Synthesis and Structure of 2,2′-Boryl-, Germyl-, Silyl-, and Stannyl-Substituted 1,1′-Binaphthyl Systems☆

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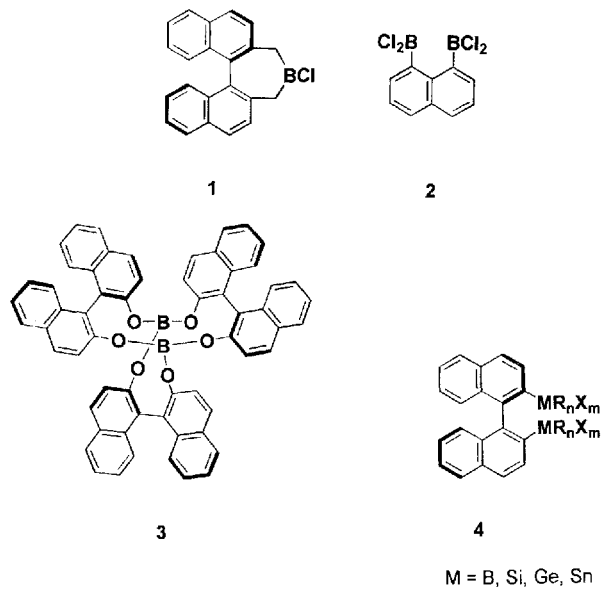
A number of Lewis acid binaphthyl systems, substituted in 2- or 2,2′-position, are synthesized by lithiation of 2,2′-dibromo-1,1′-binaphthyl (**5**), followed by addition of various electrophiles. Stepwise lithiation and subsequent borylation with trimethyl borate leads to the bromoboronic acid **6**, which can be stabilized by esterification with pinacol giving **7**. By increasing the reaction mixture to 2 equiv. of *n*-butyllithium and 2 equiv. of methyl borate the path to the binaphthylmonoboronic acid ester **9** is opened up. A further increase in the quantity of electrophile also leads to the binaphthylbisboronic acid ester **12**. The 2,2′-disubstituted silyl, germyl, and stannyl derivatives **13a–15a** are accessible in good yields. Treatment with boron halides leads exclusively to methyl/halogen exchange, giving the bidentate Lewis acids **13b–15b**, the former of which can be bridged by oxygen. Only in case of the bis(tributylstannyl)binaphthyl **16a** does *ipso* substitution occur in the presence of boron trichloride, giving the bis(dichloroboryl)-substituted binaphthyl **16b** which can then be hydrolysed to **11**. The structures of the majority of the compounds were investigated by X-ray diffraction. In case of the 2,2′-disubstituted compounds **13a–15a** the naphthyl groups are orientated perpendicular to each other. The intra- and intermolecular interactions are dominated by this binaphthyl system. In case of the oxygen-bridged compounds **13c** and **14c** the angle between the naphthyl planes decreases to about 70°. This also has an effect on the packing of the molecule; in this instance the orientation of two naphthyl in neighbouring molecules is nearly parallel. The structure of the diboronic acid is dominated by intra- and intermolecular hydrogen bonding.

During the last three decades the C_2-symmetric binaphthyl group has proved to be an extremely important and versatile artificial chiral inductor in stoichiometric and catalytic asymmetric syntheses[1]. Prominent examples of asymmetric reagents and catalysts of this kind are the β-binaphthol (BINOL) based reagents, used in asymmetric reductions, and transition metal complexes of 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (BINAP) used in catalytic enantioselective hydrogenation reactions.

Chiral organoboranes occupy a truly unique position in the field of asymmetric synthesis; this is attributable to the characteristics of the element boron. Besides playing a role in stoichiometric reactions, organohaloboranes and -borates can also act as selective Lewis acid catalysts. For example, addition of boranes can improve the rate and selectivity of Diels-Alder reactions of dienes with α,β-unsaturated carbonyl compounds by complexing, and thus activating, the carbonyl group. This addition complex is conformationally flexible if there is neither an additional steric restriction nor any stabilizing interaction, such as a π-stacking effect[2]. In the course of our investigations of the use of chiral organoboranes as catalysts for asymmetric cycloaddition reactions[3], we have synthesized the first *mono*dentate β-binaphthyl-based borane, the chlorodihyd-

Scheme 1



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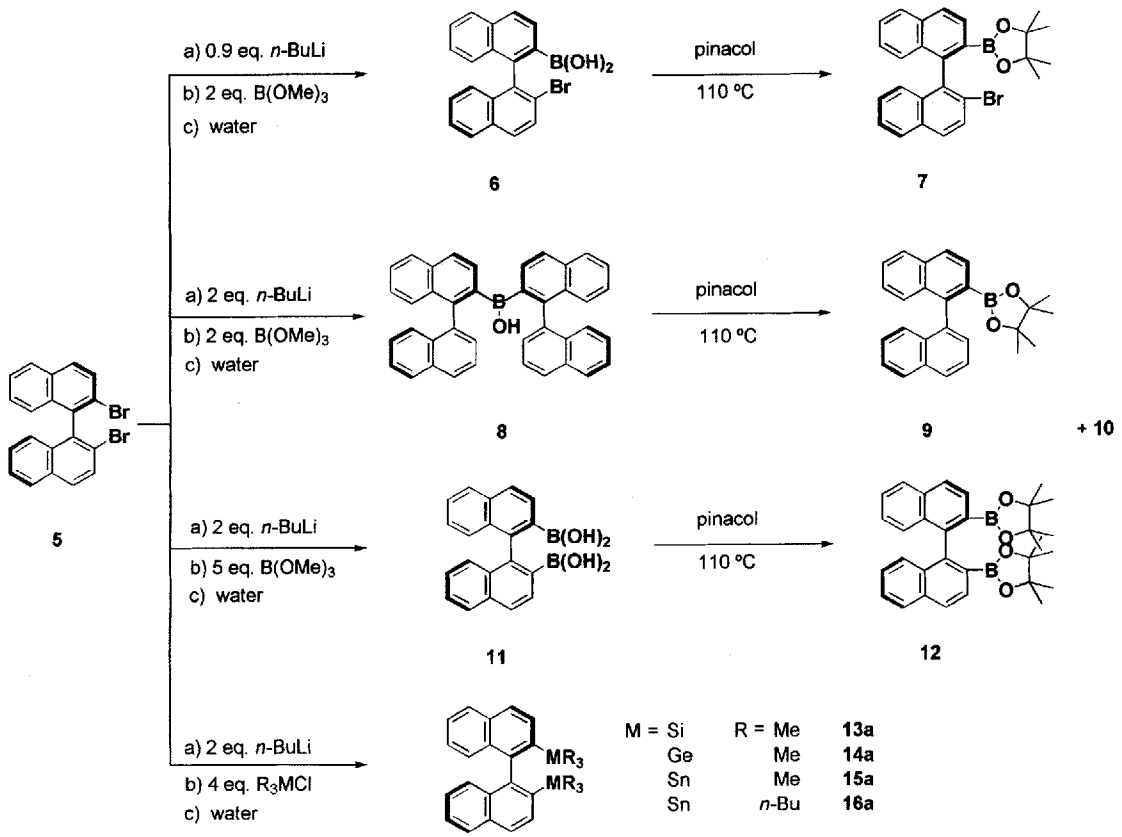
Scheme 2



rodinaphthoborepine **1**[4]. Asymmetric catalysis by bimetallic catalysts is a research field of high present interest[5]. Investigations of the interaction between *bi*dentate Lewis acids with carbonyl groups are rare[6]. Up to now, there is only one example of such an asymmetric Diels–Alder reaction catalyzed by complexes of derivatives of α-amino acids with 1,8-bis(dichloroboryl)naphthalin (**2**), where the two Lewis-acidic sites work in a cooperative manner[7]. By treating β-binaphthol with halohydroboranes we have succeeded in achieving the exclusive formation of the first example of a bidentate binaphthyl-based diborate, the C_3-symmetric tetradecacyclic diborate **3**. This molecule represents a new type of propeller compound, in which the axially chiral 1,1′-binaphthyl groups form the propeller blades[8]. In this case a cooperative interaction of both boron centers is not possible due to the bicyclic structure and we therefore directed our attention to the synthesis of 1,1′-binaphthyl systems **4** with Lewis acid groups in the 2- and 2′-positions. These molecules could open up interesting possibilities in the field of asymmetric catalysis, as hydrometallation reagents, templates, and sensor molecules for the enantioselective detection of carbohydrates[9].

