Synthesis and Characterization of a Bimetallic Boratabenzene Cobalt Complex

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Reaction of 1,4-$(BBr_2)_2C_6H_4$ with cobaltocene gives a bimetallic cobalt complex with cyclopentadienyl and boratabenzene ligands. Oxidation allows the dicationic dicobalt(III) complex to be isolated; the bis(hexafluorophosphate) salt has been structurally characterized. Variable-temperature magnetic susceptibility measurements on the neutral dicobalt(II) complex showed substantial deviation from the Curie−Weiss law; a fit to the Bleaney−Bowers equation for a singlet ground state and a triplet excited state gave an exchange interaction of $J =$ ca. -28 cm^{-1}. Electrochemical studies, as well as near-infrared data on the mixed-valence species, suggest that the interaction between the metal centers is weak.

Introduction

Bridged dinuclear or multinuclear metallocenes may exhibit interesting properties due to interactions between the metal centers[1a] and can serve as models for organometallic polymers.[1b−e] The nature and extent of the metal−metal interactions can depend on the nature of the coordinating ligand, as well as the bridging group. We have been interested in studying the properties of bridged metallocene analogues with noncyclopentadienyl ligands[2] and have now prepared a bimetallic cobalt complex featuring a boratabenzene ligand.[3] The boratabenzene anion, $[C_5H_5BR]^-$, is isoelectronic with benzene and, as a ligand, can be viewed as a six-membered-ring analogue of cyclopentadienyl. Complexes of boratabenzene ligands have been shown to possess properties similar to those of their Cp analogues.[4]

Boratabenzene complexes have generally been prepared by the reaction of a salt of a boratabenzene anion[3,5a] with an appropriate metal precursor.[3a] This approach is limited by the multistep, nontrivial syntheses of boratabenzenes.[5] The original synthesis of boratabenzene complexes, however, was via a straightforward reaction involving treatment of cobaltocene with borane reagents RBX_2 (X = halogen), leading to the insertion of boron into a cyclopentadienyl C−C bond and the formation of cyclopentadienyl(boratabenzene) cobalt complexes (eq 1).[6] The byproduct of this reaction is

$$3(C_5H_5)_2Co + RBX_2 \rightarrow (C_5H_5)Co(C_5H_5BR) + 2(C_5H_5)_2Co^+X^- \quad (1)$$

cobaltocenium halide; thus, cobaltocene also serves as a reducing agent. A second boron insertion can also occur, yielding a bis(boratabenzene) complex. While the reaction of boranes with cobaltocene to give boratabenzene complexes has been studied extensively,[3c] there appears to be only one previous example of the use of such a reaction to prepare a bimetallic species, namely the reaction of cobaltocene with $FcBBr_2$ (Fc = ferrocenyl) to give the mixed iron−cobalt complex $CpCo(C_5H_5$-BFc).[7,8]

Results and Discussion

Reaction of 1,4-$(BBr_2)_2C_6H_4$[9] with excess cobaltocene gives a bimetallic cyclopentadienyl−boratabenzene complex, $[CpCo(C_5H_5B)]_2C_6H_4$ (**Co2**; Scheme 1). In theory 6 equiv of cobaltocene is required per molecule of 1,4-$(BBr_2)_2C_6H_4$, as 2 equiv of cobaltocenium halide is also formed per boron insertion; however, less than the

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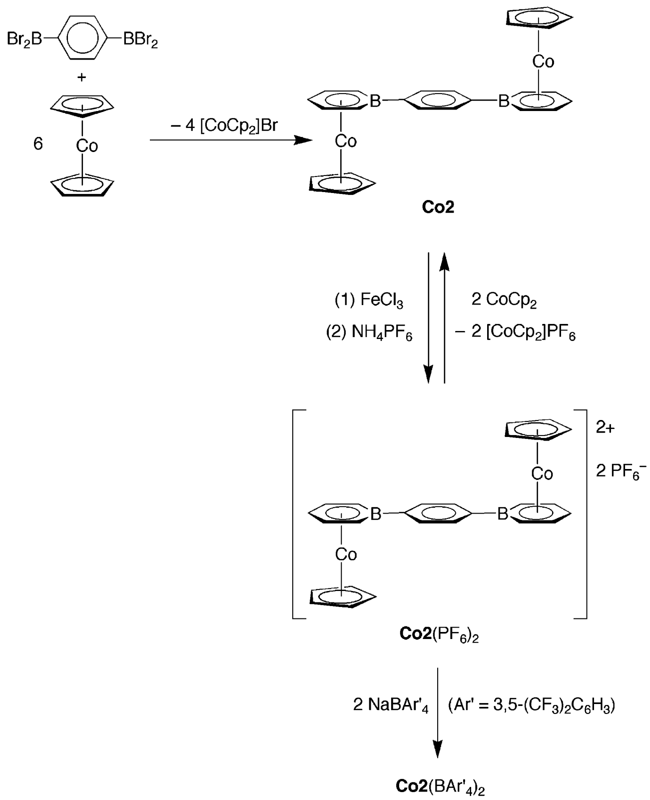
Scheme 1



