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Electron Transfer in Organometallic Clusters.[1] 7. Bis(μ_3-carbyne) Clusters of Cobalt Including Ferrocene Derivatives

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Ferrocenyl bis(carbyne) clusters $RCCo_3(Cp)_3CR'$ (R/R' = Fc/H, Fc/Fc), examples of capped clusters with multiple redox centers, have been synthesized. In general bis(carbyne) clusters undergo an electrochemically and chemically reversible one-electron oxidation (~0.6 V vs. Ag/AgCl), an irreversible oxidation at more positive potentials, and an irreversible reduction at ~−1.55 V at Pt. The electrochemistry at Hg is complicated by reaction with the electrode. When R and/or R' is a ferrocene moiety, the redox series is extended to $[FcCCo_3(Cp)_3CH]^{2+,1+,0,1-}$ and $[FcCCo_3(Cp)_3CFc]^{3+,2+,1+,0,1-}$. The cations $[RCCo_3(Cp)_3CR']^+$ have also been prepared. Nucleophiles either reduce the cations to the neutral clusters or are unreactive. Electronic spectra of cationic and neutral species and the ESR spectra of the cations are interpreted by using a qualitative bonding scheme. Trends in the spectral and electrochemical data indicate that π interactions between the carbyne and metal fragments dominate the redox chemistry of the bis(carbyne) clusters, and this is compared with other μ_3-capped clusters. It is shown that the ferrocenyl bis(carbyne) clusters are class II mixed-valence ions.

Metal clusters can function as redox centers, the activity of the center being determined by the basicity of the ligands, the nuclearity of the cluster, and the homogeneity of the metal framework. With low valency clusters, cyclopentadienylmetal (Cp_xM) fragments act as donor sites and generate electron-rich clusters[2] whereas metal-carbonyl fragments act as acceptor sites and give clusters that are readily reduced.[3] Metal carbonyl clusters may have donor sites if an appropriate number of CO ligands are replaced by a Lewis base.[4] Notwithstanding these generalizations of redox center behavior in low valency clusters, one cannot always predict a priori the thermodynamic stability of generated cationic or anionic species simply on the basis of the character of the metal-ligand group. Indeed, there are examples of apparently "electron-rich" clusters that do not function as donor redox centers. An example is $Cp_3Ni_3(\mu_3\text{-}CO)_2$, a 49-electron system where the single electron occupies a $a_2'^*$ orbital, for which only a reversible one-electron reduction was observed.[5] In this case, the capping μ_3-CO groups strongly stabilize both the radical and anionic species by d_π–π^*(CO) back-donation. Thus, with capped clusters the ability of the capping group to stabilize or destabilize the frontier orbitals of the M_x fragment can alter the donor or acceptor redox properties of the cluster.

Our interest in the electron-transfer properties of molecules containing multiple redox centers, including low-valent metal clusters, prompted a closer investigation of the role of the capping group in μ_3-capped clusters. In earlier papers we demonstrated that the μ_3-carbon-capped clusters $YCCo_3(CO)_{9-n}L_n$ can provide both acceptor (n = 0) and donor sites (n = 3)[4] and that ferrocene provides a synthetically useful redox center to link with these clusters.[6,7] The first examples of class II mixed-valent carbonyl clusters were established[7] for the cations $[FcCCo_3(CO)_6L_3]^+$. However, these compounds represented a "dead-end" as the single capping group only allowed electron transfer to or from, but not through, the cluster moiety. A bicapped Co_3 cluster overcomes this problem, and, since electron-counting requires the ligands to be cyclopentadienyl groups, the $CCo_3(Cp)_3C$ arrangement allows a comparison of CO and Cp and offers the possibility of generating an electron-rich redox center. Two references to $RCCo_3(Cp)_3CR'$ clusters were found prior to the commencement of this work; $(\mu\text{-}Et_2NC)_2Co_3(Cp)_3$[8] and $Me_3SiCCo_3(Cp)_3CSiMe_3$.[9] Vollhardt and Fritch[10] subsequently reported a general synthesis from $CpCo(CO)_2$/alkyne reactions in boiling decalin, and a low yield conversion of $(\mu\text{-}R_2C_2)Co(Cp)PPh_3$ to $RCCo_3(Cp)_3C(O)OR$ was noted by Yamayaki et al.[11] The definitive work of Vollhardt and co-workers has also demonstrated the especial reactivity of these clusters.[12]

This paper describes the synthesis of the multiple-redox center clusters $FcCCo_3(Cp)_3CH$ and $FcCCo_3(Cp)_3CFc$ (Fc = ferrocenyl) and the redox chemistry of the bis(carbyne) clusters 1–6.

$RCCo_3Cp_3CR'$	1	2	3	4	5	6
R	Ph	Ph	Me_3Si	Fc	Fc	Me_3Si
R'	Ph	H	H	H	Fc	I

Experimental Section

Preparations and manipulations were carried out under argon although the products are all stable in air. High boiling alkane

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solvents (BDH), $PhC{\equiv}CH$, and $PhC{\equiv}CPh$ were used as obtained. $CpCo(CO)_2$[13] and $Me_3SiC{\equiv}CH$[14] were synthesized by published methods. $FcC{\equiv}CH$ was prepared by the dehydrochlorination of the chlorovinylaldehyde $FcC(Cl){=}CHCHO$, according to the method of Abram and Watts.[15] $FcC{\equiv}CFc$ was obtained via a coupling reaction of iodoferrocene with copper ferrocenylacetylide.[16] Iodoferrocene was obtained via the *N*-iodosuccinimide route.[17] The bis(carbyne) clusters $RCCo_3Cp_3CR'$ (R = Ph, Me_3Si; R′ = H, Ph) were prepared by a procedure similar to that given by Fritch and Vollhardt[10,18] and $Me_3SiCCo_3Cp_3CI$ by the iodination of $Me_3SiCCo_3Cp_3CH$.[12a]

Electrochemical procedures were as described previously.[19] All measurements were vs. Ag/AgCl at the stated temperatures and were uncorrected for junction potentials. The reference electrode was calibrated by using the couple $[PhCCo_3(CO)_9]^{0,1-}$ and/or $[\text{ferrocene}]^{1+,0}$ and the electrode characteristics of the couples used to define electrochemical reversibility for the system under study.[6] Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer ^1H and ^{13}C NMR on JEOL FX-90 or Perkin-Elmer EM-390 spectrometers in $CDCl_3$ and ESR spectra on a Varian E3 spectrometer equipped with a low-temperature probe. The procedure for recording the low-temperature ESR spectra and the cells for in situ electrochemical generation of the cations have been given previously.[18b]

Preparation of $FcCCo_3Cp_3CH$ and $FcCCo_3Cp_3CFc$. A pressure-equalizing dropping funnel and a three-necked 100-cm^3 flask were charged with dodecane/tridecane (2:1) solvent mixture (20 and 35 cm^3, respectively). $FcC{\equiv}CH$ (0.42 g, 2.1 mmol) and $CpCo(CO)_2$ (1.42 g, 8 mmol) were then added to the dropping funnel. The stirred solution in the flask was heated to reflux, and the reactants were added dropwise at a rate such that $CpCo(CO)_2$ vapor was maintained in the flask (1–2 h). Once the reactants were added, the solution was refluxed for a further 30 min and then cooled and filtered. The precipitate was washed with CH_2Cl_2, and the washings were combined with the filtrate; CH_2Cl_2 was then removed in vacuo. Purple-black rhombs of the product $FcCCo_3Cp_3CH$ precipitated on standing the solution at 0 °C overnight—yield 790 mg (37%). Alternatively the high boiling solvents could be removed by chromatographic separation on a silica gel column. Elution with 4:1 hexane/CH_2Cl_2 removes the solvents followed by the product. This procedure recovers the high boiling solvents and the trace of product not precipitated in the above procedure: Anal. Calcd: C, 55.67; H, 4.47. Found: C, 55.77; H, 4.91. *m/e* 582 [M^+, calcd 582], 397, 394, 209, 201, 194, 189, 179, 166, 124, 121, 109, 100; ^1H NMR ($CDCl_3$) δ 4.33 (s, 5 ^1H), 4.47 (s, 15 ^1H), 4.63 (t, 2 ^1H), 4.92 (t, 2 ^1H), 18.13 (s, 1 ^1H); infrared (cm^{-1}) 3100 (m), 2990 (s), 2930 (ms), 1420 (mw), 1350 (mw), 1274 (mw), 1192 (m), 1114 (ms), 1065 (m), 1050 (m), 1008 (ms), 870 (s), 815 (s), 800 (vs), 666 (vs), 585 (m); λ (nm) 688, 502, 378.

$FcCCo_3Cp_3CFc$ was prepared in 31% yield by the same procedure: black plates; *m/e* 766 [M^+, calcd 766], 577, 572, 510, 453, 437, 394, 370, 189, 57; ^1H NMR ($CDCl_3$) δ 4.32 (s, 10 ^1H), 4.37 (s, 15 ^1H), 4.67 (t, 4 ^1H), 4.88 (t, 4 ^1H); infrared (cm^{-1}) 3080 (m), 2920 (s), 2850 (ms), 1420 (mw), 1370 (w), 1180 (w), 1112 (ms), 1065 (m), 1000 (m), 820 (s), 800 (vs), 695 (vs); λ (nm) 750, 510, 360.