Synthesis and Properties

In contrast to biphenyl[10], the direct regioselective bislithiation of 1,1′-binaphthyl in the 2,2′-position proved, until now, to be impossible and we therefore used 2,2′-dibromo-1,1′-binaphthyl[11] (**5**) as a starting material. Stepwise borylation was possible by lithiation with *n*-butyllithium in THF at −40 °C, followed by borylation with trimethyl borate at −78 °C. When using only 0.9 mol-equiv. of *n*-butyllithium and subsequently 2.5 mol-equiv. of trimethyl borate, 2-bromo-1,1′-binaphthyl-2′-boronic acid (**6**) was formed after hydrolysis. Purification of the product was possible by flash chromatography, but this also led to partial destruction of the boronic acid by cleavage of the B–C bond. All spectral data were in accord with the proposed structure. Due, probably, to oligomerization processes we were not able to vaporize the sterically hindered boronic acid and to obtain an EI mass spectrum. FAB-MS measurements showed an esterification reaction of **6** with 2 matrix molecules (3-nitrobenzyl alcohol, NBA) to give mass peaks at $[M + 2\ NBA - 2\ H_2O]^+$ and at $[M + 2\ NBA - 2\ H_2O - H]^-$. Moreover, a complexation of an extra matrix molecule to the esterification product was observed, giving a mass peak at $[M + 3\ NBA - 2\ H_2O - 2\ H]^-$. After esterification with pinacol in boiling toluene, the cyclic boronate **7** was isolated as a white, almost air-stable solid which could be easily purified by flash chromatography on silica gel. This simple route to **6** and **7** opens the attractive possibility of synthesizing a variety of different 2,2′-substituted 1,1′-binaphthyls.

In two subsequent runs the ratio of **5** to *n*-butyllithium and borate was altered. The substitution pattern of the binaphthyl system was different when **5** was treated with 2.2

Scheme 3

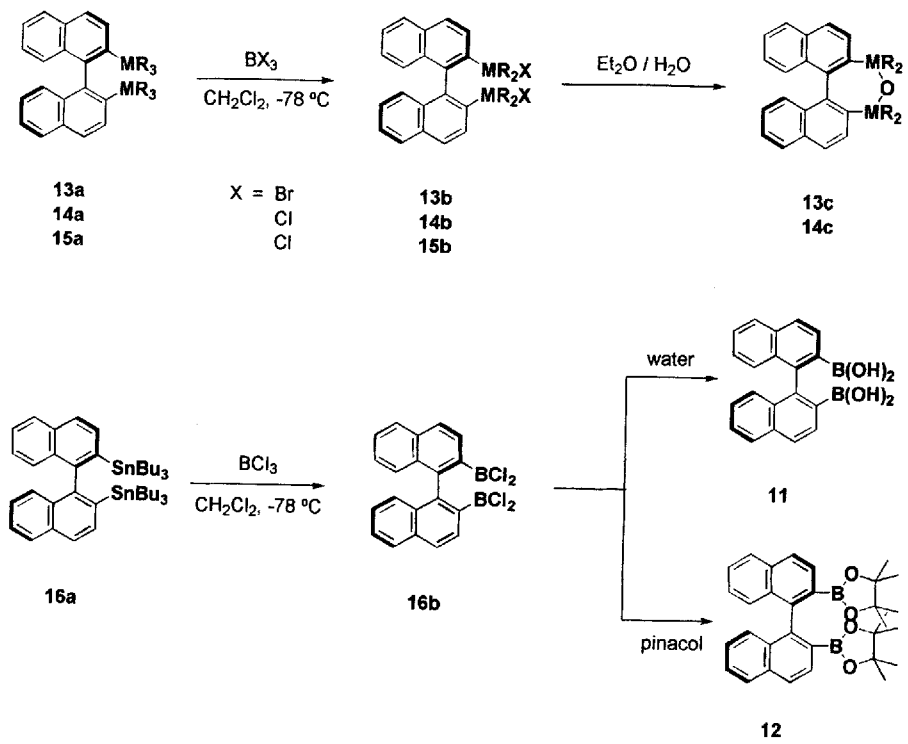


Table 1. Selected bond lengths and angles for all investigated compounds

	13a $C_{26}H_{30}Si_2$				**14a** $C_{26}H_{30}Ge_2$				**15a** $C_{26}H_{30}Sn_2$			
distances [Å]	Si1	Si2	Si3	Si4	Ge1	Ge2	Ge3	Ge4	Sn1	Sn2	Sn3	Sn4
M – C_{al}	1.856(3)	1.847(5)	1.854(4)	1.849(4)	1.917(15)	1.861(21)	1.875(16)	1.866(19)	2.119(16)	2.147(15)	2.122(27)	2.073(28)
M – C_{al}	1.861(4)	1.849(5)	1.861(4)	1.860(3)	1.933(15)	1.917(10)	1.922(16)	1.933(19)	2.123(23)	2.158(15)	2.127(14)	2.133(16)
M – C_{al}	1.876(4)	1.857(4)	1.876(4)	1.871(4)	1.983(12)	1.948(14)	1.935(11)	1.950(8)	2.127(14)	2.171(16)	2.134(18)	2.170(20)
M – C_{ar}	1.895(3)	1.903(3)	1.888(3)	1.888(3)	1.988(6)	1.958(13)	1.990(8)	1.968(11)	2.150(12)	2.183(12)	2.170(14)	2.159(15)
C_{ar} – C_{ar}	1.496(5)				1.502(16)				1.476(17)			
C_{ar} – C_{ar}	1.509(3)				1.464(17)				1.541(14)			
M1 – M2	4.5892				4.5894				4.7937			
M3 – M4	4.7279				4.7347				4.8128			
M1 – M3	5.8682				5.8658				6.6154			
M1 – M4	5.8819				5.9178				6.1099			
angle between planes [°]	C1–C10 / C11–C20		89.60(6)		C1–C10 / C11–C20		89.96(20)		C11–C110 / C21–C210		85.96(22)	
	C27–C36 / C37–C46		88.07(6)		C27–C36 / C37–C46		88.09(18)		C31–C310 / C41–C410		82.67(24)	
	(C11–C22 / C27–C36)		88.56(6)		(C11–C22 / C27–C36)		89.31(18)		(C21–C210 / C31–C310)		86.55(24)	

	13c $C_{24}H_{24}Si_2O$				**14c** $C_{24}H_{24}Ge_2O$		**11** $C_{20}H_{16}B_2O_4 \cdot 2\,(C_4H_{10}O)$			
distances [Å]	Si1	Si2	Si3	Si4	Ge1	Ge2	B1	B2		
M – C_{al}	1.863(13)	1.815(20)	1.824(16)	1.808(17)	1.939(5)	1.930(5)				
M – C_{al}	1.876(14)	1.896(15)	1.851(11)	1.856(19)	1.940(5)	1.939(5)				
M – C_{ar}	1.885(14)	1.905(13)	1.850(18)	1.860(15)	1.962(4)	1.946(5)	1.578(6)	1.583(8)		
M – O	1.635(12)	1.664(11)	1.670(11)	1.626(16)	1.789(3)	1.788(3)	1.347(6)	1.359(6)		
M – O							1.361(6)	1.365(6)		
C_{ar} – C_{ar}	1.447(21)				1.509(5)		1.506(6)			
C_{ar} – C_{ar}	1.557(20)								**H bridges**	
									Donor–H···Accept.	D···A / H···A
M1 – M2	2.9470				3.0926		4.0427		O1 – H71···O3	2.697 / 1.884
M3 – M4	2.9364								O2 – H72···O1	2.755 / 1.939
M1 – M1	4.8932				6.1279		4.1194		O3 – H73···O1	2.697 / 1.955
M3 – M3	4.9018								O4 – H74···O6	2.755 / 1.984
angle between planes [°]	C1–C10 / C11–C20		70.21(26)		C1–C10 / C11–C20	74.90(10)	C1–C10 / C11–C20	87.11(10)		
	C21–C30 / C31–C40		70.10(24)							
	(C11–C20 / C21–C30)		0.84(36)							

mol-equiv. of *n*-butyllithium, followed by 2.2 mol-equiv. of trimethyl borate. In this case, apparently, the 2,2′-dilithio-1,1′-binpahthyl[12] was formed first and the subsequent borylation led to a product mixture which was hard to separate. By flash chromatography it was only possible to isolate bis-[2-(1,1′-binaphthyl)]borinic acid (**8**), an interesting new type of a chiral diorganylborane. It is evident from the IR spectrum that the OH group is not interacting with a second molecule, due to the steric shielding by the two binaphthyl units. The distinct influence of at least one aromatic system is also reflected in the ^{1}H-NMR low-field shift of the OH proton to $\delta = 9.88$. To synthesize a stabilized, chiral, diboryl-substituted binaphthyl we attempted esterification of two molecules of **8** with pinacol in refluxing toluene. However, instead of a simple esterification of the borinic acid **8**, one B–C bond was cleaved, giving a 1:1 mixture of the cyclic pinacol ester of 1,1′-binaphthyl-2-boronic acid **9** and the hydrocarbon 1,1′-binaphthyl (**10**). An analogous cleavage reaction is known from the thermal reaction of diphenylborinic acid at higher temperatures (175°C)[13].

