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Electron Transfer in Organometallic Clusters. 2.[1] Ferrocene–Tricobalt Carbon Cluster Compounds with Multiple Redox Sites

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The redox chemistry of the cluster compounds $(R)FcCCo_3(CO)_{9-n}L_n$ [R = H, $n = 0$ and 1 for L = PPh_3, $P(C_6H_{11})_3$, and $P(OR)_3$ and $n = 2$ for L = $P(OR)_3$; R = Ac, $n = 0$] and $(R)Fc(CO)CCo_3(CO)_9$ (R = H, Me) has been studied by electrochemical and spectroscopic techniques. Regioisomers of the derivatives $AcFcCCo_3(CO)_9$ and $MeFc(CO)CCo_3(CO)_9$ were characterized. The prototypal $FcCCo_3(CO)_9$ forms a reversible redox series $[1+,0] \rightleftharpoons [0,0] \rightleftharpoons [0,1-]$. The reduction center is the cluster, and a radical anion was detected by ESR methods. Salts of the [1+,0] species were isolated and the IR, Mössbauer, and electronic spectra confirm the positive site as the Fc moiety. Replacement of one CO by a Lewis base does not change the accessible oxidation states but the formation of [0,1−] becomes irreversible; cationic salts were characterized. The [1+,1+] oxidation state becomes accessible on the coordination of an additional Lewis base. A detailed analysis of the electrochemical and spectroscopic data suggests that there is a weak interaction between the redox sites, the cluster acting as an electron-withdrawing substituent to the Cp ring which in turn acts as a π donor to the cluster. A useful model is to regard one ring acting as a fulvene moiety interacting with a $Co_3(CO)_9$ cluster.

At the present time there is widespread interest in organic[2] and inorganic[3] solid-state materials which have advantageous electrical and magnetic transport properties resulting from extensive intramolecular charge transfer. With organometallic materials the extensive chemistry of organic molecules can be augmented by significant effects associated with the variable oxidation states of the metal. While the majority of attempts to synthesize organometallic "molecular metals" have largely been unsuccessful, numerous examples[4] demonstrate that organometallic molecules strongly influence the physical properties of the solids which they form with organic donors or acceptors and promote unusual solid-state processes.

A promising area for the development of organometallic solid-state materials, which has not been explored, is the synthesis of low-dimensional solids containing low-valent metal clusters. Two recently recognized facets of homonuclear metal carbonyl cluster chemistry point to their ability to participate in cooperative transport phenomena—first, the ability to adopt a range of formal valence states[5] (given the correct ligand) and to undergo reversible one-electron transfer reactions[1,5,6] and second, the arrangement of upper bonding levels which enables them to function as electron reservoirs.[7] Cluster redox chemistry has identified systems where individual metal atoms are strongly coupled through the metal–metal bonds, a type of cooperative interaction on a local scale. Such interactions also provide effective systems for buffering perturbations in spin and charge density caused by the addition of an electron and/or substitution of CO. Cooperative interactions in multiple-redox, low-dimensional compounds incorporating cluster moieties might range from the complete coupling of redox centers, where there is an opportunity for new optical and magnetic properties to be developed (class III, $\alpha = 0.707$ according to modern usage[8]), to weak interactions producing little

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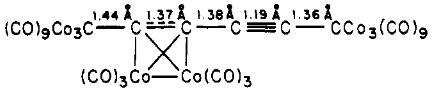
perturbation of individual centers (class I, $\alpha = 0$). An example[9] of a metal halide cluster which gives material reminiscent of organic charge-transfer TCNQ complexes is $[Nb_3Cl_6(C_6Me_6)_3]$. The reaction of this cluster with TCNQ gives a solid-state structure[9] in which there is a bent chain configuration of the cation $[Nb_3Cl_6(C_6Me_6)_3]^{2+}$ alternating with $TCNQ^-$ dimers. While no analogous systems with metal carbonyl clusters have been reported, a variety of such low-dimensional solids are, in principle, accessible via molecular tinkering such as substitution of CO or reaction at a functional atom capping the metal carbonyl clusters. In undertaking a program of synthesis of this type of material, we have initially concentrated on gaining an understanding of chemistry of metal carbonyl clusters containing multiple redox centers. This and the following[10,11] papers are concerned with one such system based on the tricobalt carbon cluster and ferrocene.

The ferrocenyl moiety was chosen as one redox component because of the ease with which it is oxidized[12] and because the mixed valence chemistry of ferrocene compounds is well understood.[13] The tricobalt carbon cluster is ideally suited as it is readily reduced to a radical anion,[14] and it participates in a facile push–pull mechanism for charge distribution to the apical substituent on the carbon atom, via the capping group.[15] Extended delocalization through C–C bonds linked to the capping group is seen in the acetylene derivatives I and II[15a] and is responsible for the stability of carbonium and acylium functional groups.[15b] Therefore with the compound $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4CCo_3(CO)_9]$ there should be an opportunity to study the cooperative interactions between the Co_3 unit and the π system of the ferrocenyl moiety via a suitable electron-conducting bridge, the capping carbon. Furthermore, it was known that the cluster redox series can be extended to include cations by replacing three carbonyl groups by Lewis bases.[5b] Thus, $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4CCo_3(CO)_{9-n}L_n]$ complexes could generate two oxidizable centers and offer a means of probing the scope and complexity of mixed-valence interactions in clusters.

$(CO)_9Co_3C-C\equiv C-CCo_3(CO)_9$

I



II

This paper deals with the redox chemistry of the prototypal $FcCCo_3(CO)_9$ and derivatives where substitution has occurred on the Cp ring and the cluster. Other papers will describe the mixed-valence and charge-transfer compounds[10] of $FcCCo_3(CO)_6L_3$ and the structure and bonding[11] in $FcCCo_3(CO)_9$.[16]

Experimental Section

Tricobalt carbon clusters[15] and ferrocene compounds[12] required as precursors for the syntheses detailed below were prepared by published methods. The ligands $P(OMe)_3$, $P(OPh)_3$, PPh_3, and $P(C_6H_{11})_3$ (Strem) were used without further purification. All reactions were carried out under an argon atmosphere, but the products were usually sufficiently stable in the crystalline phase to be handled in air. Analytical and spectral data for new compounds are given in Table I.

The IR spectra were recorded on a Perkin-Elmer 225 or Jasco IR7 spectrophotometers, ^1H and ^{13}C NMR on Perkin-Elmer EM3-90 or JEOL FX-60FT spectrometers, and electronic spectra on Schimadzu or Beckman DK2A spectrophotometers. The electrochemical instrumentation, sodium reduction, and solvent purification procedures were described earlier.[5a,14] Potentials were measured with respect to a Ag/AgCl reference electrode calibrated against the reversible $[PhCCo_3(CO)_9{}^{0/-}]$ couple which has a potential of –0.38 V in acetone and –0.56 V in CH_2Cl_2. Theoretical ΔE_p for one-electron reversible electrode processes in a particular solvent and with a particular electrode configuration were taken as those for the $[PhCCo_3(CO)_9{}^{0/-}]$ or $[Fc^{+/0}]$ couples under the same conditions. Data refer to 293 K unless otherwise specified. The drop time was normally 0.5 s^{-1} for dc polarograms, and the scan rates for the cyclic voltammograms varied between 50 mV s^{-1} and 5 V s^{-1}. The compound concentration was normally 10^{-3} mol dm^{-3} while those of the supporting electrolytes TEAP (acetone) and TBAP (CH_2Cl_2) were respectively 0.10 and 0.07 mol dm^{-3}. Controlled potential electrolyses were carried out by using a Pt basket cathode (anode) and a frit/gel separated Pt anode (cathode).

