Journal of Organometallic Chemistry, 385 (1990) 369–378
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20521

Metal complexation of thioacylferrocenes: crystal structures of pentacarbonyl(thiobenzoylferrocene-*S*)chromium and benzoylferrocene

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(Received October 4th, 1989)

Abstract

Acylferrocenes $(C_5H_5)Fe(C_5H_4COR)$ (R=CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$ or Ph) can be readily thionated to give thioacylferrocenes by use of P_4S_{10} in non-polar solvents such as CH_2Cl_2 or toluene; use of polar solvents such as THF or diglyme provides very poor conversions. Thiobenzoylferrocene reacts readily with $Et_4N^+[M(CO)_5I]^-$ (M = Cr, Mo, or W) in the presence of silver nitrate to yield $(C_5H_5)Fe[C_5H_4CPh\{SM(CO)_5\}]$, in which the $M(CO)_5$ group is bonded to the sulphur atom as revealed by an X-ray diffraction study. The structure consists of isolated molecules in which a $Cr(CO)_5$ fragment of approximate C_{4v} symmetry is bonded via sulphur to the thioacylferrocene with an Cr–S bond length of 2.412(1) Å, an S=C bond length of 1.667(2) Å and a C–S–Cr angle of 121.9(1)°. Photo oxidation of $(C_5H_5)Fe[C_5H_4CPh\{SM(CO)_5\}]$ yields benzoylferrocene the crystal structure of which was determined.

Introduction

An effective method for the stabilisation of otherwise unstable thiones involves their complexation, via the thione sulphur atom, to a soft, electron-rich metal fragment [1–3]. A particularly convenient method for the attachment of $M(CO)_5$ fragments (M = Cr, Mo, W) to such thiones has been developed by Pogorzelec and Reid [1]; in this the thione is treated with $Et_4N^+[M(CO)_5I]^-$ and silver nitrate in a

0022-328X/90/$03.50

two-phase solvent system, in reactions which, it has been suggested, proceed via the transient sixteen-electron intermediates $[M(CO)_5]$ [4]. We report here the application of this complexation reaction to some ferrocenyl thioketones, which are in general photolabile and difficult to crystallise in a manner suitable for X-ray crystallography; complexation to $[M(CO)_5]$ provides excellent crystals. We report here the crystal structure of pentacarbonyl(thiobenzoylferrocene-*S*)chromium, $(C_5H_5)Fe[C_5H_4CPh\{SCr(CO)_5\}](1)$ and that of the photodegradation product, benzoylferrocene (7).

Experimental

Infrared spectra were recorded on a Perkin Elmer model 1710 FTIR instrument. Proton NMR spectra were recorded in $CDCl_3$ solutions, at ambient temperature on a Bruker WP-80 or an AM-300 spectrometer.

The salts $Et_4N^+[M(CO)_5I]^-$ were prepared by reaction [5] of Et_4NI with $M(CO)_6$ in butanol. The acyl ferrocenes were prepared and purified by standard methods. Diethyl ether and CH_2Cl_2 were dried by refluxing with sodium benzophenone ketyl and calcium hydride, respectively.

Thionation of acylferrocenes

In a typical reaction, benzoylferrocene (10 g, 0.034 mol) was dissolved in a mixture of CH_2Cl_2 (20 cm^3) and diethyl ether (250 cm^3). Sodium hydrogencarbonate (17 g, 0.207 mol) and tetraphosphorus decasulphide (72.3 g, 0.163 mol) were added, and the mixture was heated under reflux for 3 hours. The mixture was then cooled and filtered and the filtrate was reduced to small volume and chromatographed on alumina. Elution with CH_2Cl_2 gave a purple fraction, which on evaporation yielded thiobenzoylferrocene (8.28 g, 79%) as deep purple needles, m.p. 71–72 °C. Found: C, 66.3; H, 4.9. $C_{17}H_{14}FeS$ calcd.: C, 66.7; H, 4.6%. ^1H NMR ($CDCl_3$): δ 4.18 (s, 5H, C_5H_5); 4.85 (t, 2H) and 5.10 (t, 2H), C_5H_4; 7.2–7.8 (m, 5H, C_6H_5). Infrared: ν_{max} (cm^{-1}), 1244 (C=S).

