Inorg. Chem. **1999,** *38,* 93−99

A Delocalized Analogue of the Bicobaltocene Cation Derived from Reduction of a d^6d^6 (Fulvalenediyl)bis(cobaltacarborane) Complex: Electrochemistry, ESR, Optical Spectroscopy, and IR Spectroscopy of the Carborane Group

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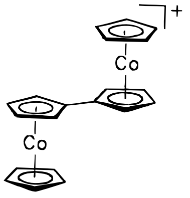
Received April 3, 1998

The electron-transfer properties of the dinuclear complex (fulvalenediyl)$Co_2(Et_2C_2B_4H_4)_2$, **4**, have been studied by electrochemical and spectroscopic methods. This d^6d^6 complex undergoes two reversible reductions ($E_{1/2} = -2.06$ and -2.52 V vs ferrocene) separated by 460 mV, indicative of a strong metal−metal interaction. ESR and optical (near-IR) spectroscopy of the ions **4**$^-$ and **4**$^{2-}$, while suggestive of significant Co−Co interactions, are ambiguous regarding the mixed-valent classification of the monoanion. IR spectra in the ν(BH) region show that the two carborane ligands in **4**$^-$ are equivalent, establishing that the monoanion is an intrinsically delocalized (class III) mixed-valent species. The oxidation of **4** proceeds in two anodic steps, only the first of which ($E_{1/2} = 1.11$ V) is reversible. The monocation **4**$^+$ decomposed rapidly, eluding spectroscopic characterization, but the small potential separation of the two oxidations of **4** (250 mV) suggests that **4**$^+$ is a valence-trapped species, in concert with other d^5d^6 systems. The BH stretching frequencies in the 2450−2650 cm^{-1} range are quite sensitive to metal charge and may be used to diagnose oxidation state changes in metal−carborane complexes. In comparing d^6d^7 complexes with d^5d^6 complexes, metal−metal interactions across a fulvalenediyl spacer appear to be significantly greater for the electronic configuration with the higher electron count. The oxidation and reduction of the mononuclear d^6 analogue $CpCo(Et_2C_2B_4H_4)$, **5**, was studied for comparison purposes.

Introduction

Dinuclear complexes with a bridging fulvalenediyl dianionic ligand have been intensely studied regarding the degree of metal−metal interactions in mixed-valent species. Complexes having a formal d^5d^6 electronic configuration have received the bulk of the attention,[1] which is generated in part from the interest in cooperative phenomena as applied to the electronic and magnetic properties of materials.[2] Far less is known about systems having two more electrons, i.e., d^6d^7 complexes, with the same molecular connectivity. The few reports to date suggest that delocalization may be more common in the more electron-rich systems (see **1**−**3**),[3−5] raising the possibility that electron injection into fulvalendiyl-based materials may lead to properties significantly different than those arising from hole injection.



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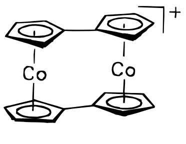

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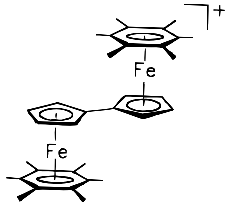

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To directly compare the d^5d^6 and d^6d^7 configurations, we now report on the electron-transfer properties of (fulvalenediyl)$Co_2(Et_2C_2B_4H_4)_2$ (**4**), a d^6d^6 complex that can be both oxidized and reduced. Formal substitution of a monoanionic cyclopentadienyl ligand by the isoelectronic metallacarborane dianion[6] facilitates generation of the $Co^{IV}Co^{III}$ state that is inaccessible from the bicobaltocenium dication.[4] Reduction of **4** is also observed, the persistence of the mono- and dianions of **4** allowing us to probe the electronic structure of the reduced forms by optical spectroscopy, electron spin resonance spectroscopy, and IR spectroscopy in the B−H stretching region. All three techniques are suggestive of strong metal−metal interactions in the d^6d^7 monoanion, with the infrared results showing conclusively that **4**$^-$ is an intrinsically delocalized system. Since it is important to determine the electrochemical and spectroscopic properties of the mononuclear "fragments" that go into making up a

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[†] University of Vermont.

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(1) (a) Dong, T.-Y.; Lee, S.-H.; Lee, T.-Y. *Organometallics* **1996**, *15*, 2354 and references therein. (b) Dong, T.-Y.; Hendrickson, D. N.; Iwai, K.; Cohn, M. J.; Geib, S. J.; Rheingold, A. L.; Sano, H.; Motoyama, L.; Nakashima, S. *J. Am. Chem. Soc.* **1985**, *107*, 7986.

(2) Leading references to fundamental studies of electron-transfer processes as applied to dimetallic systems may be found in the following references: (a) Astruc, D. *Electron-Transfer Processes in Transition Metal Chemistry*; VCH Publishers: New York, 1995. (b) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121. (c) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-P.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; DeCola, L.; Flamigini, L. *Chem. Rev.* **1994**, *94*, 993. (d) Bruce, D. W.; O'Hare, D. (Eds) *Inorganic Materials*; John Wiley and Sons: New York, 1992. (e) Brady, M.; Weng, W.; Zhou, Y., Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Boehme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775.

(3) (a) McManus, G. E.; Nielson, R. M.; Weaver, M. J. *Inorg. Chem.* **1988**, *27*, 1827. (b) Clark, S. F.; Watts, R. J.; Dubois, D. L.; Connolly, J. S.; Smart, J. C. *Coord. Chem. Rev.* **1985**, *64*, 273.

(4) Delville, M.-H.; Rittinger, S.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1992**, 519.

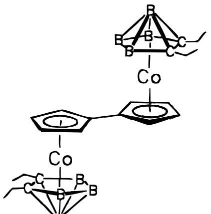
(5) Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330.

(6) Grimes, R. N. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1997; pp 321−332 and references therein.

10.1021/ic980382y CCC: $18.00

potentially mixed-valent system, analogous studies were also performed on $CpCo(Et_2C_2B_4H_4)$ (**5**).

The monocation $\mathbf{4}^+$ was characterized by electrochemical methods, but it was too unstable to yield to spectroscopic investigations. However, the separation of the $E_{1/2}$ values for the two oxidations of **4** argue strongly that its d^5d^6 ion is valence trapped. A preliminary account of part of this work has been published.[7]



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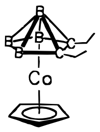

5

B = BH

Experimental Section

Chemicals and Procedures. The following compounds were prepared as previously described: cobaltacarboranes **4** and **5**;[8] $CpFe(C_6Me_6)$;[9] $[N(C_6H_3Br_2)_3][SbCl_6]$.[10] $[NO][BF_4]$ and $[O_2][SbF_6]$ were obtained from Ozark-Mahoning Co. All Manipulations were carried out using dried and degassed solvents under N_2 using either Schlenk conditions or Vacuum Atmospheres drybox.

