Cobaltocenium Metallacarboranide Mixed-Sandwich Salts, $Cp_2Co^+(Et_2C_2B_4H_4)_2M^-$ (M = Co^{III}, Fe^{III}) and $Cp_2Co^+(Et_2C_2B_3H_4\text{-}X)Co^{III}(Et_2C_2B_4H_4)^-$ (X = H, Me)[‡,1,2]

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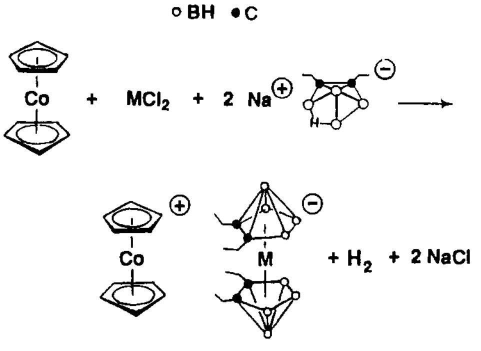
The first metallocenium metallacarboranide salts have been synthesized and isolated. The title compounds were prepared by reaction of cobaltocene and $CoCl_2$ or $FeCl_2$ with the carborane anion $Et_2C_2B_4H_5^-$ in THF solution, in which the oxidation of two M(II) metal centers to M(III) is accompanied by reduction of two B–H–B bridging protons to H_2. Orange-red, air-stable, crystalline, diamagnetic $Cp_2Co^+[(Et_2C_2B_4H_4)_2Co^{III}]^-$ (**1**) was characterized via NMR and UV–visible spectroscopy and an X-ray crystal structure determination, which revealed pairwise alignment of cobaltocenium and cobaltacarboranide sandwich units. Association of these units is also suggested in the FAB mass spectra of **1**. Decapitation of **1** in acidic media gave the *nido,closo*-cobaltacarborane $(Et_2C_2B_3H_5)Co(Et_2C_2B_4H_4)$, which was converted to its *B*5-methyl derivative; reactions of the bridge-deprotonated anions of both compounds with cobaltocene afforded the corresponding red-brown diamagnetic cobaltocenium salts $Cp_2Co^+(Et_2C_2B_3H_4\text{-}X)Co^{III}(Et_2C_2B_4H_4)^-$ (X = H, Me). The dark red, air-stable, crystalline, paramagnetic iron salt $Cp_2Co^+[(Et_2C_2B_4H_4)_2Fe^{III}]^-$ was synthesized in a procedure similar to that used for **1**. The diamagnetic anion $(Et_2C_2B_4H_4)_2Fe^{II}H^-$, detected in NMR spectra, was obtained as a minor product. Crystal data for **1**: mol wt 506.9; space group $P\bar{1}$; $Z = 4$, $a = 12.877$ (4) Å, $b = 16.554$ (5) Å, $c = 12.848$ Å, $\alpha = 92.01$ (3)°, $\beta = 90.12$ (2)°, $\gamma = 98.56$ (3)°, $V = 2707$ Å^3; $R = 0.035$ for 5051 reflections having $I > 3\sigma(I)$.

Introduction

Organometallic solid-state compounds are attracting increasing attention in the designed synthesis of new electronically or magnetically active molecular materials.[3] Prominent among these are metallocene-based systems, including covalently bonded assemblies as well as metallocenium salts. Illustrative of the former category are the recently reported silyl-bridged complexes constructed from ferrocene, nickelocene, and/or chromocene units,[4a–c] while examples of the latter class include $CpFe(arene)^+TCNQ^-$,[4d] $Cp^*{}_3Ru_2{}^+$ salts of $TCNQ^-$, $TCNE^-$, and $C_3[C(CN)_2]_3{}^-$,[4e] $Cp^*{}_2Cr^+TCNQ^-$,[4f] and $Cp_2Co^+S_3N_3{}^-$,[4g] where $Cp^* = \eta^5\text{-}C_5Me_5$, TCNQ = 7,7,8,8-tetracyanoquinodimethane, and TCNE = tetracyanoethylene. At a practical level, electropolymerized metallocenes have been incorporated into a redox diode.[5] The attraction of metal sandwiches as building blocks for new materials derives, in general, from their stability, synthetic versatility, and electronic tunability and from the prospect that with suitable tailoring they can be stacked in crystal lattices so as to promote controlled spin and/or charge transfer between metal centers.

