attempted preparation of the cyanoethyl derivative from 1-bromo-2-cyanoethane and 1^- gave only a trace of the desired product, $(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2CH_2CN)$ (10), which was characterized from its proton NMR and mass spectra.

Synthesis of Bis(cobaltacarboranyl) Complexes. The reaction of 1^- with organic dihalides (Scheme Ib), previously used to prepare xylyl-linked species,[5] was employed in the present study (using 1 equiv of the dihalide) to generate the 2-butynyl-linked compound 16 (Scheme III) in 19% yield; however, the major product was the mono(cobaltacarboranyl) 1-chloro-2-butynyl derivative 15 (48%). No effort was made to optimize the formation of 16, which presumably would be promoted by decreasing the ratio of dihalide reagent to 1^-. Two other bis(cobaltacarboranyl) species were unexpectedly isolated as minor byproducts of the synthesis of the ester 23 and 1^- and $BrCH_2OCOMe$. These species (Scheme III) were charac-

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(8) Piepgrass, K. W.; Stockman, K. E.; Sabat, M.; Grimes, R. N. Following article in this issue.

Table I. 115.8-MHz ^{11}B FT NMR Data for $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}R)$ Complexes

R	δ (J_{BH}, Hz)[a,b]
H (**1**)[c]	7.5 (146), 3.9 (134)[d]
Me (**1a**)[e]	19.4, −1.0
$CH_2—Me$ (**2**)[e]	23.1, −0.5 (118)
$CH_2—C_6H_5$ (**3**)	20.7, 0.8 (102)
$CH_2—CF_3$ (**4**)[f]	13.0, 6.8, 6.2, 4.8, 1.9
$CH_2—C_6F_5$ (**5**)	18.3, 0.6 (111)
$CH_2—C_2H_5$ (**6**)	21.7, 0.1 (110)
$CHMe_2$ (**7**)	24.9, −0.7 (123)
$CH_2—CN$ (**8**)	16.3, 2.1 (133)
$CH_2—CH_2NH_2$ (**9**)	19.0, 0.0
$CH_2—OMe$ (**11**)	16.6, 0.6 (124)
$CH_2—C(O)Me$ (**12**)	16.3, 0.5 (126)
$CH_2—C{\equiv}C—H$ (**13**)	18.8, 0.0 (127)
$CH_2—C{\equiv}C—Me$ (**14**)	20.6, 0.9 (124)
$CH_2—C{\equiv}C—CH_2Cl$ (**15**)	23.0, 0.5 (101)
$CH_2—C{\equiv}C—CH_2\text{-}5\text{-}(2,3\text{-}Et_2C_2B_3H_4)Co(C_5Me_5)$ (**16**)	19.0, 0.8 (93)
$CH_2—CH{=}CH_2$ (**17**)	22.4, 1.4 (115)
$CH_2—C(O)OMe$ (**18**)	16.6, 0.6 (122)
19[g]	8.9, 7.0
$CH_2—C(O)OH$ (**20**)[h]	16.2, 0.7
$CH_2—C(O)NH_2$ (**22**)	17.4, 0.4 (85)
$CH_2—O—C(O)—Me$ (**23**)	15.5, 1.3 (111)
$CH_2—O—CH_2\text{-}5\text{-}(2,3\text{-}Et_2C_2B_3H_4)Co(C_5Me_5)$ (**24**)	17.4, 1.2
$CH_2—(O—CH_2)_2\text{-}5\text{-}(2,3\text{-}Et_2C_2B_3H_4)Co(C_5Me_5)$ (**25**)	18.5, 2.0 (116)
$CH_2—OH$ (**26**)	18.5, 0.3 (115)
OC_4H_8 (**27**)[i]	18.3, 4.9, 4.1

[a] Shifts relative to $BF_3 \cdot OEt_2$, positive values downfield; H—B coupling constant in hertz is given in parentheses, when resolved. Spectra were recorded in *n*-hexane solution except where otherwise indicated. [b] Except where stated otherwise, the peak area ratio in each case is 1:2 and the area 1 resonance is a singlet arising from the substituted boron [B(5)]. [c] Reference 3a. [d] CH_2Cl_2 solution. [e] Reference 6. [f] Mixture of 4- and 5-CH_2CF_3 isomers. [g] $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_2\text{-}5\text{-}Br\text{-}4,6\text{-}[CH_2C(O)OMe]_2)$. [h] 1:1 hexane/$CH_2Cl_2$ solution. [i] Proposed formula is $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_3OC_4H_8)$ (see text).

terized spectroscopically as $[(C_5Me_5)Co(Et_2C_2B_3H_4)CH_2]_2O$ (**24**) and $[(C_5Me_5)Co(Et_2C_2B_3H_4)CH_2O]_2CH_2$ (**25**).

Compound Characterization. The *nido*-CoC_2B_3 cage structure has been crystallographically defined in several earlier studies[9] and in an X-ray determination on a B(5)–vinyl ester derivative[7,8] of **1**. The pure products were characterized via elemental analysis, infrared, UV–visible, and mass spectroscopy, and ^1H, ^{11}B, and ^{13}C NMR spectra. The derivatives typically exhibit strong mass spectral parent envelopes whose intensity patterns are consistent with calculated spectra. The NMR spectra (Tables I–III) reflect the idealized mirror symmetry of the B(5)-substituted cage structure. Thus, the proton-coupled boron resonances consist of a singlet and doublet in a 1:2 area ratio, corresponding respectively to B(5)–R and the equivalent B(4,6)–H groups. The proton NMR spectra similarly exhibit one set of C–ethyl signals, indicating equivalence of the cage carbons. (Symmetry lowering by asymmetric substituents on B(5) is normally not observed on the NMR time scale, owing to the averaging of group orientations via exocyclic B–C and C–C bond rotations in solution). As Table I clearly shows, substitution at B(5) produces a pronounced deshielding of the B(5) resonance relative to the parent species **1**, consistent with general observations on the NMR behavior of B-organocarboranes.[10]

The ^1H NMR shifts of the B–H–B protons have been correlated with electronic properties of the C_2B_3 open face, specifically its reactivity toward M^{2+} ions in quadruple-decker stacking reactions.[3b] This observation and its utility in synthesis are elaborated elsewhere.[8,11]

Functional Group Modification of B(5)-Substituted Derivatives. A number of the organic substituents that were attached via alkyl halide treatment of **1** are amenable to conversion to other species via standard organic procedures. Of particular interest are functional groups that contain acidic hydrogens and hence cannot be introduced directly. Several such reactions were conducted in this study.

