

C(21)	0.0616 (10)	-0.0479 (5)	0.1283 (9)	0.038 (3)
C(22)	-0.0488 (9)	-0.0275 (5)	-0.0146 (9)	0.039 (3)
C(23)	-0.0441 (11)	-0.0507 (6)	-0.1425 (10)	0.048 (4)
C(24)	0.0690 (12)	-0.0903 (5)	-0.1303 (10)	0.040 (4)
C(25)	0.1853 (10)	-0.1106 (6)	0.0110 (9)	0.038 (4)
C(26)	0.1762 (11)	-0.0884 (5)	0.1373 (10)	0.041 (4)
C(27)	0.0582 (14)	-0.0250 (7)	0.2639 (12)	0.066 (6)
C(28)	-0.1757 (11)	-0.0290 (8)	-0.2916 (11)	0.072 (5)
C(29)	0.3164 (14)	-0.1522 (8)	0.0254 (16)	0.074 (7)
C(1)	0.7013 (3)	0.1948 (2)	0.1479 (3)	0.063 (1)
C(2)	0.5501 (3)	-0.0149 (2)	-0.1469 (3)	0.064 (1)
O(5)	0.4318 (12)	0.3342 (7)	0.5649 (14)	0.111 (7)
O(6)	0.1312 (14)	0.3553 (7)	0.5493 (15)	0.125 (8)
O(7)	0.8359 (12)	0.3074 (7)	0.4140 (4)	0.111 (7)
O(8)	0.5919 (18)	0.3753 (8)	0.4177 (15)	0.126 (9)

Table 2. Selected geometric parameters (Å, °)

Ru(1)—S(1)	2.335 (3)	Ru(1)—S(2)	2.394 (2)
Ru(1)—N(1)	2.138 (7)	Ru(1)—C(11)	2.240 (10)
Ru(1)—C(12)	2.230 (11)	Ru(1)—C(13)	2.237 (9)
Ru(1)—C(14)	2.247 (8)	Ru(1)—C(15)	2.196 (13)
Ru(1)—C(16)	2.228 (13)	Ru(2)—S(1)	2.401 (2)
Ru(2)—S(2)	2.348 (3)	Ru(2)—N(2)	2.144 (6)
Ru(2)—C(21)	2.222 (11)	Ru(2)—C(22)	2.178 (10)
Ru(2)—C(23)	2.200 (9)	Ru(2)—C(24)	2.202 (10)
Ru(2)—C(25)	2.193 (11)	Ru(2)—C(26)	2.180 (10)
S(1)—C(3)	1.855 (9)	S(2)—C(8)	1.845 (6)
N(1)—C(1)	1.458 (10)	C(1)—C(2)	1.540 (15)
C(1)—C(3)	1.530 (9)	C(2)—O(1)	1.308 (15)
C(2)—O(2)	1.194 (14)	C(3)—C(4)	1.531 (13)
C(3)—C(5)	1.542 (11)	N(2)—C(6)	1.485 (9)
C(6)—C(7)	1.518 (10)	C(6)—C(8)	1.539 (12)
C(7)—O(3)	1.209 (13)	C(7)—O(4)	1.327 (11)
C(8)—C(9)	1.534 (11)	C(8)—C(10)	1.521 (12)
S(1)—Ru(1)—S(2)	78.1 (1)	S(1)—Ru(1)—N(1)	81.4 (2)
S(2)—Ru(1)—N(1)	101.5 (2)	S(1)—Ru(2)—S(2)	77.7 (1)
S(1)—Ru(2)—N(2)	101.4 (2)	S(2)—Ru(2)—N(2)	80.8 (2)
Ru(1)—S(1)—Ru(2)	102.1 (1)	Ru(1)—S(1)—C(3)	100.6 (3)
Ru(2)—S(1)—C(3)	118.2 (3)	Ru(1)—S(2)—Ru(2)	102.0 (1)
Ru(1)—S(2)—C(8)	118.0 (3)	Ru(2)—S(2)—C(8)	101.1 (2)
Ru(1)—N(1)—C(1)	119.7 (5)	N(1)—C(1)—C(2)	107.5 (7)
N(1)—C(1)—C(3)	112.1 (7)	C(2)—C(1)—C(3)	111.9 (6)
C(1)—C(2)—O(1)	117.5 (9)	C(1)—C(2)—O(2)	120.4 (11)
O(1)—C(2)—O(2)	122.0 (12)	S(1)—C(3)—C(1)	106.4 (5)
S(1)—C(3)—C(4)	107.2 (7)	C(1)—C(3)—C(4)	113.3 (7)
S(1)—C(3)—C(5)	106.9 (6)	C(1)—C(3)—C(5)	111.6 (7)
C(4)—C(3)—C(5)	111.0 (6)	Ru(2)—N(2)—C(6)	120.4 (5)
N(2)—C(6)—C(7)	106.8 (6)	N(2)—C(6)—C(8)	110.2 (6)
C(7)—C(6)—C(8)	111.5 (6)	C(6)—C(7)—O(3)	122.3 (8)
C(6)—C(7)—O(4)	116.2 (8)	O(3)—C(7)—O(4)	121.4 (7)
S(2)—C(8)—C(9)	107.0 (4)	S(2)—C(8)—C(9)	107.7 (5)
C(6)—C(8)—C(9)	112.2 (7)	S(2)—C(8)—C(10)	106.6 (6)
C(6)—C(8)—C(10)	113.1 (6)	C(9)—C(8)—C(10)	109.9 (6)
Ru(1)—C(11)—C(12)	70.7 (6)		

