

Salen-supported dinuclear and trinuclear boron compounds

Mario Sánchez^b, Timothy S. Keizer^a, Sean Parkin^a, Herbert Höpfl^b, David A. Atwood^{a,*}

^a Department of Chemistry, The University of Kentucky, Chemistry-Physics Bldg, Lexington, KY 40506-0055, USA

^b Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, C.P. 62210 Cuernavaca, Morelos, Mexico

Received 31 December 2001; received in revised form 8 February 2002; accepted 14 February 2002

Abstract

Six boron compounds have been synthesized through the combination of phenylboronic acid and various Salen (*N,N'*-ethylenebis(2-hydroxy)benzylideneimine) ligands. They contain seven- and eight-membered heterocycles with a bridging oxygen and have the formula: $L[(PhB)_2(\mu-O)]$ ($L = Acmen$ (**1**), Salen(*t*Bu) (**2**), Sal(2-OH)pen (**3**), Salpen(*t*Bu) (**4**), Acpen (**5**)) and $L[B_2(\mu-O)(O_2BPh)]$ ($L = Acen$ (**6**), Salmen (**7**)). Compounds **6** and **7** are interesting trinuclear boron derivatives with two four-coordinate and one three-coordinate boron atoms. The compounds have been characterized by MP, MS, IR, EA and ¹H- and ¹¹B-NMR, by ¹¹B-MAS for **6** and **7** and by X-ray crystallography for **2**, **4**–**7**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boron; Salen; Binuclear; Trinuclear

1. Introduction

Numerous metal containing Salen derivatives have been synthesized and extensively studied, in particular those of the middle and late d-block metals. This may be attributed to their use as asymmetric catalysts for olefin epoxidation [1], cyclopropanation [2], aziridination [3], sulfide oxidation [4], the Diels–Alder reaction [5], C–H activation [6] and the asymmetric ring-opening of epoxides [7]. These transition metal compounds are almost exclusively monometallic, that is one Salen ligand is coordinated to one transition metal atom. Many Group 13 compounds form monometallic derivatives (aluminum, [10] gallium [11] and indium [12]). However, the Group 13 elements are also capable of forming bimetallic compounds with the Salen ligands (boron, [8] aluminium, gallium, and indium [9]). There are no transition metal analogues to these compounds. The ability of the Salen ligand to produce such compounds may lead to the development of unique two-point Lewis acidic catalysts. Moreover, the boron atoms may be derivatived to have different coordination

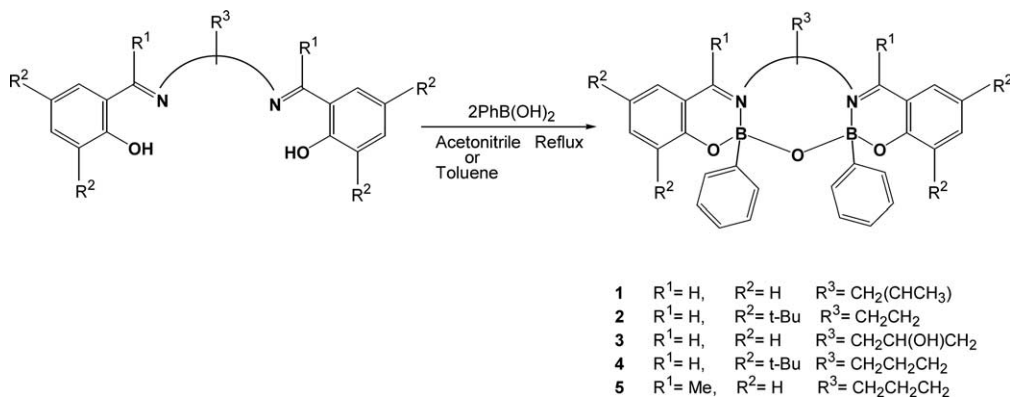
environments in these compounds, making them asymmetric.

The preparation of compounds containing seven- and eight-membered heterocycles from Salen ligands and arylboronic acids was reported recently [13]. The present work expands this effort to include the synthesis and characterization of di- and trinuclear oxo-bridged boron compounds.

2. Results and discussion

The preparation of compounds **1**–**5** was carried out in a single step by combining the corresponding Salen ligands and phenylboronic acid (Scheme 1) [13]. They can be isolated as pale yellow air-stable solids in reasonable yields by precipitation after substantial concentration of the solution or recrystallisation after cooling to –30 °C for a few days. Compounds **1** and **2** contain a seven-membered ring and **3**, **4** and **5** contain an eight-membered ring. All have bridging oxygen between the two boron atoms. Attempts to make larger-sized rings by increasing the length of the ligand backbone failed and oligomerization occurred instead. Salen ligands containing *tert*-butyl groups were utilized in an attempt to make the compounds (**2** and **4**) more

* Corresponding author. Tel.: +1-606-2574741; fax: +1-606-3231069.



Scheme 1. General reaction for the synthesis of compounds 1–5.

soluble in organic solvent but, surprisingly, they were less soluble than the compounds without *tert*-butyl groups.

The ¹H-NMR data are fairly consistent throughout the entire series. The imine CH resonances appear as singlets in the range $\delta = 8.02$ – 8.62 ppm. For compound **1**, three of the possible four diastereomers are present. The diastereomers are present due to two boron atoms and one chiral carbon atom in the ring. The presence of diastereomers can be easily deduced by ¹H-NMR, since six imino groups and three methyl groups can be distinguished. On the other hand, for compounds **2**–**4** only one diastereomer of two possible was obtained, the *cis* diastereomer (with regard to the phenyl groups attached to the boron atom).

The IR spectra for compounds **1**–**4** show that the absorptions attributed to the $\nu_{C=N}$ stretching frequency (1639 – 1644 cm^{-1}) are shifted higher by 6 – 16 cm^{-1} compared to the free ligands. This is due to the N→B intramolecular coordination which serves to reduce the electron density in the C=N bond. The shifts fall into the range of most Salen boron compounds [5]d. The MS data show no parent ion peak for compounds **1**–**4** but does show the parent ion minus phenyl group.