Twofold borylation of **5** was possible when 2.2 mol-equiv. of *n*-butyllithium and a large excess of trimethyl borate (5 mol-equiv.) were used. Subsequent hydrolysis led to 1,1′-binaphthyl-2,2′-diboronic acid (**11**). The melting point of **11** could not be determined, probably due to thermal trimerization or oligomerization. A condensation reaction of this kind could also be the reason that it was not possible to obtain an EI mass spectrum of **11**. Under FAB-MS conditions similar to those used in the case of the monoboronic acid **6**, the bisboronic acid **11** showed esterification reactions with up to 4 matrix molecules (3-nitrobenzyl alcohol, NBA). The mass peaks could be assigned to the following species $[M + 4\ NBA - 4\ H_2O]^+$, $[M + 3\ NBA - 3\ H_2O]^+$ and $[M + 4\ NBA - 4\ H_2O - H]^-$, $[M + 3\ NBA - 3\ H_2O - 2\ H]^-$. The ^{1}H-, ^{13}C-, and ^{11}B-NMR data clearly indicate the formation of the bisboronic acid. In contrast to **8** the IR spectrum of **11** shows strong intermolecular interaction of the boronic acid units. The molecular structure was also proved by X-ray crystallography **11** can also be stabilized by esterification with pinacol. This cyclic boronate **12** is as stable as both **7** and **9**. Therefore it is almost completely stable when purified by flash chromatography. This fact could open the possibility of separation of the enantiomers of **12** by chromatography on chiral phases. To the best of our knowledge **6**, **7**, **8**, **9**, **11**, and **12** are the first examples of C-borylated binaphthyl systems.

To open the route to obtaining other bidentate Lewis acids based on the binaphthyl system we also tried the synthesis of the halodialkyl-substituted silyl, germyl, and stannyl derivatives. These compounds could also prove to be interesting precursors for a high-yield synthesis of **11**, as both the silyl[14] and stannyl[15] group can usually be easily *ipso*-substituted by boron halides. In comparison to the C–Sn bond, the C–Si bond is much less reactive towards electrophilic attack[16]. The Ge–C bond should be intermediate between those two cases; up to now there is only very little known about *ipso* attack of organogermanes by boron halides[17]. In contrast the stannyl group is much larger so that, in case of sterical hindrance, it can be difficult to attack the Sn-substituted aromatic C atom. Therefore the 2,2′-bis(trimethylsilyl)-[18], -(trimethylgermyl)-, -(trimethylstannyl)-[19], and -(tributylstannyl)-substituted derivatives of the binaphthyl system **13a**–**15a** were all synthesized in good yield (68–91%) by treatment of 2,2′-dilithiobinaphthyl with the chlorotrialkylmetal derivatives in THF at −78°C. All trimethyl-substituted products were colourless solids: their molecular structures were determined by X-ray crystallography: only the tributylstannyl-substituted binaphthyl system **16a** remained as an oil, even after a period of months. All compounds were purified by flash chromatography.

The next step was to look at the reaction of **13a**–**16a** with different boron trihalides. The bis(trimethylsilyl)-substituted binaphthyl **13a** was completely inert towards boron trichloride in dichloromethane at 20°C. It was known from our previous work that simple trimethylsilyl-substituted benzene derivatives, like phenyltrimethylsilane[14], are easily *ipso*-borylated by boron trichloride or tribromide at low temperature in chlorinated solvents, especially dichloromethane. When using a solution of boron tribromide in dichloromethane at 20°C regioselective cleavage of a C_{Me}–Si bond at both silyl groups occured, giving 2,2′-bis-(bromodimethylsilyl)-1,1′-binaphthyl[18] (**13b**). This reaction is reminiscent of the reaction of trimethylsilylated biphenyls with boron halides[20]. The same type of reaction was observed when the bisgermyl- or bisstannyl-substituted binaphthyls **14a** and **15a** were introduced. Because of their higher reactivity towards electrophilic attack boron trichloride was already reactive enough for a selective methyl–chloro exchange. These compounds, **13b**–**15b**, represent a new type of inherent chiral bidentate Lewis acid of high potential value. Reduction of the M–Cl bonds leads to the chiral hydrometallation reagents.

The 2,2′-bis(chlorodimethylstannyl)-1,1′-binaphthyl[19] (**15b**) (yield 56%) was purified for complete spectral identification; the other bishalides, **13b** and **14b**, were directly transferred into the oxygen-bridged disilepine **13c**[17] and digermepine **14c**. To our suprise 2,2′-bis(tributylstannyl)-1,1′-binaphthyl (**16a**) was selectively *ipso*-substituted by boron trichloride giving exclusively 2,2′-bis(dichloroboryl)-1,1′-binaphthyl (**16b**) as a white solid. This produced both the bisboronic acid **11**, by hydrolysis in diethyl ether, and the boronate **12** by alcoholysis with pinacol.

Crystal Structure Determinations

Single crystals of the compounds **11**, **13a**–**15a**, **13c**, and **14c** (see Table 2) were investigated by X-ray diffraction. The lattice constants were determined by the automatic Search and Indexing routines of the diffractometer. Only in the case of the diboronic acid **11** it was necessary to measure under dry nitrogen and cooling (−60°C). The other crystals were stable in air and at room temperature. The detailed measuring conditions and crystal data for each compound are given in Table 2.

For Lp correction and data processing the program XCAD4[24] has been used. The space groups were deter-

mined by the reflection condition for the related crystallographic system. The structures were solved using the programs SHELXS86[21] and/or SIR92[23]. The solution by direct methods yielded almost the complete molecule. The structures were subsequently refined (anisotropic displacement parameters for non-H atoms), by a full-matrix least-squares analysis, using the program SHELXL93[22]. The hydrogen atoms were located and refined with geometrical constraints. No split position has been refined.

Discussion

The dihedral angles of the naphthyl planes and the intermetallic intramolecular distances should be the most important factors in the control of the stereochemistry in asymmetric syntheses. Therefore X-ray structural analysis of all 2,2′-disubstituted binaphthyl systems were carried out.

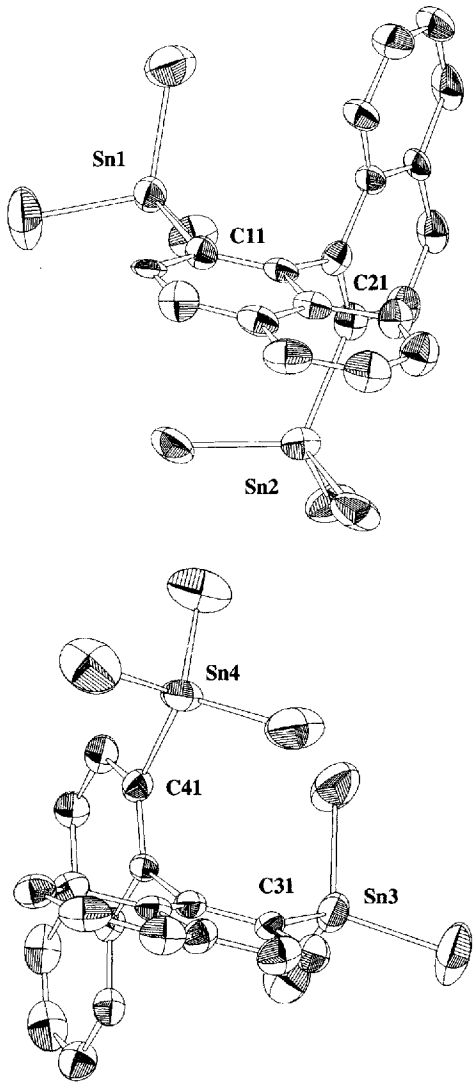
Three different types of molecular structures and three types of intermolecular packing inside the unit cell result from the crystal structure investigations. For all compounds the C–C distances of the aromatic binaphthyl systems are in the typical range of 1.35–1.43 Å; the corresponding angles are 115–125°. There is only a very small dependence of the torsion angle of the planes on the length of the central σ-bond connecting both naphthyl groups. The tetrahedral surroundings of the metal atoms are nearly undisturbed. Only one angle $C_{ar}-M-C_{al}$ is increased because of an influence of the naphthyl system. The structures do differ when the dihedral angles between the aromatic planes are compared (see Table 1). The naphthyl groups of the bismetallated compounds **13a**, **14a**, and **15a** are orientated perpendicular to each other (see Figure 1). The intra- and intermolecular interactions are dominated by the binaphthyl systems.

