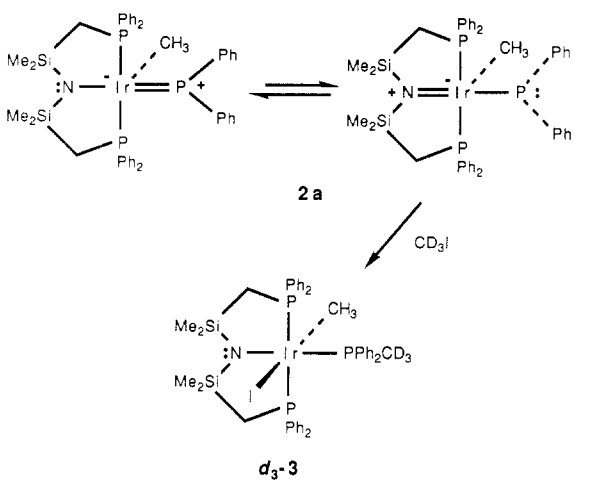
Scheme I



furthermore, a broad peak centered at the same chemical shift was detected in the $^2H\{^1H\}$ NMR spectrum, which is obviously assigned to the coordinated PPh_2CD_3 moiety. This labeling experiment (Scheme I) shows that the reaction of the phosphide complex **2a** with CH_3I or CD_3I involves intermolecular nucleophilic attack of the phosphide ligand with the electrophile and not prior reductive elimination of the methyl and phosphide ligands followed by oxidative addition.

One further aspect of this intermolecular methylation of the phosphide ligand is the relationship between the stereochemistry of the starting material **2a** and the observed, isomerically pure product **3**. By assuming that the stereochemistry of **2a** is square pyramidal with the methyl group apical (**sqp1**), then approach of the electrophile CH_3I to the open face (trans to the methyl) gives the correct product stereochemistry as **o1**. This stereoselectivity is by no means absolute proof of the stereochemistry for **2a**, but the simplicity of the mechanism and the lack of other octahedral isomers for **3** make such a proposal appealing.

Conclusions

The complexes $Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2]$ (R = Ph and *m*-tol) contain two potentially basic ligands: the disilylamide donor and the terminal diarylphosphide ligand. However, only the phosphide is nucleophilic toward methyl iodide to stereoselectively generate an octahedral complex, the structure of which can be related to the proposed stereochemistry of the starting phosphide derivative. Although the nucleophilicity of the phosphide ligand is usually associated with a pyramidal geometry at phosphorus, it is possible that the planar and pyramidal geometries are in dynamic equilibrium assisted by the lone pair[39] on the amide nitrogen.

Acknowledgment. Financial support was provided by NSERC of Canada. We gratefully acknowledge the generous loan of $IrCl_3$ from Johnson Matthey.

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[(1*R*)-1-Acetamido-3-(methylthio)propyl]boronic Acid and the X-ray Structure of Its Ethylene Glycol Ester

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[(1*R*)-1-Acetamido-3-(methylthio)propyl]boronic acid (**6**), the boronic acid analogue of *N*-acetyl-L-methionine, has been synthesized starting from (*s*)-pinanediol vinylboronate (**1**), and the structure of its ethylene glycol ester (**7**) (a 1,3,2-dioxaborolane) has been determined by X-ray diffraction. Reaction of **1** with (dichloromethyl)lithium yielded the (chloroallyl)boronate **2**, which was converted by lithiohexamethyldisilazane to the silylated amino derivative **3**. Desilylation and acylation of **3** to (acetamidoallyl)boronate **4** was followed by radical addition of methanethiol to form crystalline (*s*)-pinanediol [(1*R*)-1-acetamido-3-(methylthio)propyl]boronate (**5**), which was unsatisfactory for an X-ray structure. Cleavage with boron trichloride yielded the free boronic acid **6**, which formed a crystalline ethylene glycol ester **7**. The X-ray structure shows that the oxygen atom of the acetamido group is coordinated to the weakly acidic boron atom. The five-membered 1,3,2-dioxaborolane ring is nonplanar, in accord with the chiral induction properties of 4,5-disubstituted 2-alkyl-1,3,2-dioxaborolanes in their reactions with (dihalomethyl)lithiums.

