DOI: 10.1002/ejoc.200800787

Boron-Based Diastereomerism and Enantiomerism in Imine Complexes – Determination of the Absolute Configuration at Boron by CD Spectroscopy

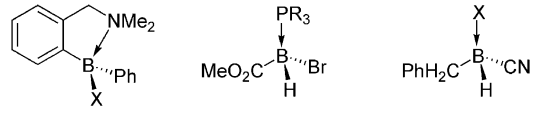
Manfred Braun,*[a] Sebastian Schlecht,[a] Marco Engelmann,[a] Walter Frank,[b] and Stefan Grimme[c]

Keywords: Boron / Chirality / Circular dichroism / Stereochemistry

Boron turns out to be a stable stereogenic center in imine complexes of aryl and alkyl boronates. Diastereomerically pure complexes **7a–c** are obtained from chiral imine ligands **5a**,**b** that are derived from the amino alcohol (*R*)-**4**. The configuration at the boron atom is determined by crystal structure analyses. Racemic boronates **10a–c**, available from a condensation of aryl boronic acids **6** with the achiral imine ligand **9**, can be separated into stable enantiomers by HPLC on a chiral column. The racemization barrier $\Delta G^{\neq}$ has been determined to amount to 105–115 kJ mol^{-1}. The comparison of calculated and measured CD spectra permits to assign unambiguously the absolute configuration to boron in the enantiomeric boronate-imine complex **10a**.

Introduction

Enantiomerism of tetrahedral main group elements other than carbon has attracted considerable interest in the past, and the features of chiral sulfur, phosphorus, nitrogen and silicon compounds have been studied comprehensively.[1] Boron, typically adopting a trigonal planar configuration, has been studied by far less intensively with respect to its ability to form a stable stereogenic center. In most of these approaches, boron was embedded in a chiral environment of enantiomerically pure ligands[2] or counterions.[3] As a consequence, an inversion of the configuration at boron results in the formation of epimers. They have been obtained in a stereoselective manner when the boron atom was incorporated in bicyclic systems, the chirality at the boron atom being induced by the chiral ligands.[2b–2d] When, on the other hand, the boron is configurationally labile, advantage has been taken of the readily occurring epimerization of the boron center in crystallization-induced asymmetric transformations.[2a] Enantiomerism at the boron center, however, has been investigated only recently in acyloxyboranes **1**, wherein electron-withdrawing substituents X are essential to avoid racemization.[4] In addition acyclic tetra-coordinated boron compounds **2**[5] and **3**[6] have been isolated as pure enantiomers (Scheme 1). In few cases only, the absolute configuration has been determined by crystal structure analyses.[4c,5]



1: X = Cl, O_2CCF_3, $O_2CC_2F_5$ **2**: R = cyclohexyl **3**: X = NMe_2, pyridine, 4-chloropyridine

Scheme 1. Enantiomeric boron-amine and boron-phosphane complexes.

Results and Discussion

In this communication, complexes of boronates are described that are obtained from 2-amino-1,2,2-triphenylethanol **4** and 2-amino-2,2-diphenylethanol **8** and isolated as pure diastereomers and/or enantiomers. We were able to determine the absolute configuration at boron in enantiomeric boronate complexes by CD spectroscopy. The imines **5** derived from (*R*)-amino alcohol **4**[7] were previously used as ligands in bis-chelated titanium complexes.[8] When *p*-chlorophenylboronic acid (**6a**) was allowed to react with the imines (*R*)-**5** by heating them in toluene, the new boronates **7a** and **7b** resulted. In order to find out whether complexes **7** with aliphatic residues at the boron atom can be obtained as well, *n*-butyldiisopropoxyborane was treated with the imine **5b**. Indeed, the complexed alkylboronate **7c** formed. The complexes **7a–c** were obtained as pure diastereomers, as shown by their ^{1}H and ^{13}C NMR spectra. Temperature-dependent NMR spectroscopy never revealed an epimeri-