Synthesis of a B-Aminomethyl Derivative. The nitrile **8**, although prepared only in low yield (vide supra), was nonetheless available in sufficient quantity to attempt its conversion to the amine. This was done via treatment with $LiAlH_4$ in THF, which following chromatographic separation afforded $(C_5Me_5)Co(Et_2C_2B_3H_4\text{-}5\text{-}CH_2CH_2NH_2)$ (**9**), a yellow oil, in 50% yield accompanied by 22% of recovered **8**. The amine function in **9** is clearly signaled by a characteristic NH_2 triplet in the proton NMR spectrum and by the identifiable C–NH_2 peak in the ^{13}C NMR spectrum.

Conversion of 18 to Carboxylic Acid and Amide Derivatives. The ester **18** was treated with Me_3SiI and NaOH by the method of Ho and Olah[12] to give the acid $(C_5Me_5)Co(Et_2C_2B_3H_4\text{-}5\text{-}CH_2C(O)OH)$ (**20**), isolated as yellow crystals in 68% yield. A trace of the ethyl ester $(C_5Me_5)Co(Et_2C_2B_3H_4\text{-}5\text{-}CH_2C(O)OEt)$ (**21**), identified from its ^1H NMR and mass spectra, was also formed, demonstrating transesterification and suggesting a considerable potential scope for applying organic chemistry to these functionalized metallacarborane species.

The acetamide $(C_5Me_5)Co(Et_2C_2B_3H_4\text{-}5\text{-}CH_2C(O)NH_2)$ (**22**) was prepared by reaction of **18** with H_2NAlMe_2 and subsequent acidification, which generated the yellow solid product in 77% yield. The ester **23** was refluxed with NaOH in ethanol to afford, following workup, a 73% yield of the B(5)–hydroxymethyl derivative **26**.

Summary. This work extends our earlier studies of regiospecific alkylation of **1** and similar complexes, and establishes that **1** can be derivatized with a variety of organic functional groups using standard procedures. The availability of these compounds, together with those incorporating electron-withdrawing groups described in the following article,[8] considerably enlarges their potential role as synthetic building blocks, by combining the metal coordination properties of the C_2B_3 open face with the specific reactivities of the organic functional groups. The broad range of available substituents, together with the stability of the metallacarborane unit under standard reaction conditions, should allow the introduction of these species into a variety of organic and biological systems. The growing interest in medical applications of boron clusters, for example in radioimmunodetection and -therapy[13] and in boron neutron capture tumor therapy,[14] suggests similar possible roles for appropriately derivatized *nido*-CoC_2B_3 complexes. In this regard the acid- and amine-substituted derivatives may be particularly useful

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(13) Paxton, R. J.; Beatty, B. G.; Hawthorne, M. F.; Varadarajan, A.; Williams, L. E.; Curtis, F. L.; Knobler, C. B.; Beatty, J. D.; Shively, J. E. *Proc. Natl. Acad. U.S.A.* **1991**, *88*, 3387.

(14) Morris, J. H. *Chem. Br.* **1991**, *27*, 331 and references therein.

Table II. 300-MHz ^1H FT NMR Data

compd	δ^{a-c}
1[d]	2.09 (m, CH_2), 1.89 (m, CH_2), 1.76 (s, C_5Me_5), 1.10 (m, CH_3), −5.54 (br s, B—H—B)
1a[e]	2.13 (m, CH_2), 1.85 (m, CH_2), 1.73 (s, C_5Me_5), 1.08 (m, CH_3), 0.34 (br s, CH_3), −5.23 (br s, B—H—B)
2[e]	2.11 (m, CH_2), 1.89 (m, CH_2), 1.72 (s, C_5Me_5), 1.09 (t, CH_3), 0.97 (t, *Et* CH_3), 0.82 (br m, BCH_2),[f] −5.36 (br s, B—H—B)
3	7.22–7.01 (m, C_6H_5), 2.27 (br, BCH_2), 2.09 (m, CH_2), 1.86 (m, CH_2), 1.79 (s, C_5Me_5), 1.03 (t, CH_3), −5.27 (br s, B—H—B)
4[g]	2.11 (m, CH_2), 1.88 (m, CH_2), 1.71 (s, C_5Me_5), 1.14 (t, CH_3), 1.12 (t, CH_3), 1.03 (t, CH_3), −5.60 (br s, B—H—B)
5	2.30 (br, BCH_2), 2.13 (m, CH_2), 1.88 (m, CH_2), 1.82 (s, C_5Me_5), 1.08 (t, CH_3), −5.42 (br s, B—H—B)
6	2.09 (m, CH_2), 1.83 (m, CH_2), 1.70 (s, C_5Me_5), 1.29 (m, *Pr* CH_2), 1.06 (t, CH_3), 0.91 (t, *Pr* CH_3), 0.78 (br m, BCH_2), −5.46 (br s, B—H—B)
7	2.12 (m, CH_2), 1.87 (m, CH_2), 1.74 (s, C_5Me_5), 1.08 (t, CH_3), 0.98 (d, CH_3), −5.55 (br s, B—H—B)
8	2.10 (m, CH_2), 1.89 (br, BCH_2), 1.85 (m, CH_2), 1.74 (s, C_5Me_5), 1.09 (t, CH_3), −5.41 (br s, B—H—B)
9	2.67 (t, NH_2), 2.12 (m, CH_2), 1.88 (m, CH_2), 1.73 (s, C_5Me_5), 1.08 (t, CH_3), −5.50 (br s, B—H—B)
10	2.29 (t, CH_2), 2.11 (m, CH_2), 1.85 (m, CH_2), 1.73 (s, C_5Me_5), 1.2 (br, BCH_2), 1.08 (t, CH_3), −5.67 (br s, B—H—B)
11	3.35 (s, OCH_3), 3.26 (br, BCH_2), 2.10 (m, CH_2), 1.87 (m, CH_2), 1.73 (s, C_5Me_5), 1.07 (t, CH_3), −5.31 (br s, B—H—B)
12	2.25 (br, BCH_2), 2.14 ($COCH_3$), 2.11 (m, CH_2), 1.87 (m, CH_2), 1.72 (s, C_5Me_5), 1.07 (t, CH_3), −5.52 (br s, B—H—B)
13	2.36 (t, CH), 2.11 (m, CH_2), 1.86 (m, CH_2), 1.73 (s, C_5Me_5), 1.09 (t, CH_3), −5.19 (br s, B—H—B)
14	2.10 (m, CH_2), 1.85 (m, CH_2, CH_3), 1.71 (s, C_5Me_5), 1.09 (t, CH_3), −5.15 (br s, B—H—B)
15	4.14 (s, CH_2Cl), 2.10 (m, CH_2), 1.87 (m, CH_2), 1.83 (br, BCH_2), 1.72 (s, C_5Me_5), 1.09 (t, CH_3), −5.25 (br s, B—H—B)
16	2.09 (m, CH_2), 1.84 (m, CH_2), 1.70 (s, C_5Me_5), 1.08 (t, CH_3), −5.11 (br s, B—H—B)
17	5.87 (m, CH), 4.86 (dd, $=CH_2$), 4.73 (dd, $=CH_2$), 2.11 (m, CH_2), 1.84 (m, CH_2), 1.73 (s, C_5Me_5), 1.08 (t, CH_3), −5.36 (br s, B—H—B)
18	3.58 s (OCH_3), 2.09 (m, CH_2), 2.03 (br, BCH_2), 1.85 (m, CH_2), 1.71 (s, C_5Me_5), 1.06 (t, CH_3), −5.32 (br s, B—H—B)
19	3.64 (s, OCH_3), 2.29 (m, CH_2), 2.10 (m, CH_2), 1.92 (m, CH_2), 1.65 (s, C_5Me_5), 1.02 (t, CH_3), −5.54 (br s, B—H—B)
20	11.4 (br s, COOH), 2.1 (m br, CH_2, BCH_2), 1.85 (m, CH_2), 1.72 (s, C_5Me_5), 1.08 (t, CH_3), −5.29 (br s, B—H—B)
21	4.03 (q, *Et* CH_2), 2.08 (m, CH_2), 2.00 (br, BCH_2), 1.70 (s, C_5Me_5), 1.20 (t, *Et* CH_3), 1.06 (t, CH_3), −5.34 (br s, B—H—B)
22	5.28, 5.08 (br s, NH_2), 2.11 (m, CH_2), 1.97 (br, BCH_2), 1.83 (m, CH_2), 1.73 (s, C_5Me_5), 1.07 (t, CH_3), −5.30 (br s, B—H—B)
23	3.94 (br, BCH_2), 2.10 (m, CH_2), 1.98 (s, $COCH_3$), 1.88 (m, CH_2), 1.73 (s, C_5Me_5), 1.08 (t, CH_3), −5.34 (br s, B—H—B)
24	3.31 (br, BCH_2), 2.08 (m, CH_2), 1.85 (m, CH_2), 1.73 (s, C_5Me_5), 1.05 (t, CH_3), −5.26 (br s, B—H—B)
25	4.63 (s, OCH_2O), 3.38 (br, BCH_2), 2.14 (m, CH_2), 1.87 (m, CH_2), 1.76 (s, CH_3), 1.11 (t, CH_3), −5.28 (br s, B—H—B)
26	3.59 (br, BCH_2), 2.11 (m, CH_2), 1.88 (m, CH_2), 1.73 (s, C_5Me_5), 1.09 (t, CH_3), −5.31 (br s, B—H—B)
27	3.99 (dt, OCH_2), 3.77 (dd, BCH), 3.60 (dt, OCH_2), 2.21 (m, CH_2), 2.05 (m, CH_2), 1.88 (m, CH_2), 1.80 (m, CH_2), 1.76 (s, CH_3), 1.13 (t, CH_3), 1.02 (t, CH_3), −5.41 (br s, B—H—B), −6.14 (br s, B—H—B)

