

# Preparation and Structural Characterization of Three Types of Homo- and Heterotrinnuclear Boron Complexes: Salen{[B–O–B][O<sub>2</sub>BOH]}, Salen{[B–O–B][O<sub>2</sub>BPh]}, and Salen{[B–O–B][O<sub>2</sub>P(O)Ph]}

Gabriela Vargas,<sup>†</sup> Irán Hernández,<sup>†</sup> Herbert Höpfl,<sup>\*,†</sup> María-Eugenia Ochoa,<sup>‡</sup> Dolores Castillo,<sup>‡</sup> Norberto Farfán,<sup>‡</sup> Rosa Santillan,<sup>‡</sup> and Elizabeth Gómez<sup>§</sup>

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, C.P. 62210 Cuernavaca, México, Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, Apdo. Postal 14-740, C.P. 07000 México D.F., México, and Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México D.F. 04510, México

Received August 17, 2004

Three types of homo- and heterotrinnuclear boron complexes have been obtained in moderate to good yields from reactions of salen-type ligands with boric acid and combinations of boric acid with phenylboronic and phenylphosphonic acid. The products are air-stable and have relatively high melting points (>290 °C) but are poorly soluble or insoluble in common organic solvents. They have been characterized as far as possible by elemental analysis, mass spectrometry, IR, <sup>1</sup>H, <sup>11</sup>B, and <sup>31</sup>P NMR spectroscopy, and X-ray crystallography. Furthermore, theoretical calculations have been performed for representative examples to permit a complete comparison of the different structure types. A detailed analysis of the molecular structures showed that the complexes are constructed around a central B<sub>3</sub>O<sub>3</sub> or B<sub>2</sub>PO<sub>3</sub> ring. The salen ligands are attached to two boron atoms of these rings, which have therefore tetrahedral coordination geometries. The complexes contain seven- and eight-membered heterocycles of the B<sub>2</sub>C<sub>n</sub>ON<sub>2</sub> (n = 2, 3) type with chair or twisted-chair and boat-chair or chair-chair conformations, respectively. In the homotrinnuclear complexes one of the three boron atoms is three-coordinate and can therefore still act as Lewis acid, thus making these products interesting for catalytic applications, e.g. in asymmetric synthesis. Depending on the substituents attached to the boron atoms, these complexes show a relationship with either trimetaboric acid, boroxine, or the tetraborate dianion found in Borax.

## 1. Introduction

Complexes with ligands of the Salen class (salenH<sub>2</sub> = *N,N'*-ethylenebis(salicylideneimine)) have been studied extensively, in particular with transition metals.<sup>1</sup> Generally, salen type ligands feature two covalent and two coordinate-covalent sites situated in a planar array, which makes them ideal ligands for the generation of specific metal polyhedra. Complexes with pentacoordinate metal centers usually have square pyramidal coordination environments, in which the

apical site is occupied by an interchangeable ligand. In hexa- and heptacoordinate complexes the ligands are usually located in the equatorial plane, leaving two or three sites for the coordination of additional ligands.<sup>2</sup> Due to these geometrical particularities salen complexes have found applications as catalytically active species for a series of chemical reactions, including asymmetric synthesis.<sup>3</sup>

The huge majority of salen complexes are mononuclear, an exception being compounds with group 13 elements, which can also be di-, tri-, and tetranuclear, especially in

\* Author to whom correspondence should be addressed. E-mail: hhopfl@buzon.uaem.mx. Fax: (+52) 777 329 79 97.

<sup>†</sup> Universidad Autónoma del Estado de Morelos.

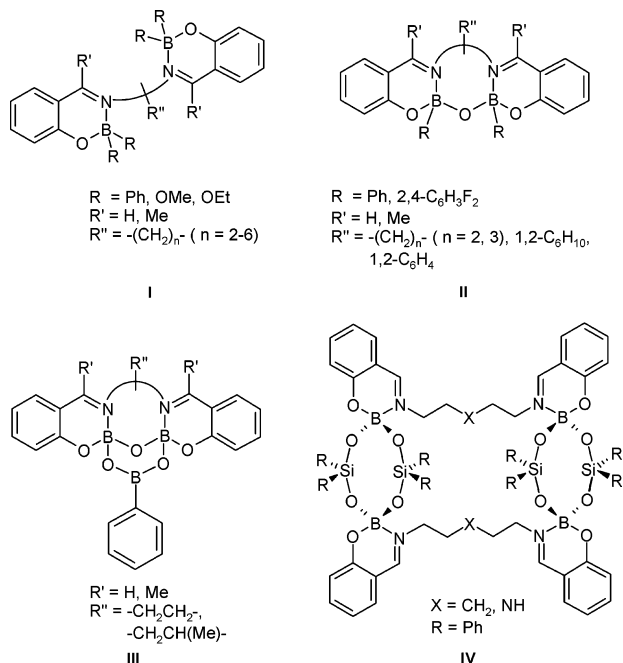
<sup>‡</sup> Centro de Investigación y de Estudios Avanzados del IPN.

<sup>§</sup> Universidad Nacional Autónoma de México.

(1) (a) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83. (b) Hobday, M. D.; Smith, T. D. *Coord. Chem. Rev.* **1972**, *9*, 311.

(2) Sánchez, M.; Harvey, M. J.; Nordstrom, F.; Parkin, S.; Atwood, D. A. *Inorg. Chem.* **2002**, *41*, 5397.

(3) (a) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. (b) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063. (c) Konsler, R. G.; Karl, J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 10780.

**Chart 1.** Reaction between a Salen Derivative as Ligand and a Boric, Boronic, or Borinic Acid Yielding Dinuclear (**I**, **II**), Trinuclear (**III**), and Tetranuclear (**IV**) Products


tetrahedral coordination environments.<sup>4,5</sup> Since the boron atom very rarely exceeds the coordination number of 4<sup>6</sup> and forms relatively strong covalent bonds with oxygen and coordinate-covalent bonds with nitrogen atoms, this element is an excellent candidate for the study of such species. So far, four different types of boron–salen complexes are known (Chart 1).

Considering that the two salicylideneimino groups of the ligands coordinate to different boron atoms, the composition of complexes **I–IV** can be described as follows: In **I** two individual BR<sub>2</sub> or B(OR)<sub>2</sub> groups are complexed,<sup>4</sup> while in **II** and **III** it is a dinuclear boroxane group, RB–O–BR,<sup>5</sup> and a trinuclear boroxane moiety, (B–O–B)–(O<sub>2</sub>BPh).<sup>5b</sup> In **IV** two diboradisiloxane rings, (B–O–SiR<sub>2</sub>–O)<sub>2</sub>, are connected through a pair of ligands to form a molecule with a large cylinder-shaped cavity.<sup>4a</sup>

Since type **III** boron complexes possess a three-coordinate boron atom, they are particularly interesting in view of

possible applications in catalytic processes, where a Lewis acid is required. The circumstance that the two tetracoordinate boron atoms are chiral and that it is relatively facile to introduce further chiral functional groups in these ligands makes them interesting for asymmetric synthesis.<sup>7</sup> Until now, only two type **III** derivatives have been described in the literature.<sup>5b</sup>

The present contribution enhances the knowledge on the preparation and structural characterization of homotrinnuclear boron–salen complexes as well as on the transformation of dinuclear oxo-bridged borates to heterotrinnuclear species containing two boron atoms and one phosphorus atom.

## 2. Experimental Section

**Instrumentation.** NMR studies were carried out with Varian Gemini 200, JEOL GSX 270, Bruker 300, and Varian Inova 400 instruments. Standards were TMS (internal, <sup>1</sup>H, <sup>13</sup>C) and BF<sub>3</sub>·OEt<sub>2</sub> (external, <sup>11</sup>B). Chemical shifts are stated in parts per million; they are positive, when the signal is shifted to higher frequencies than the standard. COSY, HMQC, and NOESY experiments have been carried out to assign the <sup>1</sup>H and <sup>13</sup>C spectra completely. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on HP 5989A and JEOL JMS 700 equipment. Elemental analyses have been carried out on Perkin-Elmer Series II 2400 and Elementar Vario ELIII instruments. It should be mentioned that elemental analyses of boronic acid derivatives are complicated by incombustible residues (boron carbide) and therefore not always in the established limits of exactitude, especially with respect to carbon.<sup>8</sup> Therefore, only the values for hydrogen and nitrogen are indicated.

**Preparative Part.** Commercial starting materials and solvents have been used. The salen, salen(<sup>t</sup>Bu), acen, salpen, salpen(<sup>t</sup>Bu), acpen, salphen, salphen(<sup>t</sup>Bu), acphen, salcen, salcen(<sup>t</sup>Bu), and accen ligands **1a–l** have been prepared according to a method reported in the literature.<sup>9</sup>

**Preparation of the Salen{[B(OH)–O–B(OH)]} Complexes.** Compounds **2b,g** have been prepared by similar methods; therefore, the experimental procedure of the preparation is only described in detail for the first case.

**Salen<sup>t</sup>Bu{[B(OH)–O–B(OH)]} (2b).** Compound **2b** was prepared from 1 equiv of ligand **1b** (2.00 g, 4.06 mmol) and 2 equiv of boric acid (0.50 g, 8.12 mmol) in 15 mL of acetonitrile. After the solution was stirred for 15 min, a yellow precipitate of **2b** had formed that was collected by filtration and dried. Yield: 60%. Mp: >300 °C. IR (KBr):  $\tilde{\nu}$  = 3429 (br, m, B–OH), 2959 (s),

(4) (a) Hohaus, E. *Fresenius Z. Anal. Chem.* **1983**, 315, 696. (b) Ghose, B. N. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, 16, 1383. (c) Kliegel, W.; Amt, H.; Becker, H.; Lauterbach, U.; Lubkowitz, G.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1994**, 72, 2118. (d) Atwood, D. A.; Jegier, J. A.; Remington, M. J.; Rutherford, D. *Aust. J. Chem.* **1996**, 49, 1333. (e) Wei, P.; Atwood, D. A. *Inorg. Chem.* **1997**, 36, 4060. (f) Wei, P.; Atwood, D. A. *Chem. Commun.* **1997**, 1427. (g) Wei, P.; Keizer, T.; Atwood, D. A. *Inorg. Chem.* **1999**, 38, 3914. (h) Agustin, D.; Rima, G.; Gornitzka, H.; Barrau, J. *Organometallics* **2000**, 19, 4276. (i) Woodgate, P. D.; Horner, G. M.; Maynard, N. P.; Rickard, C. E. F. *J. Organomet. Chem.* **2000**, 595, 215. (j) Kunkely, H.; Vogler, A. *Inorg. Chim. Acta* **2001**, 321, 171. (k) Keizer, T. S.; DePue, L. J.; Parkin, S.; Atwood, D. A. *J. Am. Chem. Soc.* **2002**, 124, 1864.

