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Preliminary communication

CARBON DISULPHIDE IRON COMPLEXES AS A SOURCE OF BIS(TRIFLUOROACETATO)IRON DERIVATIVES

H. LE BOZEC, A. GORGUES and P. DIXNEUF

Laboratoire de Chimie des Organométalliques, Campus de Beaulieu, Université de Rennes, 35042 Rennes Cédex (France)

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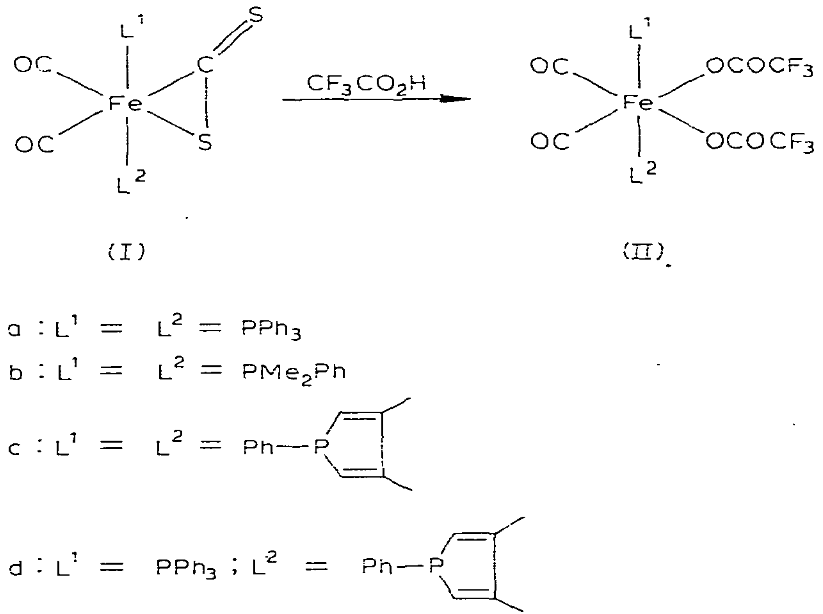
Summary

Treatment of complexes of the type $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ with trifluoroacetic acid provides a convenient route to $Fe(\eta^1\text{-}OCOCF_3)_2(CO)_2L_2$ derivatives (L = PPh_3, PMe_2Ph, Ph—P). The latter react with $(NO)^+PF_6^-$ in acetonitrile to give NO and $[Fe(\eta^1\text{-}OCOCF_3)(NCCH_3)(CO)_2L_2]\ PF_6$ complexes.

There is much interest in the enhancement by coordination of the nucleophilicity of carbon disulphide [1], and η^2-CS_2-metal compounds are useful precursors for the preparation of novel derivatives [2,3]. Moreover, presence of the η^2-CS_2 ligand on iron has been shown to favour introduction of a variety of phosphorus ligands at the apical positions [4]. After appropriate phosphorus ligands L^1 and L^2 are introduced into the very stable $Fe(\eta^2\text{-}CS_2)(CO)_2L^1L^2$ derivatives (I), it is sometimes desirable to remove the nucleophilic ligand CS_2. We now describe a simple way of removing this ligand and of preparing bis(trifluoroacetato)iron complexes II. The latter show a surprising reactivity towards the nitrosyl cation.

The uncoordinated sulfur atom in $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ derivatives I is very nucleophilic and can bring about nucleophilic substitution of alkyl halides [5]. Protonation of the complexes I using an etheral solution of HPF_6 probably takes place at the basic, uncoordinated sulphur atom, but the products cannot be identified. However when trifluoroacetic acid which yields a coordinating anion, was allowed to react with I, replacement of the carbon disulphide ligand by two *cis*-trifluoroacetato ligands took place (Scheme 1).

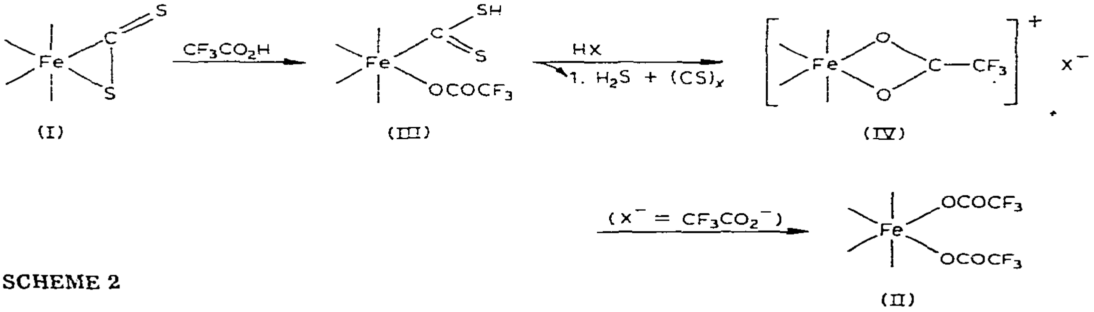
When an excess of trifluoroacetic acid was added to the red complex Ia or orange complex Ib in concentrated dichloromethane solution or in the solid state, H_2S was evolved as a yellow solution appeared. The bright yellow, photosensitive derivatives IIa (m.p. 200—205°C (dec.); ν(CO): 2040, 1986, 1680 cm^{-1}) and IIb (m.p. 185—190°C; ν(CO): 2050, 1997, 1685 cm^{-1}) were obtained in 69% and 45% yields, respectively, by use of column chromatography. The corresponding