[a] Shifts relative to Me_4Si. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. [b] B—$H_{terminal}$ resonances are broad quartets and mostly obscured by other signals. [c] $CDCl_3$ solution. [d] Reference 3a. [e] Reference 6. [f] Assignment corrected from that given in ref 6. [g] Mixture of B(4/6) and B(5) isomers.

Table III. 75.5-MHz ^{13}C FT NMR Data

compd	$\delta^{a,b}$
2	111 (C_2B_3), 92.4 (C_5), 23.0 (CH_2), 18.0 (CH_3), 17.1 (*Et* CH_3), 10.0 (C_5Me_5), 7 (BCH_2)
3	147.3 (C[1]), 128.9 (C[2]), 128.1 (C[3]), 124.6 (C[4]), 111 (br, C_2B_3), 92.6 (C_5), 24 (BCH_2), 22.9 (CH_2), 17.8 (CH_3), 10.1 (C_5Me_5)
4[c]	112 (br, C_2B_3), 92.7 (s, C_5), 22.9 (t, CH_2), 21.5 (br, BCH_2), 21.3 (t, CH_2), 18.3 (q, CH_3), 17.7 (q, CF_3), 15.9 (q, CH_3), 10.15 (q, C_5Me_5), 10.06 (q, C_5Me_5)
5	146.0 (m, C_6F_5), 142.7 (m, C_6F_5), 140.0 (m, C_6F_5), 136.1 (m, C_6F_5), 122.4 (m, C_6F_5), 111 (br, C_2B_3), 92.5 (C_5), 22.8 (CH_2), 17.7 (CH_3), 10.0 (C_5Me_5), 9.8 (br, BCH_2)
6	111 (br, C_2B_3), 92.4 (C_5), 26.0 (*Pr* CH_2), 23.0 (CH_2), 17.9 (CH_3), 17.3 (*Pr* CH_3), 10.0 (CH_3)
7	111 (br, C_2B_3), 92.3 (C_5), 24.9 (*iPr* CH_3), 23.0 (CH_2), 17.9 (CH_3), 14 (br, BCH), 9.9 (C_5Me_5)
8	122.2 (CN), 112 (br, C_2B_3), 93.0 (C_5), 22.8 (CH_2), 17.7 (CH_3), 10.0 (C_5Me_5), 1.5 (br, BCH_2)
9	111 (C_2B_3), 92.5 (C_5), 44 (br, CH_2N), 22.9 (CH_2), 17.8 (CH_3), 10.0 (C_5Me_5)
11	111 (C_2B_3), 92.6 (C_5), 65 (br, BCH_2), 61.8 (OCH_3), 22.7 (CH_2), 17.7 (CH_3), 10.1 (C_5Me_5)
12	211.6 (CO), 112 (C_2B_3), 92.7 (C_5), 35 (br, BCH_2), 30.3 ($COCH_3$), 22.8 (CH_2), 17.7 (CH_3), 10.0 (C_5Me_5)
13	112 (br, C_2B_3), 92.6 (C_5), 87.7 (CCH), 67.1 (CH), 22.9 (CH_2), 17.8 (CH_3), 10.0 (C_5Me_5), 3 (br, BCH_2)
14	111 (br, C_2B_3), 92.6 (C_5), 81.9 (C), 74.3 (CCMe), 22.9 (CH_2), 17.8 (CH_3), 10.1 (C_5Me_5), 4.1 (CCH_3), 3.5 (BCH_2)
15	111 (C_2B_3), 92.7 (C_5), 90.1 ($CCCH_2Cl$), 73.9 ($CCCH_2Cl$), 32.4 (CH_2Cl), 22.9 (CH_2), 17.8 (CH_3), 10.0 (C_5Me_5), 4 (br, BCH_2)
16	111 (C_2B_3), 92.5 (C_5), 81.3 (C), 22.9 (CH_2), 17.8 (CH_3), 10.0 (C_5Me_5), 4 (BCH_2)
17	142.4 (d, CH), 111.9 (t, CH_2), 111 (br, C_2B_3), 92.5 (s, C_5), 22.9 (t, CH_2), 21 (br, BCH_2), 17.8 (q, CH_3), 10.0 (q, C_5Me_5)
18	176.5 (s, CO), 111.5 (br, C_2B_3), 92.6 (s, C_5), 51.8 (q, OCH_3), 22.8 (t, CH_2), 22 (vbr, BCH_2), 17.7 (q, CH_3), 9.9 (q, C_5Me_5)
19	176.4 (s, CO), 106 (br, C_2B_3), 93.6 (s, C_5), 52.0 (q, OCH_3), 21.2 (t, CH_2), 21 (s br, BCH_2), 16.6 (q, CH_3), 9.1 (q, C_5Me_5)
20	183.4 (CO), 111.8 (br, C_2B_3), 92.7 (C_5), 23 (br, BCH_2), 22.8 (CH_2), 17.7 (CH_3), 9.9 (C_5Me_5)
22	179.1 (CO), 111.7 (br, C_2B_3), 92.6 (C_5), 25.5 (br, BCH_2), 22.8 (CH_2), 17.7 (CH_3), 10.0 (C_5Me_5)
23	172.0 (CO), 112 (C_2B_3), 92.9 (C_5), 57 (br, BCH_2), 22.8 (CH_2), 21.6 ($COCH_3$), 17.7 (CH_3), 10.2 (C_5Me_5)
24	111 (br, C_2B_3), 92.5 (C_5), 66.4 (br, BCH_2O), 22.9 (CH_2), 17.7 (CH_3), 10.2 (C_5Me_5)
25	112 (br, C_2B_3), 98.6 (t, OCH_2O), 92.6 (s, C_5), 58.3 (br t, BCH_2), 22.9 (t, CH_2), 17.8 (q, CH_3), 10.2 (t, C_5Me_5)
26	112 (br, C_2B_3), 92.7 (C_5), 54 (br, BCH_2), 22.9 (CH_2), 17.7 (CH_3), 10.1 (C_5Me_5)
27	112 (br, C_2B_3), 103 (br, C_2B_3), 92.9 (s, C_5), 13.3 (br d, BCH), 68.9 (t, OCH_2), 34.9 (t, $CH_2CH_2CH_2$), 27.1 (t, $CHCH_2$), 22.6 (t, CH_2), 21.8 (t, CH_2), 18.2 (q, CH_3), 16.8 (CH_3), 10.2 (q, C_5Me_5)

