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Preparation of Seven- and Eight-Membered Boron Heterocycles from Different Salen Ligands and Arylboronic Acids

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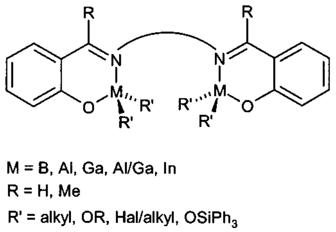
Arylboronic acids and different salen ligands have been brought to reaction in a 2:1 stoichiometry in ethanol, toluene, and acetonitrile. In all cases bimetallic boronates with chiral boron atoms could be isolated with the difference that in ethanol mostly open bimetallic boronic esters are obtained, while in toluene or acetonitrile closed bimetallic complexes with a central seven- or eight-membered heterocyclic ring are formed. Both structural types have been characterized by spectroscopic techniques and X-ray crystallography showing that the reactions are diastereoselective in the case of the bimetallic heterocyclic structures. The configurations and conformations of the seven- and eight-membered rings are different, and this may depend on steric effects and/or repulsive intramolecular $\pi-\pi$ interactions between the two salicylidene moieties attached to the central ring.

Introduction

The coordination chemistry of salen ligands with transition metal atoms has been studied extensively for many years[1] and some of the complexes already have some interesting applications, e.g., in catalytic oxidation reactions[2] and simulation of metalloenzyme-mediated catalysis.[3] Therefore, it is somewhat surprising that the coordination behavior of salen ligands with main group elements has not received much attention until recently.[4−10] An explanation might be the observation that much of the chemistry, especially with the heavier main group metals, parallels the observations with the transition metal series. Nevertheless, the coordination chemistry of some main group elements can be quite different, e.g., the group 13 elements boron, aluminum, gallium, and indium form readily bimetallic complexes with two of these elements ligated by only one ligand (Scheme 1).[6−7,11]

Scheme 1. Schematic Representation of Bimetallic Complexes between Salen Ligands and Group 13 Elements[a]



[a] More detailed representations can be seen in ref 11.

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(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) (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.

(3) Berkessel, A.; Bolte, M.; Griesinger, C.; Huttner, G.; Neumann, T.; Schiemenz, B.; Schwalbe, H.; Schwenkreis, T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1777.

(4) Complexes with group 14 elements: (a) Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Daltons Trans.* **1972**, 2003. (b) Parr, J.; Ross, A. T.; Slawin, A. M. Z. *J. Chem. Soc., Dalton Trans.* **1996**, 1509. (c) Teoh, S.-G.; Yeap, G.-Y.; Loh, C.-C.; Goong, L.-W.; Teo, S.-B.; Fun, H.-K. *Polyhedron* **1997**, *16*, 2213. (d) Agustin, D.; Rima, G.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **1999**, *592*, 1. (e) Mucha, F.; Haberecht, J.; Böhme, U.; Roewer, G. *Monatshefte. Chem.* **1999**, *130*, 117. (f) Singh, M. S.; Singh, P. K. *Main Group Met. Chem.* **2000**, *23*, 183.

(5) Complexes with group 15 elements: Agustin, D.; Rima, G.; Gornitzka, H.; Barrau, J. *Organometallics* **2000**, *19*, 4276.

(6) Bimetallic complexes with group 13 elements except boron: (a) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 2540. (b) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2093. (c) Hill, M. S.; Wei, P.; Atwood, D. A. *Polyhedron* **1998**, *17*, 811. (d) Van Aelstyn, M. A.; Keizer, T. S.; Klopotek, D. L.; Liu, S.; Muñoz-Hernández, M.-A.; Wei, P.; Atwood, D. A.; *Organometallics* **2000**, *19*, 1796.

(7) Bimetallic complexes with boron: (a) Hohaus, E. *Fresenius Z. Anal. Chem.* **1983**, *315*, 696. (b) Atwood, D. A.; Jegier, J. A.; Remington, M. J.; Rutherford, D. *Aust. J. Chem.* **1996**, *49*, 1333. (c) Wei, P. Atwood, D. A. *Inorg. Chem.* **1997**, *36*, 4060. (d) Wei, P., Atwood, D. *Chem. Commun.* **1997**, 1427. (e) Wei, P.; Keizer, T.; Atwood, D. A. *Inorg. Chem.* **1999**, *38*, 3914.

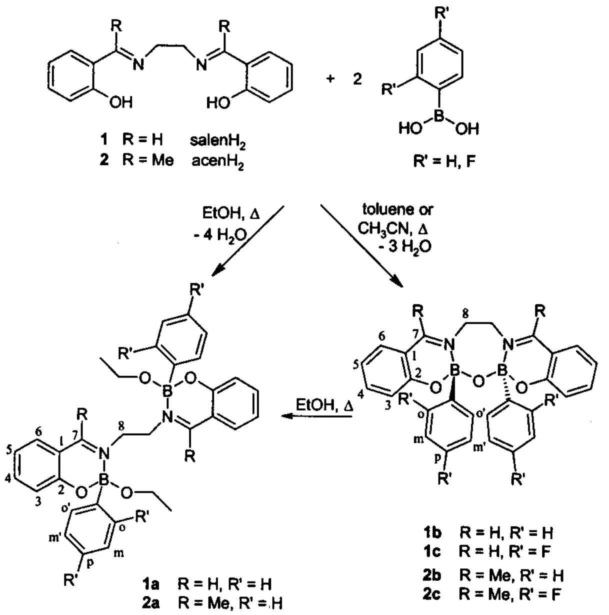
(8) Monometallic complexes with aluminium: (a) Gurian, P. L.; Cheatham, L. K.; Ziller, J. W.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1991**, 1449. (b) Rutherford, D.; Atwood, D. A. *Organometallics* **1996**, *15*, 4417. (c) Muñoz-Hernández, M.-A.; Sannigrahi, B.; Atwood, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 6747. (d) Muñoz-Hernández, M. A.; Keizer, T. S.; Parkin, S.; Patrick, B.; Atwood, D. A. *Organometallics* **2000**, *19*, 4416.

(9) Monometallic complexes with gallium: (a) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1981**, *59*, 94. (b) Hill, M. S.; Atwood, D. A. *Eur. J. Inorg. Chem.* **1998**, 67. (c) Shen, Y.-Z.; Pan, Y.; Wang, L.-Y.; Dong, G.; Jin, X.-P.; Huang, X.-Y.; Hu, H. *J. Organomet. Chem.* **1999**, *590*, 242 and ref 6a.

(10) Monometallic complexes with indium: Hill, M. S.; Atwood, D. A. *Main Group Chem.* **1998**, *2*, 191.

10.1021/ic010580g CCC: $20.00

Scheme 2. Preparation of the Boron Complexes **1a**−**c** and **2a**−**c** from SalenH$_2$ and AcenH$_2$



While in the case of the boron atom so far only bimetallic complexes are known,[7] the heavier elements aluminum,[6,8] gallium,[6,9] and indium[6,10] form also monometallic complexes. Bimetallic compounds could be interesting for applications in catalysis[6d] and might be used for further reactions with other ligands or other metal complexes. However, with exception of the preparation of a macrocyclic derivative,[7e] this chemistry has not been explored so far.

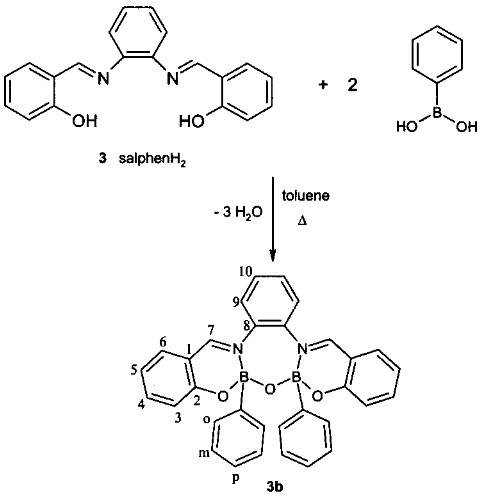
Continuing with our studies on the preparation of air-stable boron compounds with a coordinative N→B bond,[12] in this contribution we report for the first time on the synthesis as well as spectroscopic, structural, and conformational characterization of several seven- and eight-membered boron heterocyclic compounds that have been prepared from different salen ligands and arylboronic acids.

Results and Discussion

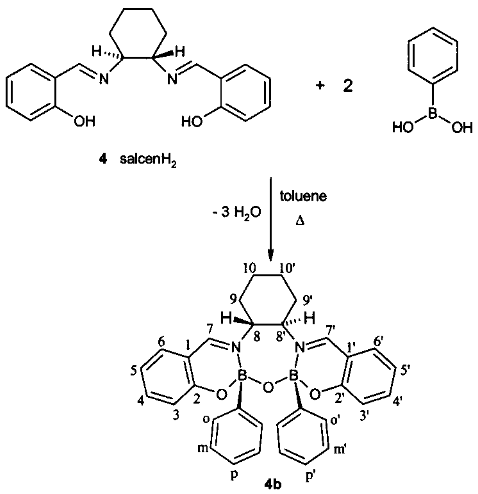
Synthesis and Spectroscopic Characterization. The preparation of the bimetallic salen complexes described here is based on condensation reactions between the corresponding ligand and an arylboronic acid. The syntheses of the boron complexes are shown in Schemes 2−6.

