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Organotransition-Metal Metallacarboranes Electrochemistry of Polymetallacarborane Staircase Oligomers[1]

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A series of linked-sandwich metallacarborane oligomers having 5–17 metal atoms was investigated via cyclic voltammetry and compared with homologous double-decker and tetradecker monomeric sandwich complexes. Systems having the general formula $[(Et_2C_2B_3H_4R)CoL]_2[(C_6H_4)LCo(Et_2C_2B_3H_2R)M(Et_2C_2B_3H_2R)CoL]_n(C_6H_4)$ (n = 1,3,5; L = η^5-C_5Me_4; M = Co, Ni; R = Cl, Me) were examined. In general, the cyclic voltammograms of these compounds are a composite of those found for the double-decker complex *nido*-$Cp^*Co(Et_2C_2B_3H_4Cl)$ and the tetradecker sandwiches $Cp^*Co(Et_2C_2B_3H_2R)Co(Et_2C_2B_3H_2R)CoCp^*$ as described in the accompanying paper.[1] Since the double-decker and tetradecker monomers correspond to the component units of the linked complexes, the absence of any large differences in the reduction potentials of the monomers and linked systems suggests that there is little intersandwich electronic communication, although there is good evidence of delocalization *within* the individual tetradecker stacks.[1] Small positive shifts are seen in the potentials of the linked species relative to the tetradecker monomers and are accounted for in terms of replacement of methyl substituents by phenylene units in the Cp* rings of the monomers.

Introduction

The construction of multidecker sandwich complexes and linked-sandwich oligomers that are stabilized by C_2B_3 carborane ring ligands has been a subject of recent publications from this laboratory.[1–4] Building-block complexes of the type $Cp^*Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}R)$ (**1** in Figure 1) are converted to $Cp^*Co(Et_2C_2B_3H_2R)M(Et_2C_2B_3H_2R)CoCp^*$ tetradecker sandwiches (e.g., **2**) via deprotonation and reaction with transition-metal ions.[2,4] Analogous stacking reactions can be conducted on bis(cobaltacarboranyl) complexes of the type $[(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}R)Co(C_5Me_4)]_2C_6H_4$ to give phenylene-linked oligomers **3**, and the sequence can be repeated to afford the 11-cobalt and 17-cobalt systems **4** and **5**.[3] Remarkably, all of these complexes are air-stable and soluble in organic solvents—important properties in the context of potential applications as precursors to new electronically, magnetically, and/or optically active materials.

Tetradecker complexes such as **2** in which M is Co, Ni, or Ru have been investigated in some detail,[2b] and the electrochemistry of 40–42-electron CoRuCo, CoCoCo, and CoNiCo systems is described in the preceding article.[1] The evidence of significant electron delocalization in these monomeric stacks, combined with a recent study of fully delocalized CoCo and CoRu triple-decker metallacarborane cations,[5] prompted the next question: what happens in linked-sandwich oligomers such as **3**–**5**? Specifically, we were interested to see how the electronic properties of these larger complexes compare with those of the monomeric tetradeckers, especially with respect to the degree of communication between the metal centers in different sandwich units.

Experimental Section

The instrumentation and techniques employed were as given in the preceding paper. The synthesis and characterization of the multisandwich oligomers **3a**–**3c**, **4**, and **5** are described elsewhere.[3]

Results and Discussion

$Cp^*Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}Cl)$ (1). Since each of the oligomeric species of interest in this study contains $(Et_2C_2B_3H_4R)Co$ end groups, it was necessary first to establish the behavior of the monomer **1**. The electrochemistry of this complex is relatively simple. Cyclic voltammetry in dimethoxyethane (DME) revealed one clearly irreversible and one quasi-irreversible reduction, both at very negative potentials (−2.70 and −2.97 V relative to ferrocene), as shown in Figure 2 and summarized in Table I. It is remarkable that no electrochemical activity is observed between +0.54 and −2.46 V in DME; in dichloromethane (DCM) the corresponding range is +0.53 to −2.57 V. There is a small wave at −0.85 V in DME (−0.92 V in DCM) that is seen only after scanning to very negative potentials. In DCM, an irreversible oxidation occurs at +0.91 V. In both solvents, the irreversibility of the processes does not change at faster scan speeds up to 1000 mV s^{-1}.

