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Synthesis of optically active boroxazolidine, borathiazolidine and boraselenazolidine and their *N*-borane adducts from the corresponding 2-imino-heteroazolidines †

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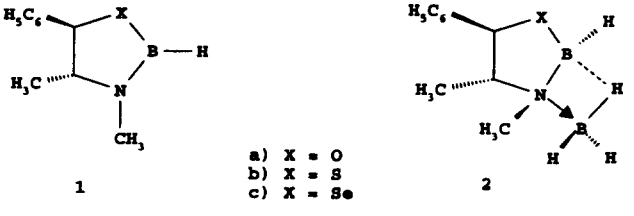
Abstract: The synthesis from the corresponding 2-imino-heteroazolidines of optically active boroxazolidine, borathiazolidine and boraselenazolidine, derived from ephedrine, and their *N*-borane adducts is reported. The X-ray diffraction structures of (4R,5R)-(+)-3,4-dimethyl-5-phenyl-2-iminium thiazolidine thiocyanate **9b**, (4R,5R)-(+)-3,4-dimethyl-5-phenyl-2-iminium-selenazolidine selenocyanate **9c**, (4R,5R)-(+)-3,4-dimethyl-5-phenyl-2-iminoselenazolidine **10b** and (4R,5R)-(+)-3,4-dimethyl-5-phenyl-2-boraselenazolidine dimer **15** were elucidated. Compounds were also studied by ^{1}H, ^{13}C and ^{77}Se NMR.

Introduction

We are interested in the reactions of aminoalcohols and boron reagents,[1a–n] especially in the synthesis of boron compounds derived from ephedrine.[1b,d–n] We have reported the preparation of heteroazoborolidines derived from ephedrines **1a** and **1b** and studied the structure of their *N*-borane adducts **2a** and **2b**[1j,k,m] (Figure 1).

We have also reported the synthesis of heterocyclic boron dihydride **4** by the reduction reaction of the thiazolidine-2-thione **3** with BH_3/THF[1m] (Figure 2). This was the first example of a cyclic five membered boron dihydride derived from an ethanethiolamine. The analogous structures for ethanolamines are not known because they are unstable.[1a]

We have also investigated easy ways to borolidines and we have recently reported several syntheses of aromatic borolidines, for example the preparation of aromatic boron hydrides, **6a–c**,[2] shown in Figure 3.



1 2

Figure 1.

† Dedicated to Professor Herbert C. Brown on the occasion of his 85th birthday.

* Corresponding author.

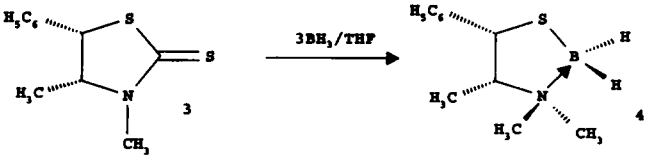


Figure 2.

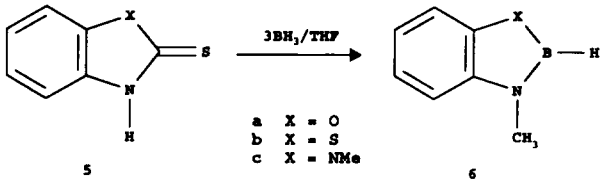


Figure 3.

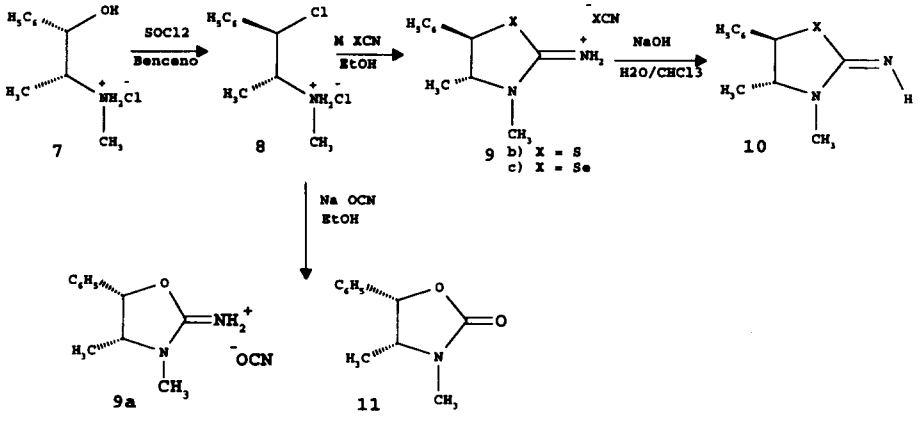


Figure 4.

