

Preliminary communication

ELECTROCHEMICAL STUDY ON $(N-N)Fe_3(CO)_9$ ($(N-N) = 2,3$ -DIAZANORBORNENE) AND RELATED COMPOUNDS. A NEW EXAMPLE OF ACTIVATION OF CARBON MONOXIDE REPLACEMENT BY ELECTRON TRANSFER.

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Summary

The compound $(N-N)Fe_3(CO)_9$ (**1**) in tetrahydrofuran undergoes two reversible one-electron reduction processes in cyclic voltammetry at the platinum electrode. A rapid electron transfer-catalyzed reaction occurs when **1** is reduced in the presence of L ($L = P(OMe)_3$) and this gives $(N-N)Fe_3(CO)_8L$ (**2**), quantitatively. Only an electron-induced nucleophilic substitution is observed for compound **2** under the same conditions, yielding $(N-N)Fe_3(CO)_7L_2$, which undergoes a similar reaction but with much lower efficiency, to give $(N-N)Fe_3(CO)_6L_3$.

The electrochemical behaviour of transition metal clusters has received considerable attention and the subject has been recently reviewed [1]. In some cases electroactivation of ligand substitution has been observed [2] in the same way as has been reported for other mono- or bi-nuclear organometallic compounds [3,4].

We report here preliminary results on a new example of activation of carbon monoxide substitution in a trinuclear iron compound by electrochemical reduction.

Results and discussion

The compound $(N-N)Fe_3(CO)_9$ (**1**) in tetrahydrofuran (THF), containing NBu_4PF_6 (0.2 M) as supporting electrolyte, at Au rotating disc electrode (RDE)

exhibits two reduction waves of equal intensity at -0.92 V (A_1) and -1.12 V (A_2) (vs. SCE) (Fig. 1).

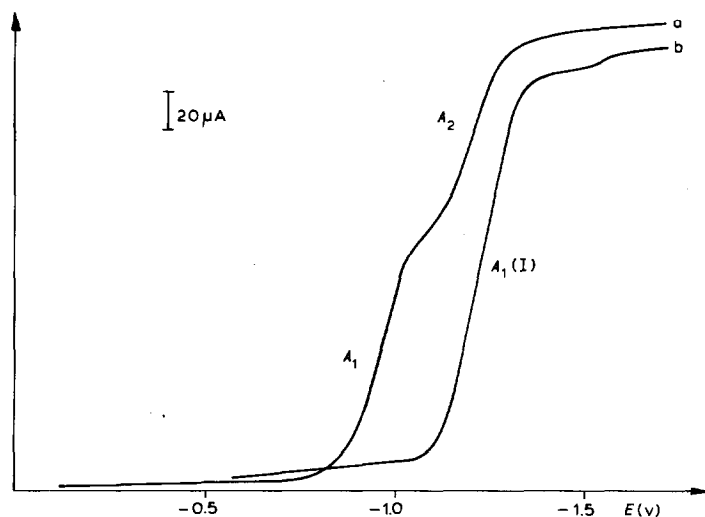


Fig. 1. Voltammogram of $(N-N)Fe_3(CO)_9$ in THF on the RDE. (a) alone, (b) with an equimolecular amount of $P(OMe)_3$.

Under the same conditions but by cyclic voltammetry (CV) the corresponding peaks A_1 ($E_p = -0.98$ V) and A_2 ($E_p = -1.18$ V) can be observed. If the potential is reversed after peak A_2 , two oxidation peaks A_2' and A_1' are obtained. The systems A_1/A_1' and A_2/A_2' can be considered electrochemically reversible ($\Delta E_p = 0.06$ V and 0.08 V, respectively; sweep rate 0.01 V s^{-1}). In potential-controlled electrolysis of compound 1 at -1.15 V approximately 2F/mol are consumed. The resulting solution exhibits the oxidation peaks A_1' and A_2' , indicating that the species $[(N-N)Fe_3(CO)_9]^{2-}$ is present in solution. Subsequent chemical changes in the solution lead to unidentified products.

The compound $(N-N)Fe_3(CO)_8L$ (**2**) ($L = P(OMe)_3$) is obtained by rapid electron transfer-catalyzed (ETC) reduction of **1**. Compound **2** shows a two-electron ($E_p = -1.22$ V; n (coulometry) = 1.90 F/mol) partially reversible reduction.

($i_o^{oxd}/i_p^{red} = 0.72$ at 0.1 V s^{-1} ; $\Delta E_p = 0.14$ V).