Scheme I



1 M = Co
4 M = Fe

Transition-metal metallacarborane sandwich complexes featuring C_2B_3 rings or C_2B_4 pyramidal ligands are electronic and steric analogues of the metallocenes.[6] A particularly clear demonstration of this close relationship is the synthesis and structural characterization[1d] of $Cp^*Co(C_2B_3Me_5H_2)$, an isoelectronic and isosteric counterpart of the decamethylcobaltocenium ion, $Cp^*{}_2Co^+$. As a group, moreover, the metallacarboranes are more versatile and chemically stable than the metallocenes[1,6,7] and are readily amenable to triple-decker and

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[‡] The systematic name for this class of ions is metallacarbaborate.

[†] Deceased March 9, 1993, in the United Kingdom. This paper is dedicated to the memory of Dr. Waterworth.

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Table I. ^{11}B and ^{1}H FT NMR Data

115.8-MHz ^{11}B NMR Data

compd	$\delta^{a,b}$	rel areas
Cp_2Co^+ $[(Et_2C_2B_4H_4)_2Co]^-$ (**1**)	4.6, –0.75	1:3
$(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_5)$ (**3a**)	4.4, 2.2, 1.0 sh, 0.0 sh, –2.9	1:2:1:1:2
$(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_4\text{-5-Me})$ (**3b**)	13.8, 2.3, –0.5, –6.0, –8.0	1:1:2:1:2
Cp_2Co^+ $[(Et_2C_2B_4H_4)_2FeH]^-$ (**5**)	9.6, 5.8, 1.6	1:2:1

300-MHz ^{1}H NMR Data

compd	δ^{c-e}
1[f]	5.92 s (C_5H_5), 2.53 m (ethyl CH_2), 2.24 m (ethyl CH_2), 1.15 t (ethyl CH_3)
1[g]	5.81 s (C_5H_5), 2.37 m (ethyl CH_2), 2.09 m (ethyl CH_2), 1.03 t (ethyl CH_3)
3a[g]	5.94 s (C_5H_5), 2.49 m (ethyl CH_2), 2.18 m (ethyl CH_2), 2.11 m (ethyl CH_2), 1.20 t (ethyl CH_3), 1.11 t (ethyl CH_3), –6.56 br s (B–H–B)
3b[g]	5.93 s (C_5H_5), 2.52 m (ethyl CH_2), 2.22 m (ethyl CH_2), 2.07 m (ethyl CH_2), 1.19 t (ethyl CH_3), 1.10 t (ethyl CH_3), 0.60 s (B–CH_3), –5.76 br s (B–H–B)
4[g]	15.9 br s, 9.2 br s, 5.74 s (C_5H_5), –2.1 br s
5[g]	5.81 s (C_5H_5), 2.48 m (ethyl CH_2), 2.15 m (ethyl CH_2), 1.04 t (ethyl CH_3), –7.67 br s (FeH)

[a] Shifts relative to $BF_3{\cdot}OEt_2$; positive values downfield. H–B coupling was not resolved in these spectra. [b] Dichloromethane solution. Integrated peak areas in all cases are consistent with the assignments given. [c] Legend: m = multiplet, s = singlet, sb = broad singlet, d = doublet, t = triplet, q = quartet. [d] B–$H_{terminal}$ resonances are broad quartets and mostly obscured by other signals. [e] Shifts relative to $(CH_3)_4Si$; all spectra proton-decoupled. [f] CD_2Cl_2 solution. [g] DMSO-d_6 solution.

tetradecker stacking.[1e,6] We have reported elsewhere[8] on the preparation of covalently linked oligomers and higher polymers incorporating tetradecker metallacarborane stacks. In the present work we have explored the synthesis of mixed-sandwich metallocenium metallacarborane salts, reasoning that the combination of metallocene and sterically compatible metallacarborane sandwich units in the same crystal lattice may allow the design of new families of electronically tunable organometallic solid-state materials.

Results

General Approach. No previous examples of metallocenium-metallacarboranide salts have been described.[9] The direct synthesis of such compounds via electron transfer, *e.g.*, in processes of the type

$$(Et_2C_2B_4H_4)_2M^{IV} + Cp_2Co \rightarrow Cp_2Co^+[(Et_2C_2B_4H_4)_2M^{III}]^-$$

might be considered, but the problem is that M(IV) complexes of small carboranes are rare.[10] Although the cyclooctatetraenyl species $(\eta^8\text{-}C_8H_8)M^{IV}(Et_2C_2B_4H_4)$ (M = V, Ti) have been reported,[10a] the only characterized example of a $(C_2B_4)_2M^{IV}$ system is the extremely air-sensitive chromium sandwich[10b] $[(SiMe_3)_2C_2B_4H_4]_2Cr$. However, we have circumvented this difficulty via an alternative strategy that involves the net reduction of carborane bridge protons to H_2 and does not require a formal +4 metal in the neutral precursor complex.

