952 *Organometallics* 1983, *2*, 952–957

Electron Transfer in Organometallic Clusters. 3.[1] Electron Transfer and Mixed-Valence Properties of Substituted Ferrocene–Tricobalt Carbon Clusters

Stephen B. Colbran, Brian H. Robinson,* and Jim Simpson*

Department of Chemistry, University of Otago, Dunedin, New Zealand

Received January 5, 1983

The oxidation state properties of the clusters $FcCCo_3(CO)_6L_3$ [L = $P(OMe)_3$, $P(OPh)_3$] have been investigated by using electrochemical and spectroscopic techniques. Both clusters form a redox series $FcCCo_3(CO)_6L_3^{2+/+/0/-}$ with discrete redox potentials, but only the cationic derivatives are stable on the electrochemical and chemical time scale. Cations were generated by electrolysis or chemical oxidation, and the physical data (infrared and visible spectra) for these species are determined by facile charge transfer between the redox sites via a "push–pull" π mechanism. In the dications [1+,1+] both Fc and Co_3C function as redox sites. Partial oxidation to the [1+,0] species generates the first examples of mixed-valence compounds of a metal carbonyl cluster which display low-energy absorption bands assigned to intravalence transfer (IT) transitions. The parameters suggest that these mixed-valence ions have localized valence sites, and the observed IT properties are consistent with the Hush model for unsymmetrical optical electron transfer in a class II (weakly interacting) species.

Detailed studies on a number of dimeric or more extensively linked molecules containing metal ions, especially those of ruthenium[2] or ferrocene (Fc)[3,4] moieties, have increased our understanding of the consequences of electronic interactions between metals in mixed-valence[5] systems. When the different redox sites are in close proximity, the compounds often have physical properties which may be characteristic of a particular compound, rather than a sum of the properties of the individual redox sites.[6]

No examples of mixed-valence compounds in which one component is a transition-metal carbonyl cluster have been reported. There is only one reported[4] example of a heteronuclear organometallic compound exhibiting mixed-valence properties, and the only cluster examples are those related to the nonheme iron proteins.[7] The availability of the cluster $FcCCo_3(CO)_9$ described in the preceding paper[1] offered the possibility of synthesizing mixed-valence cluster compounds as it was known[8] that the substitution of three CO groups by phosphite ligands generates a potential oxidizable center on the cluster. Thus, molecules of the type $FcCCo_3(CO)_6L_3$ would have two oxidation sites (Fc and Co_3C), and one requirement for mixed-valence behavior would be met. In this paper we report on the oxidation state and electron-transfer properties of the $P(OMe)_3$ and $P(OPh)_3$ derivatives and describe the first examples of heteronuclear mixed-valence[3] compounds containing a metal carbonyl cluster.[9] These molecules also enabled a study of the cooperative interactions which accrue from the incorporation of metal carbonyl clusters into multiple-redox systems.

Experimental Section

Measurements. Visible and near-infrared spectra were recorded on Beckman DK2A and Schimadzu spectrophotometers at room temperature. Because of a rapid disproportionation to the [0,0] and [1,1] species in CH_2Cl_2, spectra of the [1,0] compound were measured on freshly prepared solutions. In donor solvents such as CH_3CN and acetone-d_6, they also rapidly decompose so all spectra of the [1+,0] species were recorded in CH_2Cl_2 or CD_2Cl_2. Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer, ESR spectra on a Varian E3 spectrometer equipped with a low-temperature probe, and ^1H and ^{13}C NMR on JEOL FX-90 or Perkin Elmer EM-390 spectrometers in $(CD_3)_2CO$. Electrochemical measurements were made by using a standard three-electrode configuration described previously.[10] All measurements were vs. Ag/AgCl at the temperatures stated and are uncorrected for junction potentials. The reference electrode was frequently calibrated by using $PhCCo_3(CO)_9$ as external or internal reference (−0.56 V in CH_2Cl_2, −0.38 V in acetone). Exhaustive electrolysis at a constant potential used a standard configuration of a "basket" Pt cathode, a frit-separated Pt coil anode, a solid Ag/AgCl reference electrode, and a home-built potentiostat. The electrolysis was monitored by TLC and IR analyses.

Materials. Supporting electrolytes (TBAP, TEAP), $P(OMe)_3$, and $P(OPh)_3$ were commercial reagents, purified as necessary. For the electrochemical and spectral measurements acetonitrile was distilled from P_2O_5, dichloromethane was washed with aqueous NaOH, dried, and distilled from CaH_2, and acetone was distilled from $KMnO_4$ and then from $CaCl_2$; all solvents were stored under argon. Deuterated solvents were used without further purification. The cluster $FcCCo_3(CO)_9$ was prepared as described in the preceding paper.[1]

Preparation of $FcCCo_3(CO)_6L_3$ [L = $P(OMe)_3$ and $P(OPh)_3$]. In a typical preparation a mixture of $FcCCo_3(CO)_9$ (0.1 mmol) and excess $P(OMe)_3$ (~0.5 mmol) in hexane (25 cm) was brought to reflux temperature and then immediately cooled to room temperature (the rapid reaction is noteworthy as normally this type of reaction takes >1 h). The solvent was removed in vacuo and the residue chromatographed on a silica gel column with 3:1 hexane/CH_2Cl_2 as eluent. A small amount of $FcCCo_3(CO)_7[P(OMe)_3]_2$ was removed first, followed by the product as the major band. The compound was recrystallized from hexane as orange plates: yield 97%. Similar yields were obtained when L = $P(OPh)_3$.