[a] $CDCl_3$ solution. [b] Shifts relative to Me_4Si; all spectra broad-band-decoupled except where coupling is indicated. [c] Mixture of isomers.

in creating peptide-type linkages. Further development of this chemistry will be presented in future papers.

Experimental Section

Instrumentation and Analysis. ^{11}B (115.8 MHz), ^1H (300 MHz), and ^{13}C (75.5 MHz) NMR spectra were acquired on Nicolet NT-360 or GE QE300 spectrometers, and unit-resolution mass spectra were obtained on a Finnegan MAT 4600 GC/MS spectrometer using perfluorotributylamine (FC43) as a calibration standard. Infrared spectra were recorded on a Mattson Cygnus FTIR spectrometer, and visible–UV spectra were obtained in CH_2Cl_2 solution on a Hewlett-Packard 8452A diode array spectrophotometer with an HP Vectra computer interface. All new products gave unit-resolution mass spectra in good agreement with calculated spectra. In addition, the fragmentations exhibited in

Table IV. Infrared Absorptions (cm^{-1}, Neat Films on KBr Plates)[a,b]

compd	absorptions
2[c]	2963 (vs), 2925 (vs), 2912 (vs), 2868 (vs), 2503 (vs), 2490 (vs), 1925 (m br), 1480 (m), 1467 (s), 1448 (s), 1376 (s), 1073 (m), 1028 (m), 951 (w), 883 (s), 772 (m)
3	3164 (w), 3022 (m), 2960 (vs), 2910 (vs), 2905 (vs), 2867 (s), 2491 (vs), 1932 (m), 1599 (m), 1520 (m), 1514 (m), 1482 (vs), 1475 (s), 1451 (vs), 1376 (vs), 1222 (m)
4[d]	2964 (vs), 2927 (vs), 2871 (vs), 2509 (s), 1864 (m), 1535 (m), 1479 (m), 1470 (m), 1452 (m), 1421, 1383 (s), 1277 (s), 1299 (s), 1290 (s), 1260 (s), 1246 (s), 1100 (s), 1074 (m), 1047 (s), 1028 (m), 920 (s), 900 (w), 742 (w), 592 (w)
5	2963 (vs), 2927 (vs), 2870 (s), 2505 (vs), 1917 (w), 1885 (w), 1517 (vs), 1500 (vs), 1484 (s), 1473 (vs), 1454 (vs), 1382 (m), 1377 (s), 1280 (m), 1225 (m), 1177 (m), 1119 (m), 1028 (m), 178 (vs), 955 (vs), 896 (s), 780 (m)
6	2958 (vs), 2925 (vs), 2866 (s), 2491 (s), 1924 (w), 1497 (m), 1481 (m), 1465 (s), 1453 (s), 1382 (s), 1375 (s), 1089 (w), 1072 (w), 1028 (m), 999 (w), 931 (w), 906 (w), 876 (w), 772 (m)
7	2958 (vs), 2925 (vs), 2862 (vs), 2504 (m), 2484 (m), 1892 (w), 1563 (w), 1478 (m), 1467 (m), 1453 (m), 1383 (m), 1377 (m), 1362 (m), 1269 (w), 1251 (w), 1027 (s), 1016 (s), 995 (m), 904 (vs), 840 (s), 772 (s), 581 (m)
8	2958 (vs), 2927 (s), 2866 (s), 2531 (m), 2510 (m), 2500 (s), 2239 (s), 1882 (w), 1712 (w), 1585 (w), 1535 (m), 1521 (w), 1478 (m), 1467 (s), 1453 (vs), 1404 (m) 1387 (vs), 1220 (w), 1171 (w), 1057 (w), 1052 (m), 1031 (s), 891 (m), 787 (w), 774 (m)
9	2960 (vs), 2925 (vs), 2887 (s), 2492 (s), 1930 (w), 1661 (w), 1481 (m), 1467 (m), 1450 (m), 1435 (w), 1376 (s), 1073 (w), 1028 (m), 1001 (w), 896 (m), 776 (m)
10	2957 (vs), 2925 (vs), 2865 (s), 1925 (w), 1888 (w), 1731 (w), 1524 (w), 1508 (w), 1503 (w), 1479 (w), 1466 (m), 1463 (m), 1452 (m), 1431 (w), 1385 (s), 1075 (w), 1028 (w), 898 (w), 773 (m)
11	2961 (vs), 1925 (vs), 2908 (vs), 2865 (vs), 2829 (s), 2804 (s), 2496 (vs), 1914 (w), 1850 (w), 1731 (w), 1527 (m), 1511 (m), 1484 (m), 1466 (m), 1448 (m), 1381 (s), 1375 (s), 1114 (m), 1154 (w), 1067 (m), 1029 (m), 898 (w), 775 (m)
12	2943 (vs), 2911 (s), 2474 (vs), 1894 (w), 1685 (vs), 1430 (m), 1364 (s), 1337 (s), 1222 (s), 1174 (m)
13	3296 (s), 2959 (vs), 2927 (s), 2910 (s), 2113 (w), 2521 (m), 2503 (m), 1922 (w), 1885 (w), 1569 (w), 1517 (w), 1468 (m), 1452 (m), 1385 (s), 1377 (m), 1250 (m), 1250 (w), 1217 (w), 1030 (m), 890 (m), 821 (w), 768 (m), 639 (s), 632 (m)