$Cp_2Co^+[(Et_2C_2B_4H_4)_2Co^{III}]^-$. Treatment of the $Et_2C_2B_4H_5^-$ ion with $CoCl_2$ in the presence of cobaltocene in cold dry THF, followed by extraction with CH_2Cl_2 and crystallization from that solvent, afforded the desired salt **1** (Scheme I). The reaction is assumed to proceed through formation of a cobalt-bridged $(Et_2C_2B_4H_5)_2\text{-}\mu,\mu'\text{-}Co^{II}$ intermediate that is subsequently oxidized to the $[(Et_2C_2B_4H_4)_2Co^{III}]^-$ sandwich ion with reduction of its two B–H–B bridging protons to H_2; the redox process is balanced by the oxidation of Cp_2Co to Cp_2Co^+.

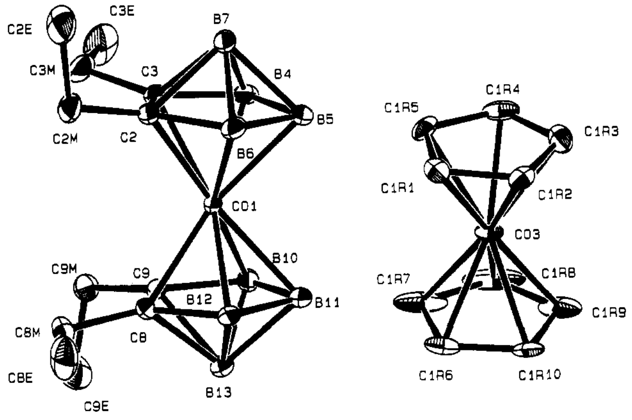

Figure 1. Molecular structure of $Cp_2Co^+(Et_2C_2B_4H_4)_2Co^-$ (**1**), showing one of the two crystallographically independent ion pairs (hydrogen atoms omitted). Nearest cation–anion distances (Å) are as follows: C1R1–B5, 3.601 (7); C1R1–B4, 3.613 (8); C1R1–B10, 3.637 (8); C1R1–B11, 3.696 (7).

Compound **1** was isolated in 40% yield as orange-red, diamagnetic, air-stable crystals. In CH_2Cl_2 solution **1** exhibits slow decomposition, but in $CHCl_3$ it degrades rapidly even under an N_2 atmosphere. The salt is not appreciably soluble in water, but it does dissolve in 1:1 DMSO/water to give stable solutions that show no decomposition over several months. The elemental analysis, ^{1}H and ^{11}B NMR data (Table I), and FAB mass spectra of **1** support the assigned formula, and some ion pairing is suggested both in the mass spectrum and in the crystal structure, to be discussed. The NMR data are typical for diamagnetic metal sandwich complexes incorporating a 7-vertex MC_2B_4 cluster, although the boron spectrum exhibits only two signals in a 3:1 ratio, reflecting overlap of the area 2 peak with one of the area 1 resonances.

An X-ray crystal structure analysis of **1** revealed a triclinic unit cell containing four Cp_2Co^+ $(Et_2C_2B_4H_4)_2Co^-$ pairs, as shown in Figures 1 and 2. Relevant data on the structure determination and refinement are collected in Table II, and bond distances and angles are listed in Table III. The asymmetric unit consists of two crystallographically independent cobaltocenium cations and two cobaltacarboranide anions. As can be seen in the stereoview (Figure 2), the two $(Et_2C_2B_4H_4)_2Co^-$ anions are mutually oriented at ~90°; each anion is roughly parallel to its nearest neighbor (paired) cobaltocenium cation. The apparent ion pairing is not

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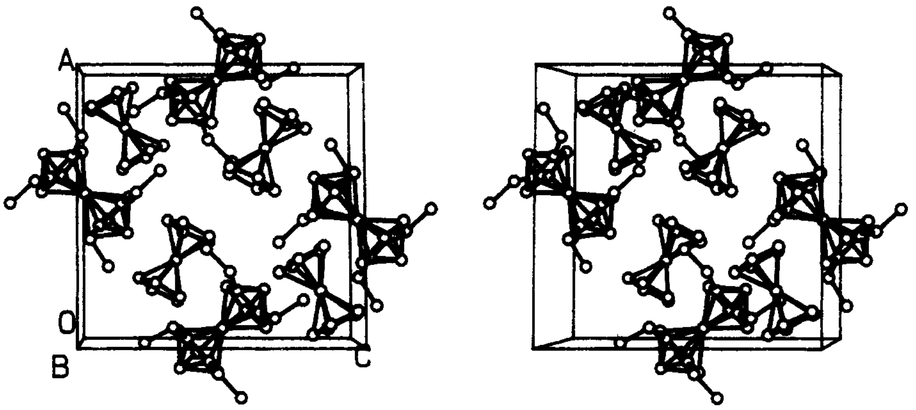

Figure 2. Stereoview of the unit cell in **1**.

