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(*SR*,1*R*,2*S*)-1-(*tert*-Butylsulfinyl)-2-(hydroxymethyl)ferrocene

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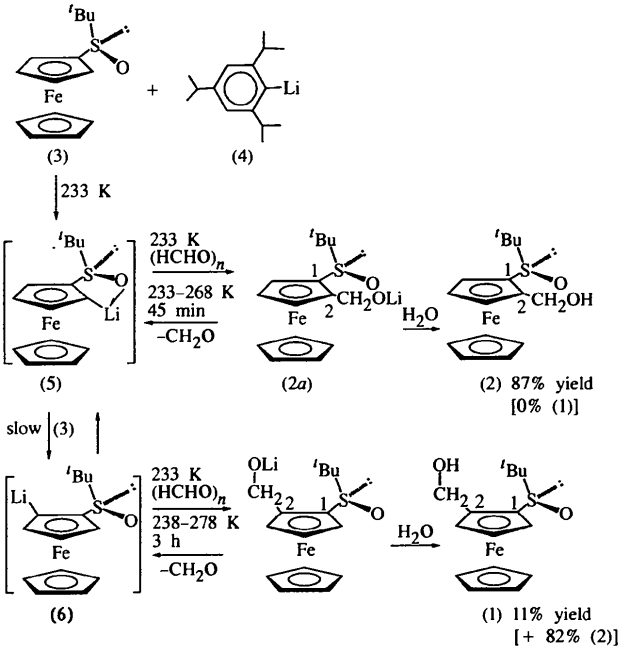
Abstract

From the reaction of (*SR*)-(–)-*tert*-butylsulfinylferrocene with (2,4,6-triisopropylphenyl)lithium followed by paraformaldehyde, the title compound, [Fe(C_5H_5)($C_{10}H_{15}O_2S$)], was obtained as an unexpected by-product along with the major product, (*SR*,1*S*,2*R*)-2-(*tert*-butylsulfinyl)-ferrocenylmethanol. The absolute structure of this by-product could not be ascertained *via* NMR, but it was characterized by X-ray diffraction as (*SR*,1*R*,2*S*)-2-(*tert*-butylsulfinyl)ferrocenylmethanol, a diastereoisomer of the major product. The two cyclopentadienyl rings are rotated away from one another by 25.5 (5)° (from an eclipsed form towards a *gauche* form), in contrast to the mutually eclipsed rings generally found in monosubstituted ferrocenes. Hydrogen bonding between sulfoxide O atoms and hydroxyl H atoms produces infinite one-dimensional chains.

Comment

The regioselective deprotonation of (*SR*)-(–)-*tert*-butylsulfinylferrocene, (3), with (2,4,6-triisopropylphenyl)-lithium, (4), provides (*SR*,1*R*,2*S*)-1-(*tert*-butylsulfinyl)-2-lithioferrocene, (5), which reacts with electrophiles to provide a facile and convenient method for the enantioselective synthesis of bidentate ferrocenes with a sulfur-containing substituent (Hua *et al.*, 1996). When the electrophile was paraformaldehyde in this process, (*SR*,1*R*,2*S*)-1-(*tert*-butylsulfinyl)-2-(hydroxymethyl)-ferrocene, (2), was isolated in 87% yield [based on reacted (3)] in 45 min. The same reaction with paraformaldehyde carried out at a slightly higher temperature over a 3 h period provided (2) [82% yield based on reacted (3)], along with one of its diastereomers, (1) [11% yield based on reacted (3)]. While the complete structure of (2) was previously determined (Hua *et al.*, 1996), that of (1) remained to be solved. Since this could not be ascertained from ^1H and ^{13}C NMR spectroscopy, an X-ray diffraction study was undertaken.



The X-ray structure of (1) with the atom numbering is shown in Fig. 1. Since the configuration at the S atom would be the same as that of substrate (3), *i.e.* *SR*, the absolute structure of (1) was assigned (*SR*,1*R*,2*S*)-1-(*tert*-butylsulfinyl)-2-(hydroxymethyl)ferrocene and was established by this analysis.