These observations on **1** reflect the comparatively high reactivity of this complex which, unlike the tetradeckers, has B–H–B bridges and is susceptible to interaction with solvent on its open face. Moreover, it is not surprising to

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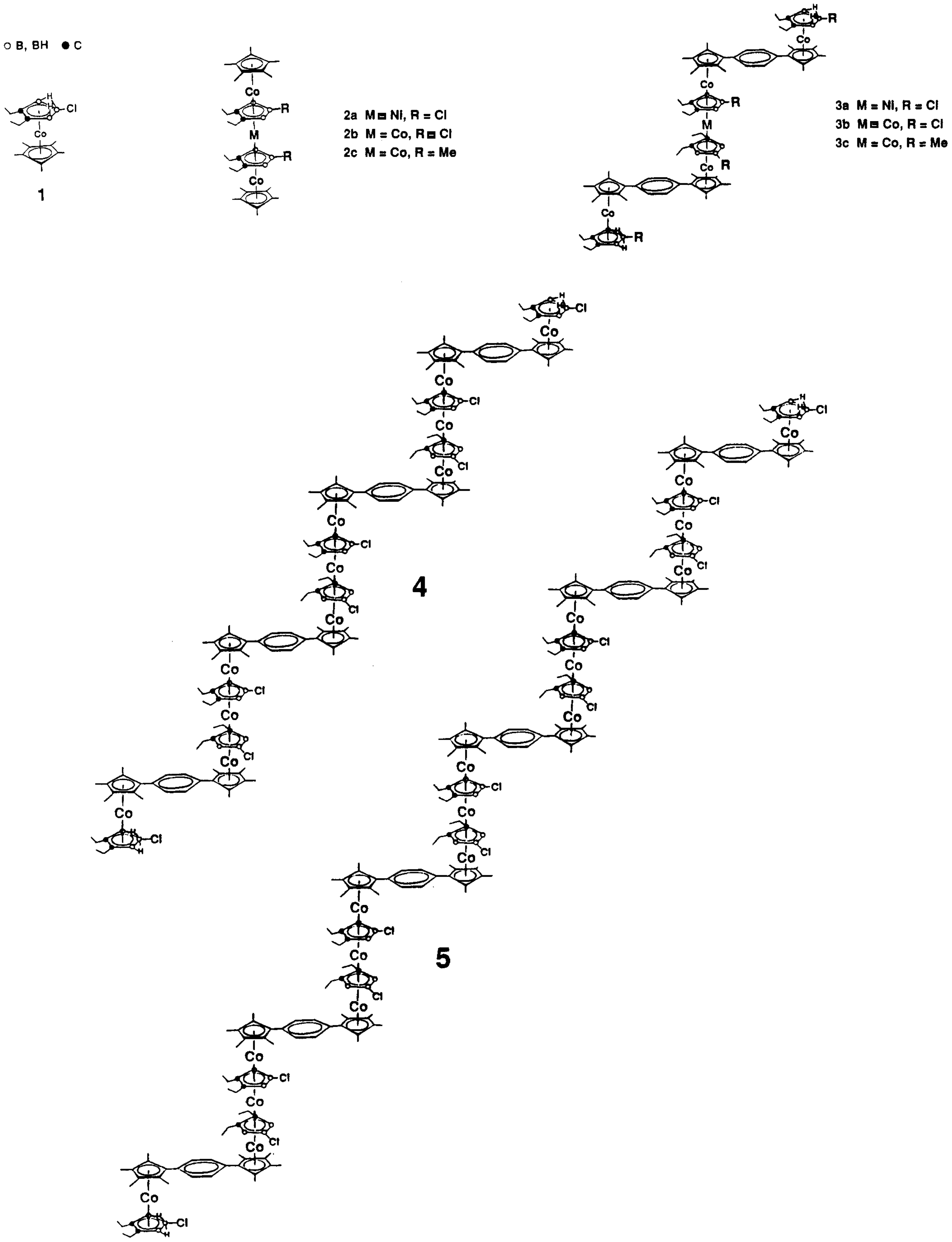

Figure 1. Structures of metallacarborane double-decker sandwich (1), tetradecker sandwiches (2 and 3), and proposed structures of linked-sandwich oligomers (4 and 5).

find that the small *nido*-CoC_2B_3 framework cannot accommodate additional electron density without undergoing irreversible change. As will be seen, the electrochemical signature of the $Co(Et_2C_2B_3H_4R)$ unit is distinctive and is readily identified in the cyclic voltammograms of the oligomers.

