Synthesis of a Bis(boronate) Compound Having *s*-Indacene Framework and Its Property as a Host Molecule for Dimethylaminopyridine

Hidehiro Sakurai, Nobuharu Iwasawa, and Koichi Narasaka*

Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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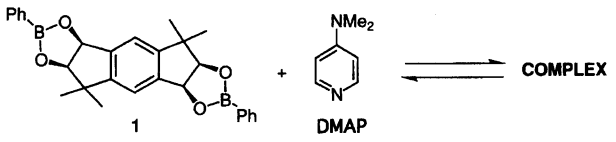
A bis(boronate) compound (**1**) in which boronate components are situated on the same side of the planar *s*-indacene framework is synthesized from 1,5-dihydro-1,1,5,5-tetramethyl-*s*-indacene by OsO_4-catalyzed dihydroxylation in the presence of dihydroxyphenylborane. The property of **1** as a host molecule has been examined with various compounds. The host **1** forms a 1 : 1 complex with 4-dimethylaminopyridine (DMAP) when an equimolar amount of DMAP is added; more concave-type complexes (**2**) are formed than convex-type complexes (**3**). When excess amounts of DMAP are present, a **1** : DMAP = 1 : 2 complex (**4**) can be isolated as a single crystal. This complex can be characterized by NMR measurements and X-ray analyses. These analyses indicate that the concave-type complex **2** does not have a bidentate coordination between the two boron–nitrogen atoms as proposed previously, but has a monodentate coordination form.

Lewis acids are widely used in organic syntheses as reaction activators. In addition, they are modified to enable highly selective and/or highly efficient reactions. For example, various kinds of Lewis acids with the chiral ligands have been recently developed to assist catalytic asymmetric reactions.[1] By introducing the concept of host–guest complexation into the chemistry of Lewis acids, it is expected that specific recognition and activation of guest molecules could be realized.[2,3] Based on such a concept, we previously designed a bis(boronate) compound **1** as a bidentate Lewis acid, in which a pair of boronate moieties are situated on the same side of the *s*-indacene framework. The bis(boronate) **1** was found to form a complex with 4-dimethylaminopyridine (DMAP) or its analogs, based on the observation of the chemical shift changes in ^{1}H NMR (Scheme 1).[4] Generation of two types of 1 : 1 complexes, the concave-type complex **2** and the convex-type complex **3** (Fig. 1), can be considered. From variable temperature NMR, we concluded that the amount of **2** is about three times more than that of **3** in a 1 : 1 mixed solution of **1** and DMAP (170 K, in CD_2Cl_2).



Scheme 1.

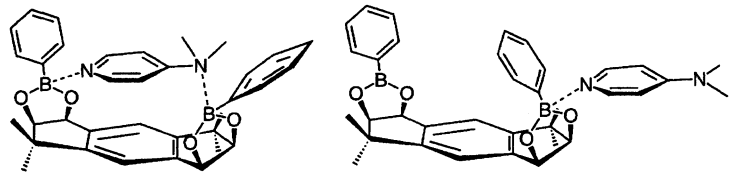
When excess amounts of DMAP were present in the solution, a **1** : DMAP = 1 : 2 complex **4** was found to be produced as the sole complex. In this, one DMAP coordinates to **1** facing the concave side of the bis(boronate) framework and the other orients outside (Fig. 2). Furthermore, a single crystal of **4** was obtained and the structure was determined by X-ray analysis. In this report, we would like to describe the details of the preparation of the bis(boronate) **1** and the analogs, and the complex formation of the bis(boronates) with amino compounds, particularly with DMAP.

Results and Discussion

For developing Lewis acid host molecules, we set up as a principal strategy to find a host molecule that could recognize the shape of guest molecules, especially the distance between two hetero atoms of guest molecules.

In designing the host molecule, we chose the *s*-indacene framework because it has a very rigid and planar structure and has no obstructive groups such as axial substituents on the steroid framework. Furthermore, aromatic–aromatic interaction could also be expected if the guest had some aromatic rings.

As the Lewis acid moieties, 1,3,2-dioxaborolane ring was chosen for the following reasons. It has a moderate Lewis



2 (Concave-type Complex) **3** (Convex-type Complex)

Fig. 1. Two possible types of 1 : 1 complexes.

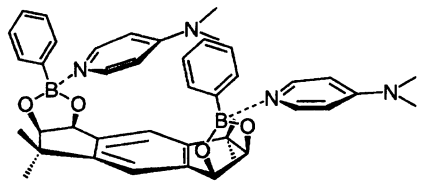
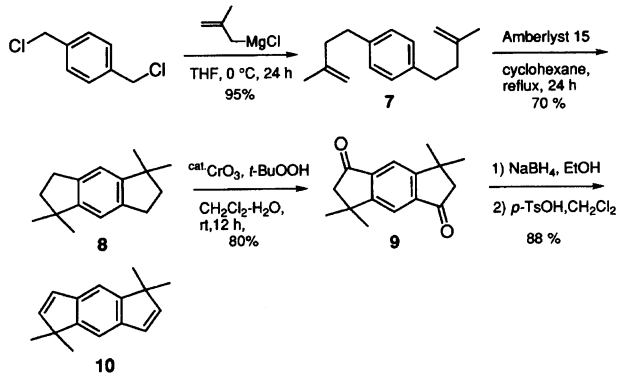


Fig. 2. 1 : 2 Complex (**4**).

acidity and keeps its rigidity because of its 5-membered ring structure. Moreover it is known that such a boronate exists as a monomer in the solution; this allows an accurate assignment of the structure of the host–guest complex. Furthermore, it is stable to chromatographic purification and can be characterized easily.

We finally designed a host molecule such as a bis(boronate) compound **1** in which phenylboronate functionalities were introduced on the same side of an *s*-indacene framework. For the comparison of the bidentate effect of **1**, the corresponding *trans* isomer **5** and the monoboronate **6** were also prepared (Fig. 3).