(5) (a) Sánchez, M.; Höpfl, H.; Ochoa, M.-E.; Farfán, N.; Santillan, R.; Rojas, S. *Inorg. Chem.* **2001**, 40, 6405. (b) Sánchez, M.; Keizer, T. S.; Parkin, S.; Höpfl, H.; Atwood, D. A. *J. Organomet. Chem.* **2002**, 654, 36.

(6) For hypervalent boron complexes, see: (a) Hillier, A. C.; Jacobsen, H.; Gusev, D.; Schmalle, H. W.; Berke, H. *Inorg. Chem.* **2001**, 40, 6334. (b) Yamashita, M.; Yamamoto, Y.; Akiba, K.; Nagase, S. *Angew. Chem., Int. Ed.* **2000**, 39, 4055.

(7) (a) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, 37, 1986. (b) Corey, E. J.; Link, J. O. *Tetrahedron Lett.* **1992**, 33, 4141. (c) Lohray, B. B.; Bhushan, V. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 729. (d) Caze, C.; El Moulaj N.; Hodge, P.; Lock, C. J.; Ma, J. J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 345. (e) Ferey, V.; Vedrenne, P.; Toupet, L.; Le Gall, T.; Mioskowski, C. *J. Org. Chem.* **1996**, 61, 7244. (f) Petasis, N. A.; Zavalov, I. A. *J. Am. Chem. Soc.* **1997**, 119, 445. (g) Davies, C. D.; Marsden, S. P.; Stokes, E. S. E. *Tetrahedron Lett.* **1998**, 39, 8513. (h) Petasis, N. A.; Zavalov, I. A. *J. Am. Chem. Soc.* **1998**, 120, 11798. (i) Batey, R. A.; MacKay D. B.; Santhakumar, V. *J. Am. Chem. Soc.* **1999**, 121, 5075. (j) Li, Y.; Liu, Y.; Bu, W.; Guo, J.; Wang, Y. *Chem. Commun.* **2000**, 1551. (k) Barringhaus, K.-H.; Matter, H.; Kurz, M. *J. Org. Chem.* **2000**, 65, 5031. (l) Bandini, M.; Cozzi, P. G.; Monari, M.; Perciaccante, R.; Selva, S.; Umami-Ronchi A. *Chem. Commun.* **2001**, 1318. (m) Chan, K.-F.; Wong, H. N. C. *Org. Lett.* **2001**, 3, 3991.

(8) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1910 and references therein.

(9) Dubsky, J. V.; Sokol, A. *Collect. Czech. Chem. Commun.* **1931**, 3, 548.

2871 (m), 1640 (C=N, s), 1567 (m), 1442 (s), 1396 (s, B-O), 1308 (m), 1245 (m), 1189 (m), 1141 (m), 971 (w), 876 (w), 831 (w), 768 (w), 679 (w), 641 (w), 516 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.01 (s, 2H, C(H)=N), 7.47, 7.00 (d, 4H, H-3, H-5), 4.21 and 3.71 (ABCD, 4H,  $\text{NCH}_2$ ,  $\text{NCH}_2$ ), 1.47, 1.28 (s, 36H,  $t$ -Bu) ppm.  $^{11}\text{B}$  NMR (96 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.0 ( $h_{1/2}$  = 270 Hz) ppm. MS (20 eV, EI):  $m/z$  (%) = 563 (23) [M + 1], 546 (31) [M - OH], 529 (46), 514 (58), 501 (66), 492 (100).

**Salphen{[B(OH)-O-B(OH)]} (2g).** Yield: 32%. Mp: >300 °C (dec). IR (KBr):  $\tilde{\nu}$  = 3357 (br, m, OH), 1625 (C=N, s), 1555 (s), 1481 (m), 1452 (m), 1371 (m, B-O), 1311 (m), 1190 (m), 1117 (s), 1022 (w), 925 (w), 916 (w), 866 (w), 808 (m), 764 (m), 684 (w), 571 (w), 456 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 8.65 (s, 2H, C(H)=N), 7.60 (m, 8H, H-10, H-9, H-3, H-5), 6.94 (m, 4H, H-2, H-4).  $^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 164.7 (C=N), 159.5 (C-1), 138.5, 137.9 (C-4, C-8), 133.1 (C-5), 129.8 (C-10), 126.0 (C-9), 118.5 (C-2, C-4), 115.9 (C-6).  $^{11}\text{B}$  NMR (64 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 3.6 ( $h_{1/2}$  = 1430 Hz) ppm.

#### Preparation of the Salen{[B-O-B][O<sub>2</sub>BOH]} Complexes.

Compounds **3a-g** have been prepared by similar methods; therefore, the experimental procedure of the preparation is only described in detail for the first case.

**Salen{[B-O-B][O<sub>2</sub>BOH]} (3a).** Compound **3a** was prepared from 1 equiv of ligand **1a** (2.00 g, 7.46 mmol) and 3 equiv of boric acid (1.38 g, 22.38 mmol) in 15 mL of acetonitrile. The mixture was refluxed for 4 h using a Dean-Stark trap, whereupon a yellow precipitate of **3a** had formed that was collected by filtration and dried. Recrystallization from acetone gave crystals suitable for X-ray crystallography. Yield: 98%. Mp: >350 °C. IR (KBr):  $\tilde{\nu}$  = 3309 (br, m, OH), 3057 (w), 2928 (w), 1639 (s, C=N), 1570 (m), 1492 (m), 1458 (m), 1408 (m, B-O), 1287 (m), 1226 (m), 1150 (m), 1069 (m), 976 (m), 940 (w), 857 (m), 812 (m), 751 (m), 647 (w), 465 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 8.64 (s, 2H, C(H)=N), 7.54 (m, 4H, H-3, H-5), 6.93 (m, 4H, H-2, H-4), 6.37 (s, 1H, OH), 4.08 and 3.98 (ABCD, 4H,  $\text{N}-\text{CH}_2$ ,  $\text{N}-\text{CH}_2$ ) ppm.  $^{11}\text{B}$  NMR (128 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 20.6 ( $h_{1/2}$  = 380 Hz), 2.7 ( $h_{1/2}$  = 190 Hz) ppm. MS (20 eV, EI):  $m/z$  (%) = 305 (100) [M -  $\text{BO}_3$ ], 277 (4), 250 (4), 236 (21), 173 (9), 152 (20), 91 (13), 77 (9). Anal. Calcd for  $\text{C}_{16}\text{H}_{15}\text{B}_3\text{N}_2\text{O}_6$  ( $M_r$  = 363.74): H, 4.15; N, 7.69. Found: H, 4.31; N, 7.71.

**Salen<sup>t</sup>Bu{[B-O-B][O<sub>2</sub>BOH]} (3b).** Yield: 64%. Mp: >350 °C. IR (KBr):  $\tilde{\nu}$  = 3435 (br, m, OH), 2959 (s), 2872 (w), 1639 (s, C=N), 1567 (w), 1446 (m), 1396 (s, B-O), 1306 (w), 1245 (w), 1141 (m), 1066 (w), 962 (w), 875 (w), 825 (w), 766 (w), 679 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 13.6 (br, s, 1H, OH), 8.44, (s, 2H, C(H)=N), 7.42 (d, 2H, H-3), 7.14 (d, 2H, H-5), 3.93 and 3.75 (ABCD, 2H,  $\text{N}-\text{CH}_2$ ,  $\text{N}-\text{CH}_2$ ), 1.47 and 1.33 (s, 36H,  $t$ -Bu) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.5 (C=N), 158.4 (C-1), 140.6, 137.1 (C-2, C-4), 127.5, 126.4 (C-3, C-5), 118.1 (C-6), 62.6, 62.2 ( $\text{N}-\text{CH}_2$ ,  $\text{N}-\text{CH}_2$ ), 35.4, 34.5 ( $t$ -Bu-C), 31.9, 29.8 ( $t$ -Bu-Me) ppm.  $^{11}\text{B}$  NMR (64 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 19.6 ( $h_{1/2}$  = 380 Hz), 0.8 ( $h_{1/2}$  = 380 Hz) ppm. MS (20 eV, EI):  $m/z$  (%) = 530 (53) [M -  $t$ -BuH], 515 (61), 473 (19), 285 (12), 236 (13), 213 (10), 57 (100). Anal. Calcd for  $\text{C}_{32}\text{H}_{47}\text{B}_3\text{N}_2\text{O}_6$  ( $M_r$  = 588.17): H, 8.05; N, 4.76. Found: H, 8.50; N, 4.75.

**Acen{[B-O-B][O<sub>2</sub>BOH]} (3c).** Yield: 98%. Mp: >350 °C. IR (KBr):  $\tilde{\nu}$  = 3411 (br, m, OH), 1618 (s, C=N), 1557 (s), 1397 (s, B-O), 1282 (s), 1240 (m), 1115 (s), 983 (m), 924 (m), 856 (m), 810 (m), 755 (s), 696 (m), 671 (m), 562 (w), 463 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 7.77 (d, 2H, H-5), 7.45 (ddd, 2H, H-3), 6.87 (m, 4H, H-2, H-4), 4.11 and 4.05 (ABCD, 4H,  $\text{N}-\text{CH}_2$ ,  $\text{N}-\text{CH}_2$ ), 2.59 (s, 6H, C(Me)=N) ppm.  $^{11}\text{B}$  NMR (64 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 19.6 ( $h_{1/2}$  = 690 Hz), 0.8 ( $h_{1/2}$  = 320 Hz)

ppm. MS (20 eV, EI):  $m/z$  (%) = 348 (0.4) [M -  $\text{BO}_2\text{H}$ ], 329 (100), 315 (7), 304 (16), 286 (12), 245 (5), 185 (47). Anal. Calcd for  $\text{C}_{18}\text{H}_{19}\text{B}_3\text{N}_2\text{O}_6$  ( $M_r$  = 391.80): H, 4.85; N, 7.15. Found: H, 5.58; N, 7.74.

**Salpen{[B-O-B][O<sub>2</sub>BOH]} (3d).** Yield: 93%. Mp: >350 °C. IR (KBr):  $\tilde{\nu}$  = 3387 (br, m, OH), 1648 (s, C=N), 1563 (m), 1484 (m), 1397 (m, B-O), 1313 (m), 1238 (m), 1148 (s), 995 (m), 924 (w), 858 (w), 824 (w), 760 (m), 711 (m), 625 (w), 458 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 8.60 (s, 2H, C(H)=N), 7.48 (m, 4H, H-3, H-5), 6.87 (m, 4H, H-2, H-4), 6.6 (br, s, 1H, OH), 3.86 and 3.80 (AB, 4H,  $\text{N}-\text{CH}_2$ ,  $\text{N}-\text{CH}_2$ ), 2.45 and 2.04 (AB, 2H, H-9) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 163.4 (C=N), 159.6 (C-1), 136.4 (C-3), 131.6 (C-5), 118.4, 118.2 (C-2, C-4), 116.2 (C-6), 54.1 ( $\text{N}-\text{CH}_2$ ), 31.8 (C-9) ppm.  $^{11}\text{B}$  NMR (128 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 20.7 ( $h_{1/2}$  = 380 Hz), 2.3 ( $h_{1/2}$  = 190 Hz) ppm. MS (20 eV, EI):  $m/z$  (%) = 319 (100) [M -  $\text{BO}_3$ ], 305 (4), 290 (14), 277 (9), 263 (4), 250 (2), 236 (18), 187 (19), 159 (24), 132 (7), 117 (4), 91 (9), 77 (8). Anal. Calcd for  $\text{C}_{17}\text{H}_{17}\text{B}_3\text{N}_2\text{O}_6$  ( $M_r$  = 377.78): H, 4.50; N, 7.42. Found: H, 4.78; N, 7.25.