The following were made similarly as deep purple oils:

(a) Thioacetylferrocene: δ_H 2.87 (s, 3H, CH_3); 4.19 (s, 5H); 4.72 (m, 2H) and 5.03 (m, 2H); ν(C=S), 1289 cm^{-1}.

(b) Thiopropionylferrocene: δ_H 1.35 (t, *J* 7Hz, 3H, CH_3); 3.06 (q, *J* 7 Hz, 2H, CH_2); 4.15 (s, 5H); 4.70 (m, 2H) and 5.04 (m, 2H); ν(C=S), 1266 cm^{-1}.

(c) Thio(2-methylpropionyl)ferrocene: δ_H 1.28 (d, *J* 6.5Hz, 6H, CH_3); 3.60 (septet, *J* 6.5Hz, 1H, CH); 4.11 (s, 5H); 4.67 (m, 2H) and 5.01 (m, 2H); ν(C=S), 1262 cm^{-1}.

(d) Thio(2,2-dimethylpropionyl)ferrocene: δ_H 1.47 (s, 9H, CH_3); 4.12 (s, 5H); 4.65 (m, 2H) and 5.10 (m, 2H), ν(C=S), 1217 cm^{-1}.

Reactions of thiobenzoylferrocene with $[M(CO)_5I]^-$ (M=Cr, Mo, W)

In a typical reaction, a mixture of thiobenzoylferrocene (0.61 g, 2.00 mmol) and tetraethylammonium pentacarbonyliodochromate(0) (1.00 g, 2.20 mmol) was stirred with CH_2Cl_2 (80 cm^3) until a homogeneous solution was formed. Aqueous silver nitrate (8.8 cm^3 of a 0.25 mol dm^{-3} solution; 2.20 mmol) was added to the mixture, with exclusion of light, and the two-phase system was stirred for 24 hours. The organic layer was then separated, dried, and filtered. The CH_2Cl_2 solution was reduced to small volume and chromatographed on silica. Elution with CH_2Cl_2 gave a blue fraction, which upon crystallisation yielded pentacarbonyl(thiobenzoylferrocene-*S*)chromium (**1**) (0.63 g, 66%) as black needles. Found: C, 53.5; H, 2.5. $C_{22}H_{14}CrFeO_5S$ calcd.: C, 53.0; H, 2.8%. Infrared: ν_{max} (cm^{-1}). (CCl_4): 2061s, 1988m, 1950vs, 1932s.

In a similar manner were prepared:

(a) Pentacarbonyl(thiobenzoylferrocene-*S*)molybdenum (**2**) (58%), as black needles; found: C, 49.2; H, 2.5. $C_{22}H_{14}FeMoO_5S$ calcd.: C, 48.6; H, 2.6%. Infrared: ν_{max}(cm^{-1}), CCl_4 solution; 2069s, 1986m, 1952vs, 1927s.

(b) Pentacarbonyl(thiobenzoylferrocene-*S*)tungsten (**3**) (84%), also as black needles; found: C, 41.9; H, 2.4. $C_{22}H_{14}FeO_5SW$ calcd.: C, 41.9; H, 2.2%. Infrared: ν_{max} (cm^{-1}) (CCl_4): 2068s, 1981s, 1945vs, 1925s.

X-ray crystallography

Crystals suitable for X-ray examination were grown from solutions in CH_2Cl_2/light petroleum. Prior to the X-ray studies, the crystals were re-examined (m.p., microanalysis) to make sure that they were of the same materials as those obtained previously from CH_2Cl_2 alone; they were found to be identical.

Crystal data

Compound **1**. $C_{22}H_{14}CrFeO_5S$, $M = 498.26$, triclinic, a 9.058(7), b 10.040(7), c 12.568(8)Å, α 113.70(5), β 93.42(6), γ 95.25(6)°, V 1036.4(12)Å^3, space group $P\bar{1}$ (No. 2), $Z = 2$, D_c 1.59 g cm^{-3}, μ (Mo–K_α) 13.34 cm^{-1}, λ 0.71069 Å, $F(000) = 500$.