Electrochemistry and Spectroscopy. General electrochemical procedures were as given previously.[11] The supporting electrolyte was $[NBu_4][PF_6]$. The experimental reference electrode was Ag/AgCl, prepared by anodizing a silver wire in HCl solution. All potentials in this paper are, however, referenced to the ferrocene scale, which was checked in every experiment by adding ferrocene as an internal standard at an appropriate point in the procedure. Voltammetry experiments were conducted with Pt disks of 2 or 0.62 mm diameter which were polished with diamond paste before use. Occasional use was made of a hanging mercury drop electrode. Rotating electrode voltammograms were obtained at a Pt bead rotating at 1800 rpm. A Luggin probe was employed in cyclic voltammetry experiments to minimize uncompensated resistance effects. In some low-temperature voltammetry experiments, positive feedback *iR* compensation was used in conjuction with the Princeton Applied Research model 173 potentiostat. Cyclic voltammetry diagnostics were applied as previously described.[12] Chronoamperometry was performed at a Pt disk the area of which (0.400 cm^2) had been calibrated with ferricyanide.[13] Bulk electrolyses were conducted with a Pt gauze cylindrical working electrode in a two-compartment cell in which the cathodic and anodic compartments were separted by a 20 mm fine frit. Temperatures for the electrochemical solutions were controlled by immersing the cell in a heptane bath in the drybox and fixing the temperature of the bath to a precision of better than one degree with an FTS systems temperature controller. IR spectroelectrochemistry was accomplished with the IR-transparent thin-layer electrode (IRTTLE) cell previously described[14] using a Mattson Polaris IR spectrometer operating at 4 cm^{-1} resolution.

Table 1. Electrochemical Formal Potentials of Cobaltacarboranes vs Ferrocene

complex	couple	solvent	$E_{1/2}$[a]	temp (K)
5	0/−	THF	−2.24	268
5	0/+	CH_2Cl_2	1.02	213
4	0/−	THF	−2.06	ambient
4	−/2−	THF	−2.52	ambient
4	0/+	CH_2Cl_2	1.11	213
4	+/2+	CH_2Cl_2	1.36[b]	213

[a] Calculated as the average of the cathodic and anodic peak potentials. [b] Irreversible wave; $E_{1/2}$ estimated as 0.04 V less than the anodic peak potential (1.40 V) at $\nu = 0.2$ V/s (the difference between E_{pc} and E_{pa} was generally 0.08 V for the reversible couples in the table).

Results and Discussion

Mononuclear **5** is part of the three-membered electron-transfer series of eq 1, and dinuclear **4** is part of the five-membered series of eq 2 (Table 1). The properties of **5** and its ions are relevant to drawing conclusions about the mixed-valent states derived from **4**.

$$\mathbf{5}^+ \xrightleftharpoons{e^-} \mathbf{5} \xrightleftharpoons{e^-} \mathbf{5}^- \qquad (1)$$

$$\mathbf{4}^{2+} \xrightleftharpoons{e^-} \mathbf{4}^+ \xrightleftharpoons{e^-} \mathbf{4} \xrightleftharpoons{e^-} \mathbf{4}^- \xrightleftharpoons{e^-} \mathbf{4}^{2-} \qquad (2)$$

$CpCo(Et_2C_2B_4H_4)$ (5) and Its Electron-Transfer Products $\mathbf{5}^-$ and $\mathbf{5}^+$. The class of Co(III) complexes represented by **5** has been shown to undergo one-electron oxidation and reduction processes yielding the corresponding Co(IV) and Co(II) states, respectively, although the spectroscopic properties of the ions were not reported.[15] Complex **5** is reduced in THF ($E_{1/2} = -2.24$ V vs Fc at 268 K) and oxidized in CH_2Cl_2 ($E_{1/2} = 1.02$ V vs Fc at 213 K), each in one-electron processes.[16] The anion $\mathbf{5}^-$ is longer-lived than is the cation $\mathbf{5}^+$. Bulk reductions of **5** at $E_{appl} = -2.4$ V (268 K) passed 0.91 F, resulting in a golden solution for which rotating Pt electrode (RPE) voltammetry established that $\mathbf{5}^-$ was the only electroactive species. Back-oxidation at $E_{appl} = -1.5$ V regenerated the original complex in 75% overall yield. Bulk oxidation ($E_{appl} = 1.3$ V) of **5** at 213 K in CH_2Cl_2 gave a dark yellow solution which, according to RPE scans, contained only 25% of the cation $\mathbf{5}^+$. Back-reduction of the solution gave 20% of the original complex and other waves at 1.44, −0.34, and −0.99 V arising from unidentified byproducts.

Samples of the anion $\mathbf{5}^-$ taken for ESR analysis revealed a rhombic spectrum at 77 K (Figure 1) with $g_1 = 2.119$, $g_2 = 2.030$, $g_3 = 1.915$, $A_1(Co) = 131 \times 10^{-4}\ cm^{-1}$, $A_2 < 10 \times 10^{-4}\ cm^{-1}$, and $A_3 = 60 \times 10^{-4}\ cm^{-1}$. A fluid solution at 250 K was ESR-silent. Reminiscent of values found for other Co(II) sandwich complexes (Table 2), these parameters are consistent with a d^7 electronic ground state descended from the e_1 pair (d_{xz}, d_{yz}) that is degenerate in complexes of cylindrical symmetry.[17] The SOMO of $\mathbf{5}^-$ appears, therefore, to be predominantly metal-based, probably 60−80% d_{xz} or d_{yz} in makeup.[18]

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(7) Chin, T. T.; Lovelace, S. R.; Geiger, W. E.; Davis, C. M.; Grimes, R. N. *J. Am. Chem. Soc.* **1994**, *116*, 9359.

(8) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776, 4884.

(9) Astruc, D.; Hamon, J.-R.; Althoff, G.; Roman, E.; Batail, P.; Michaud, P.; Mariot, J.-P.; Varret, F.; Cozak, D. *J. Am. Chem. Soc.* **1979**, *101*, 5445.

(10) (a) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719. (b) Steckhan, E. *Top. Curr. Chem.* **1987**, *142*, 1. (c) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.