Results and discussion

As part of our research into boron hydrides, we were interested in exploring the reduction reaction of 2-imino heteroazolidine with borane as an alternative synthesis of borazolidines **1c** and **2c**. Thus, we have prepared a series of 2-imino heterocycles bearing O, S and Se, **9a–c** and **10a–c** (Figure 4). The first synthesis of compound **9b** was reported by Mccarthy and Ho.[3]

The 2-iminium heteroazolidines **9a–c** are interesting chiral heterocyclic compounds because they have a delocalized electronic system between the three heteroatoms and the central planar carbon and can give stable *N*-borane adducts. Thus, we decided to prepare the series **9a–c** in order to investigate their reactions with borane. The compounds **9a–c** were prepared in good yield from the reaction of the chloride compound **8** with two equivalents of sodium or potassium cyanate, thiocyanate, or selenocyanate in ethanol. When X=S and Se, the ring formation was stereoselective, giving compounds **9a–c** with retention of configuration at C-1, as deduced from the ^{1}H and ^{13}C NMR spectra (Tables 1 and 2), and as shown in the X-ray diffraction structure of compounds **9b** and **9c** (Figure 5).

For X=O, the cyclization reaction produced a mixture of two compounds. One was the *cis*-2-iminium oxazolidine **9a** (65%), obtained stereoselectively with inversion of configuration at C-1. The other was the *cis*-oxazolidine-2-one **11**, presumably obtained by some hydrolysis of **9a**. Compounds **9a–c** are easily liberated from their salts by NaOH treatment and $CHCl_3$ extraction. For X=O, the reaction

Table 1. δ ^{1}H (ppm), J (Hz) of compounds **1–13**

Compd.	H4	H5	CH_3	N-CH_3	Aromtic	N-H or =N-CH_3
1a	3.28 m	5.41 d ^{3}J = 8.6	0.45 d ^{2}J = 6.6	2.50 s	7.15 m	
1b	3.56 m	4.14 d ^{3}J = 6.1	1.23 d ^{2}J = 6.5	2.86 s	7.31 m	
1c	3.63 m	4.24 d ^{3}J = 5.0	1.22 d ^{2}J = 6.0	2.92 s	7.27 m	
2b	3.17 m	3.89 d ^{3}J = 10.8	1.07 d ^{2}J = 6.7	2.82 s	7.35 m	
2c	3.28 m	4.05 d ^{3}J = 11.2	1.08 d ^{2}J = 6.6	2.85 s	7.33 m	
9a	4.11 m	5.74 d ^{3}J=7.9	0.76 d	2.75 s	7.37 m	
9b	4.41 m	4.92 d ^{3}J=4.9	1.39 d ^{3}J=6.3	3.22 s	7.43 m	
9c	4.46 m	4.87 d ^{3}J=2.6	1.42 d ^{3}J=5.9	3.20 s	7.37 m	
10a	3.90 m	5.45 d ^{3}J=8.1	0.75 d ^{3}J=6.7	2.85 s	7.35 m	4.46 s
10b	3.66 m	4.24 d ^{3}J=7.0	1.26 d ^{3}J=6.2	2.93 s	7.37 m	6.02 s
10c	3.77 m	4.41 d ^{3}J=5.8	1.30 d ^{3}J=6.1	2.95 s	7.30 m	4.90 s
12a	4.18 m	5.84 d	0.79 d	2.91 s	7.35 m	5.51 s
12b	3.90 m	4.29 d	1.34 d	2.94 s	7.35 m	6.23 s
12c	3.97 m	4.35 d	1.35 d	2.96 s	7.32 m	6.20 s
12d	3.97 m	4.44 d	1.38 d	3.16 s	7.32 m	6.20 s
13	3.55 m	4.20 d ^{3}J = 7.4	1.23 d ^{3}J = 6.0	2.86 s	7.35 m	3.07 s
14	3.85 m	4.28 d ^{3}J = 5.9	1.40 d ^{3}J = 6.2	3.28 s	7.35 m	3.14 s