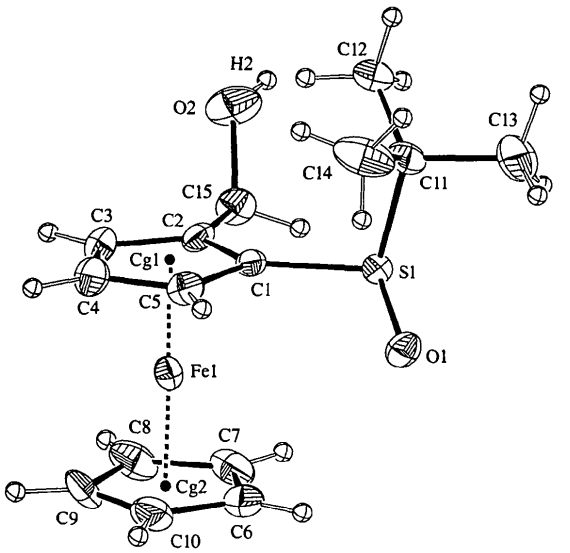


Fig. 1. The molecular structure and atom-numbering scheme for (1) with displacement ellipsoids at the 30% probability level. *Cg*1 and *Cg*2 are cyclopentadienyl-ring centroids. H atoms are shown as unlabeled isotropic spheres of arbitrary radii.

Mean C—C bond distances for the substituted and unsubstituted cyclopentadienyl rings are 1.421 (7) and 1.401 (10) Å, respectively, and the mean Fe—C distance is 2.035 (6) Å. The S1—O1 and C1—C5 bond lengths of 1.504 (4) and 1.430 (7) Å, respectively, are longer than the corresponding bonds of 1.492 (6) and 1.371 (9) Å reported for 1-(*tert*-butylsulfinyl)-2-methylferrocene by Rebiere, Riant, Ricard & Kagan (1993), but the C2—C15 bond length of 1.493 (7) Å is shorter than the distance of 1.54 (1) Å reported by that group for the corresponding bond of their methylferrocene compound. The distances from the Fe1 atom to the centroids of the cyclopentadienyl rings, *Cg*1 and *Cg*2, are 1.631 (2) and 1.656 (3) Å, respectively, and the *Cg*1—Fe1—*Cg*2 angle is 178.79 (13)°. The angle C1—S1—C11 of 101.2 (3)° is slightly larger than the C—S—C angle of dimethyl sulfoxide (100°; Bastiansen & Viervoll, 1948). The mean value of the five torsion angles C1—*Cg*1—*Cg*2—C6 through C5—*Cg*1—*Cg*2—C10 is 25.5 (5)°, indicating that the two cyclopentadienyl rings are significantly rotated with respect to one another. This conformation differs from the mutually eclipsed rings reported for monosubstituted ferrocenes by Ferguson, Glidewell & Scott (1995). The angle between the two cyclopentadienyl ring planes is 1.4 (3)°.

Hydrogen bonding between the sulfinyl O1 atom of one molecule and the hydroxyl H2 atom of an adjacent molecule related by a unit-cell translation, leads to infinite one-dimensional molecular chains extending in the **c** direction. The hydrogen-bond geometry is given in Table 1.

In a separate experiment, compound (1) was formed in high yield from the reaction of (*SR*,1*S*,2*R*)-*tert*-butylsulfinyl-2-lithioferrocene, (6), with paraformaldehyde. This result, in light of the fact that it is formed only slowly and as the minor product when (3) is the substrate, suggests that (6) is slowly generated from proton exchange between compound (5) and residual (3). It is also possible that compound (2*a*), the $-CH_2OLi$ form of (2), undergoes a reversible reaction back to (5), thereby continually providing (6) and, therefore, (1). These pathways are illustrated in the scheme above.

