

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

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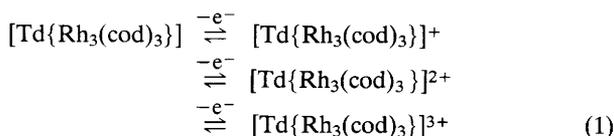
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Trinuclear manganese or rhodium complexes of the trindenyl (Td) ligand undergo three separate 1 e⁻ oxidation reactions, with an abnormally large separation in potentials between the second and third oxidations of [Td{Rh₃(cod)₃].

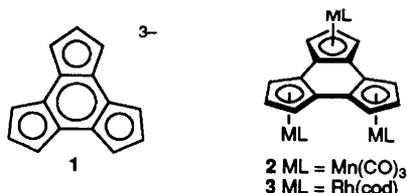
Metal complexes of the trindenyl trianion **1**⁻ (Td) offer an opportunity to study the properties of a high density of metal centres grafted onto a hydrocarbon backbone. Since the rigidity of the hydrocarbon minimizes the geometric distortions that can occur upon oxidation or reduction, these complexes 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)₃]²⁻ [ML = Mn(CO)₃] and **3**³⁻ [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⁺/2⁺ and 3²⁺/3³⁺ couples.

Cyclic voltammetry (CV) scans of **2** in CH₂Cl₂[†] show two 1e⁻ anodic waves (I and II, Fig. 1) along with their cathodic counterparts, III and IV. Waves I and IV comprise the reversible couple 2-2⁺, E^o = +0.77 V vs. Fc-Fc⁺,[†] consistent with expectations for an analogue of CpMn(CO)₃.⁴ The one-electron nature of this process was confirmed by coulometry. Wave III is a cathodic stripping peak, showing that the dication, 2²⁺, produced in wave II precipitates on the Pt electrode. An estimate of the formal potential of 2²⁺-2²⁺ is obtained from the average of II and III: +0.98 V. A third anodic wave with E_p 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⁻ 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.⁵ Oxidation of **3** proceeds, nevertheless, in three well-defined and reversible 1e⁻ steps (Fig. 2) with formal potentials of -0.33, -0.16 and +0.43 V, respectively, for the couples 3-3⁺, 3⁺-3²⁺ and 3²⁺-3³⁺ [eqn. (1)]. Bulk coulometry has confirmed the reaction stoichiometry, and an EPR spectrum of 3³⁺ in CH₂Cl₂ has been obtained [*g* = 2.0492 (fluid); g₁ = 2.0883, g₂ = 2.0579, g₃ = 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.⁶ The separation of 3-3⁺ and 3⁺-3²⁺ (170 mV) is typical of Class II⁷ M-M interactions, *i.e.* involving trapped-



valence systems.⁸ The much larger separation between 3⁺-3²⁺ and 3²⁺-3³⁺ (550 mV) is more typical of Class III (totally delocalized) systems.⁹ 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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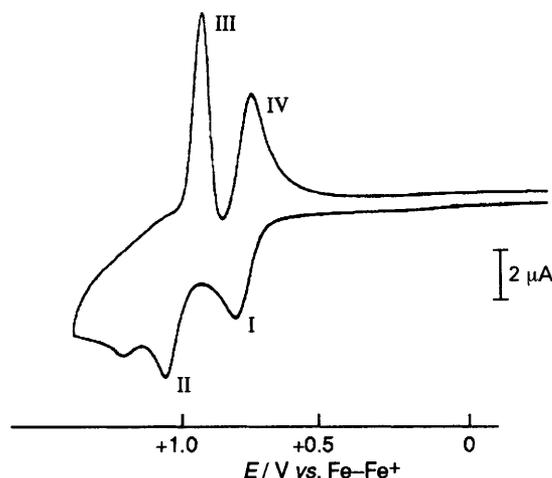


Fig. 1 CV scan of 0.44 mmol dm⁻³ **2** in CH₂Cl₂-0.1 mol dm⁻³ [NBu₄][PF₆] at Pt, T = 270 K, v = 0.1 V s⁻¹

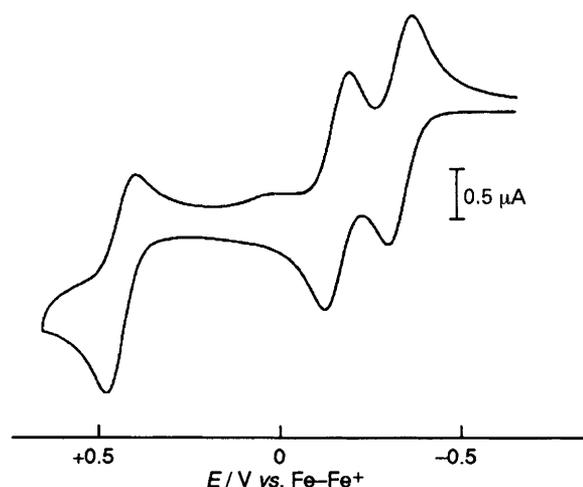


Fig. 2 CV scan of 0.27 mmol dm⁻³ **3** in CH₂Cl₂-0.1 mol dm⁻³ [NBu₄][PF₆] at Pt, T = 260 K, v = 0.1 V s⁻¹

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Footnotes

† Other electrochemical conditions: 0.1 mol dm⁻³ [NBu₄][PF₆], 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 3²⁺-3³⁺ couple required *v* > 0.2 V s⁻¹ for complete chemical reversibility.

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