Journal of Organometallic Chemistry, 353 (1988) 209–213
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Structural and Mössbauer investigations of some iron complexes containing both carbonyl and sulphur ligands

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(Received March 28th, 1988)

Abstract

A single crystal X-ray diffraction study has established that $[Fe(CO)_3\{(CF_3)_2C_2S_2\}]$ exists as a dimer in the solid state. Mössbauer parameters for this compound and its derivatives $[Fe(CO)_2(PPh_3)\{(CF_3)_2C_2S_2\}]$, $[Fe(CO)(PPh_3)_2\{(CF_3)_2C_2S_2\}]$ and $[Fe(CO)(dppe)\{(CF_3)_2C_2S_2\}]$ are reported, and compared with those of $[Fe_2(CO)_6(SPh)_3]PF_6$ and $[Fe_2(CO)_6(SPh)_2]$.

Introduction

Bis(perfluoromethyl)dithietene, $(CF_3)_2C_2S_2$, reacts with $Fe_2(CO)_9$ or $Fe(CO)_5$ to give the reactive tricarbonyl complex, $[Fe(CO)_3\{(CF_3)_2C_2S_2\}]$ [1–3]. This compound may be formulated as an iron(0) complex containing a dithioketone ligand or as an iron(II) complex containing a dithiolate ligand. The C=C stretching frequency in the complex is observed at 1481 cm^{-1} which is substantially lower than that of the free ligand (1622 cm^{-1}) suggesting that significant dithioketone character may be attributed to the ligand. Mass spectrometric measurements indicate that the complex is monomeric in the gas phase but solution molecular weight measurements in $CHCl_3$ indicate that association occurs in solution [3].

An X-ray diffraction study of $[Fe(CO)_3\{(CF_3)_2C_2S_2\}]$ has been carried out to establish the solid state structure of the complex. Mössbauer spectra have been recorded for this compound and some of its monomeric derivatives containing triphenylphosphine or 1,2-diphenylphosphinoethane (dppe) in place of CO in order to gain information on the electronic and local structure at the iron nucleii. The Mössbauer spectrum of $[Fe_2(CO)_6(SPh)_3]PF_6$ has also been recorded to provide a comparable example of an iron(II) complex with an approximately C_{3v} $\{(CO)_3S_3\}$ coordination environment, and $[Fe_2(CO)_6(SPh)_2]$ provides an example of an iron(I) complex with approximately C_s symmetry.

0022-328X/88/$03.50

Experimental

The complexes $[Fe(CO)_3\{(CF_3)_2C_2S_2\}]$, $[Fe(CO)_2(PPh_3)\{(CF_3)_2C_2S_2\}]$, $[Fe(CO)(PPh_3)_2\{(CF_3)_2C_2S_2\}]$, $[Fe(CO)(diphos)\{(CF_3)_2C_2S_2\}]$, $[Fe_2(CO)_6(SPh)_3]PF_6$ and $[Fe_2(CO)_6(SPh)_2]$ were prepared as previously described [1–4].

The iron-57 Mossbauer spectra were recorded for samples containing ca. 10 mg iron cm^{-2} with a microprocessor-controlled Mössbauer spectrometer at 298 K using a 25 mCi $^{57}Fe/Rh$ source. All the spectra were computer-fitted, and the chemical isomer shift data are quoted relative to metallic iron.

Crystal data for $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]$. $C_7F_6O_3S_2Fe$, $M = 366.04$; crystallises from dichloromethane/hexane as dark purple needles. Monoclinic, a 14.455(38), b 11.180(36), c 7.093(37) Å, β 90.30(5)°, U 1146 Å^3; D_m 2.08, D_c 2.121 g cm^{-3}, $Z = 4$, space group $P2_1/n$ (non-std. $P2_1/c$, C_{2h}^5, No. 14); Mo-K_α radiation (λ 0.71069 Å), μ(Mo-K_α) 17.42 cm^{-1}; $F(000) = 712$. Photographic data from $h(0-4)l$ and $hk(0-5)$ precession film packs; number of independent reflections 1119; absorption corrections not applied. Structure solution by heavy atom method and refinement by block-cascade, least squares. Disorder was found for one of the CF_3 groups in proportion 0.628/0.372; C_{3v} constraints were applied to each component. Final $R = 0.0937$. Thermal anisotropy for Fe and S; unit weighting scheme. Scattering factors from International Crystallographic Tables, Vol. 4. Computer program package SHELXTL(1984) on the Nova 3 *.