Compound **7**. $C_{17}H_{14}FeO$, $M = 290.15$, monoclinic, a 6.09(6), b 15.145(7), c 14.263(4) Å, β 105.9(1)°, V 1265.2(5)Å^3, space group $P2_1/c$ (No. 14), $Z = 4$, D_c 1.52 g cm^{-3}, μ(Mo–K_α) 11.10 cm^{-1}, λ 0.71069 Å, $F(000) = 592$.

Data collection

Compound **1**. A crystal of dimensions 0.20 × 0.32 × 0.76 mm was used. Cell dimensions were determined by least-squares refinement using the setting angles of 25 reflections in the range $12° \leq \theta \leq 16°$. Intensity data were collected at 22°C on a Nicolet P3 diffractometer with graphite-monochromated Mo–K_α radiation, in the $\omega/2\theta$ scan mode; ω-scan rate 2.4–2.8° min^{-1}; ω-scan width 1.2–1.4°; the maximum value of 2θ was 60°. 6084 reflections were measured, of which 6083 were unique, and 4945 had $F \geq 2\sigma(F)$. Lorentz and polarisation corrections were made: the data were also corrected for absorption.

Compound **7**. A crystal of dimensions 0.42 × 0.17 × 0.13 mm was used. Intensity data were collected at 22°C using STADI-2 diffractometer with graphite monochromated Mo–K_α radiation in the $\omega/2\theta$ scan mode: the maximum value of 2θ was 50°. 1983 reflections were measured, of which 1837 were unique, and 1652 had $F \geq 3\sigma(F)$. Lorentz and polarisation corrections, but no absorption correction, were made.

Structure solution and refinement

The structures were solved by direct methods, followed by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located and were included in the final refinements with grouped isotropic temperature factors, one for the hydrogen atoms on each ring.

Table 1

Compound **1**. Coordinates $\times 10^4$ for non-hydrogen atoms with e.s.d.'s in parentheses, $U_{eq} \times 10^3$ ^{a}

	x	y	z	U_{eq}
Fe(1)	2389(1)	6469(1)	2006(1)	35(1)
Cr(2)	8002(1)	1038(1)	2167(1)	36(1)
C(1)	2484(5)	4862(4)	385(3)	69(1)
C(2)	2063(4)	6101(5)	280(3)	72(1)
C(3)	3203(5)	7246(4)	860(3)	76(1)
C(4)	4318(4)	6730(5)	1309(3)	77(1)
C(5)	3891(5)	5252(5)	1026(3)	78(1)
C(6)	1178(3)	7900(2)	3159(2)	33(1)
C(7)	2598(3)	7864(3)	3724(2)	39(1)
C(8)	2655(3)	6421(3)	3622(2)	48(1)
C(9)	1319(3)	5546(3)	2990(3)	49(1)
C(10)	407(3)	6430(3)	2684(2)	41(1)
C(11)	712(2)	9140(2)	2985(2)	31(1)
C(12)	1663(2)	10569(3)	3583(2)	35(1)
C(13)	2276(3)	11300(3)	2950(3)	47(1)
C(14)	3147(4)	12658(4)	3532(4)	64(1)
C(15)	3367(4)	13271(4)	4720(4)	76(1)
C(16)	2783(4)	12568(4)	5362(3)	68(1)
C(17)	1940(3)	11181(3)	4805(2)	49(1)
S(18)	−888(1)	8950(1)	2180(1)	41(1)
C(19)	9431(3)	1515(3)	1292(2)	43(1)
O(20)	10245(3)	1828(3)	751(2)	65(1)
C(21)	6915(3)	−280(3)	726(3)	49(1)
O(22)	6279(3)	−1022(3)	−149(2)	76(1)
C(23)	6542(3)	551(3)	3033(2)	44(1)
O(24)	5664(2)	287(3)	3548(2)	68(1)
C(25)	9077(3)	2458(3)	3598(2)	42(1)
O(26)	9637(3)	3385(2)	4426(2)	61(1)
C(27)	6963(3)	2534(3)	2154(3)	50(1)
O(28)	6352(3)	3500(3)	2179(2)	79(1)