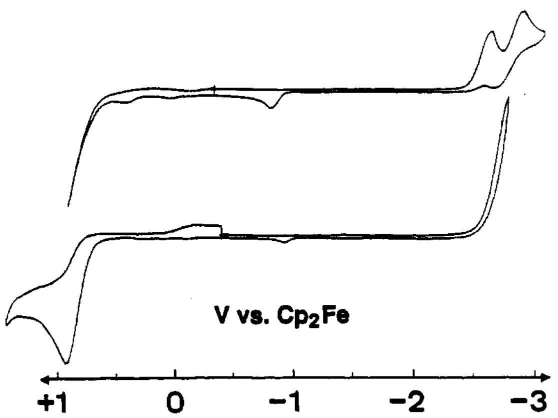

Figure 2. Cyclic voltammograms of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_2\text{-}5\text{-}Cl)$ (**1**) in dimethoxyethane (DME, top) and dichloromethane (DCM, bottom), recorded at Pt electrodes vs ferrocene at 20 °C (v = 0.2 V s^{-1}) in 0.1 M Bu_4NPF_6.

Tetradecker Monomers. Three complexes described in the accompanying report,[1] $CoNiCoCl_2$, $CoCoCoCl_2$, and $CoNiCoMe_2$ (**2a**–**2c**), are directly relevant to this study, and the salient observations are as follows. As summarized in Table I, each neutral species exhibits a 1-electron reversible oxidation and a 1-electron reversible reduction, as confirmed via controlled potential electrolysis.[1] The dichloro compounds **2a** and **2b** also show a second reversible reduction. The observation of successive, widely separated 1-electron reductions of the identical Cp*Co units in these complexes is taken as an indication of extensive electronic communication between the metal centers, an effect that appears more pronounced in the CoCoCo system (mean separation 1.49 V) than in the CoNiCo case (0.72 V).[1] Finally, in all three compounds a second, irreversible oxidation is also observed in both solvents.[1]

The redox potentials in the tetradecker systems are, in general, well separated from those of double-decker $(Et_2C_2B_3H_4R)Co$ end groups described above and conse-

Table I. Cyclic Voltammetry Data^{a}

		DME			DCM		
compd	couple	$E^{\circ\,b}$	$\Delta E_p{}^{c}$	current ratio^{d}	$E^{\circ\,b}$	$\Delta E_p{}^{c}$	current ratio^{d}
$Cp^*Co(Et_2C_2B_3H_4Cl)$ (**1**)	+/0	e			0.91^{f}		
	0/−	−2.70^{f}					
	−/2−	−2.97^{f}					
$[Cp^*Co(Et_2C_2B_3H_2Cl)]_2Ni$ (**2a**)^{h}	3+/2+				+1.20^{e}		
	2+/+	0.89^{e}			+0.88^{e}		
	+/0	+0.18	190	0.98	+0.06	130	0.92
	0/−	−1.44	190	0.98	−1.54	130	1.04
	−/2−	−2.17	195	1.00	−2.26	140	0.92
$[Cp^*Co(Et_2C_2B_3H_2Cl)]_2Co$ (**2b**)^{h}	2+/+	e, g			1.04^{e,f}		
	+/0	+0.07	125	0.88	+0.00	105	0.83
	0/−	−1.13	130	0.94	−1.19	120	0.96
	−/2−	−2.62	120	0.91			
$[Cp^*Co(Et_2C_2B_3H_2Me)]_2Co$ (**2c**)^{h}	3+/2+				+1.55^{f}		
	2+/+	+0.84^{f}			+0.79^{f}		
	+/0	−0.16	220	0.88	−0.30	150	0.93
	0/−	−1.48	210	0.93	−1.55	145	0.97
	−/2−	−3.36^{f}					
$[(Et_2C_2B_3H_4Cl)Co(C_5Me_4)C_6H_4(C_5Me_4)\text{-}Co(Et_2C_2B_3H_2Cl)]_2Ni$ (**3a**)	3+/2+				+0.99^{f}		
	2+/+	e			+0.81^{f}		
	+/0	+0.23	130	0.90	+0.13	95	0.91
	0/−	−1.35	110	0.98	−1.44	90	0.98
	−/2−	−2.07	105	0.98	−2.12	120	0.90
	2−/3−	−2.62^{f}					
	3−/4−	−2.88^{f}					
$[(Et_2C_2B_3H_4Cl)Co(C_5Me_4)C_6H_4(C_5Me_4)\text{-}Co(Et_2C_2B_3H_2Cl)]_2Co$ (**3b**)	2+/+	e					
	+/0	+0.14	140	0.82			
	0/−	−1.07	125	0.99			
	−/2−	−2.55	135	i			
	2−/3−	−2.62^{f}					
	3−/4−	−2.90^{f}					
$[(Et_2C_2B_3H_4Me)Co(C_5Me_4)C_6H_4(C_5Me_4)\text{-}Co(Et_2C_2B_3H_2Me)]_2Co$ (**3c**)	2+/+	e, g			+0.92		
	+/0	−0.10	90	0.98	−0.24	80	0.92
	0/−	−1.40	100	0.81^{j}	−1.48	0.90	0.84^{j}
	−/2−	−2.82	~150				
	2−/3−	−2.89^{f}					
	3−/4−	−3.13^{f}					
11-cobalt oligomer (**4**)	2+/+	e					
	+/0	0.15	175	0.71			
	0/−	−1.06	180	1.00			
	−/2−	−2.55	175				
	2−/3−	−2.64^{f}					
	3−/4−	−2.86^{f}					
17-cobalt oligomer (**5**)	2+/+	e					
	+/0	0.15	100	0.71			
	0/−	−1.07	120	1.09			
	−/2−	−2.56	~130				
	2−/3−	−2.62^{f}					
	3−/4−	−2.80^{f}					

