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2,4,6-Tris(1′-phenylthio-1-ferrocenyl)boroxin

Duy H. Hua,[a] James W. McGill,[a] Paul D. Robinson[b]* and Cal Y. Meyers[c]

[a]Department of Chemistry, Kansas State University, Willard Hall, Manhattan, KS 66506, USA, [b]Department of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA, and [c]Department of Chemistry and Biochemistry and Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry, Southern Illinois University-4409, Carbondale, IL 4409, USA

Correspondence e-mail: robinson@geo.siu.edu

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.016 Å
R factor = 0.047
wR factor = 0.158
Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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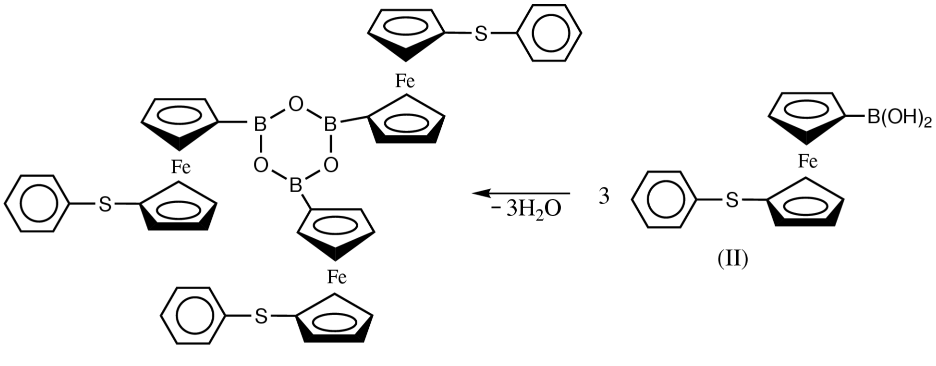
The synthesis of 1′-phenylthio-1-ferroceneboronic acid resulted in its trimerization with the loss of three molecules of water to form crystalline 2,4,6-tris(1′-phenylthio-1-ferrocenyl)boroxin, $C_{48}H_{39}B_3Fe_3O_3S_3$ or $[Fe_3(C_{15}H_{12}B_3O_3)(C_{11}H_9S)_3]$. The asymmetric unit contains two boroxin molecules conjugated with the attached cyclopentadienyl rings to form an aromatic ring. The cyclopentadienyl rings of five of the six ferrocenes are in an eclipsed conformation; the cyclopentadienyl rings of the other ferrocene are in the *gauche* form. Hydrolysis of the boroxin ring with aqueous base apparently is needed to produce the corresponding boronic acid required in a Suzuki coupling reaction.

Comment

In contrast to the identification of 2-(*N*,*N*-dimethylaminoalkyl)ferroceneboronic acids by their crystal structures (Norrild & Sotofte, 2001), our attempt to characterize 1′-phenylthio-1-ferroceneboronic acid, (II), by X-ray analysis showed that its structure was exclusively that of the corresponding boroxin, *i.e.* the title compound, (I). In our studies of chiral ferrocenyl phosphine ligands (Hua *et al.*, 2001), (I) was synthesized from the metallation of 1,1′-bis(tri-*n*-butylstannyl)ferrocene with *n*-butyllithium, followed by treatment with diphenyl disulfide, and a subsequent second metallation with *n*-butyllithium, followed by borination with trimethyl borate and acid hydrolysis. The fact that we found that water is needed in the Suzuki coupling reaction (Miyaura, 1998) when we used (I) as a substrate, and that insufficient structural characterization was afforded by spectroscopic methods, made us unsure of the unequivocal identity of the product, and we turned to X-ray analysis. Indeed, the X-ray structure of (I), shown with atom numbering in Fig. 1, indicates that the initial



(I)

boronic acid product derived from the aforementioned reactions underwent complete dehydration to form the boroxin.

Although ferroceneboronic acid underwent partial dehydration *in vacuo* after several days to give triferrocenylboroxin (Post *et al.*, 1970), 1′-phenylthio-1-ferroceneboronic acid, (II), apparently exists, at least in its crystalline state, exclusively as the boroxin (I). This anhydro structure explains the need to use water and base (such as sodium carbonate) in Suzuki reactions of (I), *i.e.* in order to hydrolyze it into boronic acid (II) so that a coupling reaction with an aryl halide may take place in the presence of palladium(0). X-ray structures of triferrocenylboroxins have not been reported previously.