Preparations of these host compounds were as follows. 1,5-Dihydro-1,1,5,5-tetramethyl-*s*-indacene **10** was prepared according to the route shown in Scheme 2. 1,4-Bis(chloromethyl)benzene was treated with 2 molar amounts of 2-methyl-2-propenylmagnesium chloride to afford **7** in 95% yield. Intramolecular Friedel–Crafts reaction of **7** was performed with Amberlyst 15 as a catalyst, giving 1,2,3,5,6,7-hexahydro-1,1,5,5-tetramethyl-*s*-indacene **8**.[5] The benzylic position was oxidized by a catalytic amount of CrO_3 and excess *t*-BuOOH[6] to yield **9**. Finally, **10** was prepared by $NaBH_4$ reduction of **9**, followed by an acidic dehydration.



Scheme 2.

The *cis* bis(boronate) **1** and the *trans* isomer **5** were obtained in 58% total yield by the modified *cis*-dihydroxylation using dihydroxyphenylborane, *N*-methylmorpholine *N*-oxide (NMO), and cat. OsO_4 (Scheme 3).[7] Each isomer could be separated by recrystallization. The monoboronate having indan moiety **6** was prepared from 1,1-dimethylindene[8] by the same procedure.

Boronate compounds **11** and **12**, in which one or more fluoro atom(s) were introduced on the phenyl group on the boron atom, were prepared by the following modified procedure. Tetrols **13** and **14** were prepared by the standard procedure using OsO_4 and NMO[9] and they were converted to the desired boronate compounds **11** and **12** by the reaction with the corresponding aryldihydroxyboranes (Scheme 4).

Examination of the Complex Formation with 1.

Host–guest complexation was examined by employing **1** as a host molecule with a variety of guest molecules. The guest molecules were mixed with **1** in a 1 : 1 ratio and their complex formation was monitored by the chemical shift changes in NMR spectra (in $CDCl_3$ at 300 K; Fig. 4).

As depicted in Fig. 4, among various guest molecules examined, apparent chemical shift changes were observed only when **1** was mixed with 4-aminopyridines. DMAP has two nitrogen atoms which are situated in an appropriate spacing such that it can coordinate to the host **1** in a bidentate form. There is a possibility that **1** is recognizing these 4-aminopyridines only by their basicity, because DMAP is known to have a strong basicity (pK_b=4.30). However, no significant changes were observed when **1** was mixed with 1,4-diazabicyclo[2.2.2]octane (DABCO; pK_b = 5.28) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; pK_b = 2.50), which has basicity comparable with that of DMAP (Fig. 5). Furthermore, the ability of the complex formation of the *trans* isomer **5** and the monoboronate **6** with DMAP was also investigated in the same way, but no significant shift change in DMAP was observed. Neither pyradine nor *N*, *N*, *N'*, *N'*-tetramethyl-*p*-phenylenediamine, which have two nitrogen atoms located in a different spacing from that of DMAP, gave any sign of the complex formation with **1** (Fig. 4). At this point, we supposed that DMAP coordinates to the host molecule **1** in

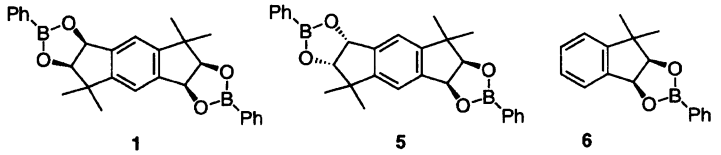
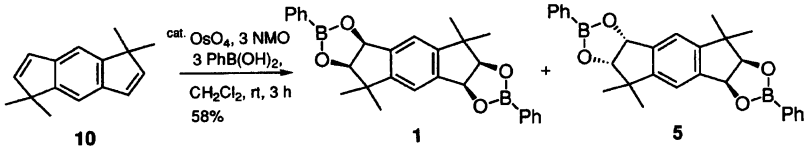
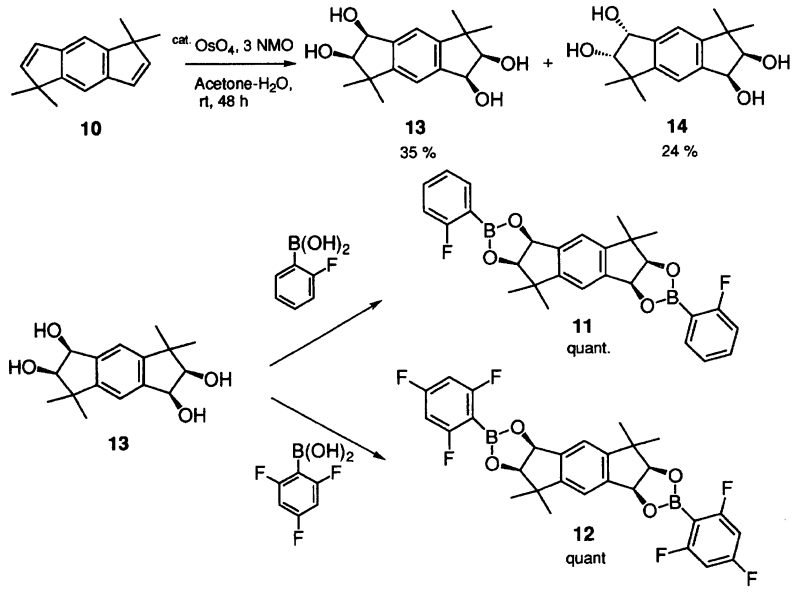


Fig. 3. Structures of the host molecules.



Scheme 3.



Scheme 4.

