

Boron and gallium esters derived from 2-(1,3,5-dithiazinan-5-yl)-ethanols

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Dedicated to Professor Rosalinda Contreras on the occasion of her 60th birthday

Abstract

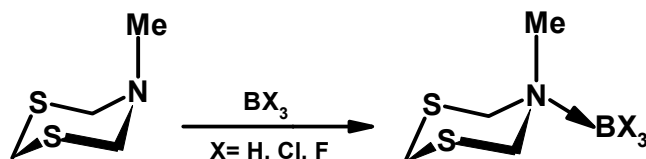
Compounds 2-(1,3,5-dithiazinan-5-yl)ethanol (**1**), 2-methyl-2-(1,3,5-dithiazinan-5-yl)ethanol (**2**) and 2-phenyl-2-(1,3,5-dithiazinan-5-yl)ethanol (**3**) reacted with BF₃·OEt₂ and BCl₃·DMS, **1** and **2** with (Ph₂B)O, and **2** and **3** with GaCl₃ giving the corresponding chelates, bearing N→BF₂O, N→BCl₂O N→BPh₂O, and N→GaCl₂O groups. The internal coordination N→M (M = B or Ga) afforded spiro-compounds, where nitrogen is the central atom. Compounds were mainly characterized by ¹¹B, ¹H and ¹³C NMR. The N→B or N→Ga coordination bond was detected in the ¹H spectra because coordination stops the ring inversion of the dithiazinane ring differentiating equatorial and axial protons. The presence of a stereogenic center at the ethanol arm (ligands **2** and **3**), differentiates C₄H₂ and C₆H₂ upon coordination. Minimum energy structures for boron compounds were calculated [*ab initio* 6-31G(d,p)]. VT NMR experiments for diphenyl borinic esters were performed in order to estimate the N→BPh₂ coordination energy. X-ray diffraction analyses of the hydrochloride of ligand **1** and of the gallium compound prepared from **2** were obtained.

Keywords: 2-(1,3,5-dithiazinan-5-yl)ethanols, boron and gallium esters, X-ray diffraction, *ab initio* calculations, VT NMR

Introduction

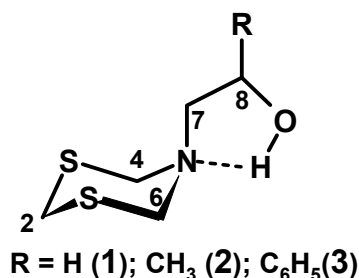
Dithiazinanes are very reactive molecules rich in lone pairs and suitable ligands for elements of group 13. They are used as flavouring agents¹ catalysts,² antibiotics^{2,3} or reagents in organic synthesis.^{4,5} The coordinating ability of the simple dithiazinanes was already tested using BX₃ reagents (X = H or halogen), in all cases the nitrogen is the more basic site,⁶⁻¹³ Scheme 1. An

important characteristic of the boron-nitrogen adducts of dithiazinanes is that the equatorial $N\rightarrow BH_3$ or $N\rightarrow BF_3$ groups stop the fluxional behavior of the ring by the presence of multiple and cooperative proton-hydride or proton-fluoride interactions.¹¹⁻¹³



Scheme 1. Borane adducts of *N*-methyldithiazinanes.¹¹⁻¹³

In the past, one of us has investigated the reactions of BH_3 and boric acid with ethanolamines.¹⁴ It was found that these reactions give selectively boric or boronic esters, amineboranes, amineboranes-boric esters or amineborane-boronic esters depending on the stoichiometry and the reaction conditions. In the reaction products, the nitrogen lone pair could be intramolecularly coordinated to boron, if the steric demand is not very high. Therefore, our interest was focused in exploring how the combination of dithiazinane and ethanolamine groups in compounds **1-3** could give better ligands for boron or gallium compounds, Scheme 2.



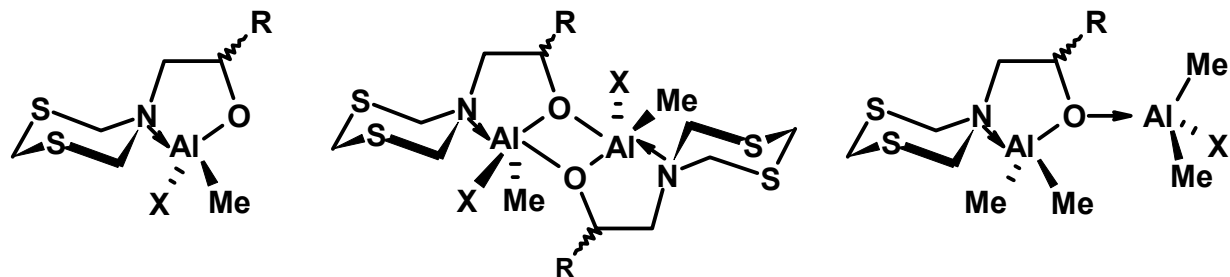
Scheme 2. Dithiazinanyl derivatives used as ligands.

The strong intramolecular hydrogen bonds $O-H\cdots N$ of compounds **1-3**¹⁵ are indicative that in the corresponding boron or gallium esters, these atoms would occupy the place of the proton, Scheme 2. This idea is supported by the report that diphenyl borinic esters of 4-hydroxypiperidine⁷ and 1,4-diethanolpiperazine²⁴ present strong intramolecular $N\rightarrow B$ coordination leading to spiro-compounds.

The preparation and the structural analysis of the dithiazinanyl-*N*-ethanols ligands (**1-3**) have been reported.¹⁵ The solid state structures obtained by X-ray diffraction showed that the ethanol moiety was placed in the axial position with a strong intramolecular hydrogen bond $OH\cdots N$, whereas the NMR analyses in $CDCl_3$ showed a ring conformational equilibrium at room temperature with a preferred conformation for the *N*-alkyl group in axial position⁸, the latter phenomenon has been attributed to the electronic repulsion between the lone pairs at sulfur and

nitrogen atoms.¹⁶ The low temperature spectra of compounds **1-3** show that the ring conformation is frozen and different signals for equatorial and axial protons are observed.¹⁵ For ligands **2** and **3**, the low temperature and the presence of a stereogenic center at C-8 (Scheme 2), make the methylene groups at C4 and C6 diastereotopic, with different ¹H-NMR chemical shifts.

We have already investigated the reaction of the neutral ligands **2** and **3** with organoaluminum compounds.¹⁷ Three types of aluminum derivatives were obtained, shown in Scheme 3.



Scheme 3. Organoaluminum compounds derived from ligands **2** and **3**.¹⁷

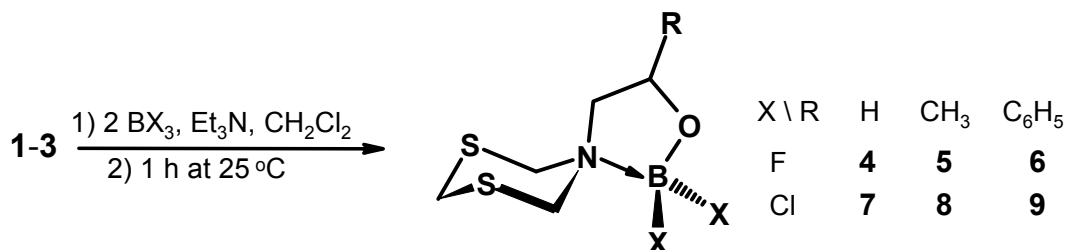
These results motivated us to test the reactions of compounds **1-3** with other group 13 elements: boron and gallium. The expected derivatives are interesting because both elements can react with the OH group giving the corresponding esters and forming chelates by coordination to the nitrogen atom. They are also of interest as gallium coordination compounds have been less well investigated than boron derivatives, despite the fact that gallium has a metallic character and that strong and stable derivatives are expected. The structure of the products was determined by NMR and the minimum energy conformations of the boron compounds were calculated by *ab initio* 6-31G(d,p). The X-ray diffraction analysis of the gallium compound (R = CH₃, **12**) as well as the hydrochloride (**15**) of compound **1** are also reported.