Preparation of $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4CCo_3(CO)_9]$. The optimum preparative route to $FcCCo_3(CO)_9$ is via the mercury derivative of ferrocene[17] rather than the Friedel-Crafts reaction.[18] In the brief description of the mercurial route reported by Seyferth and co-workers it was noted that yields were poor (~14%). The major byproduct is Fc_2Hg which precipitates from solution during the reaction, thereby reducing the yields. Effectively there are two competing reactions:

$$2FcHgCl \rightarrow Fc_2Hg + HgCl_2$$

$$FcHgCl + HCCo_3(CO)_9 \rightarrow FcCCo_3(CO)_9 + ?$$

and by keeping the concentration of $HCCo_3(CO)_9$ high, using the procedure below, the first reaction is suppressed.[19] This results in greatly increased yields of ~70% (87% based on reactant $HCCo_3(CO)_9$ consumed).

A solution of FcHgCl (2 mmol) in dry benzene (40 cm^3) was added dropwise to a stirred boiling solution of $HCCo_3(CO)_9$ (2 mmol) in benzene (40 cm^3) over a period of 2 h. After being heated under reflux for a further 1 h, the solution was cooled and filtered. Chromatographic separation on a silica gel column with hexane as elutant, removal of the solvent in vacuo, and recrystallization from hexane gave the product as dark red rhombs, identified by analysis, melting point, and IR spectrum.

Other products, in small yields, are eluted during the chromatographic separation, but there was no spectroscopic evidence for the formation of a product in which both Cp rings were substituted by a cluster. Likewise, if in the above reaction bis(chloromercuri)ferrocene is the ferrocene reagent, the only cluster product is the monosubstituted compound. All attempts to react FcLi with $XCCo_3(CO)_9$ (X = Cl, Br) also failed. Similarly, the Friedel–Crafts route from $XCCo_3(CO)_9/AlCl_3/Fc$ gave very small yields of $FcCCo_3(CO)_9$ with stoichiometric amounts of $AlCl_3$; with excess $AlCl_3$, $Fc(CO)CCo_3(CO)_9$[20] is produced in reasonable yields.

Preparation of $(Ac)FcCCo_3(CO)_9$ and $MeFcCCo_3(CO)_9$. (a) Regioisomers of $(Ac)FcCCo_3(CO)_9$. The method was that used for the preparation of $FcCCo_3(CO)_9$. The 1-acetyl-2- and 1-acetyl-1′-(chloromercuri)ferrocenes were prepared by the method

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Table I. Analytical and Spectral Data for New Compounds

compd	found C	found H	calcd C	calcd H	color	$\nu(CO)^a$	$\nu(C{=}O)^{a,b}$	^1H NMR^c
$FcCCo_3(CO)_9{}^d$	38.30	1.51	36.33	1.45	purple-black	2096, 2047, 2033, 2011		4.50 (s, H_{2-5}), 4.23 (s, $H_{1'-5'}$)^h
1,2-(Ac)$FcCCo_3(CO)_9$	39.92	1.87	39.52	1.79	purple	2099, 2048, 2034, 2015	1678	4.80 (m, $H_{3,5}$), 4.57 (m, H_4), 4.27 (s, $H_{1'-5'}$), 2.67 (s, CH_3)
1,1'-(Ac)$FcCCo_3(CO)_9$	39.41	1.76	39.52	1.79	purple-black	1098, 2048, 2035, 2014	1715	4.83 (m, $H_{2',5'}$), 4.53 (s, H_{2-5}), 4.30 (m, $H_{3',4'}$), 2.37 (s, CH_3)
1,2-(Me)$Fc(CO)CCo_3(CO)_9$		e			purple-black	2104, 2059, 2041, 2030	1578	4.80 (m, H_5), 4.68 (m, H_4), 4.40 (m, H_3), 4.13 (s, $H_{1'-5'}$), 2.08 (s, CH_3)
1,3-(Me)$Fc(CO)CCo_3(CO)_9$		e			purple	2105, 2059, 2042, 2029	1583	4.35 (d, $H_{2,5}$), 4.23 (t, H_4), 4.17 (s, $H_{1'-5'}$), 2.35 (s, CH_3)
1,1'-(Me)$Fc(CO)CCo_3(CO)_9$		e			purple	2104, 2060, 2042, 2030	1580	4.73 (t, $H_{2,5}$), 4.42 (t, $H_{3,4}$), 4.07 (s, $H_{2'-5'}$), 1.95 (s, CH_3)
$FcCCo_3(CO)_9{}^{+\,f}$	33.83	1.681	33.69	1.26	brown	2108, 2064, 2049, 2032	...	...
$FcCCo_3(CO)_8PPh_3$	52.48	3.31	51.63	2.79	maroon	2070, 2033, 2011, 1994	1893, 1864, 1852	7.48 (m, Ph), 4.45 (s, H_{2-5}), 4.17 (s, $H_{1'-5'}$)^i
$FcCCo_3(CO)_8PPh_3{}^+$		g			brown	2083, 2046, 2030, 2013	...	...
$FcCCo_3(CO)_8P(C_6H_{11})_3$	51.22	5.54	50.57	4.78	orange	2063, 2032, 2010, 1998	1885, 1858, 1844	4.22 (s, H_{2-5}, $H_{1'-5'}$), 1.65 (m, C_6H_{11})
$FcCCo_3(CO)_8P(C_6H_{11})_3{}^+$		g			brown	2076, 2033, 2020, 2009	...	...
$FcCCo_3(CO)_8P(OMe)_3$		g			maroon	2072, 2029, 2009	...	4.38 (s, H_{2-5}), 4.15 (s, $H_{1'-5'}$), 3.60 (d, CH_3, J_{P-H} = 10.2 Hz)
$FcCCo_3(CO)_7[P(OMe)_3]_2$		g			orange	2046, 1995, 1990	1882, 1854	4.14 (s, H_{2-5}), 4.13 (s, $H_{1'-5'}$), 3.70 (d, CH_3, J_{P-H} = 10.2 Hz)
$FcCCo_3(CO)_7[P(OPh)_3]_2$	55.99	4.17	54.45	3.28		2057, 2011, 1997		7.11 (m, Ph), 4.21 (s, 5 H), 4.09 (s, 4 H)

[a] In cm^{-1}. In CH_2Cl_2. [b] These are either ketonic or bridging carbonyl stretching modes. [c] In ppm in $CDCl_3$; ±0.5 ppm for other than Lewis base derivatives. In $(CD_3)_2CO$, ±0.5 ppm for Lewis base derivatives. [d] Mass spectra: *m/e* 626, 598, 570, 542, 514, 486, 458, 430, 402, 374, 348, 312, 283, 186, 121, 59, 56. [e] Stoichiometry rests on mass spectra and spectral data. [f] As BF_4^- salt. [g] Too labile to be characterized as analytically pure crystalline solids. Reversion to the [0,0] species or parent $FcCCo_3(CO)_9$ occurred very rapidly even in crystalline samples held in anaerobic conditions at low temperatures. [h] ^{13}C NMR (CD_2Cl_2): δ 200.68, 72.04, 70.82, 70.09 at 293 K. No change down to 200 K. [i] ^{13}C NMR (CD_2Cl_2): δ 208.32, 134.74, 133.52, 129.14, 71.72, 70.58, 69.68 at 293 K. There is no change down to 183 K.