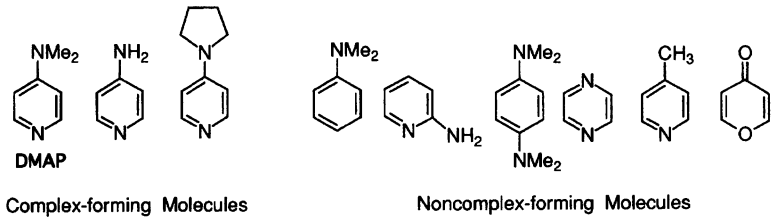


Fig. 4. Examination of the complex formation with **1**.

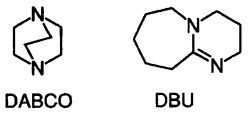


Fig. 5. DABCO and DBU.

a bidentate manner to form the concave-type complex **2** and that the ability of complexation is mainly due to the spacing of the two nitrogen atoms in the guest molecule.

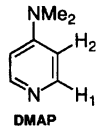
We studied the changes in chemical shifts of three protons on DMAP, all the protons showed a notable higher field shift. Two effects can be considered for the higher field shift in the complexation; the inductive effect due to the coordination of a Lewis acid to DMAP and the shielding effect by an aromatic component of the host molecule.

In order to make clear the inductive effect, the chemical shifts of DMAP were measured in 1 : 1 solutions of DMAP and various Lewis acids. The results are listed in Table 1.

It was observed that the proton of dimethylamino group (Me) and that of β-position (H2) show a lower field shift and the proton of α-position (H1) shows a higher field shift when Lewis acid coordinates to DMAP. Accordingly, the higher field shift of all the DMAP protons in the 1 : 1 mixture with bis(boronate) **1** is not due to the Lewis acid coordination, but due to shielding effect of the aromatic component of the host molecule **1**. However, little contribution from such an effect is expected if the convex-type complex **3** is formed, because both H2 and Me should be situated far from any aromatic

Table 1. Chemical Shifts of DMAP in the Presence of an Equimolar Amount of Lewis Acid

Lewis acid	Chemical shifts (ppm)		
	H1	H2	Me
None	8.22	6.49	3.00
$TiCl_4$	8.19	6.54	3.05
$SiCl_4$	8.13	6.77	3.26
Ph_2SiCl_2	8.10	6.72	3.24



components of **1**. However, if the complex is formed in the concave-type, the shielding effects against all the protons of DMAP can be explained as follows. The proton of the dimethylamino group (Me) causes a higher field shift owing to the shielding effect of a phenyl group on the boron. The proton of β-position (H2) is also shielded by the aromatic component on the *s*-indacene framework. From these observations, we concluded that the concave-type complex **2** is at least the main species in this system.

The ^{1}H NMR measurements with varying concentrations of **1** and DMAP at 300 K were tried for determination of the equilibrium state of the host–guest complexation. The complexation of **1** with DMAP and the dissociation were considered to be fast enough at room temperature judging from the dynamic NMR measurements, which will be described in a later section. Thus, $\Delta\delta$ (the difference in the chemical shifts between the protons of DMAP and those of DMAP in the presence of **1**) is at a time-average position

which can be written as a function of $\Delta\delta_{max}$ (the ultimate value for the change of chemical shift), [Host] (total concentration of **1**), [Guest] (total concentration of DMAP), and K_s. The K_s value of the complex is expressed by Eq. 1 for the 1 : 1 stoichiometric complexation.[10]

$$\text{Host}+\text{Guest} \overset{K_s}{\rightleftharpoons} \text{Host–Guest Complex}$$

$$K_s = \frac{[\text{Host–Guest Complex}]}{[\text{free Host}]\cdot[\text{free Guest}]}$$

$$\Delta\delta/\Delta\delta_{max} = \left[[\text{Host}]+[\text{Guest}]+1/K_s - [([\text{Host}]+[\text{Guest}]+1/K_s)^2 - 4[\text{Host}][\text{Guest}]]^{1/2}\right]/2[\text{Guest}] \quad (1)$$

NMR measurements were carried out for a set of solutions of **1** and DMAP in which the concentration of DMAP was maintained at 27 mmol dm^{-3} (3.3 mg/1 ml $CDCl_3$) and that of **1** was changed between 0 to 5 molar ratios to that of DMAP. Calculation was carried out according to the method of the literature using SALS system.[11] The results are shown in Fig. 6.

All the curves of each proton were fitted with Eq. 1 without any serious statistical error, which suggested that the complexes existing in this system were all of the same species and were also in a 1 : 1 stoichiometry.

The results of the calculation of K_s and $\Delta\delta_{max}$ by fitting curves in the manner shown in Fig. 6 are listed in Table 2; these indicate that 20% of the molecules form **2** and 80% of the molecules exist in a free form in the solution (0.027 mol dm^{-3}) of 1 : 1 stoichiometry at 300 K.

In the mixture of DMAP and the *trans*-bis(boronate) **5** or the monoboronate **6**, the changes in the chemical shifts were too small to calculate K_s values, indicating that both the *trans* isomer **5** and the monoboronate **6** had little ability to form a complex with DMAP. Since each boronate moiety of **1**,**5**, and **6** was considered to have the same inductive ability, any difference of the complexation ability between **1** and the other host molecules was, at this point, supposed to be due to the bidentate coordination effect of **1**.

The same measurement on the complexation between **1** and 4-(1-pyrrolidinyl)pyridine (4-PP) was also carried out in order to confirm that the protons of dimethylamino group were shielded by the phenyl group on the boron atom. 4-PP, which has nearly the same basicity as DMAP (pK_b; DMAP=4.30, 4-PP=4.10) and has the same distance between the two nitrogen atoms, was expected to have the same ability of complexation with **1**. By forming the concave-type complex of **1** and 4-PP, the chemical shift of H4 which suffers no inductive effect by Lewis acid coordination was expected to shift higher, like that of H3. The results listed in Table 3 demonstrate clearly the formation of the concave-type complex.