Anal. Calcd for $FcCCo_3(CO)_6[P(OMe)_3]_3$: C, 34.14; H, 3.94. Found: C, 35.44; H, 4.08. Calcd for $FcCCo_3(CO)_6[P(OPh)_3]_3$: C, 57.88; H, 3.67. Found: C, 57.97; H, 4.22.

---

[1] Part 2: Colbran, S. B.; Robinson, B. H.; Simpson, J. preceding paper in this issue.

[2] (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988; **1973**, *95*, 1086. (b) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443. (c) Sutton, J. E.; Taube, H. *Ibid.* **1981**, *20*, 3125.

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

[4] Dowling, N.; Henry, P. M.; Lewis, N. A.; Taube, H. *Inorg. Chem.* **1981**, *20*, 2345.

[5] Hush, N. A. *Prog. Inorg. Chem.* **1967**, *8*, 391.

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

[7] Eaton, W. A.; Palmer, G.; Fee, J. A.; Kimura, T.; Lovenberg, W. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 3015.

[8] Bond, A. M.; Dawson, P. A.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1413.

[9] Preliminary results: Colbran, S. B.; Robinson, B. H.; Simpson, J. *J. Chem. Soc. Chem. Commun.* **1982**, 1361.

[10] Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410.

0276-7333/83/2302-0952$01.50/0

Table I. Spectral Data for $FcCCo_3(CO)_6L_3$

	infrared spectra[a] ν(CO), cm^{-1}	visible spectra,[a] nm
	$L = P(OMe)_3$	
[0,0]	2003, 1979, 1968, 1863, 1825	390, 473
[1,0]	2028, 1998, 1980, 1845	390, 470, 630
[1,1]	2042, 2003, 1988, 1978, 1817	in UV tail 577
	$L = P(OPh)_3$	
[0,0]	2025, 2000, 1988, 1878, 1836	387, 485
[1,0]	2049, 2008, 1988, 1970 (sh), 1847	392, 465, 620
[1,1]	2078, 2054, 2030	in UV tail 587

[a] Data for each compound are in CH_2Cl_2.

Both complexes are orange air-stable solids, but satisfactory consistent analyses for the $P(OMe)_3$ compound were not obtained; however, the formulation is fully substantiated by the spectral data. $L = P(OMe)_3$: IR ν(CO) 2000 (m), 1984 (vs), 1972 (vs), 1945 (s), 1868 (m), 1827 (m) cm^{-1}; ^1H NMR 4.13 (s, 5 H), 3.96 (s, 4 H) 3.65 (d, J(P–H) = 10.2 Hz, 27 H) ppm. $L = P(OPh)_3$: IR ν(CO) 2025 (m), 2003 (vs), 1992 (vs), 1967 (s), 1880 (m), 1845 (m) cm^{-1}; ^1H NMR 7.10 (m, J(P–H) = 10.2 Hz, 45 H), 4.20 (s, 5 H), 4.07 (s, 4 H) ppm.

Both derivatives are soluble in all organic solvents, but TLC analysis of other than freshly made solutions invariably showed that they consisted of a mixture of $FcCCo_3(CO)_{9-n}L_n$ (n = 0–3). Therefore all physical measurements were made on solutions which were pure by TLC and IR analyses.

Preparation of Oxidized Derivatives. [1+,0]. The phosphite derivative $FcCCo_3(CO)_6L_3$ (0.10 mmol) was dissolved in 10 cm^3 of NH_4PF_6-saturated CH_2Cl_2 in a Schlenk tube. The solution was degassed, and the stoichiometric amount of $AgPF_6$ (0.10 mmol), contained in a glass boat, was added directly to the solution. On shaking the orange solution turned a dark green and after 5 min was filtered by standard Schlenk techniques. The filtrate was rapidly evaporated to dryness at 0 °C, washed with CCl_4, and dried in vacuo. All measurements were taken on these purified samples the mass being calculated from the amount of parent recovered after the oxidation. The purified sample was dissolved in CH_2Cl_2 and immediately used for spectral measurements. If these solutions are left for some time, they turn deep blue with a small amount of decomposition. When the solvent was removed at this point and the blue-black residue washed with CCl_4, almost half of the [0,0] species was recovered. The blue-black solid dissolved in CH_2Cl_2 with spectral characteristics of the [1+,1+] species. Thus the [1+,0] species rapidly disproportionates in solution,[11] and this is more rapid when $L = P(OMe)_3$.

The results with chemical oxidants were substantiated by carrying out a controlled potential oxidation of the [0,0] compound at 0.60 V (0.50, $L = P(OMe)_3$) vs. Ag/AgCl in CH_2Cl_2. The green [$P(OPh)_3$] or blue [$P(OMe)_3$] solutions had spectral properties identical with those prepared by chemical methods.

[1+,1+]. Dark blue solutions of the dications were prepared by the same methods as above but using a slight excess of the oxidant or at 1.10 V. The blue-black solids, obtained in near quantitative yields, were recrystallized from CH_2Cl_2. Like other Lewis base derivatives the compound is very labile but it is stable in CH_2Cl_2 for several months.