Table II. Electrochemical Data^a (V)

	mercury electrode^b					platinum electrode^b						
	$E_{1/2}{}^c$	$E_{1/4} - E_{3/4}$	$E_{1/2}{}^d$	$E_{1/4} - E_{3/4}$	$i_d{}^c/i_d{}^g$	$E_p(Red)^c$	ΔE_p	i_a/i_c	$E_p(Ox)^d$	ΔE_p	i_a/i_c	$E_{1/2}{}^e$
$FcCCo_3(CO)_9$	−0.42	50	0.72	50	1.0	−0.47	110	1.0	0.79	90	1.0	−1.22
1,2-(Ac)$FcCCo_3(CO)_9$	−0.53	60	0.85	55	1.0	−0.57	120	1.0	0.89	100	1.0	−1.27
1,1'-(Ac)$FcCCo_3(CO)_9$	−0.41	56	0.89	60	1.0	−0.47	150	1.0	0.91	150	1.0	...
1,2-(Me)$Fc(CO)CCo_3(CO)_9$	−0.28	56	...	...	1.0	−0.37	120	1.0	0.86	100	1.0	−1.22
1,3-(Me)$Fc(CO)CCo_3(CO)_9$	−0.28	60	...		1.0	−0.36	120	1.0	0.82	100	1.0	−1.25
1,1'-(Me)$Fc(CO)CCo_3(CO)_9$	−0.29	50	...	...	1.0	−0.37	120	1.0	0.85	100	1.0	−1.22
$Fc(CO)CCo_3(CO)_9$	−0.31	55			1.0	−0.35	100	1.0	0.90	80	1.0	−1.12
$FcCCo_3(CO)_8PPh_3$	−0.64	50	0.62	110	~2	−0.68	80	1.0	0.80	120	1.0	−0.42
$FcCCo_3(CO)_8P(C_6H_{11})_3$	−0.75	46	0.69	60	~2	−0.88	280	1.0	0.82	100	1.0	−0.42
$FcCCo_3(CO)_8P(OMe)_3$	−0.79	60	0.58	50	~2	−0.83	130	1.0	0.62	80	1.0	−0.42
$FcCCo_3(CO)_7[P(OMe)_3]_2$	−1.04	50	0.50	50	~2	−1.16	220	0.7	0.58	140	1.0	0.85^f
$FcCCo_3(CO)_7[P(OPh)_3]_2$	−0.81	85	0.60	55	~2	−0.87	290	0.4	0.65	80	1.0	1.20^f

[a] In acetone. Supporting electrolyte 0.1 M Et_4NClO_4; concentration of cluster ~10^{-3} M, all potentials vs. Ag/AgCl with $E_{1/2}[PhCCo_3(CO)_9]$ = −0.38 V as reference compound. [b] Polarography: drop time, 0.5 s; scan rate, 10 mV s^{-1}. Cyclic voltammetry: scan rate, 200 mV s^{-1}; ΔE_p depends on treatment of electrode. Under the same conditions $\Delta E_p{}^r[PhCCo_3(CO)_9]$ = 90 mV and $\Delta E_p{}^\circ$(Fc) = 100 mV. [c] For the couple [compound$^{0/-}$]. [d] Couple [compound$^{+/0}$]. [e] Other electrode processes from polarographic measurements. [f] These $E_p{}^a$ values represent the couple [compound]$^{2/2}$.

of Kovar and Rausch.[21] A complete separation of the regioisomers was essential at this stage as separation of the cluster analogues is very difficult. The reaction with $HCCo_3(CO)_9$ was as described for the preparation of $FcCCo_3(CO)_9$. Chromatographic separation was carried out on a silica gel column with CH_2Cl_2 as eluent. The 1,2-regioisomer crystallized from hot hexane as black rhombs in >50% yield; the 1,1′ compound crystallized from hot hexane as rhombs also in >50% yield.

Mercury and a yellow compound were again the main secondary products in these reactions. The yellow compound from the 1,2 reaction was recrystallized from CH_2Cl_2 and identified as bis(1-acetyl-2-ferrocenyl)mercury: mass spectrum, *m/e* molecular ion 653; ^1H NMR 4.86 (m, 2 H), 4.70 (m, 2 H), 4.55 (m, 2 H), 4.33 (s, 10 H), 2.40 (s, 6 H); IR: 3090, 1630, 1100, 1000, 910 cm^{-1}. Anal. Calcd: C, 44.17; H, 3.37. Found: C, 44.48; H, 3.81.

(b) $MeFcCCo_3(CO)_9$. All attempts to make the precursor MeFcHgCl were foiled by the facile oxidation of MeFc to the substitution-inert ferrocenium compound by mercury(II) salts. Alternative routes were sought but without success. These alternatives were as follows: (i) $MeFc/AlCl_3$ (1:1)/$XCCo_3(CO)_9$ (X = Cl, Br), no reaction; (ii) as for i but with excess $AlCl_3$, small amounts of $MeFc(CO)CCo_3(CO)_9$ (see below) formed via the acylium cation of the cluster;[15b] (iii) Seyferth has shown[22] that $R(CO)CCo_3(CO)_9$ compounds can be thermally decarbonylated. In refluxing benzene only trace amounts of the decarbonylated product are formed from $MeFc(CO)CCo_3(CO)_9$, the major product being an intractable orange solid.

Preparation of Regioisomers of $MeFc(CO)CCo_3(CO)_9$. Methylferrocene was prepared by the Emde reduction[23] of $Fc-CH_2^+NMe_3$. Following the procedures of Seyferth[24] 1.9 mmol of the acylium cation $^+[OCCCo_3(CO)_9]$ was prepared and thoroughly washed with CH_2Cl_2. The crystalline cation was slurried in 10 cm^3 of CH_2Cl_2, and to this was added 1.9 mmol of methylferrocene. After 45 min the mixture was filtered into a dilute HCl solution containing granulated zinc (to reduce ferrocenium ion) and stirred for 5 min, and the organic and aqueous layers were separated. Workup in the usual way gave a purple solid which was chromatographed on preparative silica gel plates. Development in hexane/CH_2Cl_2 (4:1) gives 10 closely spaced bands, the majority in small quantities. The slowest moving orange band is $HO_2C-CCo_3(CO)_9$. The three black bands preceding this compound were removed and replated. Elution as before gave three well-spaced black bands in order of increasing R_f: 1,2-, 1,1′-, and 1,3-$MeFc(CO)CCo_3(CO)_9$. Total yield of the regioisomers was 26%. All three are air-stable purple-black solids soluble in acetone, CH_2Cl_2, and benzene but less soluble in hexane.

It was noted that three brown bands always preceded those of the regioisomers of $MeFc(CO)CCo_3(CO)_9$. The IR spectra confirmed that they were cluster compounds without a ketonic CO. They may well be the elusive $MeFcCCo_3(CO)_9$ regioisomers, but the yields were insufficient to enable analysis etc to be carried out.

Preparation of $FcCCo_3(CO)_{9-n}L_n$. (a) L = PPh_3 and $P(C_6H_{11})_3$ (n = 1). A hexane solution (25 cm^3) containing $FcCCo_3(CO)_9$ (0.1 mmol) and ligand (0.3 mmol) was boiled for approximately 1 min. The solvent was stripped and the residue chromatographed on a silica gel column. Elution with hexane removed unreacted $FcCCo_3(CO)_9$ and ligand; the product was eluted with CH_2Cl_2. This fraction was evaporated to dryness and the residue recrystallized from hexane to give the products as purple needles (>97%).

These solid derivatives were stable in air but slowly decompose when dissolved in any organic solvent.

(b) L = $P(OMe)_3$ and $P(OPh)_3$ (n = 1 and 2). Typically to $FcCCo_3(CO)_9$ (0.1 mmol) in hexane (10 cm^3) was added the ligand (0.02 mmol) in hexane (10 cm^3). The solution was heated to reflux for 5 min, the solvent stripped, and the residue chromatographed on preparative TLC plates. Elution with hexane/CH_2Cl_2 (4:1) gave four bands, the middle two being the desired products n = 1 and 2, respectively. The maroon n = 1 derivatives are very unstable in solution or solid, converting to $FcCCo_3(CO)_9$ and the n = 2 derivatives, while the n = 2 derivatives can be isolated as pure crystalline materials, but they also are very labile in solution. Samples of the n = 1 and 2 derivatives were always freshly chromatographed before carrying out electrochemical or spectroscopic measurements.