Preparation of Cationic Derivatives $[1–3]^+$. Typically $AgPF_6$ (0.22 mmol) was added to a stirred solution of the purple $RCCo_3(Cp)_3CR'$ (0.20 mmol) in NH_4PF_6-saturated CH_2Cl_2 (20 cm^3). The solution rapidly turned brown. After 10 min the solution was filtered to remove precipitated silver and excess NH_4PF_6 and the solvent removed in vacuo to give quantitative yields of the cation $[RCCo_3(Cp)_3CR']^+PF_6^-$. The salts were washed with CCl_4 to remove any neutral material and then redissolved in CH_2Cl_2 and the spectra recorded immediately. Crystalline salts were obtained by recrystallization from CH_2Cl_2/hexane. Anal. Calcd for $[1]^+PF_6^-{\cdot}{}^1/{}_2CH_2Cl_2$: C, 48.0; H, 3.53. Found: C, 48.30; H, 3.61. Anal. Calcd for $[3]^+PF_6^-{\cdot}{}^1/{}_2C_6H_{12}$: C, 42.20, H, 4.74. Found: C, 42.37; H, 4.55. These salts are soluble in CH_2Cl_2 and CH_3CN and sparingly soluble in ethers and alcohols.

Oxidation of $FcCCo_3(Cp)_3CH$. $[4]^+$. To $FcCCo_3(Cp)_3CH$ (0.10 mmol) in 20 cm^3 of NH_4PF_6-saturated CH_2Cl_2 was added $AgPF_6$ (0.10 mmol) in a glass boat. On vigorous stirring the purple solution turned dark brown at which stage it was filtered. Sample aliquots of the filtrate were removed by syringe and their visible–near-infrared spectra recorded. The filtrate was then evaporated to dryness at 0 °C, washed with CCl_4 to remove a small quantity of unoxidized [4], and then dried in vacuo. The purified $[4]^+$ was then dissolved in CD_2Cl_2, and the visible and near-infrared spectra were run again. These spectra were identical with those recorded on the initial filtrate, and extinction coefficients were calculated with allowance made for the small amount of neutral compound recovered after oxidation.

$[4]^{2+}$. $AgPF_6$ (0.21 mmol) was added, with stirring, to $FcCCo_3Cp_3CH$ (0.10 mmol) in 20 cm^3 of NH_4PF_6-saturated CH_2Cl_2. The solution turned brown with considerable precipitation of solids. The solution was filtered; the brown filtrate had the spectral profile of $[4]^+$. Repeated washing of the brown-black precipitate with CH_2Cl_2 removed NH_4PF_6 and remaining $[4]^+$. Dissolution of the purified precipitate of $[4]^{2+}$ compound in acetonitrile gave a brown solution that was quite stable in the absence of air. Extinction coefficients for the spectra run in this solvent were calculated allowing for the small amount of $[4]^+$ compound recovered. Although the $[4]^{1,1}$ compound could be prepared in quantitative yields by using excess $AgPF_6$, the above method was favored because of problems arising from the solubility of $AgPF_6$ in acetonitrile.

Oxidation of $FcCCo_3Cp_3CFc$. To a stirred purple solution of $FcCCo_3Cp_3CFc$ (0.05 mmol) in CH_2Cl_2 (10 cm^3) was added $AgPF_6$ (0.10 mmol). The resulting brown solution was filtered, the solvent stripped, and the residue washed with CCl_4 to remove $[5]^{0,0,0}$ and then dried in vacuo. The following operations gave the required data from the one sample. The solid was dissolved in CH_2Cl_2 and the near-infrared spectrum recorded; then further CH_2Cl_2 was added to record the visible spectrum. At this point the near-infrared spectrum showed a broad absorption band rising to the solvent limit and a visible spectrum of a mixture of monocation–dication.

ESR spectra were then recorded at 298 and 77 K on the sample after the volume of solvent had been reduced. The broad signal revealed the presence of the monocation $[5]^{0,1,0}$. The solvent was stripped in vacuo and the residue dissolved in CD_2Cl_2. The near-infrared spectrum now showed a maximum at 2100 nm. A further 4.03 mg of **5** was added to the CD_2Cl_2 solution and the spectrum run again after 5 min. The band at 2100 nm had approximately doubled in intensity.

Reactions of Cationic Bis(carbyne) Clusters with Nucleophiles. A standard procedure was used for the reactions of nucleophiles, and this is illustrated for the reaction between $[1]^+PF_6^-$ and PPh_3. The cation $[1]^+PF_6^-{\cdot}{}^1/{}_2CH_2Cl_2$ (54 mg, 0.073 mmol) was dissolved in CH_2Cl_2 (10 cm^3) in air and PPh_3 (19 mg, 0.073 mmol) in CH_2Cl_2 (5 cm^3) added to this solution. Over a period of 2 min the color changed from brown to purple (the same color change is not observed if the reaction is carried out under rigorously anaerobic conditions). The solvent was removed in vacuo and the residue separated on chromatographic silica gel plates (hexane/CH_2Cl_2, 4:1). The purple band due to the neutral cluster was removed to give 39 mg (0.07 mmol) of 1 (identified by ^1H NMR, mp, and TLC). Triphenylphosphine oxide (17 mg, 0.061 mmol) was recovered from the plate (R_f 0) by extraction with acetone (characterized by comparison with the IR and melting point of an authentic sample, Strem). Formation of the neutral cluster [1–3] from the appropriate cation was also qualitatively observed for the reaction with $Et_4N^+I^-$, $Bu_4N^+I^-$, or KI (in MeCN, iodine was detected), MeO^- (in MeCN, a quantitative conversion to the neutral cluster does not require a stoichiometric amount of MeO^-, and thus 0.06 mmol of $[1]^+$-

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Table I. Electrochemical Data for $RCCo_3Cp_3CR'$[a]

At Pt[b]

apical groups R//R'	(1+, 0) E_p^{ox}	(1+, 0) E_p^{red}	(1+, 0) i_c/i_a	(2+, 1+) E_p^{ox}	(2+, 1+) E_p^{red}	(2+, 1+) i_c/i_a	(3+, 2+) E_p^{ox}	(3+, 2+) E_p^{red}	(3+, 2+) i_c/i_a	(4+, 3+) E_p^{ox}	(0, 1−) E_p^{red}
Me_3Si//H	0.63	0.57	1.0	1.41		*c*					−1.32
Me_3Si//I	0.75	0.67	1.0	1.50		*c*					−0.82
Ph//Ph	0.59	0.52	1.0	1.30		*c*					−1.63
Ph//H	0.57	0.49	1.0	1.28		*c*					−1.52
Fc//H	0.49	0.42	1.0	0.81	0.74	1.0	1.56		*c*		−1.61
Fc//Fc	0.43	0.35	1.0	0.67	0.60	1.0	0.97	0.91	1.0	1.7[c]	−1.66

At Hg[d,e]

apical group R//R'	E_p^{ox}		E_p^{red}		$E_{1/2}^{ox}$	$E_{1/2}^{red}$
Me_3Si//H	0.20	0.35	0.28	0.20	*0.34*[f,g]	*−1.57*
Ph//Ph	0.36		0.30		*0.35*[g,h]	*−1.52*
Ph//H	0.18	0.34	0.26	0.13	*0.24*[f]	*−1.44*
Fc//H	0.34	0.38	0.27		*0.31*[f]	*−1.57*
Fc//Fc					*0.27*[h]	*−1.58*

[a] V vs. Ag/AgCl; in acetone; reference $Fc^{1,0}$ or $PhCCo_3(CO)_9^{0,1-}$; supporting electrolyte 0.1 M Et_4NClO_4; ~10^{-3} M in compound; 298 K. [b] Scan rate = 200 mV s^{-1}; [c] No current on cathodic scan, i.e., completely irreversible. [d] Cyclic voltammograms in normal type and polarography in italics. [e] CV: scan rate = 500 mV s^{-1}. Polarography: scan rate = 20 mV s^{-1}; drop time = 0.5 s. Exact values are dependent on concentration, scan rate, and drop time. These data refer to oxidation of the cluster core. Data for **6** are not given as the CV and polarographs are too complex. [f] Differential pulse polarograms show two peaks. [g] A further wave is observed corresponding approximately to $E_{1/2}^{1,0}$ on Pt at high concentrations. [h] Differential pulse polarograms show a single peak.

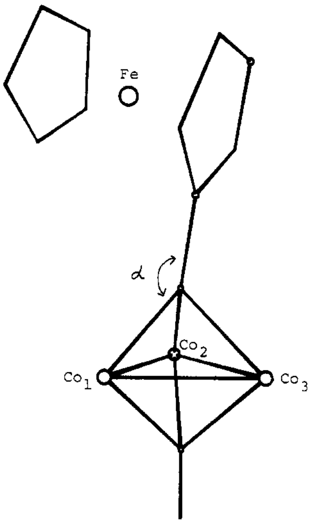

Figure 1. Molecular structure of $FcCCo_3(Cp)_3CH$: Co(1)–Co(2) = 2.365 (2) Å, Co(2)–Co(3) = 2.391 (2) Å, Co(1)–Co(3) = 2.396 (2) Å, and α = 122°.

$PF_6^-\cdot{}^1/_2CH_2Cl_2$ required ~0.03 mmol of NaOMe for conversion to 0.06 mmol of **1**), and Et_3N. No reaction was observed with H_2O (in MeCN), 1-hexene, *t*-BuO⁻, and BH_4^-.

