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Preliminary communication

Iron atom discrimination by carbon during the fragmentation of a ligand around a Fe–Fe bond. Crystal structure [μ-η^3-$RCH_2OC(S)SMeFe_2(CO)_5P(OMe)_3$]

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Abstract

The substituted compound [μ-$\eta^3RCH_2OC(S)SMeFe_2(CO)_5P(OMe)_3$] (**3**) (the structure of which was determined by X-ray diffraction), undergoes a ligand fragmentation leading to the known substituted compound [μ-$\eta^2(RCH_2OCS)Fe_2(CO)_5P(OMe)_3\mu$-SMe] (**4**). Evidently during the rearrangement the carbon atom of the bridging ligand migrates from one iron atom to the adjacent iron that bears the phosphite ligand.

Ligand exchange and ligand migration are processes of considerable importance in connection with heterogeneous and homogeneous catalysis [1–3]. In homopolynuclear compounds the indistinguishability of the metallic sites does not allow a full study of the roles played by metal atoms during reactions in their coordination sphere. We show in this paper that regiospecific labeling of one iron atom in compound **1** can be used to detect the migration of a bridging ligand during its fragmentation.

We have recently described the ligand rearrangement **1** → **2** which can occur thermally or by electron transfer catalysis at a cathode [4]. During these reactions the atom C(9) σ-bonded to Fe(1) in **1** becomes a carbene linked to iron in **2** and the

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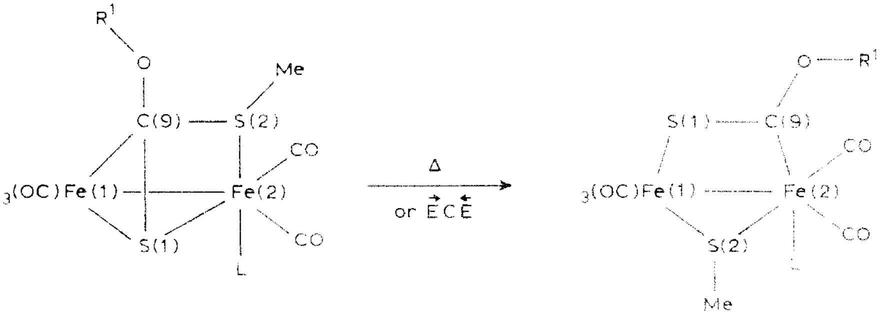

(**1**: L = CO;
3: L = P(OMe)$_3$;
R^1 = methyleneadamantane)

(**2**: L = CO;
4: L = P(OMe)$_3$;
R^1 = methyleneadamantane)

C(9)–S(2) bond is broken and the S(1) decoordinated from Fe(1). An important aspect of this reaction is that in the reactant and in the product the two iron atoms can be distinguished by their surrounding ligands. Despite this, we cannot show whether the C(9) atom remains bonded to the same iron atom during the transformation **1** → **2**. In order to clarify this point one iron atom was labeled with an additional ligand. In the light of recent results in the dithioester-Fe$_2$(CO)$_6$ series [5,6], specific ligand exchange at Fe(2) was expected provided that the replacement of CO by P(OMe)$_3$ is faster than the skeleton rearrangement. The labeling of Fe(2) with P(OMe)$_3$ was readily accomplished, under thermal activation or by using electron transfer catalysis, and compound **3** was obtained in quantitative yield [7*]. Spectroscopic studies confirm the monosubstitution and the absence of fragmentation (in the ^{13}C NMR spectrum the C(9) signal is at δ 109.6 ppm for **1** and at δ 109.4 ppm, with J(P–C) 2.5 Hz, for **3**). However the structure of **3** was uncertain, and an X-ray structure determination was necessary to prove the proposed formula in order to allow full discussion of our results.

The structure determination was carried out on a single crystal of **3** (m.p. 110 °C, hexane) from which 1582 independent diffracted intensities were observed with $I_0 > 2\sigma(I)$ from a set of 2274 independent reflections measured by a ω–2θ scan technique with graphite monochromatized Mo-K_α radiation on an Enraf–Nonius CAD4 diffractometer. The compound crystallizes with four molecules per unit cell in the space group $P2_1/c$, and the lattice constants are a 7.922(3) Å; b 17.350(8) Å; c 20.023(6) Å; α 90.0 (0)°; β 95.43 (4)°; γ 90.0 (0)°; V 2740 Å^3. 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; isotopic H) parameters converged to conventional values $R = 0.049$ and $R\omega = 0.061$. All the structural calculations were performed on a PDP 11/60 computer with SDP package [8].

