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Ferrocenyltriphenylsilane

Roger T. Palmer and Lewis J. Radonovich*

Department of Chemistry, University of North Dakota, Grand Forks, ND 58202-9024, USA

Fred B. McCormick*

3M Corporate Research Laboratories, St Paul, MN 55144-1000, USA

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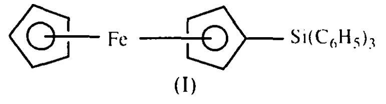
Abstract

The Fe atom of the title compound, 1-(triphenylsilyl)ferrocene, $[Fe(C_5H_5)\{C_5H_4Si(C_6H_5)_3\}]$, is symmetrically bonded to the two cyclopentadienyl ligands in an η^5 fashion and the two rings are within 2° of being parallel. The C atoms of the two cyclopentadienyl rings are within 1° of being eclipsed and the internal ring angle at the triphenylsilyl-substituted C atom is 2° smaller than other internal ring angles. The triphenylsilyl group occupies a steric volume similar to that of the ferrocenyl group.

Comment

The cyclopentadienyl ligand has played a central role in the development of organometallic chemistry. Recently, cyclopentadienyl ligands incorporating bulky substituents have received considerable attention as a means of modifying the reactivity of organometallic compounds (Janiak & Schumann, 1991). The present study was undertaken to assess the utility of the triphenylsilyl group as a bulky cyclopentadienyl substituent. The title compound, $[Fe(\eta^5\text{-}C_5H_5)\{C_5H_4Si(C_6H_5)_3\}]$, (I), was prepared from ferrocene as described by Benkeser, Goggin & Schroll (1954) and was recrystallized from hot heptane.



(I)

The atomic labeling scheme and a view down the Si(01)—C(01) bond vector are shown as *ORTEP*II (Johnson, 1971) diagrams in Figs. 1 and 2, respectively. The Fe atom is sandwiched between and is essentially equidistant from the two cyclopentadienyl rings, at an average perpendicular distance to the ring mean planes of 1.645 Å. Both cyclopentadienyl rings are planar to within 0.006 Å and are within 2° of being parallel. The ring C atoms are essentially eclipsed (rotation angle of < 1°).

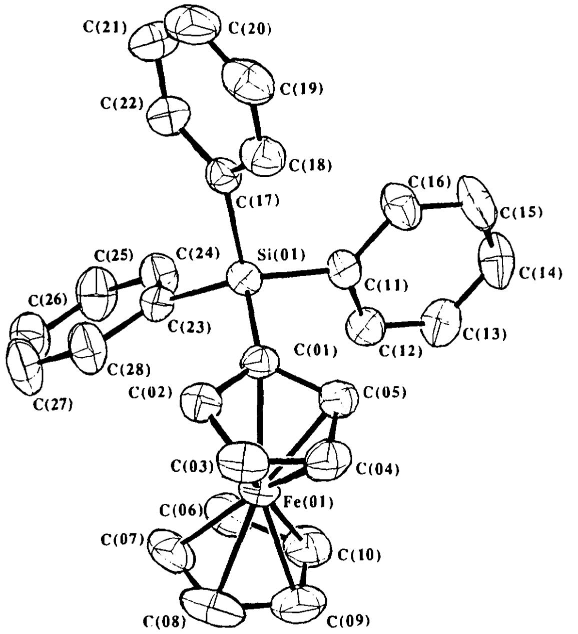


Fig. 1. An *ORTEP*II (Johnson, 1971) drawing of 1-(triphenylsilyl)ferrocene showing the atomic numbering scheme and displacement ellipsoids at 50% probability.

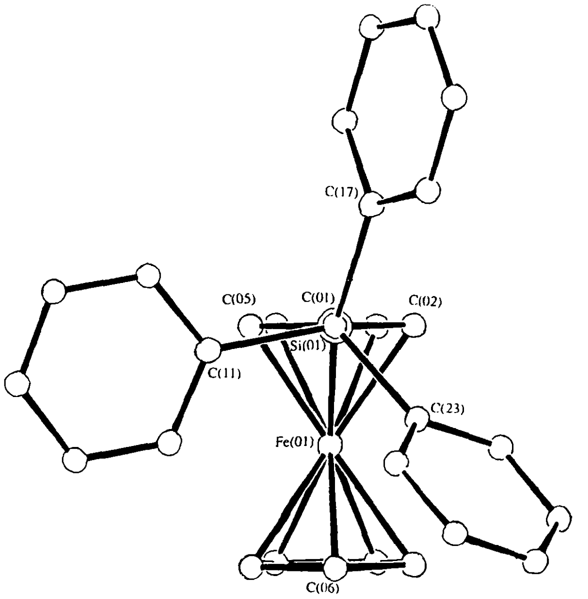


Fig. 2. An *ORTEP*II (Johnson, 1971) drawing of 1-(triphenylsilyl)ferrocene showing a view down the Si(01)—C(01) bond vector.

