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Tripodal molecules derived from ethanoldithiazinanes centered on boron and phosphorus atoms. Structural analyses by NMR and HF/6-31G(d) calculations

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ABSTRACT

A series of boric esters, phosphites, phosphates, thiophosphates and selenophosphates derived from 2-(1,3,5-dithiazinan-5-yl)-ethanol (**1**), 2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanol (**2**), and 2-(1,3,5-dithiazinan-5-yl)-1-phenylethanol (**3**) are reported. Enantiopure compounds (C3 symmetry) were prepared from **2**(−) and **3**(−) of (R) configuration. The new tripodal molecules were viscous liquids which were mainly characterized by ^{1}H, ^{13}C, ^{11}B, ^{31}P, ^{77}Se, NMR and VT-NMR experiments. BH_3, BCl_3, pyridine and PPh_3O adducts of boric esters as well as the BH_3 adducts of phosphites were synthesized. The molecular geometries were calculated by HF/6-31G(d). The modeled molecules indicated a preferred ligand conformation which led to the formation of cavities. The complex NMR spectra of isomers were interpreted by comparison with the calculated geometries.

1. Introduction

The reported tripodal molecules are mainly based on aminoborates. They are of interest as building blocks for macromolecular systems such as molecular rotors made with tris(indazolyl)borate [1]. Tripodal aminoborates are also used as polydentate ligands for metal ions [2,3]. Enantiopure tripodal ligands are relevant as enantioselective inductors. The first example of a chiral *tris*(methimazolyl)borate ligand, has been reported in 2007 [4]. An alkyltris(pyrazolyl)borate bearing a C1 symmetry alkyl group bound to boron has been used to build octahedral metal centers [5]. A chiral tripodal *tris*(oxazolinyl)ethane having carbon as the central atom and a C3 symmetry is a chelating ligand for metal atoms [6,7]. Some C3 symmetry molecules with phosphorus groups as substituents and nitrogen as the central atom have found application in asymmetric catalysis [8]. Other tripodal compounds where the central atom is a metal surrounded by phosphorus heterocycles as substituents are known [9].

In spite of the importance of tripodal molecules, to our knowledge, there are no examples where the central group is a planar tricoordinated boric ester, nor phosphites or phosphates. Consequently we decided to prepare tripodal compounds **4**–**14** using ethanoldithiazinanes **1**–**3** (Scheme 1). We were interested in exploring how the geometry of the central atom (planar, trigonal pyramidal or tetrahedral), the ligand shape and it substituents affect the conformation of these molecules.

The presence of a Lewis acid as the central atom in compounds bearing amines, makes it interesting to investigate whether, in spite of the steric demand intramolecular, coordination is possible. If the compounds are able to present intramolecular N → B coordination, then a fluxional behavior is possible by competition between the three nitrogen atoms for the boron coordination.

The symmetry of the tripodal molecules is very important. The organization of the branches and the molecular stereochemistry will depend on the presence of stereogenic centers at C8 which carry methyl or phenyl substituents. C3 symmetry molecules will be obtained if the three ligands have the same chirality and C1 symmetry compounds will be produced if they have different chirality.

The structural analysis of the isomers will be complex, particularly when crystalline structures are not available for X-ray diffraction analyses, as is the case in the present study where the compounds are viscous liquids. In this case, modelization is a very powerful tool for structural analysis, as we will discuss here.

2. Experimental

2.1. General

All solvents were freshly distilled before use. Due to the high reactivity of synthesized compounds, they were isolated pure directly from the reactions and their structure determined. The

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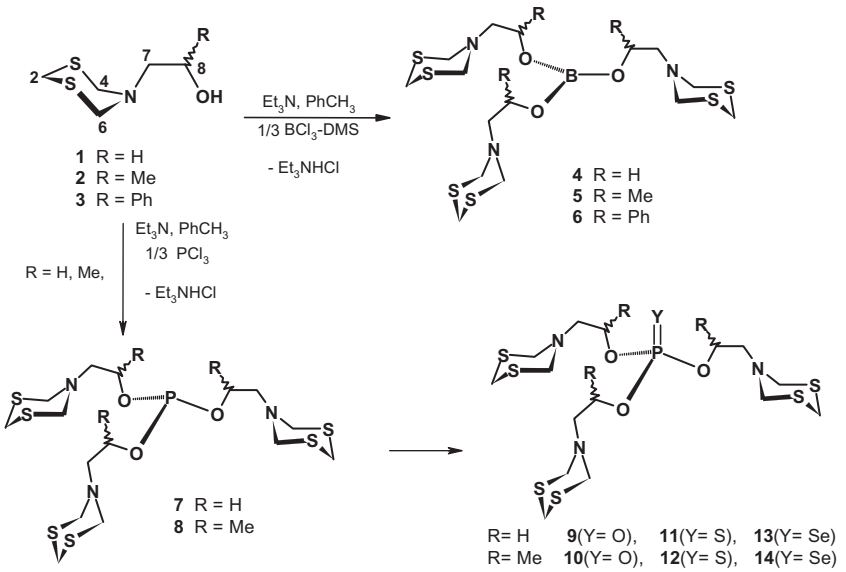


Scheme 1. Syntheses of tripodal compounds **4**–**14**.

^{1}H, ^{13}C, ^{11}B, ^{15}N, ^{31}P and ^{77}Se NMR spectra were recorded with a JEOL GXS-270 (^{1}H 270 MHz) or a JEOL Eclipse (^{1}H 400 MHz). ^{1}H and ^{13}C, ^{11}B, ^{15}N, ^{31}P and ^{77}Se δ (ppm) are referenced to TMS, $BF_3{\cdot}OEt_2$, $MeNO_2$, H_3PO_4 and $SeMe_2$, respectively. ^{1}H and ^{13}C chemical shifts were unequivocally assigned by 2D experiments HETCOR and COSY. Elemental analyses were performed on a FLASH(EA) 1112 Series, Thermo Finnigan apparatus. The MS spectra were obtained at 20 eV in a HP 5989 and +TOF high resolution spectra in an Agilent Technologies LC/MCD instrument.

2.2. X-ray crystallography

Crystal data for compound **2**(−) were obtained with an Enraf–Nonius Kappa CCD diffractometer equipped with an area detector. Relevant data are reported in the complementary information. Computation was performed by SHELXL (Sheldrick 1993) Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Bank (CCDC 777208). Copies of the data can be obtained free of charge on application to, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: Int. Code +44 (1223) 336 033; E-mail: deposit@ccdc.cam.ac.uk.

2.3. (*R*)-(−)-2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanol [**2**(−)]

Compound **2**(−) was prepared following the procedure reported for compounds **1**–**3** [9]. To (*R*)-(−)-1-amino-2-propanol (5 g, 65.2 mmol) in water (50 mL), a solution of NaSH (11.0 g, 196 mmol) and aq. formaldehyde (37%, 24.3 mL, 326 mmol) was slowly added at 5 °C. The mixture was stirred for 30 min at 0 °C and then 24 h at rt. The white solid was filtered and washed with water (20 mL). The residual solution was extracted with CH_2Cl_2, the solution was dried with Na_2SO_4 and then the solvent evaporated. Compound **2**(−) crystallized from CH_2Cl_2 (8.4 g, 72%). M.p. 70 °C. NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.37 (br s, 4H, H4, H6), 4.03 (br s, 2H, H2), 3.76 (qdd, 1H, ^{3}J 6.3, 9.9, 3.1 Hz, H8), 3.04 (dd, 1H, ^{2}J 13.5, ^{3}J 3.1 Hz, H7a), 2.59 (s, 1H, OH), 2.43 (dd, 1H, ^{2}J 13.5, ^{3}J 9.9 Hz, H7b), 1.13 (d, 3H, ^{3}J 6.3 Hz, H9). ^{13}C: 63.8 (C8), 58.8 (br s, C4, C6), 57.3 (C7), 33.7 (C2), 20.2 (C9). ^{15}N: −350.9. $[\alpha]_D$ −46.49 (CH_2Cl_2, 25 °C). MS, (20 eV) *m*/*z* (%): 179(38), 134(60), 122(37), 100(46), 76(100), 57(65), 42(72); (+)TOF *m*/*z* (amu): $(C_6H_{14}NOS_2)^+$, 180.0511, calcd. 180.0516. Anal. Calcd. for $C_6H_{13}NOS_2$: C, 40.19; H, 7.31; N, 7.81. Found: C, 40.07; H, 7.79; N, 7.83.

2.4. Tris[2-(1,3,5-dithiazinan-5-yl)-ethanyl]-boric ester (**4**) general procedure

Under an anhydrous N_2 atmosphere: compound **1** (500 mg, 3.0 mmol) was dissolved in toluene (50 mL) and NEt_3 (0.43 mL, 3.0 mmol) was added. The reaction mixture was stirred at rt for 30 min, then it was cooled to −78 °C and a solution of BCl_3 in hexane (1 M, 1 mL, 1.0 mmol) was added. The mixture was stirred for 3 h at −78 °C. The reaction was left to warm to room temperature, then it was filtered and the solvent evaporated. Compound **4** is a yellow liquid (510 mg, 98%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.34 (br s, 12H, H4, H6), 3.99 (br s, 6H, H2), 3.75 (t, 6H, ^{3}J 5.4 Hz, H8), 3.05 (t, 6H, ^{3}J 5.5 Hz, H7). ^{13}C: 61.2 (C8), 58.9 (C4, C6), 50.3 (C7), 33.9 (C2). ^{11}B: +17.5. ^{15}N: −350.7. NMR (tol-d_8, −90 °C), ^{1}H: 4.83 (d, 6H, ^{2}J 12.3, H4ax, H6ax), 4.59 (d, 3H, ^{2}J 12.3, H2ax) 4.07 (d, 6H, ^{2}J 12.3, H4eq, H6eq), 3.79 (br s, 3H, H8a), 3.59 (d, 3H, ^{2}J 12.3, H2eq), 3.50 (br t, 2H, ^{3}J 5.4 Hz, H8b), 3.09 (br s, 3H, H7a), 3.03 (br t, 3H, ^{3}J 5.4 Hz, H7b). ^{13}C: [60.0, 58.9, C8], 58.0 (C6), 57.9 (C4), [51.4, 49.8, C7], 32.9 (C2). ^{11}B: +9.0. MS, (20 eV) *m*/*z* (%): 503(3), 378(9), 247(7), 213(11), 165(12), 155(20), 100(30), 86(52), 42(100). Anal. Calcd. for $C_{15}H_{30}BN_3O_3S_6$: C, 35.77; H, 6.00; N, 8.34. Found: C, 36.03; H, 5.89; N, 8.53.

2.5. Tris[2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl]-boric ester [**5**(±)]

Compound **5**(±) was prepared following the procedure for compound **4**, from **2**(±) (500 mg, 2.8 mmol), NEt_3 (0.4 mL, 2.8 mmol) and a solution of BCl_3 in hexane (1 M, 0.93 mL, 0.93 mmol). Compound **5**(±) is a pale yellow liquid (510 mg, 98%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.34 (br s, 12H, H4, H6), 4.15 (br ddd, 3H ^{3}J 4.4, 7.3, 6.2 Hz, H8), 4.03 (br s, 6H, H2), [3.05 (dd, ^{2}J 13.6, ^{3}J 5.4 Hz), 3.04 (dd, ^{2}J 13.6, ^{3}J 3.7 Hz), 3.05 (d, ^{3}J 7.3 Hz) 2:1:1 ratio, H7a], [2.82 (dd, ^{2}J 13.6, ^{3}J 7.5 Hz), 2.76 (dd, ^{2}J 13.6, ^{3}J 7.5 Hz), 2.84 (t, ^{3}J 7.3 Hz)] 2:1:1 ratio, H7b], 1.08 (d, 9H, ^{3}J 6.2 Hz, H9). ^{13}C: [66.5, 66.4, 66.3, 1:2:1 ratio, C8], 59.6 (C4, C6), [56.4, 56.3, 56.2, 1:2:1 ratio, C7], 34.0 (C2), 20.7 (C9). ^{11}B: +17.2. ^{15}N: −350.9. NMR (tol-d_8, −90 °C), ^{1}H: 4.83 (d, 6H, ^{2}J 12.1, H4a and H6a), 4.58 (d, 3H, ^{2}J 12.1, H2a), 4.04 (d, 6H, ^{2}J 12.1, H4e, 2H6e), 3.86 (m, 1H, H8), 3.61 (d, 3H, ^{2}J 12.1, H2e), 3.02 (m, 3H, H7a), 2.77 (m, 3H,

3H7b), 1.09 (br s, 9H, H9). ^{13}C: [66.2, 66.0, 65.9, 1:2:1 ratio, C8], 59.9, 59.6 (C4 or C6), 58.0, 57.7 (C6 or C4), [56.1, 56.0, 55.8, 1:2:1 ratio, C7], 33.4 (C2), 20.1, 20.0 (C9). ^{11}B: +9.1. MS, (20 eV) *m*/*z* (%): 545(21), 420(38), 275(30), 241(36), 183(49), 134(29), 100(100), 58(82), 42(60). Anal. Calcd. for $C_{18}H_{36}BN_3O_3S_6$: C, 39.62; H, 6.65; N, 7.70. Found: C, 40.03; H, 6.96; N, 7.22.