The ORTEP drawing shown in Fig. 1 shows that P(OMe)$_3$ is linked to Fe(2) and that no fragmentation has occurred. The main structural features of **3** are identical to those of the dithioester coordination compounds **5**: [R^{1}C(S)SR^2][Fe$_2$(CO)$_6$] (**5**)

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* Reference numbers with an asterisk indicate a note in the list of references.

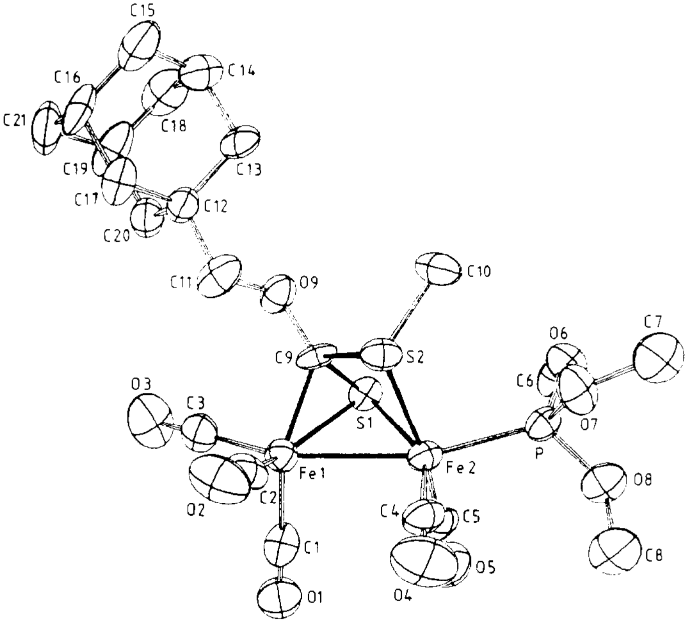

Fig. 1. ORTEP drawing of compound **3**.

and $[R^1C(S)SR^2][Fe_2(CO)_5P(OMe)_3]$ (**6**) already described [6,9]. The C(9)–Fe(1) bond is very short in compound **3**, but the high field resonance of C(9) and its tetrahedral environment are as expected for a carbon–iron bond [10]. It is known that the replacement of CO by $P(OMe)_3$ gives rise to a slight increase in the interatomic distances in the vicinity of the metal–metal axis [6]. However we notice that C(9)–S(2) and Fe(1)–S(1) are significantly longer in **3** than in compound **6** (1.82 compares with 1.79 Å, and 2.22 compared with 2.20 Å) while the other bond lengths are unchanged.

Complex **3** can be isomerized by thermal activation or electron transfer catalysis. Both methods lead to the same complex **4**, identical with the known product obtained by reaction of $P(OMe)_3$ with **2** [11]. Under thermal activation the rearrangement **3** → **4** is slower than the reaction **1** → **2** described previously [4], and a higher temperature is required to achieve a complete transformation [12]. The voltammetric curve of **3** does not reveal that the reaction can be catalyzed by electron transfer because the close proximity of the reduction potentials of **3** and **4** prevents distinction between these species at platinum cathode. However electrolysis of **3** at mercury cathode leads to **4** with a low consumption of electricity [12] *.

Under both modes of activation we observed the same fragmentation of the organic ligand ROC(S)SMe in the coordination sphere of the metallic framework. It is evident that the rearrangement is an intramolecular process because only one

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

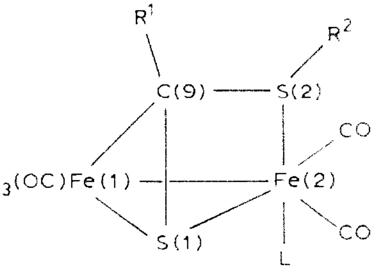
Table 1

Some relevant bond lengths (Å) and angles (°) with their e.s.d.