On the other hand, two unusual compounds (**6** and **7**) were obtained as excess PhB(OH)₂ was added to

Acen[(PhB)₂](μ -O) [13] and **1**, respectively (Fig. 1). X-ray quality crystals were formed through the recrystallization of Acen[(PhB)₂](μ -O) and **1** in acetonitrile. These compounds are air-stable, faint yellow insoluble solids and were characterized by melting point, IR, MS, elemental analysis, ¹¹B-MAS NMR and X-ray diffraction. This is an interesting product due to the fact that the B–Ph bond is broken and replaced by a B–O bond. In previous work, boron alkyl compounds were not used due to the strong, covalent nature of the B–C bond [8e]. The boron alkyl compounds do not undergo a nucleophilic displacement as well as the alkyl borates. The solid state ¹¹B-MAS NMR spectra of compounds **6** and **7** showed both three- (9.08, 19.34 ppm) and four-coordinate (1.01, 1.84 ppm) resonances. The four-coordinate sites show strong resonances with a $w_{1/2}$ of 278 and 300 Hz for **6** and **7**, respectively, whereas, the three-coordinate boron site is very weak and broad with a $w_{1/2}$ of 3882 and 1102 Hz, respectively.

2.1. Structural characterization of **2** and **4**–**7**

Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 1. Selected bonds distances and angles for these compounds are listed in Table 2. Figs. 2–6 show the

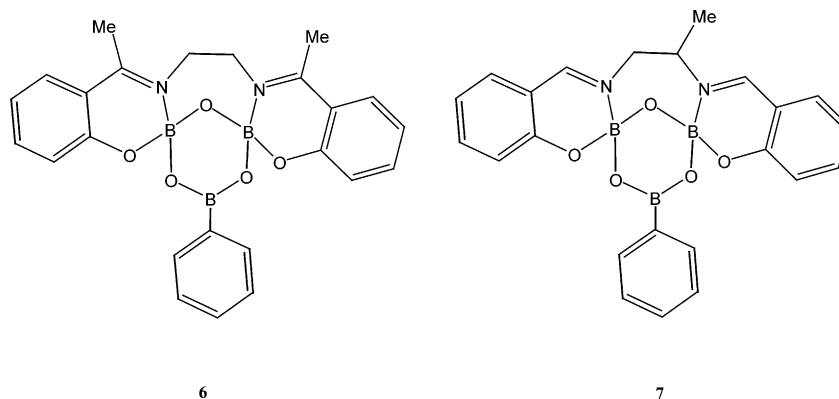
Fig. 1. Compounds **6** and **7**.

Table 1
Crystallographic data and collection parameters for compounds **2–7**

Crystal data	2	4	5	6	7
CCDC#	178691	178818	178692	178693	178819
Empirical formula	C ₄₄ H ₅₆ B ₂ N ₂ O ₃	C ₄₅ H ₅₈ B ₂ N ₂ O ₃	C ₃₁ H ₃₀ B ₂ N ₂ O ₃	C ₂₆ H ₂₆ B ₃ N ₃ O ₅ (6·CH ₃ CN)	C ₂₇ H ₃₀ B ₃ N ₂ O _{6.5} (7·THF $\frac{1}{2}$ H ₂ O)
Formula weight	682.54	696.57	500.19	492.93	518.96
<i>T</i> (°C)	–100	–100	–100	–100	20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Cc</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>Cc</i>
<i>a</i> (Å)	11.628(1)	13.818(1)	21.709(2)	9.802(1)	14.2786(14)
<i>b</i> (Å)	28.125(3)	25.397(2)	18.705(2)	11.531(2)	15.1719(15)
<i>c</i> (Å)	12.804(2)	12.690(1)	14.061(1)	12.109(2)	13.2077(13)
α (°)	–	–	–	96.94(2)	–
β (°)	99.585(10)	118.57(2)	114.381 (10)	94.75(2)	106.930(2)
γ (°)	–	–	–	113.50(2)	–
<i>V</i> (Å ³)	4128.9(9)	3911.1(5)	5200.5 (8)	1232.9(3)	2737.2(5)
<i>Z</i>	4	4	8	2	4
μ (mm ^{–1})	0.067	0.072	0.081	0.090	0.071
ρ_{calc} (g cm ^{–3})	1.098	1.183	1.278	1.328	1.254
<i>F</i> (000)	1472	1504	2112	516	992
Crystal size (mm)	0.40 × 0.20 × 0.02	0.40 × 0.08 × 0.06	0.32 × 0.24 × 0.07	0.32 × 0.18 × 0.08	0.53 × 0.35 × 0.34
θ limits (°)	1.45 < θ < 21	2.43 < θ < 22.50	1.85 < θ < 25.00	2.29 < θ < 22.50	2.01 < θ < 25.00
<i>hkl</i> limits	–11, 11; –28, 28; –12, 12	–14, 14; –27, 27; –13, 13	–25, 25; –22, 22; –16, 16	–10, 10; –12, 12; –13, 12	–16, 16; –18, 18; –15, 15
Reflections collected	15 705	10 083	17 732	6419	13 072
Independent reflections	4430	5116	4578	3221	4807
<i>R</i> _{int}	0.1005	0.0609	0.0729	0.0386	0.0386
Data/parameters/restraints	4430/473/840	5116/495/72	4578/344/602	3221/337/0	4807/365/7
<i>R</i> ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.1042	0.0508	0.0631	0.0500	0.0469
<i>wR</i> ₂ ^a (all data)	0.1358	0.0767	0.1101	0.1061	0.1161
Goodness-of-fit on <i>F</i> ²	1.396	1.030	1.153	1.022	0.90
Largest difference peak and hole (e Å ^{–3})	0.215, –0.215	0.193, –0.140	0.222, –0.187	0.154, –0.162	0.188, –0.138

$$^a R_1 = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|; wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|]^{1/2}.$$

molecular structure for the bimetallic compounds **2** and **4–7**. Compounds **2**, **4**, and **5** are in a *cis*-configuration with respect to the phenyls on the boron atoms. The average B–O bond lengths for the bridging oxygen atoms are 1.416(5), 1.418(5), and 1.419(3) Å for **2**, **4** and **5**, respectively, and the average B–O_{Ph} bond lengths are 1.503(5), 1.511(4), and 1.493(3) Å, respectively. The distances for the B–O_{Ph} bond lengths are slightly longer than those reported before [13]. The average B–O–B bond angles are 131.4(3), and 137.5(3), and 128.6(2)° for **2**, **4**, and **5**, respectively. The eight-membered ring (**4**) has a larger B–O–B bond angle than the seven-membered Salen ring (**2**) compounds. However, compound **5** (eight-membered ring) has a smaller angle than both **2** and **4**. This is probably due to the fact that compound **5** has no ^tBu groups and thus less steric interference allowing the B–O–B angle to be smaller. The deviation of the geometry around the boron can be determined by calculating the THC (tetrahedral character) value where 100% is tetrahedral and 0% is trigonal

planar [14]. The THC for these compounds is 85, 76, and 66%, respectively. It is important to notice that compound **5** has a low tetrahedral character.