14	3289 (w), 2963 (vs), 2924 (vs), 2864 (s), 2510 (vs), 2495 (s), 1918 (w), 1884 (w), 1558 (m), 1465 (m), 1456 (m), 1448 (s), 1383 (s), 1223 (w), 1031 (m), 897 (m), 816 (m), 770 (m)
15	3331 (w), 3259 (w), 2961 (vs), 2925 (vs), 2912 (s), 2867 (m), 2505 (vs), 2230 (w), 1514 (m), 1480 (m), 1467 (m), 1461 (m), 1450 (s), 1382 (s), 1376 (vs), 1261 (vs), 1028 (s), 894 (vs), 779 (s), 688 (s)
16	3322 (w), 3289 (w), 2960 (vs), 2927 (s), 2867 (s), 2510 (vs), 1922 (w), 1884 (w), 1848 (w), 1526 (m), 1512 (m), 1480 (m), 1465 (m), 1446 (s), 1430 (m), 1375 (s), 1236 (w), 1129 (w), 1025 (m), 1003 (m), 954 (w), 892 (s), 774 (m)
17	3073 (w), 2961 (vs), 2925 (vs), 2911 (vs), 2868 (s), 2494 (vs), 1923 (w), 1632 (s), 1529 (m), 1508 (m), 1481 (s), 1467 (m), 1450 (s), 1381 (s), 1376 (vs), 1199 (w), 1072 (m), 1027 (s), 1001 (m), 992 (m), 893 (vs), 776 (m)
18	2961 (s), 2926 (s), 2882 (m), 2868 (m), 2500 (s), 1918 (w), 1729 9vs), 1464 (m), 1456 (m), 1448 (m), 1435 (m), 1376 (m), 1256 (s), 1120 (s), 1015 (w), 895 (m), 775 (w), 657 (w)
19	2964 (s), 2950 (s), 2929 (s), 2871 (m), 1728 (vs), 1626 (w), 1476 (s), 1474 (s), 1460 (m), 1450 (m), 1446 (m), 1433 (s), 1377 (m), 1255 (s), 1235 (s), 1206 (m), 1121 (s), 1074 (m), 1019 (m), 856 (w), 797 (m)
20	2960 (s), 2924 (s), 2916 (s), 2656 (w), 2489 (s), 1920 (w), 1877 (w), 1688 (vs), 1590 (w), 1519 (w), 1481 (m), 1467 (m), 1460 (m), 1450 (m), 1428 (m), 1383 (m), 1378 (m), 1291 (s), 1266 (m), 1206 (m), 1136 (m), 1052 (m), 1028 (s), 954 (m), 896 (s), 783 (m), 744 (m), 628 (m)
21	2961 (s), 2926 (s), 2868 (m), 2501 (s), 1926 (w), 1883 (w), 1725 (vs), 1573 (w), 1530 (w), 1480 (m), 1466 (m), 1463 (m), 1450 (m), 1376 (m), 1365 (m), 1252 (s), 1118 (s), 1028 (s), 896 (m), 776 (w)
22	3282 (w), 3187 (w), 2962 (s), 2924 (s), 2868 (m), 2507 (s), 1918 (w), 1652 (vs), 1620 (s), 1610 (s), 1506 (w), 1456 (w), 1447 (m), 1427 (m), 1376 (s), 1209 (w), 1158 (w), 1027 (m), 1003 (w), 952 (w), 897 (m), 890 (w), 777 (w), 737 (w)
23	2961 (s), 2926 (s), 2868 (m), 2503 (s), 1920 (w), 1865 (w), 1736 (vs), 1536 (w), 1481 (m), 1467 (m), 1462 (m), 1449 (m), 1430 (w), 1376 (s), 1368 (s), 1265 (m), 1235 (vs), 1020 (s), 958 (m), 895 (m), 779 (m), 745 (m)
24	2960 (vs), 2925 (vs), 2867 (s), 2815 (m), 2497 (s), 1926 (w), 1883 (w), 1733 (w), 1590 (w), 1540 (m), 1480 (m), 1465 (m), 1450 (m), 1432 (w), 1376 (m), 1290 (w), 1072 (w), 1050 (w), 1026 (s), 1005 (m), 892 (m), 778 (m), 740 (w)
25	2960 (vs), 2923 (vs), 2836 (m), 2496 (vs), 1540 (m), 1928 (w), 1869 (w), 1480 (m), 1467 (m), 1456 (m), 1447 (m), 1377 (s), 1103 (w), 1074 (m), 1029 (vs), 896 (m), 781 (m)
26	3340 (m) br, 2960 (vs), 2925 (vs), 2868 (s), 2498 (s), 1923 (w), 1883 (w), 1710 (w), 1536 (m), 1480 (m), 1466 (m), 1450 (m), 1376 (s), 1303 (w), 1052 (w), 1027 (m), 957 (m), 892 (m), 778 (m)
27	2962 (vs), 2925 (vs), 2869 (s), 2538 (s), 2501 (s), 1857 (m), 1617 (w), 1525 (m), 1478 (m), 1470 (m), 1452 (s), 1382 (s), 1376 (s), 1043 (vs), 923 (m), 771 (w), 740 (w)

[a] Microcrystalline films obtained by evaporation of solutions. [b] Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [c] Reference 6. [d] Mixture of isomers.

the unit-resolution spectra are consistent with the proposed structures, e.g., loss of ligand or M(ligand) units from the parent ions. Elemental analyses were conducted by E&R Microanalytical Laboratory, Corona, NY 11368.

