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Novel Strained Heterocage Organoboranes: Amine Complexes of 4-Oxa- and 4-Thia-3-borahomoadamantane

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The title compounds have been obtained for the first time from 1-boraadamantane.

1-Boraadamantane and 3-borahomoadamantane are unique cage triorganoboranes containing tetrahedral (sp^3), but not trigonal (sp^2) boron atoms, as in other tricoordinate boron compounds, BX_3. This is reflected in their chemical properties, particularly in an increased tendency toward complexation.[1] For the same reason, 4-oxa-3-borahomoadamantane exists only in a dimeric form, **3**, with both B—O distances in the central four-membered ring being approximately equal (according to an X-ray study).[2] A similar feature is also characteristic of 4-aza-3-borahomoadamantane.[3]

There have been many arguments against the existence of a 4-hetero-3-borahomoadamantane monomer. Nevertheless, we have succeeded in the synthesis of a series of monomeric 4-oxa-3-borahomoadamantane–amine complexes **4**. In addition, the first synthesis of a new strained 4-thia-3-borahomoadamantane system **8** is reported in this communication (Scheme 1).

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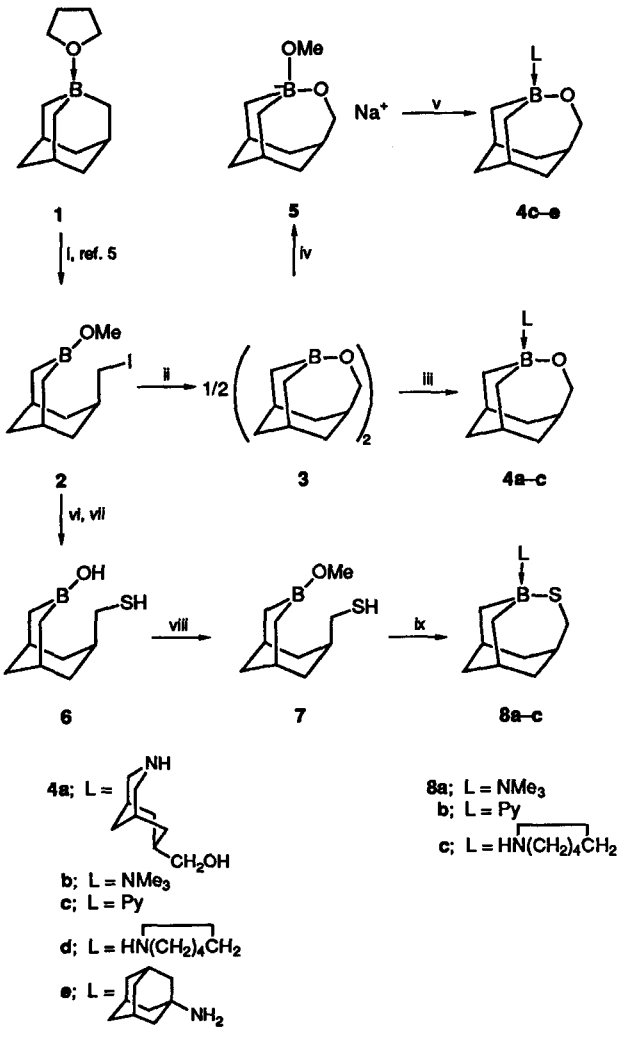


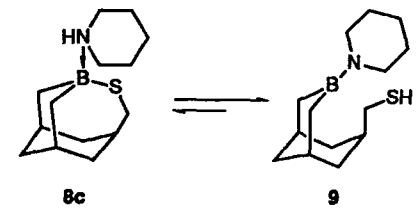
Scheme 1 *Reagents and conditions*: i, MeONa, I_2, THF, −30→20°C, 1 h (75%), ref. 5; ii, NaOH, Et_2O–H_2O, 35°C, 5 h (68%); iii, **a** ref. 4, **b** Me_3N, 20°C, 7 days, **c** pyridine (Py)–THF, 65°C, 0.5 h; iv, MeONa, MeOH–THF, 20°C, 0.5 h; v, L·HCl, MeOH–THF, 20°C, 0.5 h; vi, NaSH, DMF, 40°C, 3 h; vii, H_2O, 20°C, 0.5 h; viii, MeOH, molecular sieve 4Å, 20°C, 4 h; ix, **a** Me_3N, 20°C, 20 days, **b** Py, 50°C, 1 h, **c** piperidine, 50°C, 0.5 h

Bicyclic iodide **2** and dimeric 4-oxa-3-borahomoadamantane **3**, which are readily available from 1-boraadamantane–tetrahydrofuran (THF) adduct **1**,[5] were used as starting materials.