[a] Institut für Organische Chemie und Makromolekulare Chemie, Universität Düsseldorf,
Universitätsstr. 1, 40225 Düsseldorf, Germany
Fax: +49-211-8115079
E-mail: braunm@uni-duesseldorf.de
[b] Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf,
Universitätsstr. 1, 40225 Düsseldorf, Germany
[c] Organisch-Chemisches Institut (Abt. Theoretische Chemie) Universität Münster,
Corrensstr. 40, 48149 Münster, Germany

zation at the boron atom.[9] A final proof of structure came from the crystal structure analyses of **7a** and **7c** shown in Figure 1 and Figure 2. Therein, the distance between the nitrogen and the boron atom of 1.588 to 1.607 Å clearly indicates the existence of a coordinative bond. In addition, the crystal structures of the boron complexes **7a** and **7c** permit to determine the configuration at the boron atom to be (*R*). The structure of the related boronate **7b** was not only assigned by analogy but also by essential accordance in the CD spectra of **7b** with those of **7a** and **7c** (Scheme 2).

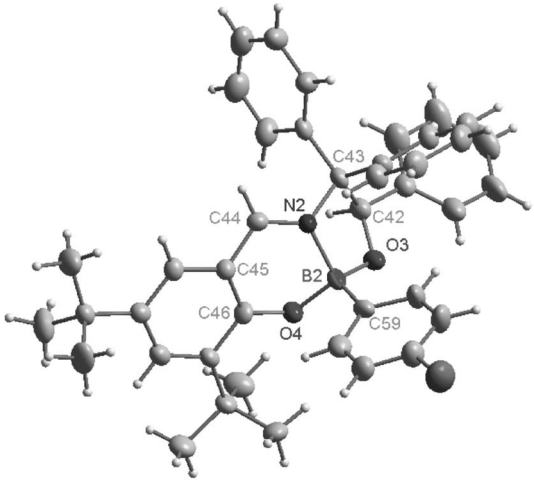


Figure 1. Diagram of one of the two crystallographically independent molecules in the crystal of **7a**. Displacement ellipsoids are set at 30% probability, radii of hydrogen atoms are chosen arbitrarily. Mean bond lengths (Å) and angles (°): B1/2–O1/4 1.495(5), B1/2–O2/3 1.439(5), B1/2–N1/2 1.607(5), B1/2–C18/59 1.599(6); O1/4–B1/2–O2/3 113.1(4), O1/4–B1/2–N1/2 104.1(3), O1/4–B1/2–C18/59 110.8(3), O2/3–B1/2–N1/2 99.4(3), O2/3–B1/2–C18/59 113.3(3), N1/2–B1/2–C18/59 115.6(3).

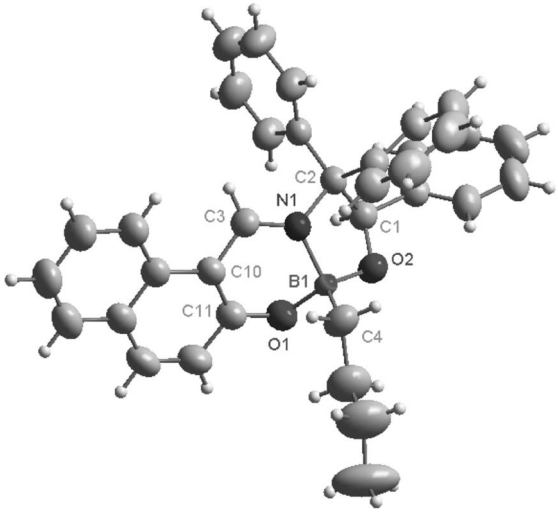
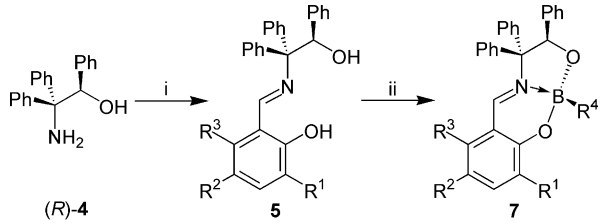


