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Synthesis and Structure of the Ferrole Complex, $[Fe_2(CO)_6\{C_4(SMe)_4\}]$

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Ferroles have been studied fairly extensively and various methods for their preparation exist, but no complexes in which the ferrocyclopentadiene ring contains sulphur substituents have been prepared before [1]. One of the general methods for their preparation involves the reaction between an iron carbonyl compound, usually $Fe_3(CO)_{12}$, and an alkyne, and although 2,5-dithiahex-3-yne, MeSC≡CSMe, has been used in a reaction with $Fe_2(CO)_9$ before [2], no ferrole complex formed. The ferrole complex, $[Fe_2(CO)_6\{C_4(OMe)_4\}]$, resulted from the reaction of $Fe_2(CO)_9$ with MeOC≡COMe [1e], but reactions with other hetero-substituted acetylenes, e.g. $Et_2NC{\equiv}CNEt_2$, led to totally different types of compounds [3, 4].

We prepared the new ferrole, $[Fe_2(CO)_6\{C_4(SMe)_4\}]$, from the reaction between $Fe(CO)_5$ and MeSC≡CSMe (eqn. (1)).

$$Fe(CO)_5 + MeSC{\equiv}CSMe \xrightarrow{h\nu} [Fe_2(CO)_6\{C_4(SMe)_4\}] \qquad (1)$$

Experimental

General methods for working under nitrogen were followed. $Fe(CO)_5$ was used as purchased and MeSC≡CSMe prepared according to the published method [5], from sodium acetylide and MeSSMe in liquid ammonia. The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 200 and a 300 MHz Bruker instrument respectively, the infrared spectrum on a Perkin-Elmer 297 and the mass spectrum on a Finnigan Mat 8200.

$[Fe_2(CO)_6\{C_4(SMe)_4\}]$ was prepared by irradiating equimolar amounts of $Fe(CO)_5$ and MeSC≡CSMe in tetrahydrofuran for 2 h. The solvent was removed under reduced pressure and the title compound separated from a mixture of lower yield products by column chromatography at −10 °C with a mixture of CH_2Cl_2 and hexane (1:4) as eluent. The compound crystallized as orange needles and the yield was less than 5%. $M^+ - CO$: 488 (M^+ required for $Fe_2C_{14}H_{12}O_6S_4$: 516.19); ^1H NMR ($CDCl_3$, ppm relative to TMS): δ 2.58 and 2.57 (SCH_3); ^{13}C NMR ($CDCl_3$, −55 °C, ppm relative to TMS): δ 20.12 (SCH_3), 24.72 (SCH_3), 124.89 (Fe–C=*C*), 185.31 (Fe–*C*) 205.3, 208.7 and 209.5 (3s, *C*O): IR (nujol, cm^{-1}): 1940vw, 1960w, 1973m, 2010m, 2040s and 2075m.

X-ray Data

Crystallographic data and details of the structure determination are given in Table I.

TABLE I. Crystallographic Data for $[Fe_2(CO)_6\{C_4(SMe)_4\}]$ and Structure Determination Details

Crystal data	
Formula	$C_{14}H_{12}O_6S_4Fe_2$
Crystal habit	orange needles
Crystal size (mm)	0.04 × 0.04 × 0.25
Symmetry	triclinic, $P\bar{1}$
Unit cell determination: least-squares fit to	25 reflections, θ(Mo) < 20°
Unit cell dimensions	*a* 8.188(1) Å
	b 8.406(1) Å
	c 15.434(1) Å
	α 78.69(1)°
	β 79.14(1)°
	γ 75.36(1)°
Packing: V ($Å^3$), Z	997, 2
D_{calc} (g cm^{-3}), M, F(000)	1.720, 516.2, 520
Experimental data	
Diffractometer	Enraf Nonius CAD4
Radiation	Mo–Kα (0.71073 Å)
Monochromator	graphite
Collection mode	ω–2θ, scans, θ range: 3–30°
scan width	(0.50 + 0.35 tan θ)°
scan speed	variable, 4.1° min^{-1} maximum
Reflections measured	5806
Observable reflections	4450 with $F > 3\sigma$
Stability	3 reflections every 60 min no variation
Corrections	Lp, absorption
μ (cm^{-1})	18.0
Absorption corrections	empirical [6]
Solution and refinement	
Program used	SHELX76 [7]
Solution	heavy atom method
Refinement	least-squares, full matrix
Number of variables	236
Reflections used	4450 observed with $F > 3\sigma$
Weighting scheme	$w = (\sigma(F))^{-2}$
Final Δ peaks	0.9 e $Å^{-3}$ near the Fe atoms
Final R, R_w	0.039, 0.028
Scattering factors	International Tables for X-ray Crystallography [8]