Complexes **4a–c** were obtained by reaction of the dimer **3** with an excess of the corresponding amine (10–50 equiv.) at room temperature or at 60–65°C (method A). An alternative route to **4** involved the transformation of the dimer **3** into the ate-complex **5** (δ_B 6.1 ppm, relative to $Et_2O \cdot BF_3$) followed by treatment with one equiv. of the amine hydrochloride in methanol (Method B). The latter route is preferable for amines with a high boiling point.

Amine complexes **4a–e** are air- and moisture-stable at room temperature (Table 1). It is noteworthy that acyclic esters R_2BOR' do not normally form complexes with amines. The enhanced stability of the 2-alkyl-1,2-oxaborolane–amine complexes has been explained in terms of a change in the boron atom hybridisation in the five-membered ring (from sp^2 to sp^3) during the course of complexation.[6]

The bicyclic iodide **2** has also been used in the first synthesis of a novel cage structure, 4-thia-3-borahomoadamantane. Reaction of **2** with sodium hydrosulfide in *N*,*N*-dimethylformamide (DMF), followed by hydrolysis, resulted in 3-hydroxy-7α-mercaptomethyl-3-borabicyclo[3.3.1]nonane **6** in 58% yield. The latter was transformed into methyl ester **7** (77%) by



reaction with methanol in the presence of molecular sieves (4Å).

The transannular cyclisation of **7** into 4-thia-3-borahomoadamantane complexes **8** was performed by treatment with an excess of amine (trimethylamine, pyridine or piperidine) and subsequent distillation of the volatiles *in vacuo*. Compounds **8a–c** are also stable in air at room temperature (Table 1).

The transformation of **7** into **8** represents an unusual reaction in boron chemistry, because the energy of the B—S bond (90 kcal mol^{-1})† is lower than that of the B—O bond (120–130 kcal mol^{-1}); therefore thioborinates, R_2BSR', are easily converted to R_2BOR'' and R'SH on the action of alcohols R''OH.[7] To our knowledge, the only exception described so far is ring-closure of $HS(CH_2)_3B(Bu)OR$ to give 2-butyl-1,2-thiaborolane on the action of piperidine.[8]

The polyhedral system of piperidine complex **8c**, which contains N—H bonds, opens up in benzene solution to give (after 7 days at 20°C) an equilibrium mixture of **8c** and aminoborane **9** (δ_B 43.8 ppm) in a ratio of 1:3 (according to ^{11}B NMR).

It should be noted that no compound **9** was observed under the conditions necessary for synthesis of **8c** from **7**. Our attempts to isolate 4-thia-3-borahomoadamantane in a free form failed.

All manipulations with organoboron compounds were performed in dry argon. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer (68.69 MHz for carbon). ^{11}B NMR sectra were obtained on a Bruker AC-200P spectrometer (standard $BF_3 \cdot Et_2O$).‡

† 1 cal = 4.184 J.

‡ *Selected spectroscopic data* for **4b**: ^1H NMR ($CDCl_3$) δ 0.30–0.60 (AB-spectrum, 4H, CH_2B, ^{AB}J 11.2 Hz), 2.44 (s, 9H, CH_3N), 3.74 (d, 2H, CH_2O, J 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 28.7 (C-1, 8), 35.1 (C-6), 38.0 (C-7, 10), 38.1 (C-9), 47.4 (CH_3N), 70.4 (CH_2O).

4c: ^1H NMR ($CDCl_3$) δ 0.53–0.77 (AB-spectrum, 4H, CH_2B, ^{AB}J 11.4 Hz), 3.92 (d, 2H, CH_2O, J 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ 29.2 (C-1, 8), 31.8 (C-2, 11), 35.3 (C-6), 38.2 (C-7, 10), 38.5 (C-9), 71.2 (CH_2O).

4d: ^1H NMR (C_6D_6) δ 0.58–0.82 (AB-spectrum, 4H, CH_2B, ^{AB}J 11.4 Hz), 3.02 (d, 2H, NCH_2^{eq}, J 10.5 Hz), 4.18 (d, 2H, CH_2O, J 2.6 Hz); ^{13}C NMR (C_6D_6) δ 27.1 (CH_2B), 29.6 (C-1, 8), 36.3 (C-6), 39.1 (C-7, 10), 39.3 (C-9), 45.3 (CH_2N), 71.9 (CH_2O).