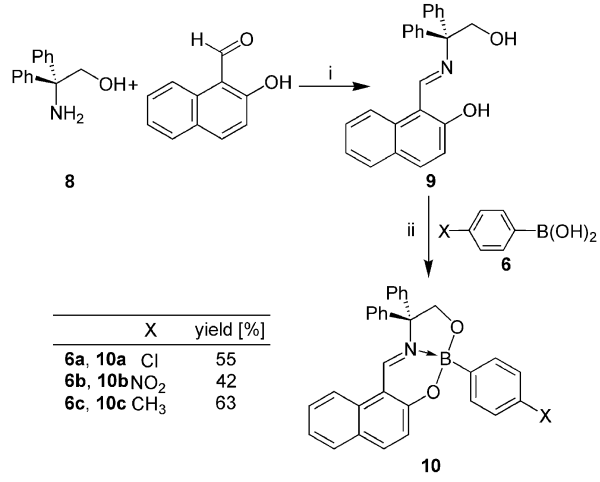
Figure 2. Molecular structure of **7c** in the crystal. Displacement ellipsoids are set at 30% probability, radii of hydrogen atoms are chosen arbitrarily. Bond lengths (Å) and angles (°): B1–O1 1.514(4), B1–O2 1.442(4), B1–N1 1.588(4), B1–C4 1.594(5), O1–B1–O2 113.2(3), O1–B1–N1 102.7(2), O1–B1–C4 108.8(3), O2–B1–N1 100.8(3), O2–B1–C4 114.4(3), N1–B1–C4 116.4(3).



	R^1	R^2	R^3	R^4
5a, **7a**	*t*Bu	*t*Bu	H	*p*-Cl-C_6H_4
5b, **7b**	H	C_6H_4		*p*-Cl-C_6H_4
5b, **7c**	H	C_6H_4		*n*Bu

Scheme 2. Synthesis of boron complexes **7**. Reagents and conditions: i) see ref. [7]; ii) **7a**, **b**: *p*-Cl-$C_6H_4B(OH)_2$ (**6a**), molecular sieves (3 Å), toluene, reflux; **7c**: $(i\text{PrO})_2B(n\text{Bu})$, toluene, reflux.

The fact that the diastereomers R_C,R_B-**7** are obtained exclusively, whereas the formation of products epimeric at the boron center are not observed, indicates the higher thermodynamic stability of the former stereoisomers, but does not answer the question of kinetic stability. This point was addressed by investigating the stability of analogous enantiomeric complexes **10** with boron as the only stereogenic center. When designing them, it was intended to keep the feature of the geminal (diphenylamino)methyl moiety in order to favor the ring closure upon complexation and to enhance the stability of the complexes. For this purpose, the achiral imine ligand **9** was synthesized from 2-amino-2,2-diphenylethanol **8**[10] and 1-formyl-2-naphthol and converted into the racemic boron complexes **10a**–**c** by treatment with boronic acids **6a**–**c**, respectively (Scheme 3).



	X	yield [%]
6a, **10a**	Cl	55
6b, **10b**	NO_2	42
6c, **10c**	CH_3	63

Scheme 3. Synthesis of racemic boron complexes **10**. Reagents and conditions: i) methanol/THF (1:1), Na_2SO_4, reflux, 75%; ii) molecular sieves 3 Å, toluene, reflux 12 to 20 h.

The crystal structure of one representative complex **10b** is shown in Figure 3. Here again, the nitrogen–boron bond becomes evident from a bond length of 1.58 Å. This is slightly shorter than the values of amine–boron bonds that range from 1.62–1.71 Å,[2c,2d,4b,6] and typical for boron-imine complexes.[2a] The structures of complexes **10a** and **10c** were confirmed by crystal structure analyses as well.