Compounds **2**, **4** and **5** have several characteristics in common. Their central heterocycles, C₂B₂N₂O and C₃B₂N₂O, have a boat conformation with the two imino-nitrogen atoms above the plane. From these results it can be concluded that the *cis*-configuration is preferred over the *trans*-configuration for seven- and eight-membered (C₂B₂N₂O and C₃B₂N₂O) heterocycles.

Compounds **6** and **7** were characterized by X-ray diffraction (Figs. 5 and 6). These compounds contain a six-membered alternating B₃O₃ ring, similar to a simple boroxine system, with an additional nitrogen dative bond to two of the three boron atoms (1.613(3) and 1.620(4) Å, respectively). The THC for **6** and **7** is 87 and 86%. The average B–O–B angles are 119.9(3) and 120.3(3)°, respectively. These angles are significantly smaller than **2**, **4**, and **5** but are similar to others compounds in the literature with B₃O₃ ring structures.

Table 2
Selected bond lengths (Å) and angles (°) for **2**, and **4–7**

Compound **2**

Bond lengths

B(1)–N(1)	1.614(6)	B(2)–N(2)	1.613(6)
B(1)–O(1)	1.510(5)	B(2)–O(2)	1.497(6)
O(1)–C(1)	1.340(5)	O(2)–C(20)	1.337(5)
C(14)–C(15)	1.430(6)	C(19)–C(18)	1.429(6)
C(15)–N(1)	1.286(5)	C(18)–N(2)	1.284(5)
N(1)–C(16)	1.459(5)	N(2)–C(17)	1.475(5)
C(16)–C(17)	1.529(6)	B(1)–C(33)	1.611(1)
B(1)–O(3)	1.419(5)	B(2)–C(39)	1.615(6)
		B(2)–O(3)	1.414(5)

Bond angles

O(2)–B2–N(2)	107.4(3)	O(1)–B1–N(1)	102.9(3)
O(2)–B2–O(3)	111.5(4)	O(1)–B1–O(3)	112.0(4)
O(2)–B2–C(39)	109.0(4)	O(1)–B1–C(33)	112.8(4)
O(3)–B2–C(39)	113.3(4)	O(3)–B1–C(33)	110.0(4)
O(3)–B2–N(2)	110.1(4)	O(3)–B1–N(1)	109.5(4)
N(2)–B2–C(39)	105.1(3)	N(1)–B1–C(33)	109.4(4)
B(1)–O3–B(2)	131.4(3)	B(1)–N1–C(16)	120.1(4)
N(1)–C16–C(17)	109.1(3)	C(16)–C17–N(2)	112.7(3)
C(17)–N2–B(2)	118.2(3)	B(1)–O1–C(1)	120.0(3)

Compound **4**

Bond lengths

B(1)–N(1)	1.631(4)	B(2)–N(2)	1.611(4)
B(1)–O(1)	1.513(4)	B(2)–O(2)	1.509(4)
O(1)–C(1)	1.336(3)	O(2)–C(21)	1.333(3)
C(14)–C(15)	1.436(4)	C(20)–C(19)	1.436(4)
C(15)–N(1)	1.289(3)	C(19)–N(2)	1.289(3)
N(1)–C(16)	1.491(3)	N(2)–C(18)	1.469(9)
C(16)–C(17)	1.523(3)	C(18)–C(17)	1.518(4)
B(1)–O(3)	1.423(4)	B(1)–C(34)	1.608(5)
		B(2)–C(40)	1.596(4)
		B(2)–O(3)	1.414(5)

Bond angles

O(2)–B2–N(2)	104.1(2)	O(1)–B1–N(1)	106.3(2)
O(2)–B2–O(3)	115.3(3)	O(1)–B1–O(3)	110.5(3)
O(2)–B2–C(40)	106.5(3)	O(1)–B1–C(34)	109.9(2)
O(3)–B2–C(40)	113.9(3)	O(3)–B1–C(34)	113.7(3)
O(3)–B2–N(2)	107.5(2)	O(3)–B1–N(1)	112.3(3)
N(2)–B2–C(40)	108.9(3)	N(1)–B1–C(34)	103.6(2)
B(1)–O3–B(2)	137.5(3)	B(1)–N1–C(16)	120.2(2)
N(1)–C16–C(17)	114.4(2)	C(16)–C17–C(18)	114.2(3)
C(17)–C18–N(2)	111.6(2)	C(18)–N2–B(2)	119.8(2)

Compound **5**

Bond lengths

B(1)–N(1)	1.626(3)	B(2)–N(2)	1.649(3)
B(1)–O(1)	1.499(2)	B(2)–O(2)	1.486(2)
O(1)–C(1)	1.329(2)	O(2)–C(15)	1.334(2)
C(9)–C(10)	1.523(3)	C(10)–C(11)	1.522(3)
C(7)–N(1)	1.299(2)	C(12)–N(2)	1.300(2)
N(1)–C(9)	1.486(3)	N(2)–C(11)	1.479(2)
C(6)–C(7)	1.457(3)	C(12)–C(14)	1.463(3)
B(1)–O(3)	1.422(3)	B(1)–C(20)	1.605(3)
		B(2)–C(26)	1.619(3)
		B(2)–O(3)	1.415(2)