**Salpen<sup>t</sup>Bu{[B-O-B][O<sub>2</sub>BOH]} (3e).** Yield: 78%. Mp: >350 °C. IR (KBr):  $\tilde{\nu}$  = 3410 (br, m, OH), 2958 (s), 2871 (m), 1644 (s, C=N), 1566 (m), 1395 (s, B-O), 1310 (m), 1259 (m), 1184 (m), 1130 (m), 936 (m), 901 (m), 821 (w), 771 (m), 681 (m), 609 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.02 (s, 2H, C(H)=N), 7.49, 7.00 (d, 4H, H-3, H-5), 4.19 and 3.70 (AB, 4H,  $\text{N}-\text{CH}_2$ ), 1.43, 1.24 (s, 36H,  $t$ -Bu) ppm.  $^{11}\text{B}$  NMR (64 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 18.5 ( $h_{1/2}$  = 680 Hz), 1.4 ( $h_{1/2}$  = 610 Hz) ppm. MS (20 eV, EI):  $m/z$  (%) = 560 (100) [M -  $\text{C}_3\text{H}_6$ ], 545 (4) [M -  $t$ -Bu], 506 (26), 489 (7), 446 (9), 273 (15), 260 (85), 247 (32), 232 (16), 230 (10), 219 (10), 204 (12), 190 (16). Anal. Calcd for  $\text{C}_{33}\text{H}_{49}\text{B}_3\text{N}_2\text{O}_6$  ( $M_r$  = 602.43): H, 8.20; N, 4.65. Found: H, 8.58; N, 4.71.

**Acpen{[B-O-B][O<sub>2</sub>BOH]} (3f).** Yield: 92%. Mp: >350 °C. IR (KBr):  $\tilde{\nu}$  = 3351 (br, s, OH), 3047 (m), 2990 (m), 1618 (s, C=N), 1558 (m), 1481 (m), 1399 (s, B-O), 1328 (s), 1266 (m), 1110 (s), 1024 (m), 944 (m), 919 (m), 843 (m), 806 (m), 759 (m), 673 (m), 586 (w), 500 (w), 468 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 7.75 (dd, 2H, H-5), 7.45 (ddd, 2H, H-3), 6.86 (m, 4H, H-2, H-4), 3.90 and 3.80 (AB, 4H,  $\text{NCH}_2$ ), 2.58 (s, 3H, C(Me)=N), 2.24 and 2.04 (AB, 2H,  $\text{CH}_2$ -9) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 170.4 (C=N), 159.0 (C-1), 135.0 (C-3), 129.4 (C-5), 119.4 (C-6), 118.4 (C-2), 118.1 (C-4), 45.9 ( $\text{NCH}_2$ ), 21.9 (C-9), 16.5 (C-(Me)=N) ppm.  $^{11}\text{B}$  NMR (64 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.0 ( $h_{1/2}$  = 540 Hz), 1.90 ( $h_{1/2}$  = 330 Hz) ppm. MS (20 eV, EI):  $m/z$  (%) = 344 (23), 329 (18), 318 (36), 303 (27), 199 (100), 185 (70). Anal. Calcd for  $\text{C}_{19}\text{H}_{21}\text{B}_3\text{N}_2\text{O}_6$  ( $M_r$  = 405.82): H, 5.22; N, 6.90. Found: H, 5.28; N, 7.05.

**Salphen{[B-O-B][O<sub>2</sub>BOH]} (3g).** Yield: 77%. Mp: >350 °C. IR (KBr):  $\tilde{\nu}$  = 3339 (br, m, OH), 3058 (m), 1627 (s, C=N), 1556 (m), 1481 (m), 1454 (m), 1408 (m, B-O), 1371 (m), 1312 (m), 1220 (m), 1192 (m), 1161 (m), 1118 (m), 1021 (m), 953 (m), 916 (m), 875 (m), 810 (m), 764 (m), 684 (m), 572 (m), 472 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 8.66 (s, 2H, C(H)=N), 7.61 (m, 8H, m, H-3, H-5, H-9, H-10), 6.94 (m, 4H, H-2, H-4) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 164.9 (C=N), 159.7 (C-1), 138.8, 138.2 (C-3, C-8), 133.3 (C-5), 130.0 (C-10), 126.2 (C-9), 118.9 (C-2), 118.6 (C-4), 116.1 (C-1) ppm.  $^{11}\text{B}$  NMR (128 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 20.6 ( $h_{1/2}$  = 260 Hz), 3.0 ( $h_{1/2}$  = 450 Hz) ppm. MS (20 eV, EI):  $m/z$  (%) = 328 (24), 326 (5), 235 (3), 221 (10). Anal. Calcd for  $\text{C}_{20}\text{H}_{15}\text{B}_3\text{N}_2\text{O}_6$  ( $M_r$  = 411.79): H, 3.64; N, 6.80. Found: H, 3.79; N, 7.05.

**Preparation of the Salen{[B-O-B][O<sub>2</sub>BPh]} Complexes.** Compounds **4a-g** have been prepared by similar methods; there-

fore, the experimental procedure of the preparation is only described in detail for the first case.

**Salen{[B–O–B][O<sub>2</sub>BPh]} (4a).** For the preparation of compound **4a** a mixture of 1 equiv of ligand **1a** (1.00 g, 3.73 mmol) and 2 equiv of boric acid (0.46 g, 7.46 mmol) was refluxed in 15 mL of acetonitrile until a yellow precipitate formed. Then 1 equiv of phenylboronic acid (0.46 g, 3.73 mmol) was added and the mixture was refluxed for 4 h using a Dean–Stark trap. The solid was collected by filtration and dried. Recrystallization from DMF gave crystals suitable for X-ray crystallography. Yield: 88%. Mp: 290–293 °C. IR (KBr):  $\tilde{\nu}$  = 3058 (w), 2930 (w), 1651(s, C=N), 1559 (w), 1478 (w), 1443 (w), 1359 (m), 1299 (m), 1232 (w), 1116 (s), 1047 (m), 973 (m), 854 (w), 800 (w), 766 (m), 698 (w), 610 (w), 466 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 8.70 (s, 2H, C(H)=N), 7.58 (m, 6H, m, H-3, H-5, *o*-BPh), 7.29 (d, 1H, *p*-BPh), 7.19 (dd, 2H, *m*-BPh), 6.98 (m, 4H, H-2, H-4), 4.01 and 4.11 (2H, ABCD, NCH<sub>2</sub>, NCH<sub>2</sub>) ppm. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 163.3 (C=N), 162.3 (*i*-BPh), 159.4 (C-1), 136.8 (C-3), 134.2 (*o*-BPh), 132.0 (C-5), 129.8 (*p*-BPh), 127.1 (*m*-BPh), 118.7 (C-2), 118.6 (C-4), 116.3 (C-6), 54.7 (NCH<sub>2</sub>) ppm. <sup>11</sup>B NMR (64 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 19.9 (*h*<sub>1/2</sub> = 380 Hz), 1.4 (*h*<sub>1/2</sub> = 190 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 424 (54) [M], 395 (12), 380 (11), 347 (95) [M – Ph], 319 (26), 303 (72), 277 (45), 249 (14), 200 (10), 174 (100), 152 (87), 132 (33). Anal. Calcd for C<sub>22</sub>H<sub>19</sub>B<sub>3</sub>N<sub>2</sub>O<sub>5</sub> (*M<sub>r</sub>* = 424.07): H, 4.51; N, 6.60. Found: H, 4.72; N, 6.71.

**SalentBu{[B–O–B][O<sub>2</sub>BPh]} (4b).** Yield: 62%. Mp: 310–312 °C. IR (KBr):  $\tilde{\nu}$  = 2958 (m), 2869 (w), 1643 (s, C=N), 1564 (m), 1515 (w), 1445 (m), 1364 (m), 1304 (m), 1258 (w), 1186 (w), 1136 (m), 1050 (m), 975 (w), 827 (w), 774 (w), 706 (w), 669 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.03 (s, 2H, C(H)=N), 7.75 (d, 2H, *o*-BPh), 7.58, 7.07 (d, 4H, H-3, H-5), 7.18 (dd, 3H, *m*-BPh, *p*-BPh), 4.18 and 3.91 (ABCD, 4H, NCH<sub>2</sub>, NCH<sub>2</sub>), 1.46, 1.28 (s, 36H, <sup>t</sup>Bu) ppm. <sup>11</sup>B NMR (64 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 20.5 (*h*<sub>1/2</sub> = 370 Hz), 1.4 (*h*<sub>1/2</sub> = 40 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 648 (1) [M], 604 (10), 546 (2), 529 (11), 501 (7), 460 (27), 446 (6), 346 (43), 264 (43). Anal. Calcd for C<sub>38</sub>H<sub>51</sub>B<sub>3</sub>N<sub>2</sub>O<sub>5</sub> (*M<sub>r</sub>* = 648.51): H, 7.92; N, 4.31. Found: H, 8.56; N, 4.33.

**Acen{[B–O–B][O<sub>2</sub>BPh]} (4c).** Yield: 62%. Mp: 314–316 °C. IR (KBr):  $\tilde{\nu}$  = 3068 (w), 1617 (s, C=N), 1555 (m), 1485 (m), 1445 (m), 1324 (s), 1118 (s), 1050 (m), 983 (m), 882 (m), 842 (m), 763 (m), 711 (m), 669 (m), 572 (m) cm<sup>-1</sup>. MS (70 eV, EI): *m/z* (%) = 452 (28) [M], 409 (22), 375 (12) [M – Ph], 345 (3), 331 (100), 305 (20), 292 (25). Anal. Calcd for C<sub>24</sub>H<sub>23</sub>B<sub>3</sub>N<sub>2</sub>O<sub>5</sub> (*M<sub>r</sub>* = 452.13): H, 5.13; N, 6.19. Found: H, 5.09; N, 6.36.