The asymmetric unit of (I) contains two chemically identical but conformationally slightly different molecules, the largest conformational variation involving the ferrocene moieties containing Fe3 and Fe3a, respectively. In molecule 1, the ferrocene moiety containing Fe3 is essentially eclipsed, while in molecule 2 the corresponding ferrocene moiety, Fe3a, is nearly perfectly staggered. In fact, all of the other ferrocene moieties are essentially eclipsed; the actual rotational values for each ferrocene moiety is tabulated in the CIF. A second significant conformational difference involves the dihedral angle between the boroxin ring and the lower cyclopentadienyl ring of the Fe3/Fe3a ferrocene moieties, the values being 16.4 (5) and 6.6 (6)°, respectively. Of course both of these differences produce several associated torsional differences. Other dihedral angles between the boroxin rings and their bonded cyclopentadienyl rings are 3.6 (5), 3.6 (5), 7.3 (5) and 5.9 (5)° for the Fe1, Fe1a, Fe2, and Fe2a ferrocene moieties, respectively. Stabilization from the aromaticity of the boroxin ring (Jug, 1983) is likely the driving force for the formation of (I). Indeed, the boroxin-ring atoms are reasonably coplanar in both molecules, the deviations from planarity ranging from -0.020 (5) to 0.020 (10) Å and −0.027 (6) to 0.021 (12) Å, respectively, for molecules 1 and 2. The sp^2-hybridized B—O bond lengths of (I) range from 1.369 (10) to 1.387 (10) Å in molecule 1 and from 1.368 (11) to 1.390 (12) Å in molecule 2. These bond lengths are in marked contrast to that of the sp^3-hybridized B—O single bond of 1.505 Å reported by Voloshin *et al.* (1997), and are consistent with an aromatic ring structure. Selected geometric parameters are listed in Table 1.

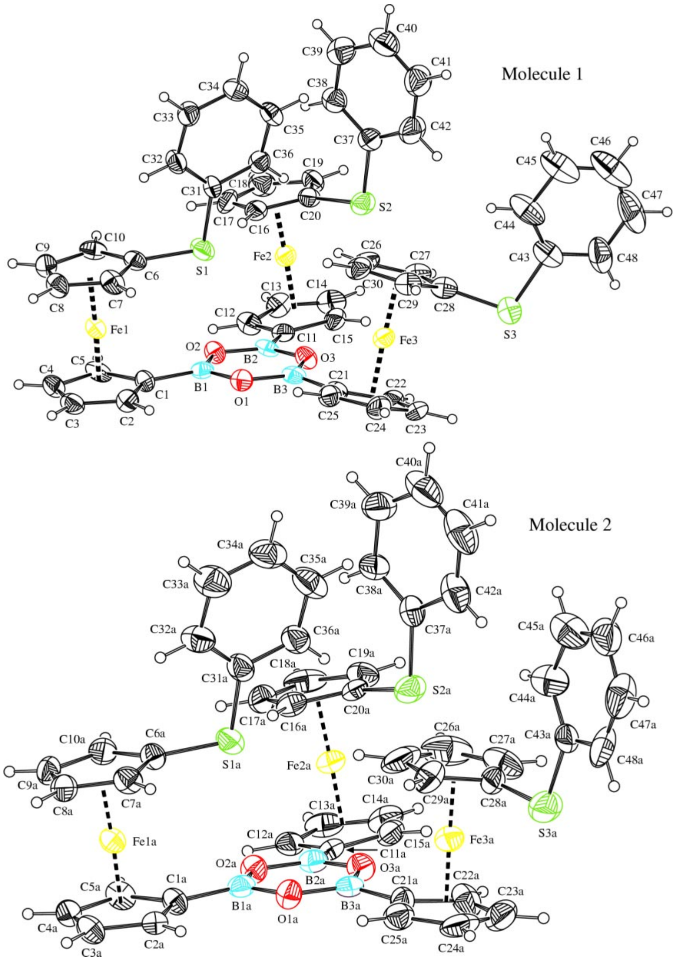


Figure 1

The molecular structure and atom-numbering scheme for (I) with displacement ellipsoids at the 30% probablilty level. The relative orientation of the two molecules in the asymmetric unit has been changed so that they can be more easily compared.

Experimental

2,4,6-Tris(1′-phenylthio-1-ferrocenyl)boroxin, (I), was prepared by treating a cold (195 K) tetrahydrofuran (10 ml) solution of 1,1′-bis(-tri-*n*-butylstannyl)ferrocene (1.56 g, 2.0 mmol) (Wright, 1990) under argon with *n*-BuLi (in hexane, 2.0 mmol) for 30 min, followed by the addition of diphenyl disulfide (0.436 g, 2.0 mmol). After the solution was stirred at 195 K for 1 h and 273 K for 3 h, the reaction was quenched with aqueous ammonium chloride, and extracted with diethyl ether, and the ether extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel to give an 89% yield of 1-(tri-*n*-butylstannyl)-1′-(phenylthio)ferrocene. The resulting sulfenylferrocene (0.60 g, 1.0 mmol) in 10 ml of tetrahydrofuran under argon was treated with *n*-BuLi (in hexane, 1.2 mmol) at 195 K for 30 min, followed by trimethyl borate (0.13 ml, 1.2 mmol). After the solution was stirred at 195 K for 1 h and 273 K for 1 h, 0.5 N HCl (10 ml) was added, and the solution was stirred at 248 K for 1 h and extracted with ether. The ether extract was dried ($MgSO_4$), concentrated, and triturated with cold hexane twice, and the remaining yellow solids were dried under vacuo to give (I) (74% yield). Recrystallization of (I) from ether gave yellow crystals (m.p. 404–406 K) suitable for X-ray analysis.