Materials. The starting material (C_5Me_5)Co($Et_2C_2B_3H_5$) (1) was prepared as reported elsewhere.[3a] Reagent grade dichloromethane and *n*-hexane were stored over molecular sieves, the THF was stored over benzophenone/Na and distilled immediately prior to use.

Synthesis of (C_5Me_5)Co($Et_2C_2B_3H_4$-5-$CH_2C_6H_5$) (3). Complex 1 (0.24 g, 0.77 mmol) was placed in a 100-mL round-bottom flask attached to a vacuum line and fitted with a septum cap, 40 mL of dry THF was added, and the flask was placed in a dry ice/ethanol bath. To the cooled, yellow solution was added, via syringe, an equimolar amount of 1.7 M *tert*-butyllithium in hexane (0.45 mL, 0.77 mmol). The solution was warmed to room temperature, during which time the color changed from yellow to deep orange. After 30 min, 0.20 mL (1.7 mmol) of $BrCH_2C_6H_5$ was added. Within 5 min the solution had become yellow again. After stirring for 1 h, the solution was opened to the air and the solvent removed by rotary evaporation. The residue was dissolved in hexane, the solution was filtered through 2 cm of silica, and the filtrate was taken to dryness. This residue was taken up in hexane and column chromatographed in hexane, yielding two bands, the first of which was pale yellow and consisted of grease and recovered 1. The second, dark yellow, band was collected and dried to give air-stable crystals of 3 (0.249 g, 0.62 mmol, 80%). Anal. Calcd for $CoC_{23}B_3H_{36}$: C, 68.40; H, 8.98. Found: C, 68.55; H, 9.24. Visible–UV absorptions (nm; percent absorbance given in parentheses): 286 (86%), 242 (38%).

Reactions of 1^- with Alkyl Halides. The procedure described above for the preparation of 3 was employed, with modifications in some cases. In each synthesis, 1 was deprotonated with an equimolar amount of 1.7 M *tert*-butyllithium in hexane, after which the alkyl halide was added (via syringe or tip-tube) and workup followed the general scheme outlined above. Except where noted, all products were isolated as yellow crystalline solids. Details of the individual syntheses and variations follow.

(C_5Me_5)Co($Et_2C_2B_3H_4$-5-CH_2CF_3) (4). $BrCH_2CF_3$ (0.4 mL, 4.0 mmol) was added to 1^- (0.339 g, 1.08 mmol) at −78 °C. The solution immediately changed from light orange to a dark red-orange. After stirring at room temperature for 2.5 h, workup was conducted as above. The first band eluted from the column was 1 (0.218 g, 64%). The second band was 4 (0.015 g, 0.04 mmol, 3.5%). Anal. Calcd for $CoF_3C_{18}B_3H_{31}$: F, 14.4; C, 54.62; H, 7.89. Found: F, 14.16; C, 55.90; H 8.20. Visible–UV absorptions: 326 (21%), 284 (95%), 242 (58%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C_6F_5)$ (5). $BrCH_2C_6F_5$ (0.5 mL, 3.3 mmol) was added to 1^- (0.307 g, 0.98 mmol) at −78 °C. The solution immediately turned yellow and was stirred at room temperature for 1 h. The first band off the column was 1 (0.046 g, 15%). The second band, barely separated from the first, was 5 (0.320 g, 0.65 mmol, 66%). Possibly owing to difficulties in separation, a satisfactory elemental analysis was not obtained for this compound, but the proton and boron NMR spectra and mass spectra were consistent with the formula given and gave no indication of major impurities. Visible–UV absorptions: 286 (86%), 236 (49%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C_2H_5)$ (6). $BrCH_2CH_2Me$ (0.15 mL, 1.7 mmol) was added to 1^- (0.190 g, 0.61 mmol) at −78 °C. There was no immediate color change, but after 3.5 h at room temperature the solution was yellow. Chromatography gave one yellow band, 6 (0.175 g, 0.49 mmol, 81%). Anal. Calcd for $CoC_{19}B_3H_{36}$: C, 64.13; H, 10.20. Found: C, 64.52; H, 10.52. Visible–UV absorptions: 286 (78%), 234 (36%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CHMe_2)$ (7). $CH_3CHBrMe$ (0.15 mL, 1.6 mmol) was added to 1^- (0.159 g, 0.51 mmol) at −78 °C. There was no immediate color change; however, following 48 h at room temperature the solution was brown. Although 7 (80 mg, 0.22 mmol, 44%) did not separate cleanly from 1 (40 mg, 25%) on a silica column, an analytically pure sample was obtained by collecting the first part of the band. Anal. Calcd for $CoC_{19}B_3H_{36}$: C, 64.13; H, 10.20. Found: C, 64.56; H, 10.52. Visible–UV absorptions: 330 (13%), 288 (93%), 236 (51%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2CN)$ (8). $BrCH_2CN$ (0.4 mL, 5.7 mmol) was added to 1^- (0.334 g, 1.07 mmol) at 0 °C. The solution immediately turned dark brown. After stirring for 4 h at room temperature, the solution was chromatographed with hexane to give 1 (0.016 g, 5%), $(C_5Me_5)Co(Et_2C_2B_3H_4Br)$ and $(C_5Me_5)Co(Et_2C_2B_3H_3Br_2)$. Subsequent washing with CH_2Cl_2 afforded 8 (0.068 g, 0.19 mmol, 18%) as dark yellow crystals. Anal. Calcd for $CoNC_{18}B_3H_{31}$: N, 3.97; C, 61.28; H, 8.86. Found: N, 3.49; C, 61.44; H, 8.85. Visible–UV absorptions: 326 (22%), 290 (95%), 242 (57%).

Conversion of 8 to $(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2CH_2NH_2)$ (9). According to procedures given elsewhere,[15] 8 (0.071 g, 0.20 mmol) was placed in a two-neck round-bottom flask fitted with a septum. The flask was evacuated, 20 mL of dry THF was added in vacuo, and 0.80 mL of 1.0 M $LiAlH_4$ (0.80 mmol) in THF was added at room temperature. The solution turned orange after 5 min. Following heating at 60 °C under vacuum for 4 h, the solution was cooled and quenched via addition of 3 g of NaOH in 20 mL of H_2O. The solution turned briefly yellow and then greenish black. The THF layer was decanted, taken to dryness, and chromatographed on a silica plate in 1:1 $MeOH/CHCl_3$. A yellow band with R_f 0.2 was collected, affording 9 (0.036 g, 0.10 mmol, 50%), a yellow oil which slowly decomposed in air. Complex 8 was recovered in 22% yield. The characterization of air-sensitive 9 was straightforward, based on its ^1H and ^{11}B NMR and mass spectra and its direct synthesis from 8.

