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Organotransition-Metal Metallacarboranes. 32. Electrochemical and Electron Spin Resonance Studies of Tetradecker Sandwich Complexes[1]

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Cyclic voltammetry and controlled potential electrolysis studies were conducted on a series of carborane-bridged tetradecker sandwich complexes of the general formula $[\text{Cp*Co}(\text{Et}_2\text{C}_2\text{B}_3\text{X}_n\text{H}_{3-n})]_2\text{M}$ (CoMCoX_{2n}) where M is Co, Ni, or Ru and X is halogen, Me, acetyl, or 2-butynyl. In dimethoxyethane (DME) or dichloromethane (DCM) solution, most of the complexes exhibited reversible reductions to a monoanion and a dianion as well as oxidation to a cation, with additional reversible or irreversible processes observed in the majority of cases. In the 42-electron diamagnetic CoNiCo series, the introduction of progressively more electron-withdrawing substituents produced a strong positive shift, but the trend was not as clear in the 41-electron CoCoCo systems. An indication of electron delocalization in the CoCoCo complexes was provided by the large separation (up to 1.69 V) in the first and second reduction potentials, which were shown via controlled potential electrolysis to be 1-electron processes. Delocalization was also observed in the CoNiCo system, whose corresponding shifts (0.73–0.84 V) were lower although still substantial. Electrochemical oxidation of the dark orange tetrachloro complex CoNiCoCl_4 to a monocation was reversible in DCM, but the second oxidation proceeded irreversibly, generating a new rose-colored species that, in turn, underwent a third oxidation. An attempt to isolate the rose complex via chromatography on silica resulted in its conversion to a different species that was characterized from NMR and mass spectra as a difluorotetrachloro complex, $\text{CoNiCoCl}_4\text{F}_2$ and subsequently studied electrochemically. Introduction of fluorine into the tetradeckers is attributed to reaction of the electrochemically generated oxidation product with the supporting electrolyte, Bu_4NPF_6. ESR spectra of several of the CoCoCo tetradecker complexes were measured and shown to be comparable to other electronically related transition-metal carborane and organoborane sandwich systems.

Introduction

Investigations of the electronic structures and properties of multidecker transition-metal sandwich complexes can furnish insight into the metal–metal interactions in such systems and are essential to their development as precursors to electroactive or magnetoactive materials.[1,2] Complexes having cyclic planar carborane (C_2B_3) or organoborane (C_3B_2, C_4B, C_4B_2) units sandwiched between metal centers are particularly useful for studies of this kind, in view of their stability, solubility in organic solvents, and ease of preparation, and the fact that they can be made with a variety of metals and substituent groups.[3] A further advantage is afforded by families of well-characterized double-, triple-, and quadruple-decker (tetradecker) stacked complexes bearing idential identical carborane or organoborane bridging rings.[3] The close structural relationships within such families facilitate direct comparisons between species and make it possible to observe changes in properties as additional metal–ligand units are added to the stack.

A recent spectroelectrochemical study[4] on the 30-electron triple-decker species $(\text{cymene})\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{cymene})$ and $(\text{cymene})\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{CoCp}$ (cymene = $p\text{-MeC}_6\text{H}_4\text{CHMe}_2$) demonstrated that the electrochemically produced 29-electron monocations of both complexes are class III (completely delocalized) mixed-valent species. In the present paper we describe an electrochemical investigation of several varieties of carborane-bridged tetradecker sandwiches:[1b] diamagnetic 42-electron $[\text{Cp*Co}(\text{Et}_2\text{C}_2\text{B}_3\text{X}_n\text{H}_{3-n})]_2\text{Ni}$ (here abbreviated as CoNiCoX_{2n}); paramagnetic 41-electron $[\text{Cp*Co}(\text{Et}_2\text{C}_2\text{B}_3\text{X}_n\text{H}_{3-n})]_2\text{Co}$ (CoCoCoX_{2n}); and a diamagnetic 40-electron ruthenium–dicobalt tetradecker, $\text{Cp*Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_2\text{Cl})\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{HCl}_2)\text{CoCp*}$ (CoRuCoCl_3). In these species the X group is a halogen or organic substituent and Cp* is ($\eta^5\text{-C}_5\text{Me}_5$). Our objectives were to probe the electronic structures and the question of electron delocalization in

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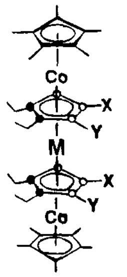
these systems and to examine the electrochemical consequences of varying the X substituents.



o B, BH ● C

M = Co, Ni, Ru

X = H, C(O)Me, Cl, Br, I, $CH_2C{\equiv}CMe$

Y = H, Cl

Experimental Section

Materials. The synthesis and characterization of most of the tetradecker sandwich compounds employed in this study have been reported previously.[1b] The solvents for electrochemistry, CH_2Cl_2 (DCM) and $(CH_3OCH_2)_2$ (DME), were purified via reflux over CaH_2 for at least 48 h under argon followed by distillation through a 1-m vacuum-jacketed Vigreux column. The first 15% and final 15% of the distillate were rejected, and the remainder was stored under argon. In most cases this process was repeated a second time, yielding solvents with a voltage window of at least 4.0 V. The supporting electrolyte, $[Bu_4N][PF_6]$, was purchased from Fluka (electrochemical grade), dried at 110 °C under vacuum for 20 h, and stored under nitrogen. Ferrocene and decamethylferrocene were obtained from Strem Chemicals and used as received.