Table 2. δ ^{13}C (ppm) of compounds **1–13**

Compd.	N-Me	C4	C5	CH_3	C-i	C-o	C-m	C-p	C2 or=N-CH_3
1a	30.25	59.62	83.58	15.42	140.02	128.13	126.59	127.32	
1b	35.52	69.07	57.43	18.57	143.33	128.56	127.42	127.31	
1c	37.01	69.32	50.59 (a)	18.44	144.77	128.48	127.00	126.87	
2b	47.92	73.80	53.79	13.03	139.95	129.33	129.17	128.51	
2c	45.68	73.15	48.50	13.94	139.08	128.63	128.44	127.53	
9a	29.88	56.50	79.28	13.55	135.56	128.16	126.27	128.07	161.11
9b	32.80	69.77	53.39	16.64	138.29	129.07	127.54	128.66	167.47
9c	33.26	70.99	50.30(b)	16.91	141.07	128.79	127.05	127.94	166.67(c)
10a	29.90	58.51	79.70	13.63	135.66	128.17	126.09	128.11	161.11
10b	31.09	67.64	54.46	17.55	138.68	128.83	127.94	128.23	164.30
10c	31.83	68.23	50.53(d)	18.02	140.61	128.85	127.74	127.88	160.52
12a	29.93	59.21	82.57	13.79	133.30	128.34	125.96	127.99	161.10
12b	31.28	69.50	54.28	17.48	137.21	129.22	127.97	128.80	170.22
12c	31.91	67.75	49.42	17.88	129.05	128.93	127.50	128.31	169.63
12d	33.31	71.02	50.03	18.61	128.93	129.05	128.08	128.64	168.77
13	32.05	66.19	53.87	16.81	138.41	128.5	127.94	127.86	40.35
14	38.27	71.75	53.80	17.95	137.73	128.98	127.08	128.56	46.27

^{2}J(Se-^{13}C) = 45 Hz, b) ^{2}J(Se-^{13}C) = 50 Hz, c) ^{2}J(Se-^{13}C) = 141 Hz, d) ^{2}J(Se-^{13}C) = 55 Hz.

products were separated by column chromatography. Compound **10b** crystallized from $CHCl_3$ and the X-ray diffraction structure was determined (Figure 6).

To our knowledge, compounds **9c** and **10c** are the first examples of optically active 2-iminium selenazolidines. Their structures were deduced from the ^{1}H, ^{13}C and ^{77}Se NMR data (Tables 1 and 2). In the ^{13}C NMR spectrum of **9c** and **10c**, the carbon atoms next to selenium are coupled with it.

The reaction of compounds **10a** and **10b** with BH_3/THF at rt afforded only one geometric isomer of the *N*-borane adducts **12a–b** (Figure 7). Compounds **12a** and **12b** presented broad signals at −22 and −20.5 ppm respectively in the ^{11}B NMR spectrum, assigned to the *N*-BH_3 group (Table 3).

In both compounds, the borane group was *trans* to the endocyclic nitrogen, as was deduced from the absence of the borane effect at the *N*-CH_3 group.

On the other hand, reaction of the 2-imino-selenazaborolidine **10c** with BH_3/THF at rt produces the mixture of *N*-borane adducts **12c** (80%) and **12d** (20%). All geometric isomers of *N*-borane adducts presented a stable imine configuration which does not change on standing in solution. A similar result was observed in other *N*-borane imine adducts studied[4] (Figure 8).

The structures of isomers **12c** and **12d** were assigned by their NMR spectra based on electronic and steric effects.[4] In the ^{11}B NMR spectrum there was a broad signal at −18.4 ppm for **12c–d**. The ^{77}Se NMR spectrum presented two signals, one at −319.5 ppm and another at −320.2 ppm. The assignment