[a] Data reported for platinum disk working electrodes at room temperature; electrolyte $[Bu_4N][PF_6]$, 0.1 M. The scan rate was 200 mV s^{-1} in all cases. [b] Volts vs Cp_2Fe/Cp_2Fe^+; E° reported for reversible systems, peak potentials ($E_p{}^{ox}$, $E_p{}^{red}$) for irreversible systems. [c] Separation in mV of anodic and cathodic peaks. [d] Ratio is given as i_a/i_c for reductions, i_c/i_a for oxidations. [e] Multielectron process. [f] Irreversible. [g] Very irreversible; E_p not measurable. [h] Data from ref 1. [i] Peak ratio not obtainable due to overlap with signal from $(Et_2C_2B_3H_4Cl)Co$ end units. [j] Small apparent ratio caused by presence of impurity in sample.

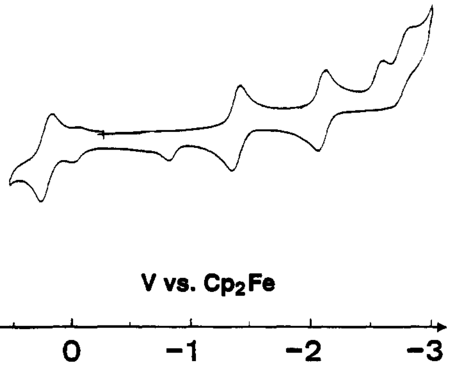

Figure 3. Cyclic voltammogram of $[(Et_2C_2B_3H_4Cl)Co(C_5Me_4)C_6H_4(C_6Me_4)Co(Et_2C_2B_3H_2Cl)]_2Ni$ (**3a**) in DME (same conditions as in Figure 2).

quently are, in most cases, readily identifiable in the multisandwich complexes to be discussed. In a few instances, there is overlap that requires careful analysis of the data in order to distinguish the processes occurring at the end units from those associated with the tetradecker stacks.

Co–CoNiCo–Co System (3a). The cyclic voltammogram (Figure 3) and electrochemical data in Table I show a reversible oxidation and two reversible reductions in both solvents, with further irreversible oxidations (in DCM) and reductions (in DME). Comparison of these data with the CoNiCo dichloro tetradecker complex **2a** reveals close similarity: the reversible formation of a monocation, a monoanion, and a dianion are seen in both species, with the potentials in **3a** shifted slightly positively in both solvents (0.05–0.14 V) relative to the monomer. The two irreversible reductions in **3a** (not observed in **2a**) clearly arise from the $(Et_2C_2B_3H_4Cl)Co$ end units. The small positive shifts in **3a** vs **2a** can be attributed to replacement of an electron-donating methyl group in the Cp* ligand of **2a** with an electron-withdrawing phenylene; thus, in going from the tetradecker monomer to the linked complex the tetradecker stack becomes slightly easier to reduce (and harder to oxidize). A similar effect is seen in the double-decker end group in **3a**, with the reductions at −2.62 and −2.88 V in **3a** slightly less negative than the corresponding values in the monomer **1**.