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Results and Discussion

The ferrole compound prepared in this study has a fairly typical structure and contains a semi-bridging carbonyl ligand, which is a regular feature of this type of compound (Fig. 1). The fractional coordinates and temperature factors are given in Table II and the bond lengths and angles in Table III.

The Fe–Fe bond is fairly long (2.53 Å) compared with other semi-bridged ferroles, as are the Fe–C σ bonds (1.970 and 1.965 Å) and the Fe–C π bonds

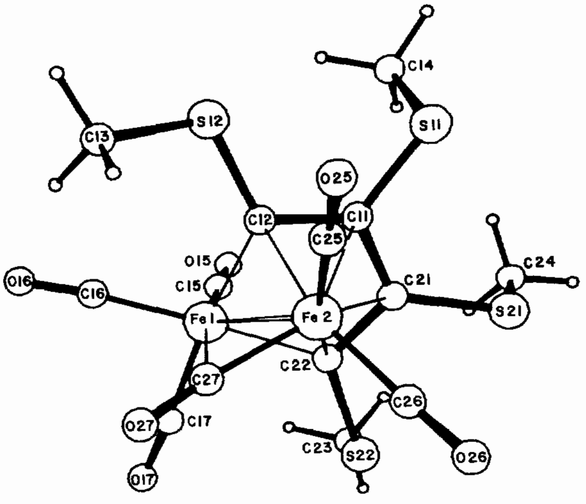

Fig. 1. Structure of $[Fe_2(CO)_6\{C_4(SMe)_4\}]$.

TABLE II. Fractional Coordinates ($\times 10^4$, $\times 10^5$ for Fe and S) and Equivalent Isotropic Temperature Factors ($Å^2$, $\times 10^3$, $\times 10^4$ for Fe and S) for the Non-H Atoms of Compound $[Fe_2(CO)_6\{C_4(SMe)_4\}]$

	x/a	*y/b*	*z/c*	U_{eq}
Fe(1)	28989(5)	–4158(5)	21868(3)	284(2)
Fe(2)	43235(5)	19090(5)	22302(3)	267(2)
S(11)	16296(12)	35011(11)	40642(6)	436(5)
S(12)	33860(12)	–3829(11)	43083(5)	412(4)
S(21)	8439(12)	52425(10)	20379(7)	462(5)
S(22)	19731(12)	26885(12)	5357(6)	444(5)
C(11)	2053(4)	2313(4)	3187(2)	31(1)
C(12)	2872(4)	574(3)	3247(2)	28(1)
C(13)	5320(5)	–1935(4)	4132(2)	55(2)
C(14)	–9(5)	2611(5)	4803(3)	69(3)
C(15)	768(4)	–606(4)	2535(2)	39(2)
C(16)	3847(4)	–2537(4)	2617(2)	37(2)
C(17)	3242(4)	–1066(4)	1094(2)	41(2)
C(21)	1682(4)	3075(3)	2307(2)	31(1)
C(22)	2190(4)	1941(4)	1676(2)	30(1)
C(23)	–42(5)	2303(6)	486(3)	73(3)
C(24)	–1318(5)	5361(6)	2343(5)	92(4)
C(25)	5645(4)	2123(4)	2980(2)	37(2)
C(26)	4984(4)	3547(4)	1412(2)	41(2)
C(27)	5790(4)	239(4)	1744(2)	36(2)
O(15)	–611(3)	–671(3)	2784(2)	64(2)
O(16)	4374(3)	–3923(3)	2829(2)	55(2)
O(17)	3442(4)	–1563(3)	435(2)	60(2)
O(25)	6465(3)	2285(3)	3466(2)	54(2)
O(26)	5442(3)	4588(3)	920(2)	58(2)
O(27)	6957(3)	–642(3)	1422(2)	50(1)