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The C(02)—C(01)—C(05) angle of 105.9 (2)° is more than 2° smaller than the other internal ring angles which average 108.2 (3)°. The Fe(01)—C(01) bond of 2.051 (2) Å is slightly longer that the remaining Fe—C bonds, which average 2.036 (5) Å. The triphenylsilyl group does not cause any other significant perturbations of the substituted cyclopentadienyl ligand. The steric volume of the triphenylsilyl group appears to be similar to that of the ferrocenyl group. The Si(01)—C(11) bond of the triphenylsilyl group lies close to the plane of the substituted cyclopentadienyl ring with a C(11)—Si(01)—C(01)—C(05) torsion angle of 10.6°. The Fe atom would thus appear to be effectively shielded from chemical approach on the triphenylsilyl side of the molecule. The structure of ferrocenyldiphenylsilane has been determined (Paton, Corey, Corey, Glick & Mislow, 1977) and is very similar to the present structure. The diphenylsilyl group of ferrocenyldiphenylsilane adopts a very similar conformation to the triphenylsilane group of the title compound, where the Si—H bond lies close to the substituted-cyclopentadienyl plane. In the unit cell of the title compound, there are no significant intramolecular contacts and the only intermolecular contact, between C(03) and H(24$^{\mathrm{i}}$) [symmetry code: (i) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$], is 0.12 Å shorter than a normal van der Waals contact (Bondi, 1964).

Experimental

(I) was synthesized by the method of Benkeser, Goggin & Schroll (1954) then recrystallized from hot heptane.

Crystal data

$[\mathrm{Fe}(\mathrm{C_5H_5})\{\mathrm{C_5H_4Si}(\mathrm{C_6H_5})_3\}]$
$M_r = 444.43$
Monoclinic
$P2_1/c$
$a = 9.468$ (2) Å
$b = 13.725$ (3) Å
$c = 17.341$ (4) Å
$\beta = 78.963$ (6)°
$V = 2211.79$ Å^3
$Z = 4$
$D_x = 1.33$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 17 reflections
$\theta = 9.53$–18.24°
$\mu = 0.745$ mm^{-1}
$T = 294$ K
Rectangular prism
0.32 × 0.30 × 0.30 mm
Orange

Data collection

Picker four circle diffractometer
θ–2θ scans
Absorption correction: analytical
$T_{\mathrm{min}} = 0.792$, $T_{\mathrm{max}} = 0.895$
6624 measured reflections
6046 independent reflections
3685 observed reflections [$I > 3\sigma(I)$]

$\theta_{\mathrm{max}} = 29.33°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = -22 \rightarrow 23$
3 standard reflections monitored every 97 reflections
intensity variation: <3% in 129.9 h

Refinement

Refinement on F
$R = 0.041$
$wR = 0.050$
$S = 1.594$
3685 reflections
272 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\mathrm{max}} = 0.027$
$\Delta\rho_{\mathrm{max}} = 1.26$ e Å^{-3}
$\Delta\rho_{\mathrm{min}} = -1.33$ 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* (Å^2)