Results and Discussion

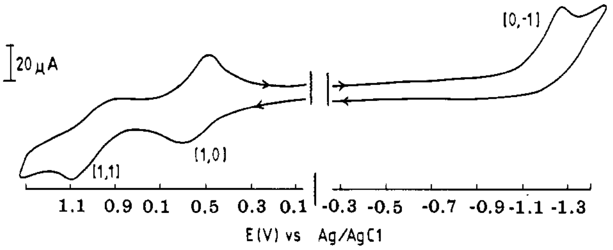
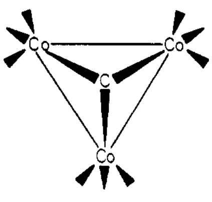
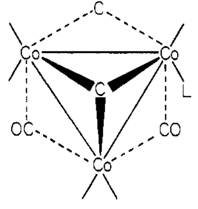


Figure 1. Cyclic voltammogram on Pt of $FcCCo_3(CO)_6[P(OPh)_3]_3$ (in CH_2Cl_2; 0.07 M TBAP at 293 K; scan rate, 200 mV s^{-1}; V vs. Ag/AgCl).

The complexes $FcCCo_3(CO)_6L_3$ [$L = P(OMe)_3$ (1) and $L = P(OPh)_3$ (2)] were prepared from $FcCCo_3(CO)_9$ as orange air-stable crystalline solids. It can be inferred[12] from the infrared spectra (Table I) that both 1 and 2 adopt the bridging carbonyl configuration[1] (*a*) shown (apical group omitted for clarity) in contrast to other $YCCo_3(CO)_6L_3$ phosphite derivatives which have no bridging carbonyls.[13] As discussed elsewhere[12] this is in response to the increased electronic charge placed on the Co_3C core by a strongly donating Fc apical substituent. Contrariwise, substitution of three carbonyl groups releases electron density to the Fc moiety, and this is manifested in increased shielding of the cyclopentadienyl protons of the substituted ring (1, 3.96 ppm, 2 4.07 ppm, compared to $FcCCo_3(CO)_9$, 4.50 ppm); the proton resonances of the unsubstituted rings are unaffected.[14] Although the interaction between the Fc and Co_3C moieties can be described as "weak" (vide infra), it is sufficient to allow a facile "push–pull" distribution of electron density. The substitution of three carbonyl groups by phosphite ligands must inevitably place an added strain on an already sterically congested cluster unit and the distortions noted[16] in the parent $FcCCo_3(CO)_9$ may well be modified in the structure of 1 and 2. Certainly, this steric congestion could account for the extreme lability of the phosphite ligands in these derivatives.



e



a

Electrochemistry. A cyclic voltammogram of 2 in CH_2Cl_2 is shown in Figure 1; half-wave potentials and other data for 1 and 2 in acetone are given in Table II; similar data were obtained in CH_2Cl_2. Uncompensated solution resistance between the reference and working electrodes, junction potentials, slow electron transfer, and poisoning of the Pt surface combined to make ΔE_p larger than the theoretical 59 mV. In our system ΔE_p for the Fc^+/Fc couple of 80 mV was used as the criterion for reversibility. It can be seen from the electrochemical data that both 1 and 2 undergo three redox processes at Pt, two oxidations and one reduction, in contrast to most other Fc–CCo_3 derivatives which exhibit one oxidation and one reduction step.[1] Reduction to the radical anion is irreversible. Ox-

---

[11] Solutions of 3 and 4 are unstable with respect to disproportionation unless light is rigorously excluded. The free energy change for the equilibrium $2[Fc^+CCo_3(CO)_6L_3] \rightleftharpoons FcCCo_3(CO)_6L_3 + Fc^+CCo_3^+(CO)_6L_3$ can be calculated to be ~240 mV, from electrochemical data for the contributing species. While this suggests that the monocation should be thermodynamically stable, a facile, light-induced excitation to an intravalence state can occur. It is this excited state which readily disproportionates to the neutral cluster and dication species.

[12] Matheson, T. W.; Robinson, B. H.; Tham, W. S. *J. Chem. Soc., Dalton Trans.* 1971, 1457.

[13] Dawson, P. A.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Dalton Trans.* 1979, 1762.

[14] It is well-known in ferrocene chemistry that the iron atom provides an effective barrier to the transmission of substituent effects from one ring to another.

[15] Rosenblum, M. "The Iron Group Metallocenes"; Wiley: New York, 1965.

[16] Colbran, S. B.; Robinson, B. H.; Robinson, W. T.; Simpson, J. *Organometallics* in preparation.

Table II. Electrochemical Data for $FcCCo_3(CO)_6L_3$ Compounds[a]

	polarography[b]				cyclic voltammetry[c]								
	oxidation [1,0]		reduction [0,1−]		oxidation [1,0]			oxidation [1,1]			reduction [0,1−][d]		
	$E_{1/2}$	$E_{3/4} - E_{1/4}$	$E_{1/2}$	$E_{1/4} - E_{3/4}$	E_p[a]	ΔE_p	i_c/i_a	E_p[a]	ΔE_p	i_c/i_a	E_p[c]	ΔE_p	i_a/i_c
L = $P(OMe)_3$	0.43	55	−1.31	50	0.46	80	1.0	0.73	120	1.0	−1.39	160	0.4
L = $P(OPh)_3$	0.51	56	−1.03	46	0.57	90	1.0	1.05	100	0.8	−1.06	110	0.1