α-Amino boronic acids have proved to be surprisingly unstable, though they survive long enough to permit the efficient synthesis of their stable *N*-acyl derivatives.[1-4] Some of these compounds have shown interesting properties as serine protease inhibitors.[1,2,5,6] As part of our program of synthesizing boron analogues of common acylated amino acids, we have prepared the *N*-acetyl-L-methionine analogue **6**. The ethylene glycol ester **7** has provided a satisfactory crystal for an X-ray structure de-

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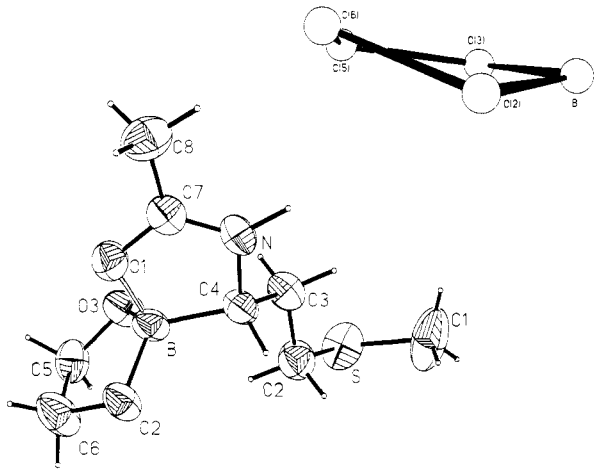
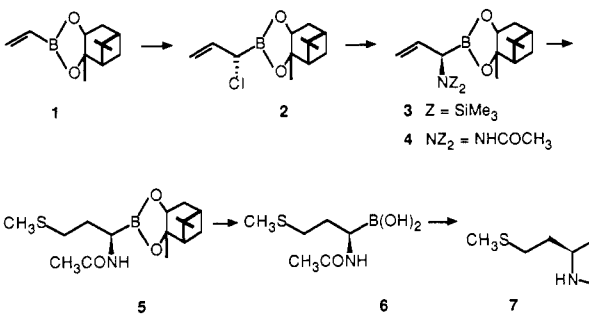


Figure 1. ORTEP diagram of ethylene glycol [(1*R*)-1-acetamido-3-(methylthio)propyl]boronate (**7**). Inset: ORTEP diagram of the 1,3,2-dioxaborolane ring of **7**.

termination, which has revealed unexpected coordination to the weakly acidic boron atom.

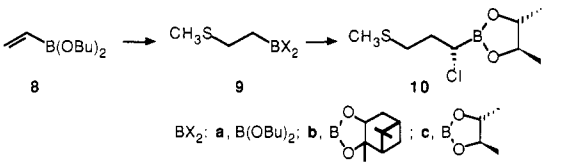
Results

The synthetic route is a straightforward application of known procedures but was found only after several seemingly equivalent alternatives proved unsuccessful. (*s*)-Pinanediol vinylboronate (**1**) reacted with (dichloromethyl)lithium in the usual manner[7,8] to provide (*s*)-pinanediol (1*S*)-1-chloroallylboronate (**2**), which with lithiohexamethyldisilazane yielded the silylated amino boronic ester **3**. Treatment with acetic acid and acetic anhydride yielded the [(1*R*)-1-acetamidoallyl]boronic ester **4**, which with methanethiol and radical initiation[9] was converted to the crystalline thioether derivative **5**. Pinanediol esters resist hydrolysis,[7] and in order to obtain a derivative which might interact with enzymes, **5** was cleaved with boron trichloride[7] to yield the free boronic acid analogue of *N*-acetylmethionine **6**.



The free boronic acid **6**, like many others, proved difficult to purify. Ethylene glycol esters equilibrate readily with free boronic acids in aqueous solution and are suitable for tests with enzymes, and we therefore made the ethylene glycol ester (1,3,2-dioxaborolane) **7**. Fortuitously, **7** formed orthorhombic crystals suitable for X-ray structure determination. An ORTEP diagram of the structure is shown in Figure 1.