It should be noted that the reaction of Lewis bases with $FcCCo_3(CO)_9$ is much more rapid and efficient compared to those with other CCo_3 substrates.[25]

Oxidation to Ferrocenium Derivatives. (a) $FcCCo_3(CO)_9$. $AgPF_6$ (0.18 mmol) was added to a stirred solution of purple $FcCCo_3(CO)_9$ (0.16 mmol) in CH_2Cl_2 (20 cm^3) saturated in NH_4PF_6. An immediate change to a brown color was observed. The reaction was monitored by IR and deemed to be completed when the band at 2096 cm^{-1} has disappeared; this usually took ~5 min. The solution was filtered to remove the precipitated silver and excess NH_4PF_6 and the solvent removed from the filtrate at 0 °C to give a virtually quantitative yield of $[FcCCo_3(CO)_9]^+PF_6^-$. The product could be recrystallized from NH_4PF_6-saturated CH_2Cl_2 as brown platelets, but considerable reversion to the parent $FcCCo_3(CO)_9$ took place during recrystallization. The recrystallized [1,0] product was washed with hexane and then CCl_4 to remove the [0,0] compound, and this gave an analytically pure sample. Polar solvents such as acetonitrile or acetone were unsatisfactory as solvents for recrystallization as reversion to the [0,0] species was rapid and almost complete. This behavior has been noted for other ferrocene[27] and cluster[28] derivatives.

Other chemical oxidants successfully used were $AgBF_4$, $AgClO_4$, and $FeCl_3$ in CH_2Cl_2; the spectroscopic properties of the BF_4^-, ClO_4^-, or Cl^- salts were identical with those of the PF_6^- salt. Crystals of these salts were not suitable for crystallographic study, and all attempts to make salts derived from Bi(III) or As(III) anions, which form crystalline ferrocenium salts,[29] were unsuccessful. Solutions of the [1+,0] are readily prepared by the controlled potential oxidation of $FcCCo_3(CO)_9$ at 0.6 V in CH_2Cl_2.

(b) $FcCCo_3(CO)_8L$ [L = PPh_3 and $P(C_6H_{11})_3$]. A similar procedure to that described above was used for these compounds. Solutions of both [1+,0] species were brown compared to purple for the parent. With these derivatives however, the conversion [1+,0] → [0,0] is much more rapid than for $FcCCo_3(CO)_9$ and it was not possible to obtain analytically pure crystalline samples.

Results and Discussion

Preparation and Structure of $(R)FcCCo_3(CO)_9$. Preparative and spectroscopic data for the prototypal compound $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4CCo_3(CO)_9]$ ($\equiv FcCCo_3(CO)_9$) (1) have been briefly reported.[17] The improved synthesis using the mercuration route given in the Experimental Section enabled a much wider investigation of its chemistry to be undertaken. In addition the clusters 1,1′-$(\eta^5\text{-}MeCOC_5H_4)Fe[\eta^5\text{-}C_5H_4CCo_3(CO)_9]$ (2) and 1,2-$(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_3(COMe)CCo_3(CO)_9]$ (3) were also accessible via the appropriate mercury chloride precursors (eq 1). It was not possible to prepare derivatives of methylferrocene by this route because of complications arising from the facile oxidation of methylferrocene to its ferrocenium ion. Furthermore, the Fc–CCo_3 linkage in this case appears to be activated to CO insertion, and the major products (in small yields) from a Friedel–Crafts reaction

$$[\eta^5\text{-}(Ac)C_5H_4]Fe[\eta^5\text{-}C_5H_4HgCl] + HCCo_3(CO)_9 \xrightarrow{\text{benzene}} [\eta^5\text{-}C_5H_4(Ac)]Fe[\eta^5\text{-}C_5H_4CCo_3(CO)_9] \quad (1)$$

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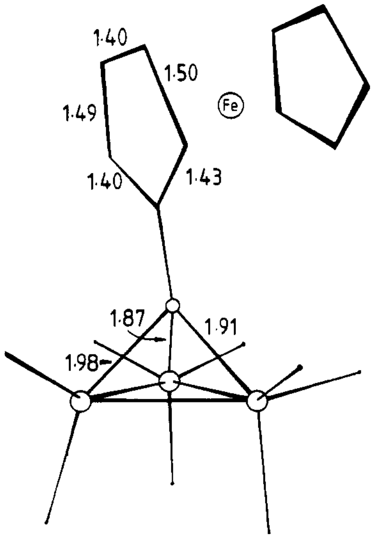

Figure 1. Skeletal structure of 1.

are the acyl clusters $(Me)Fc(CO)CCo_3(CO)_9$ (4) where the cluster is linked via a $-C(O)-$ group. A more direct route to 4 is from methylferrocene and $EtO_2CCo_3(CO)_9$ under conditions which favor the formation of the acylium ion[15b] $[OC^+CCo_3(CO)_9]$ and via this route all three regioisomers (viz., 1,2, 1,3, and 1,1′) were produced in reasonable yields (eq 2). It was hoped that the decarbonylation[22] of 4 would give the desired methylferrocene analogues of 1, but only traces of these compounds were produced.

$$^-[PF_6]^+[OCCCo_3(CO)_9] + MeFc \rightarrow MeFc(CO)CCo_3(CO)_9 + HPF_6 \quad (2)$$

The structure of 1 has been established by an X-ray analysis (Figure 1). Only the features pertinent to a description of the redox chemistry will be given here (a full stereochemical and theoretical analysis will be given elsewhere).[11] They are as follows: (a) a deformation of the Co_3C moiety from C_{3v} symmetry in response to steric congestion and overlap of the cluster π orbitals with the ring π orbitals; (b) nonequivalent C–C bonds in the substituted ring caused, it is believed, by a π interaction between the cluster and the Fc moiety. It is difficult to predict a priori the electronic consequences of having an additional electron-withdrawing substituent on the Cp ring (such as Ac), but there is no doubt that this will increase the steric congestion in the molecule. Compounds of the type $(R)Fc(CO)CCo_3(CO)_9$ are expected to have the usual[15a] C_{3v} structure of tricobalt carbon cluster.

Spectroscopic data are given in Table I. In general, it is found in other ferrocene compounds that substitution by electron-withdrawing groups on a ring leads to pronounced chemical shift differences between the $H_{2,5}$ and $H_{3,4}$ protons, whereas electron donor substituents do not promote this effect although the proton resonances of the substituted ring may be shifted to higher field.[30] In this context, it is curious that the $H_{2,5}$ and $H_{3,4}$ proton resonances are not differentiated in 1 and yet other spectroscopic evidence, and a shift of 0.27 ppm to lower field compared to those of the unsubstituted ring protons, all point to the Co_3C cluster acting as an electron-withdrawing substituent (as expected from its known chemistry[15]). Again, only a single ^1H resonance for $H_{2,5}$ and $H_{3,4}$ was found in 2, but there is a differentiation of 0.27 ppm in $H_{2',5'}$ and $H_{3',4'}$; the protons on the Ac-substituted ring are also deshielded with respect to those on the CCo_3-substituted ring. Note also that the chemical shift of the CCo_3-substituted ring protons is the same for 1 and 2. It appears that the magnetic effects of the large diamagnetic cluster are dominating the complex shielding/deshielding interaction in these ferrocene derivatives. There is no difficulty with assignments for the ^1H NMR of 3, and it is interesting that the electron-withdrawing cluster substituent ortho to the Ac group causes a shift of 0.3 ppm to lower field in the acyl resonance, relative to 2.