Bond angles

O(2)–B2–N(2)	105.4(1)	O(1)–B1–N(1)	106.8(2)
O(2)–B2–O(3)	111.5(2)	O(1)–B1–O(3)	113.8(2)
O(2)–B2–C(26)	111.2(2)	O(1)–B1–C(20)	106.2(2)
O(3)–B2–C(26)	111.7(2)	O(3)–B1–C(20)	112.7(2)
O(3)–B2–N(2)	111.5(2)	O(3)–B1–N(1)	107.9(2)

N(2)–B2–C(26)	107.1(2)	N(1)–B1–C(20)	109.4(2)
B(1)–O3–B(2)	128.6(2)	B(1)–N1–C(9)	113.7(1)
N(1)–C9–C(10)	116.2(2)		

Compound **6**

Bond lengths

B(1)–N(1)	1.624(3)	B(2)–N(2)	1.603(3)
B(1)–O(1)	1.474(3)	B(2)–O(2)	1.468(3)
O(1)–C(1)	1.348(3)	O(2)–C(18)	1.337(3)
C(6)–C(7)	1.459(4)	C(13)–C(11)	1.460(3)
C(7)–N(1)	1.301(3)	C(11)–N(2)	1.299(3)
N(1)–C(9)	1.471(3)	N(2)–C(10)	1.476(3)
C(9)–C(10)	1.528(3)	B(2)–O(5)	1.458(3)
B(2)–O(3)	1.418(3)	B(1)–O(3)	1.403(3)
B(1)–O(4)	1.451(3)	O(4)–B(3)	1.370(3)
B(3)–O(5)	1.354(3)	B(3)–C(19)	1.567(4)

Bond angles

O(2)–B2–N(2)	108.16(19)	O(1)–B1–N(1)	105.54(19)
O(2)–B2–O(3)	109.0(2)	O(1)–B1–O(3)	109.5(2)
O(2)–B2–O(5)	110.4(2)	O(1)–B1–O(4)	109.5(2)
O(3)–B2–O(5)	114.2(2)	O(3)–B1–O(4)	115.6(2)
O(3)–B2–N(2)	108.1(2)	O(3)–B1–N(1)	109.2(2)
N(2)–B2–O(5)	106.73(19)	N(1)–B1–O(4)	107.0(2)
B(1)–O3–B(2)	120.3(2)	B(1)–O4–B(3)	119.7(2)
O(4)–B3–C(19)	117.9(2)	O(4)–B3–O(5)	122.1(2)
O(5)–B3–C(19)	120.0(2)	B(3)–O5–B(2)	119.6(2)
B(1)–N1–C(9)	116.19(18)	B(2)–N2–C(10)	113.53(19)

Compound **7**

Bond lengths

B(1)–N(1)	1.627(4)	B(2)–N(2)	1.614(4)
B(1)–O(1)	1.467(4)	B(2)–O(2)	1.463(4)
O(1)–C(1)	1.349(3)	O(2)–C(18)	1.317(3)
C(6)–C(7)	1.418(4)	C(13)–C(11)	1.418(4)
C(7)–N(1)	1.288(4)	C(11)–N(2)	1.262(4)
N(1)–C(9)	1.486(4)	N(2)–C(10)	1.466(4)
C(9)–C(10)	1.499(5)	B(2)–O(5)	1.441(4)
B(2)–O(3)	1.408(4)	B(1)–O(3)	1.383(4)
B(1)–O(4)	1.463(4)	O(4)–B(3)	1.364(4)
B(3)–O(5)	1.349(4)	B(3)–C(19)	1.555(5)

Bond angles

O(2)–B2–N(2)	107.8(2)	O(1)–B1–N(1)	106.6(2)
O(2)–B2–O(3)	109.4(2)	O(1)–B1–O(3)	110.5(2)
O(2)–B2–O(5)	110.5(2)	O(1)–B1–O(4)	108.7(2)
O(3)–B2–O(5)	114.6(3)	O(3)–B1–O(4)	114.1(2)
O(3)–B2–N(2)	109.4(4)	O(3)–B1–N(1)	110.6(2)
N(2)–B2–O(5)	104.9(2)	N(1)–B1–O(4)	106.0(2)
B(1)–O3–B(2)	120.0(2)	B(1)–O4–B(3)	120.9(3)
O(4)–B3–C(19)	118.4(3)	O(4)–B3–O(5)	120.9(3)
O(5)–B3–C(19)	120.6(3)	B(3)–O5–B(2)	119.9(2)
B(1)–N1–C(9)	120.9(2)	B(2)–N2–C(10)	116.9(2)

[15–20]. The average B–O ring distances for compound **6** is 1.409(3) Å and for compound **7** is 1.401 Å. It is important to note that the B–O distances belonging to the phenylboronic acid unit are shorter than those attached to the ligand. The phenylboronic acid boron atom for **6** and **7** is three-coordinate, with angles around the boron atom of 117.9(2), 120.0(2), 122.1(2) and 118.4(3), 120.6(3), 120.9(3)°, respectively. These are only slightly distorted from trigonal planar. Thus, the boron atom has an open Lewis acid site which may be utilized for its activity in a catalytic system.

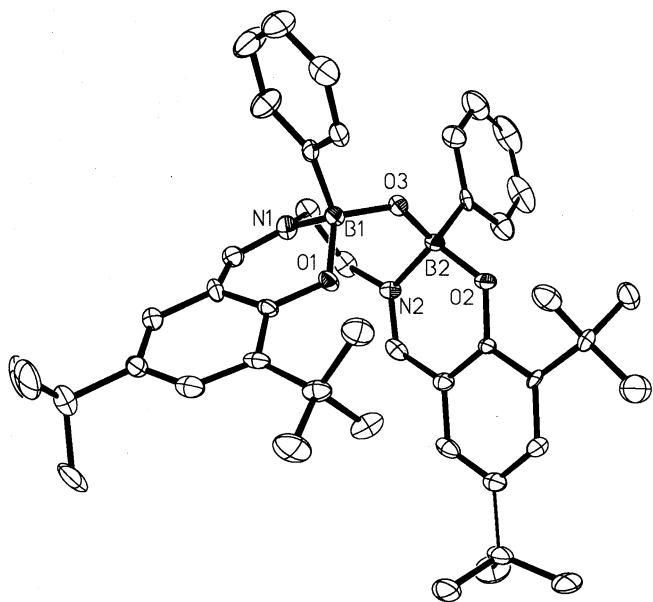


Fig. 2. Molecular structure of compound 2. Hydrogen atoms are omitted for clarity.