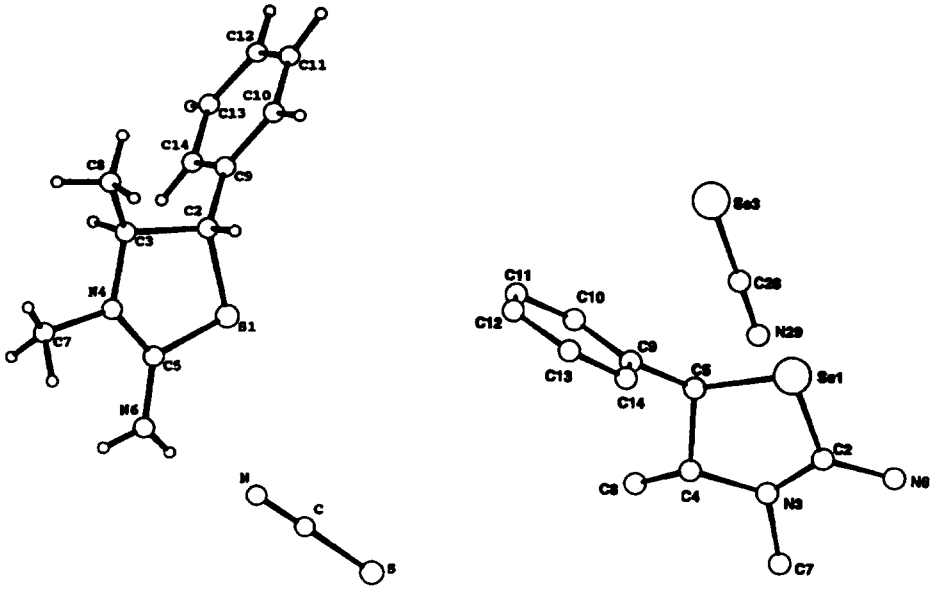


Figure 5. Perspective representation of compounds **9b** and **9c**. Selected bond lengths (Å) and angles (deg.) are as follows: **9b** S–C 1.638(4), N(4)–C(3) 1.476(4), C(2)–C(3) 1.532(4), N–C 1.151(5), N(4)–C(5) 1.324(4), C(2)–C(9) 1.506(4), S(1)–C(2) 1.823(3), N(4)–C(7) 1.464(4), C(3)–C(8) 1.515(5), S(1)–C(5) 1.737(3), N(6)–C(5) 1.303(4). C(2)–S(1)–C(5) 91.2(1), S(1)–C(2)–C(3) 105.5(2), C(2)–C(3)–C(8) 111.8(2), C(3)–N(4)–C(5) 115.0(2), S(1)–C(2)–C(9) 111.7(2), S(1)–C(5)–N(4) 113.7(2), C(3)–N(4)–C(7) 121.3(2), C(3)–C(2)–C(9) 114.5(2), S(l)–C(5)–N(6) 120.3(2), C(5)–N(4)–C(7) 121.2(3), N(4)–C(3)–C(2) 105.5(2), N(4)–C(5)–N(6) 126.0(3), S–C–N, 177.9(3), N(4)–C(3)–C(8), 113.0(3). **9c**: Se(3)–C(28) 1.78(2), N(3)–C(2) 1.30(2), C(4)–C(5) 1.53(2), N(29)–C(28) 1.14(2), N(3)–C(4) 148(2), C(4)–C(8) 1.49(2), Se(l)–C(2) 1.85(2), N(3)–C(7) 1.49(2), C(5)–C(9) 1.49(2) Se(1)–C(5) 1.92(1), N(6)–C(2), 1.32(2). C(2)–Se(l)–C(5) 88.2(7), Se(l)–C(5)–C(4) 104.9(9), C(5)–C(4)–C(8) 111.5(11), C(2)–N(3)–C(4) 118.0(13), Se(1)–C(5)–C(9) 116.0(11), Se(1)–C(2)–N(3) 112.6(11), C(4)–N(3)–C(7), 119.9(12), C(4)–C(5)–C(9) 1140(11), Se(l)–C(2)–N(6) 121.5(2), C(2)–N(3)–C(7) 120.6(12), N(3)–C(4)–C(5) 106.4(11), N(3)–C(2)N(6) 125.8(14), Se(3)–C(28)–N(29) 175.3(15), N(3)–C(4)–C(8) 113.2(13).

of the ^{1}H NMR spectrum was based on the shift (0.2 ppm) of the *N*-CH_3 signal of compound **12d** produced by the neighboring borane.[1g,f]

Methylation of the imine group in compound **10b** produces inversion of the nitrogen geometric configuration, compound **13**. Thus, the *N*-borane adduct formed by reaction of **13** and BH_3/THF afforded compound **14** that presents the borane on the same side of the *N*-methyl group. The clear effect of borane over the *N*-methyl group in compound **14** confirmed the configurational assignments in **12c** and **12d** (Figure 9).

Reaction of heterocycles **10a–c** with three equivalents of BH_3/THF in refluxing THF, afforded the B–H heterocycles **1a–c**, which were purified by distillation at reduced pressure. The borolidines were obtained after distillation in yields approaching 60% (Figure 7). The boron hydrides B–H **1a–c**, present a doublet in the ^{11}B NMR spectrum: **1a** δ=29.0 ppm, ^{1}J (B–H) 153 Hz[1k]; **1b** δ=38.7 ppm, ^{1}J (B–H) 153 Hz[1m]; **1c** δ=41.8 ppm, ^{1}J (B–H) 147 Hz. Compound **1c** presented a broad signal in the ^{77}Se spectrum at δ=223.4 ppm. The NMR data of compounds **1a–c** clearly indicate monomeric structures.

Compound **1c** crystallized on standing in $CDCl_3$ for several weeks, and the X-ray diffraction structure of the crystals indicated the formation of a dimer **15** linked by covalent bonds between boron and nitrogen atoms as can be deduced from the analogous bond length of four B–N bonds (Figure 10).

A similar X-ray diffraction structure of a dimeric structure for an amine borane was reported[5] as well as the X-ray study of a non-symmetric dimer of a boroxazolidine derived from ephedrine.