(11) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063.

(12) Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker, Inc.: New York, 1996; pp 683−717.

(13) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; p 124.

(14) Atwood, C. G.; Geiger, W. E.; Bitterwolf, T. E. *J. Electroanal. Chem.* **1995**, *397*, 279.

(15) The related complex $CpCo(C_2B_4H_6)$ has a Co^{IV}/Co^{III} couple at 1.12 V and a Co^{III}/Co^{II} couple at −2.02 V vs Fc in CH_3CN, compared to −1.34 V for the Co^{III}/Co^{II} wave of cobaltocenium ion; see: Geiger, W. E.; Brennan, D. *Inorg. Chem.* **1982**, *21*, 1963.

(16) The current functions, $i_p/\upsilon^{1/2}$, for the reduction and oxidation waves were, respectively, 0.97 and 1.10 times that of equimolar ferrocene under the same conditions. ΔE_p values ($\upsilon = 0.2$ V/s) were measured as 60−65 mV for $\mathbf{4}/\mathbf{4}^-$ at 268 K at a hanging mercury drop in THF and 58 mV for $\mathbf{4}/\mathbf{4}^+$ at 213 K at a Pt disk in CH_2Cl_2. Both waves were diffusion controlled.

(17) Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299.

(18) See arguments in: Merkert, J. W.; Geiger, W. E.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1991**, *10*, 3545.

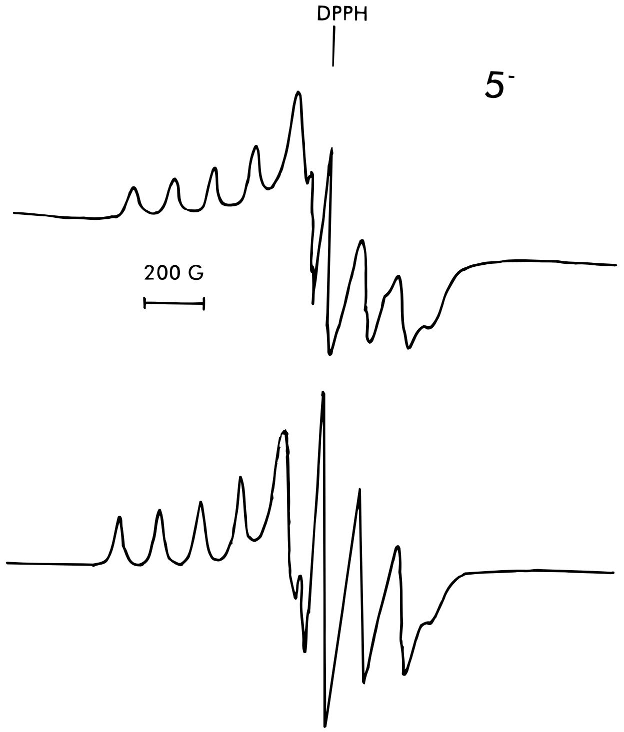

Figure 1. ESR spectrum of complex **5**$^-$ in THF at 77 K (top) produced by the electrolytic reduction of **5**. A simulation using the spectral parameters from Table 2 is shown (bottom) for comparison.

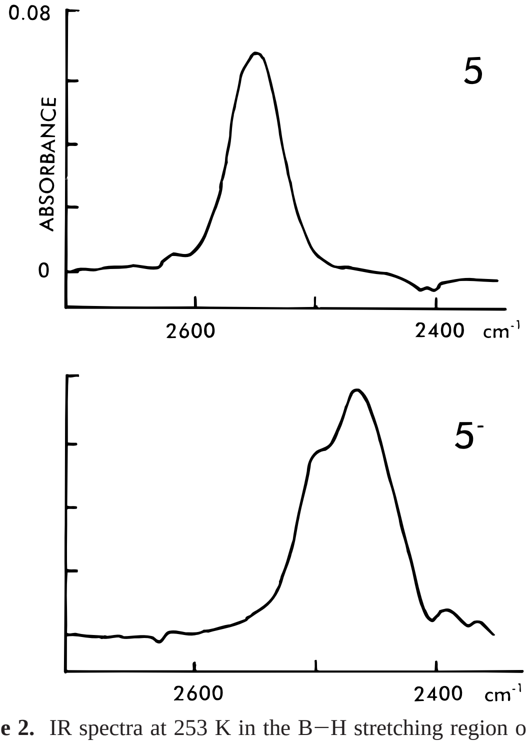

Figure 2. IR spectra at 253 K in the B$-$H stretching region of (top) 3.3 mM **5** in CH_3CN/0.3 M $[NBu_4][PF_6]$ and (bottom) the anion **5**$^-$ produced by electrolysis at -2.4 V.

IR spectra of **5**$^-$ were obtained in a separate experiment involving electrolysis ($E_{appl} = -2.4$ V) in a thin-layer IR cell at 253 K in CH_3CN/0.3 M $[NBu_4][PF_6]$. As shown in Figure 2, reduction resulted in a shift of the center of the ν(BH) band from 2552 cm^{-1} in **5** to a split band with maxima at 2465 and 2494 cm^{-1} assigned to **5**$^-$. Back-oxidation at -0.5 V gave the spectrum of **5** at 86% of its original intensity.

ESR spectra of **5**$^+$ were observed at 77 K for solutions taken from the anodic electrolysis of **5** in $CH_2Cl_2/C_2H_4Cl_2$. In this case the **g** tensor had only a small inequivalency of the g_2 and g_3 components ($g_1 = 2.35$, $g_2 = 2.04$, $g_3 = 1.98$) and a Co hyperfine splitting large enough to be resolved only in the low-field component ($A_1 = 37 \times 10^{-4}$ cm^{-1}, A_2, $A_3 < 10 \times 10^{-4}$ cm^{-1}, Table 2 and Figure 3). Fluid samples showed no resonances. Although fully interpreted spectra of d^5 Co complexes are rare,[19] by analogy with other d^5 sandwich complexes such as ferrocenium ion[17] and its carboranyl analogues,[20] the ground state of **5**$^+$ is expected to be derived from the (predominantly metal) quasi-degenerate pair d_{xy}, $d_{x^2-y^2}$.

IR spectra of the Co(IV) monocation **5**$^+$ were observed after anodic electrolysis in an IRTTLE cell at 213 K in CH_2Cl_2/0.22 M $[NBu_4][PF_6]$, a single BH band being observed at 2617 cm^{-1} (Figure 4).

