

## Stepwise Oxidation of Three Communicating Metal Centres: Electrochemistry of Trinuclear Trindenyl Complexes of Manganese or Rhodium

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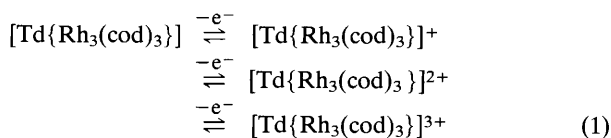
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Trinuclear manganese or rhodium complexes of the trindenyl (Td) ligand undergo three separate 1 e<sup>-</sup> oxidation reactions, with an abnormally large separation in potentials between the second and third oxidations of [Td{Rh<sub>3</sub>(cod)<sub>3</sub>}].

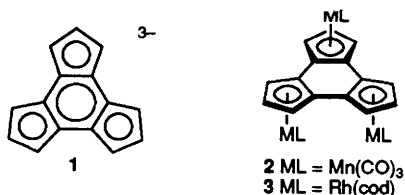
Metal complexes of the trindenyl trianion **1**<sup>-</sup> (Td) offer an opportunity to study the properties of a high density of metal centres grafted onto a hydrocarbon backbone. Since the rigidity of the hydrocarbon minimizes the geometric distortions that can occur upon oxidation or reduction, these complexes are attractive models with which to probe metal-metal interactions over known distances in mixed-valent systems. We now report the first electrochemical results on the trinuclear trindenyl complexes [Td(ML)<sub>3</sub>] **2**<sup>2-</sup> [ML = Mn(CO)<sub>3</sub>] and **3**<sup>3-</sup> [ML = Rh(cod), cod = cycloocta-1,5-diene]. Although both systems display three oxidations, **3** is particularly informative in showing three successive diffusion-controlled one-electron processes. A surprisingly large difference in formal potentials is observed for the 3<sup>+</sup>/2<sup>+</sup> and 3<sup>2+</sup>/3<sup>3+</sup> couples.

Cyclic voltammetry (CV) scans of **2** in CH<sub>2</sub>Cl<sub>2</sub><sup>†</sup> show two 1e<sup>-</sup> anodic waves (I and II, Fig. 1) along with their cathodic counterparts, III and IV. Waves I and IV comprise the reversible couple 2<sup>-</sup> ↔ 2<sup>+</sup>, E<sup>o</sup> = +0.77 V vs. Fc/Fc<sup>+</sup>,<sup>†</sup> consistent with expectations for an analogue of CpMn(CO)<sub>3</sub>.<sup>4</sup> The one-electron nature of this process was confirmed by coulometry. Wave III is a cathodic stripping peak, showing that the dication, 2<sup>2+</sup>, produced in wave II precipitates on the Pt electrode. An estimate of the formal potential of 2<sup>2+</sup> ↔ 2<sup>3+</sup> is obtained from the average of II and III: +0.98 V. A third anodic wave with E<sub>p</sub> ca. +1.2 V is of uncertain significance, owing to the problem of precipitation of the dication.

With **3**, the polycations are more soluble and all three 1e<sup>-</sup> couples are accessible. ML = Rh(cod) is perhaps an unlikely candidate for reversible electrochemical 'tag' on the trindenyl ligand, since the oxidation of the mononuclear analogue [CpRh(cod)] is irreversible in the same medium.<sup>5</sup> Oxidation of **3** proceeds, nevertheless, in three well-defined and reversible 1e<sup>-</sup> steps (Fig. 2) with formal potentials of -0.33, -0.16 and +0.43 V, respectively, for the couples 3<sup>-</sup> ↔ 3<sup>-1+</sup>, 3<sup>-1+</sup> ↔ 3<sup>-2+</sup> and 3<sup>-2+</sup> ↔ 3<sup>-3+</sup> [eqn. (1)]. Bulk coulometry has confirmed the reaction stoichiometry, and an EPR spectrum of 3<sup>3+</sup> in CH<sub>2</sub>Cl<sub>2</sub> has been obtained [*g* = 2.0492 (fluid); g<sub>1</sub> = 2.0883, g<sub>2</sub> = 2.0579, g<sub>3</sub> = 2.0024 (frozen)].



