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Preliminary communication

ELECTRON TRANSFER CATALYSIS OF THE REGIOSELECTIVE REPLACEMENT OF CO BY $P(OMe)_3$ IN DISSYMMETRICAL DIIRON HEXACARBONYL COMPLEXES

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Summary

Substitution of carbon monoxide by trimethylphosphite in two dissymetrical diiron hexacarbonyl complexes of known structure has been studied using thermal activation or electron transfer catalysis. The same regioselectivity for the monosubstitution is observed in both cases.

Replacement of carbon monoxide by other ligands is a subject of much interest in the field of polynuclear metal carbonyl complexes [1—5]. The well-known rule for this reaction under thermal activation is that there is mono-substitution at each metal nucleus but it is difficult to control the total number of carbonyl ligands which are replaced in complexes containing several metal atoms [6]. Considerable improvements have been made recently following the discovery that substitution can be monitored by using electron-transfer catalysis induced either at electrodes [7—10] or by chemical reagents [11,12]. The electrochemical method appears more useful from an analytical point of view and it also allows a facile control of the substitution, even in the presence of ligand excess, by the choice of the electrode potential [8]. Up to now such controlled CO exchange has been studied either for symmetrical complexes or for a dissymmetrical cluster for which the structures of the substitution products are not known [8]. This prompted us to investigate the regioselectivity of this reaction under both thermal and electrochemical activation. For this purpose we have chosen the dissymmetrical diiron hexacarbonyl complexes Ia and IIa having known structures [13,14]. Our conclusions concerning

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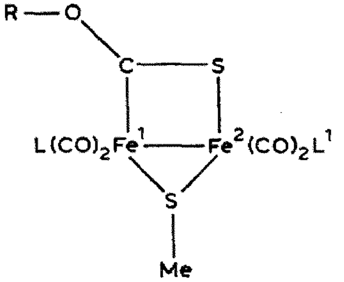
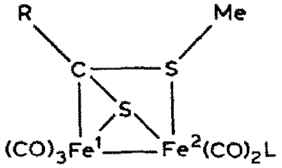
the regioselectivity of the reaction are beyond doubt because the X-ray structures of the monosubstituted products Ib and IIb, have been determined and a paper describing them is in the press.



(Ia : L = L^1 = CO;

Ib : L = $P(OMe)_3$, L^1 = CO ;

Ic : L = L^1 = $P(OMe)_3$)



(IIa : L = CO ;

IIb : L = $P(OMe)_3$)

Kochi recently showed in one case that "thermal" activation proceeds in fact by electron transfer catalysis induced by minute amounts of oxidant [15]. In our case the reactions are induced by reduction under electrochemical activation and we have confirmed that under thermal activation they are not inhibited by the presence of the classical radical scavengers of the $S_{RN}1$ [16]: O_2, p-$(NO_2)_2C_6H_4$. This proves that electrochemical and thermal activations are effectively two different processes; in addition the rate of the reaction is dramatically enhanced under electrochemical activation.

At room temperature in the presence of an excess of $P(OMe)_3$, complex Ia in acetone affords after 48 h a mixture of the monophosphite Ib (62%) and of the bis-phosphite Ic (29%) [17]. Under the same conditions complexes IIa are also slowly transformed into IIb, and the second substitution is never observed even after several days of reflux. These findings show that under electrochemical activation the contribution of thermal activation to product formation can be neglected.

Complex Ia and IIa are reduced in the same range of potential with different voltammetric behavior (Fig. 1), but both show an initial one-electron reversible or quasi-reversible reduction leading to the paramagnetic anions. The voltammetric curves related to Ia and IIa in the presence of $P(OMe)_3$ (Fig. 1) show in both cases a decrease of the peak current for the starting material and the appearance of one or two additional peaks corresponding to the products formed at the electrode surface. A qualitative estimation of the rate of the catalysed reaction can be made from the decrease of peak currents. For Ia two substitutions are observed and as for the thermal activation the first carbonyl exchange is faster than the second. For IIa only one substitution is observed under electrochemical or thermal activation. Confirmation was obtained by using bulk electrolysis, which led selectively to Ib or Ic and IIb in less than one hour with a low consumption of electricity: Ia: $E = -1.3$, vs. SCE; 0.55 e^-/mol; Ib: 71%. IIa: $E = -1.1$ vs. SCE; 0.05 e^-/mol; IIb: 88%.