**Salpen{[B–O–B][O<sub>2</sub>BPh]} (4d).** Yield: 85%. Mp: >310 °C. IR (KBr):  $\tilde{\nu}$  = 3058 (w), 1626 (s, C=N), 1555 (s), 1482 (m), 1453 (m), 1409 (m), 1370 (m), 1312 (m), 1191 (w), 1161 (m), 1117 (s), 1021 (w), 953 (w), 916 (w), 868 (w), 808 (m), 766 (m), 685 (w), 572 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 8.54 (s, 2H, C(H)=N), 7.55 (dd, 2H, *o*-BPh), 7.12 (m, 5H, H-3, *m*-BPh, *p*-BPh), 7.04 (dd, 2H, H-5), 6.48 (dd, 2H, H-4), 6.35 (d, 2H, H-2), 3.49 and 3.36 (AB, 4H, NCH<sub>2</sub>), 2.20 (m, 2H, H-9) ppm. <sup>11</sup>B NMR (96 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 20.1 (*h*<sub>1/2</sub> = 830 Hz), 1.0 (*h*<sub>1/2</sub> = 50 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 438 (1) [M], 395 (100) [M – C<sub>3</sub>H<sub>7</sub>], 394 (45), 336 (1), 319 (6), 291 (59), 248 (5), 235 (6), 188 (9), 159 (42). Anal. Calcd for C<sub>23</sub>H<sub>21</sub>B<sub>3</sub>N<sub>2</sub>O<sub>5</sub> (*M<sub>r</sub>* = 438.10): H, 4.82; N, 6.39. Found: H, 5.16; N, 6.28.

**Salpen<sup>t</sup>Bu{[B–O–B][O<sub>2</sub>BPh]} (4e).** Yield: 72%. IR (KBr):  $\tilde{\nu}$  = 2961 (w), 1641 (s, C=N), 1438 (s), 1389 (s), 1365 (s), 1168 (w), 1102 (m), 912 (w), 863 (w), 813 (w), 745 (w), 703 (w), 607 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 8.02 (s, 2H, C(H)=N), 7.68 (m, 2H, *o*-BPh), 7.50 (d, 2H, H-3), 7.41 (m, 3H,

*m*-BPh, *p*-BPh), 7.02 (d, 2H, H-5), 4.15 and 3.61 (AB, 4H, NCH<sub>2</sub>), 1.44, 1.27 (s, 36H, <sup>t</sup>Bu) ppm. <sup>11</sup>B NMR (64 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 19.4 (*h*<sub>1/2</sub> = 250 Hz), 1.1 (*h*<sub>1/2</sub> = 390 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 662 (2) [M], 647 (1), 618 (1), 585 (1) [M – Ph], 543 (3), 460 (55), 446 (29), 404 (8), 306 (21), 264 (9), 216 (13). Anal. Calcd for C<sub>39</sub>H<sub>53</sub>B<sub>3</sub>N<sub>2</sub>O<sub>5</sub> (*M<sub>r</sub>* = 662.53): H, 8.06; N, 4.22. Found: H, 8.33; N, 3.73.

**Acpen{[B–O–B][O<sub>2</sub>BPh]} (4f).** Yield: 78%. Mp: >350 °C. IR (KBr):  $\tilde{\nu}$  = 3070 (w), 2927 (w), 1619 (s, C=N), 1556 (m), 1486 (m), 1443 (m), 1336 (s), 1277 (m), 1168 (s), 1121 (s), 978 (m), 886 (w), 838 (w), 759 (m), 712 (m), 669 (m), 608 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 7.78, 7.69 (d, 4H, H-5, *o*-BPh), 7.46 (dd, 2H, H-3), 7.37 (dd, 1H, *p*-BPh), 7.28 (dd, 2H, *m*-BPh), 6.88 (m, 4H, H-2, H-4), 3.96 and 3.84 (AB, 4H, NCH<sub>2</sub>), 2.60 (6H, s, C(Me)=N), 2.33 and 1.97 (AB, 2H, H-9) ppm. <sup>11</sup>B NMR (96 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 19.5 (*h*<sub>1/2</sub> = 370 Hz), 1.0 (*h*<sub>1/2</sub> = 100 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 466 (29) [M], 389 (5) [M – Ph], 344 (77) [M – C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub>], 329 (40), 318 (85), 308 (1), 303 (61), 248 (27), 221 (23), 77 (100). Anal. Calcd for C<sub>25</sub>H<sub>25</sub>B<sub>3</sub>N<sub>2</sub>O<sub>5</sub> (*M<sub>r</sub>* = 466.15): H, 5.40; N, 6.00. Found: H, 5.49; N, 6.25.

**Salphen{[B–O–B][O<sub>2</sub>BPh]} (4g).** Yield: 31%. Mp: 316–318 °C. IR (KBr):  $\tilde{\nu}$  = 3059 (m), 2924 (w), 1625 (s, C=N), 1554 (s), 1481 (m), 1452 (m), 1369 (s), 1312 (s), 1114 (s), 1021 (m), 953 (m), 916 (w), 865 (w), 809 (m), 765 (m), 684 (w), 570 (w), 459 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 8.64 (s, 2H, C(H)=N), 7.60 (m, 10H, H-3, H-5, H-9, H-10, *o*-BPh), 6.94 (m, 7H, H-2, H-4, *m*-BPh, *p*-BPh) ppm. <sup>11</sup>B NMR (64 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 20.5 (*h*<sub>1/2</sub> = 720 Hz), 2.4 (*h*<sub>1/2</sub> = 410 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 472 (2) [M], 429 (10), 402 (11), 353 (25) [M – C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub>], 325 (63), 312 (37), 296 (60), 260 (24), 221 (100). Anal. Calcd for C<sub>26</sub>H<sub>19</sub>B<sub>3</sub>N<sub>2</sub>O<sub>5</sub> (*M<sub>r</sub>* = 472.12): H, 4.05; N, 5.93. Found: H, 3.92; N, 7.02.

**Preparation of Compound 5.** Crystals of compound **5** were obtained during attempts to crystallize acphen{[B–O–B][O<sub>2</sub>BOH]} from acetonitrile. IR (KBr):  $\tilde{\nu}$  = 3480 (m), 3434 (m), 3365 (m), 1614 (s, C=N), 1556 (m), 1483 (s), 1442 (s), 1389 (s, B–O), 1271 (m), 1208 (m), 1071 (m), 992 (m), 947 (m), 848 (m), 759 (m), 706 (m), 698 (m), 608 (w), 543 (w), 474 (w). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 7.86 (d, 2H, H-5), 7.61 (dd, 2H, H-3), 7.06–6.85 (m, 10H, H-2, H-9, H-10, H-11, H-12), 6.66 (dd, 2H, H-4), 4.90 (br, s, 4H, NH<sub>2</sub>), 2.35 (s, 6H, C(Me)=N) ppm.

**Preparation of Salen{[B–O–B][O<sub>2</sub>P(O)Ph]} (6a).** Compound **6a** was prepared from 1 equiv of ligand **1a** (1.00 g, 7.46 mmol) and 2 equiv of boric acid (0.92 g, 14.92 mmol) in 15 mL of acetonitrile. The mixture was refluxed for 4 h using a Dean–Stark trap, whereupon 1 equiv of phenylphosphonic acid (1.17 g, 7.46 mmol) was added. The yellow precipitate of **6a** that was formed after 8 h of reflux was collected by filtration and dried. Yield: 92%. Mp: 289–292 °C. IR (KBr):  $\tilde{\nu}$  = 3057 (w), 1640 (s, C=N), 1561 (m), 1479 (m), 1447 (m), 1356 (m), 1304 (w), 1236 (m), 1198 (s), 1142 (s), 985 (m), 944 (m), 820 (w), 752 (m), 705 (w), 590 (w), 538 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 8.81 (s, 2H, C(H)=N), 7.76 (ddd, 2H, <sup>3</sup>J<sub>H–P</sub> = 14 Hz, *o*-PPh), 7.62 (dd, 2H, H-5), 7.56 (ddd, 2H, H-3), 7.51 (d, 1H, *p*-PPh), 7.46 (m, 2H, *m*-PPh), 6.98 (dd, 2H, H-4), 6.91 (d, 2H, H-2), 4.40 and 4.13 (ABCD, 4H, NCH<sub>2</sub>, NCH<sub>2</sub>) ppm. <sup>11</sup>B NMR (128 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.0 (*h*<sub>1/2</sub> = 320 Hz). <sup>31</sup>P NMR (81 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 5.51 ppm. MS (FAB<sup>+</sup>): *m/z* (%) = 460 (4) [M], 307 (20), 289 (11), 154 (100), 136 (71), 107 (20), 77 (18). Anal. Calcd for C<sub>22</sub>H<sub>19</sub>B<sub>2</sub>N<sub>2</sub>O<sub>6</sub>P (*M<sub>r</sub>* = 460.00): H, 4.16; N, 6.08. Found: H, 4.85; N, 6.92.

**X-ray Crystallography.** X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector

( $\lambda_{\text{MoK}\alpha} = 0.71073 \text{ \AA}$ ; monochromator, graphite). Frames were collected at  $T = 293 \text{ K}$  (compound **3a**) and  $T = 100 \text{ K}$  (compounds **4a** and **5**) via  $\omega$ - and  $\phi$ -rotation at  $10 \text{ s/frame}$  (SMART).<sup>10a</sup> The measured intensities were reduced to  $F^2$  and corrected for absorption with SADABS (SAINT-NT).<sup>10b</sup> Corrections were made for Lorentz and polarization effects. Structure solution, refinement, and data output were carried out with the SHELXTL-NT program package.<sup>10c,d</sup> Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. All O–H and N–H hydrogen atoms have been localized by difference Fourier maps. Solvent molecules are present in each of the crystal lattices (acetone for **3a**, DMF for **4a**, and acetonitrile for **5**). Half of the acetonitrile molecules in the crystal lattice of **5** are located on crystallographic  $C_2$ -symmetry axes. A reflections-to-parameter ratio of 5:1 has been considered sufficient for the studies performed herein. Molecular structures were illustrated by the SHELXTL-NT software package.<sup>10c,d</sup> Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-247664–247666. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk; www, http://www.ccdc.cam.ac.uk).

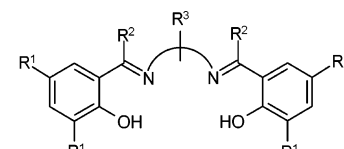
**Theoretical Calculations.** HF/6-31G(d,p) geometry optimizations were done on a PC with a Pentium III processor using the PC GAMESS software.<sup>11</sup> Structures were visualized with Molekel 4.3<sup>12</sup> and Mercury 1.1.2.<sup>13</sup> All geometry optimizations were followed by frequency calculations, using the same basis set, to characterize the stationary points as true minima.