stoichiometric amount was used, as previous related work had found that the best yields were obtained with a slight deficiency of cobaltocene, presumably because the formation of side products in which both Cp rings of cobaltocene undergo boron insertion is minimized.

Attempts to recrystallize the dicobalt species **Co2** from solution led to decomposition; therefore, the crude **Co2** was purified by oxidation in situ to give the air-stable dication, a bimetallic analogue of cobaltocenium, which could be isolated and purified as its PF_6 salt **Co2**(PF_6)$_2$. The dicationic complex is, as expected, diamagnetic and exhibits three resonances in the ^{1}H NMR spectrum due to the boratabenzene ligand in the region of δ 6.4−7.2, as well as singlets due to the Cp protons at δ 6.06 and the four equivalent protons of the arene bridge at δ 8.22. A signal is observed in the ^{11}B NMR spectrum at δ 25.0, consistent with related boratabenzene complexes.

The bimetallic dicationic cobalt complex **Co2**(PF_6)$_2$ was also characterized by X-ray crystallography, with the cation shown in Figure 1. The compound crystallizes in the space group $P\bar{1}$, with the cation located on the crystallographic inversion center. Thus, the two CpCo(C_5H_5B) units are crystallographically equivalent, and the metals are located in a trans configuration on opposite sides of the bridging ligand. The Co···Co distance within the molecule is 9.879 Å; inspection of the crystal packing reveals intermolecular Co···Co separations as short as 6.683 Å. The two boratabenzene

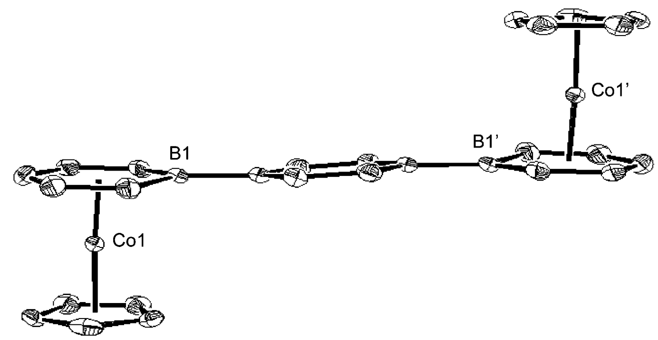


Figure 1. Molecular structure of **Co2**(PF_6)$_2$, showing the 40% thermal probability ellipsoids. Hydrogen atoms have been omitted; only the cation is shown.

rings and the bridging phenylene ring are all essentially coplanar (interplanar angle 6.8°). The boratabenzene rings are slightly distorted from planarity, with the boron atom displaced away from the metal, leading to a fold angle of ca. 7°. The boratabenzene moiety can be considered to be bound in an η^6 manner, although, as has been observed previously for the C_5H_5BPh ligand,[3] the coordination of the metal to the ring is slipped away from the boron such that the shortest boratabenzene Co−C bond length (2.056(3) Å) is to the carbon para to the boron. The Co−B distance is 2.277(3) Å, which is shorter than in the related cation $CpCo(C_5H_5BFc)^+$ (2.307(4) Å)[7] but is almost identical with the corresponding Co−B bond lengths for the neutral complexes $(CO)_2Co(C_5H_5BPh)$ (2.274(2) Å)[3c] and $Co(C_5H_5BMe)_2$ (2.283(5) Å).[3c]