Two different products can be obtained, depending on the ligand and solvent used for the reaction. In ethanol, bimetallic complexes similar to the ones reported by Hohaus,[7a] Atwood,[7b−e] and Barrau[5] are formed with salenH$_2$, acenH$_2$ (Scheme 2), and acpenH$_2$ (Scheme 6), while in toluene or acetonitrile heterocycles with a central seven- or eight-membered C$_n$B$_2$N$_2$O ($n =$

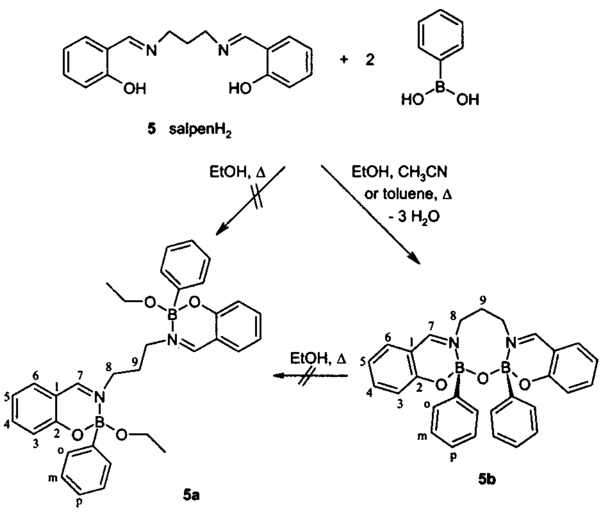
Scheme 3. Preparation of the Boron Complex **3b** from SalphenH$_2$



Scheme 4. Preparation of the Boron Complex **4b** from SalcenH$_2$



Scheme 5. Preparation of the Boron Complex **5b** from SalpenH$_2$



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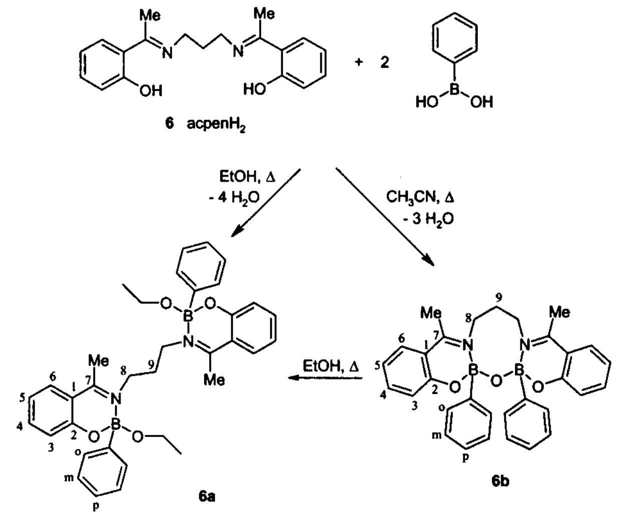
(11) Atwood, D. A.; Harvey, M. J. *Chem. Rev.* **2001**, *101*, 37.

(12) See for example: (a) Höpfl, H.; Farfán, N.; Castillo, D.; Santillan, R.; Contreras, R.; Martínez-Martínez, F.; Galván, M.; Alvarez, R.; Fernández, L.; Halut, S.; Daran, J.-C. *J. Organomet. Chem.* **1997**, *544*, 175. (b) Höpfl, H.; Farfán, N. *J. Organomet. Chem.* **1997**, *547*, 71. (c) Höpfl, H., Galván, Farfán, N.; Santillan, R. *J. Mol. Struct. THEOCHEM* **1998**, *427*, 1. (d) Höpfl, H.; Sánchez, M.; Farfán, N. *Can. J. Chem.* **1998**, *76*, 1352. (e) Höpfl, H.; Farfán, N. *Can. J. Chem.* **1998**, *76*, 1853. (f) Höpfl, H.; Sánchez, M.; Barba, V.; Farfán, N., Rojas, S.; Santillan, R. *Inorg. Chem.* **1998**, *37*, 1679. (g) Höpfl, H.; Farfán, N.; Castillo, D.; Santillan, R.; Gutierrez, A.; Daran, J.-C. *J. Organomet. Chem.* **1998**, *553*, 221. (h) Trujillo, J.; Höpfl, H.; Castillo, D.; Santillan, R.; Farfán, N. *J. Organomet. Chem.* **1998**, *571*, 21. (i) Farfán, N.; Höpfl, H.; Barba, V.; Ochoa, M. E.; Santillan, R.; Gómez, E.; Gutiérrez, A. *J. Organomet. Chem.* **1999**, *581*, 70. (j) Farfán, N.; Santillan, R.; Höpfl, H. *Main Group Chem. News* **1999**, *7*, 3. (k) Barba, V.; Cuahutle, D.; Ochoa, M. E.; Santillan, R.; Farfán, N. *Inorg. Chim. Acta* **2000**, *303*, 7. (l) Barba, V.; Luna, R.; Castillo, D.; Santillan, R.; Farfán, N. *J. Organomet. Chem.* **2000**, *604*, 273.

Scheme 6. Preparation of the Boron Complexes **6a**−**6b** from AcpenH$_2$



2, 3) ring are isolated. However, the seven-membered heterocycles **1b** and **2b** outlined in Scheme 2 can be transformed to the open bimetallic boron esters **1a** and **2a**, respectively, by heating them in ethanol. With salphenH$_2$ **3**, salcenH$_2$ **4**, and salpenH$_2$ **5**, this alcoholic hydrolysis is not possible and only closed heterocycles can be isolated, even if the boron complexation is realized in ethanol (Schemes 3−5).

All complexes obtained are stable under normal air conditions but decompose in solution partially to polymeric material. In general, the closed complexes seem to be more stable in solution, especially the eight-membered heterocycles (vide infra), since smaller quantities of decomposition products are observed in the NMR spectra.

In the case of acphenH$_2$ and accenH$_2$ with a methyl group at the imine function, boron complexation is inhibited most probably for steric reasons, since no reaction occurred with these ligands. This destabilizing effect can be also seen, if the boron complexation with salpenH$_2$ **5** and acpenH$_2$ **6** is compared. While in the former case only the closed heterocyclic derivative **5b** is obtained in either ethanol, toluene, or acetonitrile (Scheme 5), in the latter case both the open and closed bimetallic complex (**6a**, **6b**) can be prepared (Scheme 6).

Although the formulas of the open and corresponding closed bimetallic boron complexes are similar, their physical properties are quite different. The open compounds have lower melting points and are quite soluble in organic solvents such as toluene, chloroform, ethers, and alcohols. In contrast, the closed complexes have high melting points (often more than 300 °C) and are quite insoluble.

All boron complexes obtained in this study have been characterized as far as possible by spectroscopic techniques (IR and ^{1}H, ^{13}C, ^{11}B NMR) and mass spectrometry. The formation of a coordinative N→B boron bond could be confirmed by the characteristic shift displacement of the imine hydrogen or imine methyl group[12d,e] as well as by the appearance of diastereotopic NCH$_2$ hydrogens due to the chirality of the tetracoordinated boron atoms. The bidentate complexation was confirmed in some cases by ^{11}B NMR spectroscopy that is sensitive to the coordination sphere of the boron atom.[13]

Due to the complexation of two chiral boron atoms, two diastereomers with their corresponding enantiomers should be formed in all cases. Nevertheless, this happens only for the open bimetallic complexes **1a**, **2a**, and **6a**, while in the case of the seven- and eight-membered heterocycles **1b**, **1c**, **2b**, **2c**, **3b**, **4b**, **5b**, and **6b** only one diastereomer could be isolated. The formation of diastereomers can be easily deduced from ^{1}H and ^{13}C NMR spectroscopic data, since two methylene groups, two imino groups, and two B-ethoxy groups can be distinguished in the spectra of **1a** and **2a**. In the first case, one diastereomer is produced in higher yields than the other one (approximately 1.5:1), while in the latter case the stoichiometric proportion is about 1:1. For compound **6a**, the shift differences for the two diastereomers are smaller and almost undistinguishable due to the presence of three methylene groups between the imine functions. As already mentioned, the closed bimetallic heterocycles **1b**, **1c**, **2b**, **2c**, **3b**, **4b**, **5b**, and **6b** have been synthesized diastereoselectively, since in each case only signals for one diastereomer could be detected. However, the spectroscopic data do not permit prediction of which of the two possible diastereomers (*cis* or *trans* with respect to the B-phenyl group) has been formed. One reason is that both have molecular symmetry. The *SS*/*RR* enantiomeric pairs with *trans*-configuration of the B-aryl groups have C_2 symmetry, while the *RS*/*SR* mesomeric form with *cis*-configuration has a molecular plane. The only exception from this consideration is compound **4b**, with two additional stereogenic centers. For this molecule there should exist finally three diastereomers with their corresponding enantiomers as outlined in Scheme 7. The *RR*/*SS*-*trans* isomers have C_2-symmetry, while the *RS*/*SR*-*cis* isomers are completely unsymmetrical. Therefore, on the basis of NMR data it is here possible to differentiate between these two classes of diastereomers. Both in the ^{1}H and ^{13}C NMR spectrum, signals for an unsymmetrical molecule are observed, so that the configuration of the B-aryl groups in compound **4b** must be *cis*.