4e: ^1H NMR (CD_3OD) δ 0.31 (d, 4H, CH_2B, J 4.0 Hz); 3.57 (d, 4H, CH_2O, 2.6 Hz); ^{13}C NMR (CD_3OD) δ 29.8 (C-2, 11), 30.8 (C-1, 9, 8), 36.9 (C-7, 9, 10), 37.1 (C-6), 70.6 (CH_2O).

6: ^1H NMR (C_6D_6) δ 0.84 (d, 4H, CH_2B, J 4.6 Hz), 1.16 (t, 1H, SH, J 7.4 Hz), 2.28 (t, 2H, CH_2S, J 7.4Hz), 4.42 (s, 1H, B-OH); ^{13}C NMR ($CDCl_3$) δ 26.7 (C-1, 5), 27.9 (C-2, 4), 32.5 (CH_2S), 33.7 (C-9), 35.0 (C-7), 35.9 (C-8).

7: ^1H NMR ($CDCl_3$) δ 0.83–1.01 (AB-spectrum, 2H, CH_2B, ^{AB}J 17.4 Hz), 1.32 (t, 1H, SH, J 7.5 Hz), 2.40 (t, 2H, CH_2S, J 7.5 Hz), 3.61 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$) δ 25.9 (CH_2B), 26.5 (C-1, 5), 32.2 (CH_2S), 34.1 (C-9), 35.2 (C-7), 35.8 (C-6, 8), 52.8 (OCH_3).

8a: ^1H NMR ($CDCl_3$) δ 0.84–0.98 (AB-spectrum, 4H, CH_2B, ^{AB}J 12.5 Hz), 2.42 (m, 1H, 6-H), 2.66 (s, 9H, CH_3N), 2.71 (d, 2H, CH_2S, J 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ 27.6 (C-1, 8), 33.6 (C-6), 33.7 (CH_2S), 37.3 (C-9), 37.8 (C-7), 49.1 (CH_3N).

8b: ^1H NMR (C_6D_6) δ 1.30 (d, 2H, BCH_2^{β}, J 11.2 Hz), 1.72 (d, 2H, BCH_2^{α}, J 11.2 Hz), 2.75 (m, 1H, 6-H), 3.18 (d, 2H, CH_2S, J 4.2 Hz); ^{13}C NMR (C_6D_6) δ 28.3 (C-1, 8), 34.0 (C-6), 36.5 (CH_2S), 37.3 (C-9), 37.7 (C-7, 10).

8c: ^1H NMR (C_6D_6) δ 0.75 (m, 4H, CH_2B), 3.10 (m, 4H, CH_2S, NCH_2^{eq}); ^{13}C NMR (C_6D_6) δ 28.6 (C-1, 8), 34.3 (CH_2S), 34.7 (C-6), 38.3 (C-9), 38.4 (C-7, 10), 46.4 (CH_2N).

Table 1 Properties of cage (**4** and **8**) and bicyclic (**6** and **7**) compounds

Compound[a]	Yield (%)	Method	M.p./°C	δ_B (solvent)	MS: *m/z*, ion
4a[b]	4.5	A	192–196 (decomp.)	+6.6 ([$^2H_8$]THF)	155, L, [M$^+$]
					300, **3**, [M$^+$]
4b	94	A	93–97 (decomp.)	+7.2 ($CDCl_3$)	300, **3**, [M$^+$]
4c	88	A	112–116 (decomp.)	+6.4 ($CDCl_3$)	79, Py, [M$^+$]
	53	B			300, **3**, [M$^+$]
4d	60	B	151–153	+5.0 (C_6D_6)	235, **4d**, [M$^+$]
4e	82	B	160–162	+4.5 ([$^2H_8$]THF)	300, **3**, [M$^+$]
					301, **4e**, [M$^+$]
8a	45		141–144 (decomp.)	+4.4 ($CDCl_3$)	225, **8a**, [M$^+$]
8b	55		174–175	+1.6 ($CDCl_3$)	245, **8b**, [M$^+$]
8c	74		111–113 (decomp.)	+0.6 ($CDCl_3$)	251, **8c**, [M$^+$]
6	58		76–78	+53.0 ($CDCl_3$)	184, **6**, [M$^+$]
7	77		[c]	+53.5 ($CDCl_3$)	–

[a] All novel compounds have satisfactory analytical and spectroscopic data. [b]See ref. 4; [c] Liquid, b.p. 93–95°C (2 mm Hg), n_D^{20} 1.5210.

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