Results and Discussion

Ferrocene-substituted bis(carbyne) clusters were readily prepared by the established route.[10] The structure of **4**, shown in Figure 1, is typical of bis(carbyne) clusters with the exception that the ferrocenyl group is tilted from the ideal position on the C_3 axis. This feature, also found in the structure of $FcCCo_3(CO)_9$, is attributed to the nondegeneracy of the carbyne p_π orbitals arising from a mesomeric interaction between the Fc and the CCo_3C unit.[20]

The ^1H NMR of the apical carbyne substituents are characteristically affected by the strong deshielding influence of the bis(carbyne) group.[10] In **4** and **5** this is reflected in the fact that the α and β protons of the substituted ring are significantly downfield from the protons of the unsubstituted ring (Table I). From the criteria used to interpret the ^1H NMR of ferrocene compounds the chemical shift of the α and β protons would be consistent with a Fc substituent, the cluster, in this instance, acting as an electron-withdrawing group.[21] However, it is clear that these criteria are not applicable when the Fc substituent is a cluster. Clusters produce paramagnetic ring currents that give rise to strong deshielding zones for "internal" protons akin to the situation pertaining to "antiaromatic" compounds.[22] Consequently, the chemical shifts of the α and β protons should be interpreted with caution and the trend is not incompatible with the concept of an *electron-rich* cluster Fc substituent. It is interesting to note that the shift to lower field in **4** is slightly larger than that observed[6] for $FcCCo_3(CO)_9$ in which the Fc is linked via both inductive and mesomeric interactions to the powerful *electron-withdrawing* CCo_3 substituent. Another example is provided by a comparison of the ^1H chemical shift of CCo_3CH (~18 ppm) and Co_3CH (~11 ppm)[23]—a reversal of shifts expected on the basis of the respective electron-withdrawing capabilities.

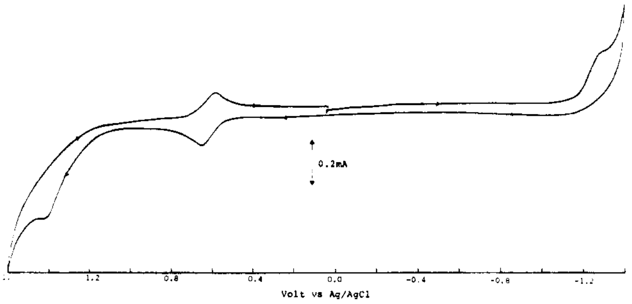

Figure 2. Cyclic voltammogram of 10^{-3} M $Me_3SiCCo_3(Cp)_3$ (**3**) over an extended range at Pt at 298 K in acetone (0.1 M Et_4NClO_4; scan rate = 200 mV s^{-1}).

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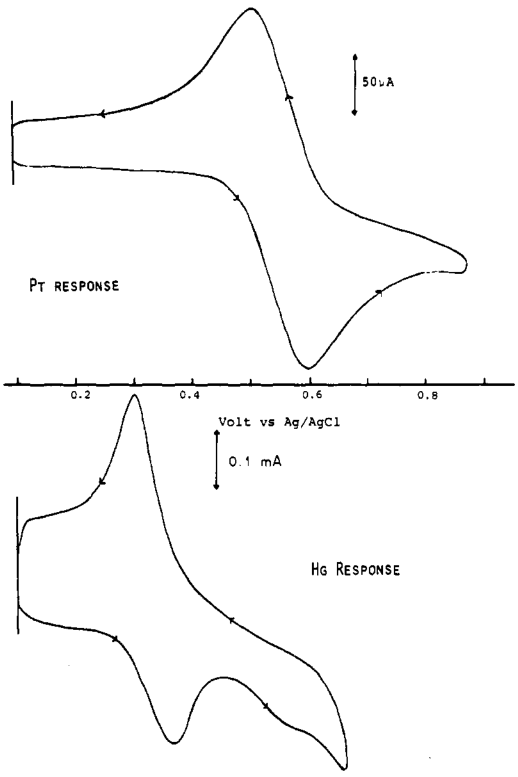

Figure 3. Cyclic voltammograms of 10^{-3} M $Me_3SiCCo_3(Cp)_3CPh$ (**1**) in acetone (0.1 M Et_4NClO_4) at 298 K (scan rate = 500 mV s^{-1}): (a) Pt, (b) Hg.

Vollhardt and co-workers[12] have highlighted the kinetic stability of the bis(carbyne)cobalt clusters, and this holds for the ferrocene derivatives as well. Fragmentation patterns of the mass spectra of **4** and **5** also reflect this stability. Parent molecular ions are observed in high abundance, and the primary fragmentation is the successive loss of Co–Cp fragments. The preferential rupture of Co–Co bonds rather than Co–C(carbyne) bonds closely resembles the breakdown found in the other kinetically stable capped cobalt clusters Co_3C.[24]

Electrode Processes for $RCCo_3(Cp)_3CR'$ ($R = R' \neq Fc$). Figure 2 shows a typical voltammogram of a CCo_3C cluster obtained at Pt over an extended potential range, and Figure 3 and 4 show cyclic voltammograms of the first oxidation wave at Hg and Pt. The electrode processes on Pt for bis(carbyne) clusters other than the ferrocene compounds **4** and **5** are characterized by an electrochemically irreversible oxidation near the solvent limit, a reversible oxidation ($E_p^{ox} \approx 0.6$ V), and an electrochemically irreversible reduction ($E_p^{red} \approx -1.55$ V) (Table I).

In CH_2Cl_2 or acetone the current–voltage response of the first oxidation step for all clusters on Pt is characteristic of an electrochemically and chemically reversible one-electron transfer with the production of a stable radical cation.

$$[RCCo_3(Cp)_3CR']^+ + e \rightleftharpoons [RCCo_3(Cp)_3CR']$$

$$E_p^{ox} = 0.50\text{–}0.65 \text{ V}$$

At scan rates up to 5 V s^{-1} and temperatures down to −70 °C both the oxidation of the radical cation and the reduction of the neutral cluster are chemically and electrochemically irreversible. No extra waves were observed on the reverse or repeat scans when the switching potential is more positive than the second oxidation step or more negative than the reduction step; presumably the disintegration products of the cluster unit are not electroactive within the accessible potential range, unlike cobalt carbonyl clusters where $Co(CO)_4^-$ can always be recognized as a product of decomposition.[4,19] The complete electron-transfer steps on Pt for these clusters are therefore[25]

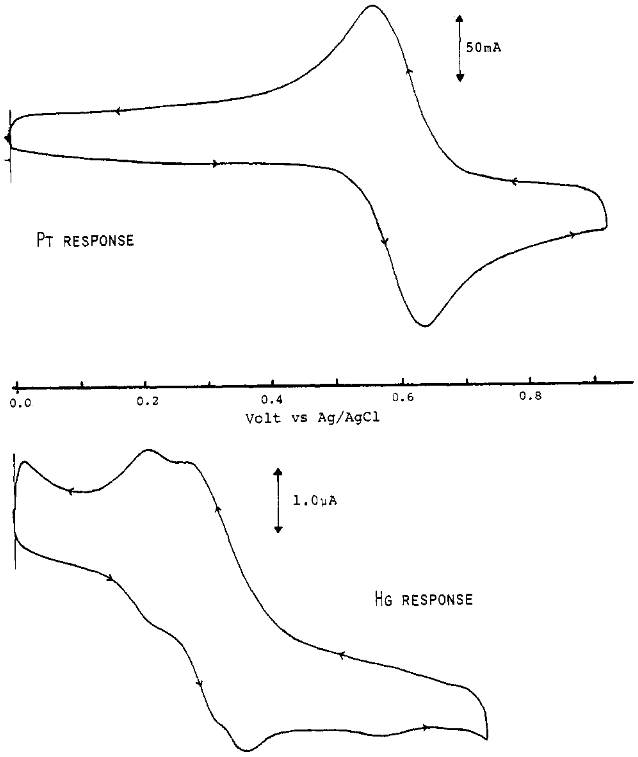

Figure 4. Cyclic voltammograms of 10^{-3} M $Me_3SiCCo_3(Cp)_3CH$ (**3**) in acetone (0.1 M Et_4NClO_4) at 298 K (scan rate = 500 mV s^{-1}): (a) Pt, (b) Hg.

$$[RCCo_3(Cp)_3CR']^{2+} \xrightarrow{\sim 1.3 \text{ V}} [RCCo_3(Cp)_3CR']^{+} \overset{\sim 0.6 \text{ V}}{\rightleftharpoons} [RCCo_3(Cp)_3CR'] \xrightarrow{\sim -1.5 \text{ V}} [RCCo_3(Cp)_3CR']^{-\cdot}$$

$$R = R' \neq Fc$$

At mercury electrodes the electrochemical responses are considerably more complicated. Polarograms are characterized by large prewaves occurring approximately 0.25 V before the chemically reversible oxidation to the cations. In solutions of concentrations $<5 \times 10^{-3}$ mol dm^{-3} the prewaves dominated to the extent that the wave corresponding to the primary oxidative process disappeared (Figure 5). Differential pulse polarograms of the prewave revealed a single peak when R or $R' \neq H$ and two peaks (Figure 5) when R or R′ = H; with the iodo derivative **6** a multitude of prewaves appeared and there was no wave due to $[6]^{1,0}$. Similarly, cyclic voltammetry at a Hg electrode **1** gives a chemically reversible response at fast scan rates, at values of E_p^{ox} corresponding to the prewave potentials, and very small peak currents for the primary oxidative process to the cation (Figures 3b and 4b). The large prewaves are suggestive of strong interactions with

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[24] Robinson, B. H.; Tham, W. S. *J. Chem. Soc. A* **1968**, 1784.