Synthesis of $[Cp^*Co(2,3\text{-}Et_2C_2B_3HCl_2)]_2Ni$ ($CoNiCoCl_4$). Following the published procedure for tetradecker synthesis,[1b] 0.380 g (0.993 mmol) of *nido*-$Cp^*Co(2,3\text{-}Et_2C_2B_3HCl_2)$ in 50 mL of dry THF was deprotonated in vacuo at ca. 0 °C with an equimolar amount of butyllithium. Nickel(II) bromide (0.108 g, 0.5 equiv) was added in vacuo with stirring, causing an immediate color change to dark brown/black. The mixture was stirred 4 h at room temperature, the flask was opened to the air, the solvent removed by rotary evaporation, and the residue taken up in a minimal volume of CH_2Cl_2. The black residue was placed on a 2-cm column of silica gel and washed successively with hexane and CH_2Cl_2 until the filtrate was clear. The hexane washing contained primarily the reagent complex (0.25 mmol recovered). The methylene chloride washing was evaporated to dryness, and the residue was chromatographed on a silica plate in 1:1 hexane:CH_2Cl_2, affording four bands, of which the second (20 mg, 0.024 mmol, 10% yield based on starting material consumed) was dark brown $CoNiCoCl_4$. Mass spectrum: cutoff at *m/z* 824, base peak *m/z* 819, strong parent envelope closely matches the calculated intensities for $NiCo_2Cl_4C_{32}B_6H_{52}$ based on natural isotope abundances. ^{11}B NMR (115.8 MHz, CH_2Cl_2, ppm relative to $BF_3{\cdot}OEt_2$, ^1H-decoupled): 12.9 (area 2, broad), 74.0 (area 1). ^1H NMR (360 MHz, $CDCl_3$, ppm relative to TMS): 2.71 (q, ethyl CH_2), 2.54 (m, ethyl CH_2), 1.60 (t, ethyl CH_3) 1.49 (s, C_5Me_5), 1.42 (t, ethyl CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm vs TMS): 101.5 (C_2B_3), 91.2 (C_5 ring), 24.7 (ethyl CH_2), 24.4 (ethyl CH_2), 14.7 (ethyl CH_3), 14.6 (ethyl CH_3), 9.9 (Cp* CH_3).

Characterization of $[Cp^*Co(2,3\text{-}Et_2C_2B_3Cl_2F)]_2Ni$ ($CoNiCoCl_4F_2$). The solution generated in the second oxidation of $CoNiCoCl_4$ in CH_2Cl_2 during cyclic voltammetry experiments (*vide infra*) was evaporated to dryness, the residue was dissolved in 1:1 CH_2Cl_2:hexane, the resulting solution was filtered through a 3.0-cm silica column to remove the supporting electrolyte, and the filtrate was chromatographed on a preparative silica TLC plate. This gave two bands, the larger of which was identified spectroscopically as $CoNiCoCl_4F_2$. Mass spectrum: cutoff at *m/z* 864, base peak *m/z* 856, strong parent envelope closely matching the calculated intensities for $NiCo_2Cl_4F_2C_{32}B_6H_{50}$. ^1H NMR (360 MHz, $CDCl_3$, ppm relative to TMS): 2.82 (q, ethyl CH_2), 2.56 (m, ethyl CH_2), 1.64 (t, ethyl CH_3) 1.53 (s, C_5Me_5), 1.46 (t, ethyl CH_3). ^{19}F NMR (338.7 MHz, $CDCl_3$, ppm relative to $CFCl_3$): −60.6 (s, broad). The smaller band was tentatively identified from its mass spectrum as a monofluorotetrachloro species ($CoNiCoCl_4F$): cutoff at *m/z* 842, base peak *m/z* 838, strong parent envelope closely matching the calculated intensities for $NiCo_2Cl_4FC_{32}B_6H_{51}$.

