

# Organotransition-Metal Metallacarboranes. 35.<sup>1</sup> Electrochemistry, ESR, and Correlated NMR Spectroscopy of Paramagnetic Mono- and Dinuclear Cp\*CoC<sub>2</sub>B<sub>4</sub> Clusters

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The redox behavior of the cobaltacarborane sandwich complexes Cp\*Co[(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (1), Cp\*Co[(Me<sub>3</sub>Si)-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>] (2), {Cp\*Co[(Me<sub>3</sub>Si)C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]CH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (4), Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>) (5), and Cp\*Co(Me<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>) (6) was investigated via cyclic voltammetry, proton NMR spectroscopy, and ESR spectra of paramagnetic anionic species. The reductions of the neutral diamagnetic monocobalt complexes 1 and 2 to their monoanions and of the dicobalt species 4 to the dianion were studied by recording in each case a series of NMR and ESR spectra during intermittent exposure to a potassium mirror until complete conversion to the anion was achieved. The NMR chemical shift correlations so obtained allow complete assignment of the paramagnetic NMR signals and afford information on the effects of reduction in different regions of the molecules. The NMR and ESR data indicate that reduction takes place primarily at cobalt. In general, as probed by <sup>1</sup>H NMR spectroscopy, the effects of reduction are strongest for the Cp\* protons and are weaker for those further from the paramagnetic metal center. The methyl protons in SiMe<sub>3</sub> groups attached to the carborane are more strongly affected than are the methyl protons of carborane-bound ethyl groups. These findings are consistent with the ESR spectra of the paramagnetic anions, which show smaller cobalt hyperfine coupling constants for the silyl-substituted species than for the ethyl derivatives.

## Introduction

The versatile role of small carborane and organoborane ligands in stabilizing organotransition-metal sandwich complexes is well documented, and a wide range of structurally varied systems is now accessible by straightforward synthetic routes.<sup>3</sup> These include multidecker, polydecker, and linked sandwiches,<sup>1a,4–6</sup> "staircase" oligomers and polymers,<sup>6c</sup> carborane-ligated metal clusters,<sup>7</sup> Fischer carbenes,<sup>8</sup> metallocene analogues,<sup>9</sup> and others. Much of the effort in the development of this chemistry has necessarily centered on synthesis and

modification of these compounds, but increasingly, attention is being directed to their detailed electronic structures and properties. This is important for both basic and practical reasons; the possible application of these complexes in the development of new conductive and magnetic materials will ultimately depend on the degree to which such properties can be tailored to meet specific requirements. Electrochemical data, ESR spectroscopy, and correlated NMR spectroscopy of paramagnetic complexes have been useful in the investigation of many of these systems. In this paper we report the application of these techniques to mono- and dicobalt species that incorporate the *nido-C*-(trimethylsilyl)carborane ligands [2,3-(SiMe<sub>3</sub>)(R)C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sup>2-</sup> (R = H, SiMe<sub>3</sub>), in which the combined data afford an unusual level of insight into the electronic structures.

## Results and Discussion

**Electrochemistry.** An earlier paper<sup>10</sup> reported the synthesis of Cp\*Co[(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (1), its catalytic desilylation to generate Cp\*Co[(Me<sub>3</sub>Si)C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>] (2) and Cp\*Co(C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>) (3), and the conversion of 2 to the xylylene-linked species {Cp\*Co-[(Me<sub>3</sub>Si)C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]CH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (4), summarized in Scheme 1. As a basis for evaluating the electrochemical behavior of the silyl derivatives, we first conducted cyclic voltammetry on the *C,C'*-diethyl and -dimethyl cobaltacarboranes 5 and 6 (Table 1). As shown in Figure 1, there is a marked solvent dependence, in that the cation 5<sup>+</sup> is stable only in dichloromethane (DCM). Thus, 5 exhibits one irreversible oxidation and one reversible reduction in 1,2-dimethoxyethane (DME), while in DCM only the oxidation (which is reversible) is observed. Not unexpectedly, the potentials are ca. 0.3 V more negative in 5 than those