Structural Characterization. To determinate which diastereomer is preferred in the case of the other seven- and eight-membered heterocycles, an X-ray crystallographic study has been undertaken for compounds **1c**, **2c**, and **5b**. Furthermore, the molecular structures of compounds **1a** and **6a** have been determined. Crystallographic data as well as selected bond lengths, bond angles, and torsion angles have been summarized in Tables 1 and 2.

Figure 1 shows the molecular structure of the open bimetallic complex **1a**. Surprisingly, the molecule has a *gauche*-conformation in the solid state with a NCCN torsion angle of 67.9°. The preference of this conformation may be explained by the formation of intramolecular hydrogen bonds between the imino hydrogens and the oxygen atoms of the corresponding adjacent BOEt functional groups (2.33 and 2.41 Å), an interaction that would not be possible in the *anti*-conformation. A similar interaction has been also reported by Atwood.[7c] As observed already in related structure types,[12f] the mean B−O$_{ph}$ bond length is significantly longer than the mean B−OEt bond length (1.495(6) Å ↔ 1.436(6) Å). The N→B bond with a length of 1.616(6) Å is relatively strong.[14]

Figures 2 and 3 show the molecular structures of the closed bimetallic seven-membered heterocycles **1c** and **2c,** and apparently in both cases the trans-configurated heterocycle is formed preferentially. The central seven-membered heterocycle has a conformation in which the imino groups are displaced significantly out of the mean plane formed by the other five atoms (0.720 Å for **1c** and 0.760 Å for **2c**). In compound **1c**, the maximum deviation of this mean plane is only 0.015 Å (for

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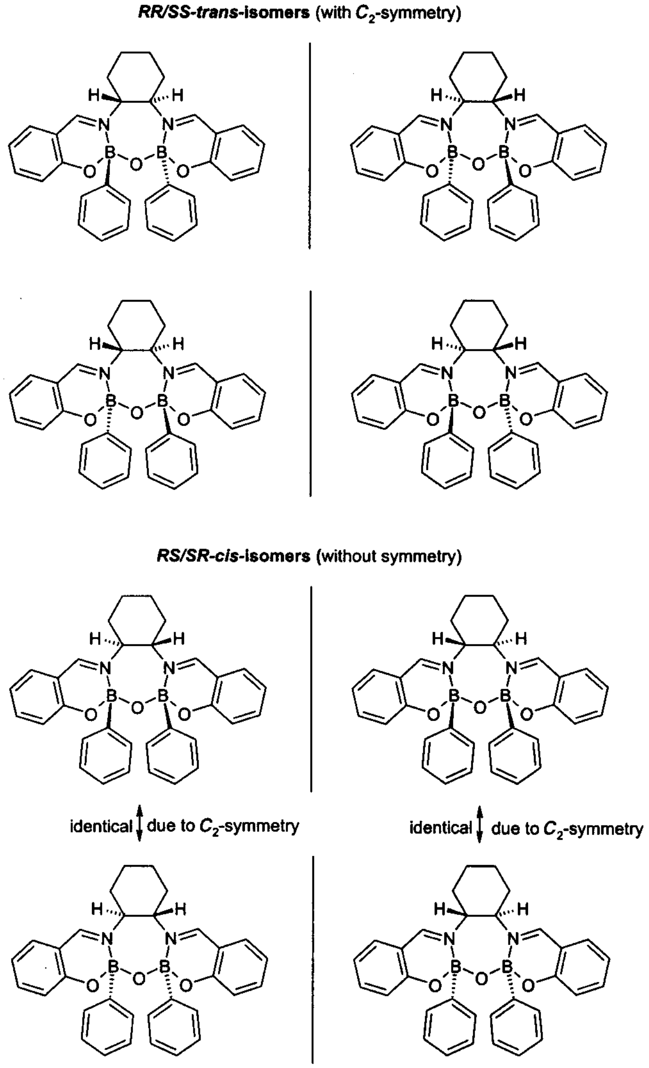
(13) Nöth, H.; Wrackmeyer, B. *NMR Basic Principles and Progress;* Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin 1978; Vol. 14.

(14) Höpfl, H. *J. Organomet. Chem.* **1999**, *581*, 129.

Scheme 7. Possible Stereoisomers for Compound **4b**[a]



[a] According to the presence of four stereogenic centers there should exist $2^4/2$ stereoisomers, because only the 1,2-*trans*-cyclohexylene derivative was used. However, there are only three different diastereomers with their corresponding enantiomers, because two of the possible four diastereomers are identical. Two of the three diastereomers have C_2-symmetry, while the third is completely asymmetrical. NMR studies proved that only this diastereomer (*RS/SR-cis*-isomer) is obtained.

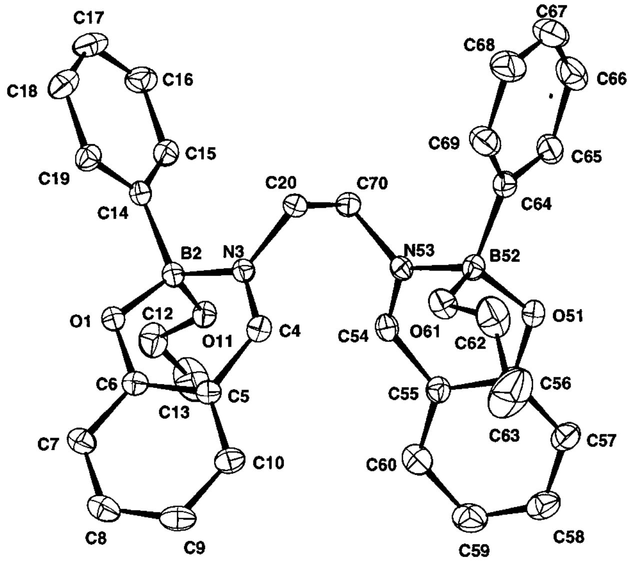


Figure 1. Perspective view of the molecular structure of compound **1a**.

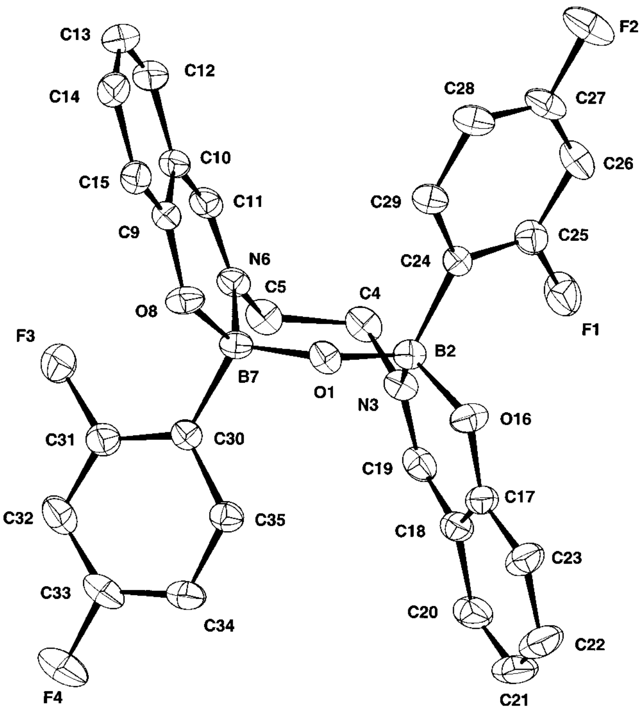


Figure 2. Perspective view of the molecular structure of compound **1c**.

atom O1), while in compound **2c** this plane is completely planar due to the fact that the molecules are located on crystallographic C_2-axes in the crystal lattice. As in the case of compound **1b**, the two types of B−O bond lengths are significantly different. The mean B−O bond lengths with the bridging oxygen atoms are 1.415(2) and 1.411(6) Å for **1c** and **2c**, respectively, and the mean $B-O_{Ph}$ bond lengths are 1.499(2) and 1.490(5) Å, respectively. The corresponding $N \rightarrow B$ bond lengths are 1.612(2) and 1.626(6) Å. The B−O−B bond angles are 135.4(1)° and 137.8(5)° for **1c** and **2c**, respectively; however, such large B−O−B bond angles are not uncommon, and similar values have been measured for a series of other boron compounds.[15] If the tetrahedral geometry of the boron atoms is compared between **1a** and **1c**, it is interesting to notice that it is more perfect in the closed bimetallic complex than in the open one. The values of the mean tetrahedral characters[14] are 74.2% and 87.1%, respectively. The main contribution to this observation results from a different $N-B-O_{B/Et}$ bond angle with a mean value of 102.6(4)° for **1a** in contrast to a mean value of 110.0(1)° for **1c**. The mean displacement of the boron atoms from the mean plane of the six-membered salicylidene heterocycles (aromatic part) is larger for **1a** (0.634 Å) than for **1c** (0.239 Å). The mean torsion angles in the seven-membered heterocycles are quite different and vary in the case of **1c** from 28.6° for the NBOB bonds to 75.9° for the $B-N-CH_2-CH_2$ bonds. The corresponding values for compound **2c** are between 28.1° and 80.0°.

