Stepwise Electrochemical Catalysis of Three Successive Replacements of the Carbonyl Group by Trimethyl Phosphite in a Tri-iron Cluster Complex
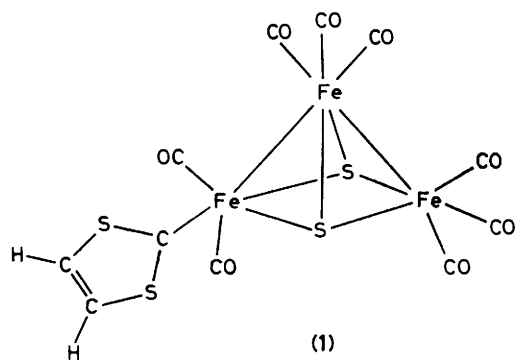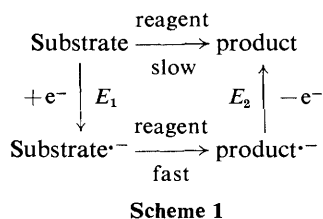
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The electrochemically catalysed replacement of the carbonyl ligand by $P(OMe)_3$ in the tri-iron cluster $Fe_3S_2CO_8L$ ($L = C_3H_2S_2$) proceeds stepwise and leads to the new clusters $Fe_3S_2CO_{8-n}L[P(OMe)_3]_n$ ($n = 1, 2,$ or 3).

In recent years electrochemists have extended their original interest in oxidation or reduction to chemical reactions where catalysis occurs with the aid of electrode or electron-transfer reagents.[1] A general mechanism for redox catalysis, depicted in Scheme 1 for the first reduction step, is efficient when (i) the reduced state (substrate·⁻) is more reactive than the starting material and (ii) E_2 is more negative than E_1.

We report here that an electrochemical method, offering

reagent
Substrate ————→ product
              slow

$+e^-$ | E_1 E_2 | $-e^-$

Substrate·⁻ ————→ product·⁻
       reagent
       fast

Scheme 1

(1)

Table 1. Synthesis of the clusters (2), (3), and (4) by electro-reduction of (1) in DMF (100 ml; 0.1 M Bu$_4$NClO$_4$) at a controlled potential E at a mercury electrode.

Cluster (1): wt./g	P(OMe)$_3$: wt./g	E/V vs. S.C.E.[a]	Electricity used, Faraday/ mol[b]	Cluster obtained[d] (% yield)	M.p.: t/°C
0.22	0.32	−0.70	0.06	(2) (59)	Oil
0.22	0.52	{ −0.75, −0.95	0.19	(3) (63)	108—109
0.42	1.0	{ −0.75, −1.00, −1.20	0.87[c]	(4) (71)	104—105

[a] The syntheses were performed in one, two, or three electro-reduction steps. [b] 1 Faraday = 96 487 Coulomb. [c] This value includes an important component due to residual current integration. [d] All compounds gave satisfactory elemental analyses (C, H, Fe, P, S). ¹H N.m.r. spectra (60 MHz): δ (CDCl$_3$; Me$_4$Si) corresponding to -CH=CH- (s, 2H); P(OMe)$_3$ (d, 9H, J 12 Hz) respectively for each compound: 8.40; 3.66 for (2); 8.21; 3.43, 3.40 for (3); 8.03; 3.60, 3.73, 3.80 for (4).
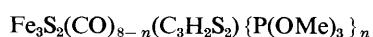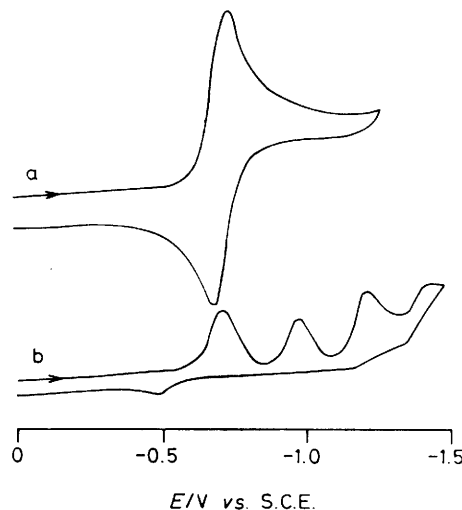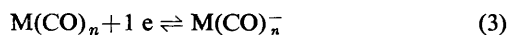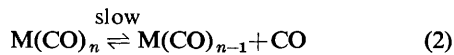
as it does an appropriate choice of electrode potential, is the most suitable method for studying the selective course of a multistep chemical reaction. We have studied the classical exchange of carbonyl by phosphite which is of great interest and widely used in organometallic chemistry [equation (1)].

$$L_x M(CO)_n + P(OMe)_3 \rightarrow L_x M(CO)_{n-1} P(OMe)_3 + CO \quad (1)$$

Substitution of carbonyl ligands is generally effected under thermal or photochemical conditions and often leads to incomplete reactions and/or to a mixture of mono- and poly-substituted compounds. It has been shown recently[2] that this reaction can also be electrochemically induced in either direction [CO or P(OMe)$_3$ exchange] depending on the ligand which is in excess.