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

	x	y	z	U_{eq}
Fe(01)	0.23333 (4)	0.46933 (3)	0.37169 (2)	0.0397 (2)
C(01)	0.0664 (3)	0.4599 (2)	0.3121 (1)	0.0350 (14)
C(02)	0.1638 (3)	0.3799 (2)	0.2926 (2)	0.0413 (16)
C(03)	0.1730 (3)	0.3282 (2)	0.3625 (2)	0.0529 (20)
C(04)	0.0814 (3)	0.3734 (2)	0.4258 (2)	0.0519 (19)
C(05)	0.0153 (3)	0.4541 (2)	0.3953 (2)	0.0422 (16)
C(06)	0.3400 (3)	0.5970 (2)	0.3434 (2)	0.0526 (20)
C(07)	0.4334 (3)	0.5176 (3)	0.3227 (2)	0.0603 (22)
C(08)	0.4375 (4)	0.4660 (3)	0.3917 (3)	0.0735 (28)
C(09)	0.3445 (4)	0.5126 (3)	0.4551 (2)	0.0717 (27)
C(10)	0.2857 (3)	0.5939 (2)	0.4242 (2)	0.0593 (22)
C(11)	−0.0946 (3)	0.6485 (2)	0.3140 (1)	0.0359 (15)
C(12)	−0.0257 (3)	0.7195 (2)	0.3508 (2)	0.0410 (16)
C(13)	−0.1017 (3)	0.7854 (2)	0.4030 (2)	0.0477 (18)
C(14)	−0.2493 (4)	0.7821 (2)	0.4197 (2)	0.0570 (21)
C(15)	−0.3202 (3)	0.7129 (3)	0.3843 (2)	0.0632 (22)
C(16)	−0.2438 (3)	0.6477 (2)	0.3316 (2)	0.0511 (19)
C(17)	−0.1134 (3)	0.4969 (2)	0.1878 (1)	0.0370 (15)
C(18)	−0.2080 (3)	0.4241 (2)	0.2199 (2)	0.0468 (18)
C(19)	−0.2991 (3)	0.3800 (2)	0.1771 (2)	0.0613 (23)
C(20)	−0.2955 (4)	0.4075 (3)	0.1006 (2)	0.0734 (28)
C(21)	−0.2052 (4)	0.4798 (3)	0.0676 (2)	0.0709 (27)
C(22)	−0.1141 (3)	0.5239 (2)	0.1101 (2)	0.0538 (20)
C(23)	0.1644 (3)	0.6120 (2)	0.1800 (1)	0.0365 (15)
C(24)	0.1571 (3)	0.7080 (2)	0.1566 (2)	0.0460 (17)
C(25)	0.2710 (3)	0.7524 (2)	0.1074 (2)	0.0548 (20)
C(26)	0.3947 (3)	0.7022 (3)	0.0806 (2)	0.0593 (21)
C(27)	0.4048 (3)	0.6064 (3)	0.1016 (2)	0.0648 (23)
C(28)	0.2904 (3)	0.5618 (2)	0.1503 (2)	0.0532 (19)
Si(01)	0.00903 (7)	0.55405 (5)	0.24783 (4)	0.0333 (4)

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

Fe(01)—C(01)	2.051 (2)	C(01)—Si(01)	1.854 (2)
Fe(01)—C(02)	2.041 (3)	C(02)—C(03)	1.422 (4)
Fe(01)—C(03)	2.034 (3)	C(03)—C(04)	1.406 (4)
Fe(01)—C(04)	2.041 (3)	C(04)—C(05)	1.423 (4)
Fe(01)—C(05)	2.037 (3)	C(06)—C(07)	1.406 (4)
Fe(01)—C(06)	2.036 (3)	C(06)—C(10)	1.398 (4)
Fe(01)—C(07)	2.033 (3)	C(07)—C(08)	1.397 (5)
Fe(01)—C(08)	2.029 (3)	C(08)—C(09)	1.422 (6)
Fe(01)—C(09)	2.034 (3)	C(09)—C(10)	1.399 (5)
Fe(01)—C(10)	2.043 (3)	C(11)—Si(01)	1.879 (3)
C(01)—C(02)	1.432 (4)	C(17)—Si(01)	1.871 (3)
C(01)—C(05)	1.433 (4)	C(23)—Si(01)	1.876 (3)
C(02)—C(01)—C(05)	105.9 (2)	C(06)—C(10)—C(09)	108.1 (3)
C(02)—C(01)—Si(01)	129.9 (2)	C(16)—C(11)—C(12)	116.8 (2)
C(05)—C(01)—Si(01)	124.2 (2)	C(18)—C(17)—C(22)	117.1 (3)
C(03)—C(02)—C(01)	108.9 (2)	C(24)—C(23)—C(28)	116.8 (2)
C(04)—C(03)—C(02)	108.4 (3)	C(01)—Si(01)—C(17)	109.1 (1)
C(03)—C(04)—C(05)	107.6 (3)	C(01)—Si(01)—C(23)	112.8 (1)
C(04)—C(05)—C(01)	109.3 (3)	C(01)—Si(01)—C(11)	107.0 (1)
C(10)—C(06)—C(07)	109.0 (3)	C(17)—Si(01)—C(23)	108.9 (1)
C(08)—C(07)—C(06)	107.1 (3)	C(17)—Si(01)—C(11)	108.8 (1)
C(07)—C(08)—C(09)	108.6 (3)	C(23)—Si(01)—C(11)	110.2 (1)
C(10)—C(09)—C(08)	107.2 (3)		