Figures 4 and 5 show the molecular structures of the eight-membered $C_3B_2N_2O$ heterocycle **5b** and the related open bimetallic complex **6a**. The X-ray study demonstrates that in the case of the eight-membered heterocycle the *cis*-configuration is preferred over the *trans*-configuration. Therefore, in this case

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(15) Höpfl, H.; Barba, V.; Vargas, G.; Farfán, N.; Santillan, R.; Castillo, D. *Chem. Heterocycl. Compounds* **1999**, *386*, 1041, and references therein.

Table 1. Crystallographic Data for Compounds 1a, 1c, 2c, 5b, and 6a

crystal data	**1a**[a]	**1c**[b]	**2c**[b]	**5b**[c]	**6a**[b]
formula	$C_{32}H_{34}B_2N_2O_4$	$C_{28}H_{20}B_2F_4N_2O_3$	$C_{30}H_{24}B_2F_4N_2O_3$	$C_{29}H_{26}B_2N_2O_3$	$C_{35}H_{40}B_2N_2O_4$
crystal size (mm)	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.4	0.3 × 0.4 × 0.4	0.2 × 0.3 × 0.3	0.1 × 0.3 × 0.5
MW (g mol^{-1})	532.26	530.08	558.15	472.16	574.31
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$Pna2_1$
			Cell Parameters		
a (Å)	13.985(1)	9.7350(4)	28.597(2)	10.150(3)	17.784(4)
b (Å)	13.831(1)	21.4186(9)	13.0190(7)	19.230(5)	7.965(2)
c (Å)	15.298(1)	12.1635(5)	20.315(1)	12.250(3)	23.028(5)
α (deg)	90	90	90	90	90
β (deg)	97.573(9)	100.936(1)	132.896(1)	95.600(13)	90
γ (deg)	90	90	90	90	90
V (Å^3)	2933.3	2490.2	5540.8	2379.6	3261.8
Z	4	4	8	4	4
μ (mm^{-1})	0.073	0.111	0.103	0.084	0.075
ρ_{calcd} (g cm^{-3})	1.21	1.41	1.34	1.32	1.17
			Data Collection		
θ limits (deg)	$2 < \theta < 24$	$2 < \theta < 26$	$2 < \theta < 25$	$2 < \theta < 25$	$2 < \theta < 25$
hkl limits	15, 0; 0, 15; 17, 17	11, 12; 24, 26; 15, 13	35, 27; 16, 16; 24, 25	12, 12; 23, 24; 15, 14	21, 18; 7, 9; 27, 25
no. collected refl	5427	16431	18378	5213	19159
no. ind. refl. (R_{int})	3033 (0.02)	4888 (0.04)	5429 (0.02)	5047 (0.03)	5398 (0.09)
no. observed refl	1882[d]	2722[e]	2159[d]	2702[e]	1820[e]
			Refinement		
R	0.045[f]	0.040[g]	0.044[f]	0.056[f]	0.046[g]
R_w	0.041[h]	0.098[i]	0.040[h]	0.060[h]	0.106[i]
w	$1/\sigma^2$	[j]	$1/\sigma^2$	$1/\sigma^2$	[k]
no. of variables	362	352	373	402	369
GOOF	0.80	0.85	1.15	3.71	0.75
$\Delta\rho_{min}$ (e Å^{-3})	0.18	0.18	0.13	0.21	0.10
$\Delta\rho_{max}$ (e Å^{-3})	0.17	0.14	0.17	0.24	0.11

[a] Data collection on an Enraf Nonius CAD4 diffractometer. [b] Data collection on a Bruker Smart 6000 diffractometer. [c] Data collection on a Rigaku Mercury diffractometer. [d] $I > 3\sigma(I)$. [e] $F_o > 4\sigma(F_o)$. [f] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [g] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$. [h] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [i] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [j] $w^{-1} = \sigma^2F_o^2 + (0.0511P)^2 + 0.00P$; $P = (F_o^2 + 2F_c^2)/3$. [k] $w^{-1} = \sigma^2F_o^2 + (0.0358P)^2 + 0.00P$; $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths, Bond Angles, and Torsion Angles for Compounds **1a**, **1c**, **2c**, **5b**, and **6a**[a]

	1a	**1c**	**2c**	**5b**	**6a**
		Bond Lengths (Å)			
N−B	1.616(6)	1.612(2)	1.626(6)	1.636(3)	1.611(7)
$B-O_{Ph}$	1.495(6)	1.499(2)	1.490(5)	1.502(3)	1.459(8)
$B-O_{Et}/B-O_B$	1.436(6)	1.415(2)	1.411(6)	1.420(3)	1.444(6)
B−C	1.595(7)	1.623(2)	1.627(6)	1.607(4)	1.610(7)
C═N	1.290(5)	1.287(2)	1.303(5)	1.290(3)	1.286(6)
$N-CH_2$	1.473(5)	1.466(2)	1.478(5)	1.477(3)	1.467(5)
CH_2-CH_2	1.529(6)	1.507(2)	1.528(8)	1.523(4)	1.527(6)
$O-CH_2$	1.417(6)				1.428(6)
OCH_2-CH_3	1.415(7)				1.414(8)
		Bond Angles (deg)			
$N-B-O_{Ph}$	105.1(4)	107.2(1)	107.3(4)	106.7(2)	107.3(5)
O−B−O	112.5(4)	109.4(2)	110.2(4)	112.1(2)	112.6(5)
N−B−C	111.0(4)	109.1(1)	109.5(4)	108.3(2)	112.3(5)
$N-B-O_{Et}/N-B-O_B$	102.6(4)	110.0(1)	110.0(4)	109.4(2)	102.5(4)
$O_{Ph}-B-C$	108.9(4)	107.3(1)	105.6(4)	108.7(2)	108.5(5)
$O_{Et}-B-C/O_B-B-C$	116.3(5)	113.8(1)	114.0(4)	111.7(2)	113.6(5)
B−N═C	119.3(4)	122.2(2)	123.2(4)	122.7(2)	123.1(5)
$B-N-CH_2$	121.8(4)	118.8(4)	115.1(4)	118.9(2)	115.7(5)
$B-O-C_{Ph}$	117.7(4)	124.0(2)	122.5(4)	126.0(2)	122.4(5)
$N-CH_2-CH_2$	110.1(4)	113.0(2)	111.3(3)	114.1(2)	114.6(4)
$B-O-CH_2/B-O-B$	117.9(4)	135.4(1)	137.8(5)	134.6(2)	117.6(4)
$CH_2-CH_2-CH_2$				115.9(2)	107.8(3)
		Torsion Angles (deg)			
N−C−C−N	67.9	63.0	67.8		
$N-CH_2-CH_2-CH_2$				59.1	178.8
$B-N-CH_2-CH_2$	74.5	75.9	80.0	54.4	101.9
$O_B-B-N-CH_2$		74.5	73.1	63.3	
B−O−B−N		28.6	28.6	51.1	
$C-B-N-CH_2$	31.2	51.0	52.9	58.2	46.7

[a] Mean values in all cases.