Discussion

The complex $[Fe(CO)_3\{(CF_3)_2C_2S_2\}]$ crystallises in the space group $P2_1/n$. Atomic coordinates are presented in Table 1 and selected bond distances and angles in Table 2. One of the CF_3 groups was found to be disordered (0.63/0.37), but the geometry of the iron coordination environment has been clearly defined. The complex is dimeric in the solid state, and contains a bridging system involving one S atom in each $(CF_3)_2C_2S_2$ ligand and the iron atom in the second $[Fe(CO)_3)\{(CF_3)_2C_2S_2\}]$ molecule, as shown in the Fig. 1. This arrangement gives the Fe atoms a coordination number of six, compared with that of five in monomeric $[Fe(CO)_3\{(CF_3)_2C_2S_2\}]$ or in the phosphine complexes $[Fe(CO)_2(PPh_3)\{(CF_3)_2C_2S_2\}]$, $[Fe(CO)(PPh_3)_2\{(CF_3)_2C_2S_2\}]$ and $[Fe(CO)(dppe)\{(CF_3)_2C_2S_2\}]$ [2,3]. Although the coordination geometry around iron is approximately octahedral, and broadly similar to that in $[Fe_2(CO)_6(SMe)_3]^+$, the bridging Fe–S(1)′ distance (2.33 Å) is slightly longer than the Fe–S(1) and Fe–S(2) distances (average 2.284 Å), whereas in $[Fe_2(CO)_6(SMe)_3]^+$ all three Fe–S distances are similar, with an average value of 2.304 Å. The C–C bond distances of 1.31 Å is consistent with an ethylene dithiolate structure for the ligand. The geometry at the bridging sulphur S(1) is, as expected, strongly pyramidalised; the iron deviates by 0.68 Å from the S_2C_2 plane. The carbonyls are linear. The iron–iron distance of 3.363 Å is in accord with the absence of any Fe–Fe interaction, as expected for an 18-electron iron(II) formulation for the complex. This distance may be compared to that of 2.537 Å in

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* Tables of anisotropic thermal vibrational parameters with esds., and lists of observed and calculated structure factors are available from the authors.

Table 1

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$)

Atom [b]	x	y	z	U_{eq} [a]
Fe(1)	3906(1)	553(2)	5093(3)	37(1)
S(1)	5344(3)	1140(3)	6046(5)	34(1)
S(2)	4224(3)	1424(4)	2250(7)	59(2)
F(1)	7153(10)	2755(18)	4266(25)	80(8)
F(2)	6277(17)	4228(10)	4801(33)	110(11)
F(3)	6587(12)	2980(16)	6907(18)	61(6)
F(4)	6144(6)	3352(15)	835(20)	166(9)
F(5)	5051(10)	4390(7)	1935(17)	118(6)
F(6)	4797(9)	3141(11)	−197(14)	111(6)
F(7)	5900(26)	3917(30)	5932(52)	124(17)
F(8)	6956(21)	2628(33)	6301(42)	100(17)
F(9)	6820(25)	3565(39)	3698(38)	118(15)
O(1)	3217(11)	2925(13)	6084(29)	123(8)
O(2)	2158(8)	−390(14)	3495(25)	109(7)
O(3)	3462(9)	−431(12)	8825(18)	70(5)
C(1)	3477(14)	2050(16)	5797(36)	91(9)
C(2)	2809(11)	−1(16)	4132(30)	68(7)
C(3)	3655(10)	−79(14)	7451(24)	41(5)
C(4)	5576(9)	2320(13)	4408(20)	34(4)
C(5)	6392(9)	3098(11)	5114(17)	70(8)
C(6)	5110(10)	2411(12)	2828(21)	38(5)
C(7)	5283(8)	3336(11)	1329(18)	59(7)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. [b] Fluorine atoms F(1)–F(3) and F(7)–F(9) comprise the trifluoromethyl groups of higher (0.628) and lower (0.372) occupancies respectively.