Complexes of bis(cyclopentadienyl)benzene and -biphenylene ligands, arene-bridged dinuclear metallocenes related to **Co2**(PF_6)$_2$, have been synthesized previously[10−13] and have been suggested as possible building blocks for organometallic polymers. Recently a hexylated version of a bis(cyclopentadienyl)benzene ligand was in fact used to prepare soluble arene-bridged poly(ferrocenes).[14] These ligands, however, suffer the disadvantage that multistep organic synthesis is required for their preparation; thus, the reaction presented here represents a significantly more facile synthesis of this type of compound.[15]

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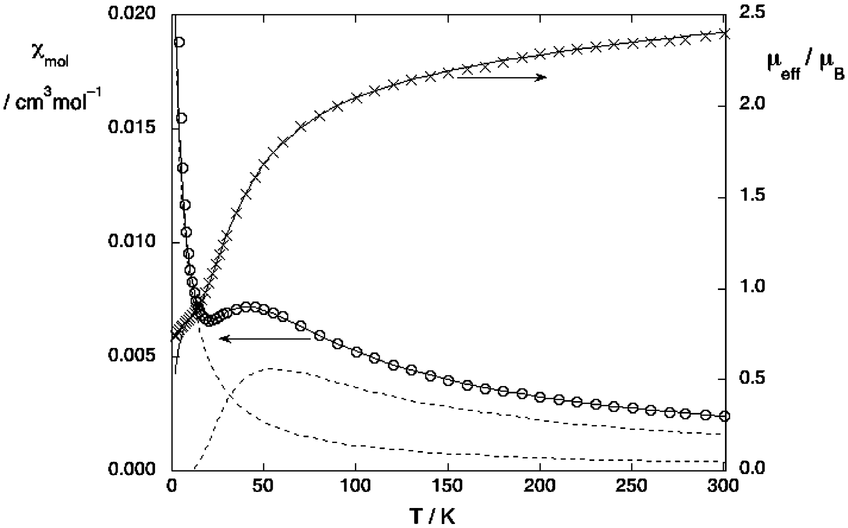

Figure 2. Variable-temperature magnetic susceptibility data (circles) and the derived effective magnetic moment (crosses) for **Co2**. The solid lines are fits to the Bleaney−Bowers equation, with additional terms added to account for a Curie paramagnet impurity and for temperature-independent paramagnetism. The broken lines show the Bleaney−Bowers and Curie components of the susceptibility fit separately.

The neutral dicobalt(II) species **Co2** could be isolated most conveniently by reduction of the dicobalt(III) salt **Co2**$(PF_6)_2$ (Scheme 1). Electrochemical data (vide supra) suggested that cobaltocene would be a suitable reducing agent, and this was indeed found to be the case. **Co2** was isolated from solution after all the cobaltocenium hexafluorophosphate was removed by multiple precipitations; the identity of the compound was confirmed by high-resolution mass spectrometry. The ^{1}H NMR spectrum of **Co2** features broad, shifted peaks, as would be expected due to the paramagnetic Co(II) centers.

The solid-state magnetic susceptibility of **Co2** was studied using SQUID magnetometry. The derived magnetic moment of **Co2** approaches ca. 2.4 μ_B at room temperature. This value is close both to that expected for two independent $S = {}^1/_2$ ($\mu_{eff} = 6^{0.5}$) cobalt centers and to that expected for a high-spin $S = 1$ configuration ($\mu_{eff} = 8^{0.5}$); however, the temperature-dependent data reveal significant deviations from Curie−Weiss behavior indicative of spin−spin exchange interactions (Figure 2). An excellent fit to the magnetic susceptibility data was obtained by considering the dinuclear species to adopt an $S = 0$ ground state and an $S = 1$ excited state, using the Bleaney−Bowers equation (eq 2) (with an additional correction for a Curie impurity)[16] with parameters $J = -28$ cm^{-1}, $\Theta = -9.6$ K, and $g = 1.73$. The g value is somewhat dependent upon how the correction is made for the Curie impurity but is of similar magnitude to the isotropic g values of 2.03, 1.77, and 1.8 obtained by EPR for $CpCo(C_5H_5BFc)$,[7] $CoCp_2$,[17] and $CoCp^*_2$,[18] respectively. The temperature dependence of the magnetic data for **Co2** is broadly similar to that previously shown for 1,4-bis(3,4,1′,2′,3′,4′,5′-heptamethylcobaltocen-1-yl)benzene (and an isoelectronic dinickel dication salt).[10b] This similarity, when compared with data for 1,3-bis(3,4,1′,2′,3′,4′,5′-heptamethylcobaltocen-1-yl)benzene,[10b] which shows much weaker magnetic interactions than its para-bridged analogue, suggests that the principal interactions in **Co2** are likely to be *intra*molecular in nature (unfortunately the magnetic couplings, J, were not reported for these dicobaltocenes). The magnetic coupling in **Co2** is somewhat stronger than in bis(1′,2′,3′,4′,5′-pentamethylcobaltocen-1-yl)dimethylsilane ($J = -15$ cm^{-1}) and bis(1′,2′,3′,4′,5′-pentamethylcobaltocen-1-yl)dimethylgermane (-12 cm^{-1})[19] but considerably weaker than in bis(fulvalene)dicobalt[20] and bis(pentalene)dicobalt,[21] which are both diamagnetic.

