Heteronuclear Mixed-valence Compounds: Transition Metal Carbonyl Clusters with Multiple Redox Centres

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Metal carbonyl clusters with multiple redox centres based on ferrocene and the tricobalt carbon cluster have been synthesised, including the first mixed-valence carbonyl clusters which display intravalence absorption bands.

At the present time, there is considerable interest in the properties of compounds with multiple-redox centres, and, in particular, those producing mixed-valence complexes.¹ A number of metal centres have been reported to form homonuclear weakly coupled systems, most examples being based on ruthenium² or ferrocene³ moieties. Heteronuclear metal systems, on the other hand, are usually best described as valence-trapped structures⁴ although Taube and co-workers have recently reported⁵ one weakly coupled system incorporating both ruthenium and ferrocene centres.

In view of the range of valence states that can be produced in metal carbonyl cluster compounds by suitable modification of the ligand environment,^{6,7} and the delocalized nature of the bonding in the cluster unit, it appeared that a new type of weakly coupled system, involving metal clusters, may be accessible. This note describes the first carbonyl cluster system with multiple-redox centres, and one which exhibits mixed valence behaviour.

The molecules (1) are readily synthesised from $HCCo_3(CO)_9$ and the appropriate $FcHgCl^{8}$ (Fc = ferrocene), and a range of phosphine and phosphite derivatives (2) by thermal⁹ or electron-transfer catalysed methods.¹⁰[†] The crystal structure of (1a) shows¹¹ that the Co₃C cluster is significantly distorted from the normal C_{3v} symmetry by displacement of the capping carbon atom towards one edge of the Co3 triangle. In addition, the substituted cyclopentadienyl ring has crystallographically significant differences in the C-C bond distances.[‡] We attribute these distortions to both steric and electronic effects arising from efficient transmission of charge between the Fc and Co_3C moiety. Cyclic voltammograms of (1a) exhibit two reversible waves in 0.1 \mbox{m} TBAP-CH₂Cl₂ (TBAP = Bu₄-NClO₄) in the potential range 1.0 to -1.0 V [equation (1)] owing to the formation of a radical anion and cation (Figure 1). By comparison with the redox properties of the model com-



† Satisfactory analytical and spectroscopic data have been obtained for all new compounds, including cationic derivatives.

‡ At present R = 5.6%: space group $Pna_{1,} a = 17.354, b = 11.463, c = 11.707 Å, Z = 2$. The three Co-Cap distances are 1.87(2), 1.91(2), 1.98(2) Å, and the five C-C bond lengths in the substituted ring are (in sequence from linking C) 1.40(3), 1.49(3), 1.40(3), 1.50(3), 1.43(3) Å.

pounds Fc and PhCCo₃(CO)₉, it is clear that the oxidation wave ($E_{\frac{1}{2}}$ 0.80 V) can be assigned to the Fc⁺-Fc[°] couple and the reduction wave ($E_{\frac{1}{2}}$ -0.59 V) to the CCo₃[°]-CCo₃^{•-} couple. The spectroscopic properties of the radical cations and anions generated by controlled potential electrolysis of (1) substantiate this assignment and show that there are small perturbations to the companion redox centre from the other positive or negatively charged centre.§

$$+1, 0 \stackrel{e}{\rightleftharpoons} 0, 0 \stackrel{e}{\rightleftharpoons} 0, -1$$
 (1)

$$+1, +1 \rightleftharpoons +1, 0 \rightleftharpoons 0, 0 \to 0, -1$$
(2)

Cyclic voltammograms of (2c) are characterised by three redox processes (Figure 1), one reversible and one quasireversible oxidation, and one irreversible one-electron reduction process [equation (2)]. The reduction centre is clearly the basal Co₃ unit {*cf.* PhCCo₃(CO)₆[P(OMe)₃]₃, $E_{\frac{1}{2}} - 1.26$ V}.⁶ An assignment for the oxidation processes can likewise be made by comparison with this tricobalt carbon derivative and (1); thus, the first oxidation centre is Fc and the second Co₃C.