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

empirical formula	$Co_2C_{22}B_8H_{38}$	Z	4
fw	506.9	μ, cm^{-1} (Mo Kα)	12.32
cryst color, habit	dark prism	transm factors	0.90–1.00
cryst dimens, mm	0.43 × 0.32 × 0.24	λ, Å	0.7107
space group	$P\bar{1}$	D(calcd), g cm^{-3}	1.244
a, Å	12.877(4)	$2\theta_{max}$, deg	46
b, Å	16.554(5)	no. of reflcns measd	7547
c, Å	12.848(3)	no. of reflcns obsd ($I > 3.00\sigma(I)$)	5051
α, deg	92.01(3)		
β, deg	90.12(2)	R	0.035
α, deg	98.56(3)	R_w	0.045
V, Å^3	2707	largest peak in final diff map, e/Å^3	0.18

reflected in any particularly short cobaltocenium-cobaltacarboranide distances that would indicate covalent bonding interaction; the smallest nonhydrogen contact is 3.6 Å between C1R1 and B5. However, the FAB mass spectrum contains an intense peak grouping at m/z 479 corresponding to $Cp_2Co^+(Et_2C_2B_4H_4)_2Co^-$ with loss of C_2H_5, and higher associations are suggested by the presence of envelopes up to m/z 957 (2 [$Cp_2Co^+(Et_2C_2B_4H_4)_2Co^-$] with loss of Co).

The two independent $(Et_2C_2B_4H_4)_2Co^-$ anions have normal molecular parameters, and the carborane ligands in each are nearly eclipsed; the respective C_2B_3 ring planes are tilted slightly (dihedral angle 5.3°) such as to increase the interligand carbon–carbon distances. The eclipsed conformation, placing the four ethyl groups on the same side of the molecule, leaves the BH vertices relatively accessible and permits closer contact with the cobaltocenium ions, thereby presumably facilitating electrostatic ion pairing.

$Cp_2Co^+(Et_2C_2B_4H_4)Co^{III}(Et_2C_2B_3H_4\text{-}5\text{-}R)^-$ (R = H, Me). The salt I was readily decapitated on treatment with acidified THF in air, generating the neutral *nido,closo*-cobaltacarborane **2a** in over 90% yield (Scheme II). Complex **2a** and its tetra-*C*-methyl homologue are previously described species.[11] The deprotonation of **2a** with butyllithium followed by reaction with $CoCl_2$ and NaCp afforded the red-brown cobaltocenium salt Cp_2Co^+-$(Et_2C_2B_4H_4)Co^{III}(Et_2C_2B_3H_5)^-$ (**3a**), shown in Scheme II. A similar sequence employing the *B5*-methyl derivative **2b** gave the corresponding *B*-methyl product **3b**. As expected, **3a** and **3b** are diamagnetic and exhibit normal ^{1}H and ^{11}B NMR spectra. However, an attempted X-ray diffraction study of **3a** revealed an unexpectedly large unit cell with one dimension over 40 Å long. Unfortunately, owing to weak diffraction the available data do not allow solution of the detailed structure; efforts to obtain better data are continuing.

$Cp_2Co^+[(Et_2C_2B_4H_4)_2Fe^{III}]^-$ and Cp_2Co^+ $(Et_2C_2B_4H_4)_2Fe^{II}H^-$. The red-orange paramagnetic iron(III) salt Cp_2Co^+-$[(Et_2C_2B_4H_4)_2Fe^{III}]^-$ (**4**) was prepared by a route similar to that employed for **1** (Scheme I), but with some adjustment of experimental conditions. Recrystallization of the CH_2Cl_2-soluble products gave dark red crystals of **4** in 25% yield, together with ca. 1% of the diamagnetic species $Cp_2Co^+(Et_2C_2B_4H_4)_2Fe^{II}H^-$ (**5**). Isolation of pure samples of the latter salt, detectable in proton NMR spectra of **4**, has not been achieved. While the iron compounds are reasonably air-stable as dry solids, they are unstable in solution on silica and hence cannot be chromatographically purified by standard methods. As in the case of **3a**, only weak diffraction was observed on the paramagnetic salt **4**, refinement of which indicates a large unit cell with one dimension exceeding 35 Å. A detailed structure is not yet available, but a curious crystal packing is apparent in which there appear to be three cation–anion pairs in the asymmetric unit with the three ferracarborane cations in parallel alignment. Attempts at further data collection on this compound are in progress.