[25] Subsequent to submission of this paper Kawamura and co-workers[26] have reported some details of the redox chemistry of **1** together with an MO diagram. Our MO diagram has a different ordering for the e″ and a_2'' levels. The stability of the radical anion is surprising in view of the electrochemistry reported therein, and we have been unable to generate the radical anion by controlled potential electrolysis in situ in the ESR cavity.

[26] Enoki, S.; Kawamura, T.; Yonozaua, T. *Inorg. Chem.* **1983**, *22*, 3821.

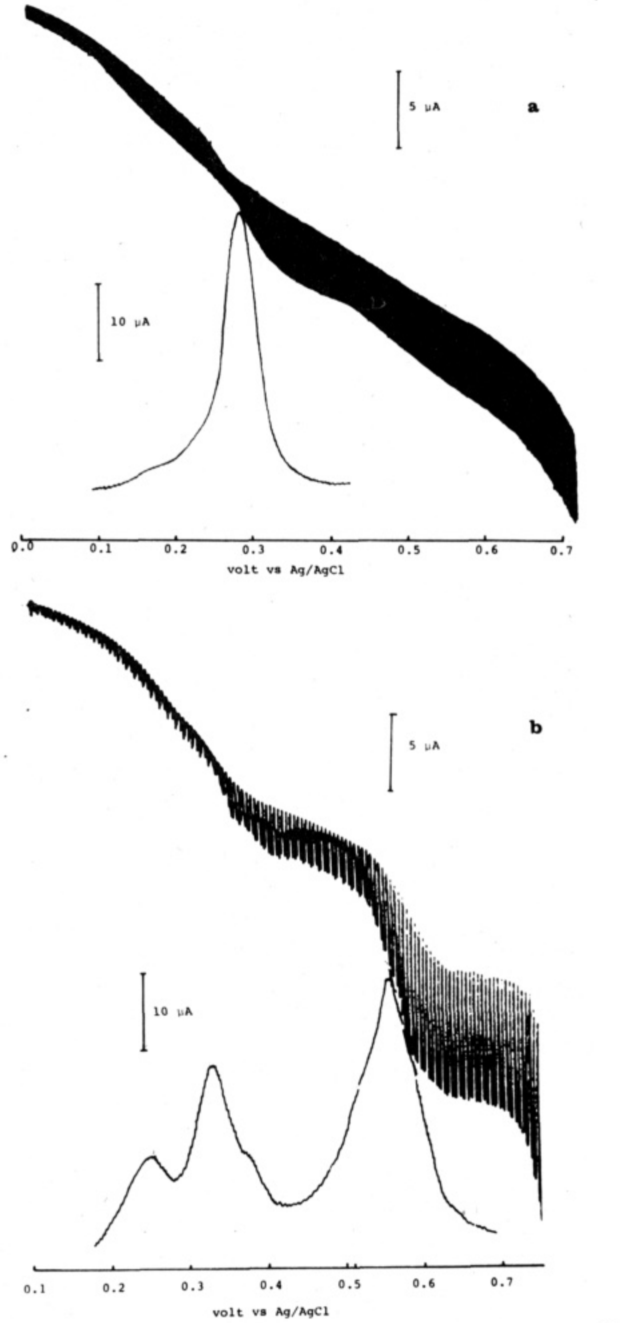

Figure 5. Polarogram and differential pulse polarogram of 10^{-3} M (a) **1** and (b) **3** in acetone (0.1 M Et_4NClO_4) at 298 K (drop time = 0.5 s; scan rate = 20 mV s^{-1}).

Hg and "complex" formation;[27] the abnormal electrochemical behavior of organometallic compounds, especially metal carbonyls, is often attributed to the formation of Hg species.[8,29] The 47-electron $[RCCo_3(Cp)_3CR']^+$ could attain the preferred 48-electron configuration by forming an edge-bridged mercury-stabilized cation of the type suggested as intermediates in electrophilic attack on the bis(carbyne) complexes.[12]

Electrode Processes for Ferrocene–Bis(carbyne) Clusters. Additional electrode processes are seen in the multicentered ferrocene clusters $FcCCo_3(Cp)_3CH$ (**4**) and $FcCCo_3(Cp)_3CFc$ (**5**). Two electrochemically and chemically reversible oxidation waves are observed in the cyclic voltammograms of **4** at Pt (Figure 6a), the electrode responses of both indicating the formation of soluble stable cations. On extended scans, a further electrochemically irreversible oxidation is observed near the solvent limit, as well as an irreversible reduction. From a comparison with the electrochemistry with the other bis(carbyne) clusters **1**–**3** it is obvious that these two *irreversible* processes are respectively oxidation of the cluster center to its dication and reduction of the cluster center to $4^{-\cdot}$ (the reduction of Fc occurs at −2.93 V[30] and will not be observed in our scans).

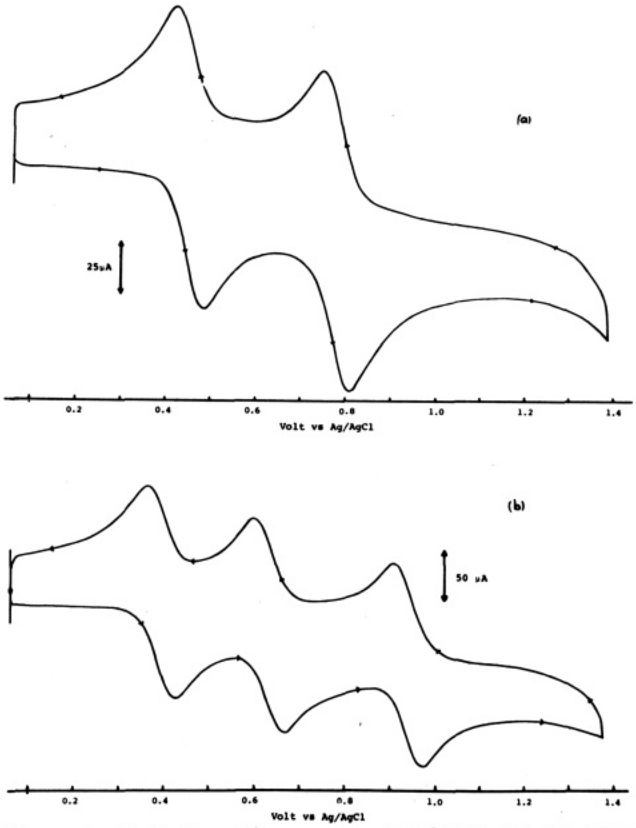

Figure 6. (a) Cyclic voltammogram of 10^{-3} M $FcCCo_3(Cp)_3CH$ (**4**) at Pt in acetone (0.1 M Et_4NClO_4; scan rate = 200 mV s^{-1}). (b) Cyclic voltammogram of 10^{-3} M $FcCCo_3(Cp)_3CFc$ (**5**) at Pt in acetone (0.1 M Et_4NClO_4; scan rate = 200 mV s^{-1}).

The first reversible oxidation process shows the same abnormal behavior on Hg described above for **1**–**3** and is therefore assigned to oxidation of the CCo_3C center. This assignment also follows from the model redox centers: $E_{1/2}[1]^{1,0}$ at 0.55 V and $E_{1/2}[Fc]^{1,0}$ at 0.63 V in the same solvent.[6] The complete electrode processes for **4** are therefore

$$[4]^{1,2} \xrightarrow{1.56} [4]^{1,1} \xrightleftharpoons{0.78} [4]^{0,1} \xrightleftharpoons{0.45} [4]^{0,0} \xrightarrow{1.61} [4]^{0,1-}$$

In contrast to **4** the electrochemistry of **5** at Pt (Figure 6b) shows, apart from the irreversible oxidation and reduction near the solvent limit, three electrochemically and chemically reversible one-electron oxidation waves. An assignment for these waves rests on a comparison with the electrochemistry of other bis(carbyne) clusters and the fact that ferrocene is a donor substituent. Therefore, because oxidation of the cluster core in **5** is expected to be easier than **4** and there is a prewave at Hg, we assign the first one-electron response to cluster oxidation. The subsequent

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[27] Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980.

[28] Blanch, S. W.; Bond, A. M.; Colton, R. *Inorg. Chem.* **1981**, *20*, 758.

[29] Further work is underway to quantify these Hg interactions. We have noted that green compounds are often found after solutions have been in contact with Hg.