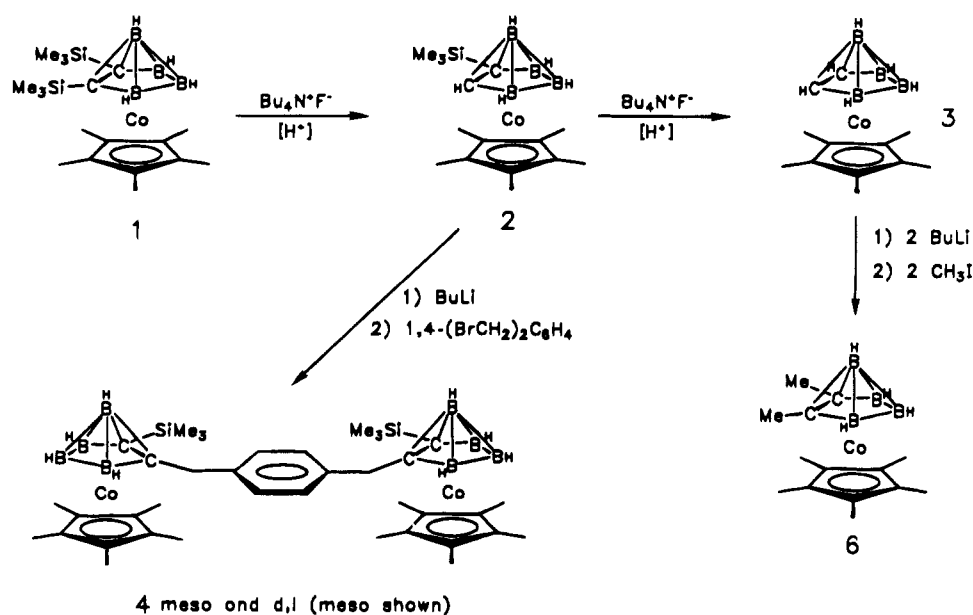
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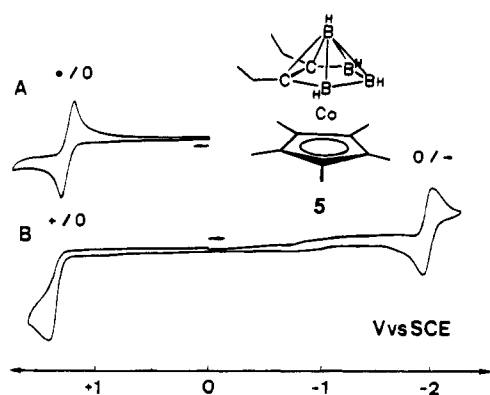
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Scheme 1

**Table 1.** Electrochemical Data for Cp\*CoC<sub>2</sub>B<sub>4</sub> Complexes<sup>a</sup>

compound	couple	$E^\circ$ <sup>b</sup>	$\Delta E_p$ <sup>c</sup>	current ratio <sup>d</sup>	$\nu$ <sup>e</sup>	solvent
Cp*Co[(Me <sub>3</sub> Si) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] (1)	+ / 0					DME
{Cp*Co[(Me <sub>3</sub> Si)C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ]CH <sub>2</sub> } <sub>2</sub> C <sub>6</sub> H <sub>4</sub> (4)	+ / 0	-1.77	100	0.99	0.05	DME
	0 / 2-	-1.84	80	0.95	0.05-1	
Cp*Co(Et <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ) (5) <sup>g</sup>	+ / 0	+1.43	<i>f</i>		0.1	DME
	0 / -	-1.99	88	0.91	0.05-2	
5 <sup>h</sup>	+ / 0	1.27	70	0.97	0.05-5	DCM
	0 / -					
Cp*Co(Me <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ) (6)	0 / -	-1.92	104	0.98	0.1-1	DME

<sup>a</sup> Data reported for platinum-disk working electrodes at room temperature; electrolyte [Bu<sub>4</sub>N][PF<sub>6</sub>], 0.1 M. <sup>b</sup> Volts vs saturated calomel electrode (SCE);  $E^\circ$  reported for reversible systems, peak potentials ( $E_p^{\text{ox}}$ ,  $E_p^{\text{red}}$ ) for irreversible systems. <sup>c</sup> Separation in mV of anodic and cathodic peaks. <sup>d</sup> Ratio is given as  $i_a/i_c$  for reductions,  $i_c/i_a$  for oxidations. <sup>e</sup> Scan rate in V s<sup>-1</sup>. <sup>f</sup> Irreversible. <sup>g</sup> No other redox processes were observed within the voltage range accessible in DME (to -3.0 V). <sup>h</sup> Oxidation is reversible at ca. -80 °C; reduction was not observed in DCM.