Magnetic measurements on the paramagnetic solid **4** as a function of temperature[12] are consistent with a spin $^1/_2$ system, but the temperature dependence is unusual and is the subject of further investigation.

Concluding Remarks

Mixed-sandwich metallocenium metallacarboranide salts present possibilities for controlled crystal lattice stacking in which the degree of intermolecular electron transfer is modulated via appropriate substitution on the carborane ligands, selection of metals, and adjustment of metal oxidation states. Given the inherent stability and tailorability of the metallacarborane cluster units,[1c,1d,6,7] there appear to be reasonable prospects for obtaining novel types of electroactive and/or magnetoactive stacked compounds through this approach. We are currently investigating the extension of this family to salts of triple-decker and tetradecker metallacarborane sandwich anions,[1e,6] which may lead to facile intervalence electron transfer via sterically enforced stacking of these relatively bulky molecular ions.

Experimental Section

Except where otherwise stated, materials, instrumentation, and procedures were as given in earlier publications.[1] Elemental analyses were obtained either in this department on a Perkin-Elmer 2400 CHN analyzer using cyclohexanone 2,4-dinitrophenylhydrazone as a standard (we thank Kenneth Stockman for performing the analyses), or by E&R Microanalytical Laboratory, Corona, NY. Column chromatography was conducted on silica gel 60 (Merck), and thick-layer chromatography was carried out on precoated silica gel plates (Merck). Unless otherwise indicated, all syntheses were conducted under vacuum or an atmosphere of nitrogen. Workup of products was conducted in air using benchtop procedures.

Synthesis of $Cp_2Co^+(Et_2C_2B_4H_4)_2Co^-$ (1). A 774-mg (6.00-mmol) sample of $CoCl_2$ was placed in a 3-neck 100-mL flask (A) which was

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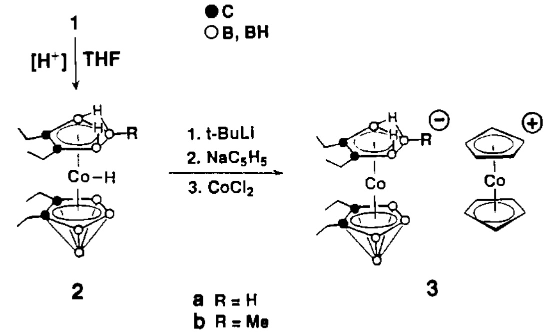
(12) We thank Professor Gordon Yee, University of Colorado, for these measurements.

Table III. Bond Distances (Å) and Selected Bond Angles (deg) for Cp_2Co^+ $[(Et_2C_2B_4H_4)_2Co]^-$ (**1**)