The tetrahedral character (THC) of the boron atom was found to be 68% in the complex **10a** and 69% in **10b** and **10c**. It was calculated according to Höpfl's equation[11] taking into account the six bond angles θ_1–θ_6 at the boron atom [Equation (1)].

$$THC = \left(1 - \frac{\sum_{n=1-6} 109.5 - \theta_n}{90}\right) \cdot 100 \quad (1)$$

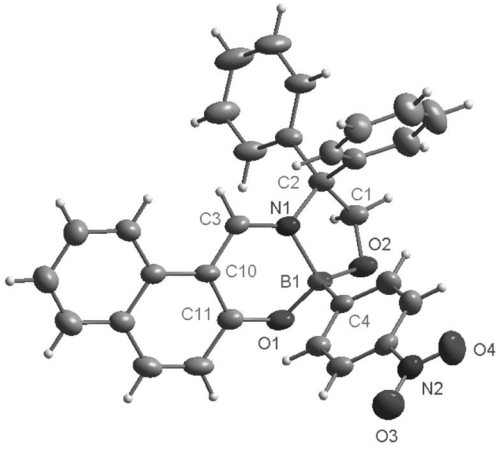


Figure 3. Molecular structure of **10b** in the crystal. Displacement ellipsoids are set at 30% probability, radii of hydrogen atoms are chosen arbitrarily. Bond lengths (Å) and angles (°): B1–O1 1.503(4), B1–O2 1.437(4), B1–N1 1.583(4), B1–C4 1.607(4), O1–B1–O2 113.7(2), O1–B1–N1 103.7(3), O1–B1–C4 109.8(2), O2–B1–N1 101.1(2), O2–B1–C4 112.3(3), N1–B1–C4 115.9(2).

On a chiral HPLC column (Chiracel OD-H), the racemic mixtures of the boron complexes **10a**–**c** displayed a split into two peaks of equal area of the two enantiomers. They were separated, the enantiomeric purity of each of the separated samples was checked by chiral HPLC, and their CD spectra were measured. Figure 4 shows the CD spectrum of the enantiomerically pure boron complex **10a**. Similar CD were obtained from the separated enantiomers of **10b** and **10c**, respectively. In all cases, the enantiomeric compounds *ent*-**10a**–**c** displayed mirror image Cotton effects.

In order to evaluate the configurational stability at the stereogenic boron center, the rate of racemization was studied by heating the separated enantiomers of boron complex **10a** in *n*-decane at 65 °C. The time dependent decrease of the optical rotation at λ = 589 nm was used as a probe of racemization. Thus, the barrier of racemization was determined for **10a** to be $\Delta G^{\neq}$ = 109 kJ mol^{-1} (k = 3.0 10^{-4}s^{-1}). The nitrophenyl-substituted boronate **10b** turned out to be slightly more, the tolyl-substituted complex **10c** less stable ($\Delta G^{\neq}$ = 115 kJ mol^{-1} and 105 kJ mol^{-1}, respectively). Obviously, the racemization increases slightly with the electron-withdrawing character of the substituents, because the stronger electron acceptor enhances the strength of the boron–nitrogen bond. This effect is underlined by the B–N bond lengths in the complexes **10a**, **10b** and **10c** (1.599, 1.583 and 1.611 Å, respectively). The racemization energy is in the same range as that measured for the acyloxyboranes **1**.[4] Nevertheless, the stability toward racemization is remarkable, as here the stereogenic boron atom in the complexes **10** forms stable enantiomers, even if it does not carry electron-withdrawing substituents, which are a prerequisite to enantiomerism in boron compounds **1**–**3**.

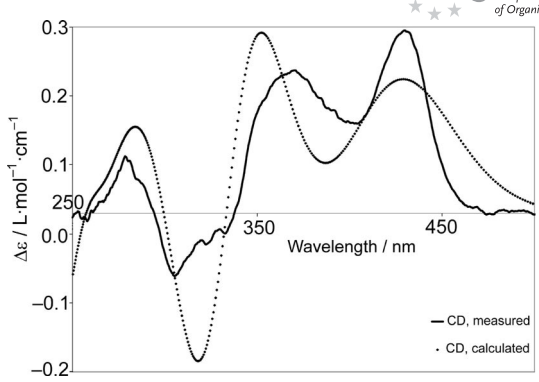


Figure 4. Comparison of experimental (in *n*-hexane) and theoretical (BHLYP/TZVP//PBE-D/TZVP) CD spectra of (*R*)-**10a**. All computed excitation energies have been red-shifted by 0.6 eV (which is the typical error of the TDDFT/BHLYP treatment). The theoretical intensities were down-scaled by a factor of 0.02.