(Fulvalenediyl)Co$_2$(Et$_2$C$_2$B$_4$H$_4$)$_2$, 4, and Its Ions. Electrochemistry. Reduction of **4** in THF at 298 K gives two reversible one-electron waves (Figure 5) at $E_{1/2} = -2.06$ V and -2.52 V vs Fc. Both waves fulfill criteria[12] for diffusion-controlled Nernstian reactions to stable electrode products. The stabilities of the mono- and dianions were confirmed with double potential step chronoamperometry experiments with 5 s step times (Cottrell constant, $it^{1/2}$/area = 80.5 μA s$^{1/2}$ cm^{-2} for step to -2.25 V; 156 mA s$^{1/2}$ cm^{-2} for step to -2.75 V; diffusion coefficient of **4** = 7.0×10^{-6} cm^2 s^{-1}). Bulk cathodic reductions, first at $E_{appl} = -2.25$ V (0.93 F/eq) and then at $E_{appl} = -2.75$ V (an additional 0.97 F/eq), gave sequentially the olive-green monoanion **4**$^-$ and the brown dianion **4**$^{2-}$. RPE scans as the electrolysis proceeded showed that no other products were formed along the way (Figure S1 of the Supporting Information). Oxidation of the solution of **4**$^{2-}$ at $E_{appl} = -1.5$ V gave back the original light yellow solution of **4** in 93% overall yield. Solutions of **4**$^-$ were ESR-active (*vide infra*), whereas those of **4**$^{2-}$ were not.

The oxidation of **4** also proceeds in two steps (Figure S2 of the Supporting Information), but only the first of these ($E_{1/2}$ = 1.11 V vs Fc) is chemically reversible. At 213 K the second, irreversible, oxidation has $E_p = 1.40$ V at $v = 0.2$ V/s. That the first oxidation wave is a one-electron process is established from the fact that its current function is equivalent to that of the already discussed one-electron reduction wave. Bulk anodic electrolysis at $E_{appl} = 1.3$ V (213 K) released 0.9 F/eq and produced a dark orange solution lacking voltammetric evidence of **4**$^+$. Decomposition product waves were observed at $E_{pc} = -0.70$, -1.04, and -1.54 V.

ESR Spectroscopy. Attempts to obtain ESR spectra of **4**$^+$ were unsuccessful, whether the cation was produced initially by electrolysis (as above) or by chemical oxidation. Even when **4** was oxidized by $[N(C_6H_3Br_2)_3]^+$ ($E_{1/2} = 1.14$ V) at 200 K in CH_2Cl_2 or by O_2^+ at the melting point of a CH_2Cl_2/freon mixture, the solutions so generated were ESR-silent at 77 K. We do not know whether the cause of the spectral inactivity is the instability of **4**$^+$ or its rapid relaxation even at 77 K. It is possible that the decomposition of **4**$^+$ goes through the dication **4**$^{2+}$ in a disproportionation-initiated sequence (eqs 3 and 4) that

$$2\mathbf{4}^{+} \rightleftharpoons \mathbf{4} + \mathbf{4}^{2+} \tag{3}$$

$$\mathbf{4}^{2+} \rightarrow \text{decomposition} \tag{4}$$

is more important at the higher concentrations used in the chemical oxidations. Although the disproportionation reaction

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(19) Rieger, P. H. *Coord. Chem. Rev.* **1994**, *135−136*, 203.

(20) Maki, A. H.; Berry, T. E. *J. Am. Chem. Soc.* **1965**, *87*, 4437.

Table 2. ESR Parameters for $\mathbf{5}^+$, $\mathbf{5}^-$, and Cobalt Sandwich Analogues

complex	electronic config	g_1	g_2	g_3	A_1(Co) (cm^{-1})	ref
$(C_5HPh_4)_2Co$	d^7	2.095	1.999	1.884	133×10^{-4}	*a*
$[CpCo(Et_2C_2B_2Me_2S)]^-$	d^7	2.14	2.04	1.98	ca. 110×10^{-4}	*b*
CpCo(helicene)	d^7	2.09	2.02	1.89	115×10^{-4}	*c*
$\mathbf{5}^-$	d^7	2.119	2.030	1.915	131×10^{-4}	this work
$\mathbf{5}^+$	d^5	2.350	2.040	1.980	37×10^{-4}	this work

[a] Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 1703. [b] Siebert, W.; El-Essawi, M. E.-D. M.; Full, R.; Heck, J. *Z. Naturforsch. B, Anorg. Chem. Org. Chem.* **1985**, *40*, 458. [c] Gilbert, A. M.; Katz, T. J.; Geiger, W. E.; Robben, M. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3199.

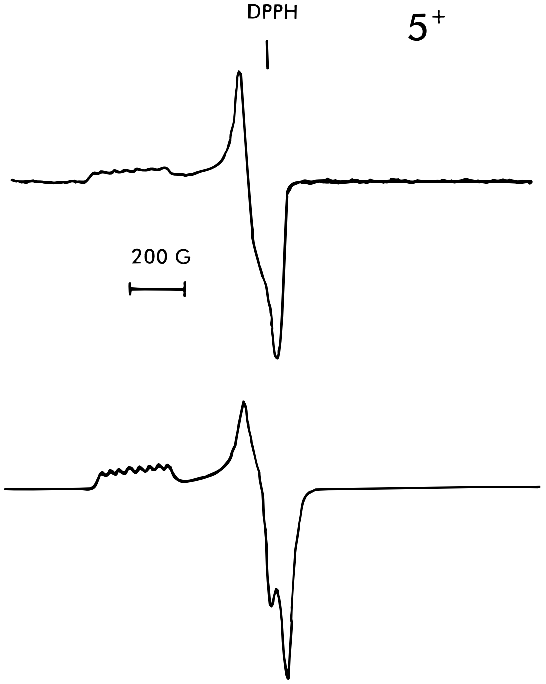

Figure 3. ESR spectrum of complex $\mathbf{5}^+$ in 1:1 $CH_2Cl_2/C_2H_4Cl_2$ at 77 K (top) produced by the electrolytic oxidation of **5**. The simulation shown below is based on the spectral parameters of Table 2.