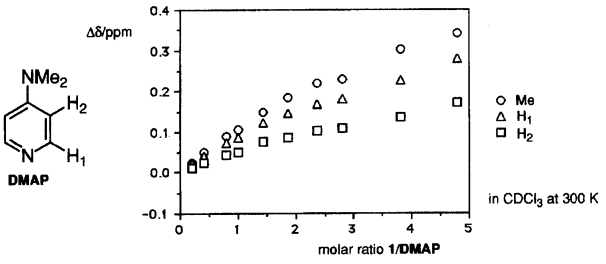


Fig. 6. Change of chemical shifts of DMAP protons $\Delta\delta$ vs. ratio of **1**/DMAP.

Table 2. K_s and $\Delta\delta_{max}$ by Fitting Curves in Fig. 6

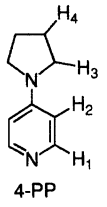
	K_s/dm^3 mol^{-1}	$\Delta\delta_{max}$/ppm
Me	7.9	0.72
H2	8.1	0.58
H1	8.4	0.35

Variable Temperature NMR Measurements of a 1 : 1 Solution of 1 and DMAP. The equilibrium rate of the complexation of **1** and DMAP was so much faster than the time of spin-lattice relaxation at room temperature that we could observe only the averaged peak in the NMR spectrum. For the purpose of direct observation of the spectra of the complexes, variable temperature NMR measurements in CD_2Cl_2 were examined.

At first, a 1 : 1 mixture of **1** and DMAP was examined (Fig. 7). At 250 K, some of the peaks started broadening. At lower temperature (170 K), they split into the peaks of the corresponding complexes. As for the peak of the dimethylamino group on DMAP, it split into two peaks: 2.31 and 3.16 ppm, with the ratio of 3 : 1. At the same temperature, the methyl peak of free DMAP appeared at 3.06 ppm. The former peak (2.31 ppm) was assigned as that of the concave-type complex **2** and the latter (3.16 ppm) as that of the convex-type complex **3** from the following observation. Judging from the calculation of curve fitting of the NMR study with

Table 3. K_s and $\Delta\delta_{max}$ in **1** and 4-PP System (300 K in $CDCl_3$)

	K_s/dm^3 mol^{-1}	$\Delta\delta_{max}$/ppm
H4	8.3	0.65
H3	8.2	0.76
H2	8.4	0.66
H1	11.0	0.41



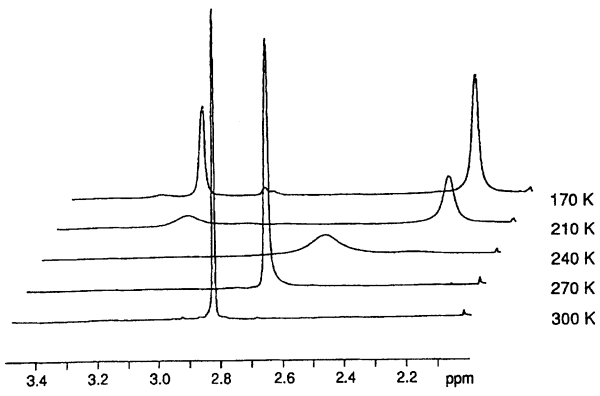


Fig. 7. Variable temperature NMR spectra of 1 : 1 mixture of **1** and DMAP. (the peak of dimethylamino group on DMAP).

varying concentrations, we expected the chemical shift of the methyl proton of **2** to be about 0.72 ppm higher than that of free DMAP at 300 K (Table 2). The former peak showed 0.75 ppm higher shift change at 170 K that corresponded well to the shift change calculated above.

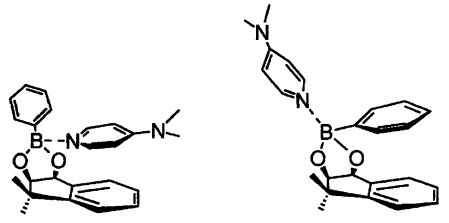
The latter peak (3.16 ppm), on the other hand, might be assigned as that of the convex-type complex **3**, since DMAP of **3** could coordinate with **1** only at the nitrogen atom on the pyridine ring. The peak of the dimethylamino group, therefore, should shift to the lower field. However, we could not exclude the possibility that the latter peak belonged to free DMAP, whose chemical shift was shifted to a lower field by some other effect. If the latter peak belonged to free DMAP, the ratio of the two peaks should depend on the concentration, but if it belonged to the convex-type complex **3**, the ratio should be independent of the concentration.

To make this assignment clear, the concentration of **1** and DMAP was changed from 27 to 5.4 mmol dm^{-3} (5 times diluted), but almost no changes in the integral ratio were observed between the two systems. It was, therefore, concluded that the higher field peak belongs to the concave-type complex **2** and the lower one belongs to the convex-type complex **3**; the concave-type complex **2** exists as a major complex compared to **3** at least in the 1 : 1 mixture.

Variable temperature NMR of a 1 : 1 mixture of the monoboronate **6** and DMAP in CD_2Cl_2 was also measured. In this **6**–DMAP system, we expected to observe the following two phenomena if the monoboronate **6** has any ability of complexation with DMAP. One was that the coalescence temperature might be different from that of the **1**–DMAP system because the **6**–DMAP system did not have such a complexation effect as was found in the concave-type complexation. The other was that two types of complex such as **15** and **16** (Fig. 8) could exist in the **6**–DMAP system and these two complexes should be observed as independent peaks at low temperature.

The complex **16** would have nearly the same chemical shift as the convex-type complex, while the complex **15** might have quite a lower field shift than the concave-type complex because no shielding effect exists by the phenyl group on the boron atom such as that in the concave-type complex **2**. The results are shown in Fig. 9.

As expected, both the change of coalescence temperature and the change of the chemical shifts of the split peaks at low temperature were observed. The broadening began at 220 K, and at 170 K, the peak of dimethylamino group split



15 **16**

Fig. 8. Two possible complexes of **6** and DMAP.

