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The Role and Nature of the Radical Anion Intermediates in Electron Transfer Catalysis of Bicapped Tri-iron Clusters

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Novel identification of a series of radical anion intermediates from bicapped tri-iron carbonyl species emphasizes the slippage of the capping bridge as an important factor in cluster activation.

Activation of transition metal clusters, which are under investigation as potential catalysts,¹ has recently been proposed in the form of electron transfer catalysis (E.T.C.).^{2,3} We now report e.s.r. spectroscopic investigations of the reactive intermediates in E.T.C. ligand substitution of the

tri-iron cluster (1), since it provides unusual insight into cluster activation. When a small cathodic current is passed through a brown solution of (1) (which is otherwise inert),⁴ it readily undergoes ligand substitution to (2) which can be isolated in ca. 70% yield. Thus CO replacement by triethylphosphine in

equation (1) is complete within 60 min at 25 °C upon the passage of only 5—10% charge at -0.8 V. This voltage corresponds to the one-electron reduction of (1), equation (2), as shown by the reversible cyclic voltammogram obtained with $E^0 = -0.79$ V vs. standard calomel electrode (s.c.e.).

$$Fe_{3}(\mu_{3}-PPh)_{2}(CO)_{9} + L \rightarrow Fe_{3}(\mu_{3}-PPh)_{2}(CO)_{8}L + CO \quad (1)$$
(1)
(2)

$$Fe_{3}(PPh)_{2}(CO)_{9} \stackrel{E_{0}}{\rightleftharpoons} Fe_{3}(PPh)_{2}(CO)_{9}^{*-}$$
(2)
(1) (1*-)

Crucial to the success of electrocatalysis is the substitution lability of the green radical anion (1^{-}) which has the



Figure 1. X-Band e.s.r. spectra of radical anions from (a) reduction of $Fe_3(\mu_3$ -PPh)_2(CO)_9, (b) (3) after standing, (c) (4) upon addition of PEt₃, and (d) (5) after standing or reduction of (2) (solvent, MeCN or THF). For the e.s.r. assignments, see Table 1. N.m.r. field markers are in kHz.

e.s.r. spectrum shown in Figure 1(a). The binomial 1:2:1 triplet splitting (a_P 13.3 G⁺) is readily assigned to the pair of equivalent bridging phenylphosphinidene caps in the symmetrical structure (3).⁵ This initially formed radical anion (3) undergoes a spontaneous rearrangement to (4), equation (3), which destroys the degeneracy of the phosphinidene caps, as shown by the appearance of two doublets in the e.s.r. spectrum, Figure 1(b). From the difference in the magnitudes of a_P (Table 1), we conclude that a geometry change resulting







Table 1. E	.s.r. parameters of	of radical	anions derived	l from tri-iroi	n clusters.ª
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		³¹ P Hyperfine splitting (G)			F 0
Tri-iron cluster radical anion	<g></g>	μ ₃ -Ρ	μ ₂ -Ρ	L	(V) ¹
(3) $Fe_3(CO)_9(\mu_3-PPh)_2$.	2.019	13.3(t)			-0.7
(4) $Fe_3(CO)_9(\mu_3-PPh)(\mu_2-PPh)^{-1}$	2.039	25.3(d)	3.4(d)		
(5) $Fe_3(CO)_8(\mu_3-PPh)(\mu_2-PPh)[PEt_3]$.	2.041	24.8(d)	3.4(d)	20.3(d)	
$Fe_3(CO)_8(\mu_3-PPh)(\mu_2-PPh)[P(OMe)_3]^{-1}$	2.041	25.3(d)	3.4(d)	25.3(d)	
(6) $Fe_3(CO)_8(\mu_3-PPh)_2[PEt_3]^{-1}$	2.027	18.3(t)		18.3(d)	-1.1
$Fe_3(CO)_8(\mu_3-PPh)_2[P(OMe)_3]^{-1}$	2.023	17.8(t)		36.0(d)	-1.0

^a In tetrahydrofuran (THF) or MeCN at 25 °C. ^b V vs. s.c.e. in THF containing 0.3 M tetrabutylammonium perchlorate.

from the cleavage of an Fe–P bond occurs. Indeed the higher g-value of the less symmetric red–brown species (4) is in agreement with an unpaired electron localized at a 17-electron iron centre.⁶

Addition of triethylphosphine to (4) leads immediately to an additional splitting in the e.s.r. spectrum, Figure 1(c), due to the ³¹P hyperfine coupling of the newly entered ligand, equation (4). This substituted radical anion (5) then reforms the Fe-P bond, equation (5), to regenerate the parent cluster framework in (6), which is tantamount to the microscopic reverse of equation (3). This is demonstrated by the appearance of the e.s.r. spectrum in Figure 1(d), which is identical with that obtained from the direct one-electron reduction of (2) $[i.e., (6) = (2^{-})]$. These interesting series of cluster transformations during E.T.C. are shown schematically in the mechanism proposed in Scheme 1. The electrocatalytic mechanism requires that (6) $[(2^{-})]$ readily undergoes electron transfer to (1) to initiate a new catalytic cycle with (3) [*i.e.* (1⁻⁻)]. This conclusion is substantiated by an exergonic driving force of 8.5 kcal mol⁻¹[‡] for electron transfer, as evaluated by the difference in the standard oxidation potentials (E^0 in Table 1).

We have thus successfully observed each step in the catalytic cycle shown in Scheme 1. Most importantly our E.T.C. catalysis studies indicate that the cluster activation occurs in the labile radical anion by first forming a reactive 17-electron iron centre *via* cleavage of a bond to the bridging cap rather than to a contiguous iron atom. This Fe–P bond breaking is central to the function of the μ_3 -phosphinidene bridge in modifying the reactivity of the cluster. Indeed this involvement of the capping ligand in the substitution behaviour of the radical anion contrasts sharply with that in neutral diamagnetic systems in which the μ_3 -bridges apparently do not participate in reactions of the cluster.⁷

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 $[\]ddagger 1 \text{ kcal} = 4.184 \text{ kJ}.$