			Bond Distances				
Co1–C2	2.051(5)	Co3–C1R9	2.017(5)	C8–B13	1.750(7)	C21–B25	1.760(7)
Co1–C3	2.063(5)	Co3–C1R10	2.026(5)	C9–C9M	1.517(6)	C21M–C21E	1.539(7)
Co1–C8	2.065(5)	Co4–C2R1	2.009(5)	C9–B10	1.567(7)	B22–B23	1.686(8)
Co1–C9	2.048(5)	Co4–C2R2	2.017(5)	C9–B13	1.755(7()	B22–B25	1.793(8)
Co1–B4	2.094(5)	Co4–C2R3	2.023(5)	C9M–C9E	1.537(7)	B23–B24	1.682(9)
Co1–B5	2.108(5)	Co4–C2R4	2.014(5)	B10–B11	1.685(8)	B23–B25	1.749(8)
Co1–B6	2.110(6)	Co4–C2R5	2.008(5)	B10–B13	1.793(8)	B24–B25	1.796(8)
Co1–B10	2.109(6)	Co4–C2R6	2.030(5)	B11–B12	1.686(8)	C1R1–C1R2	1.410(7)
Co1–B11	2.109(6)	Co4–C2R7	2.024(5)	B11–B13	1.756(8)	C1R1–C1R5	1.427(7)
Co1–B12	2.111(5)	Co4–C2R8	2.009(6)	B12–B13	1.775(8)	C1R2–C1R3	1.409(7)
Co2–C14	2.051(4)	Co4–C2R9	2.030(6)	C14–C14M	1.505(7)	C1R3–C1R4	1.403(8)
Co2–C15	2.057(5)	Co4–C2R10	2.030(5)	C14–C15	1.472(6)	C1R4–C1R5	1.398(7)
Co2–C20	2.050(5)	C2M–C2	1.509(7)	C14–B18	1.552(7)	C1R6–C1R7	1.421(7)
Co2–C21	2.054(5)	C2M–C2E	1.522(8)	C14–B19	1.752(7)	C1R6–C1R10	1.410(7)
Co2–B16	2.096(6)	C2–C3	1.470(7)	C14M–C14E	1.536(7)	C1R7–C1R8	1.40(1)
Co2–B17	2.117(6)	C2–B6	1.576(7)	C15–C15M	1.523(7)	C1R8–C1R9	1.40(1)
Co2–B18	2.097(6)	C2–B7	1.779(7)	C15–B16	1.544(7)	C1R9–C1R10	1.429(8)
Co2–B22	2.104(6)	C3M–C3	1.510(7)	C15–B19	1.765(7)	C2R1–C2R2	1.420(7)
Co2–B23	2.106(6)	C3M–C3E	1.534(8)	C15M–C15E	1.522(7)	C2R1–C2R5	1.400(8)
Co2–B24	2.107(6)	C3–B4	1.560(7)	B16–B17	1.685(8)	C2R2–C2R3	1.421(7)
Co3–C1R1	2.015(5)	C3–B7	1.763(7)	B16–B19	1.786(8)	C2R3–C2R4	1.409(8)
Co3–C1R2	2.022(5)	B4–B5	1.684(8)	B17–B18	1.664(9)	C2R4–C2R5	1.365(8)
Co3–C1R3	2.018(5)	B4–B7	1.765(8)	B17–B19	1.745(8)	C2R6–C2R7	1.447(8)
Co3–C1R4	2.010(5)	B5–B6	1.688(8)	B18–B19	1.784(8)	C2R6–C2R10	1.416(7)
Co3–C1R5	2.014(5)	B5–B7	1.751(8)	C20–C21	1.467(7)	C2R7–C2R8	1.40(1)
Co3–C1R6	2.020(5)	B6–B7	1.812(8)	C20–B24	1.551(7)	C2R8–C2R9	1.42(1)
Co3–C1R7	2.030(6)	C8M–C8	1.517(7)	C20–B25	1.770(7)	C2R9–C2R10	1.423(7)
Co3–C1R8	2.003(6)	C8M–C8E	1.513(7)	C20–C20M	1.520(7)		
C8–C9	1.468(6)	C21–C21M	1.516(7)	C20M–C20E	1.518(8)		
C8–B12	1.561(7)	C21–B22	1.550(8)				
			Selected Bond Angles				
C2M–C2–C3	123.7(4)	C14M–C14–C15	122.1(4)	C8M–C8–B12	126.5(4)	Co2–C20–C20M	135.1(4)
C2M–C2–B6	122.3(5)	C14M–C14–B18	124.5(4)	C8M–C8–B13	133.5(4)	C20M–C20–C21	120.1(4)
C2M–C2–B7	132.5(4)	C14M–C14–B19	132.4(4)	C9–C8–B12	112.3(4)	C20M–C20–B24	126.6(5)
C3–C2–B6	113.3(4)	C15–C14–B18	112.9(4)	Co1–C8–C8M	135.8(3)	C20M–C20–B25	133.4(4)
Co1–C2–C2M	137.1(4)	Co2–C14–C14M	136.0(3)	C8M–C8–C9	120.8(4)	C21–C20–B24	112.9(4)
C2–C2M–C2E	111.3(5)	C14–C14M–C14E	111.7(4)	C8–C8M–C8E	114.2(4)	C20–C20M–C20E	115.5(5)
C3M–C3–B4	127.4(5)	Co2–C15–C15M	135.6(3)	C9M–C9–B10	123.5(4)	Co2–C21–C21M	135.6(3)
C3M–C3–B7	132.6(4)	C14–C15–C15M	120.1(4)	C9M–C9–B13	134.2(4)	C20–C21–C21M	122.3(4)
C2–C3–C3M	120.1(4)	C14–C15–B16	112.0(4)	C8–C9–C9M	122.8(4)	C20–C21–B22	113.2(4)
C2–C3–B4	112.1(4)	C15M–C15–B16	127.4(4)	C8–C9–B10	113.3(4)	C21M–C21–B22	124.1(5)
Co1–C3–C3M	136.7(3)	C15M–C15–B19	133.2(4)	Co1–C9–C9M	134.7(3)	C21M–C21–B25	132.9(4)
C3–C3M–C3E	113.3(5)	C15–C15M–C15E	114.3(4)	C9–C9M–C9E	112.1(4)	C21–C21M–C21E	111.8(1)