Experimental

Formation and isolation of compound (1): to a cold (195 K) solution of (2,4,6-triisopropylphenyl)lithium, (4) [prepared from the reaction of 0.38 mmol of 1-bromo-2,4,6-triisopropylbenzene with 0.7 mmol of *tert*-butyllithium (1.7 *M* solution in pentane) for 2.5 h], in 1 ml of THF under argon was added *via* cannula a cold (195 K) solution of 101 mg (0.35 mmol) of (*SR*)-(−)-*tert*-butylsulfinylferrocene, (3) [$[\alpha]_D^{22} = -357.8°$ (c = 0.505, $CHCl_3$), 100% optically pure; literature $[\alpha]_D^{22} = -339°$ (c = 0.505, $CHCl_3$) (Diter, Samuel, Taudien & Kagan, 1994)] in 2 ml of THF. This solution was maintained at 233 K for 2.5 h and a cold (233 K) suspension of 14 mg (0.47 mmol) of paraformaldehyde in 1 ml of THF was then added *via* cannula. After the mixture was allowed to reach 278 K over a 3 h period, 30 ml of brine was added. The resulting mixture was extracted with methylene chloride three times and the extracts combined, dried ($MgSO_4$), concentrated and column-chromatographed on silica gel using hexane and ether as eluant to give 44 mg of (2) [82% yield based on 48% reacted (3)], 6 mg of (1) [11% yield based on 48% reacted (3)] and 52.5 mg of (3) (52% recovery). Recrystallization of (1) from a mixture of ether and hexane gave brown crystals suitable for X-ray analysis [m.p. 438 K (dec.), $[\alpha]_D^{22} = -165°$ (c = 0.1, CH_2Cl_2)].

Crystal data

$[Fe(C_5H_5)(C_{10}H_{15}O_2S)]$	Mo $K\alpha$ radiation
M_r = 320.24	λ = 0.71069 Å
Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	θ = 11.5–14.6°
a = 10.4082 (17) Å	μ = 1.14 mm^{-1}
b = 19.453 (4) Å	T = 296 K
c = 7.3882 (19) Å	Prism
V = 1495.9 (5) $Å^3$	0.38 × 0.27 × 0.16 mm
Z = 4	Brown
D_x = 1.4219 (5) Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-5*S* diffractometer	1299 reflections with $I > \sigma(I)$
ω scans (rate 6° min^{-1} in ω)	θ_{max} = 25°
Absorption correction: empirical (ψ scans; North, Phillips & Mathews, 1968)	$h = 0 \rightarrow 12$
	$k = 0 \rightarrow 23$
	$l = 0 \rightarrow 8$
T_{min} = 0.72, T_{max} = 0.83	3 standard reflections every 100 reflections
1565 measured reflections	intensity decay: −0.5%
1565 independent reflections	

Refinement

Refinement on F
$R = 0.039$
$wR = 0.036$
$S = 1.17$
1299 reflections
175 parameters
H atoms riding (C—H = 0.95 Å) and H2 coordinates refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.0003$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute configuration: confirmed by refinement of the alternate enantiomer which produced $R = 0.045$, $wR = 0.045$ and $S = 1.43$

Table 1. *Selected geometric parameters (Å, °) and hydrogen-bonding geometry (Å, °)*

Fe1—*Cg*1	1.631 (2)	S1—C11	1.855 (5)
Fe1—*Cg*2	1.656 (3)	O2—C15	1.407 (7)
S1—O1	1.504 (4)	C1—C5	1.430 (7)
S1—C1	1.766 (4)	C2—C15	1.493 (7)
*Cg*1—Fe1—*Cg*2	178.79 (13)	S1—C1—C5	126.7 (4)
O1—S1—C1	107.6 (2)	C1—C2—C15	128.5 (4)
O1—S1—C11	105.9 (2)	C3—C2—C15	125.0 (5)
C1—S1—C11	101.2 (3)	O2—C15—C2	108.8 (5)
S1—C1—C2	123.8 (3)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.99 (6)	1.73 (6)	2.711 (5)	172 (6)

Symmetry code: (i) $x, y, 1 + z$.

The Fe- and S-atom positions were provided by *SHELXS*86 (Sheldrick, 1985) and the remaining atomic sites were located with *DIRDIF* (Beurskens, 1984).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH* and *PLATON* (Spek, 1990).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1237). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tricarbonyl[3-(η^5-cyclopentadienylcarbonylamino)propionic acid]rhenium

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Abstract

The crystal structure of [Re{η^5-$C_5H_4CONH(CH_2)_2$-COOH}$(CO)_3$] is reported. This complex adopts a three-legged piano-stool geometry in the solid phase. The average bonding parameters are Re—C(η^5) 2.29 (1) and Re—CO 1.88 (1) Å. The dihedral angle between the planes formed by the CONH group and the cyclopentadienyl ring is 6.15°.

Comment

The selective acylation of amines with *N*-succinimidyl (Ns) esters is widely used in liquid-phase peptide synthesis (Anderson, Zimmerman & Callahan, 1964;