Results and Discussion

Boron Compounds

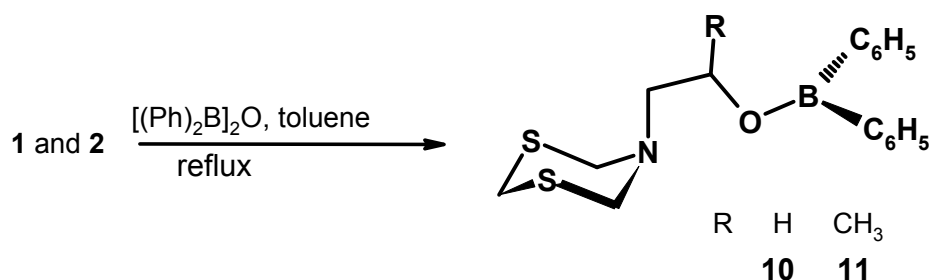
We have reacted 2-(1,3,5-dithiazinan-5-yl)ethanols **1-3** with BF₃·OEt₂, BCl₃·SMe₂, and **1** and **2** with (Ph₂B)₂O. Different products were expected because dithiazinanyl-ethanols present two active sites to boron reagents: the OH group which can form boron esters and the nitrogen that can give N→B coordination compounds. Unfortunately, we were not able to obtain crystals for X-ray diffraction analyses, however we have performed *ab initio* calculations as an alternative to study the minimum energy structures, and as we will see later, calculations are an excellent tool for the structural analyses of these compounds.

The reactions of compounds **1-3** with two equivalents of $\text{BF}_3 \cdot \text{OEt}_2$ in the presence of NEt_3 afforded the difluoroborates **4** (85%), **5** (80%) and **6** (95%); whereas with BCl_3 in CH_2Cl_2 or DMS gave the dichloroborates **7** (94%), **8** (90%) and **9** (94%), Scheme 4.



Scheme 4

The reactions of **1-2** with $(\text{Ph}_2\text{B})_2\text{O}$ in toluene afforded selectively the diphenyl borinic esters **10** (90%) and **11** (95%), Scheme 5.

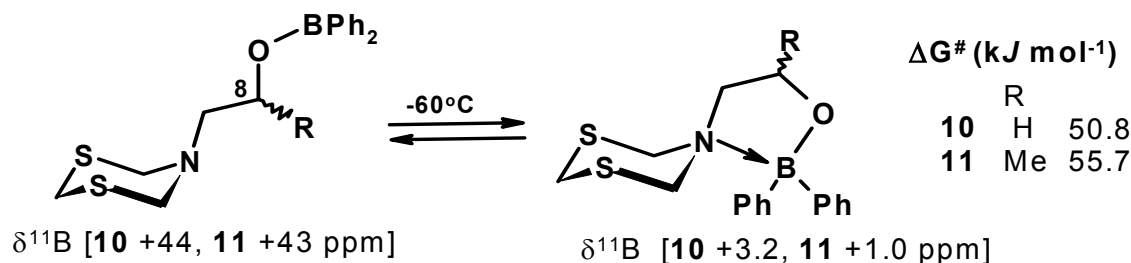


Scheme 5

From the reaction mixture of compound **7**, some crystals were obtained which were the hydrochloride (**15**) of compound **1**, its X-ray diffraction structure was determined, and is discussed below.

The ^{11}B NMR spectra show broad signals for compounds **4-6** (**4** +3.7, **5** +3.8, **6** +3.4 ppm) which correspond to $\text{OBF}_2 \leftarrow \text{N}$ groups,^{18,19} and for compounds **7-9** (**7** +9.9, **8** +10.0, **9** +10.3 ppm) characteristic of $\text{OBCl}_2 \leftarrow \text{N}$ groups.^{18,19} Reactions between two equivalents of compounds **1** and **2** and $(\text{Ph}_2\text{B})_2\text{O}$ produced esters **10-11**, the ^{11}B signals (**10** +44, **11** +43 ppm) were attributed to tricoordinated planar diphenylboronic esters, indicating the absence of nitrogen coordination, however when the ^{11}B spectra were obtained at -60° (**10** +3.2, **11** +1.0 ppm) the chemical shifts corresponded to diphenylborinic esters coordinated with nitrogen, Scheme 6. Therefore, for diphenylboron compounds, an equilibrium between the open boron esters and the intramolecular coordinated $\text{N} \rightarrow \text{B}$ molecules is proposed. The experiment indicated that the dithiazinane ring is a weaker base than piperidine or piperazine because the diphenyl borinic

esters derived from 4-hydroxypiperidine [$\delta^{11}\text{B}$ (25°C) +3.0 ppm]⁷ and 1,4-diethanolpiperazine [$\delta^{11}\text{B}$ (25°C) +6.0 ppm]²⁴ are already coordinated at room temperature.



Scheme 6. Compounds **10-11** are in equilibrium between the open structure and the spirobicyclic compound, N→B bond energies were calculated from VT NMR experiments.

Esters formation (**4-11**) was also confirmed by their ¹³C spectra. Signals for C8 are shifted to high frequencies ($\Delta\delta \approx 6.7$ ppm) with respect to the starting ethanol-dithiazinanes **1-3**, Table 1. The coupling pattern of the ¹H NMR spectra of **4-9** and of **10-11** at low temperature indicate that the inversion of dithiazinane rings is anchored as a consequence of the N→B coordination. The axial and equatorial protons appear at different chemical shift and are coupled due to the presence of stereogenic carbon atoms (C8 bearing methyl or phenyl groups) in compounds **5**, **6**, **8**, **9** and **11**. The C4H₂ and C6H₂ methylene groups are diastereotopic, and the separation of the diastereotopic signals increases with the strength of the N→B coordination bond.²⁰ In Table 1, NMR data are shown.

The difference in the chemical shift of the CH₂ protons is also due to the non symmetric contact of the halogen atoms with the methylenic protons in **4-9**. As is shown in the calculated molecules that will be discussed below, one of the halogen atoms adopt a *pseudo*equatorial position with respect to the five membered ring and is close to the two axial C4H and C6H protons, whereas the second halogen atom is *pseudo*axial and lies close to the C6H equatorial proton producing an electronic effect. Figure 1 illustrates these interactions. It is therefore expected that the highest frequency signal belongs to the equatorial C6H proton; from this assumption and using HETCOR and COSY experiments the ¹H and ¹³C signals were assigned.

From the NMR experiments the N→B coordination bond energy of **10-11** was calculated and the values are 50.8 (**10**) and 55.7 kJ mol⁻¹ (**11**); these are higher than those found for the free ligands **1** and **2** (45.4 and 49.3 kJ mol⁻¹)¹⁵ and N-methyl-dithiazinane (46 kJ mol⁻¹),^{16,21} however they are weak bonds in the range found for N→B heterocycles (50 - 81 kJ mol⁻¹).²²⁻²⁴

Table 1. ^1H and ^{13}C NMR data (δ , ppm) for compounds **1-14** and **16**

13 R = CH₃
14 R = C₆H₅

16

No	R	E	No.	R	E
1	H	H	7	H	BCl ₂
2	CH ₃	H	8	CH ₃	BCl ₂
3	C ₆ H ₅	H	9	C ₆ H ₃	BCl ₂
4	H	BF ₂	10	H	BPh ₂
5	CH ₃	BF ₂	11	CH ₃	BPh ₂
6	C ₆ H ₅	BF ₂	12	C ₆ H ₅	BPh ₂