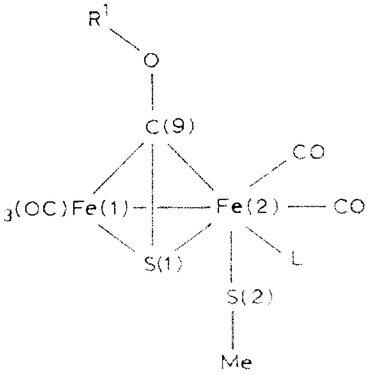
Fe(1)–Fe(2)	2.624(2)	C(9)–S(1)–Fe(1)	57.6(4)
Fe(1)–S(1)	2.224(3)	C(9)–S(1)–Fe(2)	82.6(4)
Fe(1)–C(9)	1.963(11)	Fe(1)–S(1)–Fe(2)	71.4(1)
Fe(1)–C(1)	1.831(14)	Fe(1)–C(9)–O(9)	127.5(8)
Fe(1)–C(2)	1.782(15)	Fe(1)–C(9)–S(1)	73.1(4)
Fe(1)–C(3)	1.785(15)	S(1)–C(9)–S(2)	106.4(6)
S(1)–C(9)	1.765(11)	Fe(1)–C(9)–S(2)	106.8(5)
Fe(2)–S(1)	2.272(3)	C(9)–S(2)–C(10)	103.8(6)
Fe(2)–S(2)	2.298(3)	Fe(2)–S(2)–C(10)	114.8(4)
Fe(2)–C(4)	1.762(14)	C(9)–S(2)–Fe(2)	80.7(3)
Fe(2)–C(5)	1.752(14)	Fe(2)–Fe(1)–S(1)	55.15(9)
Fe(2)–P	2.166(4)	Fe(2)–Fe(1)–C(9)	70.2(3)
S(2)–C(9)	1.819(11)	Fe(2)–Fe(1)–C(3)	161.2(4)
S(2)–C(10)	1.811(12)	Fe(1)–Fe(2)–S(1)	53.45(9)
C(11)–O(9)	1.439(13)	Fe(1)–Fe(2)–P	161.9(1)

product is obtained in good yield and without the disproportionation expected for an intermolecular reaction.

In the starting material **3** C(9) and $P(OMe)_3$ are bonded respectively to Fe(1) and Fe(2), but they are both linked to Fe(2) in the final product. Owing to the inability of $P(OMe)_3$ to migrate, this implies a movement of C(9) leading to the thermodynamically more stable compound **4**. The overall transformation **4** → **4** implies a shift of carbon from Fe(1) to Fe(2) but in the absence of characterized intermediates we cannot say exactly when it occurs. Consequently a detailed scheme for the successive steps leading from **3** to **4** remains a matter for speculation, but we suggest that the bond reorganizations occur via an intermediate such as 7 in which the carbon C(9) is a bridging ligand. A similar intermediate has been proposed to account for the redistribution of phosphite ligands in compounds analogous to **4** [13].



(**5** : L = CO , R^1 = C_4H_3S , R^2 = Me ;
6 : L = $P(OMe)_3$, R^1 = Ph , R^2 = Me)



(**7**)

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7 A solution of **1** in acetone containing 3 equiv. of $P(OMe)_3$ was stirred for 24 h under N_2 at 20 °C (quantitative transformation, 77% after crystallization). Electrolysis of **1** in acetone containing 5 equiv. of $P(OMe)_3$ and $LiClO_4$ (0.1 *M*) was carried out at a controlled potential (− 1.0 V SCE) in the dark and under N_2 with a mercury cathode. After 20 min the transformation was complete with the consumption of 0.05 e mole^{-1} (isolated yield 80%).

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12 A solution of **3** in toluene was refluxed under N_2 in the dark for 4 h (quantitative transformation, 82% isolated yield of **4**). Electrolysis of **3** in acetone/$LiClO_4$ (0.1 *M*) was carried out at a controlled potential (− 1.32 V SCE, in the dark and under N_2 at a mercury cathode). After 1 h and consumption of 0.6 e mole^{-1}, compound **4** was obtained in 64% yield (after crystallization). All the physical and spectroscopic data for **4** are identical with those of an authentic sample [11] (m.p. 117–118 °C, mixed m.p. undepressed).

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