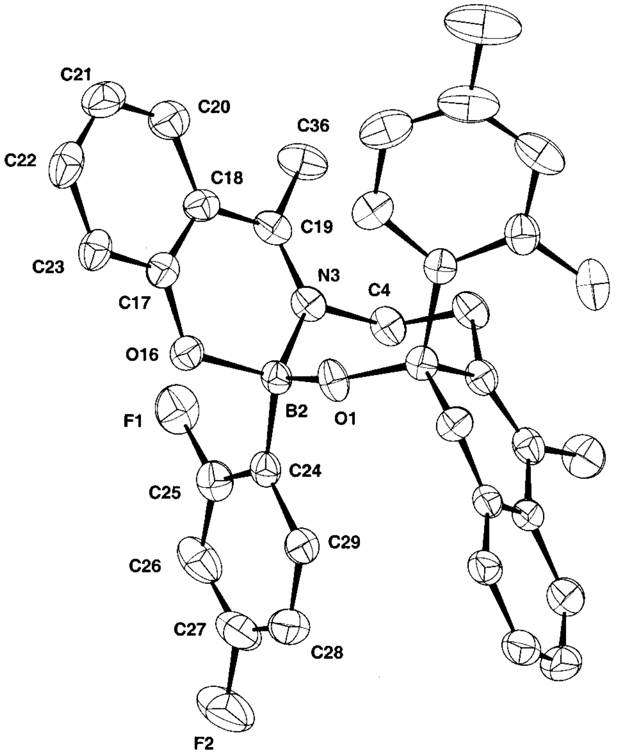

Figure 3. Perspective view of the molecular structure of compound **2c**.

a boat conformation is formed, again with the two imino-nitrogen atoms at the bow/stern positions. There may be an intramolecular C−H···O interaction, since the C18−H···O2 distance is only 2.39 Å (C18−H···O2, 110.4°), a value that is significantly smaller than the sum of the van der Waals radii of oxygen and hydrogen (2.70 Å).[16]

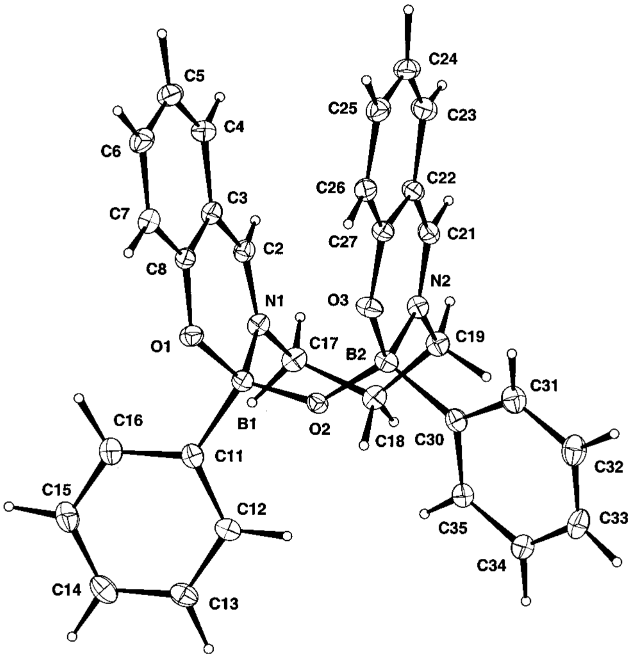

Figure 4. Perspective view of the molecular structure of compound **5b**.

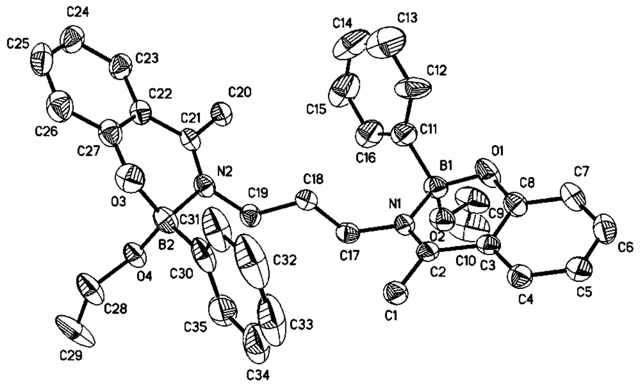

Figure 5. Perspective view of the molecular structure of compound **6a**.

Due to the *cis*-configuration of the eight-membered heterocycle **5b**, the two salicylidene groups are orientated nearly parallel to each other, but it is important to notice that they are not superposable as it would be the case for a molecule with mirror symmetry. The distance between the centroids of the aromatic rings is 3.90 Å, a distance that is longer than the sum of the van der Waals radii of two carbon atoms (3.4−3.6 Å).[16] Therefore, there should be no transannular $\pi-\pi$ interaction.[17] Again, in this case the mean B−O bond length with the phenolic oxygen atoms is much larger (1.502(3) Å) than the mean B−O bond length with the bridging oxygen (1.420(3) Å). The two N→B bonds are significantly different, 1.621(3) and 1.650(3) Å. The B−O−B bond angle with a value of 134.6(2)° is comparable to the ones found for the seven-membered heterocycles **1c** and **2c**. Furthermore, it is noteworthy that the C−C−C bond angle that is located opposite to the BOB bond angle in the heterocycle has an unusually large value of 115.9(2)°. The torsion angles in the eight-membered heterocycle are within a smaller range than in the former case and have values from 51.1° for the B−O−B−N bonds to 63.3° for the O−B−N−CH_2 bonds. This observation may indicate a higher thermodynamic stability of the eight-membered heterocycle when compared to the seven-membered one and is confirmed by the fact that the latter one can be hydrolyzed with ethanol, while the former one cannot (Schemes 2 and 5). The mean deviation of the boron atoms from the aromatic mean planes of the salicylidene moieties is 0.149 Å.

The conformation of the open derivative **6a** is *anti*. Surprisingly, in this case there is no significant length difference between the two types of B−O bonds. The mean values for the $B-O_{Ph}$ and B−OEt bond lengths are 1.459(8) and 1.444(6) Å. As in the case of the eight-membered heterocycle, the N→B bond lengths are significantly different, 1.589(6) and 1.632(7) Å. The mean tetrahedral character for the boron atoms is 77.5%, whereby the bond angle with the largest deviation from the ideal tetrahedral angle is the $NBO_{B/Et}$ bond angle with a mean value of 102.5 (4)°, as was the case for compound **1a**. For comparison, the mean $NBO_{B/Et}$ bond angle in compound **5b** is 109.4(2)° and the tetrahedral character is 88%. The mean deviation of the boron atom from the aromatic mean planes of the salicylidene moieties is 0.390 Å.

Unfortunately, we were not able to obtain single crystals for the bimetallic salphenH_2 and acpenH_2 derivatives **3b** and **6b** in order to establish their preferred configuration. According to molecular modeling, both configurations may be possible in either case, but our NMR data indicate only the formation of one diastereomer.

Conclusions

This contribution reports to the best of our knowledge for the first time on the formation of seven- and eight-membered bimetallic heterocycles from ligands of the salen type. It could be shown that both types of heterocycles are held together by two strong N→B bonds that induce a fixed conformation. For the seven-membered heterocycle with an ethylene bridge between the two imino groups, the preferred configuration is *trans* and the conformation is a practically undistorted chair with five atoms forming the central plane. If the ethylene bridge is substituted by a *trans*-1,2-cyclohexenyl bridge, the *cis*-configuration is preferred. In the case of a 1,2-phenylene unit, it is difficult to make a prediction without a crystallographic study. In boron complexes with an eight-membered heterocycle, the *cis*-configuration and boat conformation seem to be favored. As shown by the X-ray crystallographic study, they are probably more stable than the seven-membered derivatives. The reasons that different configurations and conformations are obtained for the two structure types are not clear; however, it can be shown by molecular modeling that in a *cis*-configured, seven-membered heterocycle the proximity between the two salicylidene moieties would be repulsive, due to $\pi-\pi$ interactions.

Experimental Section

Instrumental. NMR studies were carried out with Bruker 300, JEOL 270, and JEOL Eclipse+400 instruments. Standards were TMS (^{1}H, ^{13}C) and $BF_3{\cdot}OEt_2$ (^{11}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 in order to assign the ^{1}H and ^{13}C spectra completely. IR spectra were recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on a HP 5989 A equipment. Elemental analyses have been carried out on a Perkin-Elmer Series II 2400 instrument. It should be mentioned that elemental analyses of boronic

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(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(17) Glówka, M. L.; Martynowski, D.; Kozlowska, K. *J. Mol. Struct.* **1999**, *474*, 81, and references therein.

acid derivatives are complicated by incombustible residues (boron carbide) and therefore not always in the established limits of exactitude.[18]

X-ray Crystallography. X-ray diffraction studies of single crystals were realized on Enraf Nonius CAD4, Bruker Smart 6000 and Rigaku Mercury diffractometers ($\lambda_{\text{Mo K}\alpha} = 0.71069$ Å, monochromator: graphite, $T = 293$ K). Cell parameters were determined by least squares refinements on diffractometer angles for 24 automatically centered reflections or using reflections collected on three sets of 20 frames each. Absorption correction was not necessary; corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86)[19] for structure solution and the SHELXTL[20−22] (**1c** and **6a**) or CRYSTALS[23−25] (**1a**, **2c** and **5b**) software package for refinement and data output. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in all cases with the exception of **5b**, and one overall isotropic thermal parameter was refined. In the case of **5b**, the hydrogen atoms were determined with difference Fourier maps and their coordinates were refined. In general, a reflection−parameter ratio of 5 has been considered sufficient for the type of structural studies performed here. The most important crystallographic data have been summarized in Table 1. In the case of compound **2c**, the molecules are located at special positions (C_2-axis) in the crystal lattice and there are two independent molecule halves in the asymmetric unit. The B-phenyl groups in **6a** are slightly disordered, so that their bond lengths and bond angles were restrained to 1.390 Å and 120.0°.

Preparative Part. Commercial starting materials and solvents have been used. Ligands **1**−**6** are known Schiff bases and have been prepared according to refs 12b and 12f.