This behavior suggests that there is little if any electronic communication between the tetradecker and end units in **3a**; the three sandwich units are essentially electronically independent of each other. If there were significant communication, one would anticipate that, upon reduction to the monoanion, the added electron would be partially delocalized onto the end cobalts; consequently, it should be easier to add a second electron to the stack, and hence the second reduction of **3a** should show a greater positive shift in comparison to **2a**. This is evidently not the case. An inspection of Table I shows the first and second reductions are shifted by only 0.095 and 0.12 V, respectively (averaged for both solvents), a difference too small to be considered significant. This conclusion is reinforced by the observation of only small positive shifts in the reduction potentials of the end cobalts vs those in **1**, noted above.

Co–CoCoCo–Co System (3b and 3c). As was found for the nickel-centered oligomer **3a**, the electrochemistry of the pentacobalt species **3b** is essentially a composite of the waves observed for the corresponding tetradecker monomer (**2b**) and the double-decker complex **1**. However, in **3b** the second (reversible) reduction of the tetradecker stack (a 1-electron process) overlaps with the first (irreversible) reduction of the $(Et_2C_2B_3H_4Cl)Co$ end groups (a 2-electron process); the cathodic wave at −2.6 V consequently represents an overall 3-electron process. This is seen by comparing the cyclic voltammogram of **3b**, shown in Figure 4, with those of the $CoCoCoCl_2$ tetradecker (Figure 4 in the preceding paper) and **1** (Figure 2, above). The irreversible second reduction of the end units at −2.9 V is also a 2-electron process. The process that occurs near −2.6 V in **3b** has a very exaggerated cathodic component. In order to distinguish the $E_{1/2}$ for the second reduction of the CoCoCo sandwich from the first reduction of the double-decker end units, we assumed that the cathodic waves of the two entities are superimposed; hence, the voltage for the peak of the wave (−2.62 V) becomes $E_{p,c}$ for the first reduction of the end groups. Combining this value with $E_{p,a}$ (−2.48 V) yields $E_{1/2}$ = −2.55 V for the second reduction of the tetradecker stack. As a test of this determination, a differential pulse polarogram of this region was obtained, showing two peaks whose separation of 0.08 V compares closely with the value of 0.07 V obtained as described above.

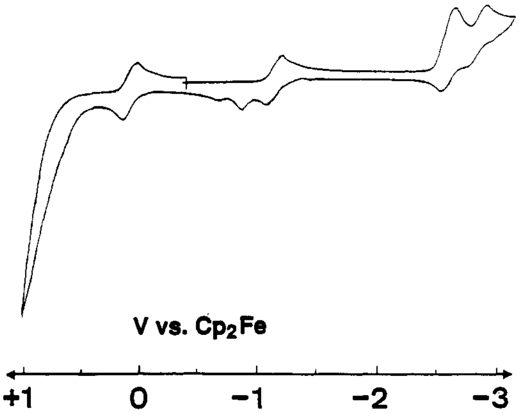

Figure 4. Cyclic voltammogram of $[(Et_2C_2B_3H_4Cl)Co(C_5Me_4)C_6H_4(C_5Me_4)Co(Et_2C_2B_3H_2Cl)]_2Co$ (**3b**) in DME (same conditions as in Figure 2).

As in the case of **3a**, there is little indication of electronic communication between the tetradecker and double-decker sandwich units. Comparison of the data for **3b** with those of the monomeric systems **2b** and **1** shows small positive shifts, comparable to those observed for **3a**. It is noteworthy that the potentials for the reduction of the double-decker end units (ca. −2.6 and −2.9 V) are nearly identical in **3a** and **3b**.

The ESR spectrum of **3b** at −170 K in toluene is very similar to that obtained earlier[2b] for the monomer **2b**, with $g_{\parallel}$ and $g_{\perp}$ values of 2.40 and 2.076, respectively; the corresponding values for **2b** are 2.37 and 2.035 under the same conditions. In both cases, there is no resolved cobalt hyperfine structure. These data imply that the presence of the end double-decker units has little effect on the paramagnetic central stack, consistent with the proposed absence of significant interstack electronic communication in the linked systems.