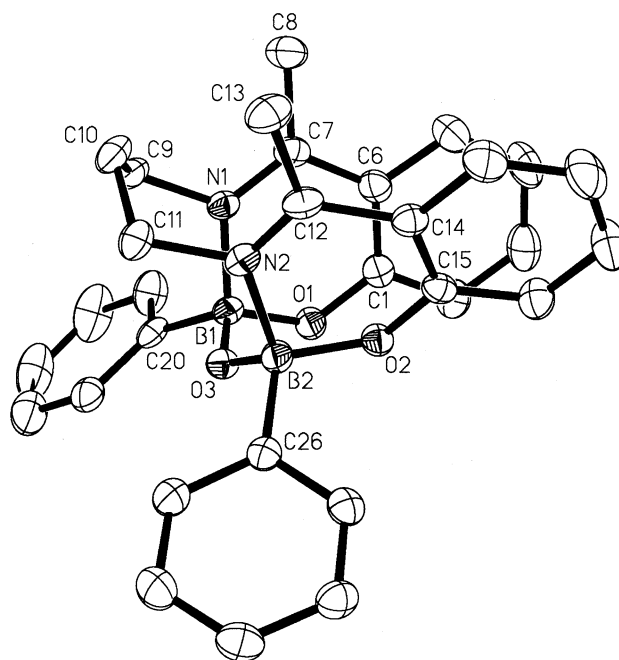


Fig. 4. Molecular structure of compound 5. Hydrogen atoms are omitted for clarity.

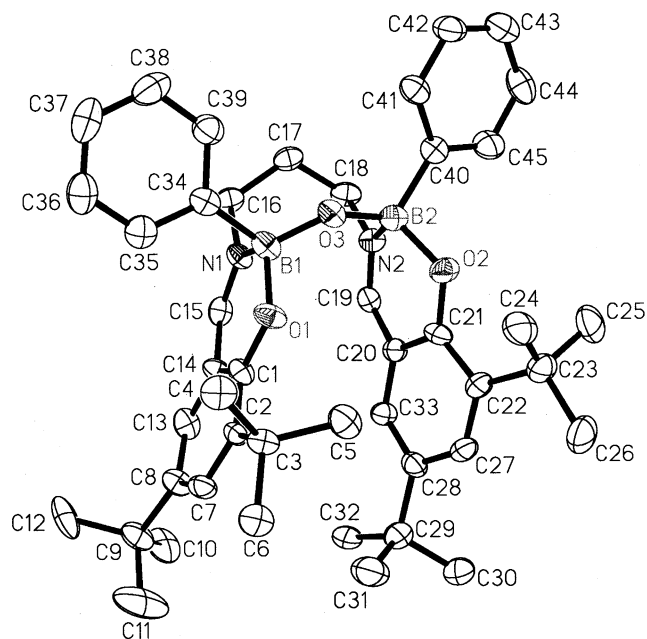


Fig. 3. Molecular structure of compound 4. Hydrogen atoms are omitted for clarity.

3. Conclusions

Seven- and eight-membered heteronuclear oxo-bridged boron compounds have been readily synthesized and further derivatized to trinuclear compounds. These compounds exhibit a similar structure to boroxine. They contain fused six- (B_3O_3) and seven-membered ($B_2C_2ON_2$) rings with both three- and four-coordinate boron atoms. The preference for either *cis* or *trans*

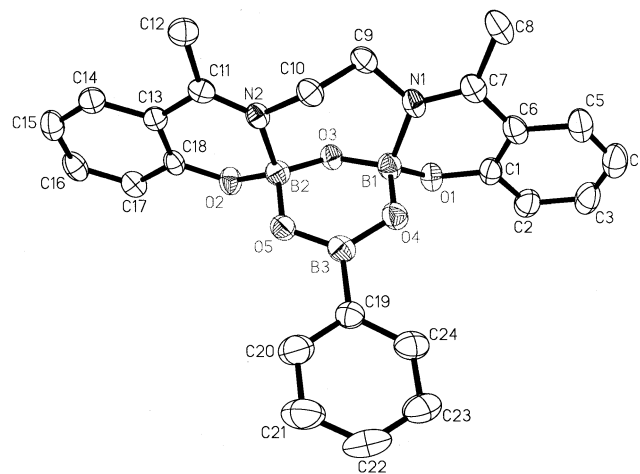


Fig. 5. Molecular structure of compound 6. Hydrogen atoms are omitted for clarity.

isomers is not well understood, but the *cis* isomer is observed in the seven- and eight-membered heterocyclic boron compounds. Also it can be concluded that ligands with four or more carbons in the backbone form polymeric structures and can be characterized only by solid-state techniques.

4. Experimental

Solvents (THF and $C_6H_5CH_3$) were rigorously dried prior to use and dispensed in the drybox. Phenylboronic acid and MeCN were used as received (Aldrich). IR

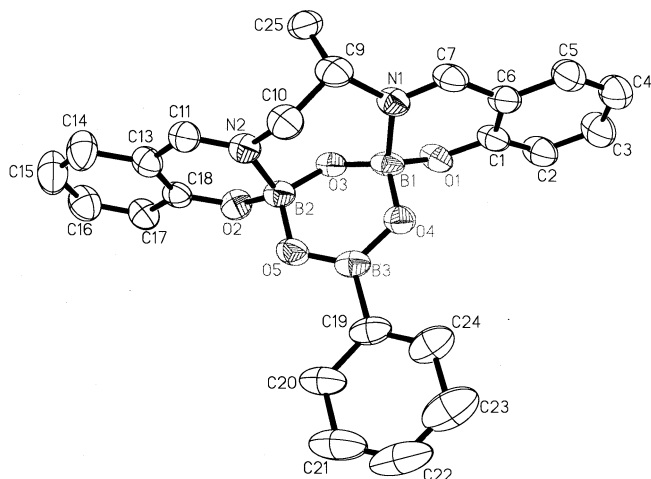


Fig. 6. Molecular structure of compound 7. Hydrogen atoms are omitted for clarity.