The magnitude of the separations between formal potentials in redox processes of homomultinuclear complexes is one indication of the degree of electronic interactions between the metals.<sup>6</sup> The separation of 3<sup>-</sup> ↔ 3<sup>-1+</sup> and 3<sup>-1+</sup> ↔ 3<sup>-2+</sup> (170 mV) is typical of Class II<sup>7</sup> M-M interactions, *i.e.* involving trapped-



valence systems.<sup>8</sup> The much larger separation between 3<sup>+</sup> ↔ 3<sup>2+</sup> and 3<sup>2+</sup> ↔ 3<sup>3+</sup> (550 mV) is more typical of Class III (totally delocalized) systems.<sup>9</sup> Whether this pattern of potential separations is unique for **3** and whether it arises from variations in delocalization among the metals or from other sources such as coulombic interactions remain to be shown. Given the synthetic versatility of cyclopentadienyl-based ligand systems, there are good opportunities to answer questions about metal-metal interactions by coordinating transition metal units with suitable spectroscopic labels to Td, and efforts are proceeding along these lines.

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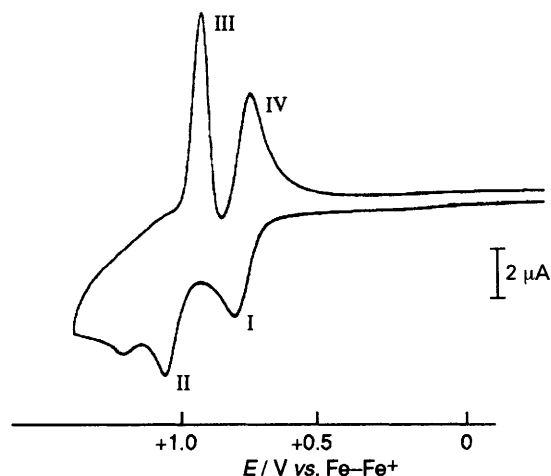


Fig. 1 CV scan of 0.44 mmol dm<sup>-3</sup> **2** in CH<sub>2</sub>Cl<sub>2</sub>-0.1 mol dm<sup>-3</sup> [NBu<sub>4</sub>][PF<sub>6</sub>] at Pt, T = 270 K, v = 0.1 V s<sup>-1</sup>

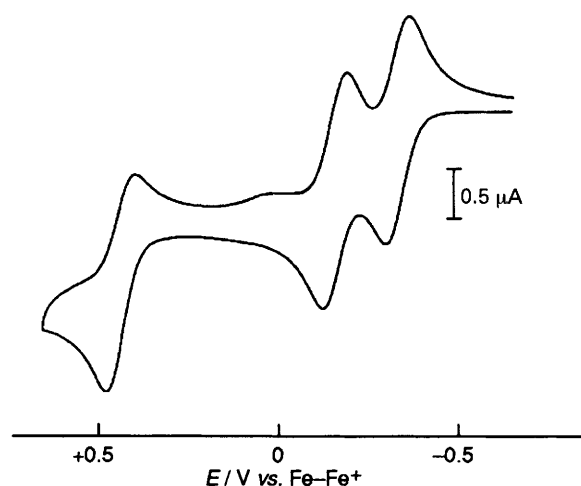


Fig. 2 CV scan of 0.27 mmol dm<sup>-3</sup> **3** in CH<sub>2</sub>Cl<sub>2</sub>-0.1 mol dm<sup>-3</sup> [NBu<sub>4</sub>][PF<sub>6</sub>] at Pt, T = 260 K, v = 0.1 V s<sup>-1</sup>

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### Footnotes

† Other electrochemical conditions: 0.1 mol dm<sup>-3</sup> [NBu<sub>4</sub>][PF<sub>6</sub>], Pt working electrode, potentials referenced to ferrocene-ferrocenium, which had a potential of +0.48 V vs. SCE in this medium. *T* = 270 K for **2**, 260 K for **3**.

‡ The 3<sup>2+</sup>-3<sup>3+</sup> couple required *v* > 0.2 V s<sup>-1</sup> for complete chemical reversibility.

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