The dimeric structure is very interesting and it was proposed as a stable derivative by the theoretical

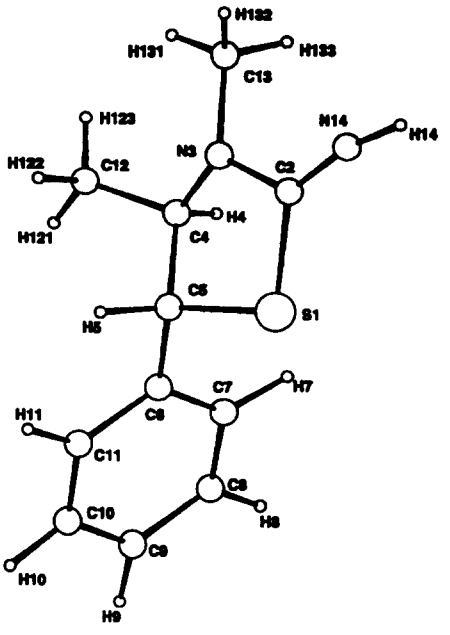


Figure 6. Perspective representation of compound **10b**. Selected bond lengths (Å) and angles (deg.) are as follows: S(1)–C(2) 1.76(1), N(3)–C(4) 142(2), C(4)–C(5) 1.54(2), S(l)–C(5) 1.14(2), N(3)–C(13) 1.50(2), C(4)–C(12) 1.46(2), N(3)–C(2) 1.37(2), N(14)–C(2) 1.24(2), C(5)–C(6) 1.46(2). C(2)–S(1)–C(5) 93.8(7), S(1)–C(2)–N(14) 127.6(13), C(5)–C(4)–C(12) 111.7(15), C(2)–N(3)–C(13) 119.3(13), N(3)–C(2)–N(14) 125.1(14), S(1)–C(5)–C(4) 103.1(11), C(4)–N(3)–C(4) 117.8(13), N(3)–C(4)–C(5) 104.5(15), S(1)C(5)–C(6) 112.9(11), C(4)–N(3)–C(13) 114.8(15), N(3)–C(4)–C(12) 114.1(15), C(4)–C(5)–C(6) 115.6(15), S(1)–C(2)–N(3) 113.3(10).

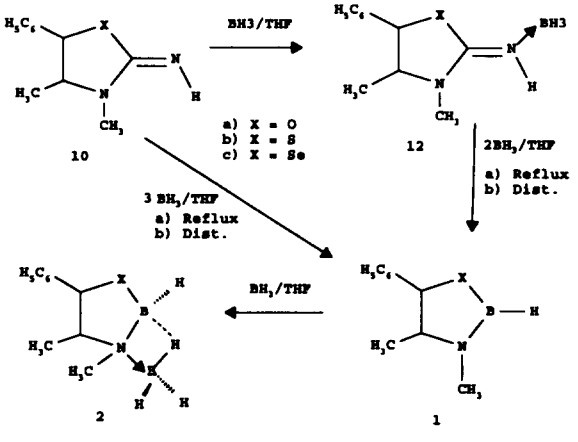


Figure 7. For X=O, methyl and phenyl groups are *cis*; for X=S or Se, methyl and phenyl groups are *trans*. In compounds **2**, the borane group is *trans* to the neighboring C4-methyl group.

studies of Nevalainen[6] and as a possible structure on the dimerization of the pseudoephedrine boroxazolidine.[7]

The reaction of compounds **1a–c** with BH_3/THF gave the diboranes **2a–c** (Figure 1). Compounds **2a**[7,1k,11] and **2b**[1m] had been previously reported. An enormous interest is focused on these borane-bearing optically active molecules as enantioselective reducing agents.[8,9] The structures of the borane adducts of borolidines were deduced from the ^{11}B NMR data, which can be attributed to diborane

Table 3. δ ^{11}B and ^{77}Se data[a]

Comp	B-H	N→BH_3	Se
1a	29.0 d, $J(^{11}B\text{-}^{1}H) = 147$		
1b	38.7 d, $J(^{11}B\text{-}^{1}H) = 149$		
1c	41.8 d, $J(^{11}B\text{-}^{1}H) = 147$		+223.4
2a	6.0 d, $J(^{11}B\text{-}^{1}H) = 173$	-20.8 c, $J(^{11}B\text{-}^{1}H) = 100$	
2b	-7.0 d, $J(^{11}B\text{-}^{1}H) = 148$	-22.2 c, $J(^{11}B\text{-}^{1}H) = 89$	
2c	-9.6 d, $J(^{11}B\text{-}^{1}H) = 149$	-20.9 c, $J(^{11}B\text{-}^{1}H) = 84$	+51.9
9c			-274.5 (+519.8 SeCN)
10c			-315.2
12a		-22.6	
12b		-20.1	
12c		-18.4	-319.5
12d		-18.4	-320.2
14		-15.7	