**Figure 1.** Cyclic voltammograms of Cp\*Co(Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>) (5): (A) in dichloromethane (DCM, 178 K); (B) in dimethoxyethane (DME, 298 K). Voltammograms were recorded at Pt electrodes vs saturated calomel electrode (SCE) ( $\nu = 0.1$  V s<sup>-1</sup>) in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

previously measured<sup>11</sup> for the Cp analogue CpCo(Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>), reflecting the higher electron density on the Cp\* species and hence greater difficulty in reducing it. It is notable that 5<sup>-</sup>, in contrast to CpCo(Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>), does not undergo reduction to the dianion within the voltage range examined (to -3.1 V) in DME. Therefore, the potential for the second reduction is shifted at least 0.6 V in the negative direction, indicating

increased stability of 5<sup>-</sup> toward reductive degradation relative to its Cp counterpart.<sup>11</sup> The C,C'-dimethyl derivative 6 shows similar behavior to 5, undergoing reduction at a slightly less negative potential than the latter compound.

It is also instructive to compare 5 with the isoelectronic (arene)ferracarboranes ( $\eta^6$ -C<sub>6</sub>Me<sub>n</sub>H<sub>6-n</sub>)Fe(Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>) ( $n = 0-6$ ), whose reduction potentials are nearly 1 V more negative (ca. -2.8 V in THF).<sup>12</sup> Paralleling the usual observation in transition-metal sandwich compounds,<sup>13</sup> the Cp\* metallacarborane complexes are better electron-acceptors than are their arene metallacarborane analogues, with the consequence that the Cp\* complexes form more stable anions.

The reduction potential of the bis(trimethylsilyl) complex 1 is shifted positively by ca. 0.2 V relative to the diethyl compound, indicative of the  $\pi$ -electron acceptor capability of the SiMe<sub>3</sub> group. The cyclic voltammogram of the dinuclear complex 4 is closely similar to those of the mononuclear species. As was found previously<sup>14</sup> for the phenylene-linked diiron carborane complexes [(Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)FeH<sub>x</sub>(C<sub>5</sub>Me<sub>4</sub>)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> ( $x = 0, 0.5, 1$ ), there is no evidence of electron exchange between the redox centers; moreover, experiments using known concentra-

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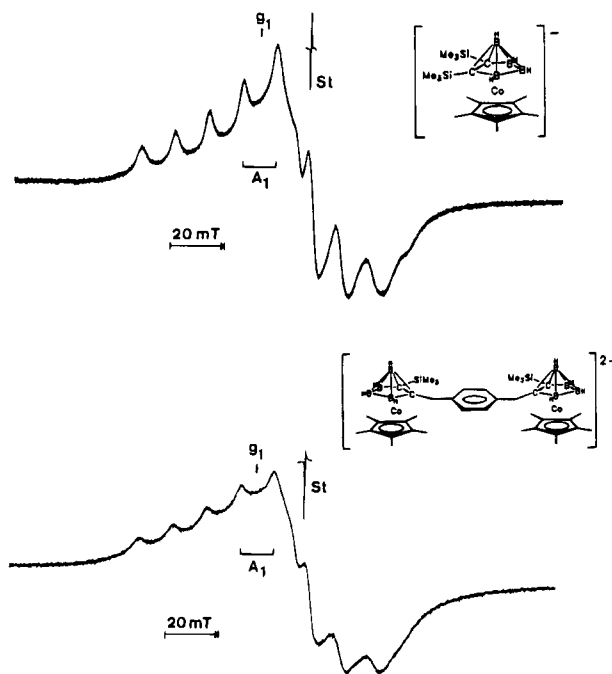
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**Table 2.** X-Band ESR Data for Complex Anions  $1^-$ ,  $4^{2-}$ , and  $5^-$  <sup>a</sup>

anion	$\langle g \rangle$	$g_1$	$g_2$	$g_3$
$1^-$	2.021	2.124 (12.0)	2.000	1.940
$4^{2-}$	2.088	2.109 (12.2)	2.078 ( $g_{2,3}$ )	
$5^-$	2.010	2.106 (13.0)	2.005	1.918

<sup>a</sup> Spectra recorded in THF glass at 110 K; coupling constants  $A_i$  (mT) are given in parentheses.