Although compound **15a** crystallizes in a comparably large unit cell the calculated density shows that the packing of **13a**–**15a** is apparently the same; the calculated density increases nearly linearly with the corresponding atomic weights of the metals. In all three cases the packing appears to be that of close-packed spheres.

When bridging the metal centers via an oxygen atom (oxadisilepin **13c** and oxadigermepin **14c**) the dihedral angle decreases to about 70°, therefore allowing intramolecular interactions. This also has an effect on the packing of the molecules. Looking at **13c** the intermolecular orientation of two naphthyl groups from one molecule to another is nearly parallel (distance 3.2 Å) and shows a layer like packing along one crystallographic axis (see Figure 2). The other type of dense packing is represented by compound **14c**, where there is a build up of zigzag chains along one crystallographic axis.

The third way to achieve intra- and intermolecular interactions between the molecules is shown in the case of the diboronic acid **11**. The structure and the packing of this compound is dominated by hydrogen bonds (see Figure 3). The intermolecular hydrogen bonds connect two molecules which thus form a planar eight membered ring (–B–O2–HH–O2–B–; see Figure 3). There is also an

Figure 1. ORTEP[29] drawing of the two independent molecules of compound **15a**



interaction with one diethyl ether molecule (O6). Because of this hydrogen bond interaction the structure of this solvent molecule was easy to refine and it does not show any disorder. The second diethyl ether molecule, however, does not show any hydrogen bond interaction with other molecules and its structure was only refineable by imposing geometrical constraints. In contrast to any other of the investigated structures the diboronic acid **11** shows nearly the same intra- and intermolecular metal–metal distances (see Table 1). This is also an effect of the intermolecular hydrogen bonds. The bismetallated compounds **13a**, **14a**, and **15a** show comparable metal–metal distances. Despite shorter intramolecular metal–metal distances this is also the case for the compounds **13c** and **14c**. This provides additional support for the assertion that there is strong intramolecular interaction in the case of the aromatic naphthyl groups.

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Figure 2. The layer-like packing of the molecules for compound **13c**; the spacing between two interacting layers is 3.2 Å; viewing is along the crystallographic *b* axis

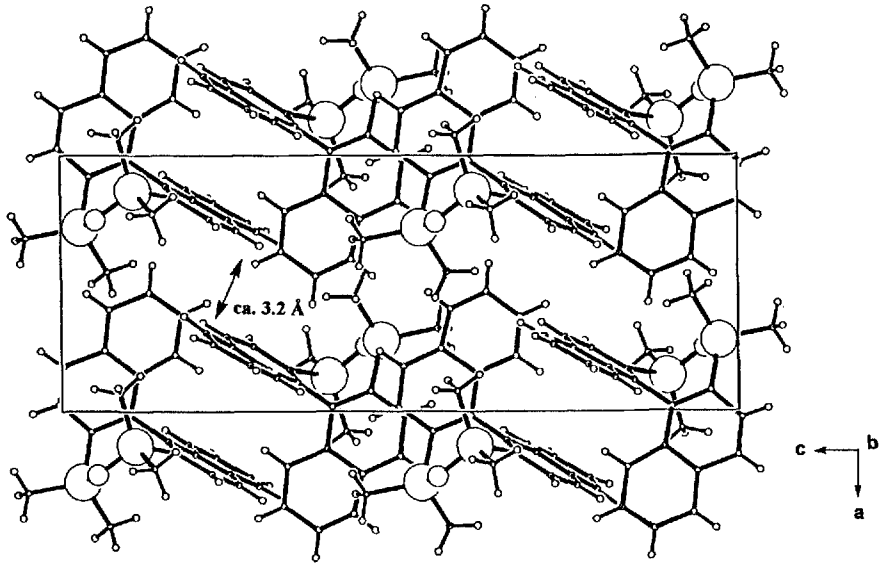
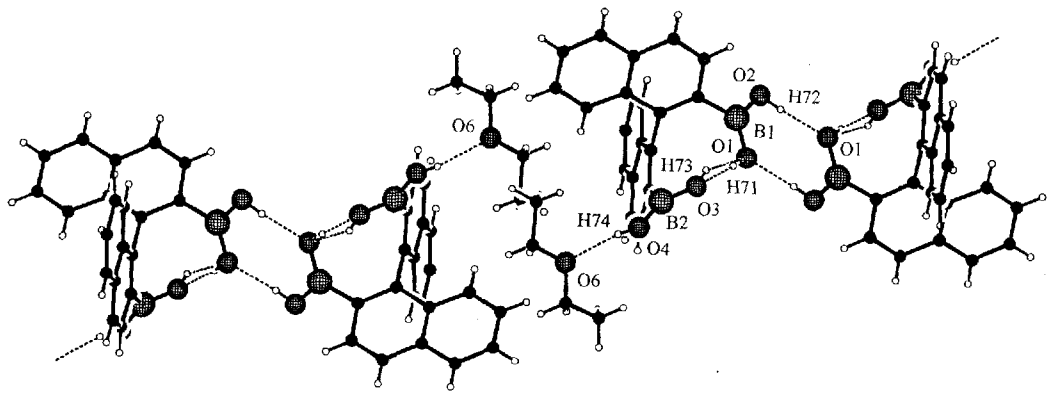


Figure 3. PLUTON[30] plot of the hydrogen-bond dominated packing of the diboronic acid **11**



and Dr. *H.-M. Schiebel* (Technische Universität Braunschweig) for MS measurements.

Experimental Section

All experiments were carried out under dry purified nitrogen or under argon in flame-dried reaction flasks. All solvents were dried by standard methods. – NMR: Bruker AMX 400 or AC 250 P with TMS (internal) and $^{11}BF_3 \cdot OEt_2$ (external) as reference. – IR: Bruker Vector 22 FT-IR. – Melting points (uncorrected): Büchi apparatus. – Elemental analyses: Institut für Pharmazeutische Chemie, TU Braunschweig. – MS (EI, CI): HP 5989B, MS (high-resolution): Finnigan MAT 95; Institut für Organische Chemie, U Göttingen, MS (FAB): Finnigan MAT 8430; Institut für Organische Chemie, TU Braunschweig. – Chromatography: flash silica gel 60 (230–400 mesh, ASTM, Merck). – Starting materials: 2,2′-dihydroxy-1,1′-binaphthyl[31] and 2,2′-dibromo-1,1′-binaphthyl[11] (**5**) were prepared according to published procedures.

Monoboryl- and Bisboryl-Substituted Binaphthyl Systems **6**, **8**, *and* **11**. – *General Procedure:* 1.6 M *n*-Butyllithium was added to a solution of 2,2′-dibromo-1,1′-binaphthyl (**5**) in THF at −40°C. After 1 h of stirring, the mixture was cooled to −78°C and added to a solution of trimethyl borate in THF. The reaction mixture was then allowed to warm to room temp. overnight. The solvents were evaporated under reduced pressure. The solid residue was dissolved in 50 ml of diethyl ether and then hydrolysed with 1 N hydrochloric acid. The product was extracted with 250 ml of diethyl ether, which was washed with a saturated aqueous sodium hydrogen carbonate solution and water. The crude product was dried with sodium sulfate.

2-Bromo-1,1′-binaphthyl-2′-boronic Acid (**6**): 2,2′-Dibromo-1,1′-binaphthyl (**5**) (2.00 g, 4.85 mmol) in THF (30 ml), 2.91 ml (4.37 mmol) of 1.5 M *n*-butyllithium, and trimethyl borate (1.35 ml, 12.13 mmol) in THF (30 ml). The crude product was purified by flash column chromatography (hexane/ethyl acetate, 4:1) to yield a white solid **6** (0.356 g, 20%), m.p. 199°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3443 (m, br. OH), 3055 (m, ArH), 1348 (m, BO), 754 (m). – ^1H NMR ($CDCl_3$): δ = 6.89 (d, *J* = 8.4 Hz, 1H, arom. CH), 6.95 (d, *J* = 8.4 Hz, 1H, arom. CH), 7.26 (dd, *J* = 8.4 and 6.8 Hz, 1H, arom. CH), 7.45–7.50 (m, 4H, 2 arom. CH and 2 OH), 7.79 (d, *J* = 8.4 Hz, 1H, arom. CH), 7.91–8.02 (m, 5H, arom. CH). – ^{13}C NMR ($[D_6]DMSO$): δ = 122.31 (arom. CBr, 1 C), 125.64, 126.02, 126.33, 126.37, and 126.58 (arom. CH, 5 C), 126.85 (arom. CH, 2 C),

Table 2. Crystal data, structure solution, and refinement of all investigated compounds[28]