[a] Potential: V vs. Ag/AgCl at 293 K in acetone. Et_4NClO_4, 0.1 mol dm^{-3}; concentration of compound, ~10^{-3} M; $E_{3/4} - E_{1/4}$ and ΔE_p in mV. [b] Scan rate, 10 mV s^{-1}; drop time, 0.5 s. [c] Scan rate, 200 mV s^{-1}. [d] Other waves in the reduction scane corresponded to those for the derivatives $FcCCo_3(CO)_{9-n}L_n$ (n = 1, 2).

idation at the first wave is electrochemically and chemically reversible while oxidation at the second wave is electrochemically quasi-reversible for 2 but reversible for 1. If due allowance is made for substituent effects, an assignment of the electron-transfer step is straightforward from a comparison with the model compounds $FcCCo_3(CO)_9$ and $MeCCo_3(CO)_6L_3$. For 2 the reduction center ($E_{1/2}{}^r$ = −1.01 V) is clearly the basal Co_3 unit of the cluster where the extra electron enters an a_2^* orbital (cf. $E_{1/2}{}^r$ for {$MeCCo_3(CO)_6[P(OMe)_3]_3$} is −1.03 V).[8] The most easily oxidized center ($E_{1/2}{}^\circ$ = 0.59 V) is the ferrocene moiety (cf. $E_{1/2}{}^\circ$ = 0.73 V in $FcCCo_3(CO)_9$),[1] and the second oxidation site ($E_{1/2}{}^\circ$ = 0.99 V) is on the cluster (cf. $E_{1/2}{}^\circ$ = 1.06 V in $MeCCo_3(CO)_6[P(OMe)_3]_3$);[8] similar assignments follow for **1**.

$$\underset{\substack{\mathbf{5},\ L = P(OMe)_3 \\ \mathbf{6},\ L = P(OPh)_3}}{Fc^+CCo_3{}^+(CO)_6L_3} \overset{e}{\rightleftharpoons} \underset{\substack{\mathbf{3} \\ \mathbf{4}}}{Fc^+CCo_3(CO)_6L_3} \overset{e}{\rightleftharpoons}$$

$$\underset{\substack{\mathbf{1} \\ \mathbf{2}}}{FcCCo_3(CO)_6L_3} \xrightarrow{e} FcCCo_3(CO)_6L_3{}^{-}\cdot$$

Triphenyl phosphite is a more effective π acceptor than $P(OMe)_3$, and this is mirrored in the values of $E_{1/2}$ [1,0] and $E_{1/2}$ [1,1]. Nevertheless, it is *easier* to oxidize the ferrocenyl center in both 1 and 2 than ferrocene itself ($E_{1/2}$ = 0.63 V), or $FcCCo_3(CO)_9$, and the shift of ~0.21 V to more positive potentials for $E_{1/2}$[1,0] relative to $FcCCo_3(CO)_9$ is dramatic when the change in electron density consequential upon phosphite substitution occurs ~7Å from the iron atom. Thus, with respect to the ferrocenyl moiety, the cluster is now acting as a *net electron donor*, in contrast to the situation in $FcCCo_3(CO)_9$ where it acts as a strong electron-withdrawing group.[1] This serves to reinforce the model of a tricobalt carbon cluster which can participate in "push-pull" cooperative interactions according to the needs of the apical substitute[17] (see below). Electrons which are gained or lost on oxidation of a ferrocene moiety come from orbitals which are largely Fe d in character and substituent effects are normally additive.[18] A substituent parameter $\delta_{CCo_3L_3}$ can be derived from the relationship

$$\delta_{CCo_3L_3} = E_{1/2}[Fc^{1/0}] - E_{1/2}[1^{1/0}] \text{ (or } [2^{1/0}]) \quad (1)$$

The values of 0.20 [L = $P(OMe)_3$] and 0.12 [L = $P(OPh)_3$] rank these substituents among net electron donors[18] such as methyl group *directly* substituted on a Cp ring. Furthermore, there is a linear relationship between $E_{1/2}$[1,0] and the number of phosphite ligands (n). Thus, the $E_{1/2}$[1,0] for a particular Lewis base derivative can be calculated from the relationship

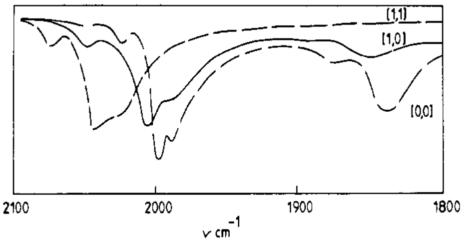
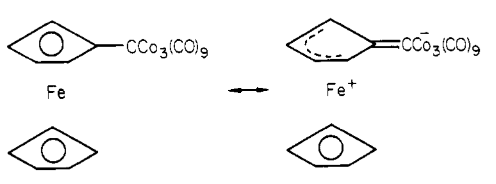


Figure 2. Infrared spectra in ν(CO) region in CH_2Cl_2 of $FcCCo_3(CO)_6[P(OPh)_3]_3$: --, [0,0]; —, [1,0]; ---, [1,1].

$$E_{1/2}[1,0] = E_{1/2}(Fc^{1/0}) + \delta_{CCo_3} - n\delta_L$$

where δ_{CCo_3} = 0.09 and δ_L = 0.10 [$P(OMe)_3$] and 0.07 [$P(OPh)_3$].