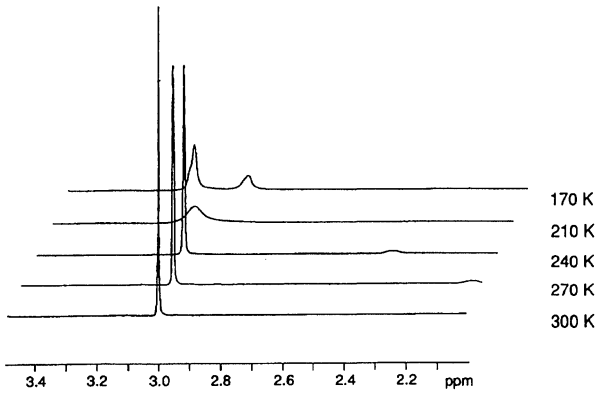


Fig. 9. Variable temperature NMR spectra of 1 : 1 mixture of **6** and DMAP. (the peak of dimethylamino group on DMAP).

into two peaks; 2.97 and 3.17 ppm, with the ratio of 1 : 1.7. The lower peak was assigned to the Me of **16** judging from the chemical shift in the convex-type complex **3** (3.14 ppm). The higher peak was considered to belong to **15**, because the chemical shift existed between the complex **2** and the complex **3**. The methyl group is probably shielded by the aromatic component on the indan framework of **15**.

It was important to note that the complex **16**, whose DMAP is coordinated to the boronate from the opposite side of the indan framework, exists predominantly over **15** which corresponds to **2**. This fact indicated that the indacene framework might not play a significant role in forming the concave-type complex **2** such as π-interaction with DMAP. It was also noted that an additional phenylboronate component is indispensable for stabilizing the concave-type complex formation.

In the ^{1}H NMR spectrum of a mixture of the *trans* isomer **5** and DMAP, the peak of dimethylamino group split into three peaks at 170 K and, as a whole, a very complicated spectrum was obtained at low temperature. It may be because **2** has two independent Lewis acid components which make the equilibrium system complicated.

As mentioned above, it became apparent that bis(boronate) **1** forms complexes with DMAP in the 1 : 1 mixture, and **2** is produced predominantly rather than **3**. Furthermore, the *cis*-bis(boronate) structure is indispensable to stabilize the concave-type complex.

Thermodynamic Parameters. At low temperature (290—250 K), the changes of chemical shifts of H1 and H2 in the monoboronate **6**–DMAP system were found large enough to calculate the stability constant K_s using Eq. 1. The thermodynamic parameters could also be obtained by Arrhenius plotting. Bidentate coordination effect might be estimated by comparing these thermodynamic parameters for the **1**–DMAP system and those for the **6**–DMAP system. As for **1**–DMAP system, nearly the same results were obtained (320—270 K) by using any proton's data (H1,H2, and Me). On the other hand, for **6**–DMAP system, the data of Me could not be fitted because the change of chemical shift was too small and complicated. The results are listed in Table 4.

Table 4. Thermodynamic Parameters of **1**–DMAP and **6**–DMAP Systems[a] ($CDCl_3$ solvent, 300 K)

	1–DMAP	**6**–DMAP
ΔH/kJ mol^{-1}	−43	−40
ΔS/J K^{-1}mol^{-1}	−130	−140
ΔG/kJ mol^{-1}	−5.3	+1.0
r	0.998	0.977

a) Calculations are performed using the data at H2 of DMAP.

As shown in Table 4, the bis(boronate) structure apparently creates a great advantage for complexation; at 300 K, the monoboronate **6** may even be disadvantageous for complexation, judging from the plus value of ΔG.

Substituent Effect at the Lewis Acid Moiety. As described above, the *cis*-bis(boronate) compound **1** was found to be a good and selective host molecule for DMAP and its analogs. However, at 300 K in the 0.027 mol dm^{-3} solution, only 20% of DMAP took the concave-type complexation and the remaining 80% of DMAP did not participate in any complex formation. Thus the limitation of the ability for the bis(boronate) **1** to complex with the Lewis basic guest might depend on its Lewis acidity. This disadvantage prompted us to increase the Lewis acidity of the boron atoms. Fluoro atom(s) were introduced into the phenyl group and their influences were investigated using 2-fluoro substituted host molecule **11** and 2,4,6-trifluoro substituted host **12**.

At first, variable temperature NMR measurements in $CDCl_3$ were carried out. The more fluoro groups were introduced, the less difference between the chemical shifts of Me of DMAP belonging to the concave-type complex and that of free DMAP ($\Delta\delta_{max}$) was observed, and the more complicated the spectrum became (Figs. 10 and 11).

The former phenomenon made it clear again that the higher field shift of DMAP in the case of the concave-type complexation is due to the shielding effect by the phenyl group on the boron atom, because the shielding effect is expected to decrease when an electron-withdrawing group is introduced. The latter, unfortunately, might indicate that there exist different kinds of complexes other than the concave-type nor the convex-type, such as a 1 : 2 complex even in the 1 : 1 mixture.

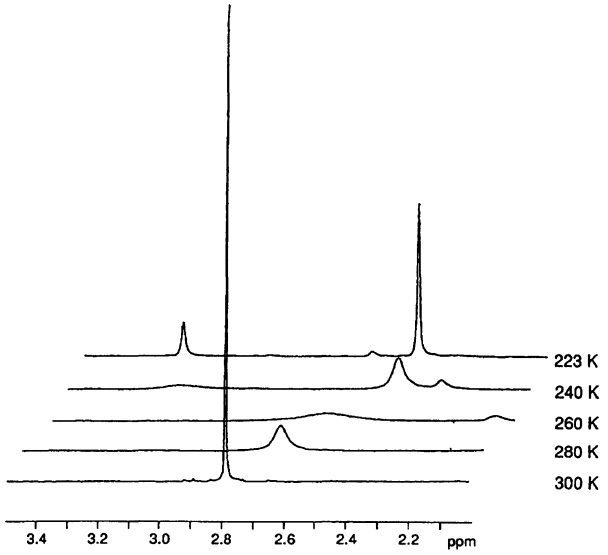


Fig. 10. Variable temperature NMR spectra of 1 : 1 mixture of **11** and DMAP. (the peak of dimethylamino group on DMAP).