[30] Mugrier, Y.; Moise, C.; Tiroflet, J.; Laviron, E. *J. Organomet. Chem.* **1980**, *186*, C49.

waves are associated with the successive oxidation of the ferrocene centers.[31]

$$[\mathbf{5}]^{1,2,1} \xrightarrow{\sim 1.7} [\mathbf{5}]^{1,1,1} \underset{}{\overset{0.94}{\rightleftharpoons}} [\mathbf{5}]^{1,1,0} \overset{0.64}{\rightleftharpoons} [\mathbf{5}]^{0,1,0} \overset{0.39}{\rightleftharpoons} [\mathbf{5}]^{0,0,0} \xrightarrow{-1.66} [\mathbf{5}]^{0,1-,0}$$

Because there are two distinct electrode responses, separated by 0.31 V, for the structurally equivalent Fc groups, they must be interacting through the oxidized carbyne cluster core. Electrode responses expected for multiredox center molecules have been evaluated.[32] Molecules with equivalent noninteracting electroactive centers have only one current–potential response with Nernstian characteristics, but the magnitude is a function of the number of electroactive centers. Conversely, molecules with interaction between equivalent electroactive centers have as many voltammetric waves, with as many one-electron diffusion currents, as there are centers. Departures from these ideal extremes are caused by slow electron transfer, structural changes upon oxidation, and adsorption at the electrode surface. Moreover, in interacting systems the separation between the one-electron waves can range from a few millivolts to several hundred millivolts. Three oxidation electrode responses for **5** therefore provide evidence that two equivalent Fc centers are strongly interacting.[32] It is interesting that the separation for the consecutive waves in **5** of ~0.3 V is of similar magnitude to that found in extensively delocalized ferrocene systems such as polyferrocenes and larger than those where Fc is linked by π-unsaturated groups (~0.1 V) in weakly interacting systems.[33] A π-interaction between the Fc moieties and the cluster provides a mechanism for hole delocalization between Fc centers in $[\mathbf{5}]^{0,1,0}$ and $[\mathbf{5}]^{1,1,0}$ species, a theme which is developed below.

Trends in Potential Data—Substituent Parameters. In keeping with the concept of a delocalized electron-rich cluster, the potentials for the oxidation of the cluster are sensitive to small variations in the electronic character of the carbyne substituents. These substituent effects are most easily seen in the substituent parameters γ derived from the relationship shown in eq 1 ($R/R' \equiv RCCo_3(Cp)_3CR'$). For example, from the data for **4** and **5** and

$$E_{1/2}[R/R']^{1,0} = E_{1/2}[H/H]^{1,0} + \gamma_R + \gamma_{R'} \qquad (1)$$

eq 2 and 3 we find $\gamma_{Fc} = -0.06$ V. Likewise γ_{Ph} derived

$$E_{1/2}[Fc/H]^{1,0} = E_{1/2}[H/H]^{1,0} + \gamma_{Fc} \qquad (2)$$

$$E_{1/2}[Fc/Fc]^{0,1,0} = E_{1/2}[H/H]^{1,0} + 2\gamma_{Fc} \qquad (3)$$

from the data for **1** and **2** is found to be 0.02 V. A negative sign for γ_{Fc} shows the Fc to be a net donor substituent, as expected, while Ph is a slightly electron-withdrawing group. With use of eq 1, $E_{1/2}[H/H]^{1,0}$ is calculated to be 0.51 V from either set of data, **1**, **2** or **4**, **5**. A value for γ_{Me_3Si} of 0.09 V is now accessible from $E_{1/2}[\mathbf{3}]^{1,0}$, which indicates that Me_3Si is functioning as an *electron-withdrawing* group. A rationale for the seemingly anomalous behavior of Me_3Si can be sought in the assistance given by the apical substituent in stabilizing the radical cation since $E_{1/2}[R/R']^{1,0}$ is a measure of the relative thermodynamic stability of the neutral and cationic species. A carbyne atom has π acceptor orbitals that have the correct symmetry to overlap with appropriate filled π orbitals on the apical substituent.[34] If such a π interaction occurs, there will clearly be a stabilization of the radical cation. Groups such as Ph and Fc, but not Me_3Si, can participate in this charge stabilization. Consequently, the cation $[\mathbf{3}]^+$ will not gain the extra thermodynamic stability—it will be more difficult to oxidize **3** than **1**, **2**, or **4** even though Me_3Si is a net electron donor. A corollary of this argument is that $E_{1/2}[HCCo_3(Cp)_3CH]^{1,0}$ calculated from the substituent parameters γ_{Ph} or γ_{Fc} will probably be more negative than the experimental parameter. Iodine, as an apical substituent, functions as an electron-withdrawing group ($\gamma_I = 0.11$ V), and consequently **6** is the most difficult cluster to oxidize. Conversely, its reduction potential $E_{1/2}[\mathbf{6}]^{0,1-}$ is much lower and comparable to those of carbonyl clusters.[3]

Table II. Electrochemical Parameters for Compounds Containing Two Ferrocenyl Groups[a]

compd	$E_{1/2}(1)^b$	$E_{1/2}(2)^b$	$\Delta E_{1/2}$
Fc—Fc[c]	0.62	0.97	0.35
FcC≡CFc[c]	0.64	0.78	0.14
$CpCo(C_4Fc_2Ph_2)^d$	0.51	0.70	0.19
5	0.73	1.03	0.30

[a] In CH_2Cl_2, vs. Ag/AgCl corrected from data in literature. [b] Calculated from peak potentials. [c] From ref 21. [d] Cis isomer ref 21.

Substituent parameters for ferrocene compounds are normally additive[35] and reflect changes in electron density in the orbitals that are largely Fe d in character. For **4** we can only calculate a substituent parameter for the oxidized cluster.

$$\delta_{CCo_3C^+} = E_{1/2}[\mathbf{4}]^{1,0} - E_{1/2}[Fc]^{1,0} = 0.15 \text{ V}$$

Thus the oxidized cluster is acting as net electron-withdrawing group. For comparison, parameters for other groups are OAc (0.25, direct ring substituent),[35] $CCo_3(CO)_9$ (0.09, "remote" bond polarizing and delocalization center) and $(CO)CCo_3(CO)_9$ (0.23, another "remote" polarization center)[6] and Fc (−0.11 V).[33]

Oxidation of $[\mathbf{5}]^{0,1,0}$ is thermodynamically easier than the oxidation of $[\mathbf{4}]^{1,0}$ presumably because of the increased opportunity for charge stabilization in $[\mathbf{5}]^{1,1,0}$. Utilizing the substituent parameter $\delta_{Fc} = -0.11$ V (derived from biferrocene),[33] $E_{1/2}$ for the oxidation of $[\mathbf{5}]^{1,1,0}$ is calculated as 0.67 V. This is close to the observed $E_{1/2}$ of 0.63 V despite the fact that a cluster unit is interposed between the two Fc moieties in **5** and the use of the additivity rule is not strictly valid. These data are indicative of the strong interaction between the two Fc moieties separated by a "through-space" distance of 4.72 Å. An extended interaction is further demonstrated by a comparison of the difference in potential for the oxidations of $[\mathbf{5}]^{0,1,0}$ and $[\mathbf{5}]^{1,1,0}$ and comparable differences in other compounds containing two Fc groups (Table II). The difference in reduction potential is nearly the same as for two Fc groups directly linked through the cyclopentadienyl rings and considerably greater than in compounds where ferrocene is linked via other bridging organic systems (note in particular $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4Fc_2Ph_2)^{46}$). As a working model, we suggest that the cluster is regarded as a bis(fulvene)

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[31] The formal oxidation state of each redox center is given by the representation $[\mathbf{4}]^{cluster,Fc}$ or $[\mathbf{5}]^{Fc,cluster,Fc}$ (e.g., $[\mathbf{5}]^{1,1,0}$) where there is more than one disparate oxidation center. For the clusters **1**–**3** the cluster is the oxidized center.

[32] Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248 and references therein.

[33] Le Vanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

[34] Kostic, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1981**, *103*, 4677; **1982**, *104*, 3879.

[35] (a) Pevevalova, E. G.; Gubin, E. Q.; Smirova, S. A.; Nesmeyanov, A. N. *Dokl. Adad. Nauk SSSR* **1964**, *155*, 847. (b) Kuwana, T.; Bubliltz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5211. (c) γ_R refers to a substituent parameter for the group attached to the cluster; δ_R is the parameter for a Fc substituent.

Table III. Spectroscopic Data for the Valence Derivatives of $RCCo_3Cp_3CR'$ Complexes[a]

compound		visible absorption bands[b]			near-infrared band[b]	ESR, (g value at 77 K)
		C	B	A		
$PhCCo_3Cp_3CPh$	[0]	430 sh (1890)	522 (3480)	730 sh (370)		
	[1+]		490 (3340)	716 sh (1130)	1250 (260)	2.19
$PhCCo_3Cp_3CH$	[0]	420 sh (2450)	507 (3250)	675 (490)		
	[1+]		~460 sh (2920)	680 (1010)	925 (250)	2.19
$Me_3SiCCo_3Cp_3CH$	[0]	396 sh (1660)	502 (3160)	698 (400)		
	[1+]		493 (2820)	690 (970)		2.21
$FcCCo_3Cp_3CH$	[0, 0]	378 sh (5120)	502 (4540)	688 (430)		
	[1+, 0]		468 (4370)	688 (1640)	2150 (560)[c,g]	2.18
	[1+, +1]		480 (4280)	685 (1360)		
$FcCCo_3Cp_3CFc$	[0, 0, 0]	360 sh (6610)	510 (3720)	750 sh (407)		
	[0, 1+, 0][d]	~340 sh	~474[f]	755 sh	2100[h]	2.16
	[1+, 1+, 0][d]		~490, ~550	~750 sh		

[a] In CH_2Cl_2. [b] nm, ϵ_M in parentheses. [c] Extinction coefficient calculated at 2100 nm in CH_2Cl_2. Maximum from spectra in CD_2Cl_2. [d] Concentration uncertain as contaminated by other valence derivatives. [f] Band has a low-energy shoulder at ~550 nm. [g] Band is very broad on low-energy side.

derivative of a Co_3Cp_3 unit functioning as an electron reservoir, analogous to the model invoked to discuss the redox chemistry of $FcCCo_3(CO)_9$.[6]

Preparation of the Cations $[1\text{-}3]^+$, $[4]^{2+/1+}$, and $[5]^{3+/2+/+}$. Brown salts of the cations $[1\text{-}4]^+$ were readily prepared by the stoichiometric oxidation of 1–4 by Ag(I) salts in CH_2Cl_2.[36]

$$RCCo_3(Cp)_3CR' + Ag^+ \xrightarrow{CH_2Cl_2} [RCCo_3(Cp)_3CR']^+ + Ag$$

These salts, in which the cluster core is oxidized, are indefinitely stable in CH_2Cl_2 and in air. Oxidation of 4 with excess Ag(I) gave the dication $[4]^{2+}$ (i.e., $[4]^{1,1}$) which precipitated from CH_2Cl_2.[2]

$$FcCCo_3(Cp)_3CH + 2Ag^+ \rightarrow {}^+FcCCo_3{}^+(Cp)_3CH + 2Ag$$

An equilibrium mixture of three species was formed by oxidation of 5 with Ag^+, and discrete solutions of the individual oxidized species of 5 were not obtained. Nevertheless, it was possible to spectroscopically distinguish each species.