All H atoms bonded to C atoms were included in calculated positions (C—H = 0.95 Å) with a single fixed isotropic displacement parameter (0.06 Å²). No other H atoms were located or included in the refinement.

Cell refinement and data collection: *XSCANS* (Fait, 1991). Data reduction and structure solution: *SHELXTL/PC* (Sheldrick, 1991). Refinement: *SHELX76* (Sheldrick, 1976) and *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC XP*.

GC thanks the SERC for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: HU1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Carter, L., Davies, D. L., Duffy, K. T., Fawcett, J. & Russell, D. R. (1994). *Acta Cryst.* **C50**, 1559–1561.
 Carter, L., Davies, D. L., Fawcett, J. & Russell, D. R. (1993). *Polyhedron*, **12**, 1599–1602.
 Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
 Sheldrick, G. M. (1991). *SHELXTL/PC*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, W. S. & Heeb, S. (1989). *J. Organomet. Chem.* **377**, 357–366.

Acta Cryst. (1995). **C51**, 580–582

The First Unsymmetrically Substituted Ring-Tilted Silicon-Bridged [1]Ferrocenophane

DANIEL A. FOUCHER, ALAN J. LOUGH,* IAN MANNERS, JOHN RASBURN AND JULIUS G. VANCSCO

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

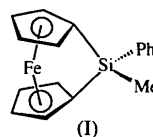
(Received 12 September 1994; accepted 19 October 1994)

Abstract

The structure analysis of the title compound, (1,1'-ferrocenediyl)methylphenylsilane, [Fe(C₁₇H₁₆Si)], is the first such study of an unsymmetrically substituted silicon-bridged [1]ferrocenophane. The strain present in this molecule results in a tilting of the cyclopentadienyl rings by 21.0 (2)° from being parallel.

Comment

As part of our overall program to investigate the structure/strain of [1]ferrocenophanes and the properties of poly(ferrocenylsilanes), we report here the first structural characterization of an unsymmetrically substituted silicon-bridged [1]ferrocenophane, [Fe{(η⁵-C₅H₄)₂SiMePh}], (I).



