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Preliminary communication

THE REDOX PROPERTIES OF ORGANOTRANSITION-METAL COMPLEXES

IV*. THE ACTIVATION OF CYCLIC POLYOLEFINIRON TRICARBONYL DERIVATIVES BY ONE-ELECTRON OXIDATION

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Summary

Cyclic polyolefiniron tricarbonyl derivatives $[Fe(CO)_2L(C_nH_m)]$ (L = CO or phosphorus donor) and oxidising agents such as Ag^+ or $[NO]^+$ in CH_2Cl_2 give reactive paramagnetic cations $[Fe(CO)_2L(C_nH_m)]^+$ which can abstract hydrogen from the solvent to give $[Fe(CO)_2L(C_nH_{m+1})]^+$.

Cyclic polyolefiniron tricarbonyl complexes (I) may undergo reaction at the coordinated organic ligand either by direct addition of reagents such as tetracyanoethylene [2], or via protonation or hydride abstraction followed by nucleophilic attack on the resulting cation [3]. We now show that I may also be activated via initial one-electron oxidation.

The addition of $[NO]X$ ($X = BF_4$ or PF_6 to $[Fe(CO)_2L(C_nH_m)]$ (I) (C_nH_m = cyclic polyolefin) in dry CH_2Cl_2 gives either $[Fe(CO)L(NO)(C_nH_m)]^+$ (II) (L = CO, C_nH_m = norbornadiene; L = PPh_3, C_nH_m = tetraphenylcyclobutadiene) or $[Fe(CO)_2L(C_nH_{m+1})]^+$ (III) in which protonation has apparently occurred (e.g. $[Fe(CO)_3(\eta^5$-cycloheptadienyl)$][BF_4]$ (IV) from $[Fe(CO)_3(\eta^4$-cycloheptatriene)$]$ (V)). Although protonations involving $[NO]^+$ have been observed [4] with alcoholic solvents, in which the equilibrium $[NO]^+ + ROH \rightleftharpoons H^+ + RONO$ occurs, the presence of protons in mixtures of $[NO]X$ and dry CH_2Cl_2 is unlikely. The possibility that the nitrosonium ion oxidises [5] (I) to $[Fe(CO)_2L(C_nH_m)]^+$ (VI) which then abstracts hydrogen from CH_2Cl_2 to give III has been confirmed by electrochemical studies and additional synthetic work.

Cyclic voltammetric studies (Table 1) in CH_2Cl_2 show that the complexes

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*For part III see ref. 1.

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TABLE 1

CYCLIC COLTAMMETRIC DATA FOR THE ONE-ELECTRON OXIDATION OF $[Fe(CO)_2L(olefin)]$ (I)

L	Olefin	Ep(V)[a]	$(ip)_{OX}$ (μA)[b]	$(ip)_{RED}$ (μA)[b]	Reversibility[c]
PPh_3	Norbornadiene	0.22	3.7	3.4	R
PPh_3	Tetraphenylcyclobutadiene	0.61	3.3	3.2	R
PPh_3	Cyclooctatetraene	0.47	4.0	—	IR
$P(OCH_2)_3CMe$	Cyclooctatetraene	0.50	4.2	—	IR
$P(OCH_2)_3CMe$	Cycloheptatriene	0.50	6.1	—	IR

[a] For the irreversible processes $(Ep)_{OX}$ is given, measured at a scan rate of 100 mV/s; all potentials are vs. a calomel 1 *M* in LiCl.

[b] For the known reversible process $[Ni\ S_2C_2(CN)_2\ _2]^{2-} \rightleftharpoons [Ni\ S_2C_2(CN)_2\ ]^{1-}$ $(ip)_{OX} = 3.5$ μA, $(ip)_{RED} = 3.8$ μA.

[c] R = reversible, IR = chemical irreversible.

I (L = phosphine or phosphite) each undergo one-electron oxidation at the platinum wire electrode*. For those complexes which afford metal nitrosyls (II with [NO]X) the electron-transfer process is reversible and addition of $Ag[PF_6]$ to solutions of these species in CH_2Cl_2 results in the formation of stable paramagnetic cations $(Fe(CO)_2L(C_nH_m))^+$ (VI) [e.g. L = PPh_3, $C_nH_m = \eta^4\text{-}C_4Ph_4$, ν(CO) (CH_2Cl_2) 2033, 2003 cm^{-1}; $\langle g_{ave} \rangle = 2.080$). For all other examples of I studied the oxidation is chemically irreversible, the initial one-electron transfer step is followed by a rapid chemical reaction. The addition of Ag^+ to those species (L = phosphine or phosphite) which are irreversibly oxidised gives products identical to those obtained from reaction with $[NO]^+$. In certain cases where L = CO only the stronger oxidising agent, $[NO]^+$ will bring about the initial electron transfer. Thus, although good yields of IV may be obtained from V and $Ag[BF_4]$, the latter will only react with I (L = PPh_3; C_nH_m = cyclooctatetraene), not with I (L = CO, C_nH_m = cyclooctatetraene).

It is clear, therefore, that not only does the formation of III from I with $[NO]^+$ not involve the direct addition of protons but that suitable oxidising agents may be used to activate I via initial one-electron transfer. Subsequent reaction of VI depends on the availability on the olefin of a site at which attack by other reagents can occur.

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References

1 N.G. Connelly and K.R. Somers, J. Organometal. Chem., 113 (1976) C39.
2 M. Green, S. Heathcock and D.C. Wood, J. Chem. Soc. Dalton, (1973) 1564.
3 E.W. Abel and F.G.A. Stone, Quart. Revs., 24 (1970) 515 and refs. therein.
4 N.G. Connelly and J.D. Davies, J. Organometal. Chem., 38 (1972) 385; B.F.G. Johnson and J.A. Segal, J. Organometal. Chem., 31 (1971) C79; J.A. Connor and P.I. Riley, J. Chem. Soc. Chem. Commun., (1976) 149.
5 N.G. Connelly, Z. Demidowicz and R.L. Kelly, J. Chem. Soc. Dalton, (1974) 2335.

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*The tricarbonyls are oxidised at more positive potentials; the phosphine and phosphite complexes lend themselves more readily to electrochemical study.