2.6. Tris[(R)-(−)-2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl]-boric ester [**5**(−)]

Compound **5**(−) was prepared following the same procedure as for compound **4**, from **2**(−) (500 mg, 2.8 mmol), NEt_3 (0.4 mL, 2.8 mmol) and BCl_3 in hexane (1 M, 0.93 mL, 0.93 mmol). Compound **5**(−) is a pale yellow liquid (510 mg, 98%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.38 (br s, 12H, H4, H6), 4.18 (qdd, 3H, ^3J = 4.7, 7.4, 6.1 Hz, H8), 4.06 (br s, 6H, H2), 2.99 (dd, 3H, ^2J 13.7, ^3J 4.7 Hz, H7a), 2.84 (dd, 3H, ^2J 13.7, ^3J 7.4 Hz, H7b), 1.09 (d, 9H, ^3J 6.1 Hz, H9). ^{13}C: 66.5 (C8), 59.5 (C4, C6), 56.2 (C7), 34.0 (C2), 20.4 (C9). ^{11}B: +17.2. ^{15}N: −351.0. NMR (tol-d_8, −50 °C), ^{1}H: 4.52 (d, 3H, ^2J 13.3, H4ax or H6ax), 4.45 (d, 3H, ^2J 3.3, H6ax or H4ax), 4.26 (qdd, 3H, ^3J 4.7, 7.7, 6.1, H8), 4.14 (d, 3H, ^2J 13.3, H2ax), 3.79 (br d, 6H, ^2J 13.3, H4eq, H6eq), 3.14 (br d, 3H, H2eq), 3.06 (dd, 3H, ^2J 13.3, ^3J 4.7, H7a), 2.76 (dd, 3H, ^2J 13.3, ^3J 7.7, H7b), 1.07 (d, 9H, ^3J 6.1, H9). ^{13}C: 65.8 (C8), 59.7 (C4 or C6), 58.0 (C6 or C4), 56.0 (C7), 33.5 (C2), 20.6 (C9). ^{11}B: +9.1.3. MS, (20 eV) *m*/*z* (%): 545(21), 420(38), 275(30), 241(36), 183(49), 134(29), 100(100), 58(82), 42(60).

2.7. Tris[2-(1,3,5-dithiazinan-5-yl)-1-phenyl-ethanyl]-boric ester [**6**(±)]

Compound **6**(±) was prepared following the procedure for compound **4**, from **3**(±) (500 mg, 2.1 mmol), NEt_3 (0.3 mL, 2.1 mmol) and BCl_3 in hexane (1 M, 0.7 mL, 0.7 mmol). Compound **6**(±) is a pale yellow liquid (500 mg, 98%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 7.40–7.10 (m, 15H, Ph), 5.10 (br dd, ^3J 7.5, 4.2 Hz, 3H, H8), 4.28 (br s, 12H, H4, H6), 4.12 (br s, 6H, H2), 3.95 (br dd, ^2J 13.5, ^3J 4.2 Hz, 3H, H7a), 3.11 (br dd, ^2J 13.5, ^3J 7.5 Hz, 3H, H7b). ^{13}C: 141.9 (Ci), 128.3 (Co), 127.6 (Cp), 126.1 (Cm), [73.7, 73.6, 73.5, 1:2:1 ratio, C8], 59.6 (br, C4, C6), [57.0, 56.9, 56.8, 1:2:1 ratio, C7], 33.7 (C2). ^{11}B: +17.8 (s). ^{15}N: −350.4. VT NMR (tol-d_8, −60 °C) ^{1}H 7.40–7.00 (m, 15H, H–Ph), 4.89 (d, 3H, ^2J 13.0, H4a or H6a), 4.83 (d, 3H, ^2J 13.0, H6a or H4a), 4.70 (m, 2H, H8), 4.60 (d, 3H, ^2J 13.3, H2a), 4.16 (d, 3H, ^2J 13.0, H4e or H6e), 4.07 (d, 3H, ^2J 13.0, H6e or H4e), 3.60 (d, 3H, ^2J 13.3, H2e), 3.22 (m, 3H, H7a), 2.91 (m, 3H, H7b). ^{13}C: 141.9, 141.8 (Ci), 128.1, 127.9 (Cm), 127.0, 126.9 (Cp), 126.0, 125.9 (Co), 73.8, 73.6(br) (C8), 59.8 (br, C6 or C4), 57.6 (br, C4 or C6), 56.8(br), 56.6 (C7), 33.0 (C2). ^{11}B: +8.9. Anal. Calcd. for $C_{33}H_{42}BN_3O_3S_6{\cdot}1/2H_2O$: C, 53.50; H, 5.85; N, 5.67. Found: C, 53.33; H, 5.55; N, 5.51.

2.8. Tris-{2-(1,3,5-dithiazinan-5-yl)-ethanyl}-phosphite (**7**)

General procedure *:* To a solution of compound **1** (500 mg, 3.0 mmol) in toluene (50 mL) NEt_3 (0.43 mL, 3.0 mmol) was added at −5 °C. The mixture was stirred 30 min at rt, then cooled to −78 °C and PCl_3 (137 mg, 1.0 mmol) dissolved in hexane (10 mL) was added. The mixture was stirred for 2 h, at −78 °C, then the reaction was left to warm to room temperature and filtered under N_2 atmosphere and the solvent evaporated. Compound **7** is a yellow liquid (500 mg, 95%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.33 (br s, 12H, H4, H6), 3.99 (br s, 6H, H2), 3.78 (dt, 6H, ^3J 5.6 Hz, H8), 3.12 (t, 6H, ^3J 5.6 Hz, H7). ^{13}C: 60.1 (d, $^2J(^{31}P–^{13}C)$ 9.9 Hz, C8), 58.8 (C4, C6), 50.0 (d, $^3J(^{13}C–^{31}P)$ 4.6 Hz, C7), 33.9 (C2). ^{31}P: +140.6, $^3J(^{31}P–^1H)$ 7.4 Hz. Anal. Calcd. for $C_{15}H_{30}N_3O_3S_6P{\cdot}CHCl_3$: C, 32.16; H, 5.58; N, 7.50. Found: C, 32.34; H, 5.96; N, 7.85.

2.9. Tris-{2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-phosphite [**8**(±)]

Compound **8**(±) was prepared following the procedure for **7**, from **5**(±) (500 mg, 2.79 mmol), NEt_3 (0.4 mL, 2.8 mmol) and PCl_3 (0.08 mL, 0.9 mmol). Compound **8**(±) is a pale yellow liquid (500 mg, 95%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.35 (br s, 12H, H4, H6), 4.22 (ddd, 3H, ^3J 3.1, 7.4, 6.3 Hz, H8), 4.05 (br s, 6H, H2), 3.07 (dd, 3H, ^2J 13.0, ^3J 3.1 Hz, H7a), 2.93 (dd, 3H, ^2J 13.0, ^3J 7.4 Hz, H7b), 1.21 (d, 9H, ^3J 6.3 Hz, H9). ^{13}C: [67.4 (d, $^2J(^{13}C–^{31}P)$ 11.5 Hz), 67.3 (d, $^2J(^{13}C–^{31}P)$ 11.2 Hz), 67.2 (d, $^2J(^{13}C–^{31}P)$ 11.2 Hz), 67.1 (d, $^2J(^{13}C–^{31}P)$ 11.7 Hz), 1:1:1:1 ratio, C8], 59.1 (C4, C6), 55.6 (C7), 33.5 (C2), 20.5 (C9). ^{31}P: +142.1 and +142.0, 3:1 ratio $^3J(^{31}P–^1H)$ 7.4 Hz. Anal. Calcd. for $C_{18}H_{36}N_3O_3PS_6$: C, 38.21; H, 6.41; N, 7.43. Found: C, 38.25; H, 6.39; N, 7.58.

2.10. Tris-{(R)-(−)-2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-phosphite [**8**(−)]

Compound **8**(−) was prepared following the procedure for **7**, from **5**(−) (500 mg, 2.8 mmol) NEt_3 (0.4 mL, 2.8 mmol) and PCl_3 (0.1 mL, 0.9 mmol). Compound **8**(−) is a pale yellow liquid (510 mg, 97%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.34 (br s, 12H, H4, H6), 4.20 (qdd, 3H ^3J 6.2, 3.3, 7.6 Hz, H8), 4.02 (br s, 6H, H2), 3.06 (dd, 3H, ^2J 13.2, ^3J 3.3 Hz, H7a), 2.92 (dd, 3H, ^2J 13.2, ^3J 7.6 Hz, H7b), 1.19 (d, 9H, ^3J 6.2 Hz, H9). ^{13}C: 67.1 (d, $^2J(^{13}C–^{31}P)$ 10.7 Hz, C8), 59.0 (C4, C6), 55.5 (C7), 33.4 (C2), 20.4 (C9). ^{31}P: +142.0, $^3J(^{31}P–^1H)$ 7.4 Hz.

2.11. Tris-{2-(1,3,5-dithiazinan-5-yl)-ethanyl}-phosphate (**9**)

General procedure*:* To a solution of H_2O_2 (30%, 80 mL, 1.0 mmol) a solution of compound **7** (500 mg, 1.0 mmol) in CH_2Cl_2 (30 mL) was added. The mixture was stirred 2 h at rt, and the solvent evaporated. Compound **9** is a colorless viscous liquid (430 mg, 83%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.35 (br s, 12H, H4, H6), 4.12 (br t, 6H, ^3J 5.5 Hz, H8), 4.02 (br s, 6H, H2), 3.29 (t, 6H, ^3J 5.5 Hz, H7). ^{13}C: 63.1 (d, $^2J(^{13}C–^{31}P)$ 6.2 Hz, C8), 58.5 (C4, C6), 49.5 (d, $^3J(^{13}C–^{31}P)$ 4.6 Hz, C7), 33.8 (C2). ^{31}P: +9.4.

2.12. Tris-{2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-phosphate [**10**(±)]

Compound **10**(±) was prepared following the procedure for **9**, from **8**(±) (500 mg, 0.9 mmol) and a solution of H_2O_2 (30%, 70 mL, 0.9 mmol). Compound **10**(±) is a colorless viscous liquid (500 mg, 97%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.32 (qdd, 3H, ^3J 5.9, 3.3, 7.3 Hz, H8), 4.27 (br s, 12H, H4, H6), 4.11 (br s, 6H, H2), 3.04 (dd, 3H, ^2J 14.2, ^3J 3.3 Hz, H7a), 2.81 (dd, 3H, ^2J 14.2, ^3J 7.3 Hz, H7b), 1.15 (d, ^3J 5.9 Hz, H9). ^{13}C: [73.4 (d, $^2J(^{13}C–^{31}P)$ 6.1 Hz), 73.3 (d, $^2J(^{13}C–^{31}P)$ 5.4 Hz), 1:1 ratio, C8], 59.3 (C4, C6), [55.1 (d, $^3J(^{13}C–^{31}P)$ 6.1 Hz), 55.0 (d, $^3J(^{13}C–^{31}P)$ 5.4 Hz), C7], 33.7 (C2), [19.8 (d, $^3J(^{13}C–^{31}P)$ 2.3 Hz), 19.7 (d, $^3J(^{13}C–^{31}P)$ 2.3 Hz), C9]. ^{31}P: −1.60 ($^3J(^{31}P–^1H)$ 7.45 Hz), −1.65 ($^3J(^{31}P–^1H)$ 7.45 Hz), 1:3 ratio. Anal. Calcd. for $C_{18}H_{36}N_3O_4PS_6{\cdot}1/6C_7H_8$: C, 38.55; H, 6.30; N, 7.04. Found: C, 38.25; H, 6.39; N, 6.58.