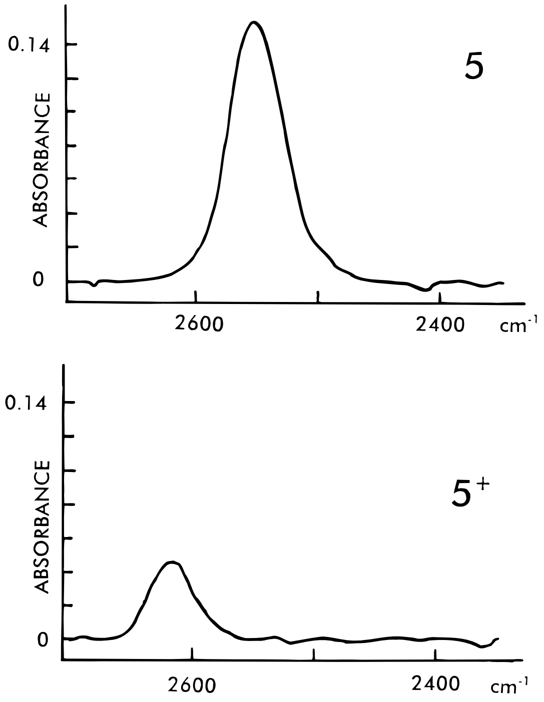

Figure 4. IR spectra at 213 K in the B−H stretching region of (top) 6.6 mM **5** in CH_2Cl_2/0.22 M $[NBu_4][PF_6]$ and (bottom) the cation $\mathbf{5}^+$ produced by electrolysis at 1.4 V.

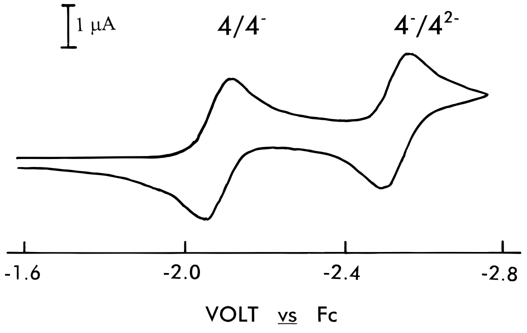

Figure 5. Cyclic voltammogram (scan rate = 0.2 V/s) of 0.57 mM **4** in THF/0.1 M $[NBu_4][PF_6]$ at Pt disk electrode showing stepwise reductions to $\mathbf{4}^-$ and $\mathbf{4}^{2-}$.

is not thermodynamically favored, it may provide a pathway if the rate of eq 4 is sufficiently high. Lending support to this possibility is our finding that a 10-fold increase in the concentration of **4** resulted in a significant decrease in the chemical reversibility of its first oxidation wave.

The frozen solution ESR spectrum of $\mathbf{4}^-$ in 2-methyltetrahydrofuran shown in Figure 6 was produced by the reaction of equimolar **4** with the strong reductant[21] $CpFe(C_6Me_6)$ ($E_{1/2} = -2.09$ V in glyme),[22] but identical spectra were found when $\mathbf{4}^-$ was prepared by bulk electrolysis in $CH_3CN/[NBu_4][PF_6]$ with and without $Na[BPh_4]$ (added as a possible ion-pairing agent). The spectra are considerably less well-resolved than those of the mononuclear analogue $\mathbf{5}^-$, especially in the low-field area, where the Co splitting is unresolved in $\mathbf{4}^-$ in contrast to the large (131×10^{-4} cm^{-1}) value of A_1(Co) in $\mathbf{5}^-$. Lacking a quantitative interpretation, we nevertheless conclude that the spectrum of $\mathbf{4}^-$ is *inconsistent* with a *trapped-valent* electronic structure of the monoanion. Delocalization of the unpaired electron over both cobalt atoms likely accounts for the larger number of hyperfine lines in a smaller *g* value spread as compared to $\mathbf{5}^-$. This phenomenon is reminiscent of results on trapped vs delocalized biferrocenium-type ions reported by Kramer and Hendrickson,[5] who also noted that spectra of the delocalized system bis(fulvalenediyl)dicobalt cation (**2**) had to be recorded under Q-band conditions in order to resolve the low-field Co hyperfine splitting (two equivalent metals, 15 lines, $A = 72 \times 10^{-4}$ cm^{-1}). High-frequency facilities were not available in the present study.

Intervalence Optical Transition of $\mathbf{4}^-$. A moderately intense (ca. 3000 L mol^{-1} cm^{-1}) optical transition for $\mathbf{4}^-$ at λ_{max} ca. 1600 nm (Table 3) is assigned to an intervalence transition (IT). It is reproducibly asymmetric (Figure 7) under all recording conditions, which include DMF, CH_3CN, and CD_3CN as

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(21) Astruc. D. *Chem. Rev.* **1988**, *88*, 1189.

(22) Herberich, G. E.; Klein, W.; Koelle, U.; Spiliotis, D. *Chem. Ber.* **1992**, *125*, 1589.

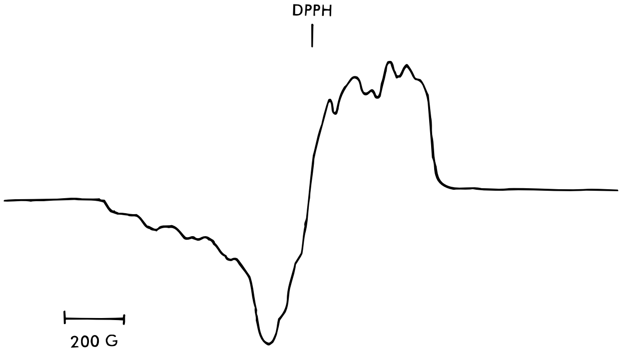

Figure 6. ESR spectrum of complex **4**$^{-}$ in 2-methyltetrahydrofuran at 77 K. The radical was produced by reduction of **4** with equimolar CpFe(C_6Me_6).

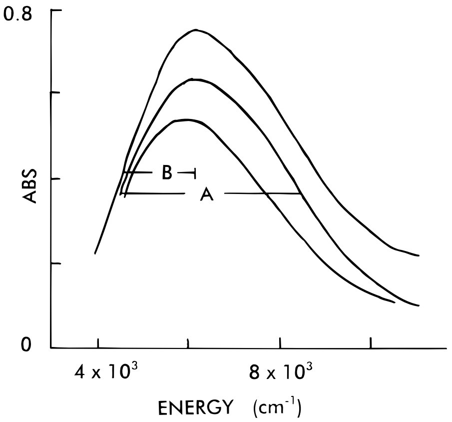

Figure 7. Optical bands assigned to intervalence transfer of **4**$^{-}$ in (top to bottom) CD_3CN, CH_3CN, and DMF (T = ambient, pathlength = 1 cm) after reduction of ca. 0.25 mM **4** with 1 equiv of CpFe(C_6Me_6). The symbols A and B refer to two different methods used to measure the spectral bandwidth (see text and Table 3).

solvents and $[NBu_4]^+$, Na^+, and $[CpFe(C_6Me_6)]^+$ as counterions. We were unable to systematically measure the solvent dependence of the band energy owing to the strong reducing nature of **4**$^{-}$, which precluded the use of several otherwise desirable solvents.

