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Diiron Complex with Three Bridging Silyl Substituents

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Abstract

The crystal structure of hexacarbonyl-μ-(chloromethylsilyl)-bis[μ-(dimethylsilyl)]diiron(*Fe—Fe*), [Fe$_2$(CH$_3$Cl-Si)(C$_2$H$_6$Si)$_2$(CO)$_6$], has been determined. The Fe—Fe distance is 2.705 (1) Å and the Fe—Si distances are 2.322 (3) Å. The combination of the sixfold screw axis and the uniqueness of the bridging SiMeCl moiety create rotational disorder within the unit cell.

Comment

The structure determination of the title compound, (I), was undertaken to establish its molecular structure. The title compound was synthesized *via* an apparent silylene-transfer reaction. Because of the low yield and low solubility, no spectroscopic evidence was available for any structural conclusions. However, crystals suitable for X-ray crystallography were available and the structure solution is given here.

(I)
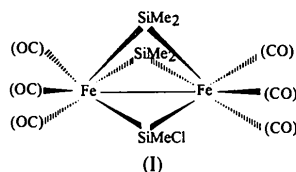
The structure of (I) is shown in Fig. 1, which illustrates the geometry of the structure as viewed down the Fe—Fe bond. Fig. 2 illustrates the packing of the title compound as viewed down a screw axis. The structure of (I) is similar to those of two other compounds which contain three Group 14 moieties bridging an Fe—Fe bond: Fe$_2$(CO)$_9$ (Cotton & Troup, 1974) and [Fe$_2$(μ-GeMe$_2$)$_3$(CO)$_3$] (Elder & Hall, 1969). Similarities are especially apparent with the latter compound. The Si and Ge compounds have similar unit-cell dimensions and both structures are solved in the centrosymmetric space group P6$_3$/m. The Fe—Fe bond distance in the silicon complex [2.705 (1) Å] is shorter than in the germanium complex [2.750 (11) Å]. Both Fe—Fe distances are significantly longer than that found in Fe$_2$(CO)$_9$ [2.523 (1) Å]. There is no lengthening of the Fe—Si bonds within the three-membered rings of (I) with respect to Fe—Si bonds in non-cyclic species. The Fe—Si distance of 2.322 (3) Å in (I) is well within the known range of Fe—Si single-bond distances (2.216–2.491 Å) (Lukevics, Pudova & Sturkovich, 1989; Sheldrick, 1989).
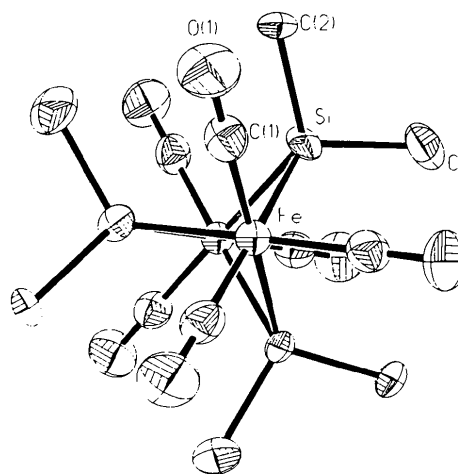
Fig. 1. Labeled ellipsoid diagram of (I). Displacement ellipsoids are drawn at the 50% probability level.
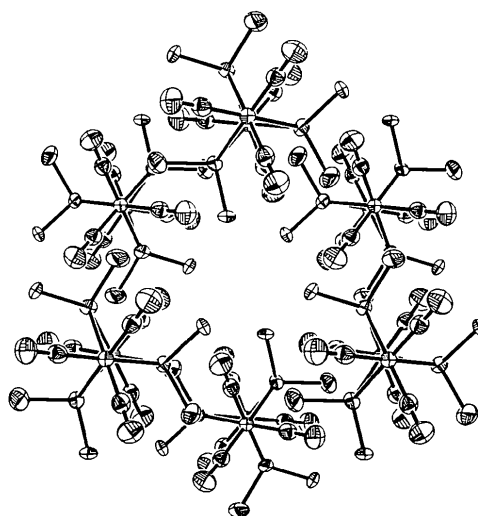
Fig. 2. Packing diagram of (I). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

For the preparation of the title compound, the compounds [(OC)₄FeSiMe₂]₂ and [(OC)₄Fe(H)(SiMe₂Cl)] (Schmid & Welz, 1979) were prepared according to the published procedures. The complex [(OC)₄FeSiMe₂]₂ (0.1 g, 0.22 mmol) was combined with excess [(OC)₄Fe(H)(SiMe₂Cl)] (0.12 g, 0.46 mmol) in 15 ml of hexane. The solution was irradiated for 3 h with a medium-pressure mercury lamp in a Pyrex vessel. The resulting red solution was filtered, removing $Fe_2(CO)_9$ as the major product. The volume of hexane was reduced to 5 ml *in vacuo*. Red needle crystals of (I) grew over a period of 30 days. Besides X-ray crystallography, no other methods of structural identification were available because of the low solubility and low yield.