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2CH_2CN)$ (10). $BrCH_2CH_2CN$ (0.15 mL, 1.8 mmol) was added to 1^- (0.235 g, 0.75 mmol) at −78 °C. The solution quickly turned yellow. After warming to room temperature and stirring for 0.5 h, the solution was placed on a silica column and washed with hexane to give 1 (99% recovery). A subsequent elution with 1:1 hexane/CH_2Cl_2 gave 10 (2 mg) as a pale yellow powder, characterized by ^1H NMR and mass spectra. Visible–UV absorptions: 328 (19%), 286 (92%), 248 (48%), 234 (49%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2OMe)$ (11). $BrCH_2OMe$ (0.4 mL, 4.9 mmol) was added to 1^- (0.315 g, 1.00 mmol) at 0 °C. The solution turned greenish brown. After 1 h at room temperature the solution was green. The solution was placed on a silica column, washed with CH_2Cl_2, and then eluted with 1:1 hexane/CH_2Cl_2. The first band eluted was 1 (0.067 g, 21%), and the second was 11 (0.233 g, 0.65 mmol, 65%). Anal. Calcd for $CoOC_{18}B_3H_{34}$: C, 60.42; H, 9.58. Found: C, 60.68; H, 9.80. Visible–UV absorptions: 328 (12%), 284 (90%), 236 (42%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C(O)Me)$ (12). Technical grade (90%) $ClCH_2C(O)Me$ (0.45 mL, 5.0 mmol) was added to 1^- (0.304 g, 0.92 mmol) at 0 °C. After 2 h at room temperature the solution was yellow. The solution was placed on a silica column, washed with CH_2Cl_2, and eluted with 1:1 hexane/CH_2Cl_2. The first band eluted was 1 (0.172 g, 57%), and the second was 12 (0.080 g, 0.22 mmol, 24%). Anal. Calcd for $CoOC_{19}B_3H_{34}$: C, 61.70; H, 9.27. Found: C, 61.93; H, 9.50. Visible–UV absorptions: 326 (12%), 286 (86%), 246 (33%), 232 (43%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C{\equiv}CH)$ (13). $BrCH_2CCH$ (0.40 mL, 3.6 mmol) was added to 1^- (0.303 g, 0.96 mmol) at −78 °C. The solution immediately turned yellow-brown. The solution was stirred at room temperature for 1 h, placed on a silica column, and washed with hexane to give 1 (0.036 g, 12%). The CH_2Cl_2 wash was column-chromatographed on silica gel in 1:1 hexane/CH_2Cl_2, yielding 13 (0.272 g, 0.77 mmol, 80%). Anal. Calcd for $CoOC_{19}B_3H_{32}$: C, 64.86; H, 9.17. Found: C, 64.66; H, 9.40. Visible–UV absorptions: 322 (17%), 286 (94%), 238 (51%).

Preparation of $MeC{\equiv}CCH_2OSO_2Me$. Using a modified literature procedure,[16] $MeCCCH_2OH$ (3.3 mL, 44 mmol) and Et_3N (6.1 mL, 44 mmol) were dissolved in 40 mL of CH_2Cl_2 at −5 °C (salt water–ice). $MeSO_2Cl$ was added over 10 min, and the solution was stirred for an additional 45 min. The solution was diluted by the addition of CH_2Cl_2 (40 mL) and washed with four 15-mL portions of H_2O. The organic layer was dried over $MgSO_4$ for 16 h and then evaporated to dryness. The residue was taken up and column-chromatographed in 1:1 hexane/Et_2O, giving a clear oil (4.45 g, 30 mmol, 68%). The product was identified by ^1H NMR and mass spectroscopy.

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C{\equiv}CMe)$ (14). $MeC{\equiv}CCH_2OSO_2Me$ (1.5 mL, 1.0 mmol) was added to 1^- (0.314 g, 1.00 mmol) at −78 °C. The solution immediately turned yellow. The solution was stirred at room temperature for 1 h, washed through silica with CH_2Cl_2, and eluted with hexane to give 1 (0.018 g, 6%). Subsequent elution with CH_2Cl_2 gave 14 (0.318 g, 0.87 mmol, 87%). Anal. Calcd for $CoC_{20}B_3H_{34}$: C, 65.66; H, 9.37. Found: C, 65.69; H, 9.59. Visible–UV absorptions: 334 (11%), 288 (92%), 242 (51%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C{\equiv}CCH_2Cl)$ (15) and $[(C_5Me_5)Co(Et_2C_2B_3H_4)CH_2]_2C{\equiv}C$ (16). $ClCH_2CCCH_2Cl$ (0.1 mL, 1.23 mmol) was added to 1^- (0.373 g, 1.19 mmol) at room temperature, stirred for 1 h, and washed through silica with hexane to give 1 (0.061 g, 16%). The silica was washed with CH_2Cl_2 and column-chromatographed in 3:1 hexane/CH_2Cl_2. The first band was yellow 15 (0.229 g, 0.57 mmol, 48%), and the second band was yellow 16 (0.077 g, 0.11 mmo, 19%). Anal. Calcd for $CoClC_{20}B_3H_{33}$ (15): C, 60.01; H, 8.31. Found: C, 60.16; H, 8.44. Visible–UV absorptions: 330 (14%), 320 (18%), 286 (94%), 238 (51%). Anal. Calcd for $Co_2C_{38}B_6H_{62}$ (16): C, 63.81; H, 9.22. Found: C, 63.63; H, 9.04. Visible–UV absorptions: 324 (14%), 286 (91%), 238 (44%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2CH{=}CH_2)$ (17). $BrCH_2CHCH_2$ (0.16 mL, 1.85 mmol) was added to 1^- (0.284 g, 0.90 mmol) at −78 °C. The solution immediately turned yellow. After 45 min at room temperature the dark golden yellow solution was washed through silica with CH_2Cl_2 and eluted with hexane. The first band eluted was yellow 1 (0.017 g, 6%), and the second was yellow 17 (0.227 g, 0.78 mmol, 87%). Anal. Calcd for $CoC_{19}B_3H_{34}$: C, 64.49; H, 9.69. Found: C, 64.03; H, 9.88. Visible–UV absorptions: 330 (21%), 292 (92%), 242 (71%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C(O)OMe)$ (18) and $(C_5Me_5)Co(Et_2C_2B_3H_2$-5-Br-4,6-$[CH_2C(O)OMe]_2)$ (19). $BrCH_2C(O)OMe$ (0.37 mL, 3.9 mmol) was added to 1^- (0.309 g, 0.98 mmol) at room temperature. The solution was stirred for 0.5 h, taken to dryness, and washed through silica with CH_2Cl_2. The residue was column-chromatographed with hexane, yielding three bands. The first was 1 (0.063 g, 0.16 mmol), the second was $(C_5Me_5)Co$-

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$(Et_2C_2B_3H_4Br)$ (0.063 g, 16%), and the third was $(C_5Me_5)Co(Et_2C_2B_3H_3Br_2)$ (0.012 g, 3%). Elution with CH_2Cl_2 afforded two more bands, 18 (0.213 g, 0.55 mmol, 56%) and 19 (0.011 g, 0.02 mmol, 2%). Anal. Calcd for $CoO_2C_{19}B_3H_{34}$ (18): C, 59.15, H, 8.88. Found: C, 58.99; H, 9.07. Visible–UV absorptions: 326 (15%), 284 (91%), 238 (48%). Anal. Calcd for $BrCoO_4C_{22}B_3H_{37}$ (19): Br, 14.89; C, 49.23; H, 6.95. Found: Br, 15.04; C, 49.26; H, 6.99. Visible–UV absorptions: 332 (16%), 290 (89%), 248 (44%), 240 (47%).