The most commonly applied criterion for assignment of mixed-valency type from IT bands involves a comparison of the experimental bandwidth ($\Delta\bar{\nu}_{1/2}$) with that predicted in eq 5 by Hush for a class II (trapped-valent) system, where $\bar{\nu}_{max}$ is the energy of the band maximum in cm^{-1}:[23]

$$\Delta\bar{\nu}_{1/2} = 48\bar{\nu}_{max}^{\ \ 1/2} \tag{5}$$

Class III (intrinsically delocalized) systems generally display bandwidths less than those calculated by eq 5. The asymmetry of the absorption for **4**$^{-}$ introduces uncertainty into application of this criterion. Measuring the bandwidth as the width at half height (method A in Figure 7) gives a value consistent with a class II ion (Table 3), whereas measuring it as twice the half-width on the low-energy side (method B) gives a value consistent with a class III ion. Reports of asymmetric IT bands are not common, and multiple ground and excited states appear to be their most common cause if one eliminates local environmental effects, which do not appear to be operative in the present case.[24]

Table 3. Optical Properties of the Intervalence Band of **5**$^{-}$

method of prepn	solvent	$\bar{\nu}_{max}$ (cm^{-1})	ϵ (M^{-1} cm^{-1})[a]	$\Delta\bar{\nu}_{1/2}$ (calc)[b]	$\Delta\bar{\nu}_{1/2}$(meas)	
					A[c]	B[c]
bulk electrolysis	CH_3CN	6242	3000	3797	3990	3600
CpFe(C_6Me_6)	CH_3CN	6250	2100	3800	4230	3600
CpFe(C_6Me_6)	CD_3CN	6329	2400	3823	4690	3670
CpFe(C_6Me_6)	DMF	6065	2250	3743	4020	3200

[a] Apparent extinction coefficient based on concentration of **5** prior to reduction. [b] Based on eq 5. [c] See Figure 7 for method of measurement.

Table 4. Mixing Coefficients for **4**$^{-}$ and Selected Mixed Valent Complexes

complex	α	reference
4^{-}	0.19	this work
1	0.17	3a
2	0.19	3a
biferrocenium	0.09	25

Table 5. BH Stretching Frequencies and Energy Shifts for Cobaltacarboranes

complex	ν(BH) (cm^{-1})	$\Delta\nu$(BH) (cm^{-1})[a]
5^{+}	2617	+65
5	2552	0
5^{-}	2494, 2465	−73 (avg)
4	2556	0
4^{-}	2515	−41
4^{2-}	2491, 2464	−79 (avg)

[a] Shift of center of absorption from energy of neutral complex.

In spite of these ambiguities, it can still be said with confidence that the IT band establishes the two metals as being strongly interacting, if not intrinsically delocalized. The basis for this statement is the value of the mixing coefficient, α, calculated based on a class II model from eq 6,

$$\alpha^2 = (4.5 \times 10^{-4})(\Delta\bar{\nu}_{1/2})(\epsilon_{max})/\bar{\nu}_{max}r^2 \tag{6}$$

where r is the calculated internuclear distance in angstroms. Using $\Delta\bar{\nu}_{1/2} = 4 \times 10^3$ cm^{-1}, $\bar{\nu}_{max} = 6.2 \times 10^3$ cm^{-1}, $r = 5$ Å, and $\epsilon_{max} = 3000$ gives $\alpha = 0.19$ for **4**$^{-}$. This is in the same range as the values calculated for the isoelectronic systems bicobaltocenium ion (**1**) and bis(fulvalenediyl)dicobalt cation (**2**) (Table 4)[3a] but is considerably larger than that of hte biferrocenium ion ($\alpha = 0.09$).[25]

IR Spectra of BH Stretching Region in 4 and Its Ions. Using the IRTTLE cell method[14] spectra were recorded from 2300 to 2700 cm^{-1}, the range expected to show the BH fundamental stretching modes of the carborane ligands in the various oxidation states of **4** (Table 5). The single absorption band of the neutral complex centered at 2556 cm^{-1} has a bandwidth (at half height) of about 50 cm^{-1} (Figure 8, top) virtually identical to **5**, befitting a complex with two identical Co(III) nuclei. When the complex is completely reduced to the dianion **4**$^{2-}$ (253 K in CH_3CN, Figure 8, bottom), the absorption shifts to lower energy, producing a split band centered at 2478 cm^{-1} (bandwidth 90 cm^{-1}), a shift (avg) of −79 cm^{-1} from **4**. Keeping in mind that the corresponding shift in going from **5** to the split band in **5**$^{-}$ is −73 cm^{-1}, it is clear that the IR spectrum of **4**$^{2-}$ is consistent with an electronic description of the dianion as Co^{II}Co^{II}. A recently reported neutral (Co(II)

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(23) Creutz, C. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley and Sons: New York, 1983; p 1.

(24) Roberts, J. A.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 157. Asymmetric bands can also be generated from a single electronic transition when the energy for vibrational reorganization is considerably larger than that of solvent reorganization. We thank a reviewer for pointing this out.

(25) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393.

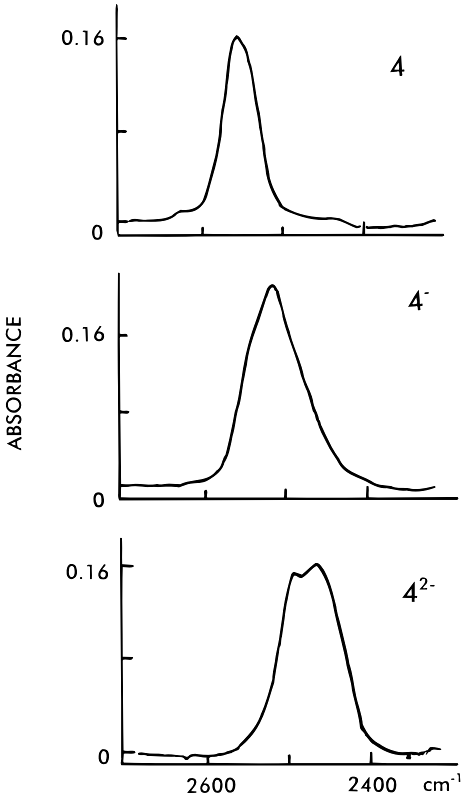

Figure 8. IR spectra at 253 K in the B−H region for the sequential reduction of 2.7 mM **4** in CH_3CN/0.3 $[NBu_4][PF_6]$. (Top) Neutral **4**; (middle) $\mathbf{4}^-$ produced by electrolysis at −2.3 V; (bottom) $\mathbf{4}^{2-}$ produced by electrolysis at −2.8 V.