spectra were obtained in KBr on a MAGNA-IR 560 spectrometer. ^1H - and ^{11}B -NMR spectra were recorded on a Varian 200 spectrometer. ^{11}B -MAS NMR spectra were recorded on a Varian 400 spectrometer. Standards were TMS and CDCl_3 for ^1H and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ for ^{11}B . Chemical shifts are stated in parts per million (ppm). EI (positive) (direct probe) spectra were acquired on a Kratos Concept IH at 70 eV for compounds 1–6. An interpretable spectrum for 7 could not be obtained. Elemental analyses were obtained on an Elementar Americas Vario EL III analyzer. X-ray diffraction studies of single crystals were performed using on a Nonius Kappa CCD and Bruker–Apex diffractometry [22] ($\lambda_{\text{Mo-K}\alpha} = 0.71073 \text{ \AA}$, monochromator: graphite, $T = 173 \text{ K}$ and 293). Cell parameters were obtained from analysis of all Kappa CCD area detector frames. Absorption correction was not necessary, but the scaling and merging routine in Scalepack [21] provide for correction of absorption effects. Solution and refinement: direct methods (SHELXS-97) for structure solution and the SHELXL-97 using a riding model software package for refinement and data output. Hydrogen atoms were refined with isotropic U tied to their respective heavy atom. The most important crystallographic data are shown in Table 1. Selected bond lengths and angles are given in Table 2.

4.1. Salmen[(PhB) $_2(\mu\text{-O})$] (1)

To a solution of (*R,S*)-2,2'-bis[(1-methyl-1,2-ethanediy]bis(nitrilomethylidyne)] phenol (1.00 g, 3.54 mmol) in $\text{C}_6\text{H}_5\text{CH}_3$ (20 ml) was added phenylboronic acid (0.43 g, 7.08 mmol). The solution was refluxed for 3 h yielding a yellow solid (1.32 g, 2.79, mmol). This was filtered under vacuum and recrystallized in THF. Yield: 79%; m.p. = 250–252 °C. $\text{C}_{29}\text{H}_{26}\text{B}_2\text{N}_2\text{O}_3$, MW = 472.15 g mol $^{-1}$. ^1H -NMR (400 MHz, $\text{Me}_2\text{SO}-d_6$, 25 °C): $\delta =$

8.62, 8.59, 8.58, 8.56, 8.39, 8.02 (2H, s, N=CH), 7.59–6.40 (18H, m, ring-H), 4.58, 4.01, 4.72 (1H, m, CHCH $_3$), 3.72, 3.30 (2H, m, CH $_2$ CH), 1.35, 1.31, 0.77 (3H, d, CHCH $_3$); ^{11}B -NMR (64 MHz, $\text{Me}_2\text{SO}-d_6$, 25 °C, $\text{BF}_3 \cdot \text{OEt}_2$): $\delta = 8.2$ ($w_{1/2} = 845 \text{ Hz}$). IR (KBr): $\nu = 3064\text{w}$, 3002w, 1640s, 1609m, 1557s, 1478m, 1460m, 1311m, 1232m, 1195s, 1150m, 1130m, 1083w 1027m cm^{-1} . MS (70 eV, EI): m/z (%): 396 (100), 291 (15), 263 (5), 248 (20), 235 (3), 187 (8), 159 (18), 130 (5), 97 (3), 69 (10), 41 (8). Anal. Calc: C, 73.77.60; H, 5.55; N, 5.93. Found: C, 73.05; H, 5.39; N, 5.86%.

4.2. Salen(^tBu)[(PhB) $_2(\mu\text{-O})$] (2)

To a solution of *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (1.00 g, 2.03 mmol) in MeCN (20 ml) was added phenylboronic acid (0.49 g, 4.06 mmol). The solution was refluxed for 8 h yielding a yellow solid (1.01 g, 1.48 mmol). Crystals were obtained in MeCN. Yield: 73%; m.p. = 298–300 °C. $\text{C}_{44}\text{H}_{56}\text{B}_2\text{N}_2\text{O}_3$, MW = 682.54. ^1H -NMR (400 MHz, $\text{Me}_2\text{SO}-d_6$, 25 °C): $\delta = 8.48$ (2H, s, N=CH), 7.45 (4H, d, ring-H), 7.34 (2H, d, ring-H), 7.14–7.07 (8H, m, ring-H), 3.86, 3.68 (4H, AB, CH $_2$ -N), 1.20 (18H, s, CCH $_3$), 1.13 (18H, s, CCH $_3$); ^{11}B -NMR (64 MHz, $\text{Me}_2\text{SO}-d_6$, 25 °C, $\text{BF}_3 \cdot \text{OEt}_2$): $\delta = 1.6$ ($w_{1/2} = 3400 \text{ Hz}$). IR (KBr): $\nu = 3049\text{w}$, 3001w, 2959s, 2868w, 1644s, 1564m, 1474w, 1443w, 1360w, 1264w, 1185s, 1119w, 1097w, 1026w cm^{-1} . MS (70 eV, EI): m/z (%): 605 (100), 528 (3), 485 (2), 413 (1), 346 (10), 295 (3), 264 (25), 57 (3). Anal. Calc: C, 77.42; H, 8.27; N, 4.10. Found: C, 75.16; H, 6.64; N, 4.06%.