TABLE III. Bond Lengths (Å) and Angles (deg) for Compound $[Fe_2(CO)_6\{C_4(SMe)_4\}]$

Fe(1)–Fe(2)	2.533(1)	Fe(1)–C(12)	1.970(3)
Fe(1)–C(15)	1.764(3)	Fe(1)–C(16)	1.803(3)
Fe(1)–C(17)	1.825(3)	Fe(1)–C(22)	1.965(3)
Fe(1)–C(27)	2.505(3)		
Fe(2)–C(11)	2.144(3)	Fe(2)–C(12)	2.102(3)
Fe(2)–C(21)	2.129(3)	Fe(2)–C(22)	2.077(3)
Fe(2)–C(25)	1.787(3)	Fe(2)–C(26)	1.795(3)
Fe(2)–C(27)	1.788(3)	S(11)–C(11)	1.769(3)
S(11)–C(14)	1.804(4)	S(12)–C(12)	1.755(3)
S(12)–C(13)	1.793(3)	S(21)–C(21)	1.772(3)
S(21)–C(24)	1.726(4)	S(22)–C(22)	1.775(3)
S(22)–C(23)	1.778(4)	C(11)–C(12)	1.439(4)
C(11)–C(21)	1.436(4)	C(15)–O(15)	1.134(4)
C(16)–O(16)	1.140(3)	C(17)–O(17)	1.142(4)
C(21)–C(22)	1.429(4)	C(25)–O(25)	1.144(3)
C(26)–O(26)	1.131(4)	C(27)–O(27)	1.147(3)

Fe(2)–Fe(1)–C(12)	53.9(1)	Fe(2)–Fe(1)–C(15)	130.8(1)
C(12)–Fe(1)–C(15)	91.4(1)	Fe(2)–Fe(1)–C(16)	120.1(1)
C(12)–Fe(1)–C(16)	97.6(1)	C(15)–Fe(1)–C(16)	95.5(1)
Fe(2)–Fe(1)–C(17)	114.2(1)	C(12)–Fe(1)–C(17)	168.0(1)
C(15)–Fe(1)–C(17)	98.9(1)	C(16)–Fe(1)–C(17)	87.5(1)
Fe(2)–Fe(1)–C(22)	53.2(1)	C(12)–Fe(1)–C(22)	81.6(1)
C(15)–Fe(1)–C(22)	92.4(1)	C(16)–Fe(1)–C(22)	172.1(1)

(continued)