Compd	2ax	2eq	4ax	6ax	4eq	6eq	C2	C4	C6
1 (-60°C)	4.50	3.54	4.77	4.77	3.97	3.97	33.8	58.4	58.4
4 (-10)	4.30	3.44	4.48	4.48	3.97	3.97	30.2	55.8	55.8
7 (25°C)	4.22	3.48	4.62	4.62	4.35	4.35	30.7	57.9	57.9
10 (-60°C)	4.43	2.54	4.66	4.66	3.93	3.93	32.2	58.2	57.9
2 (-60°C)	4.54	3.60	4.73	4.86	3.97	3.97	33.7	55.6	61.2
5 (25°C)	4.28	3.42	4.47	4.47	3.98	3.98	30.5	55.1	57.9
8 (25°C)	4.26	3.51	4.68	4.53	4.16	4.43	30.7	58.1	58.7
11 (-50°C)	4.69	3.59	4.49	4.49	3.43	3.43	31.6	56.5	57.3
12 (25°C)	4.34	3.44	4.92	4.69	3.85	4.30	31.2	53.8	57.3
16 (25°C)	4.36	3.44	4.85	5.00	3.84	3.86	32.0	56.9	53.5
3 (-60°C)	4.55	3.60	4.77	4.87	3.98	4.09	33.9	55.6	61.1
6 (25°C)	4.26	3.38	4.47	4.53	3.99	4.16	30.5	57.4	54.8
9 (25°C)	4.19	3.36	4.48	4.66	4.29	4.31	30.6	58.5	57.9
13 (25°C)	4.34	3.42	4.67	5.01	4.05	4.20	31.8	57.0	53.6

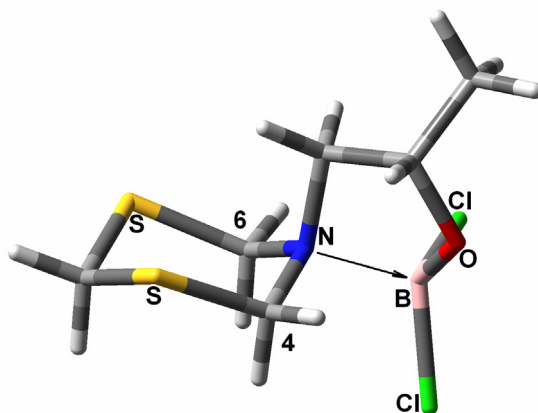


Figure 1. Minimum energy structure calculated for compound **8**. One chlorine atom is close to equatorial C6-H, whereas the other is close to axial C4-H.

Optimized structures of boron compounds 4-11

The preferred conformation of molecules **4-11** was calculated [*ab initio* 6-31G(d,p)] and found to be the same conformation for all compounds. The six membered rings have a chair conformation, the ethanol groups are in an axial position and the boron is in an equatorial position. The five membered rings formed by the coordination show an envelope conformation. For compounds **5**, **6**, **8**, **9** and **11**, the methyl or phenyl groups are found in *pseudo*equatorial positions, some examples of which are shown in Figures 1-4.

In the calculated molecules bearing boron halogen bonds, the N→B bond lengths are (**4** 1.70; **5** 1.75, **6** 1.73, **8** 1.72, **9** 1.71 Å). The N→B distances indicate this coordination and are comparable with the N→B bond distance of 1.63 Å found by X-ray diffraction analysis in the N→BH₂Cl adduct of N-methyl dithiazinane.²⁵ The calculated preferred conformations are similar to that found by X-ray diffraction analyses for the aluminium derivatives¹⁷, and for the gallium compound (**12**) reported here. For example, the calculated angles around the nitrogen (which can be related to the coordination bond) in compounds **5** (C4-N-C6 112.2; C6-N-C7 113.9 and C4-N-C7 114.9°) and **8** (C4-N-C6 110.8; C6-N-C7 112.3 and C4-N-C7 114.4°) are similar to those found in the X-ray analysis of the gallium compound **12** (C4-N-C6 110.6; C6-N-C7 111.6 and C4-N-C7 113.3°), see below. The boron atoms are also pyramidal. For example, in compound **5** the angles are: O-B-F_A 116.5, O-B-F_B 117.5, F_A-B-F_B 112.1° and in **8** O-B-Cl_A 113.9, O-B-Cl_B 115.6, Cl_A-B-Cl_B 110.0°.

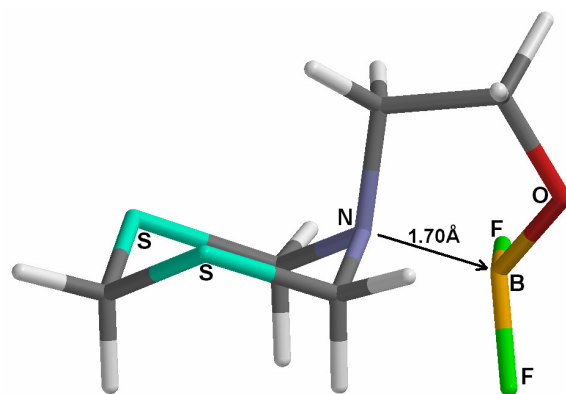


Figure 2. Preferred conformer of compound **4** found by *ab initio* 6-31G(d,p) calculations.

A view of compounds **5** and **9** in the C7-C8 bond axis (left in Figures 3 and 4) shows the preferred envelope conformation of the five membered ring, with the nitrogen atom out of the ring plane, and that the phenyl or methyl group is in the equatorial position.

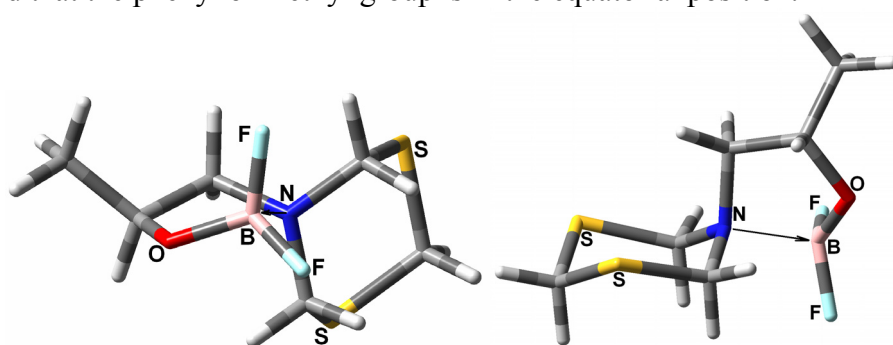


Figure 3. Two views of the calculated preferred conformation of compound **5**.

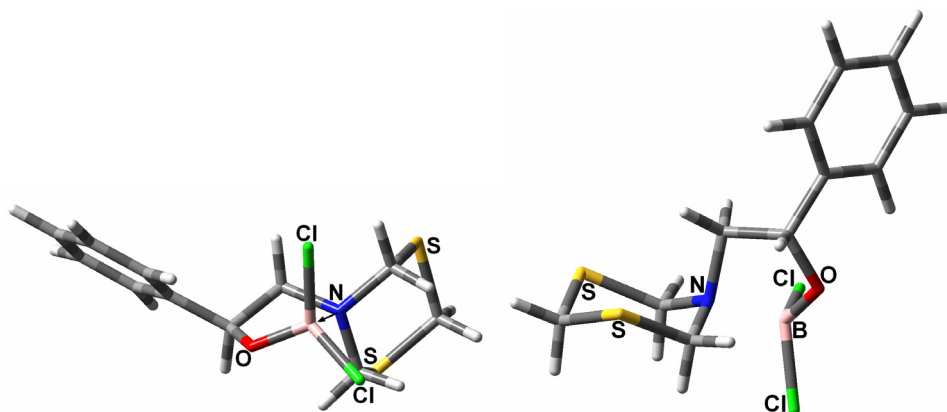


Figure 4. Two views of the calculated minimum energy structure of compound **9**.

The coordinated N→B structures of compounds **10-11** were also calculated. The most stable conformation observed for **11** is shown in Figure 5. Angles around the boron and nitrogen atoms and the N···B distances ($\approx 3.05 \text{ \AA}$) indicate a weak interaction, shorter than the sum of the van der Waals radii (3.84 \AA).²⁶ In these molecules, the boron sp^3 hybridization is minimum ($\approx 0.4 \%$) disfavoring the N→B bond coordination as was also deduced from the NMR analysis. In the preferred conformation of **11**, it is noted that the plane of the phenyl groups is close to the C4H and C6H equatorial protons, which explains the shielding effect found in the ^1H spectra of **11** (C4-H and C6-H 3.43 ppm) when compared with **8** (C4-H 4.16 and C6-H 4.43 ppm).