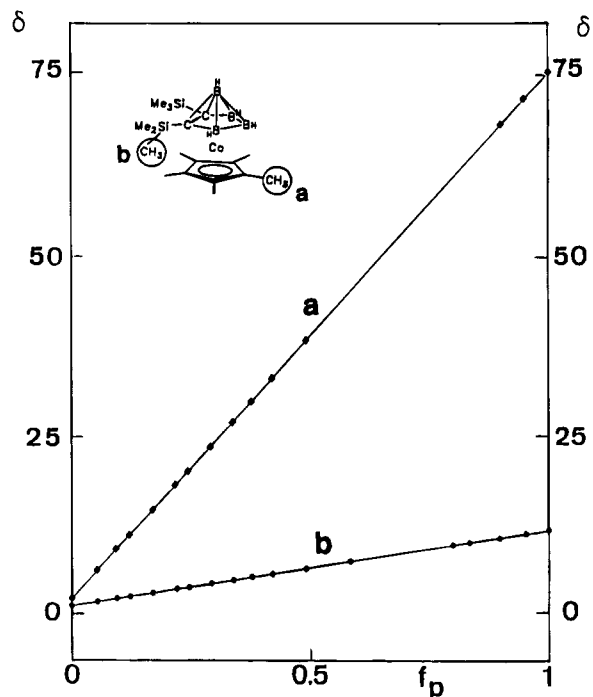


**Figure 2.** X-Band ESR spectra of  $1^-$  and  $4^{2-}$  in THF glass at 110 K referenced to LiTCNQ,  $\langle g \rangle = 2.0025$ .

tions of **5** and **4** demonstrated that the reduction of **4** is a two-electron process, as expected if the metals are in fact independent noncommunicating centers.<sup>15</sup>

**ESR Studies.** The radical anions  $5^-$ ,  $1^-$ , and  $4/4^{2-}$  were generated by reduction of the neutral compounds on a potassium mirror in THF and investigated via ESR spectroscopy. The data are listed in Table 2 and the spectra of the latter two ions are presented in Figure 2. In each case, a rhombic signal was observed with clearly resolved cobalt hyperfine splitting. Six of the eight hyperfine lines are resolved in the low-field region, with coupling constants ( $A_i$ ) from 12.0 to 13.0 mT. It is noteworthy that the coupling is smaller in the  $\text{SiMe}_3$  species  $1^-$  and  $4/4^{2-}$  than in the diethyl complex  $5^-$  (Table 2); this is consistent with NMR studies (vide infra), which show that reduction has a greater effect on the trimethylsilyl than on the ethyl  $\text{CH}_3$  protons, which are located at approximately the same distance from the metal center. Although the value of  $A_3$  was determined for  $1^-$  and  $5^-$ , and that of  $g_2$  was estimated, this was not possible for  $4/4^{2-}$ . In this case, only the mean value,  $g_{2,3} = 2.078$ , can be given. In the spectrum of  $4/4^{2-}$  no signal was found at  $H_0/2$ , indicating an absence of exchange between the metals. Further reduction of **5** and  $4/4^{2-}$  (but not  $1^-$ ) produced a signal with  $g = 2.00$ , which probably arises from organic radicals generated by reductive degradation.<sup>16</sup>

**NMR Studies.** The technique of correlated NMR spectroscopy developed by Zenneck and co-workers<sup>14,17</sup> was applied to



**Figure 3.** Correlation diagram for  $^1\text{H}$  NMR spectra of  $1/1^-$  mixtures in  $\text{THF-}d_8$ . Values of  $\delta$  (vertical axis) are plotted vs  $f_p$  ( $[1^-]/[1]$ ).