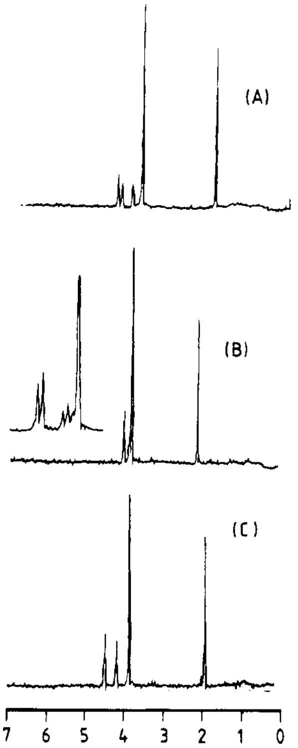

Figure 2. ^1H NMR of regioisomers of $(Me)Fc(CO)CCo_3(CO)_9$ (in $CDCl_3$): (A) 1,2; (B) 1,3; (C) 1,1′.

The ^1H NMR spectra of the three regioisomers of 4 are shown in Figure 2. The spectrum of the 1,1′-isomer is essentially a superposition of the resonances of the substituted rings of MeFc and AcFc. Recognition of the $C(O)CCo_3(CO)_9$ as an electron-withdrawing substituent then allows assignments for the other regioisomers given in Table I.

Unambiguous assignments for the ^{13}C NMR spectrum of 1 establishes the C_1 resonance at 109 ppm. ^{13}C chemical shifts of the ring carbons in ferrocene compounds are particularly sensitive to the charge distributions in the molecule, and this value for C_1 places it firmly with ferrocenylalkylium or -carbenium ion compounds. Thus, the C_1 chemical shift for neutral monosubstituted ferrocene is characteristically less than 100 ppm (cf. acetylferrocene, 77.5 ppm[31]) while that for $FcCH_2^+$ occurs at 111.8 ppm.[31] The value for 1 in fact is the highest recorded for a neutral ferrocene compound, and this underscores the powerful electron-withdrawing effect of the Co_3C moiety. Chemical shifts for $C_{2,5}$ and $C_{3,4}$ and the Cp ring carbons are very similar to those in other neutral ferrocene compounds, which is expected since these resonances seem to be relatively insensitive to the nature of the substituent on the ring. Tentative assignments only can be given for the ^{13}C spectra of 2, and 3, but again the C_1 carbon is extremely deshielded.

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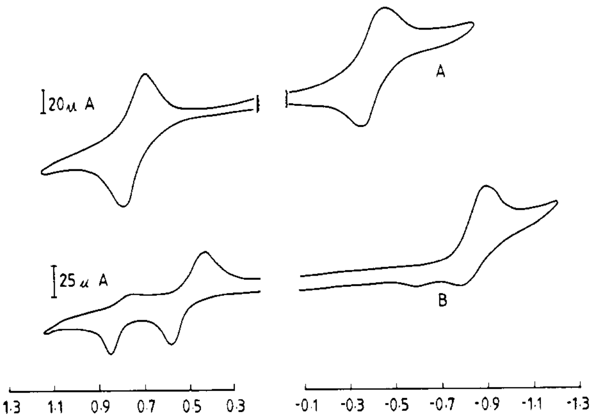

Figure 3. Cyclic voltammograms at Pt in acetone of (A) 1 and (B) $FcCCo_3(CO)_7[P(OMe)_3]_2$ (scan rate, 200 mV s^{-1}).

Electrochemistry of (R)$FcCCo_3(CO)_9$. Two discrete reversible one-electron electrode processes ($E_{1/2} = 0.72$ and -0.42 V) were exhibited in the cyclic voltammograms (Figure 3) and dc polarograms of 1 in acetone at Hg or Pt (Table II). With the close similarity of the electrochemical parameters to those of other[5] tricobalt carbon clusters ($E_{1/2}{}^{r} = -0.28 \rightarrow -0.40$ V) and ferrocene[12,32] ($E_{1/2}{}^{\circ} = 0.63$ V) in the same solvent,[33a] the electrode processes can be confidently assigned to the individual redox centers Co_3C and Fc (eq 3). Both electrode processes are electrochemically reversible although the peak separation ΔE_p in the cyclic voltammograms is characteristically larger than the theoretical 59 mV.

$$^{+}FcCCo_3(CO)_9 \overset{e}{\rightleftharpoons} FcCCo_3(CO)_9 \overset{e}{\rightleftharpoons} FcCCo_3{}^{-\cdot}(CO)_9 \quad (3)$$

This is due to the slow rate of electron transfer on Pt,[33b] poisoning of the electrodes,[33b] and uncompensated junction potentials, so the ΔE_p for the known reversible couples $[PhCCo_3(CO)_9{}^{0/-}]$ or $[Fc^{+/0}]$ were used as the standard ΔE_p. Other irreversible electrode processes were noted at more negative potentials which are probably associated with reduction to $FcCCo_3(CO)_9{}^{2-}$ (expected at -1.3 V) or reduction of the ferrocene center (in ferrocene this occurs at -2.93 V[35]). Assignments for other (R)-$FcCCo_3(CO)_9$ clusters, including the CO-inserted products are given in Table II.

It was anticipated that the trends in redox potentials in Table II would be accounted for by examining the mutual polarization of each redox site by the other, while acting as a subsequent. Substituent effects in the $[Fc^{+/0}]$ couple arise principally from inductive polarization of the energy levels which are largely nonbonding Fe d in character. Electron-donating groups lower the oxidation potential by stabilizing Fc^+—electron-withdrawing groups have the opposite effect—and, providing bond delocalization is insignificant, substituent effects are additive.[36,37] From Table II it is clear that it is more difficult to oxidize the cluster derivatives than ferrocene itself; that is, the cluster moieties act as net electron-withdrawing substituents. Thus, a substituent parameter δ_{CCo_3} can be derived for a $CCo_3(CO)_9$ group from the expression (E_1 is the oxidation potential for 1).

$$\delta_{CCo_3} = E_{1^{+/0}} - E_{Fc^{+/0}} = 0.09 \text{ V} \quad (4)$$

This value is considerably smaller than those for ring substituents like Ac but comparable (in the opposite sense) to substituents such as Fc which are "remote" bond polarizing and delocalization centers.[38] δ_{Ac} is 0.25 V, and $E_{1/2}{}^{calcd}$ for the acyl clusters 2 and 3 is therefore 1.04 V. This is ~0.1 V more positive than $E_{1/2}{}^{obsd}$ which suggests that bond polarization by Ac is offset by a reduction in the cluster substituent effect because of steric congestion. The fact that $E_{1/2}{}^{obsd}$ for the 1,2 is more negative than 1,1′ cluster supports this argument as the ortho ring substituent must interfere with the ability of the $Fc-CCo_3$ linkage to achieve maximum π overlap.

An acylium moiety $^{+}(OC)CCo_3(CO)_9$ is a more powerful electron-withdrawing group than CCo_3 and comparable to an Ac group. Thus δ_{OCCCo_3} is 0.23 V derived from $E_{1/2}$ for $Fc(CO)CCo_3(CO)_9$. Using the appropriate value[36] for δ_{Me}, $E_{1/2}{}^{calcd}$ for a methylferrocene cluster, $MeFc(CO)CCo_3(CO)_9$, is

$$E_{1/2}{}^{calcd} = E_{Fc^{+/0}} + \delta_{OCCCo_3} + \delta_{Me} = 0.88 \text{ V} \quad (5)$$

The close agreement in this case with $E_{1/2}{}^{obsd}$ (see Table II) is consistent with a bond polarization mechanism represented by eq 6.

$$Co_3CC({=}O)Fc \leftrightarrow Co_3C^{+}C({-}O^{-})Fc \leftrightarrow Co_3CC({-}O^{-}){=}^{+}Fc \leftrightarrow Co_3{}^{+}C{=}C({-}O^{-})Fc \quad (6)$$

An uncertainty in the interpretation of the reduction potentials lies in the effect of the distortions noted[11] in the structure of the CCo_3 moiety in 1. As the basal Co_3 unit is still regular, the $a_2{}^{*}$ LUMO should be little affected. This may not be so for the HOMO. Photoelectron spectra[39] and MO calculations[39,40] suggest that an a_1 orbital, a "cluster" orbital, is the HOMO but a doubly degenerate level of Co_3C character is close in energy. Distortions of the Co_3C moiety from C_{3v} symmetry may well change the ordering of these upper bonding levels, particularly by removing the degeneracy of the e level. Thus unusual trends in $E_{1/2}{}^{r}$ could be structurally as well as electronically based.