2.13. Tris-{(R)-(−)-2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-phosphate [**10**(−)]

Compound **10**(−) was prepared following the procedure for **9**, from **8**(−) (500 mg, 0.9 mmol) and a solution of H_2O_2 (30%, 70 mL, 0.9 mmol). Compound **10**(−) is colorless viscous liquid (490 mg, 95%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.38 (qdd, 3H, ^3J 4.2, 3.7, 7.3 Hz, H8), 4.30 (br s, 12H, H4, H6), 4.16 (br s, 6H, H2), 3.12 (dd, 3H, ^2J 10.2, ^3J 3.7 Hz, H7a), 2.89 (dd, 3H, ^2J 10.2, ^3J

7.3 Hz, H7b), 1.23 (d, ^3J 4.2 Hz, H9). ^{13}C: 73.4 (d, $^2J(^{13}C–^{31}P)$ 5.4 Hz, C8), 59.4 (C4, C6), 55.0 (d, $^3J(^{13}C–^{31}P)$ 4.6 Hz, C7), 33.8 (C2), 19.8 (C9). ^{31}P: −1.45, $^3J(^{31}P–^1H)$ 7.45 Hz.

2.14. Tris-{2-(1,3,5-dithiazinan-5-yl)-ethanyl}-thiophosphate (**11**)

Compound **11** was prepared by adding sulfur (100 mg, 3.0 mmol) to a solution of compound **7** (500 mg, 1.0 mmol) in CH_2Cl_2 (30 mL). After stirring for 2 h at rt, the solids were removed by filtration and then the solvent was evaporated. Compound **11** is a pale yellow liquid (490 mg, 93%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.42 (br s, 12H, H4, H6), 4.13 (dt, 6H, ^3J 5.4 Hz, H8), 4.08 (br s, 6H, H2), 3.29 (t, 6H, ^3J 5.4 Hz, H7). ^{13}C: 65.8 (d, $^2J(^{13}C–^{31}P)$ 6.1 Hz, C8), 58.8 (C4, C6), 49.1 (d, $^3J(^{13}C–^{31}P)$ 7.7 Hz, C7), 33.9 (C2). ^{31}P: +70.3.

2.15. Tris-{2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-thiophosphate [**12**(±)]

Compound **12**(±) was prepared following the procedure for **11**, from **8**(±) (500 mg, 0.9 mmol) and sulfur (90 mg, 2.7 mmol). Compound **12**(±) is a pale yellow liquid (500 mg, 95%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.56 (qdd, 3H, ^3J 5.9, 3.1, 7.4 Hz, H8), 4.36 (br s, 12H, H4, H6), 4.05 (br s, 6H, H2), 3.18 (dd, 3H, ^2J 13.2, ^3J 3.1 Hz, H7a), 2.95 (dd, 3H, ^2J 13.2, ^3J 7.4 Hz, H7b), 1.27 (d, ^3J 5.9 Hz, H9). ^{13}C: [74.3 (d, $^2J(^{13}C–^{31}P)$ 6.2 Hz), 74.2 (d, $^2J(^{13}C–^{31}P)$ 6.1 Hz), 74.1 (d, $^2J(^{13}C–^{31}P)$ 6.9 Hz), 74.0 (d $^2J(^{13}C–^{31}P)$ 6.9 Hz), 1:1:1 ratio, C8], 59.6 (C4, C6), [55.0 (d, $^3J(^{13}C–^{31}P)$ 3.1 Hz), 54.9 (d, $^3J(^{13}C–^{31}P)$ 3.1 Hz), 1:1 ratio, C7], 33.9 (C2), [19.6 (d, $^3J(^{13}C–^{31}P)$ 3.1 Hz), 19.5 (d, $^3J(^{13}C–^{31}P)$ 3.1 Hz), C9]. ^{31}P: +68.1 ($^3J(^{31}P–^1H)$ 9.9 Hz) and +67.6 ($^3J(^{31}P–^1H)$ 9.9 Hz), 1:3 ratio. Anal. Calcd. for $C_{18}H_{36}N_3O_3PS_7{\cdot}S_8$: C 25.30, H, 4.25; N, 4.92. Found: C, 25.72; H, 4.45; N, 4.57.

2.16. Tris-{(R)-(−)-2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-thiophosphate [**12**(−)]

Compound **12**(−) was prepared following the procedure for **11**, from **8**(−) (500 mg, 0.96 mmol) and sulfur (90 mg, 2.7 mmol). Compound **12**(−) is a yellow viscous liquid (500 mg, 95%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.57 (qdd, 3H, ^3J 6.2, 3.0, 7.6 Hz, H8), 4.39 (br s, 12H, H4, H6), 4.11 (br s, 6H, H2), 3.22 (dd, 3H, ^2J 13.2, ^3J 3.0 Hz, H7a), 2.96 (dd, 3H, ^2J 13.2, ^3J 7.6 Hz, H7b), 1.26 (d, ^3J 6.2 Hz, 9H, H9). ^{13}C: 73.9 (d, $^2J(^{13}C–^{31}P)$ 6.2 Hz, C8), 59.5 (C4, C6), 55.1 (d, $^3J(^{13}C–^{31}P)$ 7.6 Hz, C7), 33.7 (C2), 19.5 (d, $^3J(^{13}C–^{31}P)$ 3.2 Hz, C9). ^{31}P: +68.2, $^3J(^{31}P–^1H)$ = 9.9 Hz.

2.17. Tris-{2-(1,3,5-dithiazinan-5-yl)-ethanyl}-selenophosphate (**13**)

Compound **13** was prepared following the procedure for **11**, from compound **7** (500 mg, 0.96 mmol) and selenium (230 mg, 2.9 mmol) in CH_2Cl_2 (30 mL). Compound **13** is a pale yellow liquid (550 mg, 95%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.39 (br s, 12H, H4, H6), 4.10 (t, 6H, ^3J 5.4 Hz, H8), 4.06 (br s, 6H, H2), 3.25 (t, 6H, ^3J 5.4 Hz, H7). ^{13}C: 65.6 (d, $^2J(^{13}C–^{31}P)$ 5.3 Hz, C8), 58.0 (C4, C6), 48.1 (d, $^3J(^{13}C–^{31}P)$ 7.7 Hz, C7), 33.2 (C2). ^{31}P: +74.1 ($^1J(^{31}P–^{77}Se)$ 950.4 Hz). ^{77}Se: −365.5 (d, $^1J(^{77}Se–^{31}P)$ 950.4 Hz). (+)TOF *m*/*z* (amu): $(C_{15}H_{31}N_3O_3PS_6Se)^+$ found 603.9569 Calcd. 603.9587.

2.18. Tris-{2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-selenophosphate [**14**(±)]

Compound **14**(±) was prepared following the procedure for **11**, from **8**(±) (500 mg, 0.89 mmol) and selenium (210 mg, 2.7 mmol). Compound **14**(±) is a pale yellow liquid (550 mg, 96%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.58 (td, 3H, ^3J 3.3, 7.3, 3.3 Hz, H8), 4.33 (br s, 12H, H4, H6), 4.03 (br s, 6H, H2), 3.15 (dd, 3H, ^2J 13.3, ^3J 3.3 Hz, H7a), 2.94 (dd, 3H, ^2J 13.3, ^3J 7.3 Hz, H7b), 1.24 (d, ^3J 3.3 Hz, H9). ^{13}C: [74.9 (d, $^2J(^{13}C–^{31}P)$ 5.4 Hz), 74.8 (d, $^2J(^{13}C–^{31}P)$ 5.4 Hz), 74.7 (d, $^2J(^{13}C–^{31}P)$ 6.1 Hz), 74.6 (d, $^2J(^{13}C–^{31}P)$ 6.1 Hz), 1:1:1:1 ratio, C8], 59.6 (C4, C6), [54.9 (d, $^3J(^{13}C–^{31}P)$ 3.0 Hz), 54.8 (d, $^3J(^{13}C–^{31}P)$ 3.0 Hz), 1:1 ratio, C7], 33.9 (C2), [19.5 (d, $^3J(^{13}C–^{31}P)$ 2.3 Hz), 19.4 (d, $^3J(^{13}C–^{31}P)$ 2.3 Hz), C9]. ^{31}P: +72.0 ($^1J(^{31}P–^{77}Se)$ 934.3 Hz, $^3J(^{31}P–^1H)$ 12.4 Hz), +71.2 ($^1J(^{31}P–^{77}Se)$ 929.6 Hz, $^3J(^{31}P–^1H)$ 12.4 Hz), 3:1 ratio. ^{77}Se: [−351.4 (d, $^1J(^{77}Se–^{31}P)$ 929.6 Hz), −354.8 (d, $^1J(^{77}Se–^{31}P)$ 934.3 Hz), 3:1 ratio]. (+)TOF *m*/*z* (amu): $(C_{18}H_{37}N_3O_3PS_6Se)^+$ found 646.0040 Calcd. 646.0056. Anal. Calcd. for $C_{18}H_{36}N_3O_3PS_6Se$: C, 33.53; H, 5.63; N, 6.52. Found: C, 33.73; H, 6.13; N; 6.97.

2.19. Tris-{(R)-(−)-2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-selenophosphate [**14**(−)]

Compound **14**(−) was prepared following the procedure for **11**, from **8**(−) (500 mg, 0.9 mmol) and selenium (210 mg, 2.7 mmol). Compound **14**(−) is a pale yellow liquid (560 mg, 98%).

NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.66 (qdd, 3H, ^3J 6.3, 3.2, 7.3 Hz, H8), 4.41 (br s, 12H, H4, H6), 4.10 (br s, 6H, H2), 3.27 (dd, 3H, ^2J 13.4, ^3J 3.2 Hz, H7a), 3.01 (dd, 3H, ^2J 13.4, ^3J 7.3 Hz, H7b), 1.33 (d, ^3J 6.3 Hz, H9). ^{13}C: 74.7 (d, $^2J(^{13}C–^{31}P)$ 5.6 Hz, C8), 59.5 (C4, C6), 55.0 (d, $^3J(^{13}C–^{31}P)$ 7.7 Hz, C7), 33.9 (C2), 19.4 (d, $^3J(^{13}C–^{31}P)$ 2.8 Hz, C9). ^{31}P: +72.3 ($^1J(^{31}P–^{77}Se)$ 932.5 Hz). ^{77}Se: −358.4, d, $^1J(^{77}Se–^{31}P)$ 932.5 Hz.