CoC_2B_4 metallacarborane is reported to have a similar ν(BH), 2492 cm^{-1}.[26]

If the metal centers of the mixed-valent intermediate $\mathbf{4}^-$ were weakly interacting, then its IR spectrum would be the approximate superposition of those of **4** and $\mathbf{4}^{2-}$. Only in the case of a pair of strongly interacting metals is it possible to have a radically different type of spectrum such as that actually observed for the monoanion (Figure 8, middle). The single band centered at 2515 cm^{-1} (bandwidth 80 cm^{-1}) is consistent with the presence of *two equivalent carborane ligands* in $\mathbf{4}^-$, each linked to a cobalt atom with an effective oxidation state of 2.5 (energy shift = −41 cm^{-1} from **4**). IR spectroscopy supports, therefore, a model of *intrinsic delocalization* for the electronic structure of $\mathbf{4}^-$ (class III ion).

That attempts to generate IR spectra of the mixed-valent monocation $\mathbf{4}^+$ failed are not surprising, considering the instability of this species. In four electrolyses at 213 K in CH_2Cl_2, the band for neutral **4** (2555 cm^{-1}) was replaced by a single band at energies between 2566 and 2579 cm^{-1}, most likely arising from decomposition products.

Discussion

Magnitude of $\Delta E_{1/2}$ Values of Reductions vs Oxidations of 4. The potential differences between successive one-electron steps, i.e., the $\Delta E_{1/2}$ values, are often used to argue the relative strengths of metal−metal interactions in homodinuclear complexes.[2b,27] It has been noted that delocalized systems generally have $\Delta E_{1/2}$ values greater than about 350 mV.[28] On this basis alone, one would expect the d^5d^6 complex $\mathbf{4}^+$ to be valence trapped [$E_{1/2}(+/2+) - E_{1/2}(0/+)$ ca. 250 mV][29] and the "d^6d^7" complex $\mathbf{4}^-$ to be delocalized [$E_{1/2}(0/-) - E_{1/2}(-/2-) = 460$ mV]. Another argument to consider is whether or not there is a significant stabilization of the first one-electron process of the dinuclear complex compared to the mononuclear analogue. Considering **4** vs **5**, the reduction of the former is considerably more facile (by 180 mV), whereas the oxidation is not. This also argues for much greater metal−metal interactions in the reduced vs oxidized forms of **4**. Since we lack spectroscopic confirmation of the mixed valency class of $\mathbf{4}^+$, we must use the electrochemical values alone to conclude that, with great liklihood, the monocation is a trapped valent complex. There is little precedent for a delocalized mixed valent complex with so small a value of $\Delta E_{1/2}$.[28,30] It is important to remember, however, that mixed-valent assignments based on $\Delta E_{1/2}$ values rely on empirical correlations; actual $\Delta E_{1/2}$ values are determined by a complex combination of solvation energies and electronic factors in addition to delocalization energies.[27,31]

Vibrational Spectroscopy of the BH Group and Its Use in Assigning $\mathbf{4}^-$ as Delocalized. The strongest evidence for the intrinsic delocalization of $\mathbf{4}^-$ comes from consideration of its IR spectrum in the ν(BH) region. Boranes, carboranes, and their metal complexes display intense IR absorptions arising from terminal B−H stretching motions. A great deal of work has gone into the theoretical interpretation of these absorptions,[32] which are usually broad and often unsymmetrical. There is good reason to think that the shifts in these bands can be used to follow changes in electron density in the carborane cage, an increase in ν(BH) reflecting an increase in the BH force constant from a lowering of electron density in the B−H bond. Early indications are found in the reports of Hawthorne and coworkers, who prepared several metal−dicarbollide complexes in adjacent oxidation states and recorded their IR spectra.[33] For example, one complex isolated in Ni(II), Ni(III), and Ni(IV) forms was found to undergo an increase in the energy of its most intense ν(BH) band from 2500 to 2595 cm^{-1} between the two outlying oxidation states.[33a,34] Similarly, the frequency of the totally symmetric icosohedral vibration moves (+103 cm^{-1}) from 2517 cm^{-1} in $[B_{12}H_{12}]^{2-}$ to 2620 cm^{-1} in $C_2B_{10}H_{12}$.[35] It appears that BH frequency shifts of 40−50 cm^{-1} per unit charge occur in carboranes of approximately icosohedral size.

One might expect even larger shifts in smaller carboranes in which any additional charges are spread out over fewer atoms. Indeed, the ν(BH) energies of $C_2B_4H_6$ are about 190 cm^{-1} higher than those of the analogous borane dianion $[B_6H_6]^{2-}$.[36] In the

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(26) Hosmane, N. S.; Wang, Y.; Zhang, H.; Maguire, J. A.; Waldhoer, Kaim, W. *Organometallics* **1993**, *12*, 3785.

(27) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.

(28) (a) Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 539. (b) Gilbert, A. M.; Katz, T. J.; Geiger, W. E.; Robben, M. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3199.

(29) This value is approximate because of the necessity of estimating $E_{1/2}$ for the couple $\mathbf{4}^+/\mathbf{4}^{2+}$ from the irreversible second oxidation wave of complex **4**. See Table 1 for method of estimation.

(30) Pierce, D. T.; Geiger, W. E. *inorg. Chem.* **1994**, *33*, 373. See, however, data for the d^6d^7 complex $[(biphenyl)Fe_2Cp^*_2]^+$, which is apparently delocalized on the Mössbauer time scale (10^{-6} s) despite having a separation of only 130 mV in redox potentials: Lacoste, M.; Rabaa, H.; Astruc, D.; Ardoin, N.; Varret, F.; Saillard, J.-Y.; Le Beuze, A. *J. Am. Chem. Soc.* **1990**, *112*, 9548.

(31) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(32) Leites, L. A. *Chem. Rev.* **1992**, *92*, 279.

(33) (a) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879. (b) Warren, L. F., Jr.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 1157.