^{a} $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 2

Compound **1**. Bond distances (Å)

Fe(1)–C(1)	2.041(3)	Fe(1)–C(6)	2.042(2)
Fe(1)–C(2)	2.047(4)	Fe(1)–C(7)	2.032(2)
Fe(1)–C(3)	2.037(5)	Fe(1)–C(8)	2.051(3)
Fe(1)–C(4)	2.042(4)	Fe(1)–C(9)	2.056(4)
Fe(1)–C(5)	2.038(4)	Fe(1)–C(10)	2.036(3)
C(1)–C(2)	1.386(7)	C(6)–C(7)	1.442(4)
C(2)–C(3)	1.393(5)	C(7)–C(8)	1.409(4)
C(3)–C(4)	1.367(7)	C(8)–C(9)	1.413(4)
C(4)–C(5)	1.390(7)	C(9)–C(10)	1.409(5)
C(1)–C(5)	1.400(6)	C(6)–C(10)	1.441(3)
C(6)–C(11)	1.442(4)	Cr(2)–C(19)	1.896(3)
C(11)–C(12)	1.482(3)	Cr(2)–C(21)	1.904(3)
C(12)–C(13)	1.389(5)	Cr(2)–C(23)	1.911(3)
C(13)–C(14)	1.395(4)	Cr(2)–C(25)	1.921(2)
C(14)–C(15)	1.360(7)	Cr(2)–C(27)	1.850(4)
C(15)–C(16)	1.367(7)	C(19)–O(20)	1.138(4)
C(16)–C(17)	1.404(4)	C(21)–O(22)	1.133(3)
C(12)–C(17)	1.403(4)	C(23)–O(24)	1.132(4)
C(11)–S(18)	1.667(2)	C(25)–O(26)	1.130(3)
S(18)–Cr(2)	2.412(1)	C(27)–O(28)	1.150(5)

Table 3

Compound **1**. Selected bond angles (°)

C(1)–C(2)–C(3)	107.6(4)	C(12)–C(13)–C(14)	119.9(3)
C(2)–C(3)–C(4)	108.8(4)	C(13)–C(14)–C(15)	119.7(4)
C(3)–C(4)–C(5)	108.2(3)	C(14)–C(15)–C(16)	121.4(3)
C(4)–C(5)–C(1)	107.7(4)	C(15)–C(16)–C(17)	120.5(4)
C(5)–C(1)–C(2)	107.7(3)	C(16)–C(17)–C(12)	118.3(3)
C(6)–C(7)–C(8)	107.7(2)	C(17)–C(12)–C(13)	120.1(2)
C(7)–C(8)–C(9)	108.8(3)	C(11)–S(18)–Cr(2)	121.9(1)
C(8)–C(9)–C(10)	108.7(3)	S(18)–Cr(2)–C(19)	94.8(1)
C(9)–C(10)–C(6)	107.7(2)	S(18)–Cr(2)–C(21)	86.5(1)
C(10)–C(6)–C(7)	107.0(2)	S(18)–Cr(2)–C(23)	85.5(1)
C(7)–C(6)–C(11)	125.7(2)	S(18)–Cr(2)–C(25)	96.6(1)
C(10)–C(6)–C(11)	126.8(2)	S(18)–Cr(2)–C(27)	174.1(1)
C(6)–C(11)–C(12)	117.8(2)	Cr(2)–C(19)–O(20)	177.1(3)
C(6)–C(11)–S(18)	119.9(2)	Cr(2)–C(21)–O(22)	177.2(4)
C(12)–C(11)–S(18)	122.3(2)	Cr(2)–C(23)–O(24)	178.6(3)
C(11)–C(12)–C(13)	120.9(2)	Cr(2)–C(25)–O(26)	173.8(3)
C(11)–C(12)–C(17)	119.9(3)	Cr(2)–C(27)–O(28)	177.5(3)

For compound **1** the weighting scheme $w = 1.3944/[\sigma^2(F) + 0.000508(F^2)]$ gave final R and R_w values of 0.049 and 0.051, with 317 refined parameters. For compound **7**, the weighting scheme $w = 2.7310/[\sigma^2(F) + 0.000608(F^2)]$ gave final