2.20. N → B pyridine adduct of tris-{2-(1,3,5-dithiazinan-5-yl)-ethanyl}-boric ester (**15**)

General procedure: To compound **4** (25 mg, 0.5 mmol) in CH_2Cl_2 (30 mL), pyridine (0.04 mL, 0.5 mmol) was added at rt. The solvent was evaporated after 10 min and 15 was obtained as a yellow liquid, (29 mg, 98%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 8.17 (d, 2H, ^3J 5.9 Hz, H–Py_o), 7.18 (t, 1H, ^3J 7.6 Hz, H–Py_p), 6.80 (dd, 2H, ^3J 5.9, 7.6 Hz, H–Py_m), 4.05 (br s, 12H, H4, H6), 3.68 (br s, 6H, H2), 3.35 (t, 6H, ^3J 5.5 Hz, H8), 2.83 (t, 6H, ^3J 5.5 Hz, H7). ^{13}C: 149.4 (C–Py_o), 135.7 (C–Py_p), 123.5 (C–Py_m), 58.9 (C8), 58.4 (C4, C6), 51.3 (C7), 33.5 (C2). ^{11}B: +5.5. NMR (CD_2Cl_2, −60 °C). ^{1}H: 8.41 (br s, 2H, H–Py_o), 7.65 (br s, 1H, H–Py_p), 7.24 (br s, 2H, H–Py_m), 4.66 (br s, 12H, H4, H6), 4.39 (br s, 6H, H2), 3.90 (br s, 6H, H8), 2.94 (br s, 6H, H7). ^{13}C: 148.7 (C–Py_o), 137.3 (C–Py_p), 124.4 (C–Py_m), 58.7 (C8), 58.5 (C4, C6), 51.1 (C7), 33.8 (C2). ^{11}B: +5.6.

2.21. N → B pyridine adduct of tris-[2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl]-boric ester [**16**(±)]

Compound **16**(±) was prepared following the general procedure, from **5**(±) (251 mg, 0.46 mmol) and pyridine (0.04 mL, 0.46 mmol). Adduct **6** is a pale yellow liquid (280 mg, 98%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 8.13 (d, 2H, ^3J 5.4 Hz, H–Py_o), 7.13 (t, 1H, ^3J 7.7 Hz, H–Py_p), 6.75 (dd, 2H, ^3J 5.4, 7.7 Hz, H–Py_m), 3.99 (br s, 12H, H4, H6), 3.60 (br s, 6H, H2), 3.50 (br s, 3H, H8), 2.83 (br dd, 3H, ^2J 13.5 Hz, ^3J 3.2 Hz, H7a), 2.33 (br dd, 3H, ^2J 13.5, ^3J 8.7 Hz, H7b), 0.76 (br d, 9H, ^3J 6.2 Hz, H9); ^{13}C 149.4 (C–Py_o), 135.6 (C–Py_p), 123.4 (C–Py_m), 64.0 (C8), 58.9 (C4, C6), 56.9 (C7), 33.4 (C2), 20.8 (C9). ^{11}B: +4.2. NMR (CD_2Cl_2, −60 °C), ^{1}H: 8.46 (br s, 2H, H–Py_o), 7.67 (br s, 1H, H–Py_p), 7.27 (br s, 2H, H–Py_m), 4.75 (d, 3H, ^2J 12.8 Hz, H4ax or H6ax), 4.65 (d, 3H, ^2J 12.8 Hz, H6ax or H4ax), 4.46 (d, 3H, ^2J 13.1 Hz, H2ax), 4.10 (br s, 3H, H8), 3.91 (d, 6H, ^2J 12.8 Hz, H4e and H6e), 3.52 (d, 3H, ^2J 13.1 Hz, H2eq), 3.16 (br d, 3H, ^2J 12.8 Hz, H7a), 2.42 (br t, 3H, ^2J 12.8 Hz, H7b), 1.02 (d, 9H, ^3J 4.8 Hz, H9). ^{13}C: 148.9 (C–Py_o), 137.3 (C–Py_p), 124.4 (C–Py_m), 63.6 (C8), 56.9 (C4, C6), 60.7 (C7), 33.7 (C2), 20.7 (C9). ^{11}B: +4.0.

*2.22. N → B pyridine adduct of tris-[(R)-(−)-2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl}-boric ester [**16**(−)]*

Compound **16**(−) was prepared following the general procedure, from **5**(−) (250 mg, 0.5 mmol) and pyridine (0.04 mL, 0.5 mmol). Adduct **16**(−) is a pale yellow liquid (280 mg, 98%). NMR (δ ppm, CD_2Cl_2, −60 °C), ^{1}H: 8.54 (d, 2H, ^3J 4.5 Hz, H–Py_o), 7.18 (s, 1H, H–Py_p), 7.02 (s, 2H, H–Py_m), 4.30 (d, 3H, ^2J 13.3 Hz, H6ax or H4ax), 4.22 (d, 3H, ^2J 13.3 Hz, H4ax or H6ax), 4.02 (d, 3H, ^2J 13.4 Hz, H2ax), 3.84 (br s, 3H, H8), 3.76 (d, 3H, ^2J 13.3 Hz, H6eq or H4eq), 3.61 (d, 3H, ^2J 13.3 Hz, H4eq or H6eq), 3.21 (d, 3H, ^2J 13.0 Hz, H7a), 3.07 (d, 3H, ^2J 13.4 Hz, H2eq), 2.87 (t, 3H, ^2J 13.0 Hz, H7b), 1.29 (d, 9H, ^3J 5.6 Hz, H9). ^{13}C: 149.9 (C–Py_o), 135.9 (C–Py_p), 123.9 (C–Py_m), 64.2 (C8), 59.9 (C6 or C4), 57.6 (C4 or C6), 57.2 (C7), 33.3 (C2), 21.5 (C9). ^{11}B: +4.3.

*2.23. O → B PPh_3O adduct of tris-[2-(1,3,5-dithiazinan-5-yl)-ethanyl]-boric ester (**17**)*

General procedure: To compound **4** (25 mg, 0.5 mmol) in CH_2Cl_2 (30 mL) a solution of PPh_3O (140 mg, 0.5 mmol) in CH_2Cl_2 (30 mL) was slowly added at rt. The reaction was stirred for 10 min, then the solvent was evaporated, 17 is a yellow liquid (400 mg, 98%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 7.65–7.30 (m, 15H, H–Ph), 4.33 (br s, 12H, H4, H6), 3.97 (br s, 6H, H2), 3.58 (t, 6H, ^3J 5.4 Hz, H8), 3.10 (t, 6H, ^3J 5.4 Hz, H7); ^{13}C 132.5 (d, J(C_i–P) 103.8 Hz, C_i), 132.1 (d, J(C_o–P) 9.4 Hz, C_o), 132.0 (C_p), 128.6 (d, J(C_m–P) 11.4 Hz, C_m), 58.9 (C8), 58.5 (C4, C6), 51.4 (C7), 33.9 (C2). ^{11}B: +1.4. ^{31}P: +29.9. NMR (tol-d_8, −30 °C), ^{1}H: 7.60–7.00 (m, 15H, H–Ph), 4.48 (br s, 12H, H4, H6), 4.17(br s, 6H, H2), 3.80 (s, 6H, H8), 3.08 (s, 6H, H7). ^{13}C: 132.3 (d, J(C_i–P) 103.8 Hz, C_i), 132.2 (d, J(C_o–P) 10.0 Hz, C_o), 132.2 (C_p), 128.8 (d, J(C_m–P) 12.3 Hz, C_m), 58.8 (C8), 58.4 (C4, C6), 51.2 (C7), 33.6 (C2). ^{11}B: +1.3. ^{31}P: +29.8.

*2.24. O → B PPh_3O adduct of tris-[2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl]-boric ester [**18**(±)]*

Compound **18**(±) was prepared following the procedure for compound **17**, from **5**(±) (250 mg, 0.5 mmol) and PPh_3O (130 mg, 0.5 mmol). Adduct **18**(±) is a pale yellow liquid (400 mg, 98%). NMR (δ ppm, tol-d_8, 0 °C), ^{1}H: 7.60–7.00 (m, 15H, H–Ph), 4.14 (br s, 12H, H4, H6), 3.79 (br s, 6H, H2), 3.64 (m, 3H, H8), 3.08 (br dd, 3H, ^3J 3.4, ^2J 13.4 Hz, H7a), 2.52 (br dd, 3H, ^3J 8.8, ^2J 13.4 Hz, H7b), 1.00 (br s, 9H, H9); ^{13}C 132.3 (d, J(C_i–P) 101.7 Hz, C_i), 132.1 (d, J(C_o–P) 10.0 Hz, C_o), 132.0 (C_p), 128.7 (d, J(C_m–P) 11.5 Hz, C_m), 64.0 (C8), 59.9 (C4, C6), 56.9 (C7), 33.6 (C2), 21.1 (C9). ^{11}B: +1.2. ^{31}P: +29.9.

*2.25. O → B PPh_3O adduct of tris-[(R)-(−)-2-(1,3,5-dithiazinan-5-yl)-1-methyl-ethanyl]-boric ester [**18**(−)]*

Compound **18**(−) was prepared following the procedure for **17**, from **5**(−) (250 mg, 0.5 mmol) and PPh_3O (130 g, 0.5 mmol). Adduct **18**(−) is a pale yellow liquid (395 mg, 98%). NMR (δ ppm, tol-d_8, 0 °C), ^{1}H: 7.60–7.10 (m, 15H, H–Ph), 4.37 (br s, 12H, H4, H6), 4.01 (br s, 6H, H2), 3.77 (dd, 3H, ^3J 3.6, 6.3, 9.0 Hz, H8), 3.24 (dd, 3H, ^3J 3.6, ^2J 13.5 Hz, H7a), 2.62 (dd, 3H, ^3J 9.0, ^2J 13.5 Hz, H7b), 1.12 (d, 9H, ^3J 6.3, H9). ^{13}C: 132.6 (d, J(C_i–P) 102.3 Hz, C_i), 132.1 (d, J(C_o–P) 10.0 Hz, C_o), 132.0 (C_p), 128.7 (d, J(C_m–P) = 12.3 Hz, C_m), 64.0 (C8), 59.0 (C4, C6), 57.2 (C7), 33.8 (C2), 21.1 (C9). ^{11}B: +2.2. ^{31}P: +29.3.

*2.26. Tris[2-(5-trichloroborane-1,3,5-dithiazinan-5-yl)-ethanyl]-boric ester (**19**)*

To a solution of compound **4** (200 mg, 0.4 mmol) in toluene (30 mL), BCl_3·DMS (0.16 mL, 1.2 mmol) was added at −5 °C, then the solution was left to warm to room temperature and the solvent evaporated. Compound **19** is a yellow liquid (194 mg, 80%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.3 (br s, 12H, H4, H6), 4.0 (br s, 6H, H2), 3.76 (t, 6H, ^3J 6.3 Hz, H8), 3.46 (t, 6H, ^3J 6.3 Hz, H7). ^{13}C: 62.8 (C4, C6), 61.4 (C8), 51.0 (C7), 31.0 (C2). ^{11}B: +10.4, +17.5. Anal. Calcd. for $C_{15}H_{30}B_4Cl_9N_3O_6S_6{\cdot}C_7H_8$: C, 26.90; H, 4.04; N, 5.44. Found: C, 26.73; H, 4.27; N, 5.44.

*2.27. Tris-[2-(5-methyl-1,3,5,6-boradithiazinan-5-yl)-ethanyl]-boric ester (**20**)*

To compound **4** (200 mg, 0.39 mmol) in THF (20 mL) a solution of BH_3·THF (0.6 M, 1.2 mmol, 2.5 mL) was slowly added at −78 °C, then the solution was left to warm to room temperature and then, the solvent was evaporated. Compound **20** is a viscous yellow liquid (192 mg, 90%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.4 (br s, 12H, H4, H6), 4.2 (br s, 6H, H2), 3.8 (t, ^3J 5.9 Hz, 6H, H8), 3.5 (t, ^3J 5.9 Hz, 6H, H7), 2.7 (s, 9H, H9). ^{13}C: 63.4 (C4), 62.1 (C8), 58.2 (C7), 48.1 (CH_3), 33.8 (C2). ^{11}B: −3.8, +17.0. Anal. Calcd. for $C_{33}H_{42}BN_3O_3S_6{\cdot}3/4C_7H_8$: C, 39.60; H, 7.38; N, 6.84. Found: C, 39.17; H, 7.63; N, 7.10.

