

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

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

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

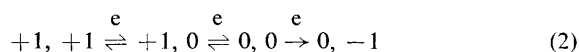
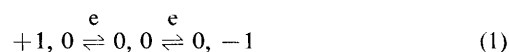
Metal carbonyl clusters with multiple redox centres based on ferrocene and the tricobalt carbon cluster have been synthesised, including the first mixed-valence carbonyl clusters which display intravalence absorption bands.

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.

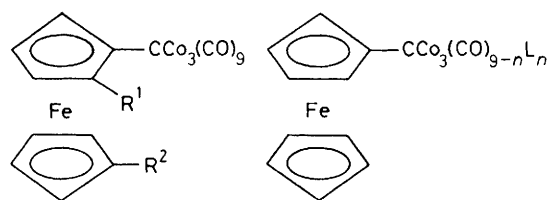
The molecules (1) are readily synthesised from $\text{HCCo}_3(\text{CO})_9$ and the appropriate FcHgCl^8 (Fc = ferrocene), and a range of phosphine and phosphite derivatives (2) by thermal⁹ or electron-transfer catalysed methods.^{10†} The crystal structure of (1a) shows¹¹ that the Co_3C cluster is significantly distorted from the normal C_{3v} symmetry by displacement of the capping carbon atom towards one edge of the Co_3 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 M TBAP- CH_2Cl_2 (TBAP = Bu_4NClO_4) 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-

pounds Fc and $\text{PhCCo}_3(\text{CO})_9$, it is clear that the oxidation wave ($E_{1/2}$ 0.80 V) can be assigned to the $\text{Fc}^+-\text{Fc}^\circ$ couple and the reduction wave ($E_{1/2}$ -0.59 V) to the $\text{CCo}_3^\circ-\text{CCo}_3^{+}$ 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.§



Cyclic voltammograms of (2c) are characterised by three redox processes (Figure 1), one reversible and one quasi-reversible oxidation, and one irreversible one-electron reduction process [equation (2)]. The reduction centre is clearly the basal Co_3 unit {cf. $\text{PhCCo}_3(\text{CO})_6[\text{P}(\text{OMe})_3]_3$, $E_{1/2}$ -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 Co_3C .

Oxidation of the red (2c) with excess of AgPF_6 generates a deep sea-green solution of the dication $^+\text{FcCCo}_3^+(\text{CO})_6[\text{P}$ -



- (1) a; $R^1 = \text{H}$; $R^2 = \text{H}$
 b; $R^1 = \text{OAc}$, Me;
 $R^2 = \text{H}$
 c; $R^1 = \text{H}$; $R^2 = \text{OAc}$
- (2) a; $n = 1$, L = PPh_3 , $\text{P}(\text{C}_6\text{H}_{11})_3$,
 $\text{P}(\text{OR})_3$
 b; $n = 2$, L = $\text{P}(\text{OR})_3$
 c; $n = 3$, L = $\text{P}(\text{OPh})_3$
 d; $n = 3$, L = $\text{P}(\text{OMe})_3$

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

‡ At present $R = 5.6\%$; space group $\text{Pna}2_1$, $a = 17.354$, $b = 11.463$, $c = 11.707$ 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.

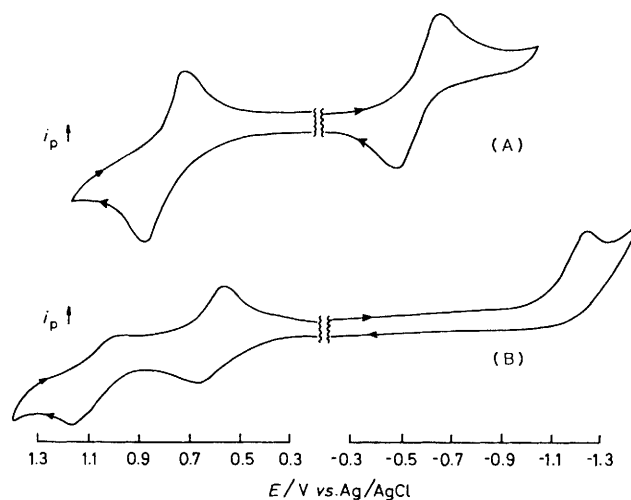


Figure 1. Cyclic voltammograms (CH_2Cl_2 , 0.1 M TBAP, 200 mV s^{-1}): (A), $\text{FcCCo}_3(\text{CO})_9$ ($E_{1/2}$ 0.79, -0.59 V); (B) $\text{FcCCo}_3(\text{CO})_6[\text{P}(\text{OPh})_3]_3$ ($E_{1/2}$ 1.08 V, estimated from voltammetric data, 0.59, -1.24 V). Under the same conditions $E_{1/2}$ values for the model compounds Fc and $\text{PhCCo}_3(\text{CO})_9$ were respectively 0.70 and -0.55 V.

§ For example, $\nu(\text{CO})\text{A}_1$ 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.