Electrochemistry. All electrochemical measurements were obtained under nitrogen in a drybox equipped with a scrubber to remove both water and oxygen. The electrochemical cells were locally constructed and contained a round glass bottom made from a 25-mm test tube and a Teflon top with holes for the electrodes. The cell volume was 10 mL but could be used with as little as 1 mL of solution. The working electrode was a Pt disk (1-mm diameter) purchased from BAS and was employed for both cyclic voltammetry and differential pulse polarography. The reference electrode consisted of a glass tube with a 5-mm Vycor frit and a Pt wire. All potentials were measured using either the Cp_2Fe/Cp_2Fe^+ (Fc) or $Cp^*_2Fe/Cp^*_2Fe^+$ (Fc*) couple as an internal standard. The potential of Fc* relative to Fc was measured in both solvents under conditions identical to those employed for the compounds. The values found based on Fc = 0.00 V were −0.55 V in CH_2Cl_2 and −0.46 V in DME.

Cyclic voltammetry measurements were obtained with a Princeton Applied Research Model 173 potentiostat/galvanostat driven by a PAR Model 175 universal programmer. The potentiostat/galvanostat included a PAR Model 179 digital coulometer which was used for controlled potential electrolysis experiments. Differential pulse polarographic measurements were conducted using a PAR Model 174A polarographic analyzer with output to an *xy* recorder. In a typical experiment, 5 mL of 0.10 M $[Bu_4N][PF_6]$ (0.14 g of solute) was placed in the cell and background CVs were taken to verify the voltage window. The preweighed sample was added to make the concentration (1.0–1.5) × 10^{-3} M, and cyclic voltammograms were taken at 200 mV s^{-1} unless otherwise noted. Following the measurements, either Fc or Fc* was added as an internal reference.

Reversibility of the waves was determined by several standard procedures. The chemical reversibility (i_{rev}/i_{for}) was measured and with rare exception gave values of 0.90–1.05 for waves having both an anodic and a cathodic component. Electrochemical reversibility was measured by comparing ΔE_p for the Fc or Fc* couple. The values of ΔE_p for the compounds studied were generally 10–20% larger than that of the reference in the same solvent, although in some cases they were smaller. In the case of $CoRuCoCl_3$ the compound was successfully reduced to the monoanion, reoxidized, and then reduced again in two steps to the dianion with acceptably consistent *n* values.

Controlled potential electrolysis experiments were conducted in a traditional H cell that was similar to the single cell used for other measurements. The auxiliary electrode was a Pt wire, and the auxiliary compartment was separated from the working electrode by two very fine glass frits. The working electrode was a 25-mm square piece of fine mesh Pt screen rolled into a cylinder. Electrical contact was made with a Pt wire. The same reference electrode and solvent system described above were used.

Electron Spin Resonance. ESR measurements were made on a Bruker ESP 300 instrument, with all work conducted at 100–130 K in small diameter quartz tubes. Electrochemically generated species were kept in sealed tubes in the drybox until immediately prior to use. Samples were dissolved in toluene (in DME if generated electrochemically) and DPPH was used as an internal reference in all cases.

Results and Discussion

Electrochemistry of the CoNiCo Complexes. Cyclic voltammetry on six diamagnetic 42-electron complexes[1b] was conducted in DME and DCM, with the results presented in Table I and voltammograms of the dibromo derivative shown in Figure 1. In the course of the study a new, fluorinated species was obtained electrochemically as described below and is included in the table. In DME, all seven complexes exhibited reductions to a monoanion

Table I. Cyclic Voltammetry Data for CoNiCo Tetradecker Complexes[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]
$CoNiCoMe_2$	4+/3+				$-1.35^{e,f}$		
	3+/2+				$+0.93^{e,f}$		
	2+/+	$+0.65^{e}$			$+0.61^{e}$		
	+/0	−0.08	220	0.90	−0.21	155	0.93
	0/−	−1.84	220	0.90	−1.91	120	0.92
	−/2−	−2.64	190	0.98			
$CoNiCo(CH_2CCMe)_2$	4+/3+				$+1.34^{e,f}$		
	3+/2+				$+0.91^{e,f}$		
	2+/+	*f, g*			$+0.61^{e}$		
	+/0	+0.04	140	0.96	−0.06	100	0.79
	0/−	−1.72	140	1.02	−1.81	120	0.79
	−/2−	−2.56	150	0.85			
$CoNiCo[C(O)Me]_2$	2+/+	*f, g*			$+0.93^{e}$		
	+/0	$+0.33^{e}$			$+0.24^{e}$		
	0/−	−1.48	210	0.88	−1.57	170	0.87
	−/2−	−2.32	215	0.82	−2.31	180	0.39
$CoNiCoCl_2$	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
$CoNiCoBr_2$	3+/2+				$+1.71^{e}$		
	2+/+	0.91^{e}			$+1.13^{e}$		
	+/0	+0.22	150	0.93	+0.15	160	0.91
	0/−	−1.37	140	0.88	−1.44	130	0.93
	−/2−	−2.10	135	0.94	−2.14	190	0.78
$CoNiCoCl_4$	3+/2+				+1.11	135	0.95
	2+/+				$+1.01^{e}$		
	+/0	+0.30	190	0.90	+0.23	155	0.89
	0/−	−1.18	200	0.95	−1.24	150	0.91
	−/2−	−1.96	180	1.03	−1.97	150	0.99
	2−/3−	-3.42^{e}					
$CoNiCoCl_4F_2$	+/0	+0.36	90	0.90	+0.31	85	0.94
	0/−	−1.04	80	1.00	−1.11	80	0.93
	−/2−	−1.76	85	0.99	−1.78	85	0.92