4.3. Sal(2-OH)pen[(PhB) $_2(\mu\text{-O})$] (3)

To a solution of *N,N'*-disalicylidene-2-hydroxy-1,3-propanediamine (1.00 g, 3.35 mmol) in MeCN (20 ml) was added phenylboronic acid (0.81 g, 6.70 mmol). The solution was refluxed for 8 h yielding a yellow solid powder (1.46 g, 2.99 mmol). Yield: 89%; m.p. = 180–183 °C. $\text{C}_{29}\text{H}_{26}\text{B}_2\text{N}_2\text{O}_4$, MW = 488.15 g mol $^{-1}$. ^1H -NMR (400 MHz, $\text{Me}_2\text{SO}-d_6$, 25 °C): $\delta = 8.39$ (2H, s, N=CH), 7.53 (4H, d, ring-H), 7.14 (10H, m, ring-H), 6.49 (2H, t, ring-H), 6.39 (2H, d, ring-H), 5.86 (1H, d, OH), 4.26 (1H, m, O-CH), 3.65, 3.39 (4H, dd, N-CH $_2$). ^{11}B -NMR (64 MHz, $\text{Me}_2\text{SO}-d_6$, 25 °C, $\text{BF}_3 \cdot \text{OEt}_2$): $\delta = 3.6$ ($w_{1/2} = 3718 \text{ Hz}$). IR (KBr): $\nu = 3064\text{w}$, 3004w, 1639s, 1608m, 1559m, 1481m, 1465m, 1430w, 1408w, 1320m, 1234m, 1180s, 1132m, 1102m, 1044m cm^{-1} . MS (70 eV, EI): m/z (%): 411 (12), 368 (2), 333 (3), 307 (100), 271 (2), 248 (38), 222 (12), 172 (12), 120 (15), 77 (11), 69 (22), 57 (28). Anal. Calc: C, 71.35; H, 5.36; N, 5.73. Found: C, 71.05; H, 5.49; N, 5.81%.

4.4. Salpen(^tBu)[(PhB)₂(μ-O)] (4)

To a solution of *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,3-propanediamine (1.00 g, 1.97 mmol) in MeCN (20 ml) was added phenylboronic acid (0.49 g, 3.94 mmol). The solution was refluxed for 8 h yielding a yellow solid (0.98 g, 1.40 mmol). Crystals were obtained in MeCN. Yield: 71%; m.p. = 318–320 °C. C₄₅H₅₈B₂N₂O₃, MW = 696.57 g mol⁻¹. IR (KBr): ν = 3063w, 2954s, 2905w, 2867w, 1642s, 1562m, 1444m, 1427m, 1362m, 1309w, 1258w, 1180s, 1110m, 1085w, 1024w cm⁻¹. MS (70 eV, EI): *m/z* (%): 619 (100), 543 (4), 515 (3), 360 (3), 300 (5), 271 (25), 256 (3), 221 (3), 129 (5), 97 (8), 85 (15), 57 (40). Anal. Calc: C, 77.59; H, 8.39; N, 4.02. Found: C, 72.96; H, 8.59; N, 3.86%.

4.5. Acen[B₂(μ-O)(O₂BPh)] (6)

To a solution of Acen[(PhB)₂](μ-O) (0.5 g, 1.77 mmol) in MeCN was added phenylboronic acid (0.21 g, 1.77 mmol) to the cloudy solution and refluxed for 12 h. The product precipitated product was filtered and washed with CHCl₃. Yield: 46%; m.p. = 332–334 °C. C₂₄H₂₃B₃N₂O₅, MW = 451.88 g mol⁻¹. ¹¹B-MAS NMR (128 MHz): δ = 1.01 (*w*_{1/2} = 278 Hz), 9.08 (*w*_{1/2} = 3882). IR (KBr): ν = 3038w, 2924w, 2854w, 1617s, 1556m, 1439m, 1323s, 1277m, 1112s cm⁻¹. MS (70 eV, EI): *m/z* (%): 452 (30), 409 (25), 375 (10), 331 (100), 305 (20), 292 (25), 248 (10), 221 (8), 201 (8), 187 (22), 166 (20), 146 (12), 121 (15), 97 (12), 69 (22), 57 (30). Anal. Calc: C, 63.79; H, 5.13; N, 6.20. Found: C, 61.70; H, 5.11; N, 5.94%.

4.6. Salmen[B₂(μ-O)(O₂BPh)] (7)

To a solution of 1,2-diaminepropane (0.5 g, 1.78 mmol) in MeCN was added boric acid (0.22 g, 3.56 mmol). Reflux the solution for 4 or 5 h. Then immediately was added phenylboronic acid (0.21 g, 1.78 mmol) to the cloudy solution in the same flask and kept refluxing for 12 more hours. The product precipitated filtered and washed with CHCl₃. Yield: 69%; m.p. = 305–307 °C. C₂₃H₂₁B₃N₂O₅, MW = 438.03 g mol⁻¹. ¹¹B-MAS NMR (128 MHz): δ = 1.84 (*w*_{1/2} = 300 Hz), 19.34 (*w*_{1/2} = 1102). IR (KBr): ν = 3061w, 2975w, 1633s, 1558s, 1481m, 1440s, 1359s, 1304s, 1234m, 1144s, 1107s, 1043m cm⁻¹. Anal. Calc: C, 63.09; H, 4.83; N, 6.39. Found: C, 69.26; H, 5.87; N, 7.32%.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 178691, 178818, 178692,

178693 and 178819 for compounds **2**, **4**, **5**, **6** and **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (int. code) +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

This work was supported by the National Science Foundation NSF-CAREER award (CHE 9816155) and CONACYT-MEXICO. NMR instruments used in this research were obtained with funds from the CRIF program of the National Science Foundation (CHE 997841), from the Research Challenge Trust Fund of the University of Kentucky and the MRI program of the NSF (DMR-9977388).