The electrochemistry of the B-methylated pentacobalt linked complex **3c** is different in some respects from its *B*-chloro analogue **3b**. The B-methyl tetradecker species **2c** exhibits only one reversible reduction,[1] indicating that the electron-donating methyl groups destabilize the monoanion. However, it is interesting that **3c** does show a second reversible reduction, which overlaps with the first reduction of the double-decker end units as in **3b**, discussed above, and requires a similar analysis of the data in order to determine the potentials. The fact that **3c**, but not **2c**, can be reversibly reduced to a dianion is readily accounted for by noting that the formal conversion of **2c** to **3c** entails replacement of a methyl substituent on the Cp* ring by a phenylene, which reduces the electron density in the system and allows a second reduction.

Once again, the first oxidation and first reduction of **3c** show small positive shifts (average 0.07 V) relative to the monomer **2c**. When one compares the potentials for reduction of the end groups in **3c** (i.e., the third and fourth reductions) with those of **1**, there is actually a *negative* shift; however, this is ascribed to the presence of *B*-chloro substituents in **1** vs *B*-methyl groups in **3c**. Replacement of an electron-withdrawing Cl with an electron-donating CH_3 group on the C_2B_3 ring will certainly make the system more difficult to reduce, as is observed. The same effect is seen by comparing the potentials for reduction of **3c** with those of **3b**; those of the former complex are much more negative (0.2–0.3 V) in both the tetradecker and double-decker regions.

11-Cobalt and 17-Cobalt Systems (4 and 5). The long-chain oligomers **4** and **5** contain CoCoCo tetradecker stacks and chloro substituents, and thus are closely related to **3b**. One expects similar electrochemical behavior, but small differences that may offer insight into the effects of increasing chain length should not be overlooked. Comparison of the data on these three complexes does indeed show close similarity, with virtually identical values of $E_{1/2}$ for the tetradecker reductions and $E_{p,c}$ for the end units. Of course, in the larger complexes the ratio of double-decker to tetradecker units is smaller, decreasing from 2:1 in **3b** to 2:3 in **4** and 2:5 in **5**; consequently, in the latter systems the double-decker signals are much less pronounced. In the cyclic voltammogram of **5**, the oxidation and first reduction show a small wave ~0.2 V negative of the principal wave, which may indicate that one of the five CoCoCo stacks in the molecule (most likely the middle one) is distinct from the others, although the possibility of an impurity is not discounted. A differential pulse polarogram of this region clearly shows a shoulder, but we were unable to further define this feature.

Conclusions

This general picture of the electronic nature of the phenylene-linked multisandwich oligomers that emerges from this study, and from NMR and electronic spectra reported earlier,[2,3] is that the individual tetradecker and double-decker end units are effectively insulated from each other electronically. This is particularly evident in compounds containing 41-electron CoCoCo tetradecker stacks, whose paramagnetism is confined to those groups and (as seen in NMR spectra[3]) does not extend to the diamagnetic $(Et_2C_2B_3H_4R)Co$ end groups. At this point, we believe that the absence of interstack delocalization is primarily a consequence of the tilt of the connecting phenylene rings relative to the planes of the attached C_5Me_4 ligands on the metallacarborane sandwiches. Such out-of-plane bending has been observed, with dihedral angles of 46–55°, in each of the four currently available crystal structures of metallacarborane complexes that incorporate the $(C_5Me_4)_2C_6H_4$ ligand[3,6] (in **3b**[3] the mean value for the two phenylenes is 46.3°). The same feature is undoubtedly present in all such species, including the oligomers **4** and **5**. The tilt is attributed to steric repulsion of the C_6H_4 bridge by adjacent methyl groups on the C_5Me_4 rings, which evidently prevents π-conjugation of the three carbocycles and thereby blocks electronic communication.

The nondelocalization in this particular class of linked-sandwich complexes would of course make them, per se, unlikely candidates as precursors to conducting polymers; on the other hand, the isolation of individual electron spins in noncommunicating CoCoCo stacks creates the possibility of molecular ferromagnetism, a subject of current study in collaboration with other groups. Related oligomers in which the phenylene bridge is coplanar with the adjacent C_5 rings may allow delocalization between stacks; better yet would be the elimination of the phenylenes entirely, as in fulvalene-bridged multisandwich systems. We have recently described the synthesis[3] of 5-cobalt and 8-cobalt fulvalene-linked oligomers incorporating CoCoCo stacks whose electronic properties are presently under exploration.[7]

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