Crystal data

$[Fe_3(C_{15}H_{12}B_3O_3)(C_{11}H_9S)_3]$
M_r = 959.98
Triclinic, $P\overline{1}$
a = 17.501 (4) Å
b = 18.875 (5) Å
c = 14.999 (4) Å
α = 113.137 (19)°
β = 101.89 (2)°
γ = 74.30 (2)°
V = 4358.4 (19) Å^3

Z = 4
D_x = 1.463 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.1–13.1°
μ = 1.17 mm^{-1}
T = 296 K
Prism, brown
0.43 × 0.17 × 0.13 mm

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Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
$T_{\min} = 0.791$, $T_{\max} = 0.859$
16 062 measured reflections
15452 independent reflections
4619 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.079$
$\theta_{\max} = 25.1°$
$h = 0 \rightarrow 20$
$k = -21 \rightarrow 22$
$l = -17 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.158$
$S = 0.93$
15452 reflections
1081 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—B1	1.378 (10)	B2a—C11a	1.548 (13)
O1a—B1a	1.380 (11)	B3—C21	1.529 (12)
B1—O2	1.372 (10)	B3a—C21a	1.523 (13)
B1a—O2a	1.381 (11)	S1—C6	1.752 (8)
O2—B2	1.387 (10)	S1a—C6a	1.742 (8)
O2a—B2a	1.368 (11)	S1—C31	1.768 (8)
B2—O3	1.377 (10)	S1a—C31a	1.768 (10)
B2a—O3a	1.390 (12)	S2—C20	1.765 (8)
O3—B3	1.369 (10)	S2a—C20a	1.731 (9)
O3a—B3a	1.390 (12)	S2—C37	1.773 (9)
B3—O1	1.378 (10)	S2a—C37a	1.758 (10)
B3a—O1a	1.385 (11)	S3—C28	1.758 (9)
B1—C1	1.537 (12)	S3a—C28a	1.743 (9)
B1a—C1a	1.542 (12)	S3—C43	1.782 (10)
B2—C11	1.521 (12)	S3a—C43a	1.796 (10)
O1—B1—O2	120.0 (8)	O1a—B3a—C21a	121.0 (10)
O1a—B1a—O2a	120.3 (9)	O3—B3—C21	121.3 (8)
B1—O2—B2	120.0 (7)	O3a—B3a—C21a	120.8 (9)
B1a—O2a—B2a	120.0 (8)	C2—C1—B1	126.3 (8)
O2—B2—O3	119.2 (7)	C2a—C1a—B1a	126.6 (9)
O2a—B2a—O3a	119.6 (9)	C5—C1—B1	128.1 (8)
B2—O3—B3	121.0 (7)	C5a—C1a—B1a	126.8 (9)
B2a—O3a—B3a	121.0 (8)	C12—C11—B2	127.6 (8)
O3—B3—O1	119.4 (8)	C12a—C11a—B2a	126.4 (9)
O3a—B3a—O1a	118.2 (9)	C15—C11—B2	126.3 (9)
B3—O1—B1	120.3 (7)	C15a—C11a—B2a	126.0 (9)
B3a—O1a—B1a	120.7 (8)	C22—C21—B3	129.2 (8)
O2—B1—C1	121.4 (8)	C22a—C21a—B3a	126.1 (10)
O2a—B1a—C1a	119.6 (9)	C25—C21—B3	125.3 (8)
O1—B1—C1	118.6 (8)	C25a—C21a—B3a	127.6 (9)
O1a—B1a—C1a	119.9 (9)	C6—S1—C31	102.9 (4)
O2—B2—C11	121.9 (9)	C6a—S1a—C31a	102.7 (5)
O2a—B2a—C11a	122.8 (10)	C20—S2—C37	104.4 (4)
O3—B2—C11	119.0 (8)	C20a—S2a—C37a	102.4 (4)
O3a—B2a—C11a	117.4 (9)	C28—S3—C43	105.1 (5)
O1—B3—C21	119.2 (8)	C28a—S3a—C43a	103.5 (5)

Although the crystal diffracted strongly at low angle and was of good quality judging by its peak shapes, it diffracted poorly at higher angles. Thus only about 30% of the approximately 15 000 possible diffraction maxima were observed at the 2σ level, despite three weeks of data collection. Certainly low-temperature data would have improved the data set considerably but our laboratory does not currently have that capability.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965) in *TEXSAN*; software used to prepare material for publication: *TEXSAN, SHELXL*97 and *PLATON* (Spek, 2000).

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