We have now studied the new tri-iron cluster complex (1) whose synthesis and X-ray structure are described elsewhere.[3] This complex contains three different iron atoms where ligand exchange can occur and we have found that thermal exchange in refluxing tetrahydrofuran (THF), even with a stoicheiometric amount of P(OMe)$_3$, affords a mixture of mono-, di-, and tri-substituted products as already reported for other clusters.[4]

We have found that a solution of the cluster (1) and 0.1 M NBu$_4$BF$_4$ in dimethylformamide (DMF) exhibits a one-electron reversible reduction at −0.73 V vs. the standard calomel electrode (S.C.E.) (Figure 1), and a multielectron irreversible oxidation near +1.0 V vs. S.C.E. At a slower scan rate (0.01 V s⁻¹) the reduction becomes irreversible ($i^p_a/i^p_c < 1$) which is consistent with an electron transfer followed by a chemical reaction. After addition of a large excess of P(OMe)$_3$ the voltammogram shows three new reduction peaks (Figure 1) but under these conditions the oxidation curve remains unchanged in agreement with the fact that no thermal exchange can be observed at room temperature. This curve and those recorded at higher scan rates are consistent with three successive ECE mechanisms leading to compounds (2), (3), and (4).

$$Fe_3S_2(CO)_{8-n}(C_3H_2S_2)\{P(OMe)_3\}_n$$

(2), $n = 1$
(3), $n = 2$
(4), $n = 3$

E/V vs. S.C.E.

Figure 1. (a) Cyclic voltammogram on Pt of a 10^{-3} M solution of the tri-iron cluster (1) in 0.1 M Bu$_4$NBF$_4$ in DMF; sweep rate 0.1 V s⁻¹; temperature 20 °C; (b) the same solution after addition of P(OMe)$_3$ (1% v/v); sweep rate 0.1 V s⁻¹. At 10 V s⁻¹ only the first reversible reduction is observed during the first scan.

In order to confirm the occurrence of stepwise electrocatalytic ligand exchange we have conducted controlled potential electrolyses at a mercury cathode with excess of P(OMe)$_3$ and we have obtained cleanly the expected clusters (2), (3), and (4) in good yield (Table 1), after addition of water to the DMF solution and extraction with diethyl ether. As for the cluster (1) i.r. spectra of the substituted clusters show only terminal carbonyl groups, the frequencies of which are shifted in agreement with the lower π-accepting character of the phosphite compared with CO. The n.m.r. data are also consistent with three successive substitutions of one carbonyl by one phosphite occurring each time at a different metal centre (Table 1). The three doublets of equal intensity found in the ¹H n.m.r. spectrum of (4) correspond to the three different sites of co-ordination in the cluster (1). Although we have no definitive proof as to where the first and second substitutions take place, the existence of two doublets of equal intensity for the cluster (3) and of one doublet for the cluster (2) prove that stepwise regiospecific substitution has occurred.
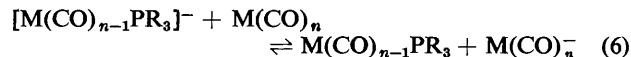
The voltammograms observed for the clusters (2) and (3) are similar to those for the cluster (1), showing reversible reduction at high scan rates and new reduction peaks when

P(OMe)$_3$ is added. Finally, the cluster (4) shows a quasi-reversible reduction which becomes reversible when trimethyl phosphite is added. The reduction of (η^5-C$_5$H$_5$)$_2$TiCl$_2$ in the presence of chloride ions has recently been shown[5] to take place similarly, and has been interpreted in terms of a ligand-removal step involving the solvent. We do not consider that the metal–metal bond breaks before the departure of one ligand,[2] but rather that the loss of one carbonyl group (equation 4) from the paramagnetic intermediate obtained after addition of one electron (equation 3) is the step which is necessary to generate a free co-ordination site. Indeed, a

$$M(CO)_n \overset{slow}{\rightleftharpoons} M(CO)_{n-1}+CO \qquad (2)$$

$$M(CO)_n+1\ e \rightleftharpoons M(CO)_n^- \qquad (3)$$

$$M(CO)_n^- \overset{faster}{\underset{than\ (2)}{\rightleftharpoons}} M(CO)_{n-1}^-+CO \qquad (4)$$

voltammetric study of (1) under one atmosphere of carbon monoxide showed that the rate of the electrocatalysed chemical reaction decreased; moreover, increasing the amount of P(OMe)$_3$ led to only a small change in the reaction rate, unexpected for a one-step replacement of CO by phosphite. Such a dissociative loss of CO has been demonstrated for diamagnetic polynuclear species[6] and may be also operative during electrocatalysed isomerisation of mononuclear complexes.[7,8]

Selectivity can be achieved in our case because the electron transfer (equation 6) which occurs after readdition of the ligand (equation 5) is thermodynamically favoured ($E_1-E_2 = 0.3$ V) and is faster than the loss of another carbonyl group.

$$M(CO)_{n-1}^- + PR_3 \rightarrow [M(CO)_{n-1}PR_3]^- \qquad (5)$$

$$[M(CO)_{n-1}PR_3]^- + M(CO)_n$$
$$\rightleftharpoons M(CO)_{n-1}PR_3 + M(CO)_n^- \qquad (6)$$

Finally, the electrochemical reversibility of the reduction of (4) with P(OMe)$_3$ in excess shows the limit of the successive ligand exchange processes. As shown by voltammetric studies the number of exchangeable CO depends on the nature of the phosphorus compound used [two for P(OPh)$_3$ and one for PPh$_3$].

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