Electron-induced nucleophilic substitution (EINS) is observed for compound **2**, leading to $(N-N)Fe_3(CO)_7L_2$ (**3**), which reacts further but with lower efficiency to the compound $(N-N)Fe_3(CO)_6L_3$ (**4**). Compounds **3** and **4** also show partially reversible two electron reduction processes (see Table 1).

If an equimolecular amount of **L** is added to the solution of compound **1** in THF, the electrochemical behaviour is completely different (Fig. 1). Work-up of the resulting solution after a single reduction sweep indicates that compound **1** is no longer present and that the monosubstituted species **2** has been formed. The latter was identified by comparing its infrared spectrum and cyclic voltammogram with those of an authentic sample [5].

Slow chemical substitution of one carbonyl group by one molecule

of ligand L takes place with compound 1 at room temperature without any electrochemical manipulation and under the conditions used for recording a cyclic voltammogram. The reaction, which can be followed by TLC, is not complete within 6 h, in contrast with the very rapid and complete substitution observed when radical anions are electrogenerated.

TABLE 1

ELECTROCHEMICAL DATA FOR COMPOUNDS 1-4 IN THF

Compound	E_p (volts) ^a		ΔE_p ^b volts	$i_p^{\text{oxd}}/i_p^{\text{red}}$ A_1/A_1^*	$n(A_1)$ ^c	E_p (volts)		ΔE_p ^e (V)	$i_p^{\text{oxd}}/i_p^{\text{red}}$ A_2/A_2^*
	A_1	A_1^*				A_2	A_2^*		
1	-0.98	-0.90	0.08	1.00	(d)	-1.16	-1.06	0.10	1.00
2	-1.22	-1.08	0.14	0.72	1.90	—	—	—	—
3	-1.54	-1.26	0.28	0.64	2.00	—	—	—	—
4	-1.80	-1.40	0.32	0.66	1.96	—	—	—	—

^a vs. SCE. ^b $\Delta E_p = E_p(A_1) - E_p(A_1^*)$. ^c By coulometry. ^d For compound 1 $n(\text{coulometry}) = 1.80$ at the potential of A_2 peak. ^e $\Delta E_p = E_p(A_2) - E_p(A_2^*)$.

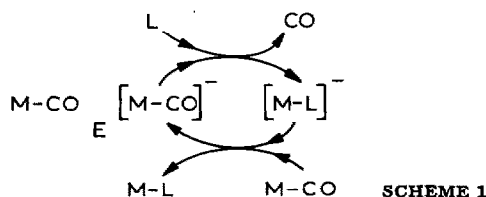
The minimum amount of charge consumed (only one linear sweep) reflects the high efficiency of the generated anions $[(N-N)Fe_3(CO)_9]^-$ and $[(N-N)Fe_3(CO)_9]^{2-}$ as catalysts for replacement of carbon monoxide by L in compound 1.

If an equimolar amount of L is added to compound 2 in THF there are changes in the cyclic voltammogram. A new high intensity reduction peak $A_2(2)$ ($E_p = -1.52$ V) appears, and the ratio $i_p(A_2)/i_p(A_1)$ increases with decreasing sweep rate. The same effect is observed on increasing the amount of ligand L.

Upon electrolysis of compound 2 in THF in the presence of an equimolar amount of L, less than two Faraday/mol are consumed (0.15–0.30 F/mol). Compound 3 can be isolated from the resulting solution. In this case the carbon monoxide activation by the electrogenerated radical anions is not catalytic, as demonstrated by the small but measurable amount of charge transferred.

Compound 3 only yields very small amounts of 4 when it is electrolyzed in the presence of L, and the charge consumption is to 2 F/mol.

The electrocatalytic substitution of carbon monoxide by L in compound 1 can be accounted for in terms of a combination of chemical and electrochemical processes as, has already been described for other mononuclear carbonyl compounds [3] (Scheme 1). However in our system the mechanism must be more complex because radical anions $[M-CO]^{2-}$ and $[M-L]^{2-}$ must also be included in the reaction scheme.



A decrease in the effectiveness of the catalytic effect is clearly observed for the reactions 2→3 and 3→4. The reason for this must lie in the fall in the stability of the radical anions with increasing carbonyl substitution [6] rather than in the propagation electron transfer process [2]. Consequently, the radical anions involved in the process can undergo chemical changes which remove them from the catalytic cycle.

The electrochemical behaviour of compound 1 and related trinuclear clusters is under further study.

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