(34) We re-recorded the IR spectrum of the Ni(III) complex $[Ni(B_9C_2H_{11})]^-$ in CH_3CN and obtained ν(BH) = 2565 cm^{-1} [cf. 2527 cm^{-1} in Nujol in ref 33a].

(35) Referrence 32, p 302.

(36) Bragin, J.; Urevig, D. S.; Drem, M. *J. Raman Spectrosc.* **1982**, *12*, 86.

cobalt carborane **5** and in an earlier reported Fe^{III}/Fe^{II} sysstem with a $C_2B_4H_4R_2$ ligand,[7] an average shift of 69 cm^{-1} (spread 58−79 cm^{-1}) per unit charge is observed.

The advantages of vibrational spectroscopy over other physical methods for the characterization of mixed valence include the short time scale (10^{-13}−10^{-14} s) of the observation and the often simple interpretation of the observed bands.[2e,37] Although the present case lacks the theoretical underpinning that comes with observation of a single fundamental band, it still allows the best spectral access to charge location in **4**$^-$. The center of gravity of the ν(BH) absorption in **4**$^-$ is almost exactly midway between those of the adjacent members of the oxidation state series, **4** and **4**$^{2-}$.

Split ν(BH) absorptions such as those seen in the Co(II) systems **4**$^-$ and **5**$^-$ have been observed previously, usually interpreted as arising from nonequivalence of the BH groups in the ligand, higher BH frequencies being assigned to terminal BH groups farther removed from the metal center.[38] The split bands in the spectra of **4**$^-$ and **5**$^-$ may therefore arise from frequency differences between the apical BH group and BH groups in the ligand face bonded to the metal, much as the apical and equatorial B−H fundamentals of $C_2B_4H_8$ are resolvable.[39] Leites warns, however, that additional factors, including spectral complications which arise from having several different fundamental modes with similar energies, must be considered in the interpretation of split BH bands.[40]

Effect of Electronic Configuration on Delocalization. A series of fulvalenediyl dicobalt mixed-valent complexes having different electronic configurations may now be compared. Considering the nominal d-orbital configurations d^5d^6, d^6d^7, d^7d^8, and d^8d^9, the strongest metal−metal interactions are found for d^6d^7 systems (see Table 6). Only complexes of this electronic structure have been shown to be intrinsically delocalized (**4**$^-$ and **2**$^+$) or on the class II/class III borderline (**1**$^+$).[3a] A similar situation appears to exist for the analogous diiron analogues (Table 6). When a molecular chain (an oligomer or polymer) contains a fulvalenediyl repeating unit, the magnitude of the metal−metal interaction within this unit will, of course, influence the electronic and magnetic properties of the chain. It appears that chains based on the d^6d^7 (fulvalenediyl)M_2 repeating group may display greater cooperativity among units than found in the corresponding d^5d^6 systems.

Table 6. Mixed-Valence Classification of Some Fulvalenediyl (Fv) Complexes and Their Reported $E_{1/2}$ Separations

nominal electronic config	classification[a]	complex	$\Delta E_{1/2}$ (mV)[b]	ref
d^5d^6	II	$[(Fv)Co_2(Et_2C_2B_4H_4)_2]^+$	250[c]	this work
d^5d^6	II	$[(Fv)Fe_2Cp_2]^+$	330−350[c]	*g*, *h*, *i*
d^5d^6	III	$[(Fv)_2Fe_2]^+$	590[c]	*h*
d^6d^7	II or III	$[(Fv)Co_2Cp_2]^+$	395[d]	3a
d^6d^7	?	$[(Fv)Co_2Cp^*{}_2]^+$	400[d]	*j*
d^6d^7	III	$[(Fv)Co_2(Et_2C_2B_4H_4)_2]^-$	460[d]	this work
d^6d^7	III	$[(Fv)Fe_2(C_6Me_6)_2]^+$	480[d]	4
d^6d^7	III	$[(Fv)_2Co_2]^+$	930[d]	3a
d^7d^8	II	$[(Fv)Co_2(COD)_2]^+$	228[e]	*k*
d^8d^9	II	$[(Fv)Co_2(COD)_2]^-$	>240[e]	*k*

[a] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. [b] Absolute values of separations of two successive one-electron processes as specified in footnotes *c* through *f* (which follow). [c] Oxidations of the d^6d^6 complex. [d] Reductions of the d^6d^6 complex. [e] Oxidations of the d^8d^8 complex. [f] Reduction of the d^8d^8 complex. The second reduction was beyond the solvent window. [g] Matsumoto, T.; Sato, M.; Ichimura, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1720. [h] Morrison, W. H., Jr.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998. [i] Brown, G. M.; Meyer, T. J.; Cowan, D. O.; Levanda, C.; Kaufman, F.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 506. [j] Rittinger, S.; Bucholz, D.; Delville-Desbois, M. H.; Linares, J.; Varret, F.; Boese, R.; Zsolnai, L.; Huttner, G.; Astruc, D. *Organometallics* **1992**, *11*, 1454. [k] Chin, T. T.; Geiger, W. E. *Organometallics* **1995**, *14*, 1316.

Acknowledgment. This work was supported by the National Science Foundation (CHE 94-16611 and CHE 97-05763 to W.E.G. and CHE 93-22490 to R.N.G.) and by the U.S. Army Research Office (DA-H0H-95-1-0145 to R.N.G.). We thank Dr. Craig Davis for preparing samples **4** and **5** and Prof. E. Steckhan for providing helpful advice and a sample of $(C_6H_3Br_2)_3N$.

Supporting Information Available: Two figures showing voltammograms (see text; 2 pages). Ordering information is given on any current masthead page.

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(37) (a) Moore, M. F.; Hendrickson, D. N. *Inorg. Chem.* **1985**, *24*, 1236. (b) Atwood, C. G.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5310. (c) Bignozzi, C. A. Argazzi, R.; Schoonover, J. R.; Gordon, K. C.; Dyer, R. B.; Scandola, F. *Inorg. Chem.* **1992**, *31*, 5260. (d) Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Joss, S. *J. Am. Chem. Soc.* **1989**, *111*, 548.

(38) See leading references in ref 32 and in: Hosmane, N. S.; Jia, L.; Zhang, H.; Bausch, J. W.; Surya Prakash, G. K.; Williams, R. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962.

(39) 2624 cm^{-1} and 2610, 2592 cm^{-1} for the apical and equatorial BH groups, respectively: Jotham, R. W.; McAvoy, J. S.; Reynolds, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 473.

(40) Reference 32, p 289.