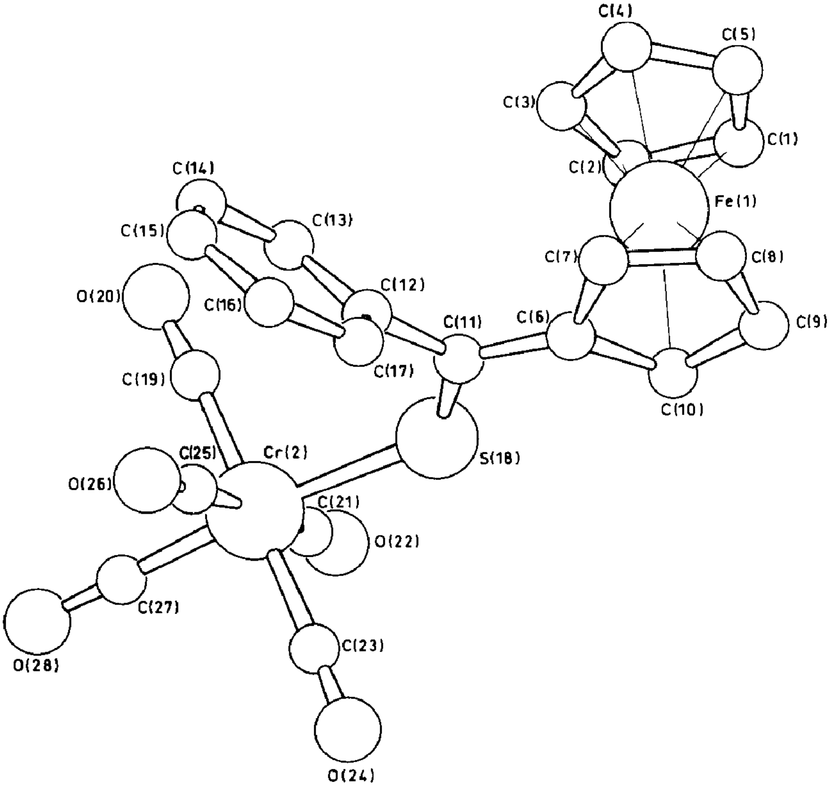


Fig. 1. Perspective view of the molecule of pentacarbonyl(thiobenzoylferrocene-*S*)chromium (1), showing the atom numbering scheme.

Table 4

Compound **7**. Coordinates $\times 10^4$ for non-hydrogen atoms with e.s.d.'s in parentheses, $U_{eq} \times 10^3$

	x	y	z	U_{eq}
Fe(1)	3557(1)	4596(1)	2330(1)	37(1)
C(1)	3614(13)	3289(4)	2015(4)	64(2)
C(2)	5629(11)	3680(4)	1989(4)	58(2)
C(3)	5196(11)	4355(4)	1294(4)	55(2)
C(4)	2866(11)	4376(4)	861(4)	54(2)
C(5)	1825(11)	3725(4)	1297(5)	64(2)
C(6)	2223(9)	5766(3)	2581(3)	38(1)
C(7)	4614(9)	5785(3)	2931(3)	40(1)
C(8)	5318(9)	5117(3)	3642(4)	41(1)
C(9)	3385(9)	4673(3)	3735(4)	46(1)
C(10)	1467(9)	5059(4)	3095(4)	42(1)
C(11)	643(9)	6325(3)	1873(4)	47(1)
C(12)	1392(8)	6928(3)	1194(3)	37(1)
C(13)	35(9)	7656(3)	848(4)	50(1)
C(14)	592(11)	8223(4)	192(4)	60(2)
C(15)	2446(11)	8054(4)	−145(4)	56(2)
C(16)	3784(9)	7337(3)	193(4)	47(1)
C(17)	3271(8)	6772(3)	868(4)	41(1)
O(18)	−1346(7)	6318(3)	1851(4)	81(1)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

R and R_w values of 0.059 and 0.069, with 179 refined parameters. Scattering factor data were taken from refs. 6–8. All calculations were performed on a Prime 6350 computer using SHELX-76 [9], SHELXS [10], and XANADU [11]. Molecular drawings were made with PLUTO [12].

