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Electrochemical Study on a Tricyclic 1,1,1-Tricarbonyl-2,3-1-diazaferrole Derivative.
II. Activation of Carbon Monoxide Replacement by Electron Transfer Processes*

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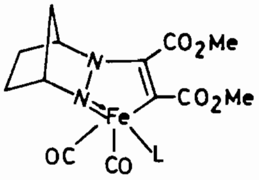
The electroactivation of ligand substitution is known for polynuclear organometallic compounds [1]. We have recently reported that an electron-transfer catalyzed reaction occurs when (N–N)$Fe_3(CO)_9$ ((N–N) = 2,3-diazanorbornene), is reduced in the presence of $P(OMe)_3$ [2].

Other authors have observed the same behaviour for 18 electron mononuclear species under oxidation conditions [3].

We do not know, however, of any reported electroactivation of ligand substitution in mononuclear organometallic compounds under reduction conditions.

We state here that such behaviour can be observed for compound **I**, when it is electrochemically reduced in the presence of $P(OMe)_3$.



I, L = CO
II, L = $P(OMe)_3$
III, L = PPh_3

Experimental

All the manipulations were carried out in an inert atmosphere.

The electrochemical experiments were carried out in a three electrode cell. The working and the auxiliary electrode were platinum, the reference electrode was a saturated calomel electrode (SCE), electrically connected to the non aqueous solution by a 'salt-bridge' containing the same non-aqueous solvent and the supporting electrolyte.

The solvent was THF freshly distilled over Na-benzophenone. The supporting electrolyte was Bu_4NPF_6, recrystallized from ethanol and dried at 80 °C under vacuum.

After electrolysis, the compounds were separated from the supporting electrolyte by removing the solvent under vacuum and dissolving the solid residue in toluene. The compounds were purified by chromatography over silica gel.

The IR spectra were obtained on a Pye-Unicam SP-2000 spectrometer and the NMR spectra on a Bruker AC-200 spectrometer using $CDCl_3$ as solvent.

Results

Compound **I** in THF shows a reduction peak A_1 at −1.67 V by cyclic voltammetry. An oxidation peak A_1' (−1.40 V) is found in the reverse sweep. The value of $\Delta E_p = E_p^{red} - E_p^{ox} = 0.27$ V is higher than that expected for a reversible system by the ratio i_p^{ox}/i_p^{red} is close to one (see Fig. 1).

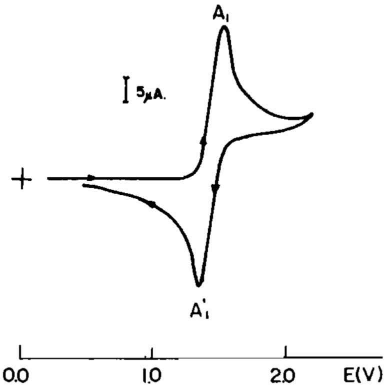


Fig. 1. Cyclic voltammogram of compound I.

The exhaustive electrolysis of compound **I** at −1.70 V consumes 2 F/mol. The resulting solution does not show the peak A_1', but other new oxidation peaks are present. This indicates that the electrogenerated anionic species is not stable and during electrolysis it undergoes chemical evolution.

The voltammogram of compound **I** in the presence of an equimolar amount of $P(OMe)_3$ shows, in addition to A_1, a new peak A_2 at −1.90 V that increases its intensity in successive sweeps (see Fig. 2).

If this solution is electrolyzed at −1.70 V, only a relatively small charge is consumed (0.4 F/mol). The resulting solution contains the new compound **II** that can be isolated as an orange oily solid. **II** reduces reversibly at −1.90 V ($\Delta E_p = 0.14$ V). In the same experimental conditions, the standard $FeCp_2/FeCp_2^+$ gave a peak separation of 0.20 V. Compound **II** shows

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*Dedicated to Professor R. Usón on the occasion of his 60th anniversary. Part I is ref. 2.

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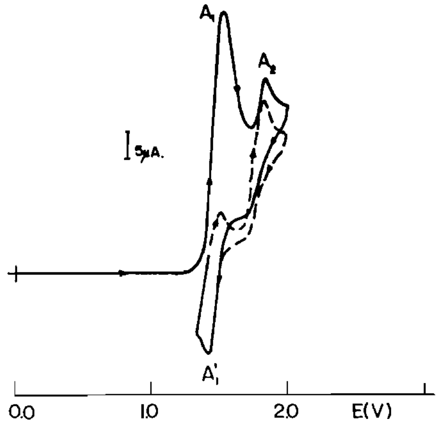

Fig. 2. Cyclic voltammogram of compound **I** in presence of $P(OMe)_3$. (—— First sweep, – – – *n*th sweep).

two carbonyl bands in the infrared spectrum in $CHCl_3$ at 1990 and 1875 cm^{-1}.