### 3. Results and Discussion

**3.1. Preparation and Characterization of Homodi- and Homotrimeric Salen-Derived Boron Complexes.** Two different synthetic methods have been reported for the preparation of the trinuclear boron complexes **III** shown in Chart 1. The first method consists of the transformation of a dinuclear boroxane **II** with phenylboronic acid to the trinuclear derivative under elimination of benzene and requires 12 h of reflux in acetonitrile. The second method starts from the intermediate formed between the ligand and 2 equiv of boric acid, to which after 4–5 h phenylboronic acid is added without isolation of the dinuclear intermediate.<sup>5b</sup>

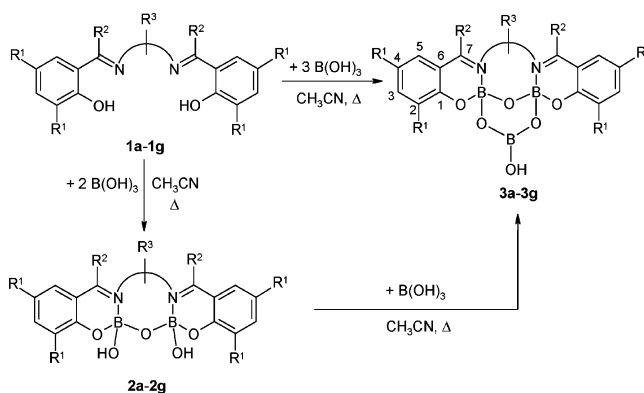
One aim of this study was to optimize the reaction conditions and to obtain information on the reaction mechanism. To reach this goal, the ligands were first reacted with

**Chart 2.** Salen Ligands Used for the Reactions Described in This Contribution



Ligand	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Name
<b>1a</b>	H	H	(CH <sub>2</sub> ) <sub>2</sub>	salen
<b>1b</b>	<sup>t</sup> Bu	H	(CH <sub>2</sub> ) <sub>2</sub>	salen( <sup>t</sup> Bu)
<b>1c</b>	H	Me	(CH <sub>2</sub> ) <sub>2</sub>	acen
<b>1d</b>	H	H	(CH <sub>2</sub> ) <sub>3</sub>	salpen
<b>1e</b>	<sup>t</sup> Bu	H	(CH <sub>2</sub> ) <sub>3</sub>	salpen( <sup>t</sup> Bu)
<b>1f</b>	H	Me	(CH <sub>2</sub> ) <sub>3</sub>	acpen
<b>1g</b>	H	H	1,2-C <sub>6</sub> H <sub>4</sub>	salphen
<b>1h</b>	<sup>t</sup> Bu	H	1,2-C <sub>6</sub> H <sub>4</sub>	salphen( <sup>t</sup> Bu)
<b>1i</b>	H	Me	1,2-C <sub>6</sub> H <sub>4</sub>	acphen
<b>1j</b>	H	H	<i>trans</i> -1,2-C <sub>6</sub> H <sub>10</sub>	salcen
<b>1k</b>	<sup>t</sup> Bu	H	<i>trans</i> -1,2-C <sub>6</sub> H <sub>10</sub>	salcen( <sup>t</sup> Bu)
<b>1l</b>	H	Me	<i>trans</i> -1,2-C <sub>6</sub> H <sub>10</sub>	accen

**Scheme 1.** Preparation of the Dinuclear and Trinuclear Complexes **2a–g** and **3a–g** Using Ligands **1a–g** and Boric Acid as Starting Materials



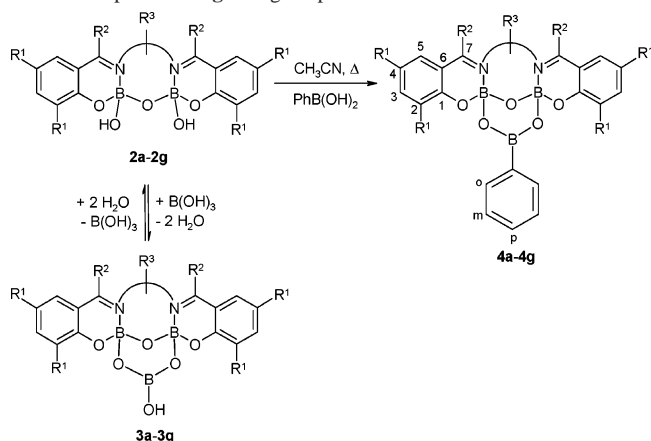
2 and then with 3 equiv of boric acid. A total of 12 known ligands **1a–l** have been used for this purpose to study also the influence of the substituents on the synthetic process and the structure of the products (Chart 2).

Interestingly, using acetonitrile as solvent the dinuclear boron complexes **2** could be isolated only in two cases, namely with salen(<sup>t</sup>Bu) (**1b**) and salphen (**1g**). With salen, acen, salpen, salpen(<sup>t</sup>Bu), and acpen precipitation of the trinuclear species **3a,c,d–f** occurred in yields ranging from 30 to 32% (Scheme 1). In contrast, with salphen(<sup>t</sup>Bu), acphen, salcen, salcen(<sup>t</sup>Bu), and accen only unseparable product mixtures were obtained that contained the trinuclear compounds, which have been identified by mass spectrometry, and oligo- or polymeric species, which have not been further characterized. As expected, the yields of the trinuclear metaboric acid esters **3a–g** could be increased significantly, when 3 instead of 2 equiv of boric acid were added to the initial reaction mixture (64–98% for **3a–g**).

As indicated in Scheme 2 the reaction between the di- and trinuclear boron complexes is apparently reversible. This conclusion can be drawn from the observation that the di- and trinuclear boric acid esters could be transformed in all cases to the trinuclear phenylboroxin derivatives **4a–g** in yields ranging from 31 to 88%, adding after 4 h 1 equiv of

- (10) (a) SMART: Bruker Molecular Analysis Research Tool, versions 5.057 and 5.618; Bruker Analytical X-ray Systems: Madison, WI, 1997, 2000. (b) SAINT + NT, versions 6.01 and 6.04; Bruker Analytical X-ray Systems: Madison, WI, 1999, 2001. (c) Sheldrick, G. M. SHELX86, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1986. (d) SHELXTL-NT, versions 5.10 and 6.10; Bruker Analytical X-ray Systems: Madison, WI, 1999, 2000.
- (11) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
- (12) (a) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *Molekel 4.3*; Swiss Center for Scientific Computing: Manno, Switzerland, 2000–2002. (b) Portmann, S.; Lüthi, H. P. Molekel: An interactive molecular graphics tool. *Chimia* **2000**, *54*, 766.
- (13) Mercury, version 1.1.2; Cambridge Crystallographic Data Center: Cambridge, U.K., 2002.

**Scheme 2.** Transformation of the Trinuclear B–OH Derivatives **3a–g** to the B–Ph Derivatives **4a–g** with an Equilibrium for the Dinuclear Species **2a–g** Being Proposed



phenylboronic acid to the initial 1:2 mixtures of ligand and boric acid.

The air-stable products **2b,g**, **3a–g**, and **4a–g** have been characterized as far as possible by elemental analysis, mass spectrometry, spectroscopic methods (IR,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR), and X-ray crystallography. Most of the products have low solubility in common organic solvents and have relatively high melting points ( $>290\text{ }^\circ\text{C}$ ).

The IR spectra for compounds **2b,g**, **3a–g**, and **4a–g** show that the absorptions that can be attributed to the  $\nu_{\text{C}=\text{N}}$  stretching vibrations ( $\tilde{\nu} = 1618\text{--}1651\text{ cm}^{-1}$ ) are shifted to higher wavenumbers compared to the free ligands ( $\Delta\tilde{\nu} = 4\text{--}22\text{ cm}^{-1}$ ).

The most conclusive evidence that molecules with a complex system of three (**2b,g**) and four boron-containing heterocyclic rings (**3a–g** and **4a–g**) have formed is provided by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy. The coordination of the nitrogen to the boron atoms and the simultaneous formation of a B–O–B bridge makes the boron atoms chiral, thus generating a diastereotopic environment for the methylene groups in **3a–f** and **4a–f**, which form part of the central heterocyclic ring. For the dinuclear derivatives **2b,g** only signals typical for tetracoordinate boron atoms are detected in the  $^{11}\text{B}$  NMR spectra,<sup>14</sup>  $\delta = 5.0\text{ ppm}$  for **2b** and  $\delta = 3.6\text{ ppm}$  for **2g**. For the trinuclear complexes **3a–g** and **4a–g** this signal is slightly high-field-shifted ( $\delta = 1\text{--}3\text{ ppm}$ ) and accompanied by a less intense signal typical for a three-coordinate boron atom ( $\delta = 18\text{--}21\text{ ppm}$ ).<sup>14</sup>

For each of the two series of trinuclear complexes one representative member could be crystallized (**3a** and **4a**), so that accurate geometric data are available. Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 1. Selected bond lengths, bond angles, and torsion angles are listed in Table 2. The crystal structure of **4c** has already been reported,<sup>5b</sup> and selected geometric parameters of this molecule have been included in Table 2 for comparison. Figure 1 shows the molecular structures for compounds **3a** and **4a**.

As can be seen from Figure 1, the molecular structures of compounds **3a** and **4a** contain a central six-membered  $\text{B}_3\text{O}_3$  ring, in which two of the three boron atoms have tetrahedral and one has a trigonal planar coordination environment. Apparently, the salen ligand has the perfect bite to coordinate to the  $\text{B}_3\text{O}_3$  moiety through the formation of two chelate rings, thus forming an additional seven-membered  $\text{B}_2\text{C}_2\text{N}_2\text{O}$  heterocycle. These heterocycles possess twisted-chair conformations. The  $\text{B}_3\text{O}_3$  rings are not completely planar but have an envelope conformation, since the oxygen O3 atoms are slightly deviated from the mean planes of the remaining five atoms (0.36 Å for **3a** and 0.35 Å for **4a**). The O4 and O5 oxygen atoms have cis-configuration with respect to the tetrahedral boron atoms. It has been demonstrated earlier for salen[B(R)–O–B(R)] complexes (type **II** in Chart 1) that cis-configured derivatives are thermodynamically more stable than trans-configured derivatives.<sup>5</sup>

Complexes **3a–g** may be considered as neutral derivatives of the tetraborate dianion  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  found in Borax, in which one of the two rings in the bicycle is closed by a N–(C)<sub>n</sub>–N ( $n = 2, 3$ ) instead of a O–B(OH)–O bridge (Figure 1, Chart 3).

The N→B bond lengths in **3a** and **4a** range from 1.597(6) to 1.625(3) Å and are therefore among the strongest N→B bonds known.<sup>15</sup> Generally, in tetrahedral boron coordination environments B–O<sub>ph</sub> bonds are significantly longer than B–O<sub>B</sub> bonds.<sup>5,16</sup> Although the experimental values for **3a** and **4a,c** range from 1.458(6) to 1.474(3) Å for B–O<sub>ph</sub> and 1.403(3) to 1.420(6) Å for B–O<sub>B</sub>, the B1–O4 and B2–O5 bond lengths do not follow this trend: 1.449(6)–1.458(3) Å.