Prior to choosing the successful synthetic route, we tried connecting the methylthio group first. Dibutyl [2-(methylthio)ethyl]boronate (**9a**) was prepared from methanethiol and dibutyl vinylboronate (**8**) by radical initiated addition.[9] Although (*s*)-pinanediol [2-(*n*-hexylthio)ethyl]boronate has reacted normally with (dichloromethyl)lithium,[8] our attempts to carry out the same reaction with the methylthio analogue **9b** failed. We then tried (*R,R*)-2,3-butanediol[10] [2-(methylthio)ethyl]boronate (**9c**) with (dichloromethyl)lithium and obtained 20–35% yields of (*R,R*)-2,3-butanediol [(1*S*)-3-(methylthio)-1-chloropropyl]boronate (**10**), which in view of the unsatisfactory yields was only partially characterized.



Discussion

In view of the excellent chiral directing properties of certain boronic ester groups,[8,10,11] all of which are substituted 1,3,2-dioxaborolanes, bond parameters suitable for molecular modeling computer programs have become of interest. However, most lower molecular weight boronic esters are liquids. Only 13 boronic ester crystal structures are listed in the Cambridge Database, plus 16 boronic anhydrides or acyloxyboron compounds. The only 1,3,2-dioxaborolanes are mannitol tris(phenylboronate)[12] and the (*p*-bromophenyl)boronate of the macrolide antibiotic streptovaricin.[13] The only alkylboron dioxy compounds include a hybrid boroxin/borazine, $(CH_3B)_3O_2NAr$,[14] a bis (ethylboryl) 2,3-dihydroxyfumarate,[15] and, with no published data, a bis(pyridine) complex of octahydroxycyclobutyl tetrakis(ethylboronate).[16] Representative of other structures reported are phenylboronic acid,[17] several of its six-membered ring esters (*B*-phenyl-1,3,2-dioxaborinanes),[18–21] and its chelated esters.[22,23]

A novel feature of interest in the structure of **7** is the internal coordination of the amide oxygen to the boron (Figure 1), even though boronic esters are not strong enough Lewis acids ($pK_a \approx 9$–11)[24] to form bimolecular complexes with amides. The coordinated O–B distance is 1.64 Å, significantly longer than the covalent B–O distances of 1.43–1.44 Å found in the ester linkages. Where the boron atom is strictly trigonal, as in phenylboronic

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acid,[17] its mannitol ester,[12] or other esters,[20,21] the B–O distance averages 1.37 Å. In diethanolamine[22] and other[20,23] tetracoordinate boron chelates, the average B–O distance is 1.46–1.47 Å.

The B–C distance in **7** is 1.61 Å. The sp^2-B–sp^3-C distance has been found to be 1.53 Å,[14,15] and the coordinated sp^3-B–sp^3-C distance 1.56 Å.[15] These are not strictly comparable compounds, **7** having relatively electron-rich oxygen atoms, which may account for the longer B–C bond in **7**. However, aryl C–B bonds can be as long, 1.61 Å in diethanolamine phenylboronate,[22] more typically 1.59 Å in chelates,[20,23] and 1.56–1.58 Å in unchelated phenylboronic esters.[12,20,21]

The intramolecular coordination is probably a general feature of α-amido boronic acid derivatives and provides a rationale for our previous observations that (1-acetamido-2-phenylethyl)boronic acid has unexpectedly high water solubility and ether insolubility and that it crystallized from aqueous hydrochloric acid as a derivative apparently containing a boron–chlorine bond.[1] Coordination also provides a basis for understanding the stability of (α-acetamidoalkyl)boron difluorides, which have been found by Kinder and Katzenellenbogen to form readily in aqueous hydrofluoric acid solution.[25]