Table 2

Selected bond lengths (Å) and angles (°)

Fe(1)–S(1)	2.279(10)	Fe(1)–S(2)	2.288(11)
Fe(1)–C(1)	1.854(20)	Fe(1)–C(2)	1.832(19)
Fe(1)–C(3)	1.853(18)	Fe(1)–S(1a)	2.328(10)
S(1)–C(4)	1.791(16)	S(2)–C(6)	1.738(17)
O(1)–C(1)	1.067(24)	O(2)–C(2)	1.129(23)
O(3)–C(3)	1.088(21)	C(4)–C(5)	1.547(20)
C(4)–C(6)	1.309(21)	C(6)–C(7)	1.505(20)
S(1)–Fe(1)–S(2)	87.2(3)	S(1)–Fe(1)–C(1)	88.1(7)
S(2)–Fe(1)–C(1)	85.6(8)	S(1)–Fe(1)–C(2)	174.1(7)
S(2)–Fe(1)–C(2)	89.6(7)	C(1)–Fe(1)–C(2)	96.6(9)
S(1)–Fe(1)–C(3)	91.4(5)	S(2)–Fe(1)–C(3)	177.2(6)
C(1)–Fe(1)–C(3)	91.9(9)	C(2)–Fe(1)–C(3)	91.9(8)
S(1)–Fe(1)–S(1a)	84.9(3)	S(2)–Fe(1)–S(1a)	86.8(3)
C(1)–Fe(1)–S(1a)	169.8(7)	C(2)–Fe(1)–S(1a)	90.0(6)
C(3)–Fe(1)–S(1a)	95.6(5)	Fe(1)–S(1)–C(4)	101.1(5)
Fe(1)–S(1)–Fe(1a)	95.1(3)	C(4)–S(1)–Fe(1a)	106.5(5)
Fe(1)–S(2)–C(6)	102.3(6)	Fe(1)–C(1)–O(1)	175.3(23)
Fe(1)–C(2)–O(2)	176.3(15)	Fe(1)–C(3)–O(3)	176.4(15)
S(1)–C(4)–C(5)	110.4(9)	S(1)–C(4)–C(6)	121.0(11)
C(5)–C(4)–C(6)	128.5(13)	S(2)–C(6)–C(4)	121.9(12)
S(2)–C(6)–C(7)	113.2(10)	C(4)–C(6)–C(7)	124.9(13)

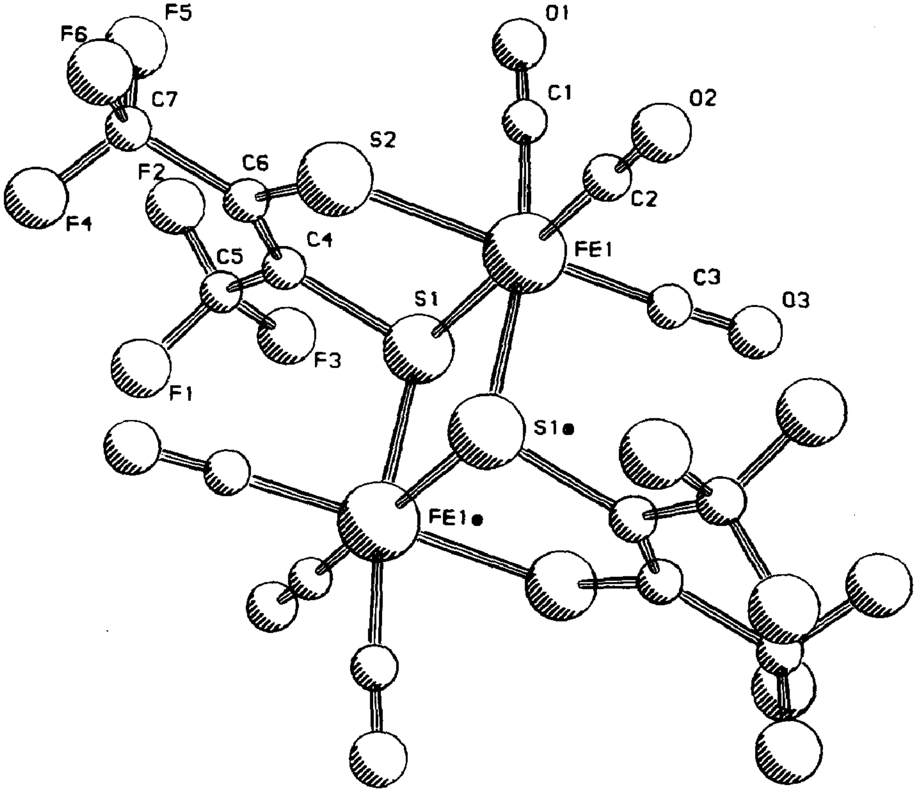

Fig. 1. The structure of $[Fe(CO)_3\{(CF_3)_2C_2S_2\}]_2$ showing the atom labelling.