*2.28. P → BH_3 adduct of tris-{2-(1,3,5-dithiazinan-5-yl)-ethanyl}-phosphite (**21**)*

To a fresh solution of compound **7** (110 mg, 0.2 mmol) in benzene (20 mL) a solution of BH_3·DMS (0.6 M, 0.44 mL, 0.2 mmol) was slowly added at −78 °C. After 5 min the solution was left to warm to room temperature and the solvent was evaporated. Compound **21** is a pale yellow liquid (100 mg, 98%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 3.97 (s, 12H, H4, H6), 3.84 (dt, ^3J 5.4, ^3J(P–H) 7.6 Hz, H8), 3.80 (s, 6H, H2), 3.08 (t, 6H, ^3J 5.4 Hz, H7); ^{13}C 64.9 (d, ^2J(^{13}C–^{31}P) 3.4 Hz, C8), 59.0 (C4, C6), 51.4 (C7), 33.9 (C2). ^{31}P: +119.4 (^2J(^{31}P–^{13}C) 3.4, ^3J(^{31}P–^{1}H) 7.6 Hz). Anal. Calcd. for $C_{15}H_{33}BN_3O_3PS_6$: C, 33.51; H, 6.36; N, 7.82. Found: C, 33.26; H, 6.45; N, 8.03.

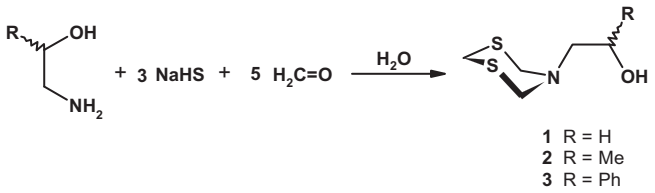
*2.29. P → BH_3 adduct of tris-{2-(5-methyl-1,3,5,6-boradithiazinan-5-yl)-ethanyl}-phosphite (**22**)*

To a fresh solution of **7** (210 mg, 0.4 mmol) in toluene (20 mL) a solution of BH_3·DMS (0.6 M, 1.8 mL, 0.84 mmol) was slowly added at −78 °C. After 5 min the solution was left to warm to room temperature and the solvent was evaporated. Compound **22** is a pale yellow liquid (208 mg, 97%). NMR (δ ppm, $CDCl_3$, 25 °C), ^{1}H: 4.40 (s, 6H, H6), 4.20 (s, 6H, H2), 3.80 (br t, ^3J 5.6 Hz, 6H, H8), 3.50 (t, ^3J 5.4 Hz, 6H, H7), 2.70 (s, 9H, H9). ^{13}C: 64.2 (C6), 60.2 (C8), 50.0 (C7), 49.1 (C9), 33.3 (C2). ^{31}P: +118.7. ^{11}B: −3.2 (br s), −44.2 (J(^{11}B–^{1}H) 98.5, J(^{31}P–^{11}B) 90.5 Hz). Anal. Calcd. for $C_{15}H_{42}B_4N_3O_3PS_6{\cdot}4/5C_7H_8$: C, 37.90; H, 7.47; N; 6.44. Found: C, 37.79; H, 8.08; N, 6.22.

3. Results and discussion

The ethanoldithiazinanes **1**–**3** were obtained by condensation of the corresponding ethanolamine with formaldehyde and NaSH in water (Scheme 2) [10]. Ethanoldithiazinanes **2** and **3** with a C8 substituent were prepared as racemic mixtures and also as an enantiopure compound **2**(−) using the ethanolamines of (R) configuration.

A crystal of the enantiopure compound **2**(−) was analyzed by X-ray diffraction (Fig. 1). The ring has a chair conformation with the nitrogen substituent in an axial position. The ethanol group forms a strong intramolecular O–H···N hydrogen bond (2.108 Å). The N5 and O10 are in an alternated *syn* conformation [dihedral angle N5–C7–C8–O10 is 46.1(1)°]. The nitrogen atom is pyramidal C4–N5–C7 114.4(3)°, C6–N5–C7 115.5(2)°, C4–N5–C6 113.0(2)° [Σ



Scheme 2. Synthesis of ethanoldithiazinanes **1**–**3**.

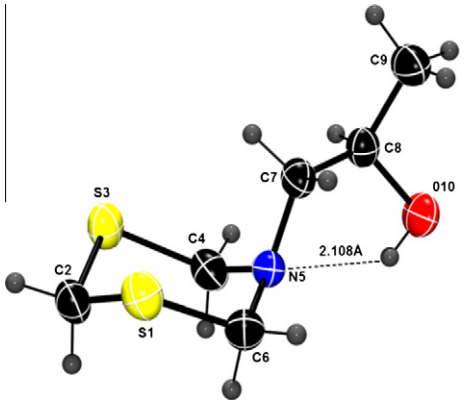


Fig. 1. ORTEP representation of compound **2**(−).

angles = 342.9°] and its geometry corresponds to 54% sp^3 hybridization. The angles at the sulfur atoms [C2–S1–C6 97.5(1)° and C2–S3–C4 96.6(1)°] indicate 36% sp^3 hybridization.

The ethanoldithiazinanes **1**–**3** have been used to synthesize a series of tris[2-(1,3,5-dithiazinan-5-yl)-ethanyl]-boric esters (**4**–**6**), tris[2-(1,3,5-dithiazinan-5-yl)-ethanyl]-phosphites (**7** and **8**), tris[2-(1,3,5-dithiazinan-5-yl)-ethanyl]-phosphates (**9** and **10**), tris[2-(1,3,5-dithiazinan-5-yl)-ethanyl]-thiophosphates (**11** and **12**) and tris[2-(1,3,5-dithiazinan-5-yl)-ethanyl]-selenophosphates (**13** and **14**) (Scheme 1). The ligand **1** will give only symmetric tripodal compounds. Racemic ligands **2**(±) and **3**(±) will produce a mixture of isomers (RRR; SSS; RRS and SSR), whereas the enantiopure ligand **2**(R) will give only one isomer (RRR) of C3 symmetry.

Compounds **4**–**14** are tripodal molecules with three bulky dithiazinane groups bound to boron or phosphorous atoms by an ethanolic chain. The dithiazinanyl heterocycles are quite interesting due to their richness in lone pairs and high reactivity. The configuration of the stereogenic center determines the conformation of the ligands in the tripodal molecules as we will discuss.

Compounds **4**–**14** are viscous liquids which could not be analyzed by X-ray diffraction studies. They were mainly characterized by ^{1}H, ^{13}C, ^{11}B, ^{31}P, ^{77}Se, and variable temperature NMR experiments, while the structure optimization has been performed by HF/6-31G(d) calculations. In order to establish the capability of the tripodal molecules to coordinate, a variety of bases and acids were added. The coordinating ability of free dithiazinanes has been tested before, using BX_3 reagents (X = H, F or Cl). In all cases the nitrogen atom is the preferred basic site [11–15]. It is also known that the free ethanoldithiazinanes are convenient ligands for aluminum organometallic compounds [16].

3.1. Synthesis of the tripodal molecules

Compounds **1**, **2**(±), **2**(−), and **3**(±) reacted with BCl_3-DMS in toluene in presence of NEt_3 (20 min, at −78 °C) to give boric esters **4**–**6** (Scheme 1). The reaction of **1**, **2**(±) and **2**(−) with PCl_3 and NEt_3 affords the phosphites **7**, **8**(±) and **8**(−). Compounds **4**–**8** are viscous yellow liquids, stable only under inert atmosphere. Phosphites **7** and **8** were oxidized with oxygenated water, sulfur or selenium, in CH_2Cl_2, to give the phosphates **9**, **10**(±), **10**(−), **11**, **12**(±), **12**(−), **13**, **14**(±) and **14**(−) which are also viscous liquids but stable in air (Scheme 1). The formation of boric esters **4**–**6** was confirmed by ^{11}B NMR spectra ($CDCl_3$, 25 °C), which shows characteristic broad signals at ~+17 ppm. These data also demonstrate that at room temperature there is no intramolecular N → B coordination (expected N → boric esters would have a chemical shift in the range of +5–10 ppm) [17]. The ^{31}P NMR ($CDCl_3$, 25 °C) spectra of the phosphorus compounds showed characteristic signals for phosphites **7** and **8** (between +140 and +142 ppm), phosphates **9** and **10** (between −2 and +9 ppm), thiophosphates **11** and **12** (between +67 and +68 ppm) and selenophosphates **13** and **14** (between +71 and +72 ppm).

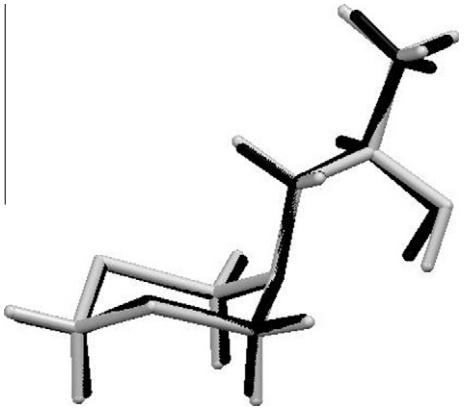


Fig. 2. Superposition of the structure of compound **2** obtained by X-ray diffraction analyses (black), with its modeled structure (gray).

3.2. HF/6-31G(d) calculations

An important aim in our investigation was the structural analysis of the different tripodal molecules and the evaluation of how the different substituents and chirality affected the overall molecular conformation. Therefore calculations were performed in order to obtain the molecular geometries using the Gaussian 98 package [18]. Geometries were checked to be the minimal by means of the frequency analysis. Validation of the calculations result from the NMR analyses and also from the reasonable superposition of the structure of compound **2** obtained by X-ray diffraction analyses (black), with its modeled structure (gray), (Fig. 2).

3.2.1. Tripodal borates

A discussion of the main results of the modeled molecules follows. In all pictorial representations, the hydrogen atoms have been omitted for better appreciation of the structures. The calculated geometry of all boric esters is trigonal planar [angles close to 120°, Σ angles = 359.98°] with the oxygen and C8 carbon atoms lying in the same plane. Two optimized conformations very close in energy were found for compound **4**, Fig. 3. In one of them (**a**) three dithiazinanes are oriented towards one face of the molecule. Distances between nitrogen atoms [N1–N2 6.51 Å, N2–N3 4.89 Å and N1–N3 4.48 Å] indicate that a cavity has been formed between the ligands. This arrangement is also promoted by the oxygen nitrogen syn conformation of the fragment O–CH_2–CH_2–N. The second one (**b**) has two arms oriented towards one face and the third in the opposite face and is slightly higher in energy than conformer **a** (0.4324 kJ/mol). In both conformers hydrogen bonds C–H···O stabilized the structure.

In Fig. 4, the (RRR) isomer of compound **6** is shown. The boron, oxygen and C8 atoms are lying in a helicoidal arrangement, as a consequence of the three hydrogen bonds between the oxygen

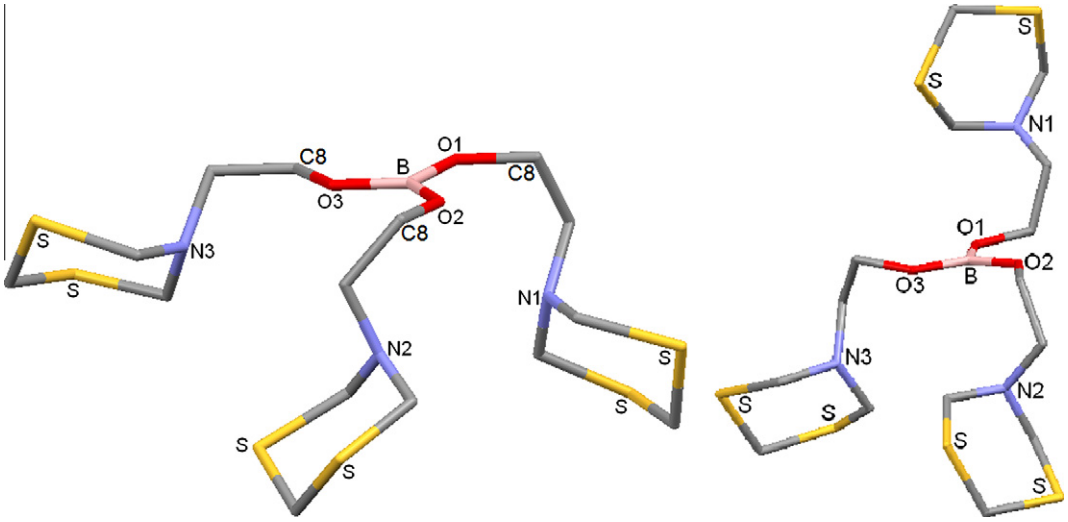


Fig. 3. Two preferred conformers were found for compound **4**. Conformer a has less energy (0.4324 kJ/mol) than conformer b.