A second feature of interest is the distortion of the five-membered 1,3,2-dioxaborolane ring (ethylene glycol boronic ester group) of **7** from planarity (inset, Figure 1), with maximum displacements of 0.137 Å for O(2) and −0.122 Å for O(3). The O–C–C–O torsional angle is 17.1°. The bonding around boron in **7** is probably a reasonable model for that in the transition state for rearrangement of (dichloromethyl)borate salts to α-chloro boronic esters, and the chiral twist in the five-membered ring as biased by substituents may be the source of the very high asymmetric inductions that have been observed.[7,8,10,11,26] The nonplanarity is somewhat less in mannitol tris(phenylboronate),[12] but the free boronic ester is not a good transition-state model. In contrast to **7**, the very complicated streptovaricin ester appears to have a nearly planar 1,3,2-dioxaborolane ring.[13] 1,3,2-Dioxaborinanes generally contain a planar C–O–B–O–C unit, with C(5) out of the plane,[18-21] and 2,4-pentanediol is a weak chiral director in the boronic ester synthesis.[27]

The X-ray data confirm that the absolute configuration of **7** is (1*R*) as indicated, which is in accord with the configurational relationships established in previous work.[7]

Experimental Section

General Data. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl. Butyllithium (1.6 M in hexane) was purchased from the Aldrich Chemical Co. and was titrated against 2-propanol to the 1,10-phenanthroline endpoint. Other chemicals were reagent grade. Proton NMR spectra were recorded with a JEOL FX-90Q at 90 MHz or a Nicolet NT-200 at 200 MHz with internal tetramethylsilane as reference. Optical rotations were measured with a Jasco DIP-181 digital polarimeter. Melting points were taken in open capillaries with a Hoover-Thomas melting point apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tn.

(*s*)-Pinanediol [(*R*)-1-(Acetamido)allyl]boronate (4). To a solution of 17.2 mmol of lithiohexamethyldisilazane (from 17.2 mmol of butyllithium and 17.5 mmol of hexamethyldisilazane) in 35 mL of THF stirred at −78 °C was added dropwise 3.75 g (14.7 mmol) of (*s*)-pinanediol [(*S*)-1-chloro-allyl]boronate[4,7] (**2**) in 10 mL of THF, which led to immediate formation of a white precipitate. The mixture was allowed to warm to 20–25 °C and kept 8 h to form **3**, which was not isolated. The solution was cooled to −78 °C, and 4.65 mL (49.1 mmol) of acetic anhydride and 1.03 mL (18 mmol) of acetic acid were added dropwise. After the solution was stirred overnight at room temperature, the solvent was removed and the residue was treated with 25 mL of ether and 25 mL of water. The aqueous layer was separated and washed with 2 × 15 mL of ether. The combined ether layers were dried over magnesium sulfate and filtered. The solution was concentrated under vacuum, and the residue was flash chromatographed through a silica gel column with 5% methanol in ether, 2.90 g (71%) of **4**; $[\alpha]^{25}_{546}$ −10.59° (*c* 1.0, toluene); mp 122–123 °C; 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 3, CH_3), 1.25 (s, 3, CH_3), 1.35 (s, 3, CH_3), 1.24–2.29 (m, 9, pinyl + CH_2CHB), 2.12 (s, 3, CH_3CO), 4.13 (dd, 1, CHOB), 4.85–4.96 (m, 2, H_2C=CH), 5.78 (m, 1, H_2C=C*H*–), 9.8 (concentration dependent) (br s, 1, N*H*). Anal. Calcd for $C_{15}H_{24}BNO_3$: C, 65.00; H, 8.73; B, 3.90; N, 5.05. Found: C, 64.85; H, 8.73; B, 4.09; N, 4.77.