All programs used were those provided by *Crystal Logic* (Strouse, 1991) and all calculations were performed on a DEC 3100 computer. A 1 ml filter was used in the data collection. Standard deviations were calculated from counting statistics and included an instability factor of 0.04. Patterson and Fourier techniques were used to locate all atoms. Full-matrix isotropic refinement produced $R(F) = 0.097$ and $wR(F) = 0.126$. Anisotropic refinement of non-H atoms produced $R(F) = 0.057$ and $wR(F) = 0.082$. Theoretical H-atom positions (C—H = 0.95 Å) and absorption corrections from average pathlength calculations were included in the final cycles of refinement.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data, complete geometry and a view of the unit cell have been deposited with the IUCr (Reference: CR1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Isothiocyanatobis(1,10-phenanthroline)-copper(II) Perchlorate, $[Cu(NCS)(phen)_2]ClO_4$

O. Jerry Parker, Jamie L. Manson
and Gary L. Breneman

Department of Chemistry and Biochemistry, MS#74, Eastern Washington University, Cheney, WA 99004, USA

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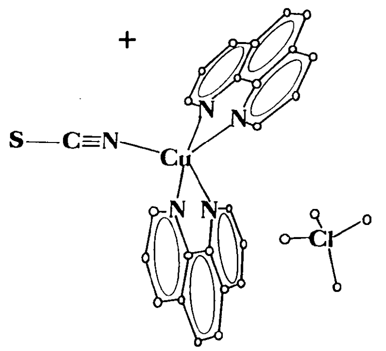
Abstract

The crystal structure of $[Cu(NCS)(C_{12}H_8N_2)_2]ClO_4$, containing a five-coordinate copper(II) atom with a distorted trigonal-bipyramidal $[Cu^{II}N_5]$ core, is reported. The Cu—NCS distance is 2.005 (5) Å with Cu bonded to the N-atom end of the isothiocyanate, while the Cu—N distances to the 1,10-phenanthrolines average 2.069 (4) Å for the equatorial positions and 2.002 (4) Å for the axial positions. The geometry is distorted from trigonal bipyramidal stereochemistry because the N—Cu—N angles of the 1,10-phenanthrolines average only 80.5 (2)°. The axial N and Cu atoms are almost linear with an angle of 174.8 (2)°. The isothiocyanate chain is approximately linear [178.7 (5)°] and bent at 166.1 (5)° from the Cu atom. This is the first report of a five-coordinate copper(II) complex containing a nitrogen-bonded thiocyanate ligand.

Comment

The stereochemistry of five-coordinate copper(II) shows molecular conformations ranging from a slightly distorted trigonal-bipyramidal (Greiner, Breneman, Parker & Willett, 1994) to a distorted square-pyramidal arrangement (Hathaway & Murphy, 1980; Harrison, Kennedy, Power, Sheahan & Hathaway, 1981). The determination of the molecular and crystal structure of $[Cu(NCS)(phen)_2]ClO_4$, (I), was initiated in order to study the bond and angle distortions displayed by five-coordinate copper(II) when one of the ligands is a bulky isothiocyanate group.



(I)

An *ORTEP* (Johnson, 1965) plot of the complex with the H atoms omitted and the numbering system indicated is shown in Fig. 1. The packing of the complex in a unit cell is shown as a stereoscopic plot in Fig. 2.

The average Cu—N(phen) distances of 2.069 (4) Å for equatorial and 2.002 (4) Å for axial positions are comparable to those reported for $[Cu(CN)(phen)_2]NO_3.H_2O$ [2.112 (10) and 2.000 (10) Å, respectively (Anderson, 1975)], $[CuCl(phen)_2]ClO_4$ [2.107 (6) and 1.995 (6) Å, respectively (Boys, Escobar & Martínez-Carrera, 1981)], $[CuCl(phen)_2]NO_3.H_2O$ [2.112 (4) and 1.989 (4) Å, respectively (Boys, 1988)] and $[CuBr(phen)_2]ClO_4$ [2.091 (3) and 1.985 (5) Å, respectively (Greiner, Breneman, Parker & Willett, 1994)]. The Cu—N(NCS) distance is 2.005 (4) Å with Cu bonded to the N-atom end of the isothiocyanate chain, with a slight bend for Cu—N1—C1 [166.1 (5)°]. The isothiocyanate moiety is very nearly linear [178.7 (5)°]. The N1—C1 and S—C1 distances [1.138 (6) and 1.629 (6) Å, respectively] of the isothiocyanate are virtually identical

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