

Preliminary communication

Carbon-ligand migration during the electron-transfer catalyzed stepwise replacement of two carbon monoxide ligands in a doubly-bridge di-iron compound

André Darchen, El Kbir Lhadi, Henri Patin,

Département de Chimie Organique, Ecole Nationale Supérieure de Chimie, Avenue du Général Leclerc, 35700 Rennes-Beaulieu (France)

Daniel Grandjean and Abdelhamid Mousser

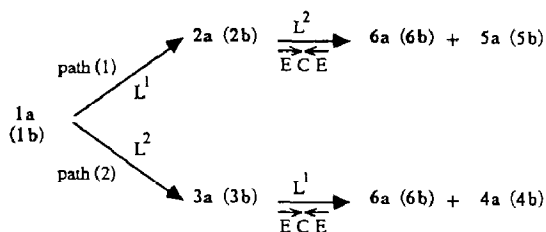
Laboratoire de Chimie du Solide et Inorganique Moléculaire, Université de Rennes I, Campus de Beaulieu, 35042 Rennes-Cedex (France)

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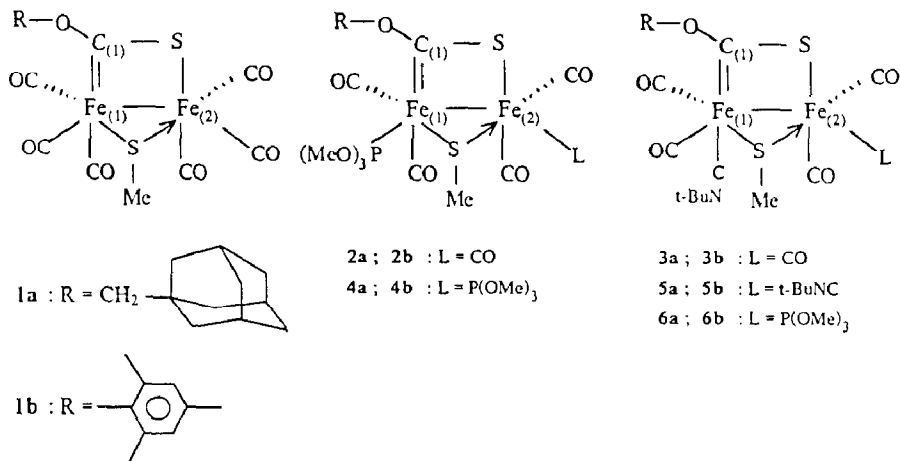
Abstract

The complexes $[(\mu\text{-}\eta^2\text{-ROC(1)S)Fe}_2(\text{CO})_6(\mu\text{-SMe})]$ (**1**), undergo selective replacement of one CO by P(OMe)_3 (L^1) or t-BuNC (L^2) to give the monosubstituted compounds **2** and **3**, respectively when L^1 or L^2 is bonded to Fe(1) bearing the carbene ligand C(1). When a second CO ligand is displaced from **2** or **3** by electron-transfer catalysis both give a complex (**6**) in which L^2 and L^1 are linked to Fe(1) and Fe(2), respectively; moreover L^1 in **2** and L^2 in **3** are displaced by the ligand present in the solution to give bis-isonitriles and bis-phosphites. The structure of **6** has been determined by X-ray diffraction and the results are discussed in terms of the assumption that the ligand exchange occurs in an intermediate in which C(1) becomes bonded to both metal atoms and consequently can rotate about the Fe–Fe axis.

Ligand exchange reactions, carried out under thermal, photochemical or electron-transfer catalysis conditions, are of major importance in organometallic and coordination chemistry in connection with catalytic processes [1,2]. Recent publications have emphasized that apparently simple substitution reactions may involve several steps. For example the classical associative and dissociative mechanisms must be completed in some mononuclear species by ligand slippage [1c] or in polynuclear compounds by vacant site transfer [3]. Consequently the full description of a ligand exchange reaction, particularly the unmasking of hidden steps, needs intensive experimental studies with appropriate substrates. We report here that ancillary ligand migration occurs in the doubly-bridged dinuclear compounds **1**



Scheme 1



during the sequential exchange of two carbonyls by two different ligands under electron-transfer catalysis [4*].