Finally, the absolute configuration had to be assigned to each of the enantiomers of boron complexes **10**. For this purpose, the CD spectrum of compound **10a** was calculated by density functional methods. All quantum chemical calculations have been performed with the TURBOMOLE suite of programs.[12] The molecular structures were fully optimized at the density functional (DFT) level employing the non-empirical PBE functional[13] with dispersion corrections (DFT-D[14]) and a Gaussian AO basis of valence-triple-zeta quality(TZVP[15]). These structures were used in subsequent calculations of the vertical CD spectra by time-dependent DFT (TDDFT) as described in detail in ref.[16] To avoid artificial excited electronic states with charge-transfer character, which often appears for large molecules when using semi-local density functionals, TDDFT calculations were carried out by the BH-LYP hybrid functional[17] with a HF-exchange fraction of 50%. The origin-independent velocity-dipole form for the rotary strengths and a full band-width (at 1/*e* height) for each electronic transition of 0.5 eV was used in the spectral simulations. The calculated CD spectrum of (*R*)-**10a** is also displayed in Figure 4. When compared with the measured CD spectra, it becomes evident that the enantiomer with the positive cotton effect at highest wavelength is *R*-configured.

Conclusions

In summary, boron has shown itself to be configurationally stable in boron complexes with chiral or achiral chelating ligands **7** and **9**. Enantiomerism has been proven in compounds **10** that form stable stereoisomers, and the first enantiomeric complexes of boronates with imine ligands have been resolved and isolated. For the first time, the abso-

lute configuration at stereogenic boron could be assigned by the evident accordance of measured and calculated circular dichroism.

Experimental Section

General Procedure for the Preparation of Boron Complexes 7 and 10: The corresponding imine, **5** or **9**, (1.0 mmol), boronic acid **6** (1.5 mmol) and 1 g of molecular sieves (3 Å) were suspended in 100 mL of dry toluene and refluxed for 20 h. After filtration, the solvent was removed in a rotary evaporatior and the residue was purified by column chromatography (Fluka; silica gel 60, chloroform/ethyl acetate, 10:1) to deliver boronates **7a**, **7b**, and **10a**–**c** as yellow, solid compounds. For the preparation of boronate **7c**, the imine **5b** was treated with $(i\mathrm{PrO})_2\mathrm{B}(n\mathrm{Bu})$ in an analogous way, however, in the absence of molecular sieves.

Selected Physical, Spectroscopic and Crystallographic Data

7a: Yellow solid, 238 mg (38%); R_f = 0.3 (chloroform/*n*-hexane, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 (s, 9 H), 1.37 (s, 9 H), 6.25 (s, 1 H), 6.27–6.31 (m, 2 H), 6.78–6.86 (m, 2 H), 6.92–6.98 (m, 2 H), 7.05–7.23 (m, 11 H), 7.36–7.40 (m, 3 H), 7.58 (s, 1 H), 7.65 (d, J_m = 2.5 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.9, 31.7, 34.7, 35.9, 83.0, 87.4, 119.5–141.6, 159.2, 161.6 ppm.

Crystallographic data: $C_{41}H_{41}BClNO_2$, M_r = 626.01, monoclinic, space group $P2_1$, a = 18.3345(9) Å, b = 10.8254(6) Å, c = 18.9903(10) Å, β = 110.593(6) °, V = 3528.3(3) Å^3, Z = 4, D_x = 1.178 g cm^{-3}, μ = 0.144 mm^{-1}, T = 291 K, crystal dimensions: 0.3 mm × 0.2 mm × 0.15 mm, STOE-IPDS, Mo-K_α radiation (λ = 0.71073 Å), θ_{max} = 26.07°, 39602 measured, 13815 unique, and 4471 observed reflections with $I > 2\sigma(I)$, LP correction, direct methods and ΔF synthesis, minimization of $\Sigma w(F_o^2 - F_c^2)^2$, 841 refined parameters, $(\Delta/\sigma)_{max}$ = 0.001, $R_1[F_o^2 > 2\sigma(F_o^2)]$ = 0.042, wR_2 = 0.085 (all data), $w = 1/\sigma^2(F_o^2)$, S = 0.828, $\Delta\rho_{max}/\Delta\rho_{min}$ = +0.166 e/Å^3 and –0.141 e/Å^3.