Compound	**13a** [25]	**14a** [26]	**15a**	**13c** [27]	**14c**	**11**
Formula	$C_{26}H_{30}Si_2$	$C_{26}H_{30}Ge_2$	$C_{26}H_{30}Sn_2$	$C_{24}H_{24}Si_2O$	$C_{24}H_{24}Ge_2O$	$C_{20}H_{16}B_2O_4 \cdot 2\,(C_4H_{10}O)$
CSD-No.	402554	402555	405496	405537	405507	405508
Formula mass [g/mol]	398.69	487.70	579.90	384.62	401.04	341.964 + 148.24
Crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group (No.)	$P\,\bar{1}$ (2)	$P\,\bar{1}$ (2)	$P\,2_1/n$ (14)	$P\,\bar{1}$ (2)	$P\,2_1/c$ (14)	$P\,2_1/c$ (14)
a [Å]	11.656(5)	11.673(2)	14.436(2)	8.654(2)	14.160(10)	16.395(2)
b [Å]	14.329(5)	14.475(3)	11.160(10)	11.502(3)	10.655(4)	9.200(3)
c [Å]	14.574(5)	14.615(10)	33.311(7)	22.821(3)	15.681(9)	19.300(4)
α [°]	87.45(2)	87.24(3)	90.0	77.76(1)	90.0	90.0
β [°]	77.00(2)	77.02(3)	100.41(1)	86.46(1)	115.94(4)	100.25(3)
γ [°]	81.64(2)	81.34(1)	90.0	72.20(1)	90.0	90.0
Volume [Å^3]	2346.4	2378.7	5278.3	2113.6	2127.5	2864.6
calc. density [g/cm^3]	1.129	1.362	1.459	1.209	1.479	1.137
Z (molec./asymm. unit)	4 (2 molec. × 2)	4 (2 molec. × 2)	8 (2 molec. × 4)	4 (2 molec. × 2)	4 (1 molec. × 4)	4 (1 molec.× 4) (2 Et_2O × 4)
Radiation	Mo-$K\alpha$ (0.71073 Å) graphite monochromator					
Diffractometer	ENRAF-NONIUS CAD4					
μ (Mo-$K\alpha$) [mm^{-1}]	0.160	2.536	1.900	0.179	2.836	0.077
Temperature [°C]	20	20	20	20	20	–60
Scan mode	ω-scan	ω-scan	ω-scan	ω-scan	ω-scan	ω-scan
Scan angle [°]	1.10 + 0.35 tg θ	1.10 + 0.35 tg θ	1.10 + 0.35 tg θ	1.10 + 0.35 tg θ	1.20 + 0.35 tg θ	1.10 + 0.35 tg θ
Scan range [°]	$2 \le 2\theta \le 54$	$2 \le 2\theta \le 64$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 56$	$2 \le 2\theta \le 60$	$2 \le \theta \le 52$
hkl range	–14/14;0/18;–18/18	0/17;0/21;0/21	0/17;0/13;–10/38	0/11;0/15;–29/30	0/19;0/14;–22/19	0/20;0/6;–23/23
max.measur.time/refl. [s]	45	60	60	60	60	40
measured refl.	10850	5764	6225	6689	6382	4146
unique refl.	10201	5764	6093	6661	6159	4007
observed refl. [$Fo \ge 2\sigma(I)$]	6512	2252	4283	1749	3552	2631
refined param.	505	506	506	496	249	325
Extinction param.	–	0.0003	0.0001	0.0002	0	0.0086
Solution program	SHELXS-86 [21]	SIR-92	SIR-92 [23]	SHELXS-86	SIR-92	SHELXS-86
Refinement program	SHELXL-93 [22]	SHELXL-93	SHELXL-93	SHELXL-93	SHELXL-93	SHELXL-93
weighting param. a/b [22]	0.1494/1.1410	0.0845/0	0.1245/16.617	0.0594/0	0.0966/0.3701	0.1357/4.4979
$R1$ for $Fo > 4\,\sigma\,(Fo)$	0.0544	0.0667	0.0579	0.0595	0.0596	0.0807
$wR2$ for all	0.2112	0.1791	0.2224	0.1972	0.1695	0.2738

128.16, 128.23, 129.09, 129.69, and 130.94 (arom. CH, 5 C), 131.44, 132.00, 133.48, 133.97, 134.48, and 139.35 (arom. quat. C, 6 C). – ^{11}B NMR ($CDCl_3$): δ = 29.5 (s). – MS (FAB$^-$, 3-nitrobenzyl alcohol; NBA); *m/z* (%): 645 (4) and 647 (4) [M + 2 NBA – 2 H_2O – H]$^-$, 797 (10) and 799 (11) [M + 3 NBA – 2 H_2O – 2 H]$^-$; MS (FAB$^+$, 3-nitrobenzyl alcohol; NBA); *m/z* (%): 646 (26) and 648 (26) [M + 2 NBA – 2 H_2O]$^+$. – $C_{20}H_{14}BBrO_2$ (377.04): calcd. C 63.71, H 3.74, B 2.87, Br 21.19; found C 66.27, H 3.71, B 2.97, Br 20.94; $C_{34}H_{24}BBrN_2O_6$; calcd. 646.0911; found 646.0917 (FAB$^+$MS, [M + 2 NBA – 2 H_2O]$^+$, ^{79}Br).

Bis[2-(1,1′-binaphthyl)]borinic Acid (**8**): 2,2′-Dibromo-1,1′-binaphthyl (**5**) (2.00 g, 4.85 mmol) in THF (30 ml), 6.67 ml (10.68 mmol) of 1.6 M *n*-butyllithium, and trimethyl borate (1.19 ml, 10.67 mmol) in THF (30 ml). The crude product was purified by flash column chromatography (hexane/ethyl acetate, 6:1) to yield a white solid **8** (0.222 g, 15%), m.p. 236°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3543 (m, OH, free), 3036 (m, ArH), 1362 (m), 1348 (m, BO), 785 (s), 744 (s). – ^{1}H NMR ($CDCl_3$): δ = 6.80 (d, *J* = 6.8 Hz, 2H, arom. CH), 7.09–7.28 (m, 11H, arom. CH and OH), 7.39–7.49 (m, 4H, arom. CH), 7.56 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.77 (d, *J* = 8.4 Hz, 4H, arom. CH), 7.82–7.90 (m, 4H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = 125.23, 125.80, 125.91, 126.30, 126.35, 126.52, 126.56, 126.92, 127.79, 127.89, 128.14, 128.31, and 130.93 (arom. CH, 26 C), 132.50, 133.02, 133.33, 133.97, 137.91 and 142.29 (arom. quat. C, 12 C). – ^{1}H NMR ([D$_6$]DMSO): δ = 6.52 (d, *J* = 8.4 Hz, 2H, arom. CH), 6.84 (d, *J* = 6.8 Hz, 2H, arom. CH), 6.89 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.04 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.10–7.16 (m, 4H, arom. CH), 7.28 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.32–7.38 (m, 4H, arom. CH), 7.43 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.77 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.87 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.90 (d, *J* = 8.4 Hz, 2H, arom. CH), 9.88 (br. s, 1H, OH). – ^{13}C NMR ([D$_6$]DMSO): δ = 125.09 and 125.58 (arom. CH, 4 C), 125.61 (arom. CH, 4 C), 125.68, 125.71, 125.80, 126.51, 127.58, 127.85, 127.97, 128.29, and 128.40 (arom. CH, 18 C), 131.61, 132.83, 132.88, 133.17, 138.41, and 139.59 (arom. quat. C, 12 C). – ^{11}B NMR ($CDCl_3$): δ = 47.1 (s). – MS, (70 eV, EI); *m/z* (%): 535 (11) [M$^+$ + 1], 534 (27) [M$^+$], 516 (7), 281 (19), 280 (13), 279 (14), 263 (39), 253 (100), 252 (95), 126 (18). – $C_{40}H_{27}BO$ (534.5): calcd. C 89.89, H 5.09; found C 89.31, H 5.00.