relative to BF_3 etherate and $(CH_3)_2Se$ as external references

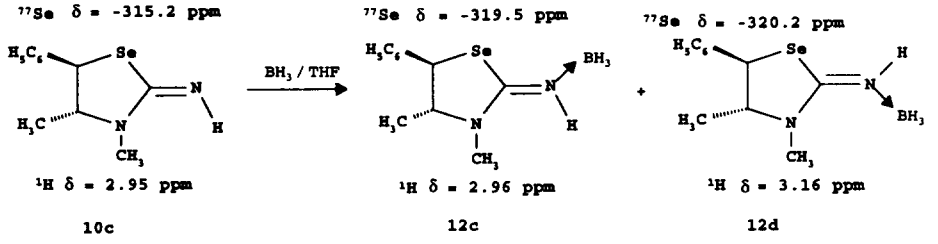


Figure 8.

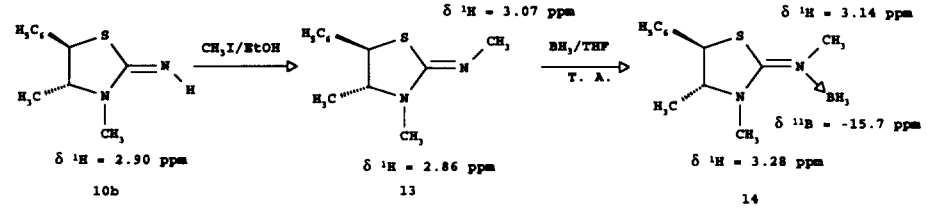


Figure 9.

derivatives, as denoted by the strong shifts of the endocyclic boron atom to lower frequencies ($\Delta\delta$ 23 ppm for **1a**; 46 for **1b**; 51 for **1c**) induced by the hydride bridge. From the latter data it can be concluded that the endocyclic boron is more acidic in going from X=O to X=Se. The strong acidity of the boron atom in **1c** also explains the dimer formation.

Infrared spectroscopy confirmed the diborane structure because the B–H–B bridge gives very strong bands at 1632, 1600 and 1576 cm^{-1}, respectively, for X=O, S and Se, whereas terminal BH_2 bond absorptions are observed at 2534, 2530 and 2536 and terminal B–H bonds at 2464, 2392 and 2474 cm^{-1}.

Experimental

The reactions were carried out under an atmosphere of dry nitrogen. All solvents were freshly distilled and dried before use according to established procedures. Melting points were measured on a Gallenkamp apparatus and are uncorrected. The IR spectra were taken as KBr discs or THF solutions using a Perkin–Elmer 16FPC IR spectrometer. All NMR spectra were obtained on a JEOL GXS-270 spectrometer. Suitable single crystals were sealed in a glass capillary and mounted on the diffractometer.