$$\chi_{mol} = \left(\frac{2N_A g^2 \mu_B{}^2}{3k(T - \Theta)}\right)\left(\frac{1}{1 - (1/3)e^{-2J/kT}}\right) \qquad (2)$$

To further assess the nature and extent of metal−metal interactions in this system, cyclic voltammetric experiments were performed. A reversible wave was observed at −0.86 V relative to the ferrocene/ferrocenium couple in THF, corresponding to the reduction of both cobalt centers of the dication to the neutral dicobalt(II) species. This represents a positive shift of ca. 0.5 V of the potential relative to cobaltocene, demonstrating the electron-withdrawing nature of the boratabenzene ligand compared to Cp. A second reversible wave was seen at −2.01 V in THF, which can be assigned to the overlapping independent reductions of the two Co centers to Co^I: i.e. overlapping **Co2**$^{0/-}$ and **Co2**$^{-/2-}$ couples. For comparison, a similar reduction to the 20-electron species was observed for $CoCp_2$ at −2.60 V vs $FeCp_2{}^{+/0}$ in THF[22] and for CoCpCp* at −2.67 V vs $FeCp_2{}^{+/0}$ in EtCN,[23] which again demonstrates that **Co2** is more readily reduced than the purely cyclopentadienyl systems. The related mononuclear boratabenzene complex $CpCo(C_5H_5BPh)$ showed reductions at −0.84

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and −1.86 V vs $FeCp_2^{+/0}$ in CH_3CN.[24,25] Thus, introduction of a *p*-phenylene bridge between two cyclopentadienyl(boratabenzene) cobalt units appears to have little effect on the electrochemistry of the species.

The separation, $\Delta E_{1/2}$, between the individual waves for the **Co2**$^{2+/+}$ and **Co2**$^{+/0}$ couples could not be resolved using either cyclic voltammetry or differential pulse voltammetry. The magnitude of $\Delta E_{1/2}$ in such systems is often indicative of the extent of communication between the metal centers. On this basis it would appear, therefore, that metal−metal interactions in **Co2** are limited. Such a separation of waves was also not observed in the purely cyclopentadienyl analogue, *p*-bis(3,4,1′,2′,3′,4′,5′-heptamethylcobaltocen-1-yl)benzene, although two oxidation waves were observed for the related iron and nickel derivatives.[10b] Furthermore, in the related ferrocene system *p*-$Fc_2C_6H_4^{2+/+/0}$ "the beginning of a splitting" was observed, and a $\Delta E_{1/2}$ value of 0.10 V was reported in chloroform.[10a]

In view of the fact that it has recently been shown that $\Delta E_{1/2}$ can be highly solvent dependent,[26] electrochemistry experiments were performed in additional solvents. CV in CH_3CN revealed the Co^{III}/Co^{II} couples as a reversible feature at $E_{1/2} = -0.82$ V vs $FeCp_2^{+/0}$, while in CH_2Cl_2 the corresponding value was −0.80 V. The reversible Co^{II}/Co^{I} redox process was also observed in CH_3CN at −1.87 V vs $FeCp_2^{+/0}$ and at −1.96 V in CH_2Cl_2. Once again the separation between the redox processes of the individual metal centers was not observed in either solvent. There was, however, evidence of imperfect reversibility ($I_{ox} < I_{red}$) and additional features possibly due to decomposition, particularly in CH_3CN, suggesting that the reduced species may be less stable in these more polar solvents.