[a] Data reported for platinum disk working electrodes at room temperature; electrolyte $[Bu_4N][PF_6]$, 0.1 M. 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] Irreversible. [f] Multielectron process. [g] Very irreversible; E_p not measurable.

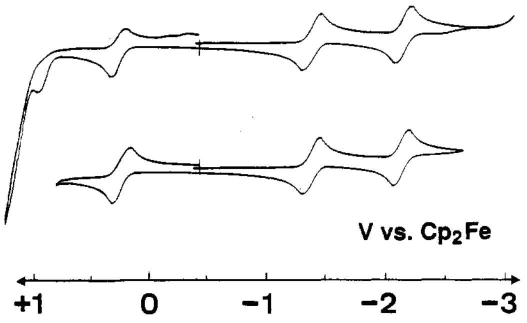


Figure 1. Cyclic voltammograms of $[(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_2\text{-}5\text{-}Br)]_2Ni$ ($CoNiCoBr_2$) at Pt electrodes vs ferrocene at 20 °C (v = 0.2 V s^{-1}) in 0.1 M Bu_4NPF_6/DME. The lower plot was recorded over a shorter scan range to demonstrate the reversibility of the first oxidation.

and a dianion as well as oxidation to a monocation, reversible in all cases except for the oxidation of the diacetyl species. The tetrachloro species produced unusual results and is discussed below.

In dichloromethane solution the findings were similar, with reversible first oxidations for all species other than the diacetyl and irreversible higher oxidations in several instances. Several of the CoNiCo complexes also gave irreversible second and third oxidations, and in the dimethyl and dibutynyl compounds even a fourth oxidation was observed. Each of the complexes exhibited a reversible first reduction, and reversible second reductions were seen for all except $CoNiCoMe_2$ and $CoNiCo(CH_2CCMe)_2$. As can be seen in Table I, most processes were shifted slightly in the negative direction (ca. 0.1 V) in DCM relative to DME.

These data clearly show the effects of introducing substituents at boron positions on the C_2B_3 rings. For the electrochemical processes

$$\text{irrev oxidation} \leftarrow CoNiCoX_2{}^+ \leftrightarrow CoNiCoX_2 \leftrightarrow CoNiCoX_2{}^- \leftrightarrow CoNiCoX_2{}^{2-}$$

the potentials, expressed as reductions, are more positive for the more electron-withdrawing substituents, as expected. What is somewhat unexpected is the magnitude of the effect: In DME the first oxidation, first reduction, and second reduction of $CoNiCoCl_4F_2$ (vide infra) are, respectively, 0.44, 0.80, and 0.88 V greater than the corresponding values for $CoNiCoMe_2$; in DCM the shifts in the potentials of the first oxidation and first reduction are 0.52 and 0.80 V (the second reduction of the dimethyl species was not observed in that solvent). A clear trend is seen in both solvents: progressively more negative values, relative to $CoNiCoCl_4F_2$, are found for the tetrachloro, dichloro and dibromo, diacetyl, dibutynyl, and dimethyl complexes, indicating a correspondingly greater ease in oxidizing (and difficulty in reducing) these species. These findings correlate in a general way with two recent observations:[1b] (i) the downfield ^1H NMR shift of the B–H–B protons induced by electron-withdrawing X groups in *nido*-$Cp^*Co(Et_2C_2B_3H_4X)$ complexes and (ii) the stabilization of C_2B_3-bridged tetradecker sandwich complexes by electronegative substituents such as C(O)Me, Cl, and Br. In sum, the electrochemical, chemical, and NMR evidence supports a model of stabilization of high oxidation state on the central metal via electron withdrawal from the carborane ring ligands.

The 1-electron nature of the reduction and oxidation waves was demonstrated via controlled potential electrolysis studies on $CoNiCoCl_2$ and $CoNiCoCl_4$. Reduction of the dichloro species to the monoanion was done on three samples with n values of 1.03, 0.95, and 0.91 (mean value 0.96), and CVs taken before and after each reduction were identical. In two of these experiments, reduction to the dianion was also achieved ($n = 0.97$ and 0.95) and again there was no change in CVs taken before and after. These data clearly establish that the reversible oxidation and two reversible reductions observed in this series of complexes are 1-electron processes.