The kinetic stability and ready formation of the cations $[RCCo_3(Cp)_3CR']^+$ raises the question as to whether they are implicated in reactions of the neutral counterparts. Pertinent to this question are the electrophilic transformations (eq 4 and 5) studied by Van Horn and Vollhardt.[12a] Iodine does not in fact oxidize any of the clusters

$$HCCo_3(CP)_3CH \xrightarrow{I_2} \text{green complex} \xrightarrow{O_2/H_2O} HCCo_3(Cp)_3CI \quad (4)$$

$$HCCo_3(Cp)_3CI \xrightarrow[MeOH]{AgBF_4} HCCo_3(Cp)_3COMe \quad (5)$$

1–5 to the cations, and we confirm Van Horn and Vollhardt's observation that a green charge-transfer complex is produced instead. $AgBF_4$ can clearly oxidize $HCCo_3(Cp)_3CI$, and the resulting cation could be activated to nucleophilic attack by OMe^-. However, treatment of any cation species $[1\text{-}5]^+$ with OMe^- regenerates the *neutral* cluster—this supports the contention that reaction 5 proceeds via electrophilic attack by Ag(I). In fact, a number of nucleophiles act in the same manner as OMe^- (see Experimental Section) and we have shown that the formal reaction with PPh_3 is quantitative (eq 6).[37]

$$[1]^+ + PPh_3 \xrightarrow[H_2O]{O_2} [1] + OPPh_3 \quad (6)$$

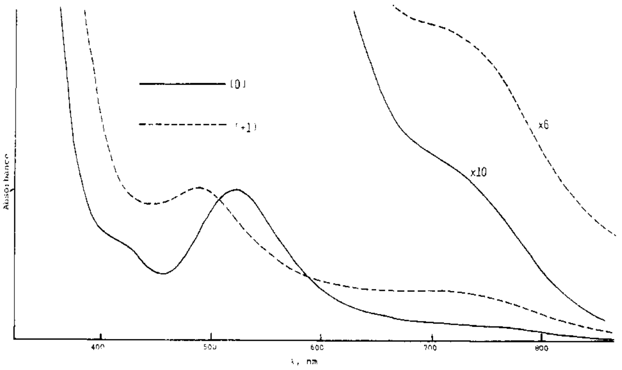

Figure 7. Electronic absorption spectra of [1] and $[1]^+$ in CH_2Cl_2 between 350 and 900 nm: —, [1]; - - -, $[1]^+$.

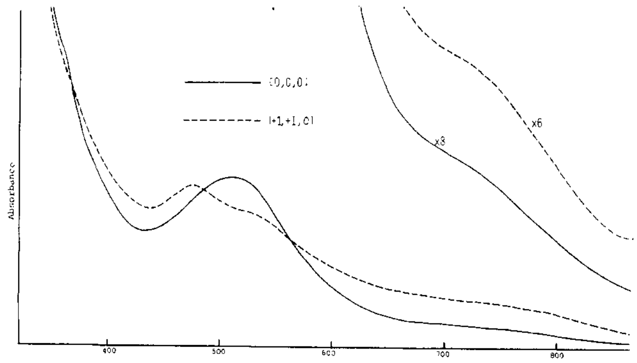

Figure 8. Electronic absorption spectra of [4] and $[4]^{1,0}$ in CH_2Cl_2 and $[4]^{1,1}$ in CH_3CN between 350 and 900 nm: —, [4]; - - -, $[4]^{1,0}$; – – –, $[4]^{1,1}$.

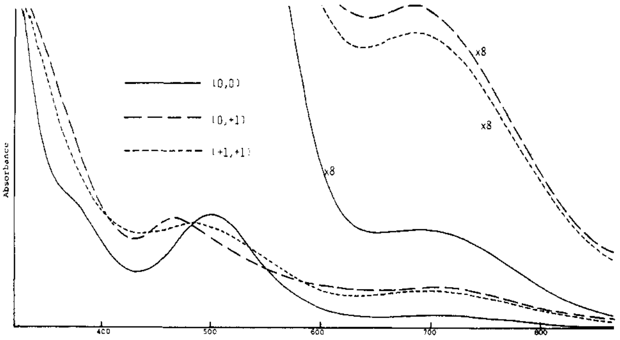

Figure 9. Electronic absorption spectra of $[5]^{0,1,0}$ and $[5]^{1,1,0}$ in CH_2Cl_2 between 350 and 900 nm: —, [5]; - - -, $[5]^{1,1,0}$.

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[36] Electrochemical oxidation by standard procedures could also be used. Coulometry showed that 1 F mol^{-1} was required.

Electronic Structure and Spectra of Neutral and Oxidized Bis(carbyne) Clusters. Neutral bis(carbyne) clusters are all purple to red-purple, regardless of the apical groups, and the similarity extends to the profiles of their electronic spectra. Each neutral cluster has three bands in the region 2000–360 nm, a weak band (A) between 550 and 750 nm, band B between 500 and 520 nm, and a well-defined shoulder (C) on a rising absorption into the UV (Figures 7–9; Table III). Different apical groups only slightly perturb the low-lying electronic absorptions, and therefore the transitions must be from levels centered on the CCo_3Cp_3C core.

Previous experience with the Co_3C clusters[7] had suggested that the visible spectra of the bis(carbyne) clusters could afford details of their upper bonding levels and give an insight into the nature of the apical group to capping atom interaction and intramolecular electron transfer. Photoelectron spectra were available to substantiate the assignments for Co_3C electronic spectra, but these are not available for bis(carbyne) clusters. We therefore start from a qualitative frontier orbital approach to the bonding and use this to assist with the assignments.

The effective symmetry of the CCo_3Cp_3C cluster core is D_{3h} even though the maximal real symmetry is C_{3v}. A picture of the upper bonding levels can be developed by analogy with the bonding in the D_{3h} dicapped clusters $(\mu_3\text{-S})_2Co_3Cp_3$ and $(\mu_3\text{-CO})_2Co_3Cp_3$. The orbitals of the symmetrical Co_3Cp_3 fragment, built up from three CoCp units, and its interaction with the capping S and CO groups have been described by Hoffmann[38] and Fenske.[39] Although symmetry arguments require the same orbital interactions with two capping μ-CR carbyne groups, the relative stabilization of the molecular orbitals, especially the e″ and e′ levels, can only be estimated. Calculations for $(\mu\text{-CO})_2Co_3Cp_3$ place the e′ and e″ levels above the "t_{2g}" set of molecular orbitals. However, there remains the possibility of orbital interaction between the μ-capping groups and the formally nonbonding "t_{2g}" set, interactions which proved to be important for charge delocalization in the Co_3C clusters.[7] Of the upper bonding orbitals only the doubly degenerate e′ and e″ are capable of π interactions with the capping group. In common with CO and S the μ-carbyne group possesses three orbitals of interest to the bonding picture: one orbital of σ symmetry with respect to the C_3 axis and two of π symmetry. The fundamental difference between the capping groups is the donor/acceptor character of their π orbitals. This is of paramount importance in determining the π interactions between the capping group and the Co_3 unit. π donor orbitals of sulfur destabilize the metal e orbitals while the converse applied to the π acceptor orbitals of CO. The e″ orbitals are stabilized/destabilized more than the e′ orbitals because the e″ orbitals point toward the capping atoms whereas the e′ are basically localized in the plane of the metal triangle. Carbyne caps have acceptor π orbitals that should also stabilize the e′ and e″ frontier orbitals of the Co_3Cp_3 fragment (this concept is developed in another paper).[20]

From the above considerations a molecular orbital diagram can be derived (Figure 10) that allows a working assignment for the electronic spectra. Assuming idealized D_{3h} symmetry for the CCo_3Cp_3C core, only ${}^1A_1' \rightarrow {}^1A_1''$ and ${}^1A_1' \rightarrow {}^1E'$ transitions are fully allowed. The simplest analysis of the visible spectra is to assign the lowest energy absorptions (B, C) to transitions from successively lower levels to the LUMO. Assignment of band A to the symmetry-forbidden $\sigma^{*\prime}$(HOMO) → σ^*(LUMO) (${}^1A_1' \rightarrow {}^1E''$) excitation and band B to the fully allowed $\sigma \rightarrow \sigma^*({}^1A_1' \rightarrow {}^1E')$ excitation is in keeping with the observed extinction coefficients. Band C is attributed to an excitation from a "t_{2g}" orbital. As this band shows a distinct trend to higher energy as the σ donor strengths of the apical groups increase (Table III), this orbital should be of correct symmetry to have contributions from the carbyne sp hybrid orbitals and thus form part of the $Co_3\text{–}C_{apical}$ σ bond (e.g., the a_1 ($d_{x^2-y^2}$)). Alternatively, band C could arise from excitations from the carbyne sp hybrids themselves (a_1' and a_2'' in the orbital scheme Figure 10).