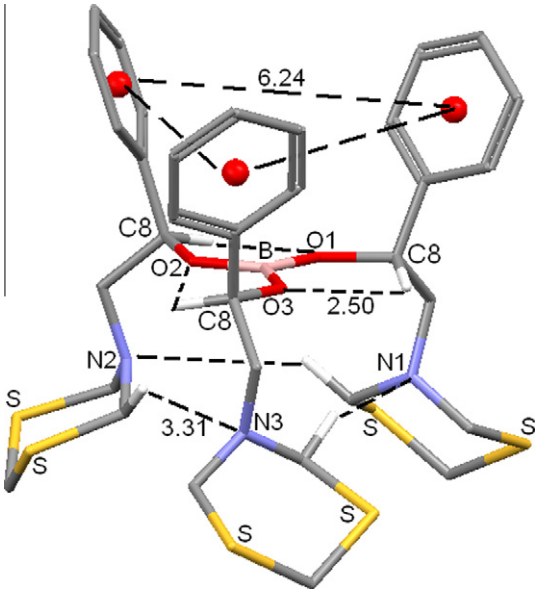


Fig. 4. View of the optimized geometry for **6**(RRR).

atoms and the C8–H protons. The phenyl groups and ethanoldithiazinanes are also helicoidally oriented. The C4–H protons are directed towards the nitrogen atoms assisting the organization of the dithiazinanyl groups. The molecule is dissymmetric (C3 symmetry). The three phenyl groups are oriented towards one boron face, whereas the dithiazinanyl groups are located on the other face. All distances between the phenyl centroids are around 6.24 Å, and all N–N distances are 5.25 Å. This arrangement leads to the formation of two different cavities. The one formed by the dithiazinanyl groups is small (0.9 Å is the distance between the axial C4–H Fig. 5a), whereas the second cavity formed by the phenyl groups has more space for the possible coordination of a small molecule (Fig. 5b).

For the isomeric mixture of compound **5**, prepared from racemic ethanoldithiazinanes **2**(±), two diasteromers, (RRR) and (SSR), were analyzed. For isomer **5**(RRR), the three methyl groups are oriented towards one face, and the three dithiazinanes are located on the other face affording two cavities. The boron, oxygen and C8 atoms form as in the previous analyzed molecule **6**(RRR), a helicoidal arrangement. The distances between the nitrogen atoms are N1–N2 6.187 Å, N2–N3 5.131 Å and N1–N3 5.066 Å and it is clear that there is more space for coordination on the face presenting the methyl groups than on the other face of the molecule (Fig. 6).

It is noteworthy that the calculated model for the **5**(SSR) isomer presented a completely different conformation (Fig. 7). One of the branches with (S) configuration is located alone on one of the faces. The opposite face has two enantiomeric branches (S) and (R). The different arrangement of the isomeric ligands has consequences in their spectral properties. In the preferred conformation of compound **5**(RRR), the three substituents are magnetically equivalent, and will give only one set of signals for all branches under NMR analyses. However, the lack of symmetry in diasteromer **5**(SSR) will make each substituent distinct.

3.2.2. Tripodal phosphites

Calculations showed that the geometry of the phosphorus atom in the modeled phosphites is trigonal pyramidal [P angles are O1–P–O2 96.53°, O2–P–O3 98.57° and O1–P–O3 103.37°]. The preferred conformation of compound **7** is described in Fig. 8. The nitrogen lone pairs are pointing in away from each other. The distances between them are bigger than in the boric esters [N1–N2 7.896 Å, N2–N3 7.737 Å, N1–N3 4.503 Å].

For compound **8**(±), which bears a methyl group at C8, isomers **8**(RRR) and **8**(SSR) were analyzed (Fig. 9). In isomer **8**(RRR), the methyl groups are situated on the same face of the plane formed by the oxygen atoms, whereas the dithiazinanyl groups are on the opposite face. The C8–H protons are oriented towards the oxygen atoms with distances 2.76, 2.79, 3.0 Å. The molecule has C3 symmetry. A helicoidal arrangement around the phosphorus is also observed. The distances between the nitrogen atoms in **8**(RRR) and **8**(SSR) highlight the differing ligand arrangements between the two diasteromers [**8**(RRR) N1–N2 5.255, N2–N3 6.693, and N1–N3 5.210 Å; **8**(SSR) N1–N2 5.389, N2–N3 5.173, and N1–N3 6.393 Å]. In isomer (SSR), the heterocycles are on the same face of the phosphate, however, the branch (R) is arranged perpendicularly to the other two of (S) configuration. It is clear that for isomer **8**(SSR), as in the boric ester **5**(SSR), asymmetry will lead to three sets of ^{1}H and ^{13}C NMR signals.

3.2.3. Tripodal phosphates

All phosphates (**9**–**14**) show the distorted tetrahedral geometry of phosphorus. Compounds **9** (P=O), **11** (P=S) and **13** (P=Se) all

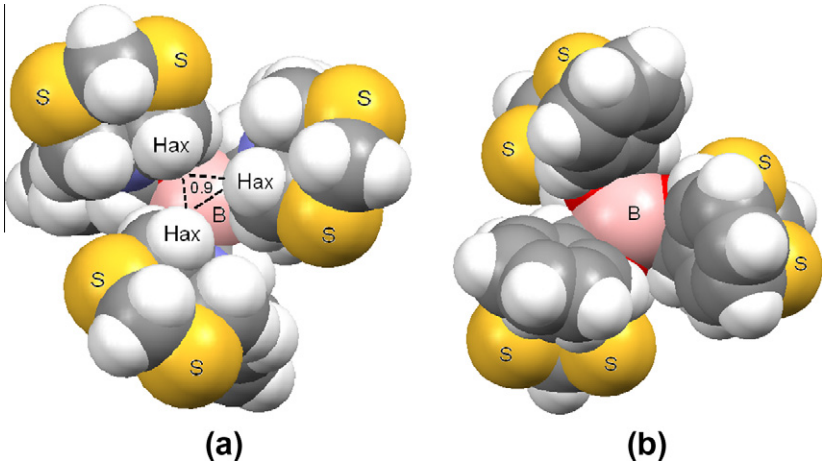


Fig. 5. Spacefill representation of compound **6**(RRR) showing two views along an axis perpendicular to the boron plane: (a) the face with ethanodithiazinanes and (b) the face with phenyl groups.

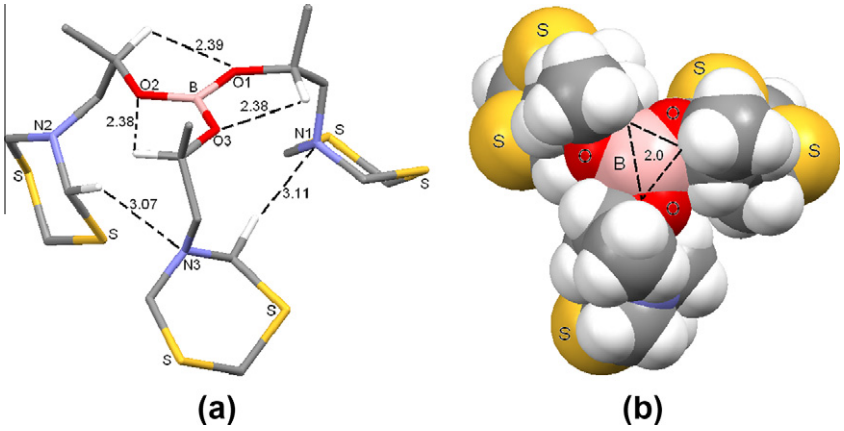


Fig. 6. (a) Distances between C–H protons and oxygen or nitrogen atoms are shown for compound **5**(RRR). (b) Spacefill representation of **5**(RRR), view of the face with methyl groups.

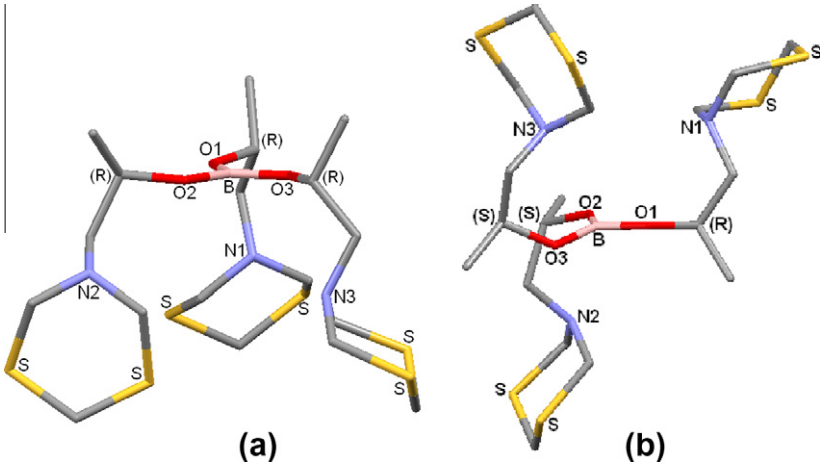


Fig. 7. Modeled conformers of **5** (a) isomer (RRR) and (b) isomer (SSR).

have O–P–O bond angles between 102.1 and 103.3°. Angles O–P=X vary in the range 114.8–116.5°. The P=Y bond lengths are characteristic [**13** (P=Se) 2.069 Å, **11** (P=S) 1.925 Å and in **9** (P=O) 1.447 Å]. As compounds **9**, **11** and **13** have a similar geometry, only compound **9** is shown (Fig. 10). Isomers (RRR) and (RRS) of compounds **10**, **12** and **14** show similar arrangements to the corresponding phosphites, with analogous stereochemical results (Fig. 11). The dithiazinane groups produce a bigger cavity in these phosphates as can be deduced from nitrogen atom distances [**14**(−) N1–N2 7.136 Å, N2–N3 4.996 Å, N1–N3 5.089 Å; **12**(−)

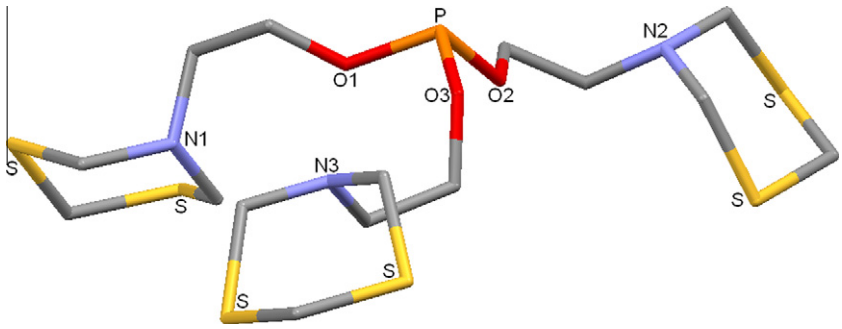


Fig. 8. Optimization of the preferred conformer of compound **7**.

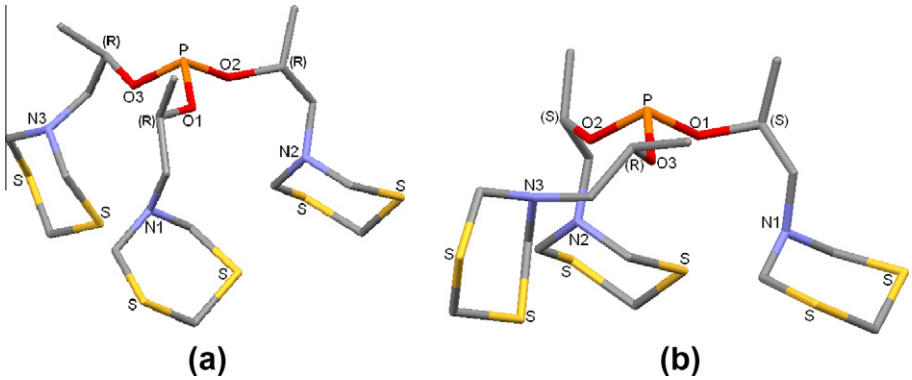


Fig. 9. Preferred conformers for isomers **8**(RRR) (a) and **8**(SSR) (b). P angles of **8**(RRR) are in the range of 97.96–98.19° and those of **8**(SSR) between 96.87° and 99.65°.