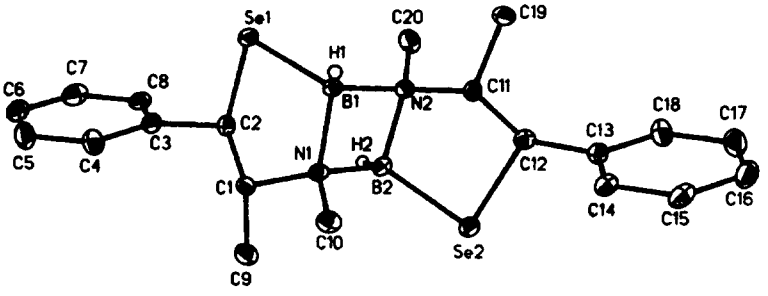


Figure 10. Perspective representation of compound **15**. Selected bond lengths (Å) and angles (deg.) are as follows: Se(1)–C(2) 1.983(4), Se(1)–B(1) 2.014(5), C(2)–C(9) 1.506(4), Se(2)–C(12) 2.001(4), Se(2)–B(2) 2.038(5), C(3)–C(8) 1.515(5), N(1)–C(10) 1.479(5), N(1)–C(1) 1.520(4), C(1)–C(2) 1.505(6), N(1)–B(1) 1.609(6), N(1)–B(2) 1.611(5), C(2)–C(3) 1.520(5), N(2)–C(20) 1.468(5), N(2)–C(11) 1.511(4), C(1)–C(9) 1.524(6), N(2)–B(2) 1.589(6), N(2)–B(1) 1.628(5), C(11)–C(19) 1.516(6), B(1)–H(1) 1.04(6), C(11)–C(12) 1.517(6), B(2)–H(2) 1.18(4), C(12)–C(13) 1.501(6). C(2)–Se(1)–B(1) 88.5(2), H(1)–B(1)–N(1) 114.3(32), C(2)–C(1)–C(9) 112.9(3), C(12)–Se(2)–B(2) 87.6(2), H(1)–B(1)–N(2) 119.6(31), N(1)–C(1)–C(9) 111.1(3), C(10)–N(1)–C(1) 108.9(3), N(1)–B(1)–N(2) 92.2(3), C(1)–C(2)–C(3) 115.8(3) C(10)–N(1)–B(1) 113.5(3), H(1)–B(1)–Se(1) 106.8(32), C(1)–C(2)–Se(1) 106.5(2), C(10)–N(1)–B(2) 117.6(3), N(1)–B(1)–Se(1) 105.8(2), C(3)–C(2)–Se(1) 108.9(3), C(1)–N(1)–B(1) 113.0(3), N(2)–B(1)–Se(1) 116.9(3), N(2)–C(11)–C(19) 113.0(4) C(1)–N(1)–B(2) 115.9(3), H(2)–B(2)–N(2) 107.8(21), N(2)–C(11)–C(12) 107.9(3), B(1)–N(1)–B(2) 86.4(3), H(2)–B(2)–N(1) 113.8(19), C(19)–C(11)–C(12) 113.8(3), C(20)–N(2)–C(11) 112.7(3), N(2)–B(2)–N(1) 93.5(3), C(13)–C(12)–C(11) 114.4(3), C(20)–N(2)–B(2) 114.6(3), H(2)–B(2)–Se(2) 112.8(20), C(13)–C12)–Se(2) 112.8(3), C(11)–N(2)–B(2) 110.2(3), N(2)–B(2)–Se(2) 105.9(2), C(11)–C(12)–Se(2) 104.0(2), C(20)–N(2)–B(1) 119.1(3), N(1)–B(2)–Se(2) 119.9(3), C(2)–C(1)–N(1) 109.9(3), C(11)–N(2)–B(1) 111.0(3), B(2)–N(2)–B(1) 86.5(3).

(1R,2R)-(−)-Chlorodesoxipseudoephedrine hydrochloride 8

The compound was prepared as reported.[9] M.p.198–200°C.

(4R,5R)-(+)-3,4-Dimethyl-5-phenyl-2-iminium-thiazolidine thiocyanate 9b

A solution of 5.05 g (22.96 mmol) of **8** and 3.72 g (45.92 mmol) of sodium thiocyanate (NaSCN) in 100 ml of ethanol was refluxed for 8 h. A precipitate was formed which was filtered and washed with ethanol. The solution was concentrated in vacuo and the reaction product crystallized (3.22 g, 53%). It was recrystallized from ethanol. M.p. 165.4–168.3°C. $[\alpha]_D^{35}$=+137.6 (c=1.2, H_2O). Crystallographic data: formula, $C_{12}H_{15}N_3S_2$; fw, 265.4, space group, triclinic P5,1,10; *a*=7.146(0) Å; *b*=7.481(0) Å; *c*=13.004(1) Å; α=86.12(4)°; β=88.38(3)°; γ=76.10(2)°; *V*=673.3 Å^3; *Z*=2; *F*(000), 280; crystal size=0.50×0.30×0.30 mm; linear abs. coeff. 3.6 cm^{-1}; ρ (calc) 1.31 g/cm^3; scan type, ω/2θ; scan range (deg.), 0.5+0.640tgθ; scan speed, 2–20 min^{-1}; data collected, 3180 used for refinement.

(4R,5R)-(+)-3,4-Dimethyl-5-phenyl-2-iminium-selenazolidine selenocyanate 9c

A solution of 2.32 g (16.1 mmol) of potassium selenocyanate and 1.77 g (8.05 mmol) of **8** in 60 ml of ethanol was refluxed for 8 h. A precipitate was formed which was filtered and washed with ethanol. The ethanol solution was concentrated and colorless crystals were formed (2.88 g, 93%). M.p. 144.1–146.2°C. $[\alpha]_D$=+203.2 (c=1.0, CH_3OH). Crystallographic data: formula, $C_{12}H_{13}N_3Se_2$; fw, 357.177, space group, $P2_1$; *a*=14.0395(3) Å; *b*=7.4981(1) Å; *c*=15.0738(3) Å; α=90.00°; β=115.08(2)°; γ=90.00°; *V*=1437.47 Å^3; *Z*=4; crystal size=0.3×0.2×0.1 mm; linear abs. coeff., 50.74 cm^{-1}; ρ (calc) 1.65 g/cm^3; scan type, ω/2θ; scan range (deg.), 0.5+0.43+0.51tgθ; data collected 2945.

(4R,SR)-(+)-3,4-Dimethyl-5-phenyl-2-imino heterocycles 10b and 10c

Compounds **9b** (3.2 g, 12 mmol) and **9c** (2.9 g, 8 mmol) were treated with one equivalent of NaOH solution and were stirred for 15 min, then the two phases were separated in a funnel and extracted with $CHCl_3$, the organic phase was dried with Na_2SO_4 and the solvent evaporated in vacuo. The reaction products were recrystallized from $CHCl_3$.