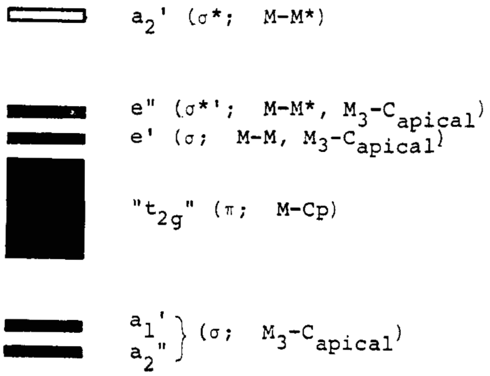

Figure 10. Orbital energy diagram suggested for $RCCo_3(Cp)_3CR'$.

Exactly the same profile for the visible spectra of the cations $[1\text{–}5]^+$ is observed (Figures 7–9). Relative to the neutral compounds there is no significant change in the energy of A, but there is a 2–3-fold increase in the extinction coefficient.[40] This is consistent with the proposed assignment as the $\sigma^{*\prime} \rightarrow \sigma^*({}^2E'' \rightarrow {}^2E'')$ transition is now fully allowed. There is a blue shift in B on oxidation and C merges into the UV tail; the extinction coefficients of B are not changed as the $\sigma \rightarrow \sigma^*({}^2E'' \rightarrow {}^2E')$ excitation is still fully allowed. It is difficult to interpret these changes in band energy in terms of the electronic structure for two reasons. First, there are no photoelectron data or calculations to give an indication of relative ordering of the LUMO and σ bonding levels on oxidation. Charge correlation, and the fact that the LUMO and e″ levels are antibonding with respect to the Co–Co interaction whereas the e′ level is bonding, could easily result in a similar HOMO–LUMO separation for the neutral and cationic species but a blue shift in the e′–LUMO separation on oxidation (the σ-bonding Co–Co interaction would be more sensitive to a change in effective nuclear charge). Perhaps of greater consequence however is that the degenerate e″ orbital is unequally occupied in the cations; as such they are susceptible to Jahn–Teller distortion. Several options can be foreseen. They could remain a symmetrical high spin species, as does $(\mu_3\text{-S})_2Co_3Cp_3$.[39] Alternatively, degeneracy of the e″ orbital could be lifted by lengthening or contracting one Co–Co bond, as in $(\mu_3\text{-X})_2Fe_3(CO)_9$ structures,[39] or the capping ligands may pause between double and triply bridged structures while keeping the Co–Co distances approximately constant. This has been explored for $(\mu_3\text{-CO})_2M_3Cp_3$ (M = Co, Rh) which have two

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(37) We noted that when CH_3CN or CH_2Cl_2 solutions of the cations are placed in contact with silica gel, there is partial conversion to the neutral clusters. Thus TLC analysis of reactions involving the cationic clusters is not recommended.

(38) (a) Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29. (b) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

(39) Rives, A. B.; Xiao-Zeng, Y.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2286.

(40) It is significant that the I_2 charge-transfer complexes of the bis(carbyne) clusters do not have the same spectral profile as the oxidized clusters in CH_3CN. Instead they have a broad absorption centered around ~560 nm with a new band at ~875 nm.

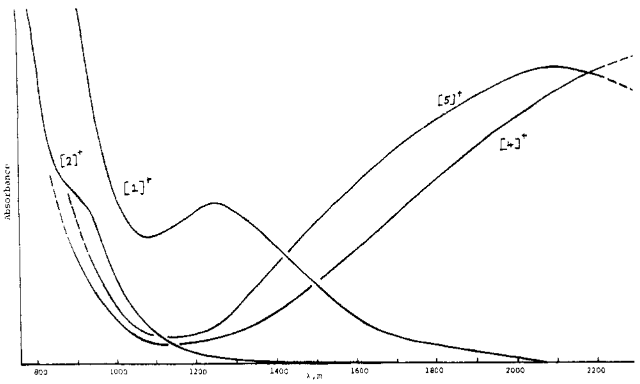

Figure 11. Near-infrared spectra at 293 K in CH_2Cl_2 of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ and in CD_2Cl_2 of $[\mathbf{4}]^{1,0}$ and $[\mathbf{5}]^{0,1,0}$.

electrons in the degenerate e″(HOMO)[38]—one electron less than $[RCCo_3Cp_3CR']^+$. In view of the chemically reversible oxidation of the neutral compounds on the electrochemical time scale, and the similar visible and ESR data for the cations, the symmetrical high spin option is likely to be preferred. The degenerate e″ level in the neutral compound would be split into b″ and a″ levels under C_{2h} symmetry and the first allowed transition would be from the a″ level. Further interpretation requires data from molecular orbital calculations. It is interesting that the blue shift in band B for all clusters other than **3** is ~35 nm whereas it is only 9 nm for **3**. In conjunction with the anomalous substituent parameter[1] γ_{Me_3Si}, and the lack of a near-infrared absorption (vide infra), it presages a different orbital ordering for **3** based on its inability to π interact with the CCo_3C core.

Oxidation of the ferrocenyl center in $[\mathbf{4}]^{1,0}$ has little effect on the transitions associated with the CCo_3C core that is expected if the Fc substituent is only slightly perturbing the σ-bonding levels. A low-energy transition $^2E_{2g} \rightarrow {}^2E_{1u}$ characterizes ferricenium ions,[41] but this was not resolved in the spectrum of $[\mathbf{4}]^{1,1}$ (Figure 8). The broadening and small red shift of band B is attributed to the ferricenium band merging with the $^2E'' \rightarrow {}^2E'$ cluster excitation, the blue shift of the $^2E_{2g} \rightarrow {}^2E_{1u}$ transition compared with that in $[Cp_2Fe]^+$ arising from the π acceptor capability of the carbyne cluster. A comparable feature was noted[9] in the visible spectrum of $[FcCCo_3(CO)_6L_3]^+$. Support for this premise comes from the spectrum of $[\mathbf{5}]^{1,1,0}$ that has a pronounced low-energy shoulder on band B (Figure 9). The red shift of the $^2E_{2g} \rightarrow {}^2E_{1u}$ ferrocenium transition on going from $[\mathbf{4}]^{1,1}$ to this species would occur because of the donor effect of the additional unoxidised ferrocenyl substituent.

Near-Infrared Spectra. Although spectra were recorded of all the valence derivatives of **1**–**5** in the near-infrared regions, only monocations $[\mathbf{1}]^+$, $[\mathbf{2}]^+$, $[\mathbf{4}]^{1,0}$, and $[\mathbf{5}]^{0,1,0}$ show absorption bands (Figure 11; Table III).

The absence of an absorption for $[\mathbf{3}]^+$ is pertinent to the origin of these transitions—note that the oxidative electrochemistry of the Me_3Si cluster was also out of step with the other clusters (vide supra). These observations can be reconciled in terms of the ability of the apical groups to stabilize the monocations by charge back-donation to the oxidized cluster center. Filled π orbitals of the Ph and Fc groups have the correct symmetry to overlap with the empty p_π orbitals of the apical carbyne atom, the resultant π donation stabilizing the oxidized CCo_3Cp_3C core. A $SiMe_3$ group has no orbitals of appropriate energy and symmetry to interact with the carbyne π orbitals (i.e., the π orbitals of the $CSiMe_3$ capping group are localized on the carbyne atom and cannot participate in charge delocalization). Similarly, when the Fc moiety is oxidized, π donation will be reduced which is consistent with no absorption band being observed in the cations $[\mathbf{4}]^{1,1}$ and $[\mathbf{5}]^{1,1,0}$ in which both the cluster and ferrocenyl redox centers are oxidized. The π-donor properties of the carbyne substituent are therefore central to an explanation for these bands. Given that a mechanism for interaction between apical substituent and cluster core exists in **1**, **2**, **4**, and **5**, we need to consider the extent of delocalization between capping carbyne function and the cluster center. Two extreme situations can be envisaged.

(a) Weak Delocalization. The near-infrared absorptions arise from the intramolecular transfer of an electron from the apical group(s) to the cluster center (i.e., a ligand to metal charge-transfer transition). For $[\mathbf{4}]^{1,0}$ and $[\mathbf{5}]^{0,1,0}$ these charge-transfer transitions represent intravalence transfer transitions characteristic of class II mixed-valence ions.[42]

(b) Strong Delocalization. I.e., the positive charge is completely delocalized over the whole cation. This would give ions in which the energy ordering of the cluster electronic levels is not the same as in their neutral precursors.[43] The near-infrared absorptions then arise from new transitions between the rearranged cluster orbitals and $[\mathbf{4}]^{1,0}$ and $[\mathbf{5}]^{0,1,0}$ would then be representatives of class III mixed-valence ions.