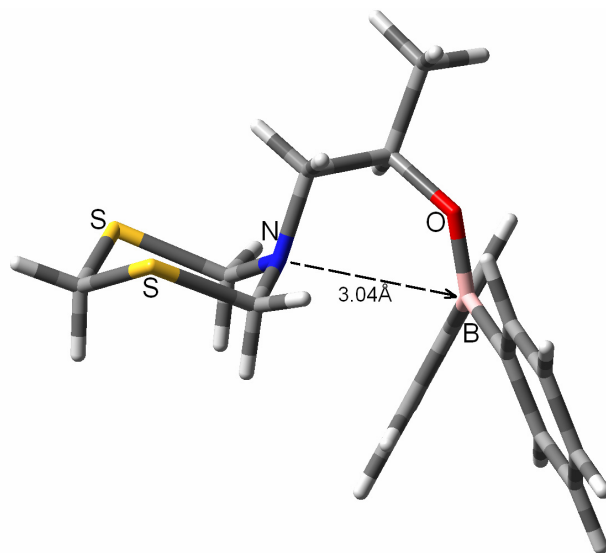
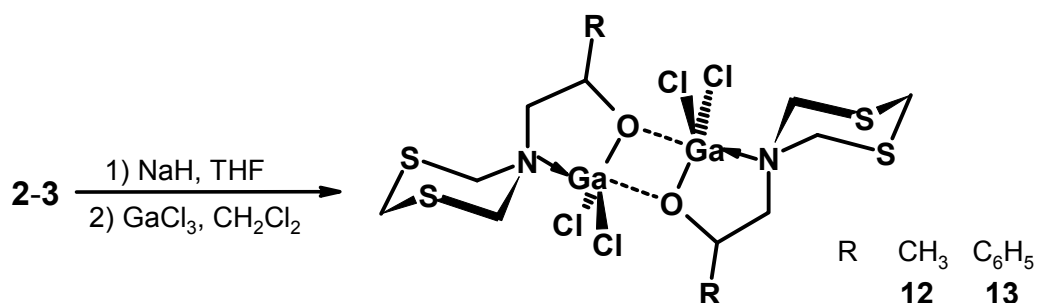


Figure 5. Structure of compound **11** found by *ab initio* 6-31G(d,p) calculations.

Gallium compounds

The gallium (dithiazinyl)ethanol compounds **12** and **13** were prepared from the reaction of the sodium ethanolate of compounds **2** and **3** and GaCl_3 in toluene, **12** (90 %) and **13** (90 %), Scheme 7. After the reaction they were directly dissolved in dried CDCl_3 and analysed by NMR. Compound **12**, crystallized directly from the NMR tube.

Compounds **12-13**, show very complex NMR coupling patterns, due to the fact that the gallium is strongly bonded to the ligand and to the stereogenic carbon atoms of the racemic ligands. The behaviour is similar to that found in the boron compounds, and the explanation was confirmed by the X-ray diffraction analyses.



Scheme 7

Compound **12** crystallized from CH₂Cl₂ as a dimer, and X-ray analysis was performed at 25 °C, Figure 6. Compound **12** is pentacyclic with two six membered rings, two five membered rings and one four membered ring. The dithiazinane rings have a chair conformation, with the gallium coordinated to the nitrogen atom in an equatorial position, and the ethanolic chain in an axial position. The five membered rings have an envelope conformation with C7 and C7a out of the ring plane and the methyl group in an equatorial position. Both stereogenic C8 carbon atoms have the same configuration in each dimer, and enantiomeric dimers are found in the crystal. The four membered ring is planar, and is formed by oxygen and gallium atoms. The gallium geometry is a distorted t_{bp} with one oxygen and one nitrogen atoms in apical positions (angles O-Ga-N 151.27° and 153.40°), Table 2. In equatorial positions, the gallium has two chlorine and one oxygen atom. The Cl-Ga-O angles are unequal around each gallium center. For the chlorine atom which is *pseudo*equatorial in the five membered ring, the angles are 133.5° and 137.4°, while for the *pseudo*axial chlorine the angles are 109.7° and 111.0°. The angles between Cl-Ga-Cl are 112.8° and 115.4°. The gallium atoms form the longest bonds with the nitrogen atoms (2.23 and 2.22 Å) and the shortest with the gallium equatorial oxygen atoms (1.89 Å), whereas with the axial oxygen atoms are 1.96 Å. The Ga-Cl bond lengths are ≈ 2.18 Å.

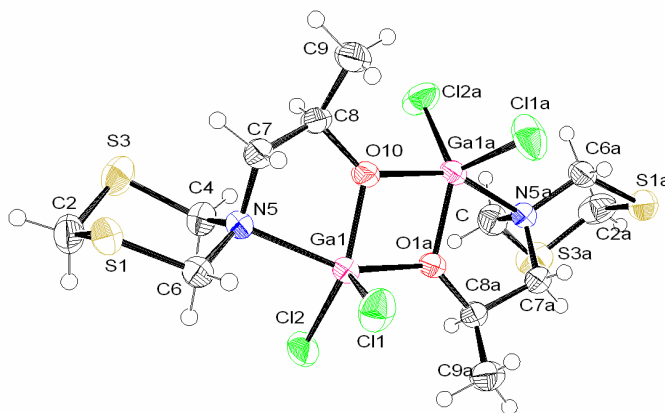


Figure 6. X-Ray diffraction structure of compound **12**.

Table 2. Compound **12**, selected bond lengths and angles

Bond lengths					
Cl2-Ga1	2.1791(8)	Ga1-O10	1.8919(2)	Ga1-N5	2.235(2)
Ga2-O10	1.968(2)	Ga1-Cl1	2.1860(8)	N5-C6	1.486(4)
O10-C8	1.439(3)	S1-C6	1.801(3)	S1-C2	1.804(4)
N5-C4	1.484(4)	C8-C9	1.515(5)	S3-C2	1.803(4)
N5-C7	1.485(4)	C8-C7	1.520(4)	S3-C4	1.813(3)
Bond angles					
C6-N5-Ga1	109.99(2)	O10-Ga1-Cl2	109.71(7)	C2-S3-C4	97.51(2)
C2a-S3a-C4a	97.15(2)	N5-C4-S3	116.5(2)	O10-Ga1-Cl1	137.43(7)
C8-O10-Ga1	121.69(2)	S3-C2-S1	112.22(2)	C8-O10-Ga1a	133.21(2)
Cl2-Ga1-Cl1	112.85(4)	Ga1-O10-Ga1a	104.99(9)	O10-Ga1-N5	79.96(9)
O10-C8-C9	110.8(3)	Cl2-Ga1-N5	97.66(6)	Cl1-Ga1-N5	93.44(6)
C6-S1-C2	96.77(2)	C7-N5-C6	111.7(2)	O10-Ga1a-Cl2a	102.40(7)
C4-N5-C7	113.3(2)	C4-N5-Ga1	109.95(2)	C4-N5-C6	110.6(2)
C7-N5-Ga1	100.99(2)	O10-Ga1a-Cl1a	94.34(6)	O10-C8-C7	107.0(2)
Cl1a-Ga1a-Cl2a	115.40(4)	C9-C8-C7	110.7(3)	N5-C7-C8	110.6(2)
N5-C6-S1	116.3(2)				

The position of the chlorine atoms with respect to the C4 and C6 methylene hydrogen bonds is important. There are four intramolecular Cl \cdots H bonds with distances between 2.67-3.16 Å. These bonds produce a very complex NMR spectrum as we have already discussed for the boron compounds, Figure 7.