SCHEME 1

reaction with the weaker acetic acid is very slow (even in the presence of acetic anhydride), and affords poor yields of the acetoxy complexes.

This reaction was used for the preparation of some phosphole containing iron complexes. A mixture of Ic and Id was formed by treating the phosphole with Ia, as in the usual substitution procedure [4], but could not be separated. However, compounds IIc (m.p. 140—145°C (dec.); ν(CO) (Nujol) 2050, 2000, 1690 cm^{-1}) and IId (m.p. 135—140°C (dec.); ν(CO) 2040, 2000, 1690 cm^{-1}) obtained by treatment of the mixture with trifluoroacetic acid were separated by chromatography.

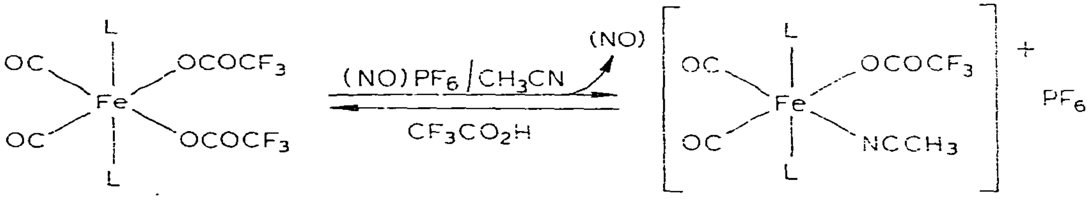


SCHEME 2

The reaction may proceed according to Scheme 2. The intermediate III is formed by protonation of the uncoordinated S atom followed by coordination of the trifluoroacetate anion. The addition of a second equivalent of acid leads to the evolution of only one equivalent of H_2S, as shown by titration [6], but the expected cationic thiocarbonyl iron derivative could not be observed.

A derivative of type IV is probably an intermediate, since when 2 equivalents of CF_3CO_2H were added to Ib in the presence of NH_4PF_6 the derivative IVb was formed and was isolated and characterized ($X = PF_6$; $\nu(C{\equiv}O)$ 2010—1945 cm^{-1}; $\nu(C{=}O)$ 1670 cm^{-1}). When X^- is $CF_3CO_2^-$ in the intermediate IV coordination of X then gives compound IIb.

The complexes II showed unexpected behaviour when treated with the nitrosyl cation. In an attempt to displace one carbonyl of the derivatives of type II, in order to destroy the C_{2v} symmetry, we treated IIa and IIb with one equivalent of $NOPF_6$ in dry dichloromethane-acetonitrile. The reaction selectively gave the cationic acetonitrile iron complexes Va and Vb (Scheme 3). Va [84%; m.p. 200°C (dec.). IR (Nujol) $\nu(C{\equiv}N)$ 2300 cm^{-1}; $\nu(C{\equiv}O)$ 2060, 2010 cm^{-1}; $\nu(C{=}O)$ 1690 cm^{-1}, ^1H NMR (CD_3COCD_3) δ 1.76 ppm (s)(CH_3CN)] and Vb (89%; m.p. 150—155°C (dec.); $\nu(CN)$ 2320—2310 cm^{-1}; $\nu(C{\equiv}O)$ 2070, 2020 cm^{-1}; $\nu(C{=}O)$ 1695 cm^{-1}; ^1H NMR δ 2.36 ppm (t); $^5J(^{31}P{-}H)$ 1.9 Hz]. An important feature is that the substitution reaction (Scheme 3) proceeds with evolution of NO gas. Therefore the first step of the process which is not yet established, may be reduction of NO^+ by the iron complexes II in a reaction analogous to that reported by Connelly et al. [7].



(II)

(V)

SCHEME 3

The reactions described above show that the stable and readily accessible complexes $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ are excellent intermediates for the formation of either neutral or cationic derivatives of iron(II).

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