In the case of the di-iron hexacarbonyl compound **1** we have shown that two CO ligands can be replaced by P(OMe)_3 or by $t\text{-BuNC}$ leading first to monosubstituted **2** or **3** and then to the disubstituted derivative **4** or **5** [5–8]. These results are apparently consistent with the empirical rule that one CO substitution occurs at each metal center [2]. However kinetic studies [9] and sequential use of P(OMe)_3 and $\text{P(OCd}_3)_3$ [10] have revealed that (i) the participation of bridging ligands must be not neglected, and (ii) the second CO substitution is not exclusively at the unsubstituted metal center. We now present new information obtained by replacing two CO ligands successively by $L^1 = \text{P(OMe)}_3$ and $L^2 = t\text{-BuNC}$ (Scheme 1).

Starting from the monosubstituted compounds **2** or **3** one would expect the formation of two different products formed by adding L^2 to **2** and L^1 to **3**. The fact that the same final compound **6** was obtained when the exchanges were performed under electron-transfer catalysis conditions reveals that a common intermediate leads to the more stable disubstituted complex in which the isonitrile occupies an axial position at $\text{Fe}(1)$ *trans* to the carbene $\text{C}(1)$ while the phosphite is linked equatorially to $\text{Fe}(2)$. Pure **6b** was obtained in 28 and 30% yield (paths 1 and 2 respectively) after chromatography and recrystallization [11]. The formation of **6** is accompanied by the production of comparable amounts of symmetrically disubsti-

* Reference number with asterisk indicates a note in the list of references.

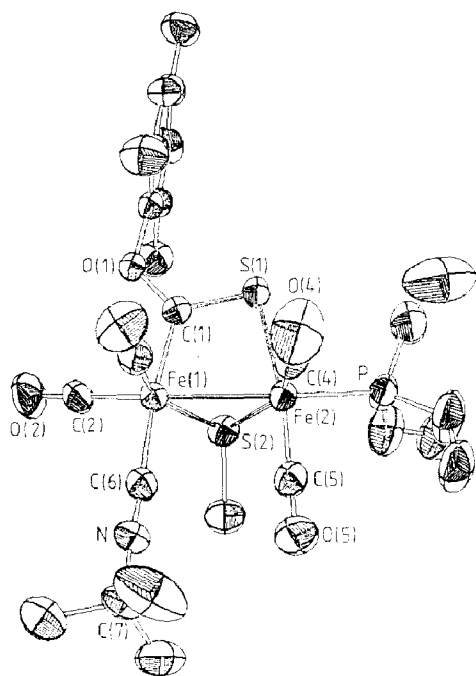


Fig. 1. ORTEP drawing of compound **6b**.

tuted complexes. For instance 25% of diisonitrile **5b** is obtained from the monophosphite **2b** (path 1) and 29% of the diphosphite **4b** is formed from the monoisonitrile **3b** (path 2). All the products were readily identified, but the regiochemistry and the stereochemistry of the $\text{P}(\text{OMe})_3$ and *t*-BuNC ligands in compounds **6** could only be established by X-ray diffraction.

The structure determination was carried out on a single crystal of **6b** (m.p. 140°C , pentane) from which 3073 independent diffracted intensities with $I_o > \sigma(I)$ were taken as observed from a set of 3292 independent reflections measured by a ω - 2θ scan technique with graphite monochromatized Mo- K_α radiation on an Enraf-Nonius CAD 4 diffractometer. The compound crystallizes with 4 molecules per unit cell in the space group $P2_1/c$ with lattice constants: a 10.477(6); b 17.785(2); c 16.793(4) Å; β $105.64(5)^\circ$; V 3013.4(3) Å³. The structure was solved by direct methods with the MULTAN program; full matrix least squares refinement of atomic positional and thermal (anisotropic Fe, S, O, C; isotropic H) parameters converged to conventional values $R = 0.039$ and $R_w = 0.57$. All the structural calculations were performed on a PDP 11/60 computer with SDP package [12]. A task of atomic coordinates and a complete list of bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.