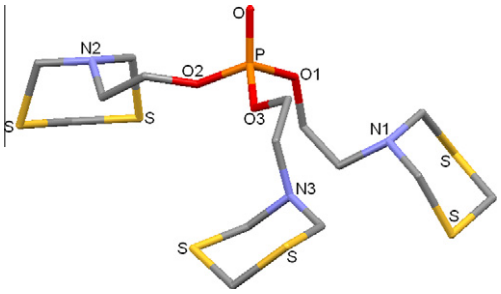


Fig. 10. Optimized geometry for compound **9**.

N1–N2 7.021 Å, N2–N3 4.926 Å, N1–N3 5.026 Å and **10**(−) N1–N2 5.125 Å, N2–N3 5.189 Å, N1–N3 7.055 Å].

3.3. Ethanolamine fragment conformation analyses by NMR

In order to establish the preferred conformation of the ethanolamine fragment in compounds **4**–**14**, we have calculated the H7a–C–C–H8 and H7b–C–C–H8 dihedral angles, from the H7a–H8 and H7b–H8 coupling constants obtained from ^{1}H NMR spectra using the Karplus equation [19]. The dihedral angles showed that the ethanolamine group in all compounds adopts a similar preferred conformation, with nitrogen (N5) and oxygen (O9) in a *syn* conformation, also found in the solid state for compound **2**(−) [N5–C7–C8–O9 torsional angle is 46.1(1)°]. In the calculated structures **4**–**14**, the averaged values for the N5–C7–C8–O9 torsional angles vary from 55.7° to 67.8°. In Table 1, the coupling constants are shown for compounds **2**(−) and **5**(−) as well as their calculated angles.

3.4. NMR and the stereochemistry

3.4.1. Stereochemical effect on central atoms

From calculations, it was clear that the tripodal compounds with ligands without substitution at C8 or having the same configuration at C8 would give only one isomer. However, the products of racemic ethanoldithiazinane would give a mixture of isomers RRR:RRS:SSR:SSS in a 1:3:3:1 ratio, though the RRR/SSS pairs are indistinguishable through NMR analysis as is also the case for the

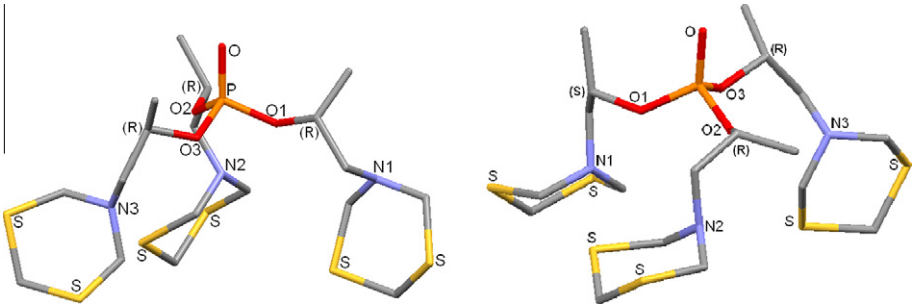
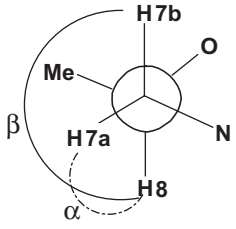


Fig. 11. Preferred conformers of isomers **10**(RRR) and **10**(RRS).

Table 1
^{1}H NMR ($CDCl_3$, 25 °C) data [δ, ppm] for **2** and **5**. Newman projection shows the preferred conformation for the ethanolamine fragment (configuration R at C8), and values of the α and β dihedral angles, calculated from coupling constants ^{3}J(H–H)



C8 R configuration

Cpd	H7a	α	H7b	β	H8
2(−)	3.04 (dd) ^{3}J 3.1	48	2.43 (dd) ^{3}J 9.9	148	3.76 (qdd) ^{3}J 9.9, 3.1
5(−)	2.99 (dd) ^{3}J 4.7	36	2.84 (dd) ^{3}J 7.4	131	4.18 (qdd) ^{3}J 7.4, 4.7

RRS/SSR pair. For this reason, NMR analysis of the reaction products of racemic ethanoldithiazinanes gives two signals in a 3:1 ratio. The ^{31}P NMR ($CDCl_3$, 25 °C) spectrum of phosphite **7** and the enantiopure compound **8**(RRR) showed as expected, only one ^{31}P signal [δ^{31}P +140.6, **7** and +142.0, **8**(−)] [20]. On the other hand, the isomers of phosphites **8**(±) synthesized from the racemic mixture **2**(±), showed two signals at +142.1 [**8**(SSR)–**8**(RRS)] and +142.0 [**8**(RRR)–**8**(SSS)] in the expected 3:1 ratio. Their assignment was checked by adding pure compound **8**(−) to the mixture **8**(±) and recording the spectrum again, with the corresponding growth of the signal for **8**(RRR) and **8**(SSS). The phosphates show a similar spectral behavior to the phosphites. The ^{31}P NMR spectrum of phosphates, **10**(±) (P═O), **12**(±) (P═S) or **14**(±) (P═Se), obtained from the racemic compound **2**(±) shows signals in the ratio 3:1. Spectra for compounds **14** are shown as an example. The ^{31}P and ^{77}Se ($CDCl_3$, 25 °C) spectra for **14**(RRR) shows a ^{31}P single resonance coupled with ^{77}Se [δ^{31}P (ppm) +72.3; ^{1}J(^{31}P–^{77}Se)

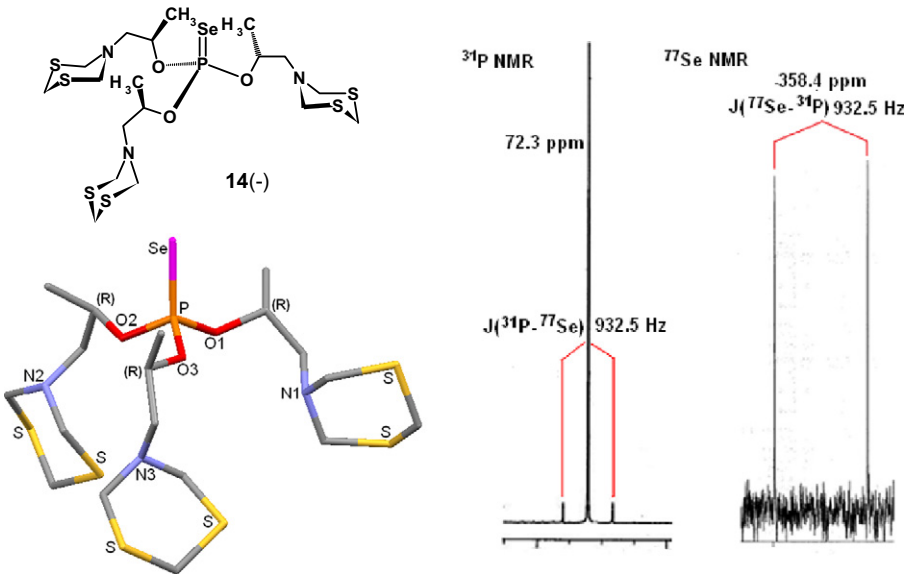


Fig. 12. δ^{31}P and ^{77}Se NMR spectra for compound **14**(RRR).

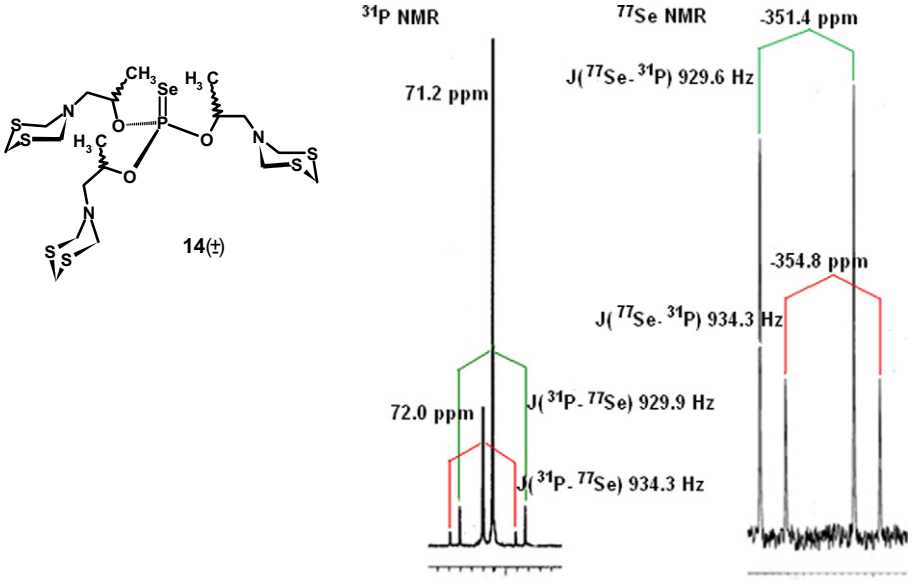


Fig. 13. δ^{31}P and ^{77}Se NMR spectra for the isomeric mixture **14**(±).

Table 2
Chemical shift data [δ, ppm] ^{13}C NMR ($CDCl_3$, 25 °C) of C7 and C8 in compounds **2**(−), **5(±)** and **5**(−).

Cpd	C7	C8
2(−)	57.2	63.6
5(−)	56.2	66.5
5(±)	56.4, 56.3, 56.2 [1:2:1] ratio	66.5, 66.4, 66.3 [1:2:1] ratio

932.5 Hz]. The ^{77}Se spectrum has a doublet at $\delta^{77}Se$ −358.4 [$^1J(^{77}Se–^{31}P)$ 932.5 Hz] (Fig. 12). Spectra of the isomeric mixture **14**(±) are in Fig. 13. Signals were assigned by comparison with pure enantiomer **14**(−).

3.4.2. Stereochemical effects on ligands

^{13}C NMR spectra of compound **5**(±) synthesized from racemic ethanolamines showed three signals for C7 and three for C8 in 1:2:1 ratio. One signal corresponds to the pair of isomers **5**(RRR) and **5**(SSS) as was equal to that observed in the spectrum of pure **5**(RRR). The other two signals in a 1:2 ratio belong to **5**(RRS)–**5**(SSR). The unequivocal assignment of the ^{13}C spectra was performed by adding to the isomeric mixture of **5**, the enantiomerically pure isomer **5**(RRR), which led to an increased signal for **5**(RRR)-**5**(SSS) allowing the identification of the pairs of isomers (Table 2). A similar stereochemical result was found for compound **6**(±). The same analysis was done with the ^1H ($CDCl_3$, 25 °C) NMR spectra.

In the ^{13}C NMR ($CDCl_3$, 25 °C) spectra of isomers **8**(±), the C8 signal presents four doublets due to $^2J(^{31}P–^{13}C)$ coupling one for RRR–SSS, and the other three for RSS–SRR (Fig. 14).

3.5. NMR variable temperature experiments

^{11}B NMR experiments at low temperature in toluene-d_8 and THF-d_8 showed that the ^{11}B signals of boric esters **4**–**6** are shifted from ∼+18 ppm (+20 °C) to ∼+9 ppm (−90°) which corresponds to boron coordination by a nitrogen atom (Scheme 3). The ^1H and ^{13}C spectra do not show two different ligands, indicating that the substituents exhibit a fluxional behavior, exchanging the coordination bond between them [21,22].