Preparation of Boronates 1a−c. Compound **1a** was prepared from salenH$_2$ **1** (0.50 g, 1.86 mmol) and phenylboronic acid (0.45 g, 3.72 mmol) in ethanol (30 mL). After 30 min of reflux the solution was concentrated with a Dean−Stark trap. A yellow precipitate formed that was filtered under vacuum and dried. Crystals were obtained after recrystallization from ethanol. Two diastereomers are obtained in a ratio of approximately 1.5:1. The product decomposes more or less rapidly in other organic solvents to polymeric material. Yield: 89%. Mp: 180−182 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS) of the mayor product: $\delta = 1.14$ (t, 6 H, CH$_3$), 3.18 and 3.52 (AB, 4 H, NCH$_2$), 3.76 (m, 4 H, OCH$_2$), 6.41 (m, 2 H, H-5), 6.80 (m, 2 H, H-3), 7.10 (m, 4 H, H-4, H-6), 7.34 (m, 2 H, p-BC$_6$H$_5$), 7.45 (m, 4 H, m-BC$_6$H$_5$), 7.80 (m, 4 H, o-BC$_6$H$_5$), 8.34 (s, 2 H, N═CH) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 18.6$ (CH$_3$), 54.6 (N−CH$_2$), 57.3 (OCH$_2$), 117.0, 118.5 (C-1, C-5), 119.4 (C-3), 127.7 (m-BC$_6$H$_5$, p-BC$_6$H$_5$), 131.5 (C-6), 133.3 (o-BC$_6$H$_5$), 137.2 (C-4), 161.0 (C-2), 165.4 (N═CH) ppm. IR (KBr): $\tilde{\nu} = 3046$ (w), 3005 (w), 2958 (w), 2864 (w), 1636 (s), 1609 (m), 1558 (m), 1479 (m), 1461 (m), 1433 (w), 1406 (w), 1315 (m), 1234 (m), 1197 (w), 1151 (s), 1136 (m), 1101 (m), 1063 (w), 1026 (w) cm^{-1}. MS (70 eV, EI), m/z (%): 487 (6) [M − OEt]$^+$, 455 (100) [M − C$_6$H$_5$]$^+$, 411 (31), 277 (19), 204 (17), 189 (15), 174 (14), 152 (26), 147 (14), 105 (25), 77 (11). Anal. Calcd (%) for C$_{32}$H$_{34}$B$_2$N$_2$O$_4$ (532.25): C, 72.21; H, 6.43; N, 5.26. Found: C, 71.01; H, 6.45; N, 5.47.

Compound **1b** was prepared from salenH$_2$ **1** (0.50 g, 1.86 mmol) and phenylboronic acid (0.45 g, 3.72 mmol) in toluene (10 mL). After 1 h of reflux, the solution was concentrated with a Dean−Stark trap. A yellow precipitate formed that was filtered under vacuum and dried. Yield: 94%. Mp: >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): $\delta = 3.50$ and 3.79 (AB, 4 H, N−CH$_2$), 6.92 (m, 10 H, H-3, H-5, m-BC$_6$H$_5$, p-BC$_6$H$_5$), 7.19 (dd, 4 H, o-BC$_6$H$_5$), 7.42 (dd, 2 H, H-6), 7.57 (dt, 2 H, H-4), 8.59 (s, 2 H, N═CH) ppm. ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C, TMS): $\delta = 56.2$ (NCH$_2$), 115.9 (C-1), 117.6 (C-5), 118.4 (C-3), 126.5 (m-BC$_6$H$_5$), 126.8 (p-BC$_6$H$_5$), 131.8 (o-BC$_6$H$_5$), 132.1 (C-6), 137.5 (C-4), 160.2 (C-2), 164.5 (N═CH) ppm. ^{11}B NMR (96.3 MHz, DMSO-d_6, 25 °C, BF$_3$·OEt$_2$): $\delta = 10$ ($h_{1/2} = 900$ Hz) ppm. IR (KBr): $\tilde{\nu} = 1638$ (s), 1608 (m), 1557 (m), 1479 (m), 1462 (m), 1431 (w), 1400 (w), 1317 (m), 1233 (m), 1198 (s), 1152 (m), 1138 (m), 1096 (w), 1028 (w) cm^{-1}. MS (70 eV, EI), m/z (%): 458 (0.2) [M]$^+$, 457 (0.9) [M − H]$^+$, 381 (100) [M − C$_6$H$_5$]$^+$, 305 (19), 248 (15), 234 (27), 152 (18), 77 (19). Anal. Calcd (%) for C$_{28}$H$_{24}$B$_2$N$_2$O$_3$ (458.14): C, 73.41; H, 5.28; N, 6.12. Found: C, 73.69; H, 5.39; N, 6.09.

Compound **1c** was prepared from salenH$_2$ **1** (0.50 g, 1.86 mmol) and 2,4-difluorophenylboronic acid (0.56 g, 3.72 mmol) in acetonitrile (20 mL). After 1 h of reflux the solution was concentrated with a Dean−Stark trap. A white precipitate formed that was filtered under vacuum and dried. Yield: 93%. Crystals were obtained from acetonitrile. Mp: >300 °C. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C, TMS): $\delta = 3.38$ and 3.90 (AB, 4 H, NCH$_2$), 6.38 (ddd, $J = 9$ and 2 Hz, 2 H, m'-BC$_6$H$_3$F$_2$), 6.77 (ddd, $J = 8$ and 2 Hz, 2 H, m-BC$_6$H$_3$F$_2$), 6.90 (m, 4 H, H-3, H-5), 7.24 (dd, $J = 16$ and 8 Hz, 2 H, o'-BC$_6$H$_3$F$_2$), 7.44 (dd, 2 H, H-6), 7.60 (dt, 2 H, H-4), 8.61 (s, 2 H, N═CH) ppm. ^{13}C NMR (67.5 MHz, DMSO-d_6, 25 °C, TMS): $\delta = 56.6$ (N−CH$_2$), 102.9 (dd, m-BC$_6$H$_3$F$_2$), 109.7 (dd, m'-BC$_6$H$_3$F$_2$), 116.5 (C-1), 118.6, 118.9 (C-3, C-5), 132.7 (C-6), 136.0 (dd, o'-BC$_6$H$_3$F$_2$), 138.3 (C-4), 160.3 (C-2), 162.4, 166.1 (dd, $J = 240$ and 11 Hz, o-BC$_6$H$_5$, p-BC$_6$H$_5$), 164.9 (N═CH) ppm. ^{11}B NMR (128.3 MHz, DMSO-d_6, 25 °C, BF$_3$·OEt$_2$): $\delta = 1.7$ ($h_{1/2} = 500$ Hz) ppm. IR (KBr): $\tilde{\nu} = 3063$ (w), 2957 (w), 1642 (s), 1603 (s), 1558 (s), 1484 (s), 1464 (s), 1448 (s), 1402 (s), 1358 (m), 1316 (s), 1284 (m), 1260 (m), 1237 (s), 1225 (s), 1171 (s), 1155 (s), 1138 (s), 1128 (s), 1113 (s), 1096 (m), 1077 (s), 1028 (m), 1012 (w), 1005 (w) cm^{-1}. MS (70 eV, EI), m/z (%): 530 (0.3) [M]$^+$, 417 (100) [M − C$_6$H$_3$F$_2$]$^+$, 415 (16), 323 (30), 304 (9), 277 (5), 270 (9). Anal. Calcd (%) for C$_{28}$H$_{20}$B$_2$F$_4$N$_2$O$_3$ (530.11): C, 63.44; H, 3.80; N, 5.28. Found: C, 63.96; H, 3.85; N, 4.82.

Preparation of Boronates 2a−c. Compound **2a** was prepared from acenH$_2$ **2** (0.50 g, 1.69 mmol) and phenylboronic acid (0.41 g, 3.38 mmol) in ethanol (30 mL). After 30 min of reflux the solution was concentrated with a Dean−Stark trap. A yellow precipitate formed that was filtered under vacuum and dried. Two diastereomers are obtained in a ratio of approximately 1:1. The product decomposes more or less rapidly in other organic solvents to polymeric material. Yield: 77%. Mp: 260−262 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS) for the mixture of the two diastereomers: $\delta = 1.06$ (m, 6 H, OCH$_2$CH_3), 2.34, 2.58 (s, 6 H, N═CCH_3), 3.17 and 3.33 (m, 4 H, OCH$_2$), 3.36−3.78 (m, 4 H, NCH$_2$), 6.83 (m, 4 H, H-3, H-5), 7.14 (m, 6 H, m-BC$_6$H$_5$, p-BC$_6$H$_5$), 7.36 (m, 4 H, o-BC$_6$H$_5$), 7.47 (m, 2 H, H-4), 7.74 (m, 2 H, H-6) ppm. IR (KBr): $\tilde{\nu} = 3066$ (w), 3043 (w), 3005 (w), 2968 (m), 2922 (w), 2862 (m), 1616 (s), 1555 (s), 1478 (m), 1458 (m), 1432 (m), 1384 (m), 1358 (m), 1334 (m), 1281 (m), 1235 (w), 1189 (m), 1172 (m), 1144 (m), 1107 (s), 1069 (m), 1022 (m) cm^{-1}; MS (70 eV, EI), m/z (%): 515 (1) [M − OEt]$^+$, 483 (14) [M − C$_6$H$_5$]$^+$, 437 (100), 391 (10), 305 (6), 248 (16), 216 (7), 203 (8), 188 (11), 166 (11), 146 (6), 105 (6). Anal. Calcd (%) for C$_{34}$H$_{38}$B$_2$F$_4$N$_2$O$_4$ (560.28): C, 72.88; H, 6.84; N, 5.00. Found: C, 72.82; H, 6.85; N, 5.02.