the trimethylsilyl compounds as a further probe of their electronic structures. Stepwise reduction of a solution of **1** in  $\text{THF-}d_8$  via intermittent exposure to a potassium mirror yielded the diagram shown in Figure 3 (shifts as a function of the  $[1]/[1^-]$  ratio are listed in supplementary tables). As can be seen, both the  $\text{Cp}^*$  and  $\text{SiMe}_3$  protons exhibit downfield shifts, the former showing the stronger effect. The behavior of this system is very similar to that observed elsewhere<sup>18</sup> for the  $\text{Cp}^*\text{Fe}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{CoCp}^*$  (**7**) monoanion: the reduction of  $7^-$  to  $7^{2-}$  shifts the  $\text{Cp}^*\text{Me}$  proton signal from  $\delta +1.50$  to  $+31.50$ . This implies that the electronic environments in **1**, an 18 VE double-decker species, and  $7^-$ , a 30 VE triple-decker, are indeed quite similar, consistent with their formal analogy as 7-vertex  $\text{CoC}_2\text{B}_3\text{E}$  clusters ( $\text{E} = \text{BH}, \text{FeCp}^*$ ). In both systems, the NMR and ESR data suggest that reduction of the diamagnetic to the paramagnetic species takes place primarily at cobalt and that the unpaired electron in the 19 (or 31) VE product is largely localized on that metal. These observations contrast with recent findings<sup>19</sup> on the 29 VE  $[\text{Cp}^*\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(i\text{-PrC}_6\text{H}_4\text{Me})]^+$  and  $[(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}_2(i\text{-PrC}_6\text{H}_4\text{Me})_2]^+$  triple-decker sandwich cations, in each of which the unpaired electron was found to be completely delocalized between the two metals; delocalization is also suggested by electrochemical studies on  $\text{C}_2\text{B}_3$ -bridged  $\text{CoCoCo}$  and  $\text{CoNiCo}$  tetradeccker sandwich complexes.<sup>20</sup>

The shift of the  $\text{SiMe}_3$  protons, while less sensitive to reduction than the  $\text{Cp}^*$  protons, nevertheless represents a greater effect ( $\delta$  0.38–11.52) than is observed for the Me signal of the

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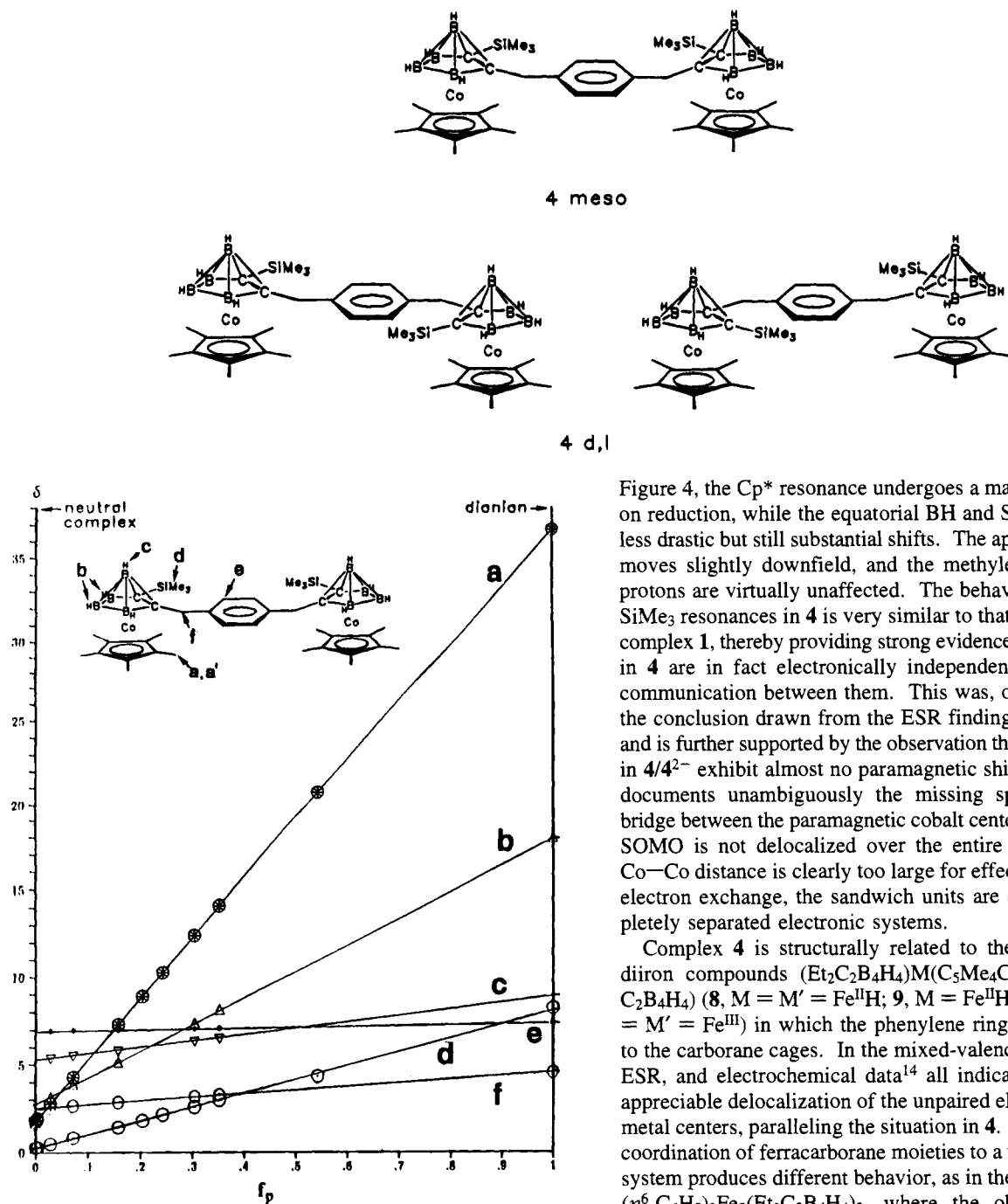
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Chart 1