As expected, B–O bonds with three-coordinate boron atoms have  $p_\pi\text{--}p_\pi$  contributions and are therefore much shorter than the B–O bond lengths discussed above for the tetrahedral boron atoms. The corresponding values for B3–O4 and B3–O5 in **3a** and **4a,c** range from 1.352(6) to 1.370(3) Å. The same is true for the B–C bond lengths: 1.564(3)–1.567(4) Å for **4a** and **4c** compared to 1.596(4)–1.627(6) Å for **II** (Chart 1).<sup>5</sup> The  $p_\pi\text{--}C_\pi$  interaction can be also evidenced by the O–B–C–C torsion angles of 9.4(3) and 11.5(4)° for **4a,c**, respectively, since otherwise an almost perpendicular orientation would be expected. An interesting result for the homotrinnuclear boron complexes containing  $\text{B}_3\text{O}_3$  moieties is that the B–O–B bond angles formed between the tetrahedral boron atoms are much smaller than the ones found in complexes of type **II**, 119.2(2)–120.3(2)° for **3a** and **4a,c** compared to 128.6(2)–137.8(5)° for **II**.

To obtain more detailed structural information on the compounds that could not be prepared in pure form or crystallized, we optimized the molecular structures of complexes **3a,d,g,j** and **4a,d,g,j** by computational methods

(15) Höpfl, H. *Struct. Bonding* **2002**, *103*, 1.

(16) (a) Höpfl, H.; Sánchez, M.; Barba, V.; Farfán, N.; Rojas, S.; Santillan, R. *Inorg. Chem.* **1998**, *37*, 1679. (b) Norman, D. W.; Edwards, J. P.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Can. J. Chem.* **2002**, *80*, 31. (c) Yalcin, N.; Kenar, A.; Arici, C.; Atakol, O.; Tastekin, M. *Main Group Met. Chem.* **2001**, *24*, 247.

(14) Nöth, H.; Wrackmeyer, B. *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978; Vol. 14.

**Table 1.** Crystallographic Data for Compounds **3a**, **4a**, and **5**

	<b>3a</b>	<b>4a</b>	<b>5</b>
Crystal Data			
formula	C <sub>16</sub> H <sub>15</sub> B <sub>3</sub> N <sub>2</sub> O <sub>6</sub> ·CH <sub>3</sub> C(O)CH <sub>3</sub>	C <sub>22</sub> H <sub>19</sub> B <sub>3</sub> N <sub>2</sub> O <sub>5</sub> ·DMF	C <sub>28</sub> H <sub>27</sub> B <sub>3</sub> N <sub>4</sub> O <sub>6</sub> ·1.5CH <sub>3</sub> CN
cryst size (mm <sup>3</sup> )	0.02 × 0.18 × 0.31	0.19 × 0.25 × 0.27	0.19 × 0.21 × 0.27
fw	421.81	496.92	609.55
space group	C2/c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	C2/c
Cell Parameters			
<i>a</i> (Å)	25.148(3)	9.9136(12)	19.790(3)
<i>b</i> (Å)	12.005(2)	10.1719(12)	14.437(2)
<i>c</i> (Å)	13.546(2)	23.553(3)	22.334(3)
β (deg)	99.232(3)	90	109.441(2)
<i>V</i> (Å <sup>3</sup> )	4036.7(10)	2375.1(5)	6017.2(14)
<i>Z</i>	8	4	8
μ (mm <sup>-1</sup> )	0.103	0.097	0.093
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.388	1.390	1.346
Data Collection			
θ limits (deg)	2 < θ < 23	2 < θ < 25	2 < θ < 23
<i>hkl</i> limits	-27, 27; -13, 13; -14, 14	-11, 11; -11, 11; -28, 28	-21, 21; -15, 15; -24, 24
no. of colld reflns	16 058	16 668	18 103
no. of indep reflns ( <i>R</i> <sub>int</sub> )	2815 (0.100)	4127 (0.039)	4204 (0.048)
no. of obsd reflns <sup>a</sup>	1834	3965	3827
Refinement			
<i>R</i> <sup>a,b</sup>	0.080	0.040	0.091
<i>R</i> <sub>w</sub> <sup>c,d</sup>	0.185	0.085	0.181
no. of variables	283	337	432
GOF	1.081	1.18	1.29
Δρ <sub>min</sub> (e Å <sup>-3</sup> )	-0.22	-0.15	-0.29
Δρ <sub>max</sub> (e Å <sup>-3</sup> )	0.24	0.20	0.77

<sup>a</sup>  $I > 2\sigma(I)$  <sup>b</sup>  $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$ . <sup>c</sup> All data. <sup>d</sup>  $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ .

using the HF/6-31G(d,p) basis set. In previous studies it has been shown that this basis set is adequate for the calculation of boron compounds having a coordinative N→B bond.<sup>17</sup> Selected geometric parameters for the calculated compounds are listed in Table 2, and the calculated molecular structures for **4a**, **d**, **g**, **j** are shown in Figure 2.<sup>18</sup>

In the case of complexes **3a** and **4a** the quality of the computational results could be evaluated by a comparison with the experimentally determined values, which showed a reasonably good agreement with respect to the bond lengths and bond angles. In the case of the bond lengths major differences are only observed for the N→B bonds (1.689/1.695 ↔ 1.597(6)/1.612(7) Å for **3a** and 1.678/1.690 ↔ 1.620(3)/1.625(3) Å for **4a**); however, similar differences have been observed for other boron complexes containing a coordinate-covalent N→B bond and have been attributed to the fact that the calculated molecular structures correspond to molecules in the gasphase.<sup>17</sup> Smaller differences occur for the B–O bonds formed between the tetrahedral and trigonal planar boron atoms (1.420/1.421 ↔ 1.449(6)/1.458(6) Å for **3a** and 1.424/1.425 ↔ 1.453(3)/1.458(3) Å for **4a**) and the C<sub>Ph</sub>–O bonds (1.299/1.299 ↔ 1.332(5)/1.342(5) Å for **3a** and 1.293/1.301 ↔ 1.332(3)/1.343(3) Å for **4a**). In the case of the bond angles, for **3a** the largest deviations are observed for the O1–B1–N1, O1–B1–O3,

O2–B2–O3, O3–B1–N1, O3–B2–N2, B1–O1–C1, and B2–O2–C17 angles with differences of -3.4, +4.3, +3.8, -4.9, -4.6, +4.5, and +6.2° (mean values). For **4a** the largest deviations correspond to the O1–B1–O3, O3–B1–N1, B1–O1–C1, B2–O2–C17, and N2–C10–C9 angles with differences of +4.1, -4.7, +5.1, +9.2, and +4.6° (mean values), respectively. Interestingly, although the overall conformations of the six- and seven-membered heterocyclic rings do not change, there are larger variations for the torsion angles (Table 2 and Supporting Information); therefore, it can be supposed that the conformations of the seven- and eight-membered heterocyclic rings present some flexibility, which allows for an accommodation according to attractive or repulsive intermolecular interactions in the solid state that are absent in the calculated gaseous phase.

In a comparison of the calculated geometric parameters within the two series of homotrinary boron complexes **3a**, **d**, **g**, **j** and **4a**, **d**, **g**, **j** in Table 2, only very small differences are observed for the B–OH/B–Ph pairs of molecules **3a/4a**, **3d/4d**, **3j/4j**, and **3g/4g**. Somewhat larger variations are only observed for that part of the torsion angles that describe the conformation of the six-membered BC<sub>3</sub>NO heterocycles in the pair **3a/4a**, thus proving that there is some conformational flexibility in the system. The N→B bond lengths are shortest for complexes **3a** and **4a** (1.678–1.695 Å) and longest for complexes **3d** (1.714 and 1.721 Å) and **3g** (1.732 and 1.738 Å). The variations in the bond angles are small, with exception of those affected by the presence of substituents in the N–C<sub>n</sub>–N bridge (see Supporting Information). One further exception are the B1–O1–C1 and B2–O2–C17 bond angles, whose values range from 121.9 to 129.9°. A comparison of the torsion angles describing the conforma-

(17) (a) Howard, S. T.; Foreman, J. P.; Edwards, P. G. *Can. J. Chem.* **1997**, *75*, 60. (b) Höpfl, H. *J. Mol. Struct. (THEOCHEM)* **1998**, *427*, 1. (c) Rayón, V. M.; Sordo, J. A. *J. Mol. Struct. (THEOCHEM)* **1998**, *426*, 171. (d) Hirao, H.; Omoto, K.; Fujimoto, H. *J. Phys. Chem. A* **1999**, *103*, 5807. (e) Sánchez, M.; Sánchez, O.; Höpfl, H.; Ochoa, M.-E.; Castillo, D.; Farfán, N.; Rojas-Lima, S. *J. Organomet. Chem.* **2004**, *689*, 811.

(18) The molecular structure for compounds **3a**, **d**, **g**, **j** are presented in the Supporting Information.

**Table 2.** Selected Experimental and Calculated Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compound **3a,d,g,j** and **4a,d,g,j**