Oxidation of the cluster center in 1 or 2 is slightly easier than for related CCo_3 derivatives, to be expected if the ferrocene moiety is acting as a net electron donor. This would appear to be in conflict with the requirement for increased electron density at the iron center (vide supra). The analysis above indicates that the latter effect arises from an inductive effect from an electron-rich cluster whereas the ferrocene moiety acts cooperatively via a π-type interaction toward the cluster; i.e., the cluster participates in "push-pull" + I, −M interactions but the π-donation from Fc is less significant than in $FcCCo_3(CO)_9$. These data are consistent with the concept of a fulvene-like ring bound to a $Co_3(CO)_9$ unit which will be developed elsewhere.[16]



Cationic Derivatives. Solutions of the deep blue [1+,1+] species, **5** and **6**, in CH_2Cl_2 were generated by the controlled electrochemical oxidation or by adding excess Ag^+ to solutions of 1 or 2, respectively. If the oxidation is carefully monitored (see Experimental Section), solutions of green [1+,0], **4**, were obtained. Progressive changes in the infrared spectra reflect both the properties of the different positively charged centers and the interaction between them (Figure 2; Table I). Oxidation of the ferrocene center shifts the A_1 ν(CO) band 23 cm^{-1} relative to the neutral species (this A_1 mode is a characteristically sensitive to the charge on the cobalt atoms). The CO-bridged *a* configuration is however retained in the [1+,0] species. To appreciate the magnitude of this shift caused by a perturbation some 7 Å from the M–CO bond, it can be noted that substitution of CO by a Lewis base on a Co_3 unit causes a shift[12] of −20 to −30 cm^{-1}. Not only is there

---

[17] (a) Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73. (b) Miller, D. C.; Brill, T. B. *Inorg. Chem.* **1978**, *17*, 240.

[18] (a) Pevevalova, E. G.; Gubin, E. Q.; Smirova, S. A.; Nesmeyanov, A. N. *Dokl. Akad. Nauk SSSR* **1964**, *155*, 847. (b) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811.

Table III. Typical Parameters for Mixed-Valence Ferrocene Compounds

compd	$\bar{\nu}_{max}$, cm^{-1}	$10^{-3}\Delta\bar{\nu}_{1/2}$, cm^{-1}	ϵ_{max}	$10^3\alpha^2$	ref
$[Fc-Fc]^+$	5550	3.0	750	~9	21
$[2\text{-}(Ac)Fc-Fc]^+$	7140	4.2	530		21
$[FcC{\equiv}CFc]^+$	6410		670	2.4	22
$[Fc(C{\equiv}C)_2Fc]^+$	8474		570		
$[(NH_3)_5RuNCFc]^{3+}$	9090	4.9	380	2.3	4
$[(NH_3)_5RuNCCH{=}CHFc]^{3+}$	8749	(4.9)	330	1.2	4
$FcCCo_3(CO)_6L_3^+$ 3	5050	2.0	840	3.5	this work
4	6472	2.5	730	2.3	this work

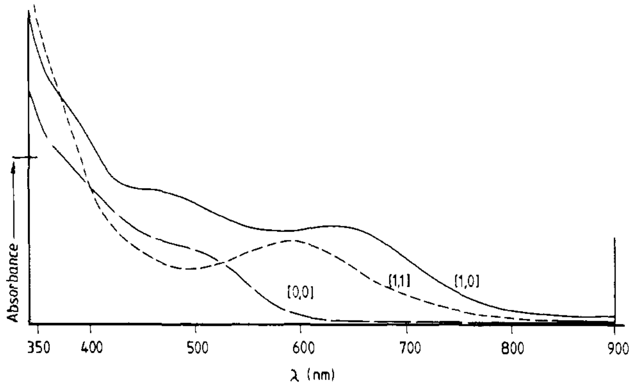


Figure 3. Visible spectra of $FcCCo_3(CO)_6[P(OPh)_3]_3{}^{2+/+/0}$ in CH_2Cl_2 at 293 K: --, [0,0]; —, [1,0]; --- [1,1].

a further shift to higher energy of the A_1 mode (~20 cm^{-1}) on oxidation of the Co_3C center, but also the removal of charge on the cobalt atoms allows the molecule to adopt the preferred nonbridged *e* configuration in **1**.

Electronic spectra of both ferrocene and tricobalt carbon compounds are sensitive to inductive and delocalization effects and will therefore reflect the degree of interaction of the redox sites. If the ground state interaction is weak, that is with localized valences, then we expect to observe electronic transitions assignable to the individual redox sites. Electronic spectra of **2**, **4**, and **6** in CH_2Cl_2 are shown in Figure 3; similar spectral profiles were found for the $P(OMe)_3$ compounds, and parameters are given in Table I.

Tricobalt carbon derivatives are characterized by two bands in the visible spectra.[1] One, band M around 500 nm, is assigned to a symmetry-allowed "cluster" transition and is relatively insensitive to changes in the apical substituents. The other (band N) involves transitions from π-energy levels and is substituent sensitive.[1] The neutral derivatives (**1** and **2**) retain this profile, but there is a blue shift (~30 nm) in band M (which is rather ill-defined in **2**) compared to $FcCCo_3(CO)_9$ because the increased electron density on the cluster increases the separation between the upper bonding orbitals and the a_2^* orbital. Band N is relatively unaffected by substitution of the CO groups by phosphite ligands.