Ferrocene is a good electron donor, comparable to a methyl group,[41] and indeed, $E_{1/2}{}^{r}$ for the $[1^{0/-}]$ couple is identical with that for $[MeCCo_3(CO)_9{}^{0/-}]$; whether this is significant is open to question. Nonetheless, the CCo_3 redox center is sensitive to changes in the regioenvironment for the Cp rings but not in the expected direction.

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[33] (a) The oxidation or reduction potentials of both ferrocene and CCo_3 compounds are very dependent on the solvent. Throughout this paper data will refer to acetone but the electrode processes are the same in CH_2Cl_2 with an appropriate shift in potential (see Experimental Section). In general, the reduction potentials become more negative in order acetone > MeCN > CH_2Cl_2 > dichloroethane; for example, $E_{1/2}{}^{r}$-$[PhCCo_3(CO)_9{}^{0/-}]$ is -0.38, -0.42, -0.52, -0.80 V vs. Ag/AgCl in the same solvent order. MeCN may participate in electron transfer catalyzed reactions[1] which may invalidate this series. Solvation and specific cation–anion association are believed[34] to be responsible for these large solvent effects with metal clusters. (b) Electrode fouling was visible and electrodes were cleaned after each scan. Slow electron transfer is characteristic of cluster electrochemistry as noted earlier.[5a]

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Whereas $E_{1/2}{}^r$ for 2 is the same as 1, substitution of an Ac group on the same ring to which the cluster is bonded (3) causes a shift of 0.12 V *to more negative potentials*. Not only is this shift too large to attribute solely to an inductive effect if $E_{1/2}{}^r$ for $[1^{0/-}]$ is accepted as the norm, but also no electronic argument can be advanced which would make *reduction more difficult*; the converse should apply. Our interpretation is that steric hindrance from the Ac groups ortho to the cluster produces an even greater deformation of the CCo_3 moiety than observed for 1 with concomitant changes in the HOMO orbital energy of the cluster.

An interesting result is the shift of the reduction potential to ~−0.28 V for all CO-inserted clusters, which puts them among the most easily reduced CCo_3 compounds. This result complements that for oxidation to the ferrocenium analogues (vide supra) and is explicable in terms of the resonance structures shown above. This type of ferrocene cluster can be regarded as a complex of the acylium cation stabilized by charge polarization from both redox centers, and this theme is developed in a later paper.[11]

Redox Chemistry of $FcCCo_3(CO)_9$. The transient redox behavior of 1 suggested that both a radical anion and cation should be accessible on the chemical time scale. This interpretation was corroborated by the detection of the radical anion $1^{-}\cdot$ and isolation of salts of the cation 1^+.

The radical anion $1^{-}\cdot$ was prepared by electrochemical or sodium reduction of 1 in THF. Its 22-line ESR spectrum ($\langle a_{Co}\rangle$ = 3.5 mT) was similar to those of other CCo_3 radical anions,[14] and an analysis of the spectrum[42] gave no features that could be attributed to the deformation of the CCo_3 moiety. That is, the LUMO is an $a_2{}^*$ orbital centered on the Co_3 unit. A qualitative measurement of the lifetime of $[Na^+ 1^{-}\cdot]$ showed that it was longer than for the archetypal $[Na^+PhCCo_3(CO)_9{}^{-}\cdot]$. This is attributed to steric hindrance by the bulky Fc moiety blocking the bimolecular decay which leads to disproportionation of the radical anion.[34]

Brown solutions of 1^+ were obtained by the electrochemical or chemical oxidation of 1 in CH_2Cl_2 and isolated as the $BF_4{}^-$ or $PF_6{}^-$ salts. Oxidation is relatively slow, and a spectrophotometric titration using $AgBF_4$ gave a well-defined end point at the correct mole ratio and an isobestic point confirming that only two cluster species were involved in the reaction. On the other hand, 1^+ rapidly reverts to 1 in solution (particularly polar solvents) both in air and under anaerobic conditions; the reducing agent may be coordinated or extraneous CO, but this has not been confirmed. Relative to 1, the A_1 ν(CO) band in 1^+ is shifted by 12 cm^{-1} to higher energy (Table I), a large shift when the polarization center is some distance from the Co–CO bond. This is good evidence for a charge polarization mechanism which allows a weak interaction between the redox sites; this mechanism will be discussed later.

ESR spectra of 1^+ were recorded down to 77 K, but no paramagnetic species were detected, a problem often encountered in ferrocenium chemistry because of fast relaxation and large anisotropies.[43]

Mössbauer Spectra. Mössbauer spectra of ferrocene compounds can be used to probe the variation in charge density around the iron atom and, in particular, the oxidation state. The large quadrupole splitting characteristic of ferrocene disappears on oxidation to the ferrocenium ion as the electric field gradient in the latter species has almost spherical symmetry. Isomer shifts on the other hand are insensitive to the change in oxidation state.[44] The Mössbauer spectra of 1 and 1^+ are shown in Figure 4, and the parameters are given in Table III. The quadrupole splitting parameters and isomer shifts are characteristic of ferrocene and ferrocenium compounds (see Table III), and these data define the positive center in 1^+ as the iron atom, as suggested by the electrochemistry.

Table III. Mössbauer Parameters at 77 K[a]

compd	isomeric shift, mm s^{-1}	quadrupole splitting, mm s^{-1}
$FcCCo_3(CO)_9$	0.52 ± 0.01	2.25 ± 0.01
$[FcCCo_3(CO)_9]^+$	0.52 ± 0.06	<0.41[d]
Fc[b]	0.48 ± 0.01	2.40 ± 0.02[b]
Fc^+[b]	0.47 ± 0.01	<0.3
$FcCH_2{}^+$[c]	0.57 ± 0.0	2.29 ± 0.0[c]

[a] Iron foil as reference. [b] Reference 44. [c] Reference 45. [d] The spectrum was analyzed in terms of a single peak and a doublet assuming Lorentzian profiles. The doublet gave QS = 0.41 (7) but as the two χ^2 values were the same there is no statistical reason for preferring the two peak fit.

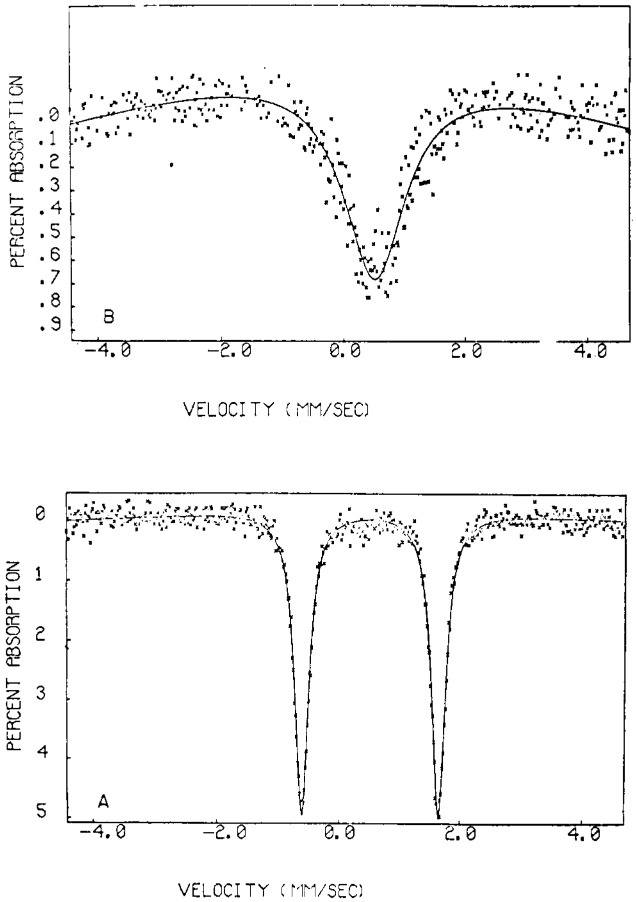

Figure 4. Mössbauer spectra of (A) 1 and (B) 1^+ (as $PF_6{}^-$ salt).