Compound **2b** was prepared from acenH$_2$ **2** (0.50 g, 1.69 mmol) and phenylboronic acid (0.41 g, 3.38 mmol) in acetonitrile (20 mL). After 1 h of reflux the solution was concentrated with a Dean−Stark trap. A white precipitate formed that was filtered under vacuum and dried. Yield: 95%. Mp: 277−280 °C. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C, TMS): $\delta = 2.47$ (s, N═CCH_3), 3.84 and 4.16 (AB, 4 H, NCH$_2$), 6.56 (d, 2 H, H-3), 6.71 (dd, 2 H, H-5), 7.11 (m, 6 H, m-BC$_6$H$_5$, p-BC$_6$H$_5$), 7.35 (dd, 2 H, H-4), 7.42 (d, 4 H, o-BC$_6$H$_5$), 7.56 (dd, 2 H, H-6) ppm. ^{13}C NMR (67.5 MHz, DMSO-d_6, 25 °C, TMS): $\delta = 16.7$ (CH$_3$), 46.4 (NCH$_2$), 117.8 (C-1), 118.9, 119.9 (C-3, C-5), 126.5 (p-BC$_6$H$_5$), 127.3 (m-BC$_6$H$_5$), 129.8 (C-6), 131.9 (o-BC$_6$H$_5$), 136.3 (C-4), 160.9 (C-2), 171.9 (N═CR) ppm. IR (KBr): $\tilde{\nu} = 3060$ (w), 3040 (w), 3000 (w), 1628 (s), 1616 (s), 1557 (s), 1479 (m), 1456 (m),

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

(19) Sheldrick, G. M. *SHELX86, Program for Crystal Structure Solution;* University of Göttingen: Göttingen, Germany, 1986.

(20) Bruker Analytical X-ray Systems. *SMART: Bruker Molecular Analysis Research Tool V. 5.057 c*, 1997−98.

(21) Bruker Analytical X-ray Systems. *SAINT + NT Version 6.01*, 1999.

(22) Bruker Analytical X-ray Systems. *SHELXTL-NT Version 5.10*, 1999.

(23) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W.; Cooper, T. I. *CRYSTALS*, Chemical Crystallography Laboratory Oxford: Oxford, 2000; Issue 11.

(24) Watkin, D. J.; Prout, C. K.; Pearce, *L. J. CAMERON;* Chemical Crystallography Laboratory Oxford, Oxford, 1996.

(25) Watkin, D. J.; Prout, C. K.; deQ. Lilley, P. M. *RC93;* Chemical Crystallography Laboratory Oxford: Oxford, 1994.

1431 (m), 1378 (w), 1347 (m), 1277 (s), 1197 (s), 1168 (m), 1141 (m), 1127 (m), 1089 (w), 1034 (m), 1025 (m) cm^{-1}. MS (70 eV, EI), *m/z* (%): 487 (0.1) [M + 1]$^+$, 409 (100) [M − C_6H_5]$^+$, 331 (15), 305 (27), 187 (17), 166 (18), 77 (10). Anal. Calcd (%) for $C_{30}H_{28}B_2N_2O_3$ (486.16): C, 74.11; H, 5.81; N, 5.76. Found: C, 74.29; H, 5.94; N, 5.69.

Compound **2c** was prepared from acenH_2 **2** (0.50 g, 1.69 mmol) and 2,4-difluorophenylboronic acid (0.53 g, 3.38 mmol) in acetonitrile (20 mL). After 1 h of reflux the solution was concentrated with a Dean−Stark trap. A white precipitate formed that was filtered under vacuum and dried. Yield: 93%. Mp: 310−312 °C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$, 25 °C, TMS): $\delta = 2.42$ (s, N═CC*H*$_3$), 3.40 and 4.21 (AB, 4 H, NCH_2), 6.37 (dt, $J = 8$ and 2 Hz, 2 H, *m′*-$BC_6H_3F_2$), 6.70 (dt, $J = 10$ and 2 Hz, 2 H, *m*- $BC_6H_3F_2$), 6.81 (dd, 2 H, H-3), 6.90 (dt, 2 H, H-5), 7.07 (dd, $J = 14$ and 8 Hz, 2 H, *o′*-$BC_6H_3F_2$), 7.52 (dt, 2 H, H-4), 7.75 (dd, 2 H, H-6) ppm. ^{13}C NMR (75 MHz, DMSO-*d*$_6$, 25 °C, TMS): $\delta = 15.4$ (CH_3), 48.3 (NCH_2), 102.2 (*m*-$BC_6H_3F_2$), 108.8 (*m′*-$BC_6H_3F_2$), 117.5 (C-1), 117.8 (C-5), 119.1 (C-3), 129.3 (C-6), 135.2 (*o′*-$BC_6H_3F_2$), 136.2 (C-4), 158.8 (C-2), 170.6 (N═*C*R) ppm. ^{11}B NMR (96.3 MHz, DMSO-*d*$_6$, 25 °C, BF_3·OEt_2): $\delta = 6$ ($h_{1/2} = 620$ Hz) ppm. IR (KBr): $\tilde{\nu} = 1616$ (s), 1555 (m), 1487 (m), 1458 (m), 1402 (m), 1357 (m), 1281 (m), 1260 (m), 1226 (w), 1169 (m), 1145 (m), 1127 (m), 1116 (m), 1100 (w), 1077 (m) cm^{-1}. MS (70 eV, EI), *m/z* (%): 445 (100) [M − $C_6H_3F_2$]$^+$, 331 (18), 305 (14), 187 (12), 166 (23), 146 (6), 114 (4), 77 (3). Anal. Calcd (%) for $C_{30}H_{24}B_2F_4N_2O_3$ (558.16): C, 64.56; H, 4.33; N, 5.02. Found: C, 65.11; H, 4.38; N, 4.53.

Preparation of Boronate 3b. Compound **3b** was prepared from salphenH_2 **3** (0.50 g, 1.58 mmol) and phenylboronic acid (0.38 g, 3.16 mmol) in acetonitrile (10 mL). After 4 h of reflux the solution was concentrated with a Dean−Stark trap. A yellow precipitate formed that was filtered under vacuum and dried. Yield: 86%. Mp: 250−253 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.94$ (m, 6 H, H-5, *m*-BC_6H_5), 6.97 (m, 2 H, *p*-BC_6H_5), 7.09 (m, 6 H, H-3, *o*-BC_6H_5), 7.14 (dd, 2 H, H-9), 7.20 (dd, 2 H, H-6), 7.43 (dd, 2 H, H-10), 7.56 (s, 2 H, N═CH), 7.59 (dd, 2 H, H-4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 118.3$ (C-1), 119.5 (C-5), 121.6 (C-3), 124.2 (C-9), 126.8 (*p*-BC_6H_5), 127.1 (*m*-BC_6H_5), 130.2 (C-10), 132.8 (*o*-BC_6H_5, C-6), 139.3 (C-4, C-8), 161.6 (C-2), 165.2 (N═CR) ppm. ^{11}B NMR (96.3 MHz, $CDCl_3$, 25 °C, BF_3·OEt_2): $\delta = 9$ ($h_{1/2} = 400$ Hz) ppm. IR (KBr): $\tilde{\nu} = 3065$ (w), 1629 (s), 1595 (w), 1552 (m), 1475 (m), 1457 (w), 1312 (w), 1218 (s), 1152 (w), 1127 (m), 1088 (w), 1049 (w) cm^{-1}. MS (70 eV, EI), *m/z* (%): 506 (0.8) [M]$^+$, 429 (100) [M − C_6H_5]$^+$, 325 (59), 221 (11), 176 (20), 77 (10). Anal. Calcd (%) for $C_{32}H_{24}B_2N_2O_3$ (506.16): C, 75.93; H, 4.78; N, 5.53. Found: C, 75.49; H, 4.99; N, 5.30.