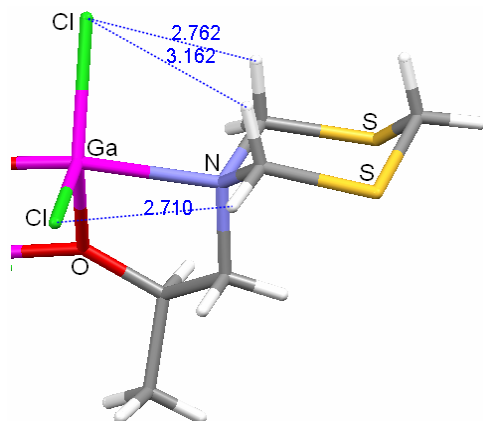


Figure 7. Short contacts between the chlorine atoms and the methylene protons found by X-ray diffraction analyses in compound **12**.

It is interesting to compare the gallium compound **12** with an analogous reported aluminum compound **17** prepared from ligand **1**,¹⁷ Figure 8. The aluminum oxygen bonds vary between 1.82 to 1.92 Å, the longest bonds are the Al-N (2.47 Å) and the shortest the Al-C 1.96-1.97 Å.¹⁷ The angles N-Al-O are similar to those of the gallium compound (151, 152°). The angles C-Al-C (124°) are more open than the Cl-Ga-Cl angles (124°).

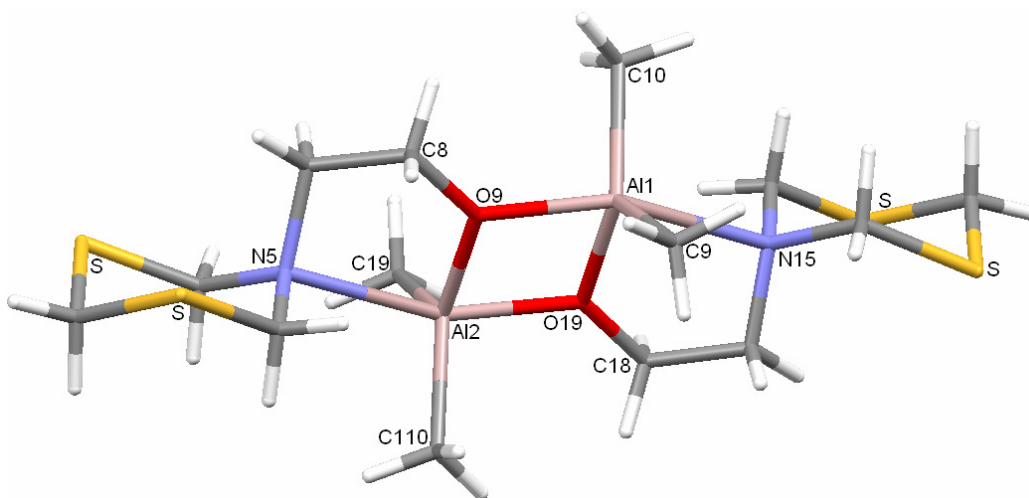


Figure 8. Aluminum compound **17** prepared from ligand **1** and AlMe_2Cl .¹⁷

In the cell of compound **12**, the chlorine atoms have intermolecular hydrogen bonds as is shown in Figure 9.

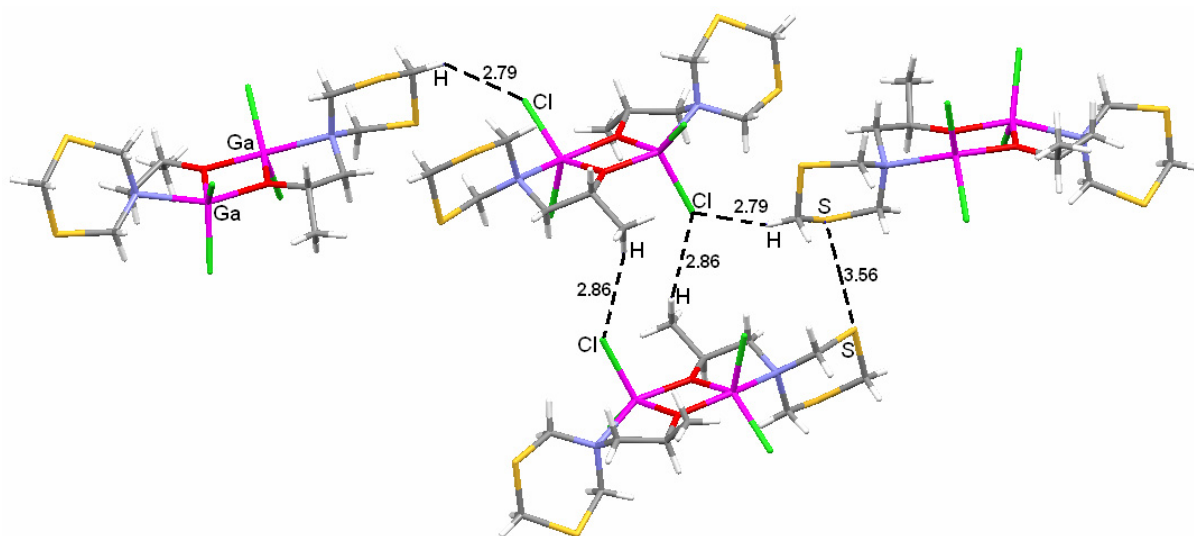


Figure 9. Compound **12** forms polymers by C-H...Cl hydrogen bonds and sulfur sulfur weak contacts.

Compound **15**, the hydrochloride of **1**, was obtained as a by-product, from the reaction of **1** with BCl_3 and its solid state structure was determined by X-ray diffraction. Selected bond lengths and angles are presented in Table 3. The ring is a chair with an unusual conformation for a protonated dithiazinane, bearing the N-ethanol group in axial and the N-H proton in equatorial positions. The opposite conformation, with the biggest group in an equatorial position was expected, because the electronic repulsion between the lone pairs of the nitrogen and the sulfur atoms no longer exists, Figure 10. One possible explanation for this unusual conformation could be the presence of two hydrogen bonds formed between the N- CH_2 protons and the sulfur atoms (2.94 and 2.80 Å) [$\sum_{\text{vdw}} = 3.26 \text{ \AA}$].²⁶ The NH proton has a hydrogen bond with the oxygen and the OH proton with the chloride (2.22 Å).

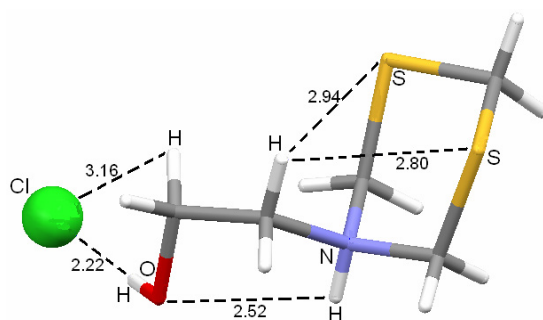
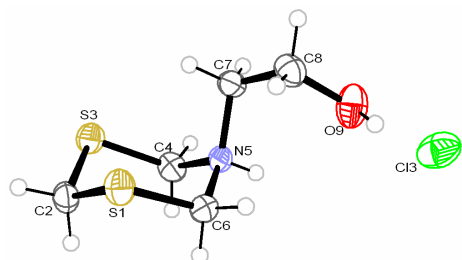


Figure 10. Solid state structure of the hydrochloride of compound **14** that shows the hydrogen bonds formed with oxygen sulfur and chloride.

Table 3. Compound **15** selected bond lengths and angles

Bond lengths					
S1- C6	1.792(2)	O9-C8	1.421(2)	N5-C6	1.505(2)
S1-C2	1.802(2)	N5-C7	1.501(2)	C7-C8	1.501(3)
S3-C4	1.794(2)	S3-C2	1.801(2)	N5-C4	1.505(2)
Bond angles					
C6-S1-C2	97.76(9)	C7-N5-C6	115.77(1)	S3-C2-S1	112.48(1)
C4-S3-C2	97.59(1)	C4-N5-C6	111.51(1)	N5-C4-S3	113.68(1)
C7-N5-C4	112.14(1)	O9-C8-C7	109.4(2)	N5-C6-S1	113.94(1)
C8-C7-N5	112.4(2)				

In the net of compound **15**, the chloride ion forms five hydrogen bonds with four molecules of the ligand, Figure 11. There is also an intermolecular bond of a geminal proton to OH with one sulfur atom, as well as S...S (3.5 Å) and S...Cl (3.78 Å) short contacts. The oxygen atom has also two cooperative intermolecular hydrogen bonds with one proton of the chain (2.57 Å) and one proton of the ring (2.56 Å), Figure 12.