	<b>3a</b> (exptl)	<b>3a</b> (calcd)	<b>4a</b> (exptl)	<b>4a</b> (calcd)	<b>4c<sup>6b</sup></b> (exptl)	<b>3d</b> (calcd)	<b>4d</b> (calcd)	<b>3g</b> (calcd)	<b>4g</b> (calcd)	<b>3j</b> (calcd)	<b>4j</b> (calcd)	<b>6a</b> (calcd)
Bond Lengths <sup>a</sup>												
B1–N1	1.597(6)	1.695	1.620(3)	1.690	1.603(3)	1.714	1.679	1.732	1.705	1.713	1.714	1.667
B2–N2	1.612(7)	1.689	1.625(3)	1.678	1.624(3)	1.721	1.681	1.738	1.705	1.705	1.705	1.656
B1–O1	1.458(6)	1.455	1.471(3)	1.460	1.468(3)	1.450	1.461	1.470	1.457	1.450	1.451	1.445
B2–O2	1.474(6)	1.458	1.471(3)	1.463	1.474(3)	1.450	1.460	1.468	1.457	1.452	1.453	1.449
B1–O3	1.420(6)	1.395	1.415(3)	1.393	1.418(3)	1.398	1.398	1.388	1.388	1.401	1.396	1.390
B2–O3	1.404(6)	1.394	1.407(3)	1.394	1.403(3)	1.402	1.397	1.389	1.389	1.396	1.395	1.384
B1–O4	1.458(6)	1.420	1.458(3)	1.425	1.458(3)	1.412	1.418	1.430	1.417	1.418	1.423	1.452
B2–O5	1.449(6)	1.421	1.453(3)	1.424	1.451(3)	1.411	1.419	1.421	1.417	1.420	1.418	1.456
B3/P1–O4	1.352(6)	1.351	1.365(3)	1.356	1.354(3)	1.363	1.355	1.373	1.355	1.350	1.355	1.572
B3/P1–O5	1.365(6)	1.364	1.363(3)	1.357	1.370(3)	1.356	1.355	1.357	1.355	1.365	1.358	1.572
B3/P1–O6	1.365(6)	1.360				1.358		1.349		1.360		1.465
B3/P1–C18			1.564(3)	1.580	1.567(4)		1.577		1.579		1.576	1.799
Bond Angles <sup>a</sup>												
O1–B1–N1	109.1(4)	105.7	107.6(2)	105.4	108.2(2)	103.3	104.1	103.8	105.6	105.2	105.2	106.2
O2–B2–N2	106.5(4)	105.6	106.2(2)	105.9	105.5(2)	103.2	104.1	104.3	105.5	105.3	105.0	105.0
O1–B1–O3	108.7(4)	113.0	109.0(2)	113.1	109.0(2)	113.1	112.7	114.4	112.0	113.4	113.6	111.8
O2–B2–O3	109.3(4)	113.1	110.7(2)	111.7	109.5(2)	113.1	112.8	115.0	112.3	113.0	113.4	113.8
O1–B1–O4	110.4(4)	111.1	110.6(2)	111.1	110.4(2)	110.4	110.2	111.5	111.0	111.5	111.0	110.4
O2–B2–O5	109.9(4)	109.5	109.8(2)	110.0	109.5(2)	110.5	110.2	110.5	110.8	109.5	109.6	109.4
O3–B1–O4	113.1(4)	115.2	114.8(2)	115.1	114.2(2)	115.6	115.7	114.9	116.1	114.4	114.6	114.8
O3–B2–O5	114.9(4)	115.7	115.8(2)	115.6	115.6(2)	115.7	115.7	115.4	116.1	115.5	115.7	115.5
O3–B1–N1	110.4(4)	105.5	109.9(2)	105.2	108.1(2)	104.7	106.1	106.9	106.2	104.8	105.2	108.5
O3–B2–N2	109.4(4)	104.8	107.8(2)	106.5	109.2(1)	103.9	106.0	107.0	105.8	104.4	104.3	107.2
N1–B1–O4	105.1(4)	105.5	104.7(2)	106.0	106.7(2)	108.7	107.0	104.1	105.1	106.7	106.3	104.4
N2–B2–O5	106.5(4)	107.5	105.9(2)	106.6	107.0(2)	109.5	107.1	103.2	105.5	108.4	108.1	104.9
B1–O3–B2	120.0(4)	118.9	119.2(2)	119.8	120.3(2)	121.1	122.1	119.3	118.2	118.5	118.1	123.3
B1–O4–B3/P1	120.6(4)	118.8	119.1(2)	119.7	119.6(2)	119.8	121.0	119.4	120.2	119.1	119.3	125.1
B2–O5–B3/P1	120.8(4)	119.4	120.6(2)	120.7	119.7(2)	120.0	121.0	119.4	120.3	119.0	120.1	128.2
O4–B3/P1–O5	121.4(5)	120.7	121.4(2)	120.1	122.1(2)	121.2	120.7	121.7	120.2	120.7	120.2	103.0
B1–O1–C1	123.1(4)	127.6	123.1(2)	128.2	123.0(2)	121.9	122.9	129.6	129.0	126.2	126.1	124.9
B2–O2–C17	120.3(4)	126.5	120.7(2)	129.9	117.7(2)	122.6	123.0	129.3	128.9	125.7	125.2	120.9
Torsion Angles <sup>a</sup>												
B1–N1–C9–C10	64.1(5)	79.6	64.6(2)	77.8	71.2(3)	37.1	86.5	52.8	51.5	84.5	84.1	62.2
B2–N2–C10–C9	45.7(6)	–17.3	45.9(2)	2.8	46.3(3)	–29.7	–87.2	–53.9	–51.5	–23.6	–25.0	48.5
O3–B1–N1–C9	–49.7(5)	–68.9	–48.7(2)	–64.0	–52.1(2)	–93.4	–87.6	–74.2	–72.1	–74.1	–74.4	–45.2
O3–B2–N2–C10	25.7(6)	71.9	28.3(2)	57.5	26.5(3)	92.2	86.9	71.9	72.9	76.7	77.9	23.9
B1–O3–B2–N2	89.1(5)	87.0	92.7(2)	84.1	94.1(2)	84.2	81.4	102.3	95.7	89.6	90.2	–92.1
B2–O3–B1–N1	–80.9(5)	–101.6	–81.4(2)	–98.1	–84.8(3)	–86.0	–80.7	–100.5	–96.1	–102.8	–103.0	81.2
N1–C9–C10–N2	–82.3(6)	–48.4	–84.8(2)	–61.9	–91.1(2)			1.4	–0.3	–45.7	–44.7	–84.5

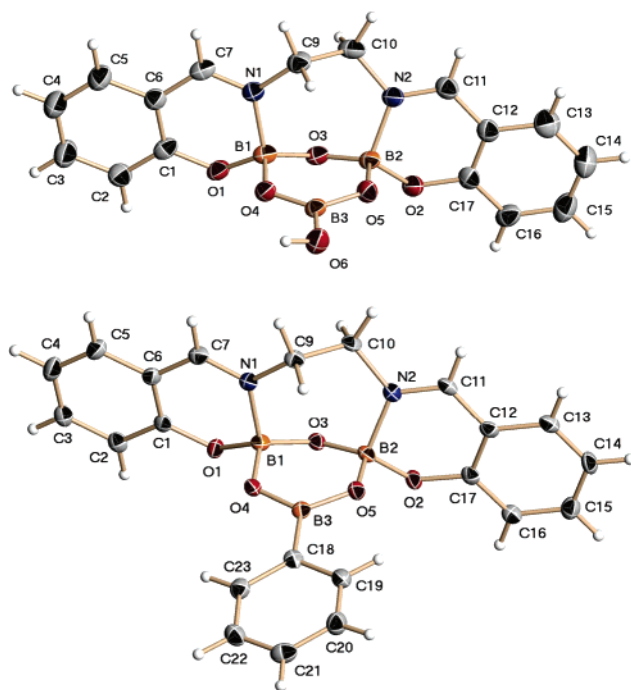
<sup>a</sup> For numeration, please see X-ray structures in Figure 1.

tion of the seven-membered heterocyclic rings in compounds **3a,g,j** and **4a,g,j** shows again that the substituents at the N–C<sub>n</sub>–N bridge have a significant influence. The calculated structures of all complexes with seven-membered heterocyclic rings have chair conformations (Figure 3). However, the distribution of the atoms within the chair is different: in the case of compounds **3a**, **4a**, **3j**, and **4j** the base of the chair is formed by the B1, O3, N2, and C10 atoms, while in compounds **3g** and **4g** it is formed by the nitrogen and boron atoms. An explanation is that the latter are obtained from the more rigid salphen ligand. It should be noticed that the experimentally determined molecular structures of compounds **3a** and **4a** have twisted-chair conformations. As shown by the theoretical calculations, in the case of the eight-membered heterocycles in compounds **3d** and **4d** the central methylene group can have two different orientations, exo or endo, which gives rise to a boat-chair or chair-chair conformation, respectively. It can be expected that there is only a very small energetic difference between these two conformations, so that a conformational equilibrium can be supposed in solution.

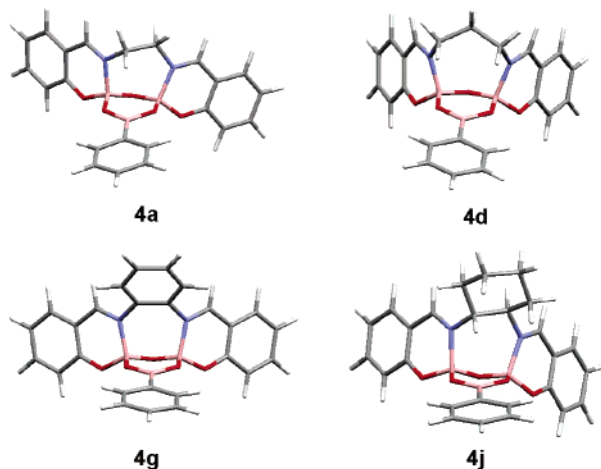
During the attempts to prepare compound **3i** crystals of a decomposition product **5** could be grown that were suitable for X-ray crystallography (Chart 4). Details of the crystal data of **5** and a summary of data collection parameters for this complex are given in Table 1. Selected bond lengths, bond angles, and torsion angles are listed in Table 3. The molecular structure of compound **5** is shown in Figure 4.

This product is a partial ester of trimetaboric acid and has structural features which can be related to complexes **3a–g**. The central part of the molecule consists of an almost planar B<sub>3</sub>O<sub>3</sub> ring, in which two boron atoms have tetrahedral and one boron atom has trigonal planar geometry. The tetrahedral boron atoms are each chelated by a fragment of the initial acphen ligand, which should have formed by partial hydrolysis. Since the coordinated ligands have opposite orientations in relation to the B<sub>3</sub>O<sub>3</sub> ring, approximate C<sub>2</sub>-symmetry can be expected in solution, whereby atoms O1, B3, and O4 are lying on the symmetry axis. Considering that atom B3 may still act as Lewis acid, this type of compound might be useful as a catalyst for asymmetric synthesis.<sup>7</sup>



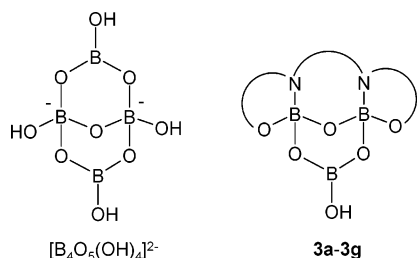


**Figure 1.** Perspective views of the molecular structures of compound **3a** (top) and compound **4a** (bottom). Ellipsoids are shown at the 30% (**3a**) and 50% (**4a**) probability level.

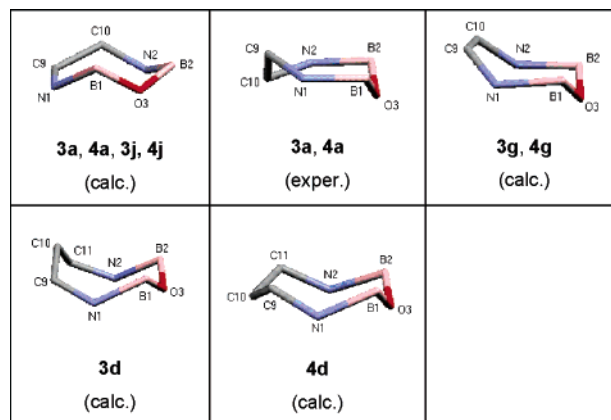


**Figure 2.** Calculated molecular structures of compounds **4a,d,g,j**.

**Chart 3.** Homotrimeric Complexes **3a–g** Considered as Derivatives of the Tetraborate Anion Found in Borax

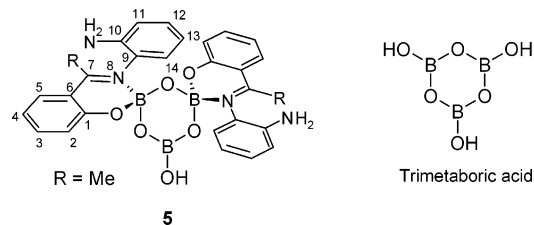


**3.2. Preparation and Characterization of a Heterotrimeric Salen-Derived Boron–Phosphorus Complex.** In the first part of this report it could be shown that it is possible to prepare homotrimeric boron complexes containing either a three-coordinate B–OH (**3a–g**) or B–Ph (**4a–g**) moiety. If this method could be extended to reactions with other



**Figure 3.** Seven-membered heterocycles in complexes **3a.g,j**, and **4a.g,f** possessing chair and twisted-chair conformations. Please note the difference between the calculated and experimental conformation of the heterocycles in **3a** and **4a**, thus indicating conformational flexibility. The eight-membered heterocycles in **3d** and **4d** have boat-chair and chair-chair conformations, respectively.