The electrochemical data do not rigorously establish electron delocalization in the tetradecker stacks, but the observed behavior is consistent with significant metal–metal communication. Each of the complexes studied incorporates two identical $Cp^*Co(Et_2C_2B_3H_nX_{3-n})^{2-}$ units coordinated to a central metal atom (M) which is in a formal +4 oxidation state. If there were no electronic communication between the two cobaltacarborane units, one would expect to see either a 2-electron process as the equivalent cobalt centers are reduced simultaneously at the same potential followed by a 1-electron reduction of M(IV) or, alternatively, an initial 1-electron reduction of M(IV) followed by a 2-electron reduction of the end cobalts (the possibility of successive reductions at M(IV), leaving the cobalts unaffected, is rejected). Neither scenario is seen, and the actual finding of successive 1-electron reductions with widely separated potentials is therefore taken as an indication of some Co–Co communication. Further evidence is afforded by the observation of 1-electron reversible oxidations in most of the CoNiCo and CoCoCo tetradeckers: oxidation of the end Co(III) centers would be seen as a 2-electron process if these equivalent cobalts were noncommunicating. A completely localized model is, in any case, highly unlikely in view of the recent finding of full delocalization in closely related C_2B_3-bridged CoCo and CoRu triple-decker systems, mentioned earlier.

The separation between successive reductions in the CoNiCo complexes is quite large; for example, in DME the second reduction occurs at a mean value of 0.78 V relative to the first (in the CoCoCo systems, discussed below, the separation is even greater). For the previously studied diruthenium triple-deckers,[4] two corresponding oxidation waves were separated by 0.95 V. In CpCo(2,3-$C_2B_3H_5$)CoCp and CpCo(2,4-$C_2B_3H_5$)CoCp, which similarly have multiple redox oxidation states,[5] the two 1-electron reductions are separated by 0.79 and 0.95 V, respectively. All of the reversible processes exhibit similar values of ΔE_p, $i_{p,c}$, and $i_{p,a}$, and the ΔE_p values are only slightly larger, in general, than those of the internal standards.

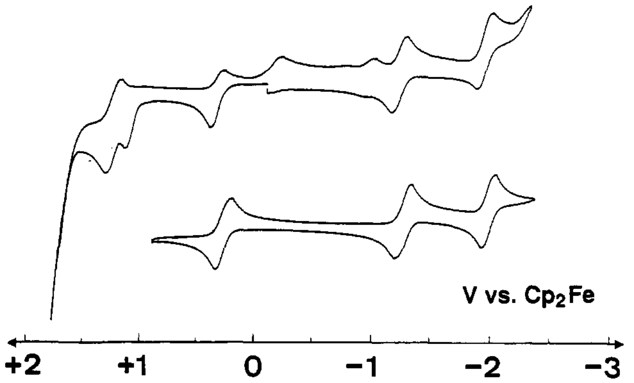


Figure 2. Cyclic voltammograms of $[(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H\text{-}4,5\text{-}Cl_2)]_2Ni$ ($CoNiCoCl_4$) at Pt electrodes vs ferrocene at 20 °C ($v = 0.2$ V s^{-1}) in 0.1 M Bu_4NPF_6/CH_2Cl_2. The lower plot was recorded over a shorter scan range to demonstrate the reversibility of the first oxidation and the first and second reductions.

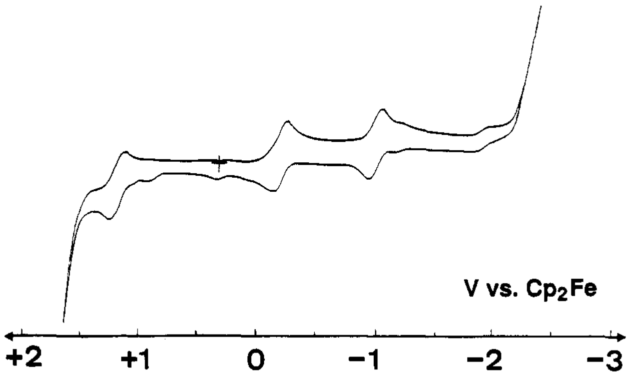


Figure 3. Cyclic voltammogram of a rose-colored complex generated via second oxidation of $CoNiCoCl_4$ (see text). Conditions were as given in Figure 2. The observed E^0 values (in volts, with ΔE_p and current ratio given in parentheses) are as follows: +/0, 1.12 (145, 1.05); 0/−, −0.24 (120, 1.01); −/2−, −1.02 (125, 0.99).