We were also interested in probing the electronic coupling between the two cobalt centers in the mixed-valence Co^{II}/Co^{III} derivative **Co2**$^+$; this can be estimated by applying Hush theory[27] to the near-infrared intervalence charge transfer expected in such a mixed-valence system.[28] The CV results described above suggested that THF might be a suitable solvent for this experiment, as there was evidence of decomposition in more polar solvents. **Co2**$^{2+}(PF_6)_2$ was insufficiently soluble in THF, however; thus, the BAr′$_4$ salt **Co2**(BAr′$_4$)$_2$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) was synthesized by metathesis of PF_6^- with NaBAr′$_4$.[29]

The mixed-valence species was generated from the dication by again using cobaltocene as the reducing agent. Addition of 1 equiv of a $CoCp_2$ solution to **Co2**(BAr′$_4$)$_2$ gave a highly air-sensitive dark orange-brown solution (solids were rapidly precipitated on exposure to air).[30] In the visible region, intense absorptions were seen with maxima at 426 and 375 nm. The reduced solution showed a very weak band in the near-IR region; accurate measurement of this band was complicated by its weakness, by solubility considerations, and by overlap with several vibrational features. Nevertheless, the band maximum, ν_{max}, was estimated as ca. 6000 cm^{-1}, and the peak molar absorptivity, ϵ_{max}, was determined to be no greater than 25 M^{-1} cm^{-1} (correction for disproportionation was made assuming K_{comp}, defined as the equilibrium constant for the reaction

$$\mathbf{Co2}^{2+} + \mathbf{Co2} \rightleftharpoons 2\mathbf{Co2}^{+}$$

to have a statistical value of 4, since K_{comp} could not be determined electrochemically due to the unresolved separation of the **Co2**$^{2+/+}$ and **Co2**$^{+/0}$ couples). The maximum possible value of the electronic coupling, *V*, was estimated to be < ca. 7 meV (60 cm^{-1}) using Hush's equation:[27]

$$V = ((4.5 \times 10^{-4})\epsilon_{max}\Delta\nu_{1/2}\nu_{max})^{1/2}/r$$

where $\Delta\nu_{1/2}$ (cm^{-1}) is the width at half-height of the intervalence band and *r* (Å) is the intermetallic distance. $\Delta\nu_{1/2}$ for **Co2**$^+$ was estimated by assuming a typical value for a class II mixed-valence species of ca. 1.3 times the Hush limit of $\Delta\nu_{1/2} = (2310\nu_{max})^{1/2}$; *r* was assumed to be equal to the Co···Co distance in the crystal structure of **Co2**$(PF_6)_2$: i.e., 9.879 Å.

While several studies of Co^{II}/Co^{III} and Fe^{II}/Co^{III} metallocene systems indicate increased M−M interactions relative to those of their Fe^{II}/Fe^{III} analogues,[31] the electronic coupling in **Co2**$^+$ is clearly rather weak in comparison to the ferrocene analogue, *p*-$Fc_2C_6H_4^+$, which shows a coupling of 43 meV,[10a] at least 6 times greater than that estimated for **Co2**$^+$. In cobaltocenium/cobaltocene systems, the increased coupling has been attributed to increased ligand character of the frontier orbitals relative to those of their iron analogues; this also explains the higher self-exchange rates found for $CoCp_2^{+/0}$ and $CoCp^*{}_2^{+/0}$ relative to those of the analogous iron systems.[32] Although the redox centers in **Co2** are isoelectronic with those of cobaltocene, perhaps the inclusion of the boron atoms in the coordinated rings significantly reduces the metal−metal coupling. On the other hand, electrochemical data appear to suggest weaker interactions in the closely analogous 1,4-bis(3,4,1′,2′,3′,4′,5′-heptamethylcobaltocen-1-yl)benzene system than in 1,4-$Fc_2C_6H_4$; unfortunately, near-IR data for the 1,4-bis(3,4,1′,2′,3′,4′,5′-heptamethylcobaltocen-