**Figure 4.** Correlation diagram for  $^1\text{H}$  NMR spectra of  $4/4^{2-}$  mixtures in  $\text{THF}-d_8$ . Values of  $\delta$  (vertical axis) are plotted vs  $f_p$  ( $[4^{2-}]/[4]$ ).

carboranyl ethyl groups in **7**, which is virtually unchanged on reduction to the anion. We interpret this as further evidence for interaction between the silyl groups and the cage, probably via a  $\pi$ -acceptor mechanism.

A similar correlated NMR study of the xylylene-linked bis-(cobaltcarboranyl) complex **4** was conducted, the diagram for which is presented in Figure 4. The signals for each of the six types of protons were followed as a function of mole fraction of the reduced (dianion) species. The observation of BH signals in a correlated NMR experiment is, to our knowledge, unprecedented (the resonances of the equatorial protons on B(4,6) and B(5) were superimposed). This complex has three isomers, an achiral meso form and a pair of enantiomers (Chart 1), whose spectra are essentially indistinguishable; all data were measured on an unresolved mixture of these species. As is apparent from

Figure 4, the  $\text{Cp}^*$  resonance undergoes a major downfield shift on reduction, while the equatorial BH and  $\text{SiMe}_3$  signals show less drastic but still substantial shifts. The apex BH proton peak moves slightly downfield, and the methylene and phenylene protons are virtually unaffected. The behavior of the  $\text{Cp}^*$  and  $\text{SiMe}_3$  resonances in **4** is very similar to that in the monocobalt complex **1**, thereby providing strong evidence that the Co centers in **4** are in fact electronically independent with little or no communication between them. This was, of course, precisely the conclusion drawn from the ESR findings, described above and is further supported by the observation that the arene protons in  $4/4^{2-}$  exhibit almost no paramagnetic shift (Figure 4). This documents unambiguously the missing spin density in the bridge between the paramagnetic cobalt centers, proving that the SOMO is not delocalized over the entire molecule. As the Co—Co distance is clearly too large for effective through-space electron exchange, the sandwich units are consequently completely separated electronic systems.