Although symmetrically substituted silicon-bridged [1]ferrocenophanes have been known for almost twenty years (Osborne & Whiteley, 1975; Stoeckli-Evans, Osborne & Whiteley, 1976; Finckh, Tang,

Foucher, Zamble, Ziembinski, Lough & Manners, 1993), the first report of unsymmetrical silicon-bridged [1]ferrocenophanes appeared only earlier this year (Foucher, Ziembinski, Petersen, Pudelski, Edwards, Ni, Massey, Jaeger, Vancso & Manners, 1994). Polymers prepared from unsymmetrical monomers of this type may lead to the preparation of syndiotactic or isotactic poly(ferrocenylsilanes) (Foucher *et al.*, 1994).

In a substituted silicon-bridged [1]ferrocenophane, the silicon group acts as a 'strap' between the cyclopentadienyl rings and imposes considerable strain upon the molecule. In the title molecule, the substituted bridging silicon group has a much smaller C(1)—Si—C(6) angle than expected [96.2(2)°] and a larger than expected C(11)—Si—C(17) angle [112.4(2)°]; this geometry at the Si atom in turn results in a tilt of the cyclopentadienyl rings towards the silicon bridge, giving an angle between the least-squares ring planes of 21.0(2)°. The ring tilt can also be seen with respect to the differences in the Fe—C distances of the ferrocene group, which range from 2.003(4) Å for the Fe—C(6) bond to 2.083(4) Å for the Fe—C(3) bond. Furthermore, the short Fe···Si non-bonded distance of 2.692(1) Å is indicative of a significant dative interaction, which may assist in stabilizing the ring-tilted structure. In addition, the displacement of the Fe atom from the midpoint of the two centroids of the cyclopentadienyl rings is only 0.218(4) Å. In comparison, the tetramethylethylene-bridged [2]ferrocenophane (Laing & Trueblood, 1965), which has a similar ring-tilt angle to that of the title compound and where no dative interaction is possible, has a much larger Fe displacement of 0.432(12) Å. The shorter Fe displacement in the title compound suggests that the Fe···Si interaction may play an important role in defining the degree of ring tilt in silicon-bridged [1]ferrocenophanes.

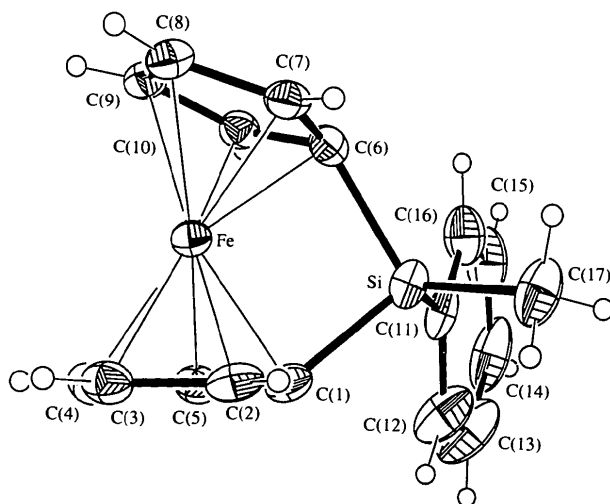


Fig. 1. A view of the title molecule with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 25% probability level. H atoms are shown as spheres of arbitrary radii.

Experimental

Details of the synthesis of the title compound have been published elsewhere (Foucher *et al.*, 1994).

Crystal data

[Fe(C₁₇H₁₆Si)]
M_r = 304.2
 Monoclinic
*P*2₁/*c*
a = 18.205(2) Å
b = 7.282(2) Å
c = 11.022(2) Å
 β = 100.62(2)°
V = 1436.2(5) Å³
Z = 4
D_x = 1.407 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 22 reflections
 θ = 6.2–18.1°
 μ = 1.116 mm⁻¹
T = 293(2) K
 Needle
 0.50 × 0.32 × 0.24 mm
 Reddish orange