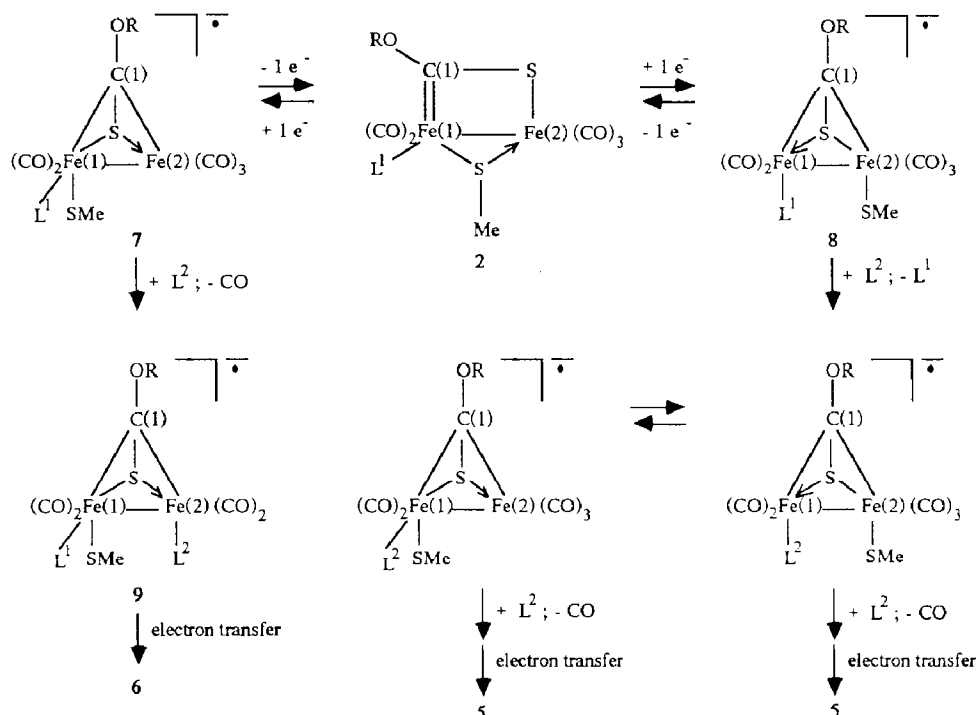
The ORTEP drawing (Fig. 1) shows that *t*-BuNC is coordinated axially to Fe(1) while $\text{P}(\text{OMe})_3$ equatorially linked to Fe(2) occupies the same half-space as the bridging ligand SME. Some selected bond lengths and bond angles are given in Table 1. There is a shortening of the metal-metal bond and lengthening of the metal-carbene bond compared with other complexes in the same series. The ¹³C NMR resonance of C(1) appears at 307.6 ppm (³ $J(\text{P}-\text{C})$ 4.95 Hz) and in the carbonyl region four signals are present at room temperature, consistent with the loss of fluxionality when both metal atoms are substituted [5,6,13].

Table 1 Selected bond lengths (Å) and angles (°) with e.s.d.'s

Fe(1)–Fe(2)	2.608(1)	Fe(1)–C(6)–N	175.2(3)
Fe(1)–C(1)	1.916(3)	Fe(1)–Fe(2)–S(1)	76.65(2)
Fe(1)–S(2)	2.266(1)	Fe(1)–Fe(2)–S(2)	55.10(2)
Fe(1)–C(6)	1.902(3)	Fe(1)–Fe(2)–P	157.51(4)
Fe(2)–S(1)	2.323(1)	Fe(2)–Fe(1)–S(2)	54.20(2)
Fe(2)–S(2)	2.241(1)	Fe(2)–Fe(1)–C(1)	76.72(9)
Fe(2)–P	2.168(1)	Fe(2)–Fe(1)–C(6)	95.6(1)
C(1)–S(1)	1.679(3)	S(2)–Fe(1)–C(1)	83.79(6)
C(1)–O(1)	1.330(4)	S(2)–Fe(1)–C(6)	95.7(1)
S(1)–Fe(2)–S(2)	82.78(4)	C(3)–Fe(1)–C(6)	89.4(2)
S(2)–Fe(2)–P	104.43(4)	S(1)–Fe(2)–P	92.66(3)
P–Fe(2)–C(5)	95.0(1)	P–Fe(2)–C(4)	102.8(1)
Fe(2)–S(1)–C(1)	89.7(1)	Fe(1)–S(2)–Fe(2)	70.70(3)
C(6)–N–C(7)	173.2(4)	Fe(1)–C(1)–S(1)	116.9(2)
Fe(1)–C(1)–O(1)	122.0(2)	S(1)–C(1)–O(1)	121.1(2)