Final refined coordinates for compound **1** are given in Table 1, and selected bond lengths and angles in Tables 2 and 3: a perspective view, showing the atom numbering scheme is in Fig. 1. Final refined coordinates for compound **7** are given

Table 5

Compound **7**. Bond distances (Å)

Fe(1)–C(1)	2.032(7)	Fe(1)–C(6)	2.022(6)
Fe(1)–C(2)	2.022(8)	Fe(1)–C(7)	2.023(6)
Fe(1)–C(3)	2.031(9)	Fe(1)–C(8)	2.042(6)
Fe(1)–C(4)	2.049(7)	Fe(1)–C(9)	2.038(7)
Fe(1)–C(5)	2.043(8)	Fe(1)–C(10)	2.015(8)
C(1)–C(2)	1.372(10)	C(6)–C(7)	1.405(7)
C(2)–C(3)	1.398(8)	C(7)–C(8)	1.413(7)
C(3)–C(4)	1.384(9)	C(8)–C(9)	1.393(8)
C(4)–C(5)	1.406(9)	C(9)–C(10)	1.398(7)
C(5)–C(1)	1.436(8)	C(10)–C(6)	1.443(8)
C(12)–C(13)	1.384(7)	C(6)–C(11)	1.460(7)
C(13)–C(14)	1.380(9)	C(11)–C(12)	1.491(8)
C(14)–C(15)	1.366(10)	C(11)–O(18)	1.203(7)
C(15)–C(16)	1.364(8)		
C(16)–C(17)	1.387(8)		
C(17)–C(12)	1.369(8)		

Table 6

Compound 7. Selected bond angles (°)

C(1)-C(2)-C(3)	109.8(5)	C(6)-C(7)-C(8)	108.7(5)
C(2)-C(3)-C(4)	107.8(6)	C(7)-C(8)-C(9)	108.5(4)
C(3)-C(4)-C(5)	108.5(5)	C(8)-C(9)-C(10)	108.2(5)
C(4)-C(5)-C(1)	107.0(6)	C(9)-C(10)-C(6)	108.4(5)
C(5)-C(1)-C(2)	107.0(6)	C(10)-C(6)-C(7)	106.2(4)
C(7)-C(6)-C(11)	131.1(5)	C(12)-C(13)-C(14)	120.2(6)
C(10)-C(6)-C(11)	122.7(5)	C(13)-C(14)-C(15)	120.1(5)
C(6)-C(11)-C(12)	122.9(5)	C(14)-C(15)-C(16)	119.7(6)
C(6)-C(11)-O(18)	118.8(6)	C(15)-C(16)-C(17)	120.7(6)
C(12)-C(11)-O(18)	118.3(5)	C(16)-C(17)-C(12)	119.8(5)
C(11)-C(12)-C(13)	117.4(5)	C(17)-C(12)-C(13)	119.3(5)
C(11)-C(12)-C(17)	123.2(4)		

in Table 4, and selected bond lengths and angles in Table 5 and 6: a perspective view, showing the atom numbering scheme is given in Fig. 2.

Tables of refined hydrogen coordinates, anisotropic temperature factors for non-hydrogen atoms have been deposited with the Cambridge Crystallographic Data Centre, and lists of observed and calculated structure factors are available from the authors.

Results and discussion

Acylferrocenes $(C_5H_5)Fe(C_5H_4COR)$ for $R = CH_3$, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$, or C_6H_5 were readily thionated to give the thioacyl derivatives $(C_5H_5)Fe(C_5H_4CSR)$ by use [13] of phosphorus pentasulphide in the presence of sodium hydrogencarbonate: after work-up, chromatography on alumina provided the thioacyl ferrocenes as deep purple oils (R = alkyl) or as low melting black-purple needles ($R = C_6H_5$). We found that the choice of solvent employed is critical for the