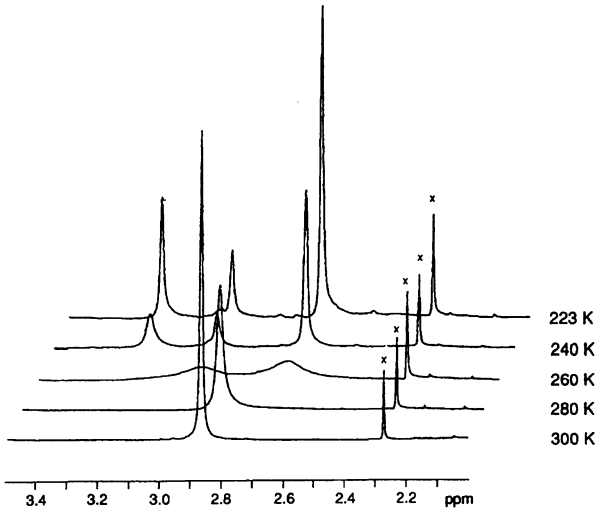


Fig. 11. Variable temperature NMR spectra of 1 : 1 mixture of **12** and DMAP. (the peak of dimethylamino group on DMAP).

The measurements with varying concentrations also showed similar phenomena. A characteristic phenomenon is that $\Delta\delta_{max}$ diminishes, which is in parallel to the observation of the variable temperature NMR measurements as shown in Figs. 10 and 11. Another is that the statistical error for the K_s value increases as the number of fluoro groups increases (Table 5).

The reasons for the increase in the statistical error may include two factors. One is that it is due to the existence of other kinds of complexes. The other is some substantial error in the calculations. The calculation using Eq. 1 is performed on the assumption that complexation and decomplexation is at its equilibrium and on the assumption that only a single kind of complex exists. However, strong Lewis acidity might cause the absence of the free form even at 300 K, especially in the case of **12**, making the equilibrium present only between the different complexes, including the concave-type and the convex-type complexes. This fact must cause a serious error in the calculation using Eq. 1.

NMR Studies on the Solution Which Contains Excess

Table 5. Comparison of K_s and $\Delta\delta_{max}$ between **1**-, **11**-, and **12**–DMAP Systems

	1–DMAP	**11**–DMAP	**12**–DMAP
K_s	7.9	1.1×10^2	2.2×10^2
$\Delta\delta_{max}$	0.72	0.48	0.20
r	0.998	0.992	0.924

Calculations are performed using the data at Me of DMAP.

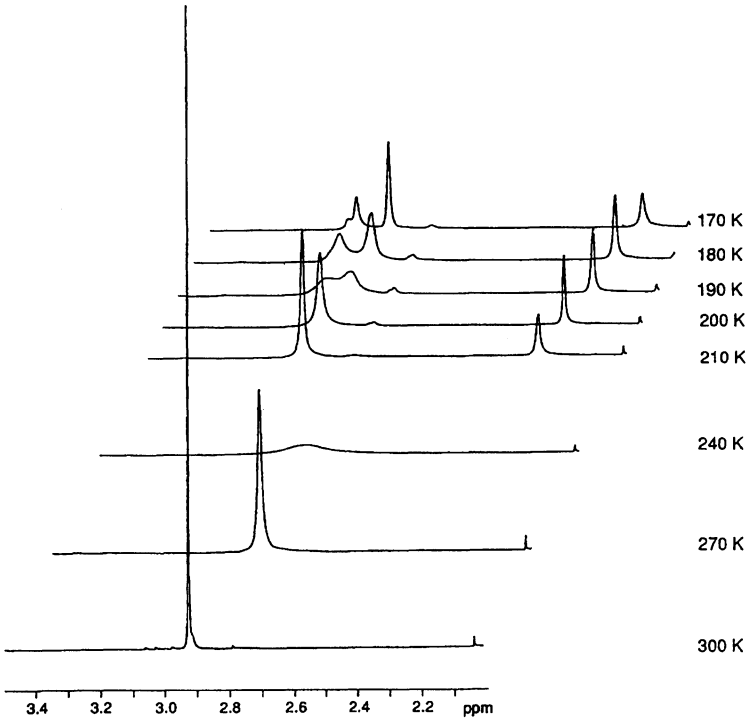


Fig. 12. Variable temperature NMR spectra of 1 : 3 mixture of **1** and DMAP. (the peak of dimethylamino group on DMAP).

Amounts of DMAP. In the section of variable temperature NMR study, we described the assignment of the two split peaks to be of **2** and of **3** in the **1**–DMAP system at low temperature. We also described that the temperatures at which the broadening began were different between **1**–DMAP system and the monoboronate **6**–DMAP system. Accordingly, variable temperature NMR was studied for the solutions which contained an excess amount of DMAP to that of **1**. There were two purposes in this experiment. The one was to observe the two coalescence steps derived from the concave-type complexation and the convex-type complexation, and the other was to make clear assignments of the peaks belonging to the convex-type complex because the free DMAP and the convex-type complex might be observed independently at low temperature.

The **1**:DMAP=1:3 mixed CD_2Cl_2 solution was measured, because at least one molar amount of free DMAP would remain in the system even if all boron atoms are coordinated with DMAP in 1 : 1 manner. The spectrum is shown in Fig. 12.