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: ψ scans
 T_{\min} = 0.276, T_{\max} = 0.920
 3293 measured reflections
 2906 independent reflections

1968 observed reflections [*I* > 2σ(*I*)]
 R_{int} = 0.0229
 θ_{\max} = 26.3°
 h = 0 → 22
 k = -9 → 0
 l = -13 → 13
 3 standard reflections
 frequency: 120 min
 intensity decay: <4%

Refinement

Refinement on *F*
 R = 0.0399
 wR = 0.0468
 S = 1.55
 1968 reflections
 174 parameters
 H atoms riding
 $w = 1/[\sigma^2(F) + 0.0002F^2]$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$

Extinction correction: *SHELXTL/PC* (Sheldrick, 1990)
 Extinction coefficient: 0.00171(17)
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Fe	0.62845 (3)	0.05776 (6)	0.68328 (4)	0.0389 (2)
Si	0.7680 (1)	0.0470 (2)	0.6349 (1)	0.0521 (4)
C(1)	0.6865 (2)	0.2019 (5)	0.5776 (3)	0.049 (1)
C(2)	0.6186 (2)	0.1285 (5)	0.5032 (3)	0.056 (1)
C(3)	0.5559 (2)	0.1989 (5)	0.5465 (3)	0.057 (1)
C(4)	0.5821 (2)	0.3175 (5)	0.6473 (4)	0.057 (2)
C(5)	0.6612 (2)	0.3198 (5)	0.6657 (3)	0.050 (1)
C(6)	0.7196 (2)	-0.0964 (5)	0.7383 (3)	0.047 (1)
C(7)	0.6577 (2)	-0.2108 (5)	0.6817 (3)	0.051 (1)
C(8)	0.5993 (2)	-0.1943 (5)	0.7489 (3)	0.051 (1)
C(9)	0.6225 (2)	-0.0724 (5)	0.8482 (3)	0.052 (1)
C(10)	0.6959 (2)	-0.0131 (5)	0.8428 (3)	0.046 (1)
C(11)	0.8452 (2)	0.1842 (7)	0.7255 (4)	0.061 (2)
C(12)	0.8612 (3)	0.3569 (8)	0.6844 (5)	0.096 (2)
C(13)	0.9201 (4)	0.4609 (10)	0.7479 (6)	0.127 (3)
C(14)	0.9644 (3)	0.3920 (12)	0.8501 (7)	0.116 (3)

C(15)	0.9482 (3)	0.2275 (11)	0.8944 (6)	0.105 (3)
C(16)	0.8899 (3)	0.1219 (8)	0.8330 (4)	0.082 (2)
C(17)	0.7988 (3)	-0.0877 (7)	0.5103 (4)	0.083 (2)

Table 2. Selected geometric parameters (Å, °)

Fe—C(1)	2.007 (4)	Fe—C(8)	2.077 (4)
Fe—C(2)	2.026 (4)	Fe—C(9)	2.071 (4)
Fe—C(3)	2.083 (4)	Fe—C(10)	2.017 (3)
Fe—C(4)	2.080 (4)	Si—C(1)	1.879 (4)
Fe—C(5)	2.019 (4)	Si—C(6)	1.880 (4)
Fe—C(6)	2.003 (4)	Si—C(11)	1.858 (4)
Fe—C(7)	2.028 (4)	Si—C(17)	1.856 (5)
C(1)—Si—C(6)	96.2 (2)	C(11)—Si—C(17)	112.4 (2)
C(1)—Si—C(11)	109.3 (2)	Si—C(1)—C(2)	120.4 (3)
C(6)—Si—C(11)	111.5 (2)	Si—C(1)—C(5)	117.7 (2)
C(1)—Si—C(17)	113.3 (2)	Si—C(6)—C(7)	118.3 (3)
C(6)—Si—C(17)	113.2 (2)	Si—C(6)—C(10)	119.6 (3)

H atoms were placed in calculated positions (C—H 0.96 Å) and included in the refinement as riding atoms with a general isotropic displacement parameter which refined to 0.093 (4) Å².