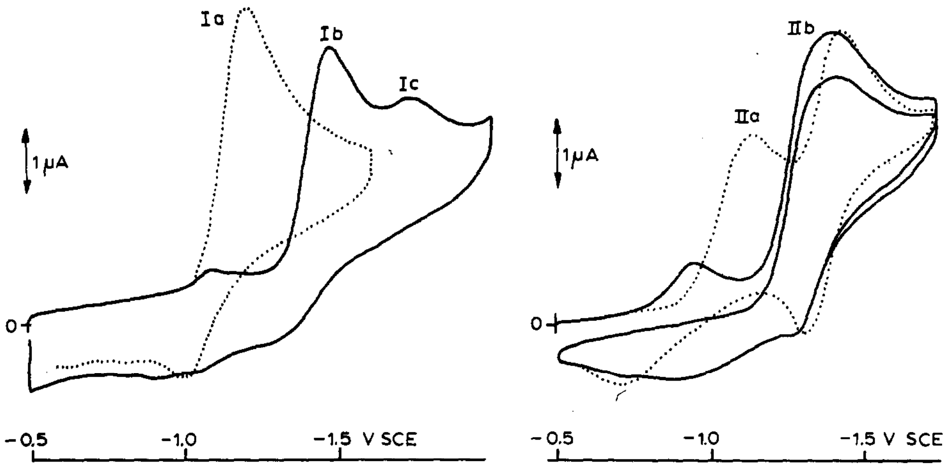


Fig. 1. Cyclic voltammetry of Ia and IIa (10^{-3} *M*) in n-Bu_4N^+ BF_4^- 0.1 *M* acetone, at platinum electrode (v = 0.2 V s^{-1}) in the presence of $P(OMe)_3$. . . . without $P(OMe)_3$, —— with $P(OMe)_3$ 8 × 10^{-3} *M*.

The products obtained using electrochemical activation are identical (^1H NMR and IR spectra, melting points and mixed melting points) to those isolated after chromatographic separation of the mixture obtained from thermal activation.

Our results show that an appreciable rate increase can be attained under electrochemical activation and that the same regioselectivity is observed using both activation modes. The monophosphites Ib and IIb are undoubtedly the thermodynamic products. If a kinetic product of different structure can be formed under electrochemical activation it is likely to consider that an irreversible isomerisation leading to the stable product will occur either by thermal induction or due to the presence of the unpaired electron before deactivation. Examples of isomerisation reactions induced by electron transfer catalysis are known [18]. Prediction of the substitution site by considering arguments such as metal—CO bond lengths, electronic or steric effects of the ligands attached remains hazardous. For instance, in the case of IIa the carbonyls are fluxional at room temperature on both iron atoms and the carbonyl removed effectively corresponds to the longest metal—CO bond length [19]. In contrast for compound Ia the carbonyls are not fluxional on the Fe^1 atom [17] and the substitution occurs on the carbonyl for which one of the shortest metal—CO distance has been recorded [13].

References

1 D.C. Sonnenberger and J.D. Atwood, J. Am. Chem. Soc., 104 (1982) 2113.
2 D.J. Darensbourg and B.J. Baldwin-Zuschke, J. Am. Chem. Soc., 104 (1982) 3906.
3 D.J. Darensbourg, B.S. Peterson and R.E. Schmidt, Jr., Organometallics, 1 (1982) 306.
4 D.C. Sonnenberger and J.D. Atwood, Organometallics, 1 (1982) 694.
5 D. Labroue, R. Queau and R. Poilblanc, J. Organometal. Chem., 233 (1982) 359.
6 A.J. Deeming, in B.F.G. Johnson (Ed.), Transition Metal Clusters, John Wiley, New York, 1980, p. 391.
7 G.J. Bezems, P.H. Rieger and S. Visco, J. Chem. Soc. Chem. Commun., (1981) 265.
8 A. Darchen, C. Mahé and H. Patin, J. Chem. Soc. Chem. Commun., (1982) 243.

9 C.M. Arewgoda, B.H. Robinson and J. Simpson, J. Chem. Soc. Chem. Commun., (1982) 284.
10 C.M. Arewgoda, P.H. Rieger, B.H. Robinson and J. Simpson, J. Am. Chem. Soc., 104 (1982) 5633.
11 M.I. Bruce, D.C. Kehoe, J.G. Matisons, B.K. Nicholson, P.H. Rieger and M.L. Williams, J. Chem. Soc. Chem. Commun., (1982) 442.
12 M.I. Bruce, J.G. Matisons, B.K. Nicholson and M.L. Williams, J. Organometal. Chem., 236 (1982) C57.
13 H. Patin, G. Mignani, A. Benoit, J.Y. Le Marouille and D. Grandjean, Inorg. Chem., 20 (1981) 4351.
14 A. Benoit, J.Y. Le Marouille, C. Mahé and H. Patin, J. Organometal. Chem., 218 (1981) C67.
15 J.W. Hershberger, R.J. Klingler and J.K. Kochi, J. Am. Chem. Soc., 104 (1982) 3034.
16 N. Kornblum, Angew. Chem. Int. Ed., 14 (1975) 734.
17 H. Patin, G. Mignani, A. Benoit and M.J. McGlinchey, J. Chem. Soc. Dalton Trans., (1981) 1278.
18 R.D. Rieke, H. Kojima and K. Öfele, Angew. Chem. Int. Ed., 19 (1980) 538.
19 C. Mahé, Thesis, Rennes, 1982.