**Chart 4.** Compound **5** as a Decomposition Product of a Homotrimeric Complex and Considered as Derivative of Trimetaboric Acid

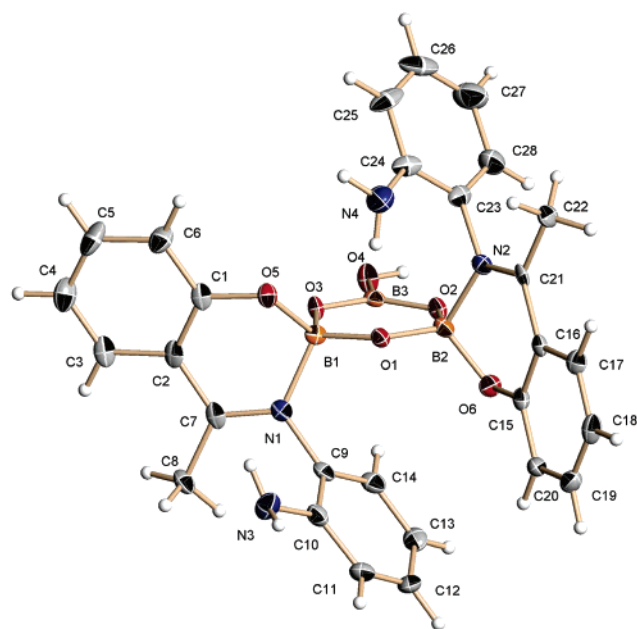


**Table 3.** Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compound **5**

Bond Lengths			
B1–N1	1.624(6)	B1–N2	1.628(6)
B1–O1	1.403(6)	B2–O1	1.424(6)
B1–O3	1.447(6)	B2–O2	1.455(6)
B1–O5	1.466(6)	B2–O6	1.454(6)
B3–O2	1.374(6)	B3–O3	1.344(6)
B3–O4	1.360(6)		
Bond Angles			
O1–B1–N1	111.6(3)	O1–B2–N2	106.0(4)
O3–B1–N1	104.3(3)	O2–B2–N2	108.2(4)
O5–B1–N1	104.7(3)	O6–B2–N2	105.8(4)
O1–B1–O3	115.4(3)	O1–B2–O2	114.8(4)
O1–B1–O5	110.4(4)	O1–B2–O6	113.3(4)
O3–B1–O5	109.7(4)	O2–B2–O6	108.3(4)
O2–B3–O3	121.7(4)	O2–B3–O4	121.6(4)
O3–B3–O4	116.6(4)		
Torsion Angles			
B1–O1–B2–O2	–4.0(6)	O1–B2–O2–B3	–4.0(6)
B2–O2–B3–O3	–3.9(6)	O2–B3–O3–B1	–3.7(6)
B3–O3–B1–O1	10.9(6)	O3–B1–O1–B2	10.8(6)
B1–N1–C9–C10	112.3(4)	B2–N2–C23–C24	90.1(5)
N1–C9–C10–N3	5.7(7)	N2–C23–C24–N4	5.8(7)

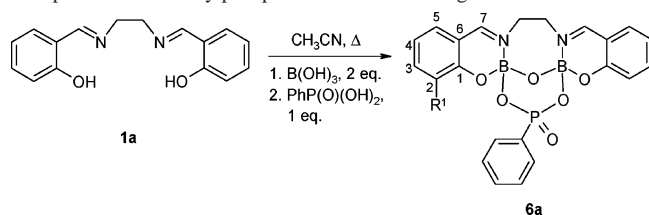
acidic diols, a number of heterotrimeric derivatives of the  $B_2EO_3$  type could be prepared.

In a first approach we experimented with phenylphosphonic acid, and from Scheme 3 it can be seen that the synthetic pathway established for the preparation of compounds **4a–g** can be extended to the preparation of the boron–phosphorus complex **6a**. Complex **6a** was obtained from the reaction between the salen ligand **1a** and 2 equiv of boric acid, to



**Figure 4.** Perspective view of the molecular structure of compound **5**. Ellipsoids are shown at the 50% probability level.

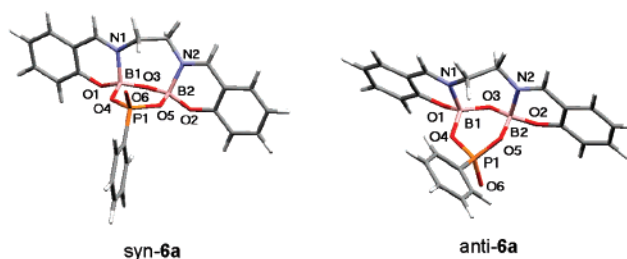
**Scheme 3.** Preparation of the Heterotrimeric Complex **6a** Using Complex **2a** and Phenylphosphonic Acid as Starting Materials



which after 4 h phenylphosphonic acid was added without isolation of the dinuclear intermediate (yield: 92%). The molecular structure of compound **6a** was established by elemental analysis and mass spectrometry as well as  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{31}\text{P}$  NMR spectroscopy. Unfortunately, crystals could not be grown for this derivative.

As expected, the chemical shifts measured in the  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of compound **6a** are very similar to the ones observed for **4a**. The signals for the methylene hydrogen atoms that are forming part of the seven-membered central heterocycle of the heterotrimeric complex are diastereotopic, and the  $^{11}\text{B}$  NMR shift is  $\delta = 2.0$  ppm. The  $^{31}\text{P}$  NMR shift is  $\delta = 5.51$  ppm, and similar shift differences have been measured for a series of borophosphonates  $[\text{RPO}_3\text{-BR}']_4$  ( $\text{R}, \text{R}' = \text{alkyl, aryl}$ ).<sup>19</sup>

Since theoretically two configurations are possible for compound **6a** (Figure 5), *ab initio* calculations at the HF/6-31G(d,p) level have been performed to determine their relative energies. The energy difference between the thermodynamic more stable *syn* and the less stable *anti* configuration is 5.9 kcal/mol. This difference can be attributed to



**Figure 5.** Calculated molecular structures of compounds *syn-6a* and *anti-6a*. Two configurations are possible for the heterotrimeric phosphonate **6a**; however, the *syn* conformers are thermodynamically more stable.

the steric repulsion that arises from the interaction of the P-phenyl group with the N-C-C-N backbone of the seven-membered heterocycle. The calculated molecular structures for *syn*- and *anti-6a* are shown in Figure 5.

A comparison of the bond lengths, bond angles and torsion angles in the molecular structure of **6a** (Table 2) with the values calculated for **3a** and **4a** shows differences for the N→B bond, which is significantly shorter (1.656/1.667 Å for **6a** ↔ 1.678–1.695 Å for **3a** and **4a**), the B–O–B bond angle, which is larger (123.3° for **6a** ↔ 118.9 for **3a** and 119.8° for **4a**), and the torsion angles in the six- and seven-membered heterocycles (Table 2). These variations indicate again the conformational flexibility of these heterocycles. The P–O, P=O, and P–C bond lengths are 1.572, 1.465, and 1.799 Å, and agree with the values reported for compounds containing P(O)–O–B bonds.<sup>19,20</sup>

#### 4. Conclusions

This contribution has shown that salen ligands and boric acid can be combined to homodinuclear and homotrimeric boron complexes; apparently, these reactions are reversible in polar solvents. Both boron atoms in the dinuclear species are tetrahedral, while the homotrimeric derivatives contain additionally a three-coordinate boron atom. In the presence of acidic diols such as phenylboronic or phenylphosphonic acid, the B–OH moiety can be interchanged by a B–Ph or a P(O)Ph group and probably also by other functional groups such as  $\text{SiR}_2$  and  $\text{SnR}_2$ .

The homo- and heterotrimeric boron derivatives discussed herein contain an almost planar  $\text{B}_3\text{O}_3$  or  $\text{B}_2\text{PO}_3$  heterocycle; therefore, these complexes can be considered as derivatives of trimetaboric acid,  $\text{B}_3\text{O}_3(\text{OH})_3$ , boroxine,  $\text{B}_3\text{O}_3\text{R}_3$ , or the tetraborate dianion found in Borax,  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ . The seven-membered  $\text{B}_2\text{C}_2\text{N}_2\text{O}$  heterocycles possess chair or twisted-chair conformations, while the eight-membered  $\text{B}_2\text{C}_3\text{N}_2\text{O}$  heterocycles prefer boat-chair and chair-chair conformations.

According to theoretical calculations, for the heterotrimeric boron–phosphorus derivatives the *syn* configuration,

(19) (a) Walawalkar, M. G.; Murugavel, R.; Roesky, H. W.; Schmidt, H.-G. *Inorg. Chem.* **1997**, *36*, 4202. (b) Diemert, K.; Englert, U.; Kuchen, W.; Sandt, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 241. (c) Walawalkar, M. G.; Murugavel, R.; Roesky, H. W.; Schmidt, H.-G. *Organometallics* **1997**, *16*, 516.

(20) (a) Bontchev, R. P.; Junghwan, D.; Jacobson, A. J. *Inorg. Chem.* **1999**, *38*, 2231. (b) Bontchev, R. P.; Junghwan, D.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1937. (c) Zhao, Y.; Zhu, G.; Zou, Y.; Pang, W. *Chem. Commun.* **1999**, 2219. (d) Yang, G.-Y.; Sevov, S. C. *Inorg. Chem.* **2001**, *40*, 2214. (e) Asnani, M.; Ramanan, A.; Vittal, J. J. *Inorg. Chem. Commun.* **2003**, *6*, 589.

in which the P-phenyl group is oriented in opposite direction to the salen ligand, is thermodynamically more stable.

The three-coordinate boron atoms in the salen{[B–O–B][O<sub>2</sub>BR]} derivatives and in (acphen')<sub>2</sub>{[B–O–B][O<sub>2</sub>B–(OH)]} should still have Lewis acidic properties and are embedded in environments that makes them interesting catalysts for asymmetric reactions.

**Acknowledgment.** The authors thank the CONACyT for financial support.

**Supporting Information Available:** Figures for the calculated structures of compounds **3a,d,g,j**, atomic coordinates for all calculated structures, additional geometric data for the calculated structures, and complete lists of geometric data for the structures determined by X-ray crystallography in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. This material is also available directly from the corresponding author.

IC048862E