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *XCAD-4 Software* (Siemens, 1993). Program(s) used to solve structure: *SHELXTL/PC XS* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC XLS*. Molecular graphics: *SHELXTL/PC XP*. Software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

This research was supported by NSERC Canada and the University of Toronto.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Enraf-Nonius (1989). *CAD-4 Software*. Version 5. Enraf-Nonius, Delft, The Netherlands.
- Finckh, W., Tang, B. Z., Foucher, D. A., Zamble, D. Z., Ziembinski, R., Lough, A. J. & Manners, I. (1993). *Organometallics*, **12**, 823–829.
- Foucher, D. A., Ziembinski, R., Petersen, R., Pudelski, J., Edwards, M. E., Ni, Y., Massey, J., Jaeger, C. R., Vancso, J. G. & Manners, I. (1994). *Macromolecules*, **27**, 3992–3999.
- Laing, M. B. & Trueblood, K. N. (1965). *Acta Cryst.* **19**, 373–381.
- Osborne, A. G. & Whiteley, R. H. (1975). *J. Organomet. Chem.* **101**, C27–C28.
- Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Siemens (1993). *XCAD-4 Software. Program to Extract Intensity Data from the Enraf-Nonius CAD-4 Program*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stoekli-Evans, H., Osborne, A. G. & Whiteley, R. H. (1976). *Helv. Chim. Acta*, **59**, 2402–2406. [Note: unit-cell parameter *a* reported as 14.18 (2) should be 14.81 (2) Å.]

Acta Cryst. (1995). **C51**, 582–584

The Twinned Crystal Structure of Bis(η⁶-mesitylene)ruthenium(II) Tetrafluoroborate at 150 K

ALEXANDER J. BLAKE, PAUL J. DYSON,
ROBERT O. GOULD,* BRIAN F. G. JOHNSON*
AND SIMON PARSONS

*Department of Chemistry, The University of Edinburgh,
West Mains Road, Edinburgh EH9 3JJ, Scotland*

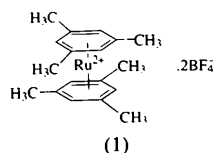
(Received 15 July 1994; accepted 6 September 1994)

Abstract

The title compound, [Ru(C₉H₁₂)₂]₂BF₄, forms cubic crystals twinned on (110). The [Ru(mesitylene)₂]²⁺ cation resides on a $\bar{3}$ special position and therefore adopts a staggered conformation.

Comment

There is considerable interest in the structures and properties of bis(η⁶-arene) complexes of the transition metals. Both the physical and chemical properties of these materials may be readily modified and this has led to their use as components in one-dimensional charge-transfer conductors. Bis(arene) complexes typically exhibit very low energy barriers to changes in the relative orientation of the arene ligands. The conformation that these complexes adopt is therefore subject to crystal packing forces and this furnishes a potential tool for the fine tuning of their properties. Bis(benzene)ruthenium(II) dications have been employed in several one-dimensional solids (Suravajjala, Polam & Porter, 1993) and we now report the crystal structure of its close relative, bis(η⁶-mesitylene)ruthenium(II) tetrafluoroborate, (1) (mesitylene is 1,3,5-trimethylbenzene), derived from a crystal twinned on (110).



In the solid state, compound (1) consists of discrete [Ru(mesitylene)₂]²⁺ cations (Fig. 1) and BF₄⁻ anions, with bond distances and angles as listed in Table 2. In common with many 1:2 salts, compound (1) adopts the fluorite structure (Fig. 2) with the site symmetries of the cation and anion reduced from *m* $\bar{3}$ *m* and $\bar{4}3m$ to $\bar{3}$ and 3, respectively. The cations thus adopt the same staggered conformation as in [Ru(mesitylene)₂]²⁺[C₆(CN)₆]²⁻, (2)