The ^1H NMR spectrum ($CDCl_3$) solution of **II** contains a doublet corresponding to coordinated $P(OMe)_3$, at $\delta = 3.4$ ppm ($J_{P-H} = 11$ Hz) in addition to the resonances observed in compound **I** assigned to the diazanorbornene ligand.

A single resonance at $\delta = 124.2$ ppm appears in the ^{31}P NMR spectrum.

The ^{13}C NMR spectrum also shows one signal in the carbonyl region at $\delta = 215.4$ ppm ($J_{P-C} = 40$ Hz).

The cyclic voltammogram of compound **I** does not change in the presence of equimolar amounts of PPh_3. The electrolysis of this solution at −1.70 V consumes 1.5 F/mol. A red crystalline compound **III** was isolated from this solution with a yield of 18%. Compound **III** reduces irreversibly at −1.84 V. It shows two infrared bands in the carbonyl region at 1980 and 1910 cm^{-1}.

The ^1H, ^{13}C, and ^{31}P NMR spectra (see Table I) and elemental analysis allow us to identify compound **III**.

If **I** is reduced in the presence of equimolar amounts of $P(OPh)_3$, 2 F/mol are consumed and no definite compound is isolated from the resulting solution.

Discussion

We already know that under reduction conditions $(N-N)Fe_3(CO)_9$, ((N–N) = 2,3-diazanorbornene) yields $(N-N)Fe_3(CO)_8[P(OMe)_3]$ [2] in the presence of equimolar amounts of $P(OMe)_3$ in a practically quantitative way. The catalytic process is very efficient, only a minimum amount of charge is required and substitution is completed in a few seconds.

Other trinuclear iron compounds exhibit the same behaviour but in a less efficient way [1].

It is an accepted fact that the reduction of these clusters locates electrons in a molecular orbital having an antibonding character with respect to the metal–metal bond [1].

This makes the nucleophilic attack on the radical anions easier and consequently the ligand substitution is faster than in the neutral complexes.

There are examples of activation of ligand substitution in mononuclear complexes of manganese [3] and chromium [4]. In these cases the active species are obtained by electrochemical oxidation of the neutral complexes and are 17 electron species.

The results described in this paper represent the first example, as far as we know, of electron induced nucleophilic substitution (EINS) observed in a mononuclear complex under reduction conditions.

The same scheme of reactivity already described for the activation of $(N-N)Fe_3(CO)_9$ can be used to explain the behaviour of compound **I**. The reduced species can easily undergo ligand substitution, yielding substituted anionic species which experiment an electron transfer process with the starting product.

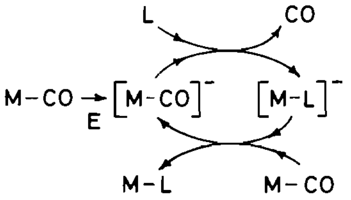

TABLE I. Spectroscopic Data for the Compounds

Compound	ν_{C-O} (cm^{-1})	^1H NMR[a] (ppm)	^{13}C NMR[b] (ppm)	^{31}P NMR (ppm)	J_{P-C} (Hz)	J_{P-H} (Hz)
I	2020 1980		210.8			
II	1990 1875	3.48 3.42	215.8 215.0	124.2	40	11.5
III	1980 1910	7.50	216.5 216.1	64.5	17	

[a] Only the signals corresponding to $P(OMe)_3$ or PPh_3. [b] Only the signals in the carbonyl region.

The reason for such behaviour must be attributed to the particular electronic properties of the metallocyclic system.

The reduced species might weaken the metal–carbon bond (or metal–nitrogen bond) and consequently would be activated for nucleophilic attack in a similar way as has been proposed for polynuclear compounds [1].

In both cases the substituted compounds reduce at a more negative value than the tricarbonyl compound. The lower efficiency observed for the EINS process when PPh_3 is present must be due to the irreversibility of the reduction of compound **III**.

We must add that no substitution has been observed after irradiation for two hours of compound **I** in THF in the presence of equimolar amounts of $P(OMe)_3$.

Acknowledgements

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References

1 M. Arewgoda, B. H. Robinson and J. Simpson, *J. Am. Chem. Soc., 105,* 1893 (1983) and refs. therein.
2 P. Lahuerta, J. Latorre, M. Sanaú and H. Kisch, *J. Organomet. Chem., 286,* C27 (1985).
3 J. W. Hersberg, R. J. Klinger and J. K. Kochi, *J. Am. Chem. Soc., 105,* 61 (1983).
4 J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasine, R. M. Wightman and J. K. Kochi, *J. Am. Chem. Soc., 106,* 3968 (1984).