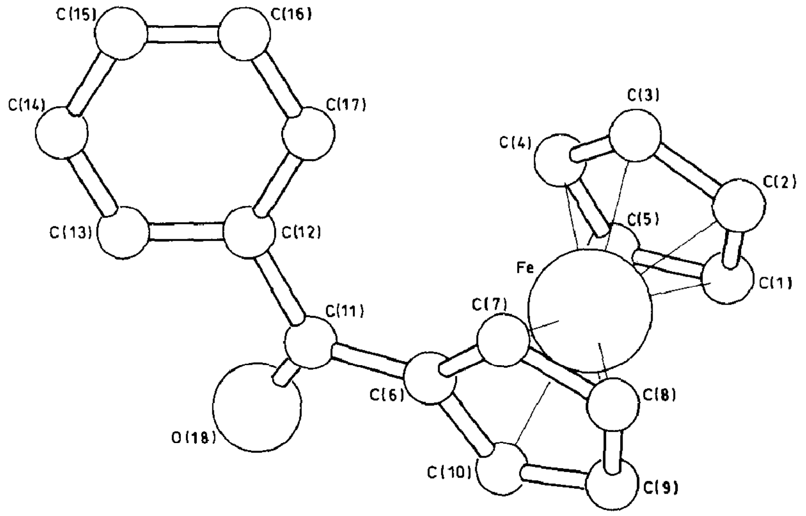
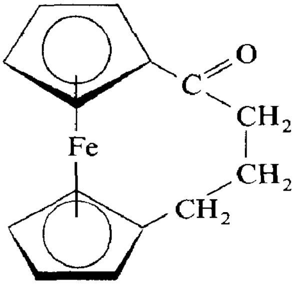


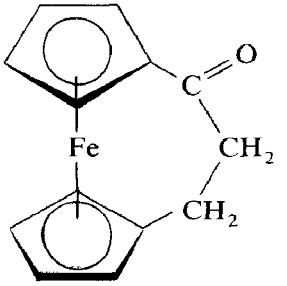
Fig. 2. Perspective view of the molecule of benzoylferrocene (7), showing the atom numbering scheme.

effectiveness of the thionation procedure for acylferrocenes. When dry benzene, toluene or CH_2Cl_2 was employed, good yields were obtained, but when one of the more polar solvents, such as THF or diglyme which have been recommended [13] for such thionations, was employed, the yields of thioacylferrocenes were poor: not only was unchanged starting material still present, but other unidentified impurities were also formed. With dry solvents of low polarity, satisfactory yields of pure thioacylferrocenes were readily achieved.

These compounds all have low melting points, and are readily photooxidised to give the parent acylferrocene as one product. In order to form crystalline derivatives suitable for X-ray study, we employed the reaction of $(C_5H_5)Fe(C_5H_4CSPh)$ with Et_4N^+ $[M(CO)_5I]^-$ and silver nitrate in a two-phase aqueous/CH_2Cl_2 system: work-up of the organic phase, followed by chromatography on silica gave good yields of compounds **1**–**3**: $(C_5H_5)Fe[C_5H_4CPh\{SM(CO)_5\}]$ M = Cr(**1**), Mo(**2**), and W(**3**), all readily crystallised from CH_2Cl_2 as black needles.



(9)



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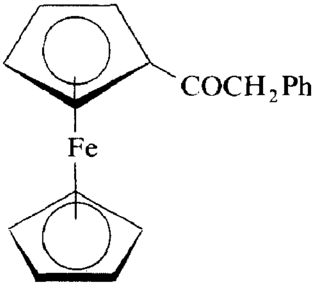

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Crystal and molecular structure of 7

The structure of benzoylferrocene **7** presents few unusual features. We note however that, as usual, the mean Fe–C distances for the two independent cyclopentadienyl rings are identical within experimental uncertainty: likewise there is no significant difference between the mean C–C distances in the substituted ring, 1.410 Å, and the unsubstituted ring, 1.399 Å. The structure of **7** thus resembles in this respect those of **10** and **11**, rather than those of **1** and **9**: no reason is obvious for this dichotomy of behaviour.