$[Fe_2(CO)_6(SEt)_2]$ [5], which contains an Fe–Fe bond, and that of 3.062 Å in $[Fe_2(CO)_6(SMe)_3]^+$ [5], which contains non-bonded 18-electron iron(II) centres linked by three bridging MeS ligands.

The ^{57}Fe Mössbauer spectrum of the complex $[Fe(CO)_3\{(CF_3)_2C_2S_2\}]_2$ showed a single quadrupole split absorption with a chemical isomer shift (Table 3) characteristic [7] of low spin iron(II). The chemical isomer shift data for the monomeric derivatives containing triphenylphosphine or dppe in place of carbon monoxide

Table 3

^{57}Fe Mössbauer parameters obtained at 298 K for some iron carbonyl complexes containing thiolate ligands

Compound	$\delta \pm 0.01$ (mm. s^{-1})	$\Delta \pm 0.02$ (mm. s^{-1})
$[FE(CO)_3\{(CF_3)_2C_2S_2\}]_2$	−0.01	0.35 [a]
$[Fe(CO)_2(PPh_3)\{(CF_3)_2C_2S_2\}]$	−0.10	1.29 [b]
$[Fe(CO)(PPh_3)_2\{(CF_3)_2C_2S_2\}]$	0.00	1.18 [b]
$[Fe(CO)(dppe)\{(CF_3)_2C_2S_2\}]$	−0.10	1.45 [b]
$[Fe_2(CO)_6(SPh)_3]^{PF}_6$	0.01	0.26 [a]
$[Fe_2(CO)_6(SPh)_2]$	−0.04	1.09 [c]

[a] Iron with coordination number 6. [b] Iron with coordination number 5. [c] Iron(I) with near C_s local symmetry.

were all identical within the experimental errors, and not significantly different from those of the binuclear complexes [$Fe_2(CO)_6(SPh)_3$]PF_6 and [$Fe_2(CO)_6(SPh)_2$]. In contrast, the quadrupole splitting found for [$Fe(CO)_3\{(CF_3)_2C_2S_2\}$]$_2$ was smaller than that from the monomeric derivatives, and this is consistent with the results of the X-ray structural determination which showed the atoms in [$Fe(CO)_3\{(CF_3)_2C_2S_2\}$]$_2$ to be in near octahedral coordination sites. The Mössbauer parameters of the triply bridged dimer [$Fe_2(CO)_6(SPh)_3$]$^+$, which also contains six-coordinate iron(II) with essentially similar C_{3v} local symmetry [6] were very similar to those for [$Fe(CO)_3\{(CF_3)_2C_2S_2\}$]$_2$. The quadrupole splittings for iron in the monomeric derivatives [$Fe(CO)_2(PPh_3)\{(CF_3)_2C_2S_2\}$], [$Fe(CO)(PPh_3)_2\{(CF_3)_2C_2S_2\}$] and [Fe(CO)(diphos)$\{(CF_3)_2C_2S_2\}$] were larger, and consistent with a more distorted five-fold coordination for the iron(II) in these compounds. Of interest is the similarity between the Δ values for these compounds and for the iron(I) complex [$Fe_2(CO)_6(SPh)_2$], in which iron adopts near C_s symmetry.

It has been noted previously that the substitution of carbonyl by phosphine ligands in thiolate bridged binuclear iron compounds of this type causes little change in the isomer shift [8,9]. This may be due to the ability of the π-acid carbonyl ligands to compensate for changes in the donor properties of the coligands present [10,11]. In the case of [$Fe(CO)_3\{(CF_3)_2C_2S_2\}$]$_2$ phosphine substitution is accompanied by cleavage of the dimer to produce monomeric 5-coordinate iron complexes, and this is reflected in the substantial increase in the quadrupole splitting.

Acknowledgement

We are grateful to the SERC for their support (to J.S.).

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