On oxidation to **3** or **4** a new band appears at ~630 (**3**) and 620 nm (**4**): band N has essentially the same energy as comparable bands in the neutral derivatives, whereas there is a small blue shift in band M. All ferricenium compounds display an intense absorption in the region of 600 nm, which has been assigned to a ligand e_{1u} to metal e_{2g} ($^2E_{2g} \rightarrow {}^2E_{2u}$) excitation.[3] This is clearly the origin of the new bands in **3** and **4**, an assignment which firmly establishes the ferrocene moiety as the cationic center. Furthermore, the energy of this excitation in **3** and **4** reinforces the concept of inductive transfer from the cluster to the Fc moiety established from the electrochemical data. Thus, there is a progressive red shift from the molecule where the cluster is acting as a net –I group, $FcCCo_3(CO)_9{}^+$ (~560 nm), through those where the cluster has no pronounced inductive or mesomeric effect, $FcCCo_3(CO)_8L^+$ ($^2E_{2g} \rightarrow {}^2E_{2u}$ energy very similar to Fc^+), to the $FcCCo_3(CO)_6L_3{}^+$ species where the cluster is a net electron donor. Oxidation to the [1+,1+] species, **5** and **6**, causes a major change in the profile of the transitions associated with the cluster unit, consistent with the postulate that the Co_3C core represents the second valence-localized oxidation site. Thus, both bands, M and N, undergo the anticipated blue shift such that they merge with the ultraviolet tail. A similar shift to higher energy is observed in the $^2E_{2g} \rightarrow {}^2E_{2u}$ transition as expected if the cluster is a less effective net donor because of the higher effective nuclear charge on the cobalt atoms. The fact that the energy of this Fc-based transition is dependent on the effective electron-withdrawing capacity of the cluster offers cogent evidence for the cooperative interaction between the two redox sites discussed above. Furthermore, the magnitude of the effect is commensurate with the weak interaction expected for a class II, mixed-valence ion.

The ESR spectra of ferricenium compounds are often difficult to detect because of large anisotropies and fast relaxation.[19] This was the case for the [1+,0] clusters, no paramagnetic species being detected down to 77 K.

Intravalence Transfer Bands. The spectroscopic and electrochemical data for the [1+,0] species provide evidence for discrete donor and acceptor sites with some degree of delocalization or interaction between them. Providing this delocalization is within the "weak interaction" criteria defined by Hush[5] (or class II in Robin and Day's terminology[6]) intravalence charge-transfer (IT) bands may arise due to optically induced electron transfer from Fc to the Co_3C cluster in the mixed-valence species **3** and **4**.

Near-infrared spectra of sea-green solutions of $Fc^+CCo_3(CO)_6[P(OPh)_3]_3$, **4**, in CH_2Cl_2 exhibited[20] a broad feature with λ_{max} at 1545 nm (ϵ_{max} 730) which was not present in solutions of the neutral precursor or the dication **6**. The comparable IT band for **3** in CD_2Cl_2 was on the edge of the solvent limit at λ_{max} 1980 nm (ϵ_{max} 840), but again this band was absent in species in other oxidation states. Unfortunately, it was not possible to study the solvent dependence of these IT bands because of the rapid decomposition in more polar solvents. Because of tailing of the IT bands into the background solvent absorptions, only high-energy bandwidths at half-height, $\Delta\bar{\nu}_{1/2}$, were measured and we were unable to use the procedure recommended by Hush[5] for the measurement of $\Delta\bar{\nu}_{1/2}$. The parameters of the IT bands, $\Delta\bar{\nu}_{1/2}$, ϵ_{max}, and band profiles may be compared with other mixed-valence compounds with trapped ground states[3,21,22] (Table III) and can be seen to be consistent with molecules which can have the ferrocene moiety as their acceptor site. Biferrocene ions

---

[19] Prins, R. *Mol. Phys.* **1970**, *19*, 603.

[20] *The profile of the near-infrared spectrum is given in ref 9.*

[21] Le Vanda, C.; Bechgaard, K.; Cowan, D. O.; Rausch, M. O. *J. Am. Chem. Soc.* **1977**, *99*, 2964.

[22] Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393.

which have delocalized ground states have much narrower bandwidths ($<3.5 \times 10^3$ cm^{-1}) and a non-Gaussian profile.[23]

A significant difference between the metal carbonyl cluster mixed-valence compounds and most mixed-valence ferrocene systems is the disparity in the nature of the donor and acceptor sites. In the unsymmetrical cluster compounds electron transfer will result in the formation of an energetically unfavorable valence isomer, and there will be a marked distortion in the transformation from one valence isomer to another. With polyferrocene systems on the other hand the difference in energy between different oxidation state isomers rarely exceeds 10–20 kJ mol^{-1}. An application of Hush's theoretical analysis to these cluster systems is therefore of some interest. In the high-temperature limit the half bandwidth should be related to the energy of the IT transition $\bar{\nu}_{max}$ at λ_{max} by the relation

$$\bar{\nu}_{max} - \bar{\nu}_0 = (\Delta\bar{\nu}_{1/2})^2/2310 \text{ (in cm}^{-1}\text{)} \quad (2)$$

where $\bar{\nu}_0$ the internal energy difference between the two oxidation state isomers Fc^+–Co_3C and Fc–$Co_3{}^+C$, is not directly accessible from spectroscopic or electrochemical data. By assuming that $\Delta S \approx 0$ and neglecting charge factors, it is possible to calculate the free energy difference between the two oxidation state isomers from the redox potentials of the appropriate couples [L = $P(OPh)_3$, values for L = $P(OMe)_3$ in parentheses; in CH_2Cl_2 to match the spectral solvents].