Preparation of Boronate 4b. Compound **4b** was prepared from salcenH_2 **4** (0.50 g, 1.55 mmol) and phenylboronic acid (0.37 g, 3.10 mmol) in toluene (10 mL). After 2 h of reflux the solution was concentrated with a Dean−Stark trap. A white precipitate formed that was filtered under vacuum and dried. Yield: 38%. Mp: 304−306 °C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$, 25 °C, TMS): $\delta = 0.71$−1.97 (m, 8 H, H-9, H-9′, H-10, H-10′), 3.51 (m, 1 H, H-8), 4.41 (m, 1 H, H-8′), 6.61, 6.77, 7.14 (m, 10 H, H-3, H-3′, H-5, H-5′, *m*-BC_6H_5, *m′*-BC_6H_5, *p*-BC_6H_5, *p′*-BC_6H_5), 7.34, 7.48 (m, 2 H, H-6, H-6′), 8.53 (s, 1 H, H-7), 8.66 (s, 1 H, H-7′) ppm. IR (KBr): $\tilde{\nu} = 3063$ (w), 3043 (w), 3001 (w), 2941 (w), 2863 (w), 1637 (s), 1608 (m), 1558 (s), 1522 (w), 1508 (w), 1480 (m), 1461 (m), 1431 (m), 1405 (w), 1364 (w), 1322 (s), 1258 (m), 1198 (s), 1151 (s), 1130 (s), 1085 (m), 1027 (m) cm^{-1}. MS (70 eV, EI), *m/z* (%): 435 (100) [M − C_6H_5]$^+$, 331 (25), 277 (15), 236 (11), 179 (18), 77 (20), 51 (14). Anal. Calcd (%) for $C_{32}H_{30}B_2N_2O_3$ (512.20): C, 75.04; H, 5.90; N, 5.47. Found: C, 75.47; H, 6.04; N, 5.36.

Preparation of Boronate 5b. Compound **5b** was prepared from salpenH_2 **5** (0.50 g, 1.77 mmol) and phenylboronic acid (0.43 g, 3.54 mmol) in ethanol (30 mL). After 1 h of reflux the solution was concentrated with a Dean−Stark trap. A yellow precipitate formed that was filtered under vacuum and dried. Yield: 97%. Mp: >300 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25 °C, TMS): $\delta = 1.98$ (m, 2 H, H-9), 3.49 (m, 4 H, NCH_2), 6.35 (d, 2 H, H-3), 6.47 (dd, 2 H, H-5), 7.04 (d, 2 H, H-6), 7.14 (m, 4 H, H-4, *p*-BC_6H_5), 7.19 (m, 4 H, *m*-BC_6H_5), 7.56 (d, 4 H, *o*-BC_6H_5), 8.54 (s, 2 H, N═CH) ppm. ^{13}C NMR (75 MHz, DMSO-*d*$_6$, 25 °C, TMS): $\delta = 31.5$ (C-9), 53.0 (NCH_2), 116.0 (C-1), 117.2 (C-5), 118.4 (C-3), 126.5 (*p*-BC_6H_5), 127.2 (*m*-BC_6H_5), 131.6 (C-6), 131.8 (*o*-BC_6H_5), 137.0 (C-4), 161.1 (C-2), 164.1 (N═CH) ppm. ^{11}B NMR (96.3 MHz, DMSO-*d*$_6$, 25 °C, BF_3·OEt_2): $\delta = 8$ ($h_{1/2} = 320$ Hz) ppm. IR (KBr): $\tilde{\nu} = 3065$ (w), 3047 (w), 2930 (w), 1646 (s), 1610 (m), 1560 (m), 1482 (m), 1459 (m), 1446 (w), 1432 (w), 1415 (w), 1364 (w), 1321 (m), 1228 (m), 1192 (s), 1151 (m), 1117 (s), 1080 (m), 1066 (m), 1029 (w), 1000 (w) cm^{-1}. MS (70 eV, EI), *m/z* (%): 471 (0.1) [M − H]$^+$, 395 (100) [M − C_6H_5]$^+$, 291 (39), 159 (24), 77 (4). Anal. Calcd (%) for $C_{29}H_{26}B_2N_2O_3$ (472.38): C, 73.77; H, 5.55; N, 5.93. Found: C, 73.67; H, 5.64; N, 5.89.

Preparation of Boronates 6a,b. Compound **6a** was prepared from acpenH_2 **6** (0.50 g, 1.61 mmol) and phenylboronic acid (0.391 g, 3.22 mmol) in ethanol (30 mL). After 30 min of reflux the solution was concentrated with a Dean−Stark trap. A yellow precipitate formed that was filtered under vacuum and dried. The product decomposes more or less rapidly in other organic solvents to polymeric material, so the NMR spectra could not be obtained pure. Data are therefore only reported for the major compound **6a**. Yield: 77%. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C, TMS: $\delta = 0.74$ (m, 2 H, H-9), 1.08 (q, 6 H, OCH_2CH_3), 1.88 (s, 6 H, N═CCH_3), 3.20 and 3.40 (AB, 4 H, OCH_2), 2.93 and 3.49 (m, 4 H, NCH_2), 6.82 (m, 2 H, H-5), 6.99 (m, 2 H, H-3), 7.23 (m, 6 H, *m*-BC_6H_5, *p*-BC_6H_5), 7.43 (m, 4 H, H-4, H-6), 7.55 (m, 4 H, *o*-BC_6H_5) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 15.9$ (N═C*C*H_3), 18.1 (OCH_2CH_3), 27.9 (C-9), 46.1 (NCH_2), 56.9 (OCH_2), 117.2 (C-1), 118.3 (C-5), 120.2 (C-3), 127.0 (*p*-BC_6H_5, 127.4 (*m*-BC_6H_5), 128.2 (C-6), 133.1 (*o*-BC_6H_5), 136.4 (C-4), 160.1 (C-2), 170.4 (N═CR) ppm. ^{11}B NMR (128.3 MHz, $CDCl_3$, 25 °C, BF_3·OEt_2): $\delta = 4$ ($h_{1/2} = 360$ Hz) ppm. IR (KBr): $\tilde{\nu} = 3066$ (w), 3043 (w), 3004 (w), 2963 (m), 2923 (m), 2870 (m), 1619 (s), 1556 (s), 1483 (m), 1457 (m), 1433 (m), 1386 (m), 1358 (m), 1340 (m), 1272 (m), 1185 (m), 1169 (m), 1145 (m), 1105 (m), 1081 (m), 1000 (m); MS (70 eV, EI), *m/z* (%): 497 (4) [M − C_6H_5]$^+$, 482 (11), 451 (100), 423 (9), 396 (10), 319 (98), 262 (39), 246 (46), 234 (74), 206 (19), 185 (19), 173 (10), 161 (6), 146 (11), 105 (14), 77 (26), 51 (12). Anal. Calcd (%) for $C_{35}H_{40}B_2N_2O_4$ (574.36): C, 73.19; H, 7.01. Found: C, 72.81; H, 7.35.

Compound **6b** was prepared from acpenH_2 **6** (0.50 g, 1.61 mmol) and phenylboronic acid (0.39 g, 3.22 mmol) in acetonitrile (15 mL). After 1 h of reflux the solution was concentrated with a Dean−Stark trap. A white precipitate formed that was filtered under vacuum and dried. Yield: 78%. Mp: 294−296 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.02$ (m, 2 H, H-9), 2.42 (s, 6 H, N═CC*H*$_3$), 3.53 and 4.09 (m, 4 H, N−CH_2), 6.45 (dt, 2 H, H-5), 6.62 (dd, 2 H, H-3), 7.13 (m, 4 H, H-4, H-6), 7.24 (m, 6 H, *m*-BC_6H_5, *p*-BC_6H_5), 7.72 (dd, 4 H, *o*-BC_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 16.0$ (CH_3), 29.3 (C-9), 48.9 (NCH_2), 116.7 (C-5), 120.7 (C-3), 126.4, 126.8 (C-6, *p*-BC_6H_5), 127.0 (*m*-BC_6H_5), 131.8 (*o*-BC_6H_5), 136.0 (C-4), 169.4 (N═*C*R) ppm. ^{11}B NMR (128.3 MHz, $CDCl_3$, 25 °C, BF_3·OEt_2): $\delta = 3$ ppm; IR (KBr): $\tilde{\nu} = 3065$ (m), 3042 (m), 3002 (m), 2915 (m), 1623 (s), 1557 (s), 1481 (s), 1459 (s), 1431 (m), 1382 (m), 1365 (m), 1341 (m), 1296 (m), 1272 (s), 1234 (m), 1192 (s), 1143 (m), 1115 (s), 1087 (m), 1061 (m), 1028 (m) cm^{-1}. MS (70 eV, EI), *m/z* (%): 423 (100) [M − C_6H_5]$^+$, 345 (18), 319 (33), 262 (6), 234 (4), 201 (7), 173 (19), 146 (4), 77 (6). Anal. Calcd (%) for $C_{31}H_{30}B_2N_2O_3$ (500.19): C, 74.44; H, 6.04; N, 5.60. Found: C, 74.60; H, 6.14; N, 5.74.

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Supporting Information Available: CIF files, tables of crystallographic details, atomic coordinates and *U* values, distances and angles, anisotropic displacement parameters, torsion angles, and mean planes and deviations. This material is available free of charge via the Internet at http://pubs.acs.org.

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