Scheme II



attached to a vacuum line via a vertical column containing a frit. A two-neck flask (B), which was equipped with a septum and attached to the column above the frit, was charged with ca. 12 mmol of NaH. Both flasks contained magnetic stirbars. Approximately 100 mL of dry THF were transferred in vacuo to each of the flasks, and 6 mmol of NaCp in 2.0 M THF solution was added to flask A via syringe under a N_2 atmosphere at 0 °C. The solution was warmed to room temperature and stirred for 2 h. During this period, 6 mmol of $Et_2C_2B_4H_6$ in 0.5 M THF solution was added to flask B via the septum at −78 °C and this reaction was allowed to proceed for 1 h at room temperature. At this point the solution of $Na^+(Et_2C_2B_4H_5)^-$ was filtered (in vacuo) through the frit into flask A. This produced an immediate color change in the A-flask solution from dark green to dark brown. The combined solution was stirred 4 h at room temperature and exposed to air, and the THF was removed by rotary evaporation. The residue was dried under vacuum and washed twice with 15-mL portions of hexane, and the hexane solution was removed via syringe. The residue remaining was dissolved in CH_2Cl_2, and the solution was filtered and concentrated via evaporation. The saturated solution was refrigerated overnight, generating orange crystals of **1** (0.610 g, 40% yield), mp (under N_2) 210 °C dec. Visible–UV absorptions (nm, in CH_2Cl_2): 262 (96%), 288 (100%); the 288 nm peak disappears in dilute solution and is interpreted as a charge-transfer band. Anal. Calcd for $Co_2C_{22}B_8H_{38}$: C, 52.13; B, 17.06; H, 7.56. Found: C, 52.37; B, 16.79; H, 7.59.

Conversion of $Cp_2Co^+(Et_2C_2B_4H_4)_2Co^-$ to $(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_4$-5-R) (2a, R = H; 2b, R = Me). Treatment of samples of **1** with a molar excess of acidified ethyl acetate (prepared from 7 mL of concentrated HCl solution and 25 mL of ethyl acetate) in THF solution afforded **2a**, a yellow oil,[11] as the only isolable product. Purification by washing with hexane on 2 cm of silica gave yields of ca. 90%.

Methylation of **2a** was achieved by treatment of 0.310 g (1.00 mmol) in THF with 1.00 mmol of *n*-butyllithium (0.40 mL of 2.5 M solution injected through a rubber septum) in an ice bath, which produced an instant color change from yellow to orange. The solution was warmed to room temperature, stirred for 25 min, and cooled to −78 °C, and 1.00 mmol of methyl iodide was added through the septum. After being stirred overnight at room temperature, the brown solution was opened to the air, THF was removed by rotary evaporation, and the solution was flashed through 2 cm of silica gel, affording a pale yellow band. This material was washed with dichloromethane and acetone, both eluents giving bright yellow solutions. Each fraction was evaporated and chromatographed in the corresponding solvent, giving in both cases yellow **2b**, total yield 0.132 g (0.409 mmol, 41% yield).

Synthesis of $Cp_2Co^+(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_4$-5-R)$^-$ (3a, R = H; 3b, R = Me). Three-neck flasks A and B, fitted with septums, were connected in series and attached to a vacuum line. Flask A was charged with 0.325 g (2.52 mmol) of $CoCl_2$, and flask B was charged with 0.780 g (2.52 mmol) of $(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_5)$ (**2a**). The apparatus was evacuated, THF was distilled into both flasks, flask A was cooled to 0 °C, and 1.26 mL of 2.0 M NaCp was added to flask A via the septum. The dark green solution was warmed to room temperature and stirred for 2 h. Flask B was cooled to 0 °C and 1.01 mL of 2.5 M BuLi was injected via the septum, producing a color change from yellow to orange, indicating deprotonation had occurred. The solution was warmed to room temperature and stirred for 20 min. The contents of flask B were tipped into flask A, causing an immediate color change to black. After this mixture was stirred for 4 h at room temperature, the solvent was removed by rotary evaporation, and the dark brown residue was washed through a coarse frit, first with hexane and then with CH_2Cl_2. The hexane portion was chromatographed on silica, yielding the starting material **2a** (0.228 g, 0.073 mmol). The CH_2Cl_2 fraction was rotary evaporated to dryness and the brown residue was taken up in a minimum amount of CH_2Cl_2 and eluted in that solvent on a silica TLC plate. A broad yellow band was obtained that hardly moved from the baseline; several other, more mobile, bands were not characterized. The yellow band was collected and washed through with CH_2Cl_2, and evaporated to dryness, producing yellow crystals of the salt **3a** (0.359 g, 0.72 mmol, 41% yield based on **2a** consumed). Anal. Calcd for $Co_2C_{22}B_7H_{39}$: C, 53.16; H, 7.91. Found, C, 53.26; H, 8.09. Ir (neat film, cm^{-1}): 2803 vvs, 2512 m br, 2350 vw br, 1646 m br, 1461 w, 1070 s, 904 s.