$$Fc^+\text{–}CCo_3 + e \rightleftharpoons Fc\text{–}CCo_3 \qquad 0.54\ \text{V}\ (0.44\ \text{V})$$

$$Fc\text{–}CCo_3{}^+ + e \rightleftharpoons Fc\text{–}CCo_3 \qquad ?$$

The potential of the second couple is not directly available from the electrochemical data, but an upper estimate can be obtained from the couple

$$Fc^+\text{–}CCo_3{}^+ + e \rightleftharpoons Fc^+\text{–}CCo_3 \qquad 1.04\ \text{V}\ (0.76\ \text{V})$$

where ΔG ($\sim\bar{\nu}_0$) is thus respectively 0.50 V (3.9×10^3 cm^{-1}) and 0.32 V (2.5×10^3 cm^{-1}) for **3** and **4**. From eq 2 the respective bandwidths ($\Delta\bar{\nu}_{1/2}$ (calcd)) are 2.4×10^3 and 2.4×10^3 cm^{-1} which may be compared with $\Delta\bar{\nu}_{1/2}$(obsd) of 2.44×10^3 cm^{-1} and 2.6×10^3 cm^{-1}. Typically[2,24,25] for mixed-valence compounds of the weakly coupled type (class II) the agreement between observed and calculated $\Delta\bar{\nu}_{1/2}$ is of the order $\Delta\bar{\nu}_{1/2}(\text{obsd})/\Delta\bar{\nu}_{1/2}(\text{calcd}) = 1.1$–$1.3$; thus the value is 1.1 for $[Fc^+\text{–}Fc]$[3] and 1.3 for the heteronuclear $[(NH_3)_5RuNCFc]$.[4] For the cluster compounds **3** and **4** the agreement factors are respectively 1.0 and 1.1. These results reinforce the view that the near-IR bands originate in IT transitions between valence-localized Fc^+ and Co_3C sites.

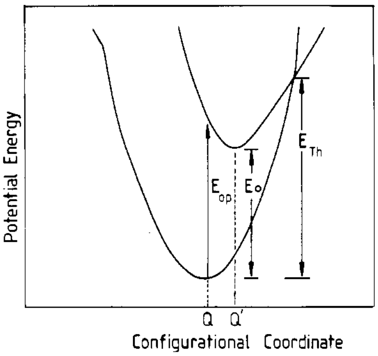


Figure 4. Potential energy–configurational coordinate diagram for system with widely different valence isomers. E_0 difference in free energy for the valence isomers: Q, equilibrium normal coordinate for $Fc^+CCo_3(CO)_6L_3$; Q', equilibrium normal coordinate for $FcCCo_3(CO^+)_6L_3$.

The difference of $\sim$1490 cm^{-1} in the energy of the IT transition between **3** and **4** suggests that the rate of electron transfer for these transitions is sensitive to the steric and electronic constraints imposed by $P(OMe)_3$ or $P(OPh)_3$. This is not unexpected since it is known that slight changes in environment may be sufficient to tip the balance between trapped and delocalized ground states in mixed-valence biferrocene ions. According to Hush the origin of valence trapping lies in the vibrational changes which occur upon oxidation and the vibrational trapping energy corresponds to the thermal activation barrier to electron transfer between Co_3C and Fc^+. Because there is the disparity in the nature of the donor and acceptor sites, electron transfer will result in the formation of an energetically unfavorable valence isomer and there will be a marked distortion when transferring from one valence isomer to another. Reference to the potential energy diagram (Figure 4) shows that a difference in band energy may be due to changes in the configuration coordinate as well as in the difference in energy between the final and initial states (E_0). Data for unsymmetrically substituted mixed-valence ferrocene compounds indicate that changes in the configuration coordinate are relatively important. The red shift of the IT band from **3** to **4** is not most likely, however, due to an energetically more favorable valence isomer with $P(OMe)_3$ as the Lewis base. Indeed, the oxidation potentials show that the $P(OMe)_3$ ligand is effectively a weaker acceptor than $P(OPh)_3$; the difference in the calculated ν_0 values (1.4×10^3 cm^{-1}) could be taken as a measure of the relative stabilization of the valence isomer of $P(OMe)_3$ (cf. observed 1.5×10^3 cm^{-1}).

If we assume that the Hush treatment of mixed-valence complexes applies to these cluster compounds, then an activation energy (E_τ) for the thermal electron transfer can be roughly estimated from the relationship $E_{obsd} \geq 4E_\tau$, where E_{obsd} is the energy of the IT transition.[5] Taking the entropy of activation to be zero, then

$$k \approx (kT/h) \exp[(-E_{obsd}/4 - RT)/RT] \quad (3)$$

The values of k for the two clusters are calculated to be 5×10^9 s^{-1} (**4**) and 4×10^{10} s^{-1} (**3**), and the difference in k is consistent with a slower rate of electron transfer when L = $P(OPh)_3$. This must be related to the energy separation between the respective valence isomers of **3** and **4**. It also suggests that in cluster systems where there are weak interactions between redox centers the rates of intramolecular electron transfer can be systematically and widely varied by tinkering with the coordination sphere of the cluster.

If there are valence-localized sites in the Fc–CCo_3 clusters, then an approximate measure of the extent of delocalization of the optical electron can be obtained from the expression

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\Delta\nu_{1/2}\epsilon_{max}}{\nu(\text{obs})d^2}$$

Since the oxidation site on the cluster portion of the mixed-valence species cannot be strictly defined in the sense that it can be for a mononuclear metal center, there is some tolerance in the measurement of d, the distance separating the redox sites. When a molecular radius[22] for

---

[23] Morrison, W. H.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331.