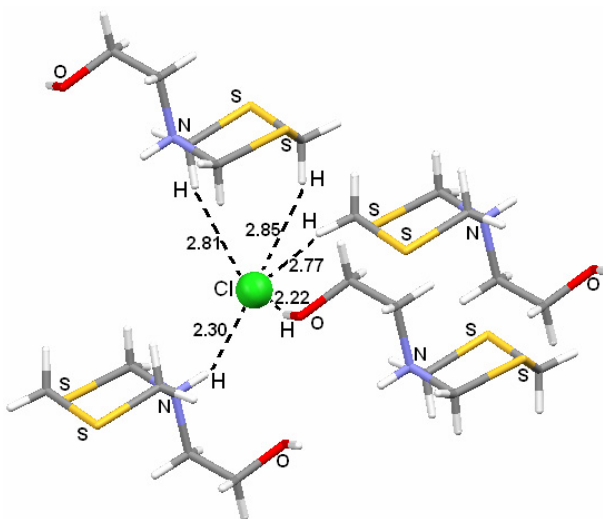


Figure 11. Intermolecular chloride connections with different dithiazinanium ions for compound **15**. The values of the atomic distances in C-H...Cl, N-H...Cl and O-H...Cl hydrogen bonds are shown.

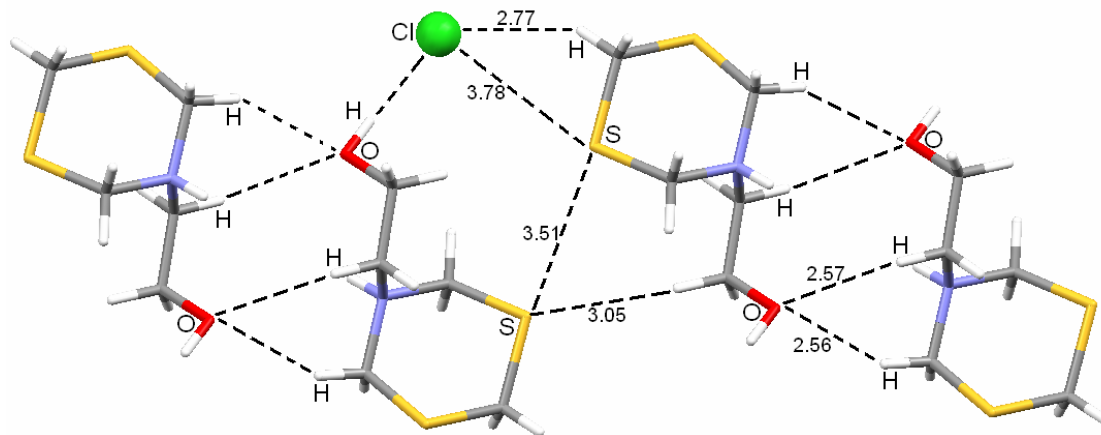


Figure 12. Molecular association of the crystalline net of compound **15** showing CH \cdots O, CH \cdots S, CH \cdots Cl, OH \cdots Cl, hydrogen bonds.

Conclusions

New boron and gallium esters derived from ethanol dithiazinanes were prepared and their structures were studied by NMR and in one gallium compound by X-ray diffraction. The difluoro and dichloroboron compounds gave spiranic compounds formed by the N \rightarrow B coordination whereas diphenylborinic esters were not coordinated in the same conditions. VT NMR experiments were performed for diphenylboron compounds in order to estimate the N \rightarrow B energy. The minimum energy conformation for all boron compounds was calculated, and they are similar to the solid state gallium structure. The boron and gallium coordination stops the fluxional behaviour of the dithiazinane and the equatorial hydrogen atoms become different from the axial ones. The presence of a stereogenic center in the ethanol arm, differentiates the C4 and C6 methylene groups upon coordination. Therefore the ^1H spectra are useful tools for the structural study of these interesting ligands.

Internal coordination N \rightarrow B was found for difluoro, dichloro and diphenylborinic esters, the N \rightarrow B energy for the latter indicating weak coordination. The X-ray diffraction structure of the gallium compound **12** showed formation of hypervalent t_{bp} gallium atoms by dimeric association.

Experimental Section

General Procedures. All solvents were freshly distilled before use. The ^1H , ^{13}C and ^{11}B NMR spectra were recorded with a JEOL GXS-270 (^1H 270 MHz) or a JEOL Eclipse (^1H 400 MHz). ^1H , ^{13}C and ^{11}B δ (ppm) are referenced to TMS and $\text{BF}_3\cdot\text{OEt}_2$. Melting points were measured on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed by Oneida

Research Services, Whitesboro, New York and at Cinvestav Mexico on an Eager 300. The MS spectra were obtained to 20 eV in a HP 5989 spectrometer. Compounds **1-3** were prepared as reported.¹⁵ Compounds **2** and **3** are racemic. For the crystallographic study, data were measured on a Nonius Kappa CCD instrument with area detector using graphite-monochromated Mo K α radiation. Intensities were measured using $\varphi + \omega$ scans. All structures were collected at rt. Crystals of **15** were obtained from CHCl₃, they are triclinic space group P-1 [$a = 6.569(1)$, $b = 7.854(2)$, $c = 8.848(2)$ Å; $\alpha = 79.09(3)$, $\beta = 89.35(3)$, $\gamma = 79.48(3)$; $R_1 = 0.0418$; $wR_2 = 0.0694$]. Crystals of compound **12** were obtained from CHCl₃, they are orthorhombic space group P b c a [$a = 12.0621(2)$, $b = 18.8830(3)$, $c = 21.0366(4)$; $R_1 = 0.0666$; $wR_2 = 0.086$]. In both structures, all hydrogen atoms were located and their positions were refined and solved by direct methods using SHELX-97, and the refinement (based on F^2 of all data) was performed by full matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as numbers: 653943 (**15**) and 653944 (**12**). Copies of the data can be obtained, free of charge, on applications to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

General Procedure for the reaction of 2-(dithiazinyl)ethanol **1-3** with haloboranes

1,1-Difluoro-2-oxa-7,9-dithia-5-aza-1-bora-spiro[4.5]decane (4). To a solution of **1** (100 mg, 0.6 mmol) in CHCl₃ (20 mL) and NEt₃ (0.16 mL, 1.2 mmol) at -40 °C, BF₃·OEt₂ (1.2 mmol, 0.1 mL) was slowly added. After 5 min, the solvent was evaporated and the mixture was dissolved in toluene, filtered and compound **4** was obtained as a white solid (120 mg, 94%). ¹H NMR (CDCl₃) $\delta = 4.38$ (s, 4H, 2H-4, 2H-6), 4.02 (s, 2H, H-2), 3.87 (t, 2H, H-8, ³J 6.70 Hz), 3.67 (t, 2H, H-7, ³J 6.70 Hz). ¹³C $\delta = 57.8$ (C-8), 55.8 (C-4, C-6), 49.9 (C-7), 30.2 (C-2). ¹H NMR (CDCl₃, -10 °C) $\delta = 4.48$ (d, 2H, H-4_{ax}, H-6_{ax}, ²J 14.0 Hz), 3.97 (br d, 2H, H-4_{eq}, H-6_{eq}, ²J 14.0 Hz), 4.30 (d, 1H, H-2_{ax}, ²J 14.0 Hz), 3.44 (br d, 1H, H-2_{eq}, ²J 14.0 Hz), 3.84 (t, 2H, H-8, ³J 8.0 Hz), 3.67 (t, 2H, H-7, ³J 8.0 Hz). ¹¹B NMR $\delta = +3.7$ (br t, ¹J 18.5 Hz). Anal. Calcd. for C₅H₁₀NOS₂BF₂: C (31.45), H (6.16), N (6.11). Found: C (32.02), H (6.26), N (6.40).