These results provide confirmation of our suggestion that we have made previously and reveal a new fact, namely that ligands exchange can occur at a metal center already substituted by the non-carbonyl ligands, L^1 or L^2 , involving their ejection and replacement by the incoming ligand present in the reaction medium [14].

The exclusive formation of the regioisomer **6** is another illustration of the need to postulate a pre-equilibrium leading to a reaction intermediate such as **7** or **8** [10,15] in which the biatomic bridge becomes symmetrically linked to the metal–metal bond (Scheme 2). Under electron-transfer catalysis one of the metal atoms bears 19



Scheme 2

electrons a situation which favors the replacement of one CO at Fe(2) in **7** or of the more labile L ligand at the electron-rich metal-center Fe(1) in **8**. The last step involves electron loss and bridge reformation. If two non-carbonyl ligands are present in the reaction intermediates **9** the redox potential of these species are lower than those of the starting materials and electron transfer occurs readily to give the disubstituted compound **6**. However, the ligand exchange occurring at Fe(1) in **8** leads to the intermediate $3^{\cdot-}$ which is involved in a second CO replacement at Fe(2) before electron loss, possibly after SMe migration from Fe(2) to Fe(1). If $3^{\cdot-}$ loses the electron and gives **3**, at the working potential used compound **3** is reactivated towards a second CO substitution and this leads to the final symmetrically disubstituted compounds **5**. Our results, and particularly the formation of comparable amounts of symmetrical and dissymmetrical disubstituted complexes show that ligand exchange can occur with the same probability at both metal centers. The rotation of the carbon–sulfur bridge is governed by the stability of the final compound, which appears to favour a *t*-BuNC ligand axially linked to Fe(1) and *trans* to the carbene.

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- After the voltammetric studies, electrolysis of **2a** (**2b**) and of **3a** (**3b**) in acetone containing 5 equiv. of P(OMe)₃ or *t*-BuNC and LiClO₄ (0.1 M) was carried out at a controlled potential (–1.55 VSCE for **2** and –1.50 VSCE for **3**) in the dark, under N₂ at a mercury cathode. After 1 h the transformation was complete and the solvent was removed. The residue was treated with water and the product extracted with Et₂O. The isolated crude product (60–65%) was fractionated by chromatography on silica plates with the Et₂O/hexane (1/4 by volume) as eluent. The *R_f* of compounds **4**, **6** and **5** are respectively 0.32, 0.50 and 0.60. The yields are: path (1) **5a** (20%), **5b** (25%), **6a** (26%) and **6b** (28%); path (2) **4a** (30%), **4b** (29%), **6a** (30%) and **6b** (34%). Compounds **4** and **5** were readily characterized (see ref. 5–8), and the new compounds **6a** (mp. 145 °C) and **6b** (mp. 140 °C) were identified by the usual analytical and spectroscopic techniques including an X-ray diffraction study for **6b**.
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- RMN ¹³C(CDCl₃): δ 307.65 (d, *J* 4.95 Hz); 156.3 (m); 212.0 (*J* 9.9 Hz); 215.6 (*J* 18.1 Hz); 218.2 (*J* < 0.2 Hz); 218.9 (*J* < 1 Hz) ppm. RMN ³¹P (CDCl₃): δ 179.6 ppm.
- For an example of P(OPh)₃ replacement by PBu₃ in an iridium cluster see ref. 23 in D.C. Sonnenberger and J.D. Atwood, *Organometallics*, 1 (1982) 694.
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