References

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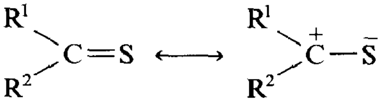
thioacylferrocene. The Cr(2)–S(18)–C(11) bond angle is 121.9(1)° and the Cr(2)–S(18) bond is almost eclipsed by the C(11)–C(12) bond (dihedral angle 10.2°) (see Fig. 1 for atom-numbering scheme). In a similar fashion, the C(11)–S(18) bond is almost eclipsed by the Cr(2)–C(25) bond (dihedral angle 18.8°). This conformation of the $Cr(CO)_5$ fragment relative to the thioacylferrocene fragment leads to some close non-bonded contacts between O(26) and C(16), 3.31 Å and between O(26) and C(17), 3.32 Å: these are both only a little greater than the sum, 3.2 Å of the Van der Waals radii [15]. These close contacts are presumably responsible for the small but significant bending of the Cr(2)–C(25)–O(26) fragment from linearity: the Cr–C–O bond angle is 173.8(3)°, compared with a mean bond angle for the other three equatorial ligands of 177.6° and an axial bond angle of 177.5°. Within the $Cr(CO)_5$ fragment the axial Cr–C and C–O bond lengths are 1.850(4) and 1.150(5) Å, respectively, compared with the mean values for the equatorial bonds of 1.908 and 1.134 Å, respectively. These values are consistent with much stronger metal–ligand π-bonding at the axial carbonyl ligand than at the equatorial carbonyls, confirming that thione ligands compete very poorly with carbonyls for metal π-electron density [2,16,17].

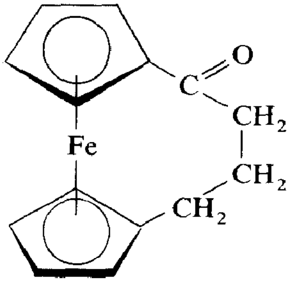
The Cr–S distance observed, 2.412(1) Å, lies almost mid-way between the values observed for $Cr(CO)_5SCMe_2$, 2.377(4) Å [16], and $Cr(CO)_5S(Et)CH_2Ph$, 2.458(2) Å [18], although it is very much shorter than the value of 2.510(2) Å found for $Cr(CO)_5SPMe_3$ [17]. The S=C bond length, S(18)–C(11) of 1.667(2) Å, while essentially identical to that found [2] in **4**, 1.68(1) Å, is significantly longer that the corresponding bond length, 1.618(8) Å in $Cr(CO)_5SCMe_2$ [16]. These differences may be rationalised in terms of the electronic nature of the substituents in the thione fragment. In both **1** and **4** the thione has one extremely electron rich substituent, the ferrocenyl group in **1** and the dihydro-4*H*-benzodithiole group in **4**: such groups readily stabilise the polar form **8b** at the expense of the doubly-bonded form **8a** of the thione.



(8a) **(8b)**

Consequently, in the presence of such electron donor substituents as R^1 and R^2, it may be expected that in complexes $R^1(R^2)CSM(CO)_5$ the unique C–S bond is longer than it is when $R^1 = R^2 = CH_3$: such thiones will also be poorer π-acceptors from $M(CO)_5$ than $(CH_3)_2CS$, so that the M–S bonds will likewise be longer when R^1 and R^2 are electron donors.

In the ferrocenyl fragment, the mean Fe–C distances for the two independent rings are identical within the experimental uncertainty: however the mean C–C distances within the two cyclopentadienyl rings are significantly different. In the unsubstituted ring the mean C–C distance is 1.387 Å, and in the substituted ring it is 1.423 Å. Such a difference between rings carrying or not carrying an acyl substituent has been observed previously in **9** [19], although not in **10** [20] or **11** [21].



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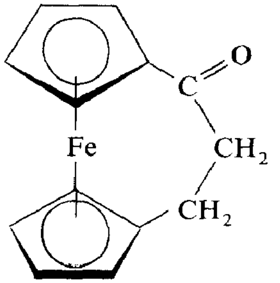

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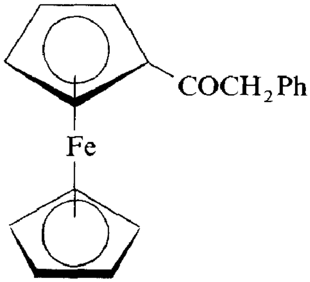

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