(*s*)-Pinanediol [(1*R*)-1-Acetamido-3-(methylthio)propyl]boronate (5). In a Vycor round-bottom flask, 5.92 g (21.3 mmol) of **4** and 0.1 g of azobis(isobutyronitrile) were dissolved in 10.2 g (213 mmol) of methanethiol. The mixture was stirred at −10 °C and irradiated with a 100-W mercury vapor lamp until the vinyl protons disappeared from the NMR spectrum (4 h).[9] The mixture was allowed to warm to room temperature, dissolved in 15 mL of ethyl acetate, and concentrated under vacuum. The product **5** was recrystallized from ethyl acetate/petroleum ether: 5.57 g (81%); mp 158–159 °C; $[\alpha]^{22}_{546}$ −46.5 °C (*c* 1, $CHCl_3$); 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.81 (s, 3, CH_3), 1.22 (s, 3, CH_3), 1.34 (s, 3, CH_3), 1.33–2.40 (m, 8, pinyl + CH_2), 2.05 (accidentally degenerate s, 6, CH_3S + CH_3CO), 2.62 (m, 3, SCH_2 + CH(N)B), 4.11 (dd, 1, CHOB), 9.5 (concentration dependent) (br s, 1, N*H*). Anal. Calcd for $C_{16}H_{28}BNO_3S$: C, 59.08; H, 8.68; B, 3.32; N, 4.31; S, 9.86. Found: C, 58.90; H, 8.63; B, 3.36; N, 4.34; S, 10.19.

Ethylene Glycol [(1*R*)-1-Acetamido-3-(methylthio)propyl]boronate (7). Boron trichloride (10 mL) was condensed under argon in a 100-mL round-bottom flask and stirred at −78 °C during the addition of 4.91 g (17.7 mmol) of **5** dissolved in 10 mL of dichloromethane.[7] The cooling bath was removed, and the mixture was stirred 8 h as the boron trichloride partially evaporated. The remainder of the boron trichloride was evaporated under a stream of argon, and the residue was treated with 30 mL of water and 75 mL of ether. The aqueous phase was separated and washed with 3 × 20 mL of ether. Lyophilization of the aqueous phase yielded a residue of crude [(1*R*)-1-acetamido-3-(methylthio)propyl]boronic acid (**6**), which was freed from boric acid by treatment with 50 mL of methanol and distillation until the distillate showed no green boron color in the flame when ignited. The excess methanol was distilled under vacuum, and the residue was treated with 25 mL of ether and 10 mL of ethylene glycol and then distilled. The product **7**, bp 158–161 °C (0.03 Torr), solidified on cooling and was recrystallized from ethyl acetate; 3.19 g (83%); mp 132–134 °C; $[\alpha]^{25}_{546}$ −78.6° (*c* 1, $CHCl_3$); 200-MHz ^{1}H NMR ($CDCl_3$) δ 1.79 (m, 2, CH_2CH_2CH), 2.10 (s, 3, CH_3CO), 2.14 (s, 3, CH_3S), 2.45–2.71 (m, 3, $-SCH_2CH_2CHB$), 3.95 (m, 4, $-OCH_2CH_2O-$), 9.0 (position varies with concentration) (s, 1, N*H*). Anal. Calcd for $C_8H_{16}BNO_3S$: C, 44.26; H, 7.43; B, 4.98; N, 6.45; S, 14.77. Found: C, 44.09; H, 7.53; B, 5.25; N, 6.24; S, 14.50.

Structure of Ethylene Glycol [(1*R*)-1-Acetamido-3-(methylthio)propyl]boronate (7). A selected crystal was analyzed with the data collection parameters summarized in Table I.[28] The absolute configuration was established by comparison of the refinements of the two enantiomorphs, which established with statistical certainty that the (1*R*)-enantiomer was the observed form. Atomic coordinates and isotropic thermal parameters are summarized in Table II, bond lengths in Table IIIa, and bond angles in Table IIIb.[29]

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Table I. Data Collection and Refinement Parameters