1,1′-Binaphthyl-2,2′-diboronic Acid (**11**): 2,2′-Dibromo-1,1′-binaphthyl (**5**) (1.03 g, 2.51 mmol) in THF (30 ml), 3.68 ml (5.52 mmol) of 1.5 M *n*-butyllithium, and trimethyl borate (1.40 ml, 12.55 mmol) in THF (50 ml). The crude product was dissolved in 5 ml of dichloromethane and then precipitated by adding 30 ml of hexane. The precipitate was separated by filtration and thoroughly washed with hexane to yield a white solid **11** (0.581 g, 68%). The melting point could not be determined, as thermal dehydration led, probably, to the formation of anhydrides or oligomers. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3600 (m, OH, free), 3328 (s, br. OH), 3054 (w, ArH), 1380 (s, br. BO). – ^{1}H NMR ([D$_6$]DMSO): δ = 6.94 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.19 (dd, *J* = 7.6 and 7.6 Hz, 2H, arom. CH), 7.42 (dd, *J* = 7.6 and 7.6 Hz, 2H, arom. CH), 7.68 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.93 (d, *J* = 7.6 Hz, 2H, arom. CH), 7.95 (d, *J* = 7.6 Hz, 2H, arom. CH), 8.14 (br. s, 4H, OH). – ^{13}C NMR ([D$_6$]DMSO): δ = 125.89 (arom. CH, 4 C), 126.35, 126.45, 127.96 and 128.78 (arom. CH, 8 C), 132.78 and 133.46 (arom. quat. C, 4 C), 141.17 (arom. quat. C, 2 C). – ^{11}B NMR ([D$_6$]DMSO): δ =

24.2 (s). – MS (FAB$^-$, 3-nitrobenzyl alcohol; NBA); *m/z* (%): 881 (14) [M + 4 NBA – 4 H_2O – H]$^-$, 745 (28) [M + 3 NBA – 3 H_2O – 2 H]$^-$; MS (FAB$^+$, 3-nitrobenzyl alcohol; NBA); *m/z* (%): 882 (3) [M + 4 NBA – 4 H_2O]$^+$, 747 (2) [M + 3 NBA – 3 H_2O]$^+$. – $C_{20}H_{16}B_2O_4$ (342.0): calcd. 70.25, H 4.72, B 6.32; found C 70.41, H 4.80, B 6.03.

Reaction of **6**, **8** *and* **11** *with Pinacol to Obtain* **7**, **9**, *and* **12**. – *General Procedure:* A solution of the borylated compound and 2,3-dihydroxy-2,3-dimethylbutane (pinacol) in 20 ml of toluene was heated under reflux for 48 h. The resulting water was removed by azeotropic distillation. After completion of the reaction the solvent was removed under reduced pressure.

2-Bromo-1,1'-binaphthyl-2'-boronic Acid Pinacol Ester (**7**): 2-Bromo-1,1'-binaphthyl-2'-boronic acid (**6**) (0.200 g, 0.53 mmol) and 2,3-dihydroxy-2,3-dimethylbutane (0.069 g, 0.58 mmol). The crude product was purified by flash column chromatography (hexane/ethyl acetate, 25:1). The product **7** was isolated as a white solid (0.140 g, 58%), m.p. 59°C. – IR (film, cm^{-1}): $\tilde{\nu}$ = 3055 (w, ArH), 2977 (m) and 2927 (m, CH), 1378 (s) and 1305 (s, BO). – ^{1}H NMR ($CDCl_3$): δ = 0.79 and 0.94 [2 s, 12H, $C(CH_3)_2$], 7.07 (d, *J* = 8.4 Hz, 1H, arom. CH), 7.17–7.29 (m, 2H, arom. CH), 7.38–7.52 (m, 3H, arom. CH), 7.74 (d, *J* = 8.4 Hz, 1H, arom. CH), 7.79 (d, *J* = 8.4 Hz, 1H, arom. CH), 7.84–7.96 (m, 4H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = 24.22 and 24.31 [$C(CH_3)_2$, 4 C], 83.07 (OC, 2 C), 122.87 (arom. CBr, 1 C), 125.54, 126.18, 126.42, 126.48, 126.73, 126.77, 127.20, 127.56, 128.11, 128.56, 129.58, and 130.61 (arom. CH, 12 C), 131.74, 132.10, 134.80, 135.19, 138.95, and 144.52 (arom. quat. C, 6 C). – ^{11}B NMR ($CDCl_3$): δ = 30.8 (s). – MS (70 eV, EI); *m/z* (%): 460 (72) and 458 (75) [M$^+$], 445 (4) and 443 (4), 380 (2), 344 (24) and 342 (38), 293 (100), 278 (73), 261 (68), 252 (28). – $C_{26}H_{24}BBrO_2$ (459.19): calcd. C 68.01, H 5.27; found C 66.05, H 5.23; calcd. 458.1053; found 458.1052 (MS).

1,1'-Binaphthyl-2-boronic Acid Pinacol Ester (**9**): Bis[2-(1,1'-binaphthyl)]borinic acid (**8**) (0.089 g, 0.17 mmol) and 2,3-dihydroxy-2,3-dimethylbutane (0.062 g, 0.52 mmol). The crude product was purified by flash column chromatography (hexane/ethyl acetate, 25:1). The by-product 1,1'-binaphthyl (**10**) (0.043 g, 69%) was obtained. The product **9** was isolated as a white solid (0.028 g, 66%), m.p. 53–54°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3054 (w, ArH), 2977 (m) and 2927 (m, CH), 1377 (s) and 1359 (s, BO), 781 (m). – ^{1}H NMR ($CDCl_3$): δ = 0.76 and 0.90 [2 s, 12H, $C(CH_3)_2$], 7.18–7.33 (m, 3H, arom. CH), 7.37–7.60 (m, 5H, arom. CH), 7.82–7.96 (m, 5H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = 24.09 and 24.29 [$C(CH_3)_2$, 4 C], 83.21 (OC, 2 C), 124.92, 125.34, 125.61, 125.78, 126.45, 126.55, 126.76, 127.20, 127.25, 127.77, 127.89, 128.04, and 129.87 (arom. CH, 13 C), 132.72, 133.41, 133.88, 134.55, 138.89, and 144.74 (arom. quat. C, 6 C). – ^{1}H NMR ([D$_6$]DMSO): δ = 0.72 and 0.83 [2 s, 12H, $C(CH_3)_2$], 7.06 (d, *J* = 8.4 Hz, 1H, arom. CH), 7.22 (d, *J* = 8.4 Hz, 1H, arom. CH), 7.26 (dd, *J* = 8.4 and 6.8 Hz, 1H, arom. CH), 7.32 (dd, *J* = 8.4 and 6.8 Hz, 1H, arom. CH), 7.35 (d, *J* = 6.8 Hz, 1H, arom. CH), 7.45 (dd, *J* = 8.4 and 6.8 Hz, 1H, arom. CH), 7.52 (dd, *J* = 8.4 and 6.8 Hz, 1H, arom. CH), 7.59 (dd, *J* = 8.4 and 6.8 Hz, 1H, arom. CH), 7.76 (d, *J* = 8.4 Hz, 1H, arom. CH), 7.97–8.03 (m, 4H, arom. CH). – ^{13}C NMR ([D$_6$]DMSO): δ = 24.14 and 24.22 [$C(CH_3)_2$, 4 C], 83.12 (OC, 2 C), 125.23, 125.67, 125.89, 125.95, 126.41, and 126.52 (arom. CH, 6 C), 126.90 (arom. CH, 2 C), 127.55, 128.00, 128.15, 128.24 and 129.86 (arom. CH, 5 C), 132.20, 133.22, 133.24, 134.24, 138.22, and 144.18 (arom. quat. C, 6 C). – ^{11}B NMR ($CDCl_3$): δ = 30.8 (s). – MS (70 eV, EI); *m/z* (%): 381 (29) [M$^+$ + 1], 380 (100) [M$^+$], 365 (3), 294 (9), 293 (9), 280 (20), 279 (38), 264 (83), 253 (25), 252 (59), 84 (8). – $C_{26}H_{25}BO_2$ (380.3): calcd. C 82.12, H 6.63; found C 82.25, H 6.81.

1,1'-Binaphthyl-2,2'-diboronic Acid Bispinacol Ester (**12**): 1,1'-Binaphthyl-2,2'-diboronic acid (**11**) (0.268 g, 0.78 mmol) and 2,3-dihydroxy-2,3-dimethylbutane (0.185 g, 1.57 mmol). The crude product was purified by flash column chromatography (hexane/ethyl acetate, 20:1) to yield a white solid **12** (0.278 g, 70%), m.p. 65°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3051 (w, ArH), 2976 m and 2929 (w, CH), 1379 (s) and 1304 (s, BO). – ^{1}H NMR ($CDCl_3$): δ = 0.80 and 0.88 [2 s, 24H, $C(CH_3)_2$], 7.18 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.27 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.41 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.82–7.90 (m, 6H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = 24.22 and 24.30 [$C(CH_3)_2$, 8 C], 82.77 (OC, 4 C), 125.23, 125.89, 126.01, 127.42, 127.52, and 129.93 (arom. CH, 12 C), 133.75, 134.30, and 146.42 (arom. quat. C, 6 C). – ^{11}B NMR ($CDCl_3$): δ = 31.1 (s). – MS (70 eV, EI); *m/z* (%): 507 (30) [M$^+$ + 1], 506 (86) [M$^+$], 505 (38), 448 (3), 406 (7), 321 (4), 306 (20), 279 (35), 263 (25), 252 (22), 84 (32), 41 (100). – $C_{32}H_{36}B_2O_4$ (506.3): calcd. C 75.92, H 7.17; found C 76.08, H 7.28; calcd. 506.2800; found 506.2799 (MS).