7b: Yellow solid, 304 mg (54%); R_f = 0.61 (chloroform/ethyl acetate, 10:1); m.p. 214 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.2 (s, 1 H), 6.87 (t, J_o = 7.7 Hz, 2 H), 6.9 (d, J_o = 8.1 Hz, 2 H), 7.1 (d, J_o = 8.0 Hz, 2 H), 7.1–7.3 (m, 13 H), 7.3 (d, J_o = 9.0 Hz, 1 H), 7.32 (t, J_o = 7.6 Hz, 1 H), 7.39 (t, J_o = 7.6 Hz, 1 H), 7.5 (d, J_o = 8.1 Hz, 1 H), 7.74 (d, J_o = 8.0 Hz, 1 H), 7.98 (d, J_o = 9.1 Hz, 1 H), 8.0 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 82.8, 87.2, 113.5, 120.6, 121.4, 124.7, 126.7, 126.8–129.0, 127.7, 127.8, 129.1, 129.4, 131.8, 133.1, 135.2, 138.7, 139.0, 139.6, 156.2, 163.6 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 6.82 ppm.

7c: Yellow solid, 469 mg (92%); R_f = 0.69 (chloroform/ethyl acetate, 10:1); m.p. 197 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.7 (t, ^3J = 7.1 Hz, 3 H), 1.2 (m, 6 H), 6.1 (s, 1 H), 7.0–7.3 (m, 15 H), 7.2 (d, J_o = 9.1 Hz, 1 H), 7.28 (t, J_o = 7.1 Hz, 1 H), 7.38 (t, J_o = 7.7 Hz, 1 H), 7.5 (d, J_o = 8.2 Hz, 1 H), 7.7 (d, J_o = 7.9 Hz, 1 H), 7.86 (s, 1 H), 7.9 (d, J_o = 9.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 26,1, 27.4, 82.2, 88.1, 113.9, 120.6, 121.8, 124.2, 127–130, 127.5, 128.6, 129.2, 132, 136.1, 138.5, 139.1, 139.3, 155, 163.4 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 8.8 ppm.

Crystallographic data: $C_{35}H_{32}BNO_2$, M_r = 509.43, orthorhombic, space group $P2_12_12_1$, a = 11.019(2) Å, b = 14.315(3) Å, c = 18.275(4) Å, V = 2882.8(10) Å^3, Z = 4, D_x = 1.174 g cm^{-3}, μ = 0.071 mm^{-1}, T = 293 K, crystal dimensions: 0.5 mm × 0.1 mm × 0.05 mm, STOE-IPDS, Mo-K_α radiation (λ = 0.71073 Å), θ_{max} = 25.00°, 37818 measured, 2860 unique, and 1970 observed reflections with $I > 2\sigma(I)$, LP correction, direct methods and ΔF synthesis, minimization of $\Sigma w(F_o^2 - F_c^2)^2$, 353 refined parameters, $(\Delta/\sigma)_{max}$ = 0.000, $R_1[F_o^2 > 2\sigma(F_o^2)]$ = 0.037, wR_2 = 0.079 (all data), $w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 0.7P]$ where $P = (F_o^2 + 2F_c^2)/3$, S = 1.013, $\Delta\rho_{max}/\Delta\rho_{min}$ = +0.256 e/Å^3 and –0.129 e/Å^3.

10a: Yellow solid, 268 mg (55%); R_f = 0.58 (chloroform/ethyl acetate, 10:1); m.p. 179 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.6, 4.92 (d, ^2J = 9.7 Hz, 2× 1 H), 6.8 (m, 4 H), 7.2–7.34 (m, 10 H), 7.28 (d, J_o = 9.1 Hz, 1 H), 7.31 (m, 1 H), 7.42 (d, J_o = 8.0 Hz, 1 H), 7.58 (d, J_o = 8.0 Hz, 1 H), 7.72 (d, J_o = 8.0 Hz, 1 H), 7.95 (d, J_o = 9.1 Hz, 1 H), 8.32 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 77.1, 77.4, 112.7, 120.5, 121.3, 124.6, 126.8, 127.7, 127.8, 128.3–129.0, 129.0, 129.4, 131.8, 132.8, 138.5, 139.6, 140.5, 155.5, 162.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 7.3 ppm.