[24] Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064.

[25] Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 7827.

Fc^+ of 3.90 Å and the appropriate molecular parameters[17] for Co_3C are used and if the oxidation center is taken to be the centroid of the tetrahedral cluster, then d is ~6.5 Å. This gives values for α^2 of 2.7×10^{-3} and 2.8×10^{-3} for **3** and **4**, respectively, values which are comparable with those of $FcC{\equiv}CFc^+$ (2.4×10^{-3}) and $[(NH_3)_5RuNCFc]^{3+}$ (2.3×10^{-3}) but less than that for the directly coupled system $Fc\text{–}Fc^+$ (9×10^{-3}). Nonetheless this is a tenuous comparison for two reasons. First the result for the cluster species is very dependent on the definition of the acceptor site in the multiatom cluster as α^2 is proportional to $1/d^2$; e.g., if there is a direct interaction between the Fe and cluster, α^2 increases to 5×10^{-3} for **4**. Second, there is a difference in the nature of the orbital interaction between the redox sites in the clusters and the other mixed-valence ions mentioned above. In particular, the contribution from "pure" d (metal) is significant in other examples of mixed-valence ions, whereas an already delocalized multimetal unit mixing with a (C_5H_5-cap) bridge "carries" Co_3C character to the Fe(III) site. In a sense, the Co_3C could act as a "buffer" and one might anticipate a reduced effective ground-state delocalization parameter α^2 in mixed-valence cluster ions. The α^2 parameter for the cluster suggests that the optical electron spends between 1 and 2% of its time on the cluster.

Conclusion

The present study has extended the range of organometallic clusters which can exhibit multiple oxidation states to include heteronuclear Lewis base substituted metal carbonyl clusters. Furthermore, the cationic species, [1+,0], provide the first examples of a class II intramolecular mixed-valence compound (within the categories defined by Day) which include an organometallic cluster as one of the redox sites. The conclusion that there are localized valence sites in these $[FcCCo_3]$ compounds is supported by the energy, intensity, and bandwidth of the IT transition, the correlation between the spectral and electrochemical data, the fact that transitions are seen in the visible spectra appropriate to either of the constituent redox sites, and the magnitude of various parameters deduced from the Hush model. The internal consistency between the observed and calculated parameters indicates that the Hush model is valid for cluster systems.

Vibrational changes which occur in the respective coordination environments are responsible for the valence trapping, the vibrational trapping energy being related to the thermal activation barrier to electron transfer between the unsymmetrical redox sites. The extent of electronic delocalization between the redox sites will determine whether the magnitude of the electronic resonance energy will compensate for the loss of vibrational trapping energy if the system is fully delocalized. To the extent that the coordination spheres of the two redox sites are grossly different, this is unlikely to happen. It is important to note that intravalence transfer transitions are only found in mixed-valence ferrocene compounds when the redox sites are directly fused or bridged by electron-conducting π groups (this includes Fc–Ru systems). It is reasonable to propose that the (ring) C–C (cluster) link must be playing the role of an electron-conducting bridging group via π overlap. Indeed, the mixed-valence properties are consequent upon the particular electronic makeup of the Co_3C core which allows for this type of overlap. The extent of overlap will be reduced by any structural distortion which reduces the coplanarity of the respective orbitals. Tricobalt carbon clusters are sterically congested molecules[17] so we can anticipate that the electron-transfer properties will be sensitive to the ligand configuration adopted around the basal Co_3 moiety. The phosphite derivatives **3** and **4** have a bridging CO configuration, and therefore it is not possible to extrapolate directly from the crystal structure parameters of the parent $FcCCo_3(CO)_9$;[16] that is, whether the Cp ring and the Co_3C unit are still distorted. Nonetheless, it seems likely that unfavorable steric interactions in molecules of this type will serve to reduce delocalization of electron density between the ferrocene and cluster moieties and hence the interaction leading to intravalence charge transfer.

In this study emphasis has been placed on multicenter clusters which have a capping carbon functionality, but noncapped clusters could equally well be suitable substrates as the general trends in redox potential noted in Co_3C compounds apply to these clusters. With noncapped clusters the conceptual problem is synthetic—how to link clusters and at the same time incorporate a suitable bridge for efficient electron transfer. The simplest bridge is an unsaturated organic moiety and examples of this type have been prepared in this laboratory. Whereas transition-metal carbonyl clusters are suitable reduction centers, cyclopentadienyl metal clusters are often electron rich and behave as oxidation centers; coupling of a ferrocene moiety with a cyclopentadienyl metal cluster may present an opportunity for mixed-valence compound formation. Clusters with multiple redox sites provide an opportunity to probe the variety and complexity of cooperative interactions as will be demonstrated in further papers in this series.

Registry No. **1**, 85369-68-2; **2**, 85369-69-3; **3**, 85369-70-6; **4**, 85369-71-7; **5**, 85369-72-8; **6**, 85369-73-9; $FcCCo_3(Co)_6(P(OMe)_3)_3^{-}\cdot$, 85442-16-6; $FcCCo_3(CO)_6(P(OPh)_3)_3^{-}\cdot$, 85442-15-5; $FcCCo_3(CO)_9$, 52215-96-0; $P(OMe)_3$, 121-45-9; $P(OPh)_3$, 101-02-0; Co, 7440-48-4.