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(25) Corrected by assuming that the potential of the $Cp_2Fe^{+/0}$ couple is +0.40 V vs SCE in CH_3CN/0.1 M $Bu_4N^+PF_6^-$. See: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

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(29) BAr′$_4^-$ salts of related species have been prepared previously by similar metatheses of BF_4^- or PF_6^- salts with NaBAr′$_4$. See for example: (a) Chávez, I.; Alvarez-Carena, A.; Molins, E.; Roig, A.; Maniukiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manriquez, J. M. *J. Organomet. Chem.* **2000**, *601*, 126−132. (b) Barlow, S.; Cowley, A. R.; Green, J. C.; Brunker, T. J.; Hascall, T. *Organometallics* **2001**, *20*, 5351−5359. (c) Barlow, S.; Henling, L. M.; Day, M. W.; Schaefer, W. P.; Green, J. C.; Hascall, T.; Marder, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 6285−6296.

(30) The solution was reinvestigated by cyclic voltammetry after spectroscopic analysis; features due to **Co2**$^{2+/+/0/-/2-}$ and $CoCp_2^{+/0}$ were observed in the expected ratios, and no additional features were seen, indicating that the reduced neutral dicobalt species had not significantly decomposed during the spectroscopic measurements.

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1-yl)benzene monocation, which might help resolve the reasons behind the weak coupling in **Co2**$^+$, have not been reported.

In summary, a bimetallic cobalt complex with boratabenzene ligands linked by a *p*-phenylene bridge has been synthesized. Magnetic data for the neutral species, showing antiferromagnetic interactions between the metal centers, and electrochemical data, showing no resolvable separation between the two Co^{III}/Co^{II} couples, are similar to those reported for a structurally similar dicobaltocene system. The near-IR spectrum of the mixed-valence derivative shows only rather weak metal–metal interactions.

Experimental Details

General Considerations. All manipulations were performed under an inert atmosphere of N_2 using a combination of drybox and Schlenk techniques, except for the oxidation of **Co2** and workup of its PF_6^- salt, which could be performed in air. 1,4-$(BBr_2)_2C_6H_4$[9] and NaBAr′$_4$[33] were synthesized by following literature procedures. NMR spectra were recorded using a Varian Unity Plus 500 MHz spectrometer or a Varian Mercury VX-Works 300 MHz spectrometer. ^{1}H and ^{13}C chemical shifts (δ) are quoted in ppm relative to tetramethylsilane and were referenced via the residual protio solvent peak (^{1}H) or a ^{13}C resonance of the solvent. ^{11}B spectra were referenced using $BF_3 \cdot OEt_2$ as an external standard.

Variable-temperature magnetic susceptibility data were acquired in a field of 0.1 T using a MPMS-5 SQUID magnetometer, with the sample loaded in a gelatin capsule mounted between other gelatin capsules in a nonmagnetic plastic straw. The data were corrected for sample diamagnetism using Pascal's constants.[34] The molar susceptibility data were fitted to the Bleaney–Bowers equation[16] with additional terms to account for a paramagnetic impurity ($\chi = C/(T - \Theta)$) and for temperature-independent paramagnetism. Without knowledge of the molecular weight and spin state of the Curie paramagnetic impurity, it is difficult to quantify the exact level present; however, if for example the impurity is assumed to have $S = {}^3/_2$ (typical for inorganic Co(II) species) and to have a molecular weight similar to that of **Co2**, it would correspond to ca. 6% of the sample.

Electrochemical measurements were carried out under argon, with solutions in deoxygenated, dry solvents ca. 10^{-4} M in analyte (**Co2**(BAr′$_4$)$_2$ for experiments in THF and CH_2Cl_2; **Co2**$(PF_6)_2$ for experiments in CH_3CN) and 0.1 M in [^{n}Bu$_4$N][PF$_6$], using a BAS or CH Instruments CHI600A potentiostat, a glassy-carbon working electrode, a platinum auxiliary electrode, and a Pt wire, or a AgCl-coated Ag wire, as a pseudo-reference electrode. Potentials were referenced to $Cp_2Fe^{+/0}$ by adding ferrocene to the cell. The reversibility of a redox couple was judged by comparison with the behavior of the $Cp_2Fe^{+/0}$ couple under the same conditions. Near-IR measurements were conducted using a Varian Cary 5 spectrometer.