compd name	ethylene glycol [(1*R*)-1-acetamido-3-(methylthio)propyl]boronate (**7**)
empirical formula	$C_8H_{16}BNO_3S$
mol wt	217.096 g/mol
A. Data Collection	
diffractometer system	upgraded Syntex $P2_1$
cryst class	orthorhombic
space group	$P2_12_12_1$
lattice constants	a = 8.555 (2) Å b = 8.862 (2) Å c = 14.910 (4) Å V = 1133 Å^3 based on 22 reflections in the range $17 < 2\theta < 28$
$F(000)$	464
radiatn	Mo Kα with graphite monochromator
abs coeff	2.55 cm^{-1}
calcd density	ρ = 1.27 g/cm^3 (Z = 4)
type of abs correctn	none applied
temp	room temp
data collectn technique	ω scan
scan range	0.8°
scan speed	4°/min (min); 29.3°/min (max)
check reflctns	0, 4, 0; 4, 2, 2; monitored every 100 reflections
total reflctns	1643
2θ(max)	45°
unique reflectns	888 with 761 with $F > 3\sigma(F)$
h,k,l	$-8 < h < 0$; $0 < k < 9$; $0 < l < 16$
B. Solution and Refinement	
structure soln package	Nicolet SHELXTL
structure soln technique	direct methods
$R = \sum\|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.0445
$R_w = \{[\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]\}^{1/2}$	0.0457
with $w = 1/[\sigma^2(F) + g(F)^2]$	g = 0.00031
functn minimized	$\sum w(\|F_o\| - \|F_c\|)^2$
goodness of fit	1.472
$\|\Delta/\sigma\|$(mean)	0.012
$\|\Delta/\sigma\|$(max)	0.059
total parameters refined	127
thermal parameters	anisotropic on all non-hydrogen atoms
hydrogen atoms	constrained to C–H and N–H = 0.96 Å, thermal parameters fixed at 0.10 or 0.15
largest peak on final diff map	1/4 e/Å^3; near S
most negative peak on final diff map	−1/4 e/Å^3
extinctn correctns	none applied

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $C_8H_{16}BNO_3S$ (7)

	x	y	z	U^a
S	1813 (2)	922 (2)	9998 (1)	70 (1)
B	2934 (6)	3391 (6)	7124 (4)	39 (2)
N	5428 (4)	2168 (4)	7255 (3)	44 (1)
O(1)	3958 (4)	3147 (4)	6206 (2)	47 (1)
O(2)	2496 (4)	4954 (4)	7175 (2)	46 (1)
O(3)	1521 (4)	2551 (3)	7015 (2)	49 (1)
C(1)	3448 (8)	687 (4)	10709 (4)	101 (3)
C(2)	2547 (5)	2257 (6)	9195 (4)	56 (2)
C(3)	3640 (6)	1570 (5)	8501 (3)	50 (2)
C(4)	4195 (5)	2789 (5)	7843 (3)	41 (2)
C(5)	289 (5)	3566 (6)	6840 (3)	51 (2)
C(6)	994 (6)	5114 (5)	6770 (4)	66 (2)
C(7)	5197 (5)	2426 (6)	6417 (4)	43 (2)
C(8)	6309 (6)	1924 (6)	5711 (4)	59 (2)

[a] The equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Dibutyl [2-(Methylthio)ethyl]boronate (9a). A solution of 62.6 g (0.34 mol) of dibutyl vinylboronate[9] and 0.1 g of azobis(isobutyronitrile) in 49 g (1.0 mol) of methanethiol in a Vycor flask at −10 °C was stirred and irradiated with a 100-W mercury vapor lamp until the NMR spectrum showed disappearance of the vinyl protons (4 h). Vacuum distillation yielded 66.2 g (98%) of **9**: bp 84–89 °C (2 Torr); 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 6, CH_2CH_3), 1.12 (t, 2, CH_2B), 1.24–1.61 (m, 8, CH_2CH_2), 2.11 (s, 3, CH_3S), 2.62 (t, 2, SCH_2), 3.80 (t, 4, OCH_2). Anal. Calcd for $C_{11}H_{25}BO_2S$: C, 56.90; H, 10.85; B, 4.66; S, 13.81. Found: C, 57.02; H, 10.93; B, 4.63; S, 13.92.