From the VT-NMR experiments, the activation energy for the breaking of the N → B bond was calculated as 37.8 kJ mol^{-1} for compound **4** and 37.9 kJ mol^{-1} for compound **5**(RRR). The low value observed is typical for a weak coordination bond. They are in the range of similar molecules (30–60 kJ mol^{-1} [23–25]). The weak coordination is attributed to steric effects, and to the nature of the nitrogen geometry, which is in between tetrahedral and planar, due to the ring tension, as along with the weak Lewis acid nature

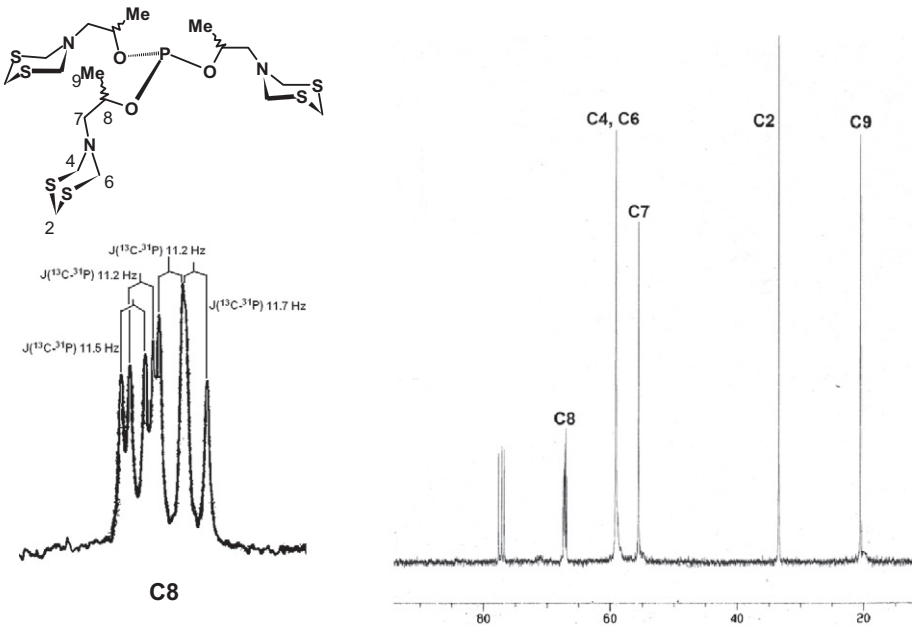
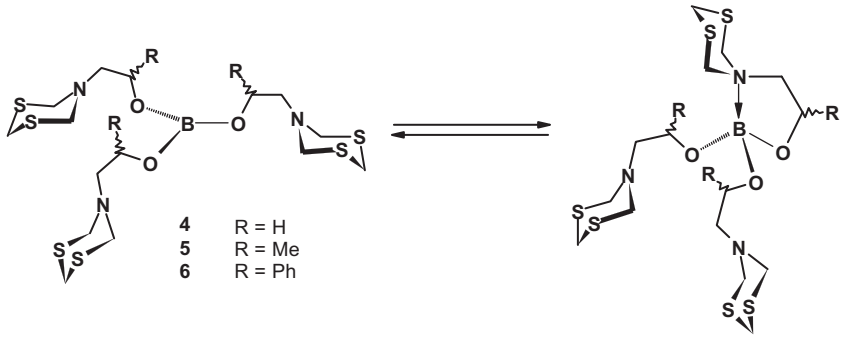
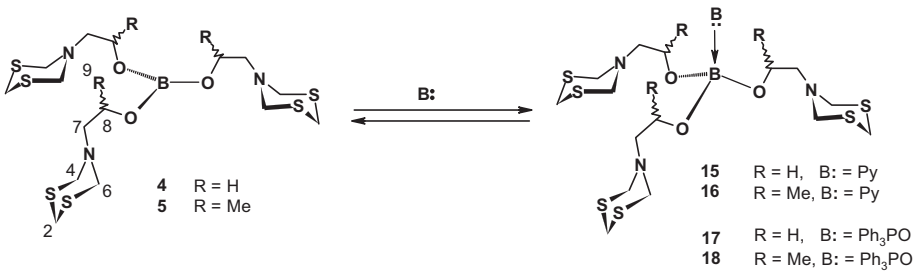


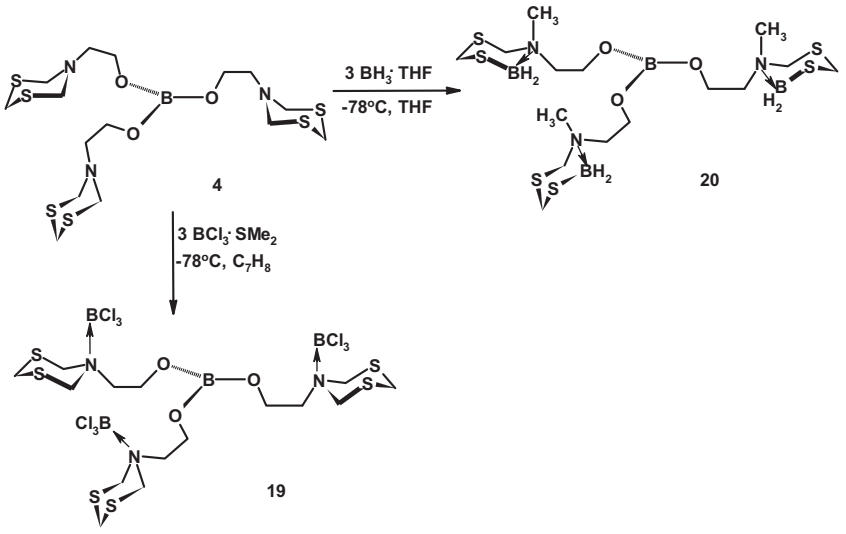
Fig. 14. ^{13}C NMR spectrum of the isomeric mixture: **8**(RRR)–**8**(SSS) and **8**(RRS)–**8**(SSR). Amplification of C8 signals is shown.



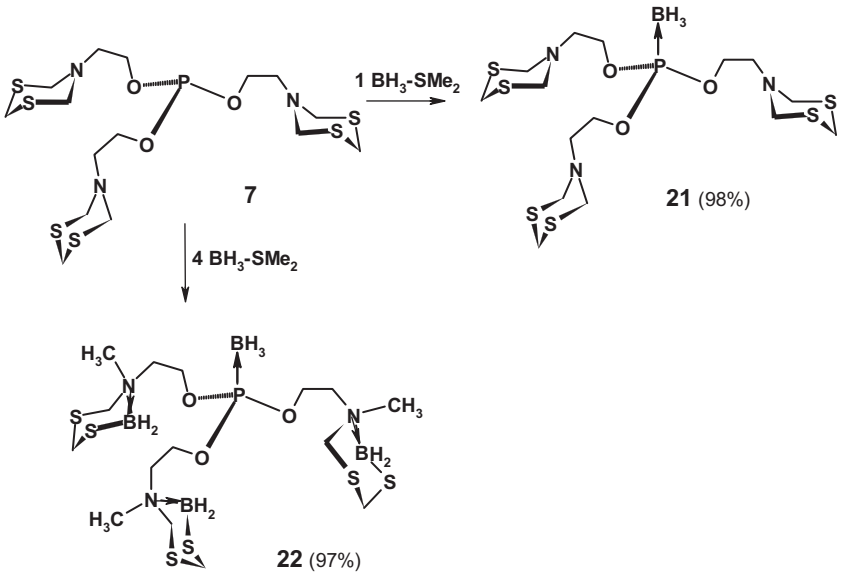
Scheme 3. N → B intramolecular coordination of boric esters **4**–**6**.



Scheme 4. Pyridine and PPh_3O adducts of boric esters **4** and **5**.



Scheme 5. Reactions of boric ester **4** with boron reagents.



Scheme 6. Borane adducts of compound **7**.

of the borate. The presence of alkyl or aryl groups in the chains diminishes the bond strength due to steric effects.

From the VT ^1H and ^{13}C NMR experiments in THF-d_8 and toluene-d_8, the ring inversion energy was measured as 47.4 kJ mol^{-1} for **4**, 49.1 kJ mol^{-1} for **5** and 48.4 kJ mol^{-1} for **6**. The presence of an alkyl or aryl group in the chain increases the energy by 1.7 and 1.0 kJ mol^{-1}, respectively.

3.6. Lewis base addition to the boric esters

We were interested in establishing whether the ligands surrounding the boron atom were sufficiently bulky to prevent the coordination of bases. Accordingly, we added a variety of bases to the boric esters and evaluated the reaction by ^{11}B NMR. Benzylamine, α-methylbenzylamine and pyridine were added to the boric

esters **4** and **5** and the ^{11}B spectrum recorded (Scheme 4). The experiments did not show any coordination of benzylamine nor of α-methylbenzylamine even at low temperature. In contrast, pyridine, adducts were observed (^{11}B δ +5.6 ppm for **15** and +4.0 for **16**). The difference in the coordinating behavior of these amines is attributed to the lesser volume of the pyridine.

Addition of PPh_3 to the boric esters did not show any P → B coordination. However, PPh_3O which is a less hindered base with a greater affinity for boron, was coordinated (Scheme 4). The spectrum of the boric esters **4** or **5** and ten equivalents of $(Ph)_3PO$ at room temperature showed the coordinated species $Ph_3PO \rightarrow B$ **17** ($\delta^{11}B$ +1.3 ppm, $\delta^{31}P$ +29.8 ppm) and **18** ($\delta^{11}B$ +1.2 ppm, $\delta^{31}P$ +29.5 ppm). These results indicate that these esters are capable of small bases ligands are useful for small bases coordination.

3.7. Reactions of boric ester 4 with BCl_3 and BH_3

In order to establish whether the amine groups of the boric esters are free enough to coordinate a Lewis acid, three equivalents of $BCl_3{\cdot}SMe_2$ were added to the boric ester **4** and compound **19** was obtained in quantitative yield. Its ^{11}B NMR spectrum showed two signals in 1:3 ratio, one at +17.5 for $B(OR)_3$, and another at +10.4 for the N → BCl_3 group. All three nitrogen atoms were coordinated, and the rings were found to be in conformational equilibrium (Scheme 5). The reaction of three equivalents of $BH_3{\cdot}THF$ with boric ester **4** at −78 °C gave compound **20** by a reductive ring opening and rearrangement (Scheme 5). The endocyclic BH_2 group give a broad band in the ^{11}B spectrum (δ −3.8 ppm) together with the resonance for the boric atom at +17.0 ppm, in a 3:1 ratio. The ^{13}C NMR spectrum of **20** has a signal for an N–CH_3 group at 48.1 ppm and C4 is shifted from 58.8 to 63.4 ppm. The structure was established by comparison with the reported data for 5-methyl-5-borane-dithiazinane and 5-methyl-6,1,3,5-boradithiazinane [11,12,15].

3.8. Reactions of phosphites with BH_3

The equimolar reaction of phosphite **7** with BH_3–SMe_2 gave the P → BH_3 adduct **21** as the only product, demonstrating that the phosphorus has enough space for coordination. In an excess of borane (four equivalents) the borata heterocycles **22** are obtained (Scheme 6).

4. Conclusions

A series of tripodal boric esters (**4**–**6**), phosphites (**7** and **8**), phosphates (**9** and **10**), thiophosphates (**11** and **12**) and selenophosphates (**13** and **14**) were synthesized. C3 symmetry enantiopure compounds were obtained, which may have application in asymmetric synthesis or a building blocks in material sciences. The effect of the bulky ethanoldithiazinanes on their structure was analyzed. The chirality at C8 affected the preferred conformation of the tripodal compounds. Calculations were very useful for structural analyses of the compounds. Modeled molecules indicated the preferred conformations and how they depend on the size and chirality of substituents. Analyses were confirmed by NMR. ^{1}H, ^{13}C, ^{31}P and ^{77}Se spectra allowed the diasteromer and conformer assignments. The boric esters presented a fluxional N → B coordination as was observed by ^{11}B NMR at low temperature. The preferred conformations in the tripodal molecules led to the formation of cavities which left in some of them enough space for coordination of molecules of low steric demand.

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