1,1-Difluoro-3-methyl-2-oxa-7,9-dithia-5-aza-1-bora-spiro[4.5]decane (5) was prepared, following the same procedure as for **4**. Compound **2** (107 mg, 0.6 mmol), NEt₃ (0.16 mL, 1.2 mmol) and BF₃·OEt₂ (0.1 mL, 1.2 mmol). A white solid was obtained, 136 mg, 92%. NMR (CDCl₃) ¹H $\delta = 4.60$ (ddq, 1H, H-8, ³J 9.4, 6.0, 5.9 Hz), 4.47 (d, 2H, H-4_{ax}, H-6_{ax}, ²J 13.9 Hz), 4.28 (d, 1H, H-2_{ax}, ²J 13.9 Hz), 4.18 (dd, 1H, H-7A, ²J 12.5, ³J 6.0 Hz), 3.98 (br d, 2H, H-4_{eq}, H-6_{eq}, ²J 13.9 Hz), 3.42 (br d, 1H, H-2_{eq}, ²J 13.9 Hz), 2.71 (dd, 1H, H-7B, ²J 12.5, ³J 9.4 Hz), 1.21 (d, 3H, H-9, ³J 6.0 Hz). ¹³C $\delta = 65.0$ (C-8), 57.9 (br s, C-6), 57.0 (C-7), 55.1 (br s, C-4), 30.5 (C-2), 21.6 (C9). ¹¹B $\delta = +3.8$ (br s). Anal. Calcd. for C₆H₁₂NOS₂BF₂: C (34.58), H (6.63), N (5.76). Found: C (34.30), H (6.60), N (5.63).

1,1-Difluoro-3-phenyl-2-oxa-7,9-dithia-5-aza-1-bora-spiro[4.5]decane (6) was prepared as **4**. Compound **3** (145 mg, 0.6 mmol), NEt₃ (0.16 mL, 1.2 mmol) and BF₃·OEt₂ (0.1 mL, 1.2 mmol). A white solid was obtained, 136 mg, 92%. NMR (CDCl₃) ¹H $\delta = 5.01$ (dd, 1H, H-8, ³J 6.7, 7.7

Hz), 4.53 (d, 1H, H-4_{ax}, ²J 13.0 Hz), 4.47 (d, 1H, H-6_{ax}, ²J 14.0 Hz), 4.44 (dd, 1H, H-7A, ²J 12.2, ³J 6.7 Hz), 4.41 (dd, 1H, H-7B, ²J 12.2, ³J 7.7 Hz), 4.26 (d, 1H, H-2_{ax}, ²J 13.8 Hz), 4.16 (br d, 1H, H-4_{eq}, ²J 13.0 Hz), 3.99 (br d, 1H, H-6_{eq}, ²J 14.0 Hz), 3.38 (d, 1H, H-2_{eq}, ²J 13.8 Hz). ¹³C δ = 138.2 (C_i), 128.8 (C_o), 128.2 (C_p), 125.7 (C_m), 70.6 (C-8), 57.4 (br s, C-6), 57.0 (C-7), 54.8 (br s, C-4), 30.5 (C-2). ¹¹B δ = +3.4 (br s). Anal. Calcd. for C₆H₁₂NOS₂BF₂: C (34.58), H (6.63), N (5.76). Found: C (34.30), H (6.60), N (5.63).

1,1-Dichloro-2-oxa-7,9-dithia-5-aza-1-bora-spiro[4.5]decane (7). To a solution of **1** (100 mg, 0.6 mmol) in CH₂Cl₂ (20 mL) and NEt₃ (0.16 mL, 1.2 mmol) at -78 °C, BCl₃·(1.2 mmol, 0.16 mL) was slowly added, after 1 h, the solvent was evaporated. The mixture was dissolved in toluene and filtered, then, the toluene was evaporated in vacuum and **7** was obtained as a white solid (120 mg, 94%). NMR (CDCl₃) ¹H δ = 4.62 (d, 2H, H-4_{ax}, H-6_{ax}, ²J 14.1 Hz), 4.35 (dt, 2H, H-4_{eq}, H-6_{eq}, ²J 14.1, ⁴J 1.5 Hz), 4.22 (d, 1H, H-2_{ax}, ²J 14.1 Hz), 4.04 (t, 2H, H-7, ²J 6.6 Hz), 3.90 (t, 2H, H-8, ²J 6.6 Hz), 3.48 (dt, 1H, H-2_{eq}, ²J 14.1, ⁴J 1.5 Hz). ¹³C δ = 59.5 (C-8), 57.9 (C-4, C-6), 48.6 (C-7), 30.7 (C-2). ¹¹B δ = +9.9. Anal. Calcd. for C₅H₁₀BCl₂NOS₂: C (24.41), H (4.10), N (5.69). Found: C (25.13), H (4.54), N (5.11).

1,1-Dichloro-3-methyl-2-oxa-7,9-dithia-5-aza-1-bora-spiro[4.5]decane (8) was prepared following the same procedure as for **7**. Compound **2** (107 mg, 0.6 mmol), NEt₃ (0.16 mL, 1.2 mmol) and BCl₃ (0.16 mL, 1.2 mmol). A white solid was obtained, 143 mg, 92%. NMR (CDCl₃) ¹H δ = 4.68 (d, 1H, H-6_{ax}, ²J 14.1 Hz), 4.53 (d, 1H, H-4_{ax}, ²J 14.1 Hz), 4.43 (dt, 1H, H-4_{eq}, ²J 14.1, ⁴J 3.0 Hz), 4.16 (dt, 1H, H-6_{eq}, ²J 14.1, ⁴J 3.0 Hz), 4.28 (qdd, 1H, H-8, ³J 11.2, 5.7, 4.5 Hz), 4.26 (d, 1H, H-2_{ax}, ²J 13.9 Hz), 4.23 (dd, 1H, H-7A, ²J 13.9, ³J 4.5 Hz), 3.51 (dt, 1H, H-2_{eq}, ²J 13.9, ⁴J 3.0 Hz), 3.19 (dd, 1H, H-7B, ³J 11.2, ²J 13.9 Hz), 1.28 (d, 3H, H-9, ³J 5.7 Hz). ¹³C δ = 67.9 (C-8), 58.7 (C-4), 58.1 (C-6), 54.9 (C-7), 30.7 (C-2), 21.1 (C-9). ¹¹B δ = +10.0. Anal. Calcd. for C₆H₁₂BCl₂NOS₂·1/5 C₇H₈: C (31.92), H (4.92), N (5.03). Found: C (31.37), H (5.54), N (5.11).