10b: Yellow solid, 209 mg (42%); R_f = 0.53 (chloroform/ethyl acetate, 10:1); m.p. 240 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.6, 4.97 (d, ^2J = 9.8 Hz, 2× 1 H), 7.0–7.35 (m, 10 H), 7.29 (d, J_o = 9.1 Hz, 1 H), 7.32 (m, 2 H), 7.35 (m, 1 H), 7.46 (m, 1 H), 7.62 (d, J_o = 8.1 Hz, 1 H), 7.65 (m, 2 H), 7.75 (d, J_o = 8.1 Hz, 1 H), 7.99 (d, J_o = 9.1 Hz, 1 H), 8.39 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 77.1, 77.7, 112.5, 120.5, 121.0, 121.5, 124.9, 127.8, 127.8, 128.5–129.0, 129.2, 129.5, 131.7, 138.1, 139.6, 140.0, 147.1, 155.6, 162.3 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 6.9 ppm.

Crystallographic data: $C_{31}H_{23}BN_2O_4$, M_r = 498.32, orthorhombic, space group *Iba*2, a = 12.5991(9) Å, b = 18.5482(10) Å, c = 21.6143(12) Å, V = 5051.1(5) Å^3, Z = 8, D_x = 1.311 g cm^{-3}, μ = 0.087 mm^{-1}, T = 291 K, crystal dimensions: 0.4 mm × 0.2 mm × 0.2 mm, STOE-IPDS, Mo-K_α radiation (λ = 0.71073 Å), θ_{max} = 25.00°,11612 measured, 2276 unique, and 1430 observed reflections with $I > 2\sigma(I)$, LP correction, direct methods and ΔF synthesis, minimization of $\Sigma w(F_o^2 - F_c^2)^2$, 343 refined parameters, $(\Delta/\sigma)_{max}$ = 0.000, $R_1[F_o^2 > 2\sigma(F_o^2)]$ = 0.029, wR_2 = 0.053 (all data), $w = 1/[\sigma^2(F_o^2) + (0.018P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, S = 0.965, $\Delta\rho_{max}/\Delta\rho_{min}$ = +0.095 e/Å^3 and –0.099 e/Å^3.

10c: Yellow solid, 294 mg (63%); R_f = 0.48 (chloroform/ethyl acetate, 10:1); m.p. 192 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 4.65, 4.89 (d, ^2J = 9.5 Hz, 2× 1 H), 6.7 (d, J_o = 7.8 Hz, 2 H), 6.8 (d, J_o = 7.8 Hz, 2 H), 7.2–7.35 (m, 10 H), 7.27 (d, J_o = 9.1 Hz, 1 H), 7.27 (t, J_o = 8.0 Hz, 1 H), 7.39 (t, J_o = 8.0 Hz, 1 H), 7.56 (d, J_o = 8.2 Hz, 1 H), 7.68 (d, J_o = 8.0 Hz, 1 H), 7.91 (d, J_o = 9.1 Hz, 1 H), 8.29 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1, 77.1, 77.2, 112.9, 120.5, 121.5, 124.4, 127.5, 127.7, 127.7–128.7, 128.8, 129.3, 131.9, 132.3, 136.3, 138.9, 139.2, 141.5, 147.1, 155.6, 162.6 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 4.6 ppm.

CCDC-689995 (for **7a**), -689999 (for **7c**), -689997 (for **10a**·*n*-C_6H_{12}), -689996 (for **10b**), and -689998 (for **10c**·0.5Et_2O) contain the supplementary crystallographic data. These data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG). We are grateful to Sabine Houben for her assistance with the preparation of several compounds.