References

- [1] (a) E.N. Jacobsen, Asymmetric, catalytic epoxidation of unfunctionalized olefins, in: I. Ojima (Ed.), *Catalytic Asymmetric Synthesis*, VCH Publishers, New York, 1993, pp. 159–202; (b) T. Katsuki, *Coord. Chem. Rev.* 140 (1995) 189; (c) A.K. Jørgensen, *Chem. Rev.* 1989 (89) 431; (d) P.J. Pospisil, D.H. Carsten, E.N. Jacobsen, *Chem. Eur. J.* 2 (1996) 974; (e) S.L. Vander-Velde, E.N. Jacobsen, *J. Org. Chem.* 60 (1995) 5380; (f) K. Srinivasan, P. Michand, J.K. Kochi, *J. Am. Chem. Soc.* 108 (1986) 2309.
- [2] T. Fukuda, L. Katsuki, *Tetrahedron* 53 (1997) 7201.
- [3] (a) J. Du Bois, C.S. Tomoka, J. Hong, E.M. Carreira, *Acc. Chem. Res.* 30 (1997) 364; (b) H. Noshikori, T. Katsuki, *Tetrahedron Lett.* 37 (1996) 9245.
- [4] (a) C. Sasaki, K. Nakajima, M. Kojima, J. Fujita, *Bull. Chem. Soc. Jpn.* 64 (1991) 1318; (b) C. Bolm, F. Bienewald, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2640; (c) M. Palucki, P. Hanson, E.N. Jacobsen, *Tetrahedron Lett.* 33 (1992) 7111; (d) T. Fukuda, T. Katsuki, *Tetrahedron Lett.* 38 (1997) 3435.
- [5] (a) S.E. Schaus, J. Branalt, E.N. Jacobsen, *J. Org. Chem.* 63 (1998) 403; (b) Y. Yamashita, T. Katsuki, *Synlett* (1995) 829; (c) T.K. Hollis, W. Oldenkirk, N.P. Robinson, J. Whelan, B. Bosnich, *Tetrahedron* 49 (1993) 5415.
- [6] (a) M.D. Kaufman, P.A. Greico, D.W. Bougie, *J. Am. Chem. Soc.* 115 (1993) 11648; (b) J.F. Larrow, E.N. Jacobsen, *J. Am. Chem. Soc.* 116 (1994) 12129; (c) K. Hamachi, R. Irie, L. Katsuki, *Tetrahedron Lett.* 37 (1996) 4979.
- [7] (a) E.N. Jacobsen, F. Kakiuchi, R.G. Konsler, J.F. Larrow, M. Tokunaga, *Tetrahedron Lett.* 38 (1997) 773; (b) M. Tokunaga, J.F. Larrow, F. Kakiuchi, E.N. Jacobsen, *Science* 277 (1997) 936; (c) L.E. Martinez, J.L. Leighton, D.H. Carsten, E.N. Jacobsen, *J. Am. Chem. Soc.* 117 (1995) 5897; (d) J.L. Leighton, E.N. Jacobsen, *J. Org. Chem.* 61 (1996) 389.

- [8] (a) E. Hohaus, *Fresenius Z. Anal. Chem.* 315 (1983) 696;
(b) D.A. Atwood, J.A. Jegier, M.J. Remington, D. Rutherford, *Aust. J. Chem.* 49 (1996) 1333;
(c) P. Wei, D.A. Atwood, *Inorg. Chem.* 36 (1997) 4060;
(d) P. Wei, D.A. Atwood, *Chem. Commun.* (1997) 1427;
(e) P. Wei, T. Keizer, D.A. Atwood, *Inorg. Chem.* 38 (1999) 3914;
(f) T.S. Keizer, L.J. DePue, S. Parkin, D.A. Atwood, *J. Can. Chem.* (2002) in press;
(g) T.S. Keizer, L.J. DePue, S. Parkin, D.A. Atwood, *J. Am. Chem. Soc.* 124 (2002) 1864.
- [9] (a) K.S. Chong, S.J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* 55 (1977) 2540;
(b) D.A. Atwood, J.A. Jegier, D. Rutherford, *Bull. Chem. Soc. Jpn.* 70 (1997) 2093;
(c) M.S. Hill, P. Wei, D.A. Atwood, *Polyhedron* 17 (1998) 811;
(d) M.A. Van Aelstyn, T.S. Keizer, D.L. Klopotek, S. Liu, M.-A. Muñoz-Hernández, P. Wei, D.A. Atwood, *Organometallics* 19 (2000) 1796;
(e) D.A. Atwood, M.J. Harvey, *Chem. Rev.* 101 (2001) 37.
- [10] (a) P.L. Gurian, L.K. Cheatham, J.W. Ziller, A.R. Barron, *J. Chem. Soc. Dalton Trans.* 11 (1991) 1449;
(b) D. Rutherford, D.A. Atwood, *Organometallics* 15 (1996) 4417;
(c) M.-A. Muñoz-Hernández, B. Sannigrahi, D.A. Atwood, *J. Am. Chem. Soc.* 121 (1999) 6747;
(d) M.A. Muñoz-Hernández, T.S. Keizer, S. Parkin, B. Patrick, D.A. Atwood, *Organometallics* 19 (2000) 4416.
- [11] (a) K.S. Chong, S.J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* 59 (1981) 94;
(b) M.S. Hill, D.A. Atwood, *Eur. J. Inorg. Chem.* (1998) 67;
(c) Y.-Z. Shen, Y. Pan, L.-Y. Wang, G. Dong, X.-P. Jin, X.-Y. Huang, H. Hu, *J. Organomet. Chem.* 590 (1999) 242.
- [12] M.S. Hill, D.A. Atwood, *Main Group Chem.* 2 (1998) 191.
- [13] The synthesis of compound **5**: M. Sánchez, H. Höpfl, M.E. Ochoa, N. Farfan, R. Santillan, S. Rojas, *Inorg. Chem.* 40 (2001) 6405.
- [14] H. Höpfl, *J. Organomet. Chem.* 581 (1999) 129.
- [15] P.V.R. Schleyer, G. Subramanian, H. Jiao, K. Najafian, M. Hofmann, in: W. Siebert (Ed.), *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, 1977, p. 3.
- [16] C.H. Chang, R.F. Porter, S.H. Bauer, *Inorg. Chem.* 8 (1969) 1689.
- [17] S.H. Bauer, J.Y. Beach, *J. Am. Chem. Soc.* 63 (1941) 1394.
- [18] R. Boese, M. Polk, D. Blaser, *Angew. Chem. Int. Ed. Engl.* 26 (1987) 245.
- [19] C.P. Brok, R.P. Minton, K. Nieddenzu, *Acta Crystallogr.* C43 (1987) 1775.
- [20] M.A. Beckett, G.C. Strickland, K.S. Varma, D.E. Hibbs, M.B. Hursthouse, K.M.A. Malik, *J. Organomet. Chem.* 535 (1997) 33.
- [21] Z. Otwinowski, W. Minor, *Methods Enzymol.* 276 (1997) 307.
- [22] Bruker Analytical X-ray Structures, SAINT-NT Version 6.0A, 1999.