1,1-Dichloro-3-phenyl-2-oxa-7,9-dithia-5-aza-1-bora-spiro[4.5]decane (9) was obtained following the same procedure as for **7**. Compound **3** (145 mg, 0.6 mmol) in CH₂Cl₂ (20 mL) and NEt₃ (0.16 mL, 1.2 mmol), BCl₃·(1.2 mmol, 0.16 mL). Compound **9** was obtained as a white solid, (120 mg, 94%). ¹H NMR (CDCl₃) δ = 7.25 (m, 5H, Ph), 5.06 (dd, 1H, H-8, ³J 7.8, 7.0 Hz), 4.66 (d, 1H, H-4_{ax}, ²J 14.6 Hz), 4.48 (d, 1H, H-6_{ax}, ²J 14.1 Hz), 4.40 (dd, 1H, H-7A, ²J 10.4, ³J 7.0 Hz), 4.31 (br d, 1H, H-4_{eq}, ²J 13.5 Hz), 4.29 (br d, 1H, H-6_{eq}, ²J 13.5 Hz), 4.19 (d, 1H, H-2_{ax}, ²J 13.8 Hz), 3.40 (dd, 1H, H-7B, ²J 10.4, ³J 7.8 Hz), 3.36 (br d, 1H, H-2_{eq}, ²J 13.8 Hz). ¹³C δ = 139.6 (C_i), 128.7 (C_o), 128.2 (C_p), 125.8 (C_p), 73.0 (C-8), 58.5 (C-6), 57.9 (C-4), 55.5 (C-7), 30.6 (C-2). ¹¹B δ = +10.3. Anal. Calcd. for C₁₁H₁₄BCl₂NOS₂. Calcd: C 41.02, H 4.38, N 4.35. Found C 41.53, H 4.45, N, 4.74

2-(1,3,5-Dithiazinan-5-yl)ethyl)diphenylborinic ester (10). A solution of **1** (140 mg, 0.83 mmol) and (Ph₂B)₂O (140 mg, 0.41 mmol) in toluene (60 mL) was refluxed for 12 h, the solvent was evaporated and compound **10** was obtained as a viscous yellow liquid, 270 mg, 90%. NMR ¹H (CDCl₃) δ = 7.67 (br s, 2H, Ph), 7.32 (m, 8H, Ph), 4.30 (s, 4H, 2H-4, 2H-6), 4.21 (t, ³J 5.50 Hz, 2H, H-8), 4.02 (s, 2H, H-2), 3.31 (t, 2H, H-7, ³J 5.50 Hz). ¹H NMR (THF-*d*₈, -60 °C) δ =

7.79 (s, 2H, Ph), 7.40 (br s, 8H, Ph), 4.66 (d, 3J 12.6 Hz, 2H, H-4_{ax}, H-6_{ax}), 4.43 (d, 3J 13.0 Hz, 1H, H-2_{ax}), 4.25 (br s, 2H, H-7), 3.93 (d, 3J 12.6 Hz, 2H, H-4_{eq}, H-6_{eq}), 2.54 (d, 3J 13.0 Hz, 1H, H-2_{eq}), 3.40 (br s, 2H, H-8). ^{13}C δ = 137.8 (Ci), 134.2 (Co), 129.8 (Cp), 127.5 (Cm), 65.5 (C-8), 58.8 (C-4, C-6), 50.7 (C-7), 33.3 (C-2). ^{13}C (THF-*d*₈, -60 °C) δ = 140.3 (Ci), 129.7 (Cp), 131.6 (Co), 130.0 (Cm), 63.7 (C-8), 58.2, 57.9 (C-4, C-6), 50.2 (C-7), 32.2 (C-2). ^{11}B (THF-*d*₈) δ = +44.0 at 25°C; +3.2 at -60°C. Anal. Calcd. of C₁₇H₂₀BNOS₂: C (62.01), H (6.12), N (4.25). Found: C (62.38), H (6.21), N (4.77).

[2-(1,3,5-Dithiazinan-5-yl)-1-methylethyl]diphenylborinic ester (11) was prepared following the procedure described for **10**. Compound **2** (150 mg, 0.84 mmol) and (Ph₂B)₂O (140 mg, 0.42 mmol) in toluene (60 mL). Compound **11** is a yellow liquid, 274 mg, 95%. NMR (THF-*d*₈, -50°C) ^1H δ = 8.35-7.44 (m, 10H, Ph), 4.57 (br s, 1H, H-8), 4.69 (d, 2J 13.1 Hz, 1H, H-2_{ax}), 4.49 (d, 2J 13.4 Hz, 2H, H-4_{ax}, H-6_{ax}), 3.93 (br d, 2J 12.6 Hz, 1H, H-7A), 3.59 (d, 2J 13.1 Hz, 1H, H-2_{eq}), 3.43 (d, 2J 13.4, 2H, H-4_{eq}, H-6_{eq}), 2.88 (br d, 2J 12.6 Hz, 1H, H-7B). ^{13}C (THF-*d*₈, -90°C) δ = 141.8, 136.7, 135.2, 134.8, 133.2, 131.6, 128.5, 128.2, 127.9, 127.6 (2Ph), 69.3 (C-8), 60.15 (C-7), 57.3, 56.5 (C-4, C-6), 31.6 (C-2), 20.6 (C-9). ^{11}B (THF-*d*₈) δ = +43.0 at 25°C; +1.0 at -50°C. Anal. Calcd. for C₁₈H₂₂BNOS₂: C (62.97), H (6.46), N (4.08). Found: C (63.45), H (6.77), N (4.57).

O-Dichlorogallium-1-methyl-2-(1,3,5-dithiazinan-5-yl)ethanolate dimer (12). To a suspension of NaH (1.34 mmol) in THF (0.5 mL) at rt, a solution of **2** (200 mg, 1.11 mmol) in THF (30 mL) was added. After 30 min, the excess of NaH was filtered and the solvent evaporated. The colourless viscous liquid obtained was dissolved in toluene (30 mL) and a 0.05 M solution of GaCl₃ (210 mg, 1.19 mmol) in toluene (30 mL) was added. The mixture was stirred for 30 min, filtered and the solvent evaporated. Compound **12** was obtained as a white solid which was crystallized from CH₂Cl₂ or CDCl₃ (350 mg, 90 %). Mp 147-149 °C. NMR (CDCl₃) ^1H = 4.92 (d, Hax-6, 2J = 14.4 Hz), 4.69 (d, Hax-4, 2J = 14.2 Hz), 4.34 (d, Hax-2, 2J = 13.8 Hz), 4.31 (dd, H-7b, 2J = 12.4, 3J = 5.8 Hz), 4.30 (dt, Hec-4, 2J = 14.20, 4J = 2.2 Hz), 4.13 (m, H-8, 3J = 6.0, 11.4, 5.8 Hz), 3.85 (dt, Hec-6, 2J = 14.4, 4J = 2.2 Hz), 3.44 (dt, Hec-2, 2J = 13.8, 4J = 2.2 Hz), 2.46 (dd, H-7a, 2J = 12.4, 3J = 11.4 Hz), 1.40 (d, 3H-9, 3J = 6.0 Hz). ^{13}C δ = 62.9 (C-8), 57.3 (C-4), 53.8 (C-6), 52.9 (C-7), 31.8 (C-2), 21.0 (C-9). Anal. Calc. for C₁₂H₂₄Cl₄Ga₂N₂O₂S₄: C (22.60), H (3.79), N (4.39). Found: C (22.42), H (4.12), N (4.20).

O-Dichlorogallium-1-phenyl-2-(1,3,5-dithiazinan-5-yl)ethanolate dimer (13). The procedure followed was as described for **12** (210 mg, 0.87 mmol) and a 0.05 M solution of GaCl₃ (0.15 g, 0.85 mmol) in toluene (30 mL). Compound **13** was obtained as a yellow powder (300 mg, 90 %). Mp 175-177 °C. NMR (CDCl₃) ^1H δ = 7.40-7.20 (br s, 5H), 5.01 (d, Hax-6, 2J = 14.3 Hz), 5.00 (dd, 1H-8, 3J = 4.4, 4.0 Hz), 4.67 (d, Hax-4, 2J = 14.3 Hz), 4.41 (dd, 1H-7b, 2J = 12.6, 3J = 4.0 Hz), 4.34 (d, Hax-2, 2J = 13.9 Hz), 4.20 (dt, Heq-6, 2J = 14.3, 4J = 2.6 Hz), 4.05 (dt, Heq-4, 2J = 14.3, 4J = 2.6 Hz), 3.42 (dt, Heq-2, 2J = 13.9, 4J = 2.6 Hz), 2.85 (dd, 1H-7a, 2J = 12.6, 3J = 4.4 Hz). ^{13}C δ = 137.9 (Ci), 129.1 (2C_m), 128.6 (2C_p), 127.9 (C_o), 69.0 (C-8), 57.0 (C-4), 53.6 (C-6), 53.0 (C-7), 31.8 (C-2). Anal. calcd. for C₁₂H₂₈Cl₄Ga₂N₂O₂S₄: C (34.68), H (3.70), N (3.68). Found: C (34.49), H (3.82), N (4.00).

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