[1] For reviews, see: M. R. Barbachyn, C. R. Johnson, in *Asymmetric Synthesis*, vol. 4 (Eds.: J. D. Morrison, J. W. Scott), Academic Press, San Diego, **1984**, chapter 2; D. Valentine Jr., in *Asymmetric Synthesis*, vol. 4 (Eds.: J. D. Morrison, J. W. Scott),

Academic Press, San Diego **1984**, chapter 3; F. A. Davis, R. H. Jenkins Jr., in *Asymmetric Synthesis*, vol. 4 (Eds.: J. D. Morrison, J. W. Scott), Academic Press, San Diego **1984**, chapter 4; C. A. Maryanoff, B. E. Maryanoff, in *Asymmetric Synthesis*, vol. 4 (Eds.: J. D. Morrison, J. W. Scott), Academic Press, San Diego, **1984**, chapter 5.

[2] a) E. Vedejs, R. W. Chapman, S. Lin, M. Müller, D. R. Powell, *J. Am. Chem. Soc.* **2000**, *122*, 3047–3052; b) C. S. Shiner, C. M. Garner, R. C. Haltiwanger, *J. Am. Chem. Soc.* **1985**, *107*, 7167–7172; c) H. I. Beltrán, L. S. Zamudio-Rivera, T. Mancilla, R. Santillan, N. Farfán, *J. Organomet. Chem.* **2002**, *657*, 194–204; d) H. I. Bertrán, S. J. Alas, R. Santillan, N. Farfán, *Can. J. Chem.* **2002**, *80*, 801–812.

[3] D. J. Owen, D. VanDerveer, G. B. Schuster, *J. Am. Chem. Soc.* **1998**, *120*, 1705–1717.

[4] a) S. Toyota, T. Hakamata, N. Nitta, F. Ito, *Chem. Lett.* **2004**, *33*, 206–208; b) S. Toyota, F. Ito, N. Nitta, T. Hakamata, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2081–2088; c) S. Toyota, F. Ito, T. Yamamoto, H. Akashi, T. Iwanaga, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 796–798.

[5] T. Imamoto, H. Morishita, *J. Am. Chem. Soc.* **2000**, *122*, 6329–6330.

[6] L. Charoy, A. Valleix, L. Toupet, T. Le Gall, P. Pham van Chuong, C. Mioskowski, *Chem. Commun.* **2000**, 2275–2276.

[7] M. Braun, R. Fleischer, B. Mai, M.-A. Schneider, S. Lachenicht, *Adv. Synth. Catal.* **2004**, *346*, 474–482.

[8] M. Braun, A. Hahn, M. Engelmann, R. Fleischer, W. Frank, C. Kryschi, S. Haremza, K. Kürschner, R. Parker, *Chem. Eur. J.* **2005**, *11*, 3405–3412.

[9] In a low-temperature ^{1}H NMR spectrum (223 K) of **7a** (H instead of Cl), one of the geminal phenyl rings displayed a set of five anisochronous protons (ABCDE system), indicating their hindered rotation.

[10] S. Jones, C. Smanmoo, *Tetrahedron Lett.* **2004**, *45*, 1585–1588; M. Murakata, H. Tsutsui, O. Hoshino, *Org. Lett.* **2001**, *3*, 299–302.

[11] H. Höpfl, *J. Organomet. Chem.* **1999**, *581*, 129–149. Slightly different values resulted, when the tetrahedral character was calculated according to Ōki's equation, which is based on the three angles between boron and the covalently bound neighbouring atoms: **10a**: 74%, **10b**: 77%, **10c**: 74%; cf.: S. Toyota, M. Ōki, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1832–1840.

[12] TURBOMOLE (vers. 5.8): R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, H. Korn, C. Huber, U. Huniar, M. Kattannek, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, H. Weiss, University of Karlsruhe **2006**, siehe http://www.turbomole.com.

[13] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[14] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787–1799.

[15] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.

[16] a) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454–464; b) F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Vögtle, S. Grimme, *J. Am. Chem. Soc.* **2000**, *122*, 1717–1724; c) C. Diedrich, S. Grimme, *J. Phys. Chem. A* **2003**, *107*, 2524–2539.

[17] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.

Received: August 12, 2008
Published Online: September 17, 2008