Conversion of 18 to $(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C(O)OH)$ (20). According to the method described elsewhere,[12] Me_3SiI (0.16 g, 0.80 mmol) and 18 (0.12 g, 0.38 mmol) under a nitrogen atmosphere were placed in a tube fitted with a vacuum stopcock. The solution was frozen and the tube evacuated. The lower part of the tube was placed in a boiling water bath for 2 h, after which the initially red solution became yellow brown. The solution was opened to the air and diluted with 10 mL of diethyl ether (tech grade). This solution was then washed with two 10-mL portions of 0.5 M NaOH, and the aqueous layers were combined and acidified to a pH of 3 using 1 M HCl. The yellow precipitate which formed was collected and washed with 50 mL of H_2O. The solid was dissolved in CH_2Cl_2, filtered, and evaporated to dryness, affording yellow crystals of 20 (0.098 g, 0.26 mmol, 68%). Anal. Calcd for $CoO_2C_{18}B_3H_{32}$ (20): C, 58.15; H, 8.67. Found: C, 57.96; H, 8.77. Visible–UV absorptions: 294 (91%), 242 (65%). The ether layer was found to contain a trace of $(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C(O)OEt)$ (21), identified from its ^1H NMR and mass spectra. Visible–UV absorptions for 21: 324 (18%), 286 (92%), 238 (56%).

Conversion of 18 to $(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2C(O)NH_2)$ (22). According to the procedure of Bashra et al.,[17] 18 (0.098 g, 0.25 mmol) was placed in a tip tube attached to a 25-mL round-bottom flask fitted with a septum. The flask was evacuated, and 10 mL of dry CH_2Cl_2 was condensed in. NH_3 (0.55 mmol) was added, and as the solution warmed, $AlMe_3$ (0.28 mL of a 2 M solution in hexane, 0.56 mmol) was added via syringe. The solution was stirred for 15 min, 0.25 mmol of 18 was tipped in, and the solution was heated at 40 °C for 15 h. Upon cooling, 10 mL of 1 M HCl was introduced with a syringe, the organic layer was collected, and the aqueous layer was washed with 10 mL of CH_2Cl_2. The organic fractions were combined, the solvent was removed, the residue was taken up in MeOH, and the solution was filtered through 2 cm of silica. The solution was evaporated and the residue chromatographed in CH_2Cl_2, giving a single yellow band, 22 (0.071 g, 0.19 mmol, 76%). Anal. Calcd for $CoONC_{18}B_3H_{33}$ (22): N, 3.78; C, 58.30; H, 8.97. Found: N, 3.65; C, 58.49; H, 8.97. Visible–UV absorptions: 326 (20%), 290 (92%), 282 (90%), 248 (52%), 240 (57%).

$(C_5Me_5)Co(Et_2C_2B_3H_4$-5-$CH_2OC(O)Me)$ (23), $[(C_5Me_5)Co(Et_2C_2B_3H_4)CH_2]_2O$ (24), and $[(C_5Me_5)Co(Et_2C_2B_3H_4)CH_2O]_2CH_2$ (25). $BrCH_2OC(O)Me$ (0.30 mL, 3.1 mmol) was added to 1^- (0.293 g, 0.93 mmol) at 0 °C. The solution was stirred for 1 h, taken to dryness, and washed through silica with CH_2Cl_2. The residue was chromatographed with hexane, giving yellow 1 (0.112 g, 38% recovery). Elution with 1:1 hexane/CH_2Cl_2 afforded three bands: 24 (9 mg, 0.01 mmol, 2%), 25 (21 mg, 0.03 mmol, 6%), 23 (0.091 g, 0.24 mmol, 25%). Anal. Calcd for $CoO_2C_{19}B_3H_{34}$ (23): C, 59.15; H, 8.88. Found: C, 59.28; H, 9.03. Visible–UV absorptions for 23: 328 (21%), 288 (95%), 242 (63%). Anal. Calcd for $Co_2OC_{34}B_6H_{62}$ (24): C, 60.99; H, 9.33. Found: C, 62.21; H, 9.60. Visible–UV absorptions for 24: 360 (12%), 286 (93%), 238 (60%). Anal. Calcd for $Co_2O_2C_{35}B_6H_{64}$ (25): C, 60.09; H, 9.22. Found: C, 60.41; H, 9.47. Visible–UV absorptions for 25: 326 (12%), 284 (87%), 236 (47%).

Conversion of 23 to $(C_5Me_5)Co(Et_2C_2B_3H_4$–$CH_2OH)$ (26). Complex 23 (0.040 g, 0.10 mmol) was dissolved in 50 mL of ethanol in a 100-mL round-bottom flask. Excess NaOH (0.5 g) was added and the solution was refluxed for 0.5 h at which point it was greenish in color. The solution was cooled, acidified (pH paper) with 1 M HCl, evaporated to dryness, the residue was dissolved in CH_2Cl_2, and the resulting solution was filtered. The residue was thin-layer-chromatographed in 1:1 hexane/CH_2Cl_2. The third band (R_f 0.1) was 26 (0.025 g, 0.07 mmol, 73%). Anal. Calcd for $CoOC_{17}B_3H_{32}$ (26): C, 59.39; H, 9.38. Found: C, 59.72; H, 9.47. Visible–UV absorptions: 330 (20%), 286 (94%), 240 (61%).

$(C_5Me_5)Co(Et_2C_2B_3H_3$–$C_4H_8O)$ (27). Complex 27 was obtained in trace amounts in the preparations of 4, 6, 7, and 10, and in attempted (unsuccessful) reactions of 1^- with 1-bromoadamantane, 2-bromoadamantane, and *tert*-butyl bromide. These were all experiments which gave low or zero yields of product and usually involved extended reaction times. Quantities of 27 were accumulated over a number of experiments, and the compound was purified by TLC in 1:1 hexane/CH_2Cl_2 (R_f 0.3), collected as yellow crystals, and characterized from its NMR and mass spectra. Extended reflux of 1^- in THF did not produce a significant amount of 27.

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