Table III. Bond Lengths (Å) and Bond Angles for $C_8H_{16}BNO_3S$ (7)

a. Bond Lengths

S–C(1)	1.769 (7)	O(1)–C(7)	1.279 (6)
S–C(2)	1.798 (5)	O(2)–C(6)	1.427 (6)
B–O(1)	1.641 (7)	O(3)–C(5)	1.412 (6)
B–O(2)	1.438 (6)	C(2)–C(3)	1.523 (7)
B–O(3)	1.431 (6)	C(3)–C(4)	1.536 (7)
B–C(4)	1.613 (7)	C(5)–C(6)	1.503 (7)
N–C(4)	1.479 (6)	C(7)–C(8)	1.489 (7)
N–C(7)	1.286 (7)		

b. Bond Angles

C(1)–S–C(2)	101.6 (3)	S–C(2)–C(3)	113.8 (3)
O(1)–B–O(2)	108.1 (4)	C(2)–C(3)–C(4)	110.1 (4)
O(1)–B–O(3)	106.8 (4)	B–C(4)–N	101.9 (4)
O(2)–B–O(3)	106.7 (4)	B–C(4)–C(3)	116.8 (4)
O(1)–B–C(4)	98.8 (3)	N–C(4)–C(3)	109.8 (4)
O(2)–B–C(4)	117.4 (4)	O(3)–C(5)–C(6)	107.2 (4)
O(3)–B–C(4)	118.0 (4)	O(2)–C(6)–C(5)	104.0 (4)
C(4)–N–C(7)	113.6 (4)	N–C(7)–O(1)	117.1 (4)
B–O(1)–C(7)	107.7 (4)	N–C(7)–C(8)	122.5 (4)
B–O(2)–C(6)	108.0 (4)	O(1)–C(7)–C(8)	120.4 (4)
B–O(3)–C(5)	108.7 (3)		

(*s*)-Pinanediol [2-(Methylthio)ethyl]boronate (9b). This compound was made either by transesterification of **9a** with an equimolar amount of pinanediol or by reaction of pinanediol vinylboronate[30] with methanethiol under the conditions described for preparation of **9a**: bp 107–111 °C (0.2 Torr); 200-MHz ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3, CH_3), 1.15–2.5 (m, 17, with CCH_3 singlets at δ 1.31 and 1.39, CH_3S δ 2.10), 2.62 (t, 2, SCH_2), 4.30 (dd, 1, OC*H*). Anal. Calcd for $C_{13}H_{23}BO_2S$: C, 61.43; H, 9.12; B, 4.25; S, 12.61. Found: C, 61.51; H, 9.24; B, 4.29; S, 12.80.

(*R*,*R*)-2,3-Butanediol [2-(methylthio)ethyl]boronate (9c). Transesterification of **9a** with an equimolar amount of (*R*,*R*)-2,3-butanediol in ether yielded 87–97% **9c**: bp 92–94 °C (0.2 Torr); 200-MHz ^{1}H NMR ($CDCl_3$) δ 1.14–1.38 (m, 8, CH_2B and $CHCH_3$), 2.10 (s, 3, CH_3S), 2.62 (t, 2, SCH_2), 4.01 (m, 2, $OCHCH_3$); $[\alpha]^{21}_{546}$ −6.22°. Anal. Calcd for $C_7H_{15}BO_2S$: C, 48.30; H, 8.69; B, 6.21; S, 18.42. Found: C, 48.41; H, 8.78; B, 6.20; S, 18.60.

(*R*,*R*)-2,3-Butanediol [(1*S*)-1-Chloro-3-(methylthio)propyl]boronate (10). Reaction of **9c** with (dichloromethyl)lithium at −100 °C followed by 1.7 mol of zinc chloride according to the usual procedure[8] followed by workup with petroleum ether and magnesium sulfate[10] and chromatography on silica with 10% ethyl acetate in hexane yielded 20–35% **10**: 200-MHz ^{1}H NMR ($CDCl_3$) δ 1.1–1.48 (m, 8, CH_2CH_2CHCl and $CHCH_3$), 2.10 (s, 3, CH_3S), 2.61 (t, 2, SCH_2), 3.81 (t, 1, *C*HClB), 4.11 (m, 2, O–*CHCH*–O). In view of the low yield, characterization was not pursued further.

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Supplementary Material Available: Tables of thermal parameters and hydrogen atom coordinates (2 pages); a listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

(30) Tsai, D. J. S.; Matteson, D. S. *Organometallics* **1983**, *2*, 236–241.