Bismetallated Systems **13a**, **14a**, **15a**, *and* **16a**. – *General Procedure:* 1.6 M *n*-Butyllithium was added to a solution of 2,2'-dibromo-1,1'-binaphthyl (**5**) in 30 ml THF at –40°C. After 1 h of stirring, the green slurry was cooled to –78°C and a solution of the electrophile, in 30 ml of THF, was added. The reaction mixture was allowed to warm to room temp. overnight and was then hydrolysed with a saturated ammonium chloride solution. The product was extracted with 150 ml of diethyl ether (**16a**: 400 ml), and was then washed with a saturated aqueous sodium hydrogen carbonate solution and water. The crude product was dried with sodium sulfate.

2,2'-Bis(trimethylsilyl)-1,1'-binaphthyl (**13a**): 2,2'-Dibromo-1,1'-binaphthyl (**5**) (2.48 g, 6.02 mmol), 8.27 ml (13.23 mmol) of 1.6 M *n*-butyllithium, and chlorotrimethylsilane (3.17 ml, 25.10 mmol). The crude product was recrystallized from toluene to yield **13a** (1.88 g, 78%) as colourless single crystals, m.p. 114.5°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3041 (w, ArH), 2953 (m, CH), 1246 (s, SiC), 829 (s, SiC). – ^{1}H NMR ($CDCl_3$): δ = –0.29 [s, 18H, $Si(CH_3)_3$], 7.12 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.19 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.43 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.75 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.87 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.93 (d, *J* = 8.4 Hz, 2H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = –0.03 [$Si(CH_3)_3$, 6 C], 125.65, 126.12, 126.66, 127.29, 127.59 and 130.56 (arom. CH, 12 C), 133.38, 133.64, 137.95, and 145.10 (arom. quat. C, 8 C). – MS (70 eV, EI); *m/z* (%): 399 (5) [M$^+$ + 1], 398 (10) [M$^+$], 310 (5), 295 (37), 252 (7), 73 (100). – $C_{26}H_{30}Si_2$ (398.7): calcd. C 78.33, H 7.58; found C 78.25, H 7.62.

2,2'-Bis(trimethylgermyl)-1,1'-binaphthyl (**14a**): 2,2'-Dibromo-1,1'-binaphthyl (**5**) (2.43 g, 5.90 mmol), 7.87 ml (11.81 mmol) of 1.5 M *n*-butyllithium, and chlorotrimethylgermane (3.00 ml, 24.29 mmol). The crude product was purified by flash column chromatography (hexane/diethyl ether, 98:2) to afford crystalline **14a** (1.98 g, 69%). Single crystals (colourless prisms) were obtained from diethyl ether, m.p. 105°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3038 (m, ArH), 2967 (m, CH), 1233 (m), 828 (s). – ^{1}H NMR ($CDCl_3$): δ = –0.20 [s, 18H, $Ge(CH_3)_3$], 7.14 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.21 (dd, *J* = 8.2 and 6.8 Hz, 2H, arom. CH), 7.43 (dd, *J* = 8.2 and 6.8 Hz, 2H, arom. CH), 7.70 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.88 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.93 (d, *J* = 8.2 Hz, 2H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = –0.58 [$Ge(CH_3)_3$, 6 C], 125.67, 125.91, 126.90, 127.05, 127.68 and 130.16 (arom. CH, 12 C), 133.33, 133.57, 140.50, and 144.19 (arom. quat. C, 8 C). – MS (70 eV, EI); *m/z* (%): 490 (6), 488 (8), 486 (7), 484 (3), and 482 (1) [M$^+$], 475 (9), 473 (12) and 471 (11) [M$^+$ – CH_3], 341 (100), 339 (73), 337

(54), 252 (38), 119 (55), 117 (44), 115 (33). – $C_{26}H_{30}Ge_2$ (487.7): calcd. C 64.03, H 6.20; found C 64.05, H 6.14.

2,2'-Bis(trimethylstannyl)-1,1'-binaphthyl (**15a**): 2,2'-Dibromo-1,1'-binaphthyl (**5**) (2.00 g, 4.85 mmol), 6.67 ml (10.68 mmol) of 1.6 M *n*-butyllithium, and chlorotrimethylstannane (4.03 g, 20.24 mmol). The crude product was purified by flash column chromatography (hexane/diethyl ether, 98:2) to yield **15a** (2.01 g, 71%) as, initially, a colourless viscous oil which finally solidified. Single crystals (colourless prisms) were obtained from diethyl ether, m.p.80.5°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3038 (w, ArH), 2969 (m, CH), 771 (s, SnC). – ^{1}H NMR ($CDCl_3$): δ = −0.34 [s, $J(^{119}Sn,CH_3)$ = 53.8 Hz, 18H, $Sn(CH_3)_3$], 7.18–7.25 (m, 4H, arom. CH), 7.43 (dd, *J* = 8.2 and 6.0 Hz, 2H, arom. CH), 7.72 [d, *J* = 8.2 Hz, $J(^{119}Sn,CH)$ = 40.9 Hz, 2H, 3-H and 3'-H], 7.90 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.91 (d, *J* = 8.2 Hz, 2H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = −8.72 [s, $J(^{119}Sn,CH_3)$ = 348.1 Hz, $Sn(CH_3)_3$, 6 C], 125.81 and 125.94 (arom. CH, 4 C), 126.82 [s, $J(^{119}Sn,CH)$ = 45.1 Hz, C-3 and C-3', 2 C], 126.92 and 127.86 (arom. CH, 4 C), 132.06 [s, $J(^{119}Sn,CH)$ = 38.5 Hz, C-4 and C-4', 2 C], 133.20 (arom. quat. C, 2 C), 133.66 [s, $J(^{119}Sn,CH)$ = 9.4 Hz, C-2 and C-2', 2 C], 142.52 and 147.48 (arom. quat. C, 4 C). – MS (70 eV, EI); *m/z* (%): 567 (36), 565 (45), 563 (41), 561 (19), and 559 (6) [$M^+ - CH_3$], 387 (86), 385 (68), 383 (38), 252 (100), 165 (40), 163 (28), 161 (18). – MS (70 eV, CI, reactant gas: CH_4, ^{120}Sn); *m/z*: 567 [$M^+ - CH_3$]. – $C_{26}H_{30}Sn_2$ (579.9): calcd. C 53.85, H 5.21; found C 54.26, H 4.93.

2,2'-Bis(tributylstannyl)-1,1'-binaphthyl (**16a**): 2,2'-Dibromo-1,1'-binaphthyl (**5**) (5.69 g, 13.81 mmol), 18.99 ml (30.38 mmol) of 1.6 M *n*-butyllithium and tributylchlorostannane (15.57 ml, 57.79 mmol). The crude product was purified by flash column chromatography (hexane/diethyl ether, 98:2) to yield **16a** (10.5 g, 91%) as a colourless viscous oil. – IR (film, cm^{-1}): $\tilde{\nu}$ = 3035 (m, ArH), 2956 (m, CH), 2853 (s, br. CH), 1462 (s), 866 (m). – ^{1}H NMR ($CDCl_3$): δ = 0.23–0.51 (m, 12H, $SnCH_2CH_2$), 0.77 (t, *J* = 7.4 Hz, 18H, CH_2CH_3), 1.05–1.20 (m, 24H, $SnCH_2CH_2CH_2CH_3$), 7.19 (d, *J* = 4.0 Hz, 4H, arom. CH), 7.41 (m, 2H, arom. CH), 7.68 [d, *J* = 8.0 Hz, $J(^{119}Sn,CH)$ = 35.2 Hz, 2H, 3-H and 3'-H], 7.87 (d, *J* = 8.0 Hz, 2H, arom. CH), 7.88 (d, *J* = 8.0 Hz, 2H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = 9.85 [s, $J(^{119}Sn,CH_2)$ = 326.7 Hz, $SnCH_2CH_2$, 6 C], 13.55 (s, CH_3, 6 C), 27.32 [s, $J(^{119}Sn,CH_2)$ = 63.9 Hz, $SnCH_2CH_2$, 6 C], 28.91 [s, $J(^{119}Sn,CH_2)$ = 18.1 Hz, $SnCH_2CH_2CH_2$, 6 C], 125.54 and 125.72 (arom. CH, 4 C), 126.37 [s, $J(^{119}Sn,CH)$ = 40.1 Hz, C-3 and C-3', 2 C], 126.87 and 127.78 (arom. CH, 4 C), 132.91 [s, $J(^{119}Sn,CH)$ = 32.4 Hz, C-4 and C-4', 2 C], 133.46 (arom. quat. C, 2 C), 133.62 [s, $J(^{119}Sn,CH)$ = 7.6 Hz, C-2 and C-2', 2 C], 143.07 and 147.98 (arom. quat. C, 4 C). – MS (70 eV, EI); *m/z* (%): 832 (1) and 830 (1) [M^+], 777 (48), 775 (61), 773 (54), 771 (26), and 769 (9) [$M^+ - C_4H_9$], 492 (6), 429 (33), 373 (73), 372 (42), 291 (100), 252 (100), 235 (71), 179 (72). – $C_{44}H_{66}Sn_2$ (832.4): calcd. C 63.49, H 7.99; found C 63.01, H 7.98.