TABLE III. *(continued)*

C(17)–Fe(1)–C(22)	92.0(1)	Fe(1)–Fe(2)–C(11)	75.6(1)
Fe(1)–Fe(2)–C(12)	49.2(1)	C(11)–Fe(2)–C(12)	39.6(1)
Fe(1)–Fe(2)–C(21)	75.8(1)	C(11)–Fe(2)–C(21)	39.3(1)
C(12)–Fe(2)–C(21)	69.2(1)	Fe(1)–Fe(2)–C(22)	49.3(1)
C(11)–Fe(2)–C(22)	69.0(1)	C(12)–Fe(2)–C(22)	75.9(1)
C(21)–Fe(2)–C(22)	39.7(1)	Fe(1)–Fe(2)–C(25)	131.4(1)
C(11)–Fe(2)–C(25)	93.1(1)	C(12)–Fe(2)–C(25)	92.6(1)
C(21)–Fe(2)–C(25)	123.1(1)	C(22)–Fe(2)–C(25)	161.8(1)
Fe(1)–Fe(2)–C(26)	134.3(1)	C(11)–Fe(2)–C(26)	123.0(1)
C(12)–Fe(2)–C(26)	162.3(1)	C(21)–Fe(2)–C(26)	94.1(1)
C(22)–Fe(2)–C(26)	95.2(1)	C(25)–Fe(2)–C(26)	91.8(1)
Fe(1)–Fe(2)–C(27)	68.4(1)	C(11)–Fe(2)–C(27)	139.5(1)
C(12)–Fe(2)–C(27)	100.6(1)	C(21)–Fe(2)–C(27)	138.3(1)
C(22)–Fe(2)–C(27)	99.0(1)	C(25)–Fe(2)–C(27)	96.9(1)
C(26)–Fe(2)–C(27)	95.9(1)	C(11)–S(11)–C(14)	100.8(2)
C(12)–S(12)–C(13)	106.6(2)	C(21)–S(21)–C(24)	101.4(2)
C(22)–S(22)–C(23)	101.5(2)	Fe(2)–C(11)–S(11)	127.2(2)
Fe(2)–C(11)–C(12)	68.6(2)	S(11)–C(11)–C(12)	125.4(2)
Fe(2)–C(11)–C(21)	69.8(2)	S(11)–C(11)–C(21)	121.1(2)
C(12)–C(11)–C(21)	113.4(2)	Fe(1)–C(12)–Fe(2)	76.9(1)
Fe(1)–C(12)–S(12)	130.1(2)	Fe(2)–C(12)–S(12)	127.5(1)
Fe(1)–C(12)–C(11)	114.6(2)	Fe(2)–C(12)–C(11)	71.8(2)
S(12)–C(12)–C(11)	114.5(2)	Fe(1)–C(15)–O(15)	176.6(3)
Fe(1)–C(16)–O(16)	173.2(3)	Fe(1)–C(17)–O(17)	176.0(3)
Fe(2)–C(21)–S(21)	125.1(2)	Fe(2)–C(21)–C(11)	70.9(2)
S(21)–C(21)–C(11)	122.0(2)	Fe(2)–C(21)–C(22)	68.2(2)
S(21)–C(21)–C(22)	124.6(2)	C(11)–C(21)–C(22)	113.2(2)
Fe(1)–C(22)–Fe(2)	77.5(1)	Fe(1)–C(22)–S(22)	124.8(2)
Fe(2)–C(22)–S(22)	123.7(2)	Fe(1)–C(22)–C(21)	115.3(2)
Fe(2)–C(22)–C(21)	72.1(2)	S(22)–C(22)–C(21)	119.6(2)
Fe(2)–C(25)–O(25)	178.6(3)	Fe(2)–C(26)–O(26)	177.1(3)
Fe(2)–C(27)–O(27)	166.5(3)		

(2.077 Å, Fe2–C22; 2.102 Å, Fe2–C12; 2.144 Å, Fe2–C11; 2.129 Å, Fe2–C21). The bond lengths between the bridging carbonyl ligand and the iron atoms are regular (2.505 Å, Fe1–C27; 1.788 Å, Fe2–C27).

The ^{13}C NMR chemical shifts for the ferrocyclopentadiene ring of the new ferrole (125 and 185 ppm) are within the range of chemical shifts reported for other compounds [1a, 9]. The signals for the CO ligands (209.5, 208.7 and 205.3 ppm), have the 3:1:2 intensity pattern characteristic of this type of compound. The CO signals could not be observed above −25 °C. In the proton NMR spectrum, a very small difference in the chemical shifts for the two non-equivalent SMe groups was observed.

The infrared spectrum has a complex pattern in the ν(CO) region, which is normal for ferroles [1a], and the mass spectrum shows the consecutive loss of five CO units from the $M^+ - $ CO peak.

The compound is stable in air in the solid state, and in an inert atmosphere in solution. It is soluble in polar solvents (CH_2Cl_2, thf), but only slightly soluble in hydrocarbons (hexane).

Supplementary Material

Tables containing anisotropic temperature factors and calculated hydrogen positions are available from the authors on request.

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