Synthesis of {[CpCo(C$_5$H$_5$B)]$_2$C$_6$H$_4$}$^{2+}$(PF$_6^-$)$_2$ (Co2(PF$_6$)$_2$). A solution of 1.13 g of *p*-$(BBr_2)_2C_6H_4$ (2.71 mmol) in ca. 40 mL of toluene was added dropwise to a solution of 2.80 g of cobaltocene (14.8 mmol) in ca. 60 mL of toluene at −78 °C. A light brown precipitate began to form immediately. The reaction mixture was allowed to return to room temperature slowly and then stirred for 1 h. The mixture was filtered and the solvent removed from the red filtrate under vacuum. To the residue was added 50 mL of ether, followed by a solution of 1.69 g of $FeCl_3 \cdot 6H_2O$ (6.25 mmol) in 50 mL of H_2O. This yielded an orange aqueous layer and a yellow organic layer, which was removed. To the aqueous layer was added a solution of 1.13 g of NH_4PF_6 (6.93 mmol) in 20 mL of H_2O, giving an orange precipitate of **Co2**$(PF_6)_2$ which was isolated by filtration. The product was purified by dissolving in acetone (150 mL), filtering the solution, and adding diethyl ether to give an orange precipitate, which was dried under vacuum. Yield: 0.87 g (46% based on $CoCp_2$). X-ray quality crystals were grown by diffusion of Et_2O into a saturated CH_3CN solution. NMR data are as follows. ^{1}H (acetone-d_6): δ 6.06 (s, 10 H [C$_5$*H*$_5$Co(C$_5$H$_5$B)]$_2$C$_6$H$_4$); 6.37 (d, J_{H-H} = 9 Hz, 4 H, C$_5$*H*$_5$B); 7.06 (dd, J_{H-H} = 6, 9 Hz, 4 H, C$_5$*H*$_5$B); 7.21 (t, J_{H-H} = 6 Hz, 2 H, C$_5$*H*$_5$B); 8.22 (s, 4 H, [C$_5$H$_5$Co(C$_5$H$_5$B)]$_2$C$_6$*H*$_4$). ^{13}C{^{1}H} (CD$_3$CN): δ 88.3 ([*C*$_5$H$_5$Co(C$_5$H$_5$B)]$_2$C$_6$H$_4$); 90.7 ([C$_5$H$_5$Co(*C*$_5$H$_5$B)]$_2$C$_6$H$_4$); 95.6 ([C$_5$H$_5$Co(*C*$_5$H$_5$B)]$_2$C$_6$H$_4$); 108.2 ([C$_5$H$_5$Co(*C*$_5$H$_5$B)]$_2$C$_6$H$_4$); 133.7 ([C$_5$H$_5$Co(C$_5$H$_5$B)]$_2$*C*$_6$H$_4$); 139.2 (B–*C* of [C$_5$H$_5$Co(C$_5$H$_5$B)]$_2$*C*$_6$H$_4$). ^{11}B (CD$_3$CN): δ 25.0 (br s). Anal. Calcd for $C_{26}H_{24}B_2Co_2P_2F_{12}$: C, 40.8; H, 3.2. Found: C, 41.0; H, 3.2.

Synthesis of {[CpCo(C$_5$H$_5$B)]$_2$C$_6$H$_4$}$^{2+}$(BAr′$_4^-$)$_2$ (Co2(BAr′$_4$)$_2$). CH_2Cl_2 (25 mL) was added to a mixture of 0.14 g of **Co2**$(PF_6)_2$ (0.18 mmol) and 0.33 g of NaBAr′$_4$ (0.37 mmol). The mixture was gently warmed (35 °C) and stirred for 90 min, before filtering through Celite to remove the fine white precipitate that had formed. The CH_2Cl_2 was removed in vacuo, the orange solid was extracted with ether (2 × 15 mL), and the extracts were filtered through Celite. The solvent was removed from the resulting clear orange solution under reduced pressure to give an orange solid. Yield: 0.34 g (84% based on **Co2**$(PF_6)_2$). NMR data are as follows. ^{1}H (CD$_2$Cl$_2$): δ 5.61 (s, 10 H, [C$_5$*H*$_5$Co(C$_5$H$_5$B)]$_2$C$_6$H$_4$), 6.14 (d, J_{H-H} = 9 Hz, 4 H, C$_5$*H*$_5$B), 6.72 (dd, J_{H-H} = 6, 9 Hz, 4 H, C$_5$*H*$_5$B), 6.85 (t, J_{H-H} = 6 Hz, 2 H, C$_5$*H*$_5$B), 7.56 (s, 8 H, B[C$_6$*H*$_3$(CF$_3$)$_2$]$_4$), 7.71 (m, 16 H, B[C$_6$*H*$_3$(CF$_3$)$_2$]$_4$), 8.09 (s, 4 H, [C$_5$H$_5$Co(C$_5$H$_5$B)]$_2$C$_6$*H*$_4$). Anal. Calcd for $C_{90}H_{48}B_4Co_2F_{48}$: C, 49.1; H, 2.2. Found: C, 49.0; H, 2.1.