The B5-methyl derivative **3b** was prepared via an identical procedure from 0.200 g (0.62 mmol) of **2b**, 0.080 g (0.62 mmol) of $CoCl_2$, 0.25 mL of 2.5 M BuLi, and 0.31 mL of 2.0 M NaCp. A 40-mg (0.12-mmol) quantity of **2b** was recovered, and the yield of **3b** was 0.143 g (0.28 mmol, 56%). Ir (neat film, cm^{-1}): 2803 vvs, 2500 m br, 2340 vw br, 1646 m br, 1417 w.

Synthesis of $Cp_2Co^+(Et_2C_2B_4H_4)_2Fe^-$ (4). A 250-mL 3-neck flask (B) was connected via Teflon stopcocks (and standard taper greased joints to permit rotation) to two 2-neck flasks A and C (each equipped with a rubber septum) and to a vacuum line. All three vessels contained magnetic stirbars. Flasks A, B, and C were charged, respectively, with 0.387 g (3.00 mmol) of $CoCl_2$, 0.378 g (3.00 mmol) of $FeCl_2$, and 0.700 g of NaH (50% mineral oil dispersion). The entire assembly was evacuated and ca. 50 mL of THF was condensed into each flask. A solution of NaC_5H_5 (6 mmol of a 2M solution) was added to A via syringe, and the reaction was allowed to proceed overnight at room temperature. Following this, 0.792 g (6 mmol) of $Et_2C_2B_4H_6$ was added via syringe to C, and the flask was slowly warmed to room temperature and allowed to stand undisturbed for 30 min to permit unreacted NaH to collect at the bottom. A liquid nitrogen bath was placed around flask B, and the cobaltocene solution in A and the clear solution in C were decanted into B via rotation of the flasks, after which B was placed in a dry ice/ethanol bath. The solution in B was stirred for 10 min and then allowed to warm to room temperature over a 4-h period with stirring. The THF solvent was distilled off in vacuo, the flask was opened to the air, and the residue was washed with two 10-mL portions of hexane. At this point, all further operations were conducted under nitrogen on a Schlenck line or in a drybox. Dry, distilled dichloromethane was added via syringe, the mixture was filtered, and the solution was concentrated by evaporation and refrigerated overnight. This produced dark red crystals of **4** (0.374 g, 25%), which contained ca. 5% of the diamagnetic $Fe^{II}H$ species as detected by proton NMR. Mp (under N_2): 295–300 °C dec. Visible-UV absorptions (nm, in CH_2Cl_2): 268 (88%), 294 (100%) (in dilute solution the relative intensities of the 268 and 294 nm bands are 100% and 41%, respectively). Anal. Calcd for $CoFeC_{22}B_8H_{38}$: C, 52.45; H, 7.60. Found, C, 52.94; H 8.01.

X-ray Structure Determination on 1. Measurements were carried out on a Rigaku AFC6S diffractometer at −120 °C using Mo $K\alpha$ radiation. Table II lists information on the data collection and structure determinations. Preliminary measurements indicated a triclinic unit cell; cell reduction calculations using the program TRACER II did not yield a cell of higher symmetry. Unit cell dimensions were obtained using the setting angles of 25 high-angle reflections. The intensities of three standard reflections were monitored, showing no significant variation. Absorption corrections were applied using the Ψ scanning of several reflections. All calculations were performed employing the TEXSAN crystallographic software package.[13] The structure was solved by direct methods (SIR88).[14] Full-matrix least-squares calculations with anisotropic thermal displacement parameters for all non-hydrogen atoms gave the final residuals reported in Table II. Hydrogen atoms were located from difference Fourier maps and included as fixed contributions to the structure factors. The final difference Fourier map was featureless.

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Supplementary Material Available: Tables of atomic coordinates, thermal displacement parameters, intermolecular distances, and calculated mean planes and a numbering diagram (13 pages). Ordering information is given on any current masthead page.

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(13) TEXSAN 5.0: TEXRAY Structure Analysis Package. Molecular Structure Corporation, The Woodlands, TX, 1989.

(14) SIR88: Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D., *J. Appl. Crystallogr.* **1989**, *22*, 389.