Isomer shifts are also insensitive to ring substitution, but the quadrupole splitting undergoes small changes when electron-withdrawing substituents are incorporated. Relative to ferrocene, there is a reduction in the quadrupole splitting on substitution of the cluster on the ring consistent with the cluster acting as a net electron-withdrawing group.[44] Note, however, the close similarity between the parameters for the carbonium ion[45] $FcCH_2{}^+$ and

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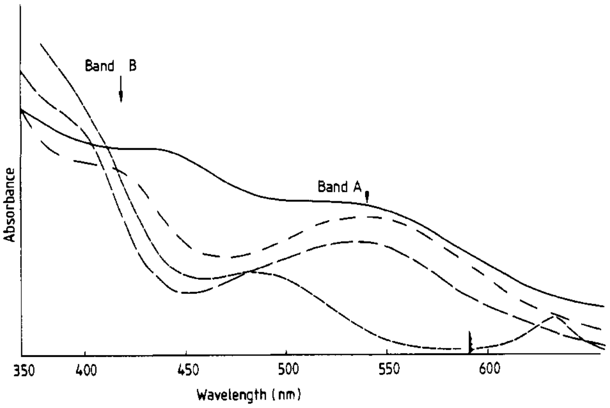
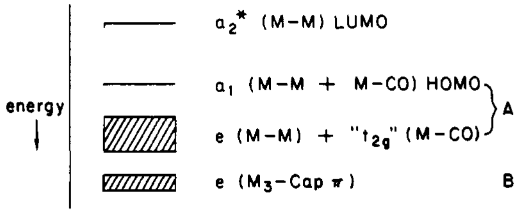


Figure 5. Visible spectra, in CH_2Cl_2, of (i) (- - -) 1, (ii) (—) 1^+, (iii) (— —) $ClCCo_3(CO)_9$, and (iv) (- - -) $[FcCCo_3(CO)_8P(C_6H_{11})_3]^+$ (change of absorbance scale at 580 nm).

Chart I

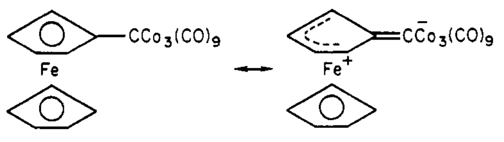


1. Without placing too much emphasis on this analogy, it does support a bonding model in which the interaction between the ferrocene and the cluster is regarded as being between a fulvene moiety and a $Co_3(CO)_9$ group, with a possible component from the interaction between the iron atom and the exo-fulvene link.[46] This provides a raison d'etre for the distortion of the substituted ring as elaborated elsewhere.[11] The arguments[45] advanced to account for the quadrupole splitting of $FcCH_2^+$ involving π-transmission effects equally well apply to 1.

Electronic Spectra. The electronic spectra of 1 and 1^+ are given in Figure 5. Qualitative interpretations of the visible spectra of CCo_3 compounds have been published,[39b,47] but a more definitive description was required for this work. Visible spectra of neutral CCo_3 compounds are characterized by two transitions: band M (λ_{max} ~510 nm, ϵ ~3400) and band N (λ_{max} ~380 nm, ϵ ~4000). The intensity of these bands indicate that they involve levels which are not pure d in character.

An insight into the nature of the transitions can be obtained from recent MO and photoelectron spectra[39] analyses. The important valence orbitals are shown in Chart I. The LUMO is strongly localized on the Co_3 unit. The HOMO, a truly cluster orbital, is only indirectly affected by the inductive and hyperconjugative capacity of the apical group, any π effects being primarily distributed via the upper degenerate bonding orbitals. Photoelectron spectra of CCo_3 compounds display bands in three distinct regions, A (6.0–9.5 eV), B (9.5–13.5 eV), C (13.5–20.0 eV); only the first need concern us. This broad band, which displays a shoulder on the low-energy side (probably ionization from the HOMO), results from several closely spaced ionizations from the upper cluster bonding levels and is relatively insensitive to the type of apical substituent. We attribute band M in the visible spectra to σ (Co_3) → a_2* transitions and band N to transitions from π (Co_3–C_{ap}) bonding levels derived from the t_{2g} set.[48] Bands M and N in the visible spectra are therefore due to closely spaced transitions from the same type of bonding orbitals involved in the first region of ionization in the PE spectra.

Two features distinguish the visible spectra of 1 and 1^+. First, the maxima for band M occurs at 520 nm irrespective of the oxidation state. The fact that the ferrocene moiety does not perturb the energy levels participating in band A is expected from the MO analyses providing the cluster–ferrocene linkage is π in origin. These bands are of slightly lower energy than those for other homonuclear CCo_3 clusters which might be related to the distortions in the CCo_3 unit. Second, there is a pronounced red shift in the energy of band N for 1 relative to those for other apical substituents which can function as net π donors (e.g., Cl, see Figure 5); there is a further red shift on oxidation to 1^+. These data confirm that the Fc moiety is perturbing the π levels of the cluster and support the model used to interpret the Mössbauer spectra, namely, a cluster linked to a fulvene-like ring (eq 7). The magnitude of the hypochromic shift may be due in part to the distortion of the Co_3C unit as well as the net donor properties of Fc.



(7)

Ferrocenium compounds characteristically[12,13] have a band ~620 nm assigned to a ligand (e_{1u}) → $Fe(e_{2g}(3d))$ transition; for example, Fc^+ λ_{max} is 617 nm. No such band was discerned in the spectrum of 1^+ although there is no doubt that the molecule has a ferrocenium center. Extinction coefficients of these bands are often <1000 so it is possible that the band for 1^+ is submerged beneath the cluster transition (band A). Against this explanation is that these bands in other Fc–cluster compounds (vide supra) are of comparable intensity to the cluster transition. Electron-withdrawing substituents on a Cp ring of Fc cause a blue shift in the $^2E_{2g}$ → $^2E_{2u}$ transition and delocalization of electron density from the ring via the π mechanism, believed to be operating in the cluster derivatives, and the consequential ring distortion will also increase the separation between the $^2E_{2g}$ and $^2E_{2u}$ states. Therefore it seems likely that the broad $^2E_{2g}$ → $^2E_{2u}$ transition for 1^+ has merged into the equally broad σ→σ* cluster transition. A conservative estimate of the shift relative to Fc^+ is 2500 cm^{-1}, and this may be compared with a blue shift of 2700 cm^{-1} for ring substitution by Ac.

Redox Chemistry of $FcCCo_3(CO)_{9-n}L_n$ (*n* = 1 and 2). Previous work had shown that the range of redox states accessible to the tricobalt carbon cluster can be extended by replacing CO groups by Lewis bases.[5b] For the redox studies described in this paper the derivatives $FcCCo_3(CO)_{9-n}L_n$ [*n* = 1, PPh_3, $P(C_6H_{11})_3$, $P(OPh)_3$, $P(OMe)_3$; *n* = 2, $P(OPh)_3$, $P(OMe)_3$] were prepared and characterized; the redox chemistry of $FcCCo_3(CO)_6L_3$ is the subject of the following paper.[10]

Lewis base derivatives adopt either of the configurations shown. The *a* configuration is preferred in situations where the cluster is "electron rich".[25] The PPh_3 and $P(C_6H_{11})_3$ complexes crystallize with an *a* structure, but in solution they are stereochemically nonrigid through the established *a* ⇌ *e* interconversion.[49] In contrast the

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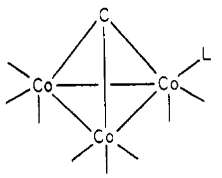
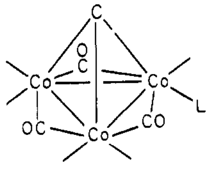


e



a

phosphite analogues have an *e* configuration in both solid and solution. Nonetheless, the $n = 2$ phosphite derivatives revert to an *a* structure, the first phosphite–CCo_3 complexes to have a CO-bridged configuration.[26] These observations are in accord with the ferrocene moiety acting as a net electron donor.