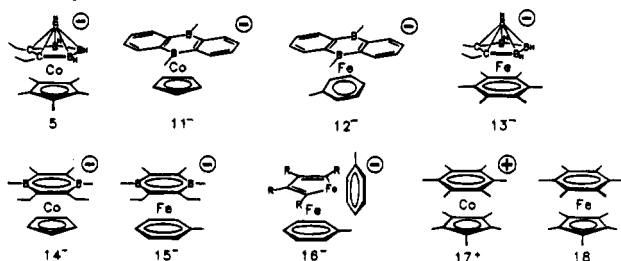
Complex **4** is structurally related to the phenylene-linked diiron compounds  $(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{M}(\text{C}_5\text{Me}_4\text{C}_6\text{H}_4\text{C}_5\text{Me}_4)\text{M}'(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$  (**8**,  $\text{M} = \text{M}' = \text{Fe}^{\text{IIH}}$ ; **9**,  $\text{M} = \text{Fe}^{\text{IIH}}$ ,  $\text{M}' = \text{Fe}^{\text{III}}$ ; **10**,  $\text{M} = \text{M}' = \text{Fe}^{\text{III}}$ ) in which the phenylene ring is directly bonded to the carborane cages. In the mixed-valence species **9**, NMR, ESR, and electrochemical data<sup>14</sup> all indicate that there is no appreciable delocalization of the unpaired electron between the metal centers, paralleling the situation in **4**. On the other hand, coordination of ferracarborane moieties to a fused-ring aromatic system produces different behavior, as in the biphenyl complex  $(\eta^6\text{-C}_6\text{H}_5)_2\text{Fe}_2(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)_2$ , where the observation of two reversible one-electron oxidations clearly implies Fe—Fe communication.<sup>21</sup>

The electrochemical and ESR properties of the 19 VE radical anions investigated in this work are consistent with results obtained on structurally related toluene iron and cyclopentadienyl-cobalt complexes of comparable structure, as can be seen in Table 3. Despite the variation in ligands among the species listed, the similarity in ESR data underline the common electronic structure shared by these complexes. In all cases shown, the ESR spectra indicate that the unpaired electron is not occupying a low-lying ligand SOMO. This is true even for the 1,3-diphosphate complex anion  $[(\eta^6\text{-MeC}_6\text{H}_5)\text{Fe}(\eta^4\text{-P}_2\text{C}_2\text{-tBu}_2)]^-$ , which exhibits a rhombic ESR spectrum that reveals

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Table 3. X-Band ESR Data for Related Complexes<sup>a</sup>

anion	$g_1$	$g_2$	$g_3$	$T$ (K)	ref
5 <sup>-</sup>	2.106	2.005	1.918	110	this work
11 <sup>-</sup>	2.166	2.018	1.978	110	4c
12 <sup>-</sup>	2.123	2.035	1.966	110	4c
13 <sup>-</sup>	2.062	1.999	1.909	77	12
14 <sup>-</sup>	2.140	2.040	1.990	110	22
15 <sup>-</sup>	2.072	1.994	1.939	110	22
16 <sup>-</sup>	2.092	1.986	1.967	110	23, 24
17 <sup>+</sup>	2.103	2.022	1.912	3.5	25
18	2.063	2.000	1.864	3.5	26

<sup>a</sup> Key:

coupling of the unpaired electron to both phosphorus nuclei of the four membered ring.<sup>24</sup> Extended Hückel MO calculations give evidence that nearly 60% of the electron spin is concentrated on the metal  $d_{yz}$  orbital and 10% on the phosphorus  $\pi$ -orbitals, the latter being responsible for the observed coupling.<sup>24</sup> Ab initio studies by Ammeter et al. on  $[(\eta^6\text{-C}_6\text{Me}_6)\text{-}$

$\text{CoCp}^*\text{J}^+$  (17<sup>+</sup>)<sup>25</sup> and  $(\eta^6\text{-C}_6\text{Me}_6)\text{FeCp}^*$  (18)<sup>26</sup> suggest that 60–75% of the spin density of the SOMO is located in a metal-centered MO; in the case of 18, further calculations indicate extensive covalent bonding between the metal and the ligand.

This study exploits the remarkable ability of metallocarborane sandwich complexes to undergo redox processes without decomposition, allowing one to reversibly interconvert paramagnetic and diamagnetic species in solution and thereby bring to bear ESR and NMR spectroscopies, as well as electrochemistry, on systems of interest. Information on electronic structure generated in this way will be helpful in designing metal–boron cluster assemblies having specific properties, an essential aspect of efforts to develop new materials based on compounds of this type.

### Experimental Section

The trimethylsilyl-substituted cobaltacarboranes employed in this work were prepared as described elsewhere.<sup>10</sup> The instrumentation and techniques used in the ESR, NMR, and electrochemical studies were as reported in an earlier paper.<sup>14</sup>

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**Supplementary Material Available:** Tables of <sup>1</sup>H NMR chemical shifts of 1/1<sup>-</sup> and 4/4<sup>2-</sup> as a function of mole fraction of reduced species (2 pages). Ordering information is given on any current masthead page.

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