Oxidation of the red (2c) with excess of AgPF₆ generates a deep sea-green solution of the dication $+FcCCo_3+(CO)_6[P-CCO_3+(CO)_6]$



Figure 1. Cyclic voltammograms (CH₂Cl₂, 0.1 M TBAP, 200 mV s⁻¹): (A), $FcCCo_3(CO)_9(E_4 0.79, -0.59 V)$; (B) $FcCCo_3(CO)_6$ -[P(OPh)₃]₃(E_4 1.08 V, estimated from voltammetric data, 0.59, -1.24 V). Under the same conditions E_4 values for the model compounds Fc and PhCCo₃(CO)₉ were respectively 0.70 and -0.55 V.

§ For example, $\nu(CO)A_1$ shifts by +12 cm⁻¹ from (1a) \rightarrow (1a)⁺ even though the positive centre is the Fc. Conversely, the ¹H n.m.r. signal of the substituted ring is 0.27 p.p.m. to lower field compared to that of the unsubstituted ring.



Figure 2. Near-infrared intravalence-transfer band for a 1.37 mmol dm $^{-3}$ solution of (4) in CH₂Cl₂.

 $(OPh)_3]_3$ (3). The electronic spectrum of (3) is characterised by an absorption at 590 nm and the absence of the usual absorption band of neutral Co₃C derivatives around 460 nm. Compared to (2c) there is a shift of +53 cm⁻¹ in the v(CO) bands and a structural change to a non-carbonyl bridged configuration.

$$F_{cCCo_{3}^{+}(CO)_{6}}[P(OPh)_{3}]_{3} \{F_{cCCo_{3}}(CO)_{6}[P(OPh)_{3}]_{3}\}^{+,0}$$
(3) (4)

However, stoicheiometric oxidation of (2c) gave a green solution of the mixed-valence compound {FcCCo₃(CO)₆-[P(OPh)₃]₃}+,⁰ (4). Of particular significance is the fact that the near-infrared spectrum of (4) exhibits a broad band at 1545 nm ($\epsilon = 270$ dm³ mol⁻¹ cm⁻¹) typical of an intravalence transfer transition, which was absent from the spectrum of (2c) or (3) (Figure 2). With (4) there is a shift of +28 cm⁻¹ in the v(CO) bands relative to (2c) and retention of the parent carbonyl-bridged structures.

The energy of the intravalence-transfer band $\overline{\nu}$ (in cm⁻¹) should be related¹ to the band width $\Delta \overline{\nu}_{3}$ by the expression (3).

$$\overline{\nu} - \overline{\nu}_0 = (\Delta \overline{\nu}_4)^2 / 2310 \tag{3}$$

Although $\bar{\nu}_0$, the internal energy difference between the two oxidation isomers, is not directly accessible from the present data, an upper limit (6.45 × 10³ cm⁻¹) can be estimated from

the redox potentials. The agreement between $\Delta \bar{v}_{\frac{1}{2}}$ (calc.) of 2.3 \times 10³ cm⁻¹ and $\Delta \bar{v}_{\frac{1}{2}}$ (obs.) of 2.1 \times 10³ cm⁻¹ is of the order expected for mixed-valence ions of the weakly interacting type and substantiates the assignment of the band at 1545 nm to a radiation-induced electron transfer between the ferrocene and cluster centres. An estimate of the ground-state delocalization is given by the Hush interaction parameter α . Using the appropriate internuclear separation from the structure of (1), α^2 is calculated to be 3.4 \times 10⁻³, a value comparable to other classical Class II mixed-valence ions.^{1,2}

Metal carbonyl clusters are obviously suitable redox centres for incorporation in multiple-redox and mixed-valence compounds. Functionalization of the tricobalt carbon centre or ferrocene has provided other examples and preliminary work¹¹ suggests that linked metal cluster systems can also be utilized.

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