The tetrachloro complex $CoNiCoCl_4$ showed unusual behavior and accordingly was studied extensively. In DME the usual reversible oxidation and two reversible reductions were observed, as was a third reduction which was irreversible. In comparison to the dichloro species, the waves for the tetrachloro compound are shifted positively by 0.1–0.2 V, reflecting the presence of two additional chlorines in the latter species; however, a second oxidation was not seen. In DCM the behavior was more complex, as depicted in Figure 2. In addition to the reversible generation of a monocation and mono- and dianions, there is an irreversible (probably 1-electron) second oxidation at $E° = +1.01$ V and a third oxidative process at +1.11 V that, remarkably, appears reversible based on its i_c/i_a value of 0.95 and a ΔE_p of 0.135 V. On the assumption that the formation of the dication initiated an electrochemical generation of a new species which in turn gave rise to the third oxidation, we conducted a controlled potential electrolysis study. In separate trials, oxidation to the monocation and dication gave mean n values of 0.90 and 0.92, respectively. A CV taken after the first oxidation was unchanged from the original, but following the second oxidation a new CV was obtained (Figure 3), accompanied by a dramatic color change of the solution from nearly black to rose-red. Although this voltammogram is similar in appearance to those of the other tetradecker sandwiches, exhibiting a reversible oxidation and two reversible reductions, there are pronounced positive shifts (see figure caption); the observed potentials are 0.9 V more positive than those of the starting $CoNiCoCl_4$ complex. A third reduction was not directly observed, but at ca. −2.2 V the current rose exponentially.

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Table II. Cyclic Voltammetry Data for CoCoCo and CoRuCo Tetradecker Complexes[a]

		DME			DCM		
compd	couple	E° [b]	ΔE_p [c]	current ratio[d]	E° [b]	ΔE_p [c]	current ratio[d]
$CoCoCoMe_2$	3+/2+				+1.55[e]		
	2+/+	+0.84[e]			+0.79[e]		
	+/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[e]					
$CoCoCo[C(O)Me]_2$	2+/+	+0.60[e]			+0.69	135	
	+/0	+0.15[e]	165	0.21	+0.07[e]	125	0.38
	0/−	−1.08	190	0.88	−1.19	120	0.96
	−/2−	−2.77	180	0.80			
$CoCoCoCl_2$	2+/+	*f, 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			
$CoCoCoI_2$	+/0	+0.18	215	0.95			
	0/−	−1.03	210	0.94			
	−/2−	−2.53[e]	205	0.38			
	2−/3−	−3.10[e,h]					
$CoRuCoCl_3$	3+/2+				+1.34[e]		
	2+/+	+1.02[e]			+1.02[e]		
	+/0	+0.48[e]			+0.39[e]		
	0/−	−1.09	165	0.92	−1.16	150	0.98
	−2/−	−2.23	145	0.99	−2.27	125	0.86

[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. 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] Irreversible. [f] Multielectron process. [g] Very irreversible; E_p not measurable. [h] Possible third reduction; not conclusively identified.

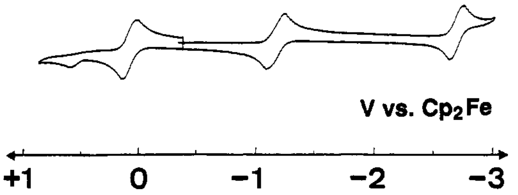

Figure 4. Cyclic voltammogram of $[(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_2\text{-}5\text{-}Cl)]_2Co$ ($CoCoCoCl_2$) at Pt electrodes vs ferrocene at 20 °C (v = 0.2 V s^{-1}) in 0.1 M Bu_4NPF_6/DME.

In an effort to isolate the rose complex, the electrolysis solution was worked up in air as described in the Experimental Section, affording a dark orange-brown product that was characterized from mass spectra and ^1H NMR and ^{19}F NMR spectra as $CoNiCoCl_4F_2$, an air-stable compound whose electrochemical data are reported in Table I. A minor product was isolated and tentatively identified as a monofluorotetrachloro complex, $CoNiCoCl_4F$. These findings suggest that the second electrochemical oxidation of $CoNiCoCl_4$ is accompanied by reaction with the electrolyte Bu_4NPF_6, the only source of fluorine in the system. From the CVs of the isolated complex $CoNiCoCl_4F_2$ and its rose-colored precursor, there is no doubt that these are different species. In the absence of other than electrochemical data on the latter compound, its identity at present is a matter for speculation, but the fact that it gives rise to the tetrachlorodifluoro complex strongly implies that it retains the essential CoNiCo tetradecker structure.