Synthesis of [CpCo(C$_5$H$_5$B)]$_2$C$_6$H$_4$ (Co2). A solution of 0.12 g of $CoCp_2$ (0.63 mmol) in 10 mL of CH_2Cl_2 was added dropwise at room temperature to a slurry of 0.25 g of **Co2**$(PF_6)_2$ (0.33 mmol) in 15 mL of CH_2Cl_2. After the mixture was stirred overnight, the **Co2**$(PF_6)_2$ had completely dissolved and a pale yellow precipitate ([CoCp$_2$]PF$_6$) had formed. The precipitate was removed by filtration and washed with CH_2Cl_2, and the washings were combined with the filtrate. Ether was added to the solution, and the remaining [CoCp$_2$]PF$_6$ that precipitated was removed by filtration and washed with ether. The solvent was removed from the red-orange solution to give a brown powder, which was dried under vacuum. Yield: 0.11 g (73% based on $CoCp_2$). Because of its highly air-sensitive nature, we were unable to obtain a satisfactory elemental analysis for this complex. NMR data are as follows. ^{1}H (CD$_2$Cl$_2$): δ −61.4 (10 H), −47.7 (4 H), 12.7 (4 H), 15.8 (4 H), 30.2 (2 H). UV–vis (CH$_2$Cl$_2$): λ_{max} (ϵ_{max}) 485 (1300), 358 (5000), 318 (8500), 274 (18 000) nm (M^{-1} cm^{-1}). MS (EI): *m/z* 476 (M$^+$, 100%), 411 (M$^+$ − Cp, 5%), 238 (M^{2+}, 4%), 189 ([Cp$_2$Co]$^+$, 10%). MS (ES): *m/z* 476 (M$^+$, 3%), 238 (M^{2+}, 100%). High-resolution MS (EI): calcd for $C_{26}H_{24}B_2Co_2$, 476.0728; found, 476.0746. Anal. Calcd for $C_{26}H_{24}B_2Co_2$: C, 65.6; H, 5.1; Co, 24.8. Found: C, 62.3; H, 4.7; Co, 20.8.

X-ray Crystallography Study on Co2(PF$_6$)$_2$. A single crystal (red-brown block, ca. 0.08 × 0.18 × 0.18 mm) was mounted on a glass fiber using perfluoropolyether oil and cooled from ambient temperature to 150 K at a rate of 120 K/h in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å). Intensity data were processed using the DENZO-SMN package.[35] A total of 9742 reflections were measured (3192 unique). Crystal data:

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triclinic, $a = 7.0697(2)$ Å, $b = 9.9528(3)$ Å, $c = 10.4818(3)$ Å, $\alpha = 88.1016(12)°$, $\beta = 78.4576(12)°$, $\gamma = 77.1226(14)°$, $V = 704.4$ Å^3.

The structure was solved in the space group $P\bar{1}$ (No. 2) using the direct-methods program SIR92,[36] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[37] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R = 0.0397$ and $R_w = 0.0401$ for 2481 observed reflections ($I > 3\sigma(I)$) and 247 refined parameters: $C_{26}H_{24}B_2Co_2F_{12}P_2$, $Z = 1$, $\rho_{calcd} = 1.805$ Mg/m^3, $\mu = 1.389$ mm^{-1}.

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Supporting Information Available: Additional data from the X-ray crystal structure determination of **Co2**$(PF_6)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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