10b (2.5 g, quantitative yield). MS, M^+ 206 (65%). M.p. 74.9–75.4°C. $[\alpha]_D$=+66.2 (c=1.0, $CHCl_3$). Crystallographic data: formula, $C_{11}H_{14}N_2S$; fw, 206.3, space group, $P2_12_12_1$; *a*=8.073 Å; *b*=8.848 Å; *c*=15.787 Å, α=90.00°; β=90.00°; γ=90.00°; *V*=1127.7 Å^3; *Z*=4; crystal size=0.1×0.2×0.2 mm; F(000) 440, linear abs. coeff., 2.39 cm^{-1}; ρ (calc) 1.215 g/cm^3; scan type, ω/2θ; scan range (deg.), 0.42+0.78gθ; data collected 1186.

10c (2.03 g, quantitative yield), MS, M^+ 254 (79%). M.p. 86–88°C. $[\alpha]_D$=+67.9 (c=0.07, $CHCl_3$).

*(4R,5S)-3,4-Dimethyl-5-phenyl-2-iminoxazolidine **10a***

A solution of 2.76 g (12.5 mmol) of **8** and 2.03 g (25 mmol) of potassium cyanate (KOCN) in 60 ml of ethanol, was refluxed for 8 h. A precipitate formed, the solid was filtered and washed with ethanol, the solution was concentrated by evaporation and 0.5 g (12.5 mmol) of NaOH in water (25 ml) was added and stirred for 15 min. The reaction product was extracted with $CHCl_3$ and purified on a silica gel column with ethanol:$CHCl_3$ (80:20) as the eluent. Compound **10a** was obtained as a white crystalline powder (1.4 g, 60%). MS, M^+ 190 (23%). M.p. 90–93°C.

N-*borane adducts **11a–c***

The compounds were formed by reaction of 2-iminoheterocycles **10a–c** with an equivalent of BH_3/THF (2 M) in an NMR tube at room temperature and observed directly.

*(4R,5S)-3,4-Dimethyl-5-phenyl-2-boroxazolidine **1a**, (4R,5R)-(+)-3,4-dimethyl-5-phenyl-2-borathiazolidine **1b** and (4R,5R)-(+)-3,4-dimethyl-5-phenyl-2-boraselenazolidine **1c***

The preparation of compound **1c** illustrates the general procedure.

Compound **10c** (2.5 g, 10 mmol) was dissolved in 10 ml of dry THF and cooled in an ice bath, then 15 ml (30 mmol) of a 2 M BH_3/THF solution was added. The reaction mixture was refluxed for 4 h and then distilled in vacuo (bp 109°C at 1.1 mmHg). A viscous transparent liquid (**1c**) was obtained (1.43 g, 60% yield). $[\alpha]_D$=+59.7 (c=2.1, $CHCl_3$).

Compound **1a**, bp (100°C, 0.01 mmHg) $[\alpha]_D$=+108.0 (c=1.0, $CHCl_3$).

Compound **1b**, bp (100°C, 1 mmHg) $[\alpha]_D$=+67.3 (c=0.05, THF).

*(4R,5R)-(+)-3,4-Dimethyl-5-phenyl-2-boraselenazolidine dimer **15***

Compound **1c** was dissolved in $CDCl_3$ and the solution was left for several weeks in an NMR tube. The crystals formed were suitable for an X-ray study. Crystallographic data: formula, $C_{20}H_{28}B_2N_2Se_2$; fw, 475.98, space group, $P2_1$; *a*=6.320(2) Å; *b*=11.971(3) Å; *c*=13.861(3) Å; α=90.00°; β=94.91(1)°; γ=90.00°; *V*=1044.7 Å^3; *Z*=2; crystal size=0.3×0.15×0.15 mm; F(000) 480, linear abs. coeff., 35.45 cm^{-1}; ρ (calc) 1.513 g/cm^3; scan type, hemisphere; 2θ range for data collection 2.94 to 58.40°; data collected 6093.

*Compounds **2a–c***

The preparation of compound **2c** also illustrates the preparation of **2a** and **2b**.

trans-*(3R,4R,5R)-3-Borane-3,4-dimethyl-5-phenyl-1,3,2-selenazaborolidine **2c***

136 mg (0.6 mmol) of selenazaborolidine **1c** was placed in an NMR tube with 0.28 ml (0.6 mmol) of BH_3/THF solution (2.0 M) The solvent was eliminated in vacuo and $CDCl_3$ was added and the reaction product characterized by NMR.

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