The fact that a near-infrared absorption is found for $[\mathbf{4}]^{1,0}$ but not for $[\mathbf{4}]^{1,1}$ allows these two situations to be distinguished. When no near-infrared absorption bands are found in a fully oxidized class III mixed-valence ion, there is an implied difference between the energy ordering of the electronic levels in the mixed-valence and fully oxidized ions. This would not appear to be the case however for the ferrocenyl clusters as the profile and intensity of the electronic spectra of $[\mathbf{5}]^{0,1,0}$ and $[\mathbf{5}]^{1,1,0}$ imply the same order of orbital energies. Note also that a $^2E_{2g} \rightarrow {}^2E_{2u}$ ferrocenium ion transition is observed in $[\mathbf{5}]^{1,1,0}$ which would not be expected in a fully delocalized system. We therefore consider that the near-infrared band in $[\mathbf{4}]^{1,0}$ and $[\mathbf{5}]^{0,1,0}$ arises from an IT transition in a class II mixed-valence ion. Furthermore, the similarities in the ESR (vide infra) and electronic spectra suggest that there is only weak delocalization between the cluster core and carbyne capping group in all $RCCo_3(Cp)_3CR'$ clusters. Consequently, the near-infrared bands observed in $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ represent charge-transfer transitions between the PhC carbyne fragment and the Co_3Cp_3 core.

Although detailed Hush parameters[45] cannot be derived for $[\mathbf{4}]^{1,0}$ or $[\mathbf{5}]^{0,1,0}$, a qualitative comparison with the other cluster mixed-valence ions,[7] $[FcCCo_3(CO)_6L_3]^+$, shows some interesting features. Most conspicuous is the decrease in energy of the near-infrared band on going from the carbonyl clusters $CCo_3(CO)_9$ to the cyclopentadienyl clusters $CCo_3(Cp)_3C$. Both types of clusters represent unsymmetrical mixed-valence ions and are isostructural with respect

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[41] Cowan, D. O.; Le Vanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1.

[42] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

[43] Delocalization of the positive charge is, in principle, equivalent to the relaxation of negative charge from the apical groups to the d orbitals of the Co_3Cp_3 core. As the $e''(Co_3)/\pi$ (carbyne–apical group) combination (HOMO in the neutral species) is most suited for charge delocalization, ionization from a lower orbital level may give a more stable orbital configuration (i.e., the order of electronic levels may change an oxidation). For example, the class III ion bis(fulvalene)diiron.[44]

[44] Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T. *Inorg. Chem.* **1976**, *15*, 2665.

[45] Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

to the conformation of the Fc–CCo_3 fragment.[20] In particular, there is little difference in the formal distance between the ferrocene and cluster halves of the mixed-valence ions. From the Hush model it follows from the low energy that less reorganizational energy is required for electron transfer in the bis(carbyne) clusters. Within an isostructural group this can be interpreted as a greater delocalization in the ground state for **4** or **5** than $[FcCCo_3(CO)_6L_3]^+$, a conclusion in keeping with the electrochemical data. Intensities of the near-infrared bands [**4**]^{1,0} and [**5**]^{0,1,0} appear to be comparable to those observed in $[FcCCo_3(CO)_6L_3]^+$ and other class II mixed-valence ions.[41,46] The large distances between redox centers and the absence of direct Fc–cluster overlap suggest that the dominant interaction between the disparate redox centers must take place via overlap of the appropriate ferrocene and cluster π orbitals. The carbyne cap in the cluster mixed-valence ions is providing for similar processes of valence transfer to those involved in both directly fused and acetylene-bridged diferrocene cations.

ESR Spectra. ESR spectra of cationic organometallic paramagnetic species are often characterized by large anisotropies and fast relaxation.[23] The cationic bis(carbyne) clusters were no exception, and ESR spectra of [**1–3**]$^+$, [**4**]^{1,0}, and [**5**]^{0,1,0} were only observed in frozen CH_2Cl_2 solutions.[25] The notable features of the spectra were the $\langle g \rangle$ values of ~2.2 (Table I) that are much larger than those of cluster radical *anions* and the broad lines (line width ≈ 60 mT) with no hyperfine structure. Spin–orbit coupling between energy states arising from the singly occupied e″ level, or Jahn–Teller splitting of the upper bonding levels (vide supra), could cause the larger $\langle g \rangle$ values. Cluster radical anions by comparison have the unpaired electron in a singly degenerate a_2^* orbital.[19,47]

Conclusion

A molecule in which a Co_3Cp_3 unit is bicapped by two carbyne groups generates an electron-rich oxidizable center in contradistinction to a mono-capped $Co_3(CO)_9$ unit that has a reducible center. Electrochemical studies on a number of μ_3-capped clusters have now been carried out, and it is possible to discern the factors that determine their redox behavior.

(a) First, the electron density at the metal atom of the component fragments forming the metal triangle increases in the order

$$M(CO)_3 < M(CO)_3P(OR)_3 < M(CO)_2PR_3 < MCp < M(\eta^5\text{-}C_5Me_5)$$

This series reflects the decreasing stabilization of the fragment frontier orbitals by the π^*(ligand) orbitals (which increase in energy from CO to C_5Me_5). For a given μ_3-cap, successive replacement by isolobal fragments having more destabilized frontier orbitals will lead to an overall destabilization of the cluster molecular orbitals. Thus oxidation will be thermodynamically easier and reduction conversely more difficult. Provided no gross structural changes accompany successive replacement, then there is often a linear correlation between $E_{1/2}$ and the degree of fragment replacement. For example, in the series $(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}Cp)_2$ (n = 0–5) the reduction potential steps in increments of −33 mV as n is increased. Similar incremental series are found with $YCCo_3(CO)_{9-n}L_n$ reduction potentials.[19]

(b) Second, the ability of the μ_3-capping group to destabilize/stabilize the frontier orbitals of the M_3 fragment (i.e., its donor–acceptor character). As the acceptor capacity increases, the cluster molecular orbitals are stabilized and oxidation is more facile. The three most common μ_3 caps are μ_3-S, μ_3-CO, and μ_3-C. Sulfur has low-lying π orbitals and is a net donor whereas both C and CO have higher lying π orbitals making them π acceptors.[34] There are several pertinent examples illustrating this point. For the isostructural and isoelectronic $(\mu_3\text{-}S)FeCo_2(CO)_9$[3] and $HCCo_3(CO)_9$[19] only the former has an oxidation process ($E_{1/2}$ = 1.1 V) whereas reduction is relatively facile for the latter ($E_{1/2}$ = −0.37 V). The 49-electron cluster $(\mu_3\text{-}CO)_2Ni_3Cp_3$ for which an oxidation process might be expected undergoes a reversible one-electron reduction step.[5] In this case the μ_3-CO groups stabilize the anionic species by d_π–π^*(CO) bonding. Another example is provided by a comparison of CCo_3C clusters and the isoelectronic $(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}Cp)_2$. μ_3-CO is a better π acceptor carbyne function, and a reversible one-electron reduction is observed whereas the CCo_3C clusters are reversibly oxidized. Finally, the electronegativity of the apical carbyne substituent alters the acceptor capability of the μ_3-carbyne atom and systematic trends in the reduction potentials of CCo_3C and CCo_3 clusters are found.

With respect to the apical substituent/CCo_3C interaction (or more precisely the RC/Co_3 interaction) the picture that has emerged from this study of the redox chemistry is one of weak delocalization between the two entities in situations where the RC carbyne group has suitable π orbitals (i.e., Ph, Fc). These weak interactions give rise to transitions in the near-infrared and, in the ferrocenyl derivatives, class II mixed-valence ion behavior. It should be noted that the two empty π levels of the carbyne fragment, CPh and CFc, are nonequivalent and a nonsymmetrical π interaction with the symmetrical Co_3Cp_3 core is permissable. Structural consequences of this nonequivalence are discussed elsewhere.[20] The weak interaction observed in the systems described in this paper encourages us to believe that compounds in which bis(carbyne) clusters are linked by delocalized bridging groups such as –C≡C– or –N≡N– may display advantageous electrical and magnetic properties, and work is underway to test this hypothesis.

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Registry No. **1**, 72271-50-2; [**1**]$^+$PF$_6^-$, 90763-96-5; [**1**]$^{2+}$, 90763-97-6; [**1**]$^-$, 87482-31-3; **2**, 90790-63-9; [**2**]$^+$, 90763-98-7; [**2**]$^{2+}$, 90763-99-8; [**2**]$^-$, 90764-00-4; **3**, 74143-43-4; [**3**]$^+$PF$_6^-$, 90764-02-6; [**3**]$^{2+}$, 90764-03-7; [**3**]$^-$, 90764-04-8; **4**, 90764-05-9; [**4**]$^+$, 90764-06-0; [**4**]$^{2+}$, 90764-07-1; [**4**]$^{3+}$, 90764-08-2; [**4**]$^-$, 90764-09-3; **5**, 90764-10-6; [**5**]$^+$, 90764-11-7; [**5**]$^{2+}$, 90764-12-8; [**5**]$^{3+}$, 90764-13-9; [**5**]$^{4+}$, 90764-14-0; [**5**]$^-$, 90764-15-1; **6**, 90764-16-2; [**6**]$^+$, 90764-17-3; [**6**]$^{2+}$, 90764-18-4; [**6**]$^-$, 90764-19-5; FcC≡CH, 1271-47-2; CpCo$(CO)_2$, 12078-25-0.

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