Electrochemistry of the CoCoCo Complexes. The 41-electron tricobalt stacks were anticipated to show more difficult oxidations and more facile reductions than their 42-electron CoNiCo counterparts having identical X substituents. While this was found to be true in part, the results reveal a complex pattern. The CV data for the four compounds studied are summarized in Table II, and the voltammogram of the dichloro species is presented in Figure 4. The dimethyl, diacetyl, dichloro, and diiodo compounds showed reversible first oxidations and first reductions in DME, except for $CoCoCo[C(O)Me]_2$ whose oxidation was irreversible. The diacetyl and dichloro species also exhibited a second reversible reduction, and $CoCoCoMe_2$ showed a second, irreversible, reduction process at the solvent limit; the diiodo complex underwent a second, and possibly a third, reduction, both irreversible. The correlation between these data and the electron-withdrawing ability of X is less clearcut than in the CoNiCo systems discussed above. The first oxidation and reduction of $CoCoCoMe_2$ are shifted negatively relative to those of $CoCoCoCl_2$, as expected; however, the potentials of the dichloro, diiodo, and diacetyl species are close, with no clear trend. This behavior contrasts with that of the CoNiCo series and is perhaps surprising given the electronegativity difference between I and Cl. We believe that these observations are related to a highly delocalized electronic structure in the 41-electron CoCoCo system, which is proposed to contain a vacancy in an MO that is bonding throughout the molecule (discussed below); electronic effects of substituents on such a system would likely be complex, involving the entire sandwich.

In DCM the general results were similar, with reversible reductions for the dimethyl, dichloro, and diacetyl complexes (the diiodo species was not examined) and reversible oxidations for the first two. The irreversibility of the oxidation of $CoCoCo[C(O)Me]_2$ in both solvents matches the observations for $CoNiCo[C(O)Me]_2$ and points to the acetyl groups as the loci of oxidative chemical change. However, significant differences are apparent in these species. In the CoNiCo diacetyl complex, the first oxidation was irreversible at scan speeds up to 1000 mV s^{-1}, indicating rapid decomposition of the cation; for the CoCoCo diacetyl species, the $i_{p,c}/i_{p,a}$ ratio increased from 0.28 V at 50 mV s^{-1} to 0.77 V at 2000 mV s^{-1}, revealing a much slower process. Moreover, while the CoNiCo compound showed an irreversible second oxidation, its CoCoCo counterpart exhibited a nominally *reversible* process at 0.69 V that disappeared at high scan speeds. This is similar to the behavior of $CoNiCoCl_4$ upon oxidation to the 40-

electron dication, discussed in detail above, and accordingly suggests that a similar fate—fluorination by the PF_6^- electrolyte—may be occurring in the case of CoCoCo[C(O)Me]$_2$.

The argument for communication between the equivalent redox centers in the CoCoCo species is analogous to that given above for the CoNiCo systems. The values of 1.49 V for $CoCoCoCl_2$ and 1.69 V for the diacetyl complex can be compared to the corresponding shifts for the seven CoNiCo species, which range from 0.73 to 0.84 V (mean value 0.78 V). Controlled potential electrolysis of $CoCoCoCl_2$ demonstrated that the oxidation and reduction are reversible 1-electron processes with n = 0.85 and 0.79 V; efforts to reduce the anion to a dianion were unsuccessful even in a drybox, owing to the high negative potentials required.

Comparison with related multidecker systems is useful. The 0.79-V separation in the first and second reductions of the $CpCo(2,3\text{-}C_2B_3H_5)CoCp$ triple-decker,[5] a diamagnetic 30-electron stack, is essentially the same as that found in the CoNiCo tetradeckers. The 43-electron tetradecker complex[6] $[CpCo(Et_2HC_3B_2Me_2)]_2Co$ in CH_2Cl_2 exhibits only one reduction but two oxidations, separated by 1.94 V; this behavior reflects in part the presence of C_3B_2 rings as well as the eight alkyl substituents, all of which shift the redox processes in the negative direction. Finally, the "hybrid" tetradecker complex[7] $CpCo(Et_2MeC_3B_2Et_2)Co(Et_2C_2B_3H_3)CoCp^*$, a 42-electron CoCoCo system, is unsymmetrical and, as expected, shows two 1-electron reductions. If the cobalt centers were not in communication, these should occur at similar potentials; in fact, they are separated by 0.91 V in DME, implying substantial delocalization.

Electrochemistry of $CoRuCoCl_3$. The cyclic voltammetry data on this complex (Table II) reveal that it does not survive oxidation in either solvent, even at high (1000 mV s^{-1}) scan speeds. It undergoes two 1-electron reductions, both of which were confirmed by controlled potential electrolysis (0/–, n = 0.97; –/0, n = 0.96; –/2–, n = 1.20. Given the unsymmetrical structure[1b] with one ring monochlorinated and the other dichlorinated, two separate reductions are expected for the inequivalent cobalts, as is indeed found. However, the large separation (ca. 1.1 V) in both solvents once again is consistent with electron delocalization. This point is particularly emphasized if one compares the first reduction of $CoNiCoCl_2$ with that of $CoNiCoCl_4$: adding a second Cl to each ring in the former species produces positive shifts of only 0.26 V in DME and 0.30 V in DCM. Hence, in $CoRuCoCl_3$, a similarly small effect should be anticipated in the reductions of its two rings if there were minimal electronic communication between them. Obviously, such is not the case.