Reaction of Bismetallated Compounds with Boron Trihalide to Obtain **13c**, **14c** *and* **15b**. – *General Procedure:* A solution of the bismetallated compound in 20 ml of dichloromethane was added to the boron trihalide at −78°C. The mixture was kept at this temperature for 1 h and then allowed to warm to room temp. overnight. The solvents were evaporated under reduced pressure. The solid residue was dissolved in diethyl ether and hydrolyzed with water. The crude product was dried with sodium sulfate and then dissolved in 2 ml of a mixture of hexane and dichloromethane. The product was again precipitated, under cold conditions, after a while. The precipitate was separated by filtration.

2,2,7,7-Tetramethyldinaphtho[2,1-c;1',2'-e]-1,2,7-oxadisilepin (**13c**): 2,2'-Bis(trimethylsilyl)-1,1'-binaphthyl (**13a**) (0.298 g, 0.75 mmol) and 0.14 ml (1.39 mmol) of boron tribromide. Recrystallization from toluene yielded **13c** (0.168 g, 58%) as colourless crystals, m.p. 186°C. – IR (KBr, cm $^{-1}$): $\tilde{\nu}$ = 3051 (w, ArH), 2960 (w, CH), 1250 (m), 965 (s), 817 (s). – ^{1}H NMR ($CDCl_3$): δ = −0.65 and 0.55 [2 s, 12H, $Si(CH_3)_2O$], 7.04 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.15 (dd, *J* = 8.2 and 6.8 Hz, 2H, arom. CH), 7.44 (dd, *J* = 8.2 and 6.8 Hz, 2H, arom. CH), 7.77 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.90 (d, *J* = 8.2 Hz, 2H, arom. CH), 7.96 (d, *J* = 8.2 Hz, 2H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = −0.48 and −0.30 [$Si(CH_3)_2O$, 4 C], 125.91, 126.25, 127.39, 127.46, 127.96, and 129.35 (arom. CH, 12 C), 133.41, 133.84, 137.12 and 144.96 (arom. quat. C, 8 C). – MS (70 eV, EI); *m/z* (%): 385 (38) [M^+ + 1], 384 (100) [M^+], 370 (31), 369 (93), 354 (12), 353 (40), 323 (1), 295 (15), 252 (5). – $C_{24}H_{24}Si_2O$ (384.6): calcd. C 74.95, H 6.29; found C 75.27, H 6.43.

2,2,7,7-Tetramethyldinaphto[2,1-c;1',2'-e]-1,2,7-oxadigermepin (**14c**): 2,2'-Bis(trimethylgermyl)-1,1'-binaphthyl (**14a**) (0.500 g, 1.03 mmol) and 2.73 ml (4.10 mmol) of a 1.5 M solution of boron trichloride in dichloromethane. Recrystallization from toluene yielded **14c** (0.201 g, 41%) as colourless crystals, m.p. 228°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3050 (w, ArH), 2975 (w, CH), 819 (m), 744 (s). – ^{1}H NMR ($CDCl_3$): δ = −0.53 and 0.75 [2 s, 12H, $Ge(CH_3)_2O$], 7.13 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.21 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.46 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.78 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.93 (d, *J* = 8.0 Hz, 2H, arom. CH), 7.99 (d, *J* = 8.0 Hz, 2H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = −0.22 and 1.29 [$Ge(CH_3)_2O$, 4 C], 126.20, 126.35, 127.29, 127.86, 128.12, and 128.94 (arom. CH, 12 C), 133.46, 133.72, 139.27, and 143.90 (arom. quat. C, 8 C). – MS, (70 eV, EI); *m/z* (%): 476 (22), 474 (29), 472 (28), 470 (15) and 468 (5) [M^+], 461 (75), 459 (100), 457 (86), 455 (46), 453 (17), 341 (43), 339 (33), 337 (27), 326 (13), 324 (21), 322 (14), 252 (53). – $C_{24}H_{24}Ge_2O$ (473.7): calcd. C 60.86, H 5.11; found C 61.34, H 4.95; calcd. 476.0251; found 476.0250 (MS).

2,2'-Bis(chlorodimethylstannyl)-1,1'-binaphthyl (**15b**): 2,2'-Bis-(trimethylstannyl)-1,1'-binaphthyl (**15a**) (0.257 g, 0.44 mmol) and 1.18 ml (1.77 mmol) of a 1.5 M solution of boron trichloride in dichloromethane, no hydrolysis. Recrystallization from ethanol yielded **15b** (0.154 g, 56%) as colourless crystals, m.p. 169°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3040 (m, ArH), 2972 (w, CH), 1306 (w), 817 (s), 744 (s). – ^{1}H NMR ($CDCl_3$): δ = 0.03 [s, $J(^{119}Sn,CH_3)$ = 59.8 Hz, 12H, $Sn(CH_3)_2Cl$], 7.25 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.34 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.54 (dd, *J* = 8.4 and 6.8 Hz, 2H, arom. CH), 7.97 (d, *J* = 8.4 Hz, 2H, arom. CH), 7.99 (d, *J* = 8.4 Hz, 2H, arom. CH), 8.07 (d, *J* = 8.4 Hz, 2H, arom. CH). – ^{13}C NMR ($CDCl_3$): δ = −0.82 [$Sn(CH_3)_2Cl$, 4 C], 126.47, 127.16, 127.39, 128.38, and 128.76 (arom. CH, 10 C), 131.07 [s, $J(^{119}Sn,CH)$ = 39.2 Hz, C-3 and C-3', 2 C], 132.89, 134.29, 142.62, and 145.55 (arom. quat. C, 8 C). – MS (70 eV, EI); *m/z* (%): 609 (5), 607 (9), 605 (10) and 603 (7) [M^+ − 15], 387 (66), 385 (50), 383 (29), 372 (18), 371 (24), 370 (21), 368 (15), 252 (100). – $C_{24}H_{24}Sn_2Cl_2$ (620.8).

1,1'-Binaphthyl-2,2'-diboronic Acid (**11**): A solution of 2,2'-bis-(tributylstannyl)-1,1'-binaphthyl (**16a**) (3.60 g, 4.32 mmol) in 20 ml of dichloromethane 11.52 ml (17.28 mmol) was added to a 1.5 M solution of boron trichloride in dichloromethane at −78°C. The mixture was held at this temp. for 1 h and was then allowed to warm to room temp. overnight. The solvents were evaporated under reduced pressure. The solid residue was dissolved in 5 ml of dichloromethane and precipitated again by adding 20 ml of hexane. The precipitate was separated by filtration and thoroughly washed with hexane. The solid was then dissolved in a mixture of 20 ml of diethyl ether and 20 ml of ethanol. The product was hydrolysed

with 1 ml of water and then dried with sodium sulfate. The crude product was recrystallized from a mixture of ethanol, dioxane, and toluene to afford a white solid **11** (1.05 g, 71%). Single crystals (colourless needles) were obtained by recrystallization from diethyl ether. A melting point could not be determined as thermal dehydration probably led to formation of anhydrides or oligomers.

1,1'-Binaphthyl-2,2'-diboronic Acid Bispinacol Ester (**12**): 0.397 g (0.48 mmol) of 2,2'-bis(tributylstannyl)-1,1'-binaphthyl (**16a**) was treated with 1.27 ml (1.91 mmol) of a 1.5 M solution of boron trichloride in dichloromethane to give 2,2'-bis(dichloroboryl)-1,1'-binaphthyl (**16b**). This was then separated and added in situ to 0.169 g (1.43 mmol) of 2,3-dihydroxy-2,3-dimethylbutane in 20 ml of toluene. The mixture was stirred at room temp. for 24 hours. After completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (hexane/ethyl acetate, 20:1) to yield the product **12** (0.107 g, 44%).

☆ Dedicated to Professor *Hans Paulsen* on the occasion of his 75th birthday.

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