Crystal data

[Fe₂(CH₃ClSi)(C₂H₆Si)₂-
(CO)₆]
$M_r = 474.6$
Hexagonal
$P6_3/m$
$a = 9.5660 (10)$ Å
$c = 12.042 (2)$ Å
$V = 954.3 (2)$ Å³
$Z = 2$
$D_x = 1.652$ Mg m⁻³

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
reflections
$\theta = 10–15°$
$\mu = 1.870$ mm⁻¹
$T = 291$ K
Needle
$0.3 \times 0.1 \times 0.1$ mm
Red

Data collection

Syntex $P2_1$ diffractometer
$2\theta–\theta$ scans
Absorption correction:
none
437 measured reflections
437 independent reflections
352 observed reflections
[$F > 4\sigma(F)$]

$\theta_{max} = 22.5°$
$h = -10 \rightarrow -1$
$k = 1 \rightarrow 8$
$l = 0 \rightarrow 12$
3 standard reflections
monitored every 97
reflections
intensity decay: <5%

Refinement

Refinement on F
$R = 0.0351$
$wR = 0.0429$
$S = 1.44$
352 reflections
44 parameters
$w = 1/[\sigma^2(F) + 99F^2]$
$(\Delta/\sigma)_{max} = 0.514$

$\Delta\rho_{max} = 0.50$ e Å⁻³
$\Delta\rho_{min} = -0.29$ e Å⁻³
Extinction correction: none
Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent
isotropic displacement parameters* (Å²)

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

	x	y	z	U_{eq}
Fe(1)	2/3	1/3	0.1377 (1)	0.030 (1)
Si(1)	0.4851 (3)	0.3619 (3)	1/4	0.037 (1)
Cl(1)†	0.4881 (6)	0.5718 (6)	1/4	0.071 (3)
C(1)	0.4941 (8)	0.1855 (8)	0.0650 (6)	0.043 (3)
C(2)	0.2604 (9)	0.2047 (10)	1/4	0.037 (4)
O(1)	0.3843 (6)	0.0921 (6)	0.0151 (5)	0.071 (3)

† Occupancy = 1/3Cl + 2/3C.

Table 2. *Selected geometric parameters* (Å, °)

Fe(1)—Si(1)	2.322 (2)	Si(1)—Cl(1)	1.994 (7)
Fe(1)—C(1)	1.777 (6)	Si(1)—C(2)	1.910 (7)
Fe(1)—Fe(1ⁱ)	2.705 (1)	C(1)—O(1)	1.152 (7)
Si(1)—Fe(1)—C(1)	85.9 (3)	C(1)—Fe(1)—C(1ⁱⁱⁱ)	97.8 (3)
Si(1)—Fe(1)—Fe(1ⁱ)	54.4 (1)	Fe(1)—Si(1)—Cl(1)	118.9 (1)
C(1)—Fe(1)—Fe(1ⁱ)	119.5 (2)	Fe(1)—Si(1)—C(2)	121.4 (3)
C(1)—Fe(1)—Si(1ⁱⁱ)	86.4 (3)	Cl(1)—Si(1)—C(2)	103.7 (4)
Si(1)—Fe(1)—Si(1ⁱⁱ)	89.5 (1)	Fe(1)—Si(1)—Fe(1ⁱ)	71.2 (1)
C(1)—Fe(1)—Si(1ⁱⁱⁱ)	173.9 (2)	Fe(1)—C(1)—O(1)	178.0 (7)

Symmetry codes: (i) $x, y, \frac{1}{2} - z$; (ii) $1 - y, -y+x, z$; (iii) $1 -x+y, 1 -x, z$.

The systematic absences 00l, $l = 3n + 1$, $3n + 2$, indicated either the space group $P6_3$ or $P6_3/m$. Structure solution in both $P6_3$ and $P6_3/m$ indicated that the higher symmetry space group was correct. The asymmetric unit consists of an OC—Fe—SiRR' fragment where R = C, and R' = 2/3(C) + 1/3(Cl). The Si, R, and R' atoms lie on the mirror plane at (x, y, 1/4). R was refined as C(2). R' was refined as Cl(1) with the occupancy fixed at 0.56863. The fixing of the occupancy of Cl(1) constitutes the disorder model used to accommodate the uniqueness of the SiMeCl moiety. Fe lies on a sixfold axis with atomic coordinates (2/3, 1/3, z). C(1) and O(1) of the carbonyl group are in general positions. H atoms were omitted from the final structure solution for three reasons: (*a*) they were not located on the difference map, (*b*) placement of H atoms in calculated positions did not improve the R value, and (*c*) inclusion of the H atoms would place H atoms on Cl(1). However, H atoms were included in the calculations of the density, absorption correction and molecular weight. All atoms were refined with anisotropic parameters and the R value is acceptable.

All calculations were performed using *SHELXTL-Plus* (Sheldrick, 1987).

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