The derivatives $FcCCo_3(CO)_8L$ (Fc–CCo_3L) show two discrete one-electron electrode processes in acetone with the appropriate shift to more negative potentials relative to 1 for the formation of the radical anion and cation. The couple [Fc–$CCo_3L^{+/0}$] displays Nernstian behavior over the range 298–203 K, whereas the couple [Fc–$CCo_3L^{0/-}$], unlike [$1^{0/-}$], is chemically irreversible at 293 K (eq 8). The

$$^{+}FcCCo_3L \overset{e}{\rightleftharpoons} FcCCo_3L \xrightarrow{e} FcCCo_3L^{-}\cdot \xrightarrow{\text{fast}} 1^{-}\cdot + \text{decomp} \quad (8)$$

chemical irreversibility of the reduction is due to kinetic lability of the ligand and additional waves appeared on the anodic scan, and subsequent complete cycles of the cyclic voltammograms, which correspond to the couple [$1^{0/-}$]. A small wave at ~0.34 V can be attributed to the oxidation of $Co(CO)_4^-$; additional ill-defined electrode processes at potentials >1.1 V were not assigned.

An unexpected trend in $E_{1/2}^{r}$ (Table II) was that it is more difficult to reduce the phosphite than phosphine derivatives; the converse is true for $E_{1/2}^{o}$. Not only is this trend contrary to the results obtained for other CCo_3 derivatives,[5b] but also it runs counter to simple electronic arguments. Nonetheless, the results are consistent with the hypothesis that ligands with a large cone angle interfere with the apical Fc group, tilting the Fc moiety and thereby decreasing the favorable π donation to the cluster. Tilting of the smaller apical methyl group in response to steric constraints was noted[15a] in the structure of $CH_3CCo_3(CO)_8PPh_3$; this effect would be magnified in the more sterically congested ferrocene clusters.

Cationic derivatives $^{+}FcCCo_3L$ [L = PPh_3, $P(C_6H_{11})_3$] were isolated by chemical oxidation of the neutral analogues and the spectroscopic data is given in Table I. The significant features of the IR spectra were the shift to higher frequency for ν(CO) bands and the reversion to a nonbridged *e* configuration in response to the decrease in electron density on the cluster, even though the cationic site is not on the cluster. In the electronic spectra, band N has apparently merged in the UV envelope. Band M is a sensitive guide to the coordination environment of the Co_3 unit,[48] and the shift to higher energy is the result of a stabilization of the "cluster" bonding orbitals involved in transitions incorporated in band M, caused by the increased electron density on the cobalt atoms, and destabilization of the LUMO. An increase in electron density will also cause a reduction in the π-donor component from the apical substituent with consequential changes to band N. Because of the hypochromic shift in bands M and N, the ferrocene transition $^2E_{2g} \rightarrow {}^2E_{2u}$ is now well resolved (Figure 5).

A cyclic voltammogram for a $FcCCo_3(CO)_7L_2$ derivative is shown in Figure 3. At this point in the series a second one-electron oxidation process at very positive potentials is accessible, but it is completely irreversible and a dication could not be isolated. On the basis of the unequivocal assignment for $FcCCo_3(CO)_6L_3$ derivatives (discussed in the following paper[10]) the second cationic site is believed to be the CCo_3 moiety. The couple [$FcCCo_3L_2^{0/-}$] is chemically irreversible, and additional waves are seen on the anodic and repetitive scans. The overall electron-transfer steps are therefore

$$^{+}FcC^{+}Co_3L_2 \xleftarrow{-e} FcC^{+}Co_3L_2 \overset{e}{\rightleftharpoons} FcCCo_3L_2 \xrightarrow{e} FcCCo_3L_2^{-} \rightarrow 1^{-}\cdot + \text{decomp}$$

Conclusion

The prototypal compounds $(R)FcCCo_3(CO)_{9-n}L_n$ reported in this study give an insight into the properties of molecules in which a transition-metal cluster is linked to another redox center. At least with carbon-capped carbonyl clusters this coupling of redox sites leads to a modification of each individual site and mutual cooperative interactions between them. By suitable molecular architecture a molecule can be synthesized which has a range of redox states, and this theme is developed further in the following paper[10] in which mixed-valence compounds are formed by further Lewis base substitution of carbonyl groups. Further papers in this series will describe molecules in which the range of oxidation states is further elaborated by changing the functionality of the ferrocene moiety.

The cooperative interaction between the two redox sites in $FcCCo_3(CO)_9$ is weak, but sufficient perturbation occurs to cause structural and spectral changes relative to the parent molecules Fc and $(R)CCo_3(CO)_9$. The capping carbon in the CCo_3 moiety has been described as electron rich while the CCo_3 moiety itself is "electron withdrawing". This dichotomy is reconcilable because both inductive and mesomeric parameters must be considered, not necessarily operating in the same sense. Overall, the trends in electrochemical and spectral data for these ferrocene clusters suggest that Fc is acting both as +I and +M substituent, the +M component arising from a π interaction between the appropriate orbitals of the Cp ring and the e_π orbitals of the cluster, and a weaker Fe → exo carbon component. This theoretical concept is elaborated further in another paper[11] in which the structural effects of this π interaction are also considered.

Acknowledgment. We are most grateful to Dr. C. Childs, D.S.I.R., Wellington, New Zealand, for obtaining the Mössbauer spectra.

Registry No. 1, 52215-96-0; $1^{-}\cdot$, 85356-64-5; **2**, 85356-50-9; **3**, 85356-51-0; 1,2-4, 85356-52-1; 1,1'-4, 85356-53-2; 1,3-4, 85369-74-0; $[FeCCo_3(CO)_9]BF_4$, 85356-55-4; $FcCCo_3(CO)_8PPh_3$, 85356-56-5; $FcCCo_3(CO)_8PPh_3^+$, 85356-57-6; $FcCCo_3(CO)_8P(C_6H_{11})_3$, 85356-58-7; $FcCCo_3(CO)_8P(C_6H_{11})_3^+$, 85356-59-8; $FcCCo_3(CO)_8P(OMe)_3$, 85356-60-1; $FcCCo_3(CO)_7[P(OMe)_3]_2$, 85356-61-2; $FcCCo_3(CO)_7[P(OPh)_3]_2$, 85356-62-3; $[FcCCo_3(CO)_9]PF_6$, 85356-63-4; FcHgCl, 1273-75-2; $HCCo_3(CO)_9$, 15664-75-2; $ClCCo_3(CO)_9$, 13682-02-5; $BrCCo_3(CO)_9$, 19439-14-6; $AlCl_3$, 7446-70-0; Fc, 102-54-5; $[OCCCo_3(CO)_9]^+$, 47314-15-8; MeFc, 1271-44-9; PPh_3, 603-35-0; $P(C_6H_{11})_3$, 2622-14-2; $P(OMe)_3$, 121-45-9; $P(OPh)_3$, 101-02-0; Co, 7440-48-4; 1-acetyl-2-(chloromercuri)ferrocene, 85356-65-6; 1-acetyl-1'-(chloromercuri)ferrocene, 85356-66-7; bis(1-acetyl-2-ferrocenyl)mercury, 85356-67-8.