Electron Spin Resonance Spectra. The ESR spectrum of the 41-electron $CoRuCoCl_3^-$ anion at –170 °C shows a $g_\parallel$ of 2.40 and a $g_\perp$ of 2.051, very close to the values (2.37, 2.035) previously reported[1b] for the 41-electron $CoCoCoCl_2$ species (it will be noted that both complexes have a formal +3 central metal). There is no sign of hyperfine splitting in either case. These data can be compared with those of the indenyl complex[8] $(\eta^5\text{-}C_9H_7)Fe^{III}(Et_2C_2B_4H_4)$ for which $g_\parallel$ and $g_\perp$ are 2.535 and 2.008 respectively, and the closely related species[8] $(\eta^5\text{-}C_5Me_5)Fe^{III}(Et_2C_2B_4H_4)$ for which $g_\parallel$ and $g_\perp$ are 2.689 and 1.979, respectively. Both spectra are almost identical in appearance with that of $CoRuCoCl_3^-$.

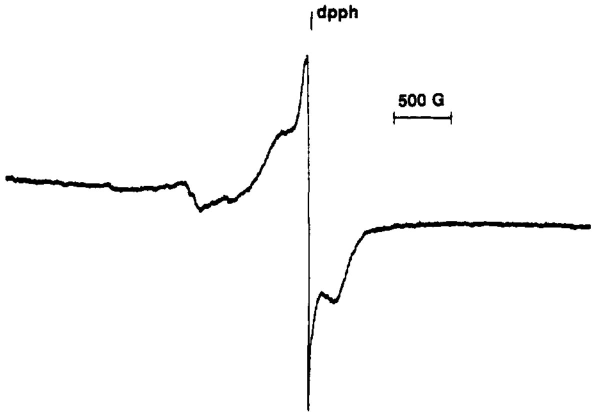

Figure 5. X-band ESR spectrum of the electrochemically generated $CoNiCoCl_2^-$ monoanion in DME glass at –160 °C with dpph as the internal reference. The small low-field signal is attributed to a sample impurity.

The ESR spectrum of the electrolytically generated 43-electron $CoNiCoCl_2^-$ anion, shown in Figure 5, is indicative of an orthorhombic g tensor with $g_1 = 2.19$, $g_2 = 2.027$, and $g_3 = 1.88$. This species contains a formal Ni(III) (d^7) center and can be compared with the Fe(I) (d^7) anion[9] $(\eta^6\text{-}C_6Me_6)Fe^I(Et_2C_2B_4H_4)^-$, which gave $g_1 = 2.062$, $g_2 = 1.999$, and $g_3 = 1.909$.

Electronic Structure of Chlorinated Tetradeckers. It is appropriate here to compare the three complexes $CoRuCoCl_3$, $CoCoCoCl_2$, and $CoNiCoCl_2$, which are respectively 40-, 41-, and 42-electron systems having similar substituents (all have been fully characterized including X-ray structure determinations[1b]). None of these survives oxidation to a 39-electron system, and $CoNiCoCl_2$ cannot be reversibly oxidized even to a 40-electron species; each of the complexes, however, can be reduced in two steps to a dianion having, respectively, 42, 43, and 44 electrons. A theoretical study of the idealized 46-electron $CpCoCpCoCpCoCp^+$ tetradecker system[10] found that the HOMOs are a degenerate $3e_{1u}$ pair. In our 40–42-electron complexes, those orbitals are empty and the HOMO would correspond either to the a_{1g}, located primarily on the central metal, or the $2e_{1u}$ pair, which are expected to be nondegenerate in our systems owing to the lower symmetry of the heterocyclic carborane rings. Although these data permit no firm conclusions about orbital occupancy, the latter assignment is probable for the ground state, in view of the irreversible oxidations of the 40-electron CoRuCo and $CoCoCo^+$ systems; the catastrophic effect of removing the electron is more consistent with its occupying the $2e_{1u}$ MO (or its equivalent in our systems), which is bonding throughout the molecule, rather than the nonbonding a_{1g}. As a further point, we note that UV–visible spectra of the neutral carborane-bridged tetradeckers, including those under discussion here, all contain intense bands (extinction coefficients 28 000 to 43 000 M^{-1} cm^{-1}) that have been interpreted as charge-transfer excitations from ligand bonding MOs to empty metal antibonding orbitals.[1b]

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Summary. The electrochemical evidence points to significant electron delocalization between equivalent metal centers in the diamagnetic CoNiCo and CoRuCo anions and in the paramagnetic CoCoCo systems. This raises the possibility that extended complexes composed of suitably linked CoCoCo or CoNiCo tetradecker units may exhibit long-range metal–metal communication and could open the way to new families of conducting or semiconducting polymers. Recent work in our laboratory has demonstrated that CoCoCo-based linked-sandwich oligomers can be systematically constructed,[1a] and in an accompanying paper we report an electrochemical study of several such systems.[11]

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