As expected, two different coalescence steps are observed. These coalescence temperatures nearly correspond to the results of the **1**–DMAP system and the **6**–DMAP system. At 170 K, three types of peaks of DMAP are observed, which resemble those of the concave-type complex **2**, the convex-type complex **3**, and free DMAP, respectively. However, the ratio of the peaks of these three components is 1 : 1 : 1, and the chemical shifts are apparently different from the results observed in the **1** : DMAP=1 : 1 solution. Furthermore, these peaks are markedly sharp even at 170 K, indicating the absence of such an equilibrium process as is observed between **2** and **3** in the system of **1** : DMAP=1 : 1 solution at 170 K. From these results, we concluded that the only one species, such as **4** containing **1** and DMAP in the ratio of 1 : 2, is produced in which one DMAP is coordinated toward the concave side of **1** and the other coordinated from the outside (Fig. 13).

The Crystal Structure of 4. The fact that the 1 : 2 complex **4** exists nearly as the single isomer in the solution which contains excess amounts of DMAP gave the possibility of obtaining the appropriate crystal for an X-ray analysis, although we failed to achieve crystallization of the 1 : 1 concave-type complex **2**. In fact, single crystals of the 1 : 2 complex **4** were obtained from ether and dichloromethane mixed solution containing 1 : 2 ratio of **1** and DMAP. The molecular structure of **4** is shown in Fig. 14 (Table 6).

This structure corresponds well to the structure of **4** assigned by NMR in the last section. The information from the crystal structure, therefore, would help in confirming the conformation of the 1 : 2 complex **4** in the solution. 1) All the methyl nitrogen atoms have planar structure and both boron atoms are tetrahedral. 2) The distance between N2 and B2 is over 4 Å, and it is not plausible to suppose that any interactions occur between them. Furthermore, no intermolecular interaction such as π-stacking effect is observed. As for π-interaction, there is no stacking nor T-shape ge-

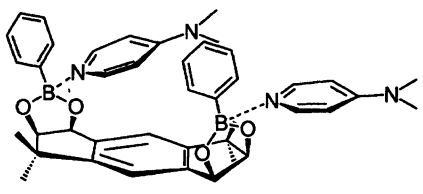


Fig. 13. 1 : 2 Complex **4**.

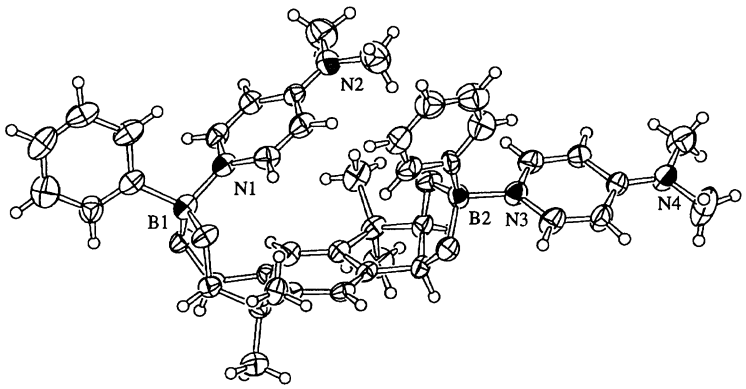


Fig. 14. ORTEP drawing of **4**.

Table 6. Crystallographic Data of **4**

Color	Colorless
Crystal shape	Block
Molecular formula	$C_{42}H_{48}B_2N_4O_4$
Formula weight	694.49
Crystal size/mm	$0.50\times0.60\times0.70$
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.660(3)
b/Å	9.650(3)
c/Å	31.930(5)
β/°	97.15(2)
V/Å^3	3870(1)
Z	4
D_c/g cm^{-3}	1.192
μ(Mo $K\alpha$)/cm^{-1}	0.76
Total no. of observed reflections	9333
No. of unique reflections with $I>3\sigma(I)$	2483
Final no. of variables	469
Final rediduals	
R	0.060
R_w	0.040

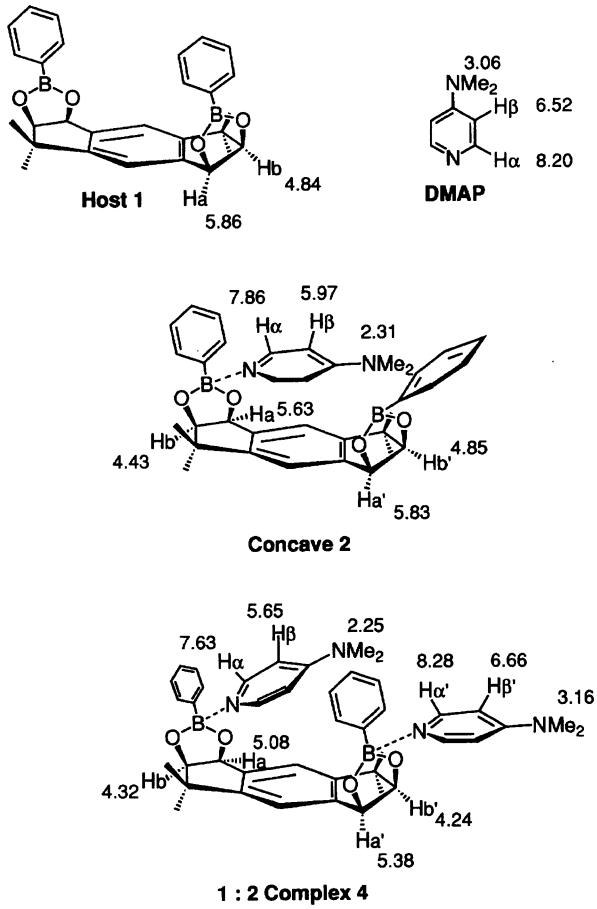


Fig. 15. ^{1}H NMR chemical shifts of complexes (170 K in CD_2Cl_2).

ometry between any of the aromatic rings even in an intermolecular relationship which is often observed in the crystal structure. Therefore, at least in crystal **4**, the concave-type DMAP (settled inside of **1**) is stabilized neither by bidentate coordination nor by π-interaction.

Comparison of Chemical Shifts of Complexes. The crystal structure of the 1 : 2 complex **4** may correspond to the conformation of the complex in the solution state. The conformation of the concave-type complex **2** in the solution would be also obtained by comparing the chemical shifts between **2** and the 1 : 2 complex **4**. Though we could not assign all the protons in each of the complexes described above, owing to bad separation of peaks especially at the phenyl position, the chemical shifts of the representative protons are listed in Fig. 15.

Methine protons (Ha, Ha′, Hb, Hb′) at an α-position of the boronate are shifted to higher field by the coordination of DMAP to the boron atom(s), because the boron atom changes from a planar to a tetrahedral structure, which causes the phenyl group on the boron to shield these protons. As for the concave-type complex **2**, the protons Ha and Hb, which are located near the boron atom coordinating to the pyridine nitrogen atom, are shifted from 5.86 and 4.84 to 5.63 and 4.43, respectively. Similarly, the four protons of the Ha, Hb, Ha′, and Hb′ in the 1 : 2 complex **4** shift to 5.08, 4.32, 5.38, and 4.24. On the contrary, Ha′ and Hb′ of the concave-type complex **2** have nearly the same chemical shifts as those of the free host, which indicates that the boron atom on this side still keeps the planar structure and thus suggests that the bidentate coordination, which we proposed

in a previous communication, is not crucial in the formation of the concave-type complex **2**.

Furthermore, the DMAP belonging to **2** and the DMAP coordinated at the inside of guest in **4**, have relatively close chemical shifts. This indicates that the DMAP of **2** is located in an environment similar to that of the corresponding DMAP of **4**.

Because Ha and Hb of the 1 : 2 complex **4** shift more than Ha and Hb of **2**, the benzene ring on the boron atom of **4** is considered to be inclined more horizontal to the indacene framework than that of **2**. Thus, the DMAP of **2** may be located considerably closer to the indacene framework than the DMAP of **4**. This fact confirms that there should be some interactions between DMAP and the host molecule **1** in the case of the concave-type complexation. However, as for the second B–N coordination at the nitrogen atom of the dimethylamino group, it makes little contribution to the formation of the concave-type complex.

Conclusion

As discussed above, DMAP of the concave-type complex **2** does not form a bidentate coordination but exists in a monodentate form. Even if the second boron–nitrogen coordination exists, the coordination energy is too low to be observed by the above investigation. Nevertheless, it is evident that the concave-type complex **2** is produced preferentially to the convex-type complex **3**, though **2** seems to be located in a crowded structure, indicating there should be some other interactions between the host and the guest molecules.

Experimental

General. All melting points are uncorrected. The IR spectra were measured with a Horiba FT-300S spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded on a Bruker AM500 spectrometer with $CHCl_3$ (δ=7.24 and 77) or CH_2Cl_2 (δ=5.33 and 53.6) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating at 70 eV. X-Ray diffraction intensities were collected on a Rigaku AFC-5R goniometer with graphite monochromatized Mo $K\alpha$ (λ=0.71069 Å) radiation.

Flash column chromatography was carried out on silica gel (Merck Silica gel 60) and preparative TLC was carried out using Wakogel B-5F. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl. Dichloromethane was distilled from P_2O_5, then from CaH_2, and dried over Molecular Sieves 4A (MS4A). Ethanol was distilled from magnesium ethoxide and dried over MS3A. Acetone and cyclohexane were reagent grade and were used without further purification. All of the operations were performed under an argon atmosphere. 1,1-Dimethylindene[8] was prepared according to a method from the literature.

Preparation of 1,4-Bis(3-methyl-3-butenyl)benzene (7):[5] To a THF (200 ml) solution of 1,4-bis(chloromethyl)benzene 50.8 g (290 mmol) was added 1.1 M THF solution (1 M=1 mol dm^{-3}) of 2-methyl-2-propenylmagnesium chloride (850 ml) dropwise at 0 °C. The mixture was stirred for 24 h. The reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo, and the crude product was distilled under reduced pressure to give **7** (59.3 g, 95% yield). Colorless oil; bp 120 °C/1.5 mmHg (1 mmHg=133.322 Pa) (lit,[5] 85 °C/0.1 mmHg); IR (neat) 1649, 1450, 887, 811 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.80 (6H, s), 2.34 (4H, t, J=8.1 Hz), 2.76 (4H, t, J=8.1 Hz), 4.75 (2H,s), 4.77 (2H, s), 7.14 (4H, s). Found: C, 89.36, H, 10.30%. Calcd for $C_{16}H_{22}$: C, 89.65, H, 10.35%.

Preparation of 1,2,3,5,6,7-Hexahydro-1,1,5,5-tetramethyl-*s*-indacene (8):[5] A mixture of **7** (27.8 g, 13 mmol), and Amberlyst 15 (33 g) in 1 dm^3 of cyclohexane was heated to reflux for 24 h. The reaction mixture was cooled and Amberlyst 15 was filtered off. The filtrate was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane) to give **8** (19.5 g, 70% yield). Colorless crystals (from petroleum ether); mp 94 °C (lit,[5] 94—95 °C); IR (KBr) 1473, 1307, 875 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.23 (12H, s), 1.91 (4H, t, J=7.1Hz), 2.83 (4H, t, J=7.1 Hz), 6.94 (2H, s). Found: C, 89.46; H, 10.21%. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35%.

Preparation of 2,3,6,7-Tetrahydro-3,3,7,7-tetramethyl-*s*-indacene-1,5-dione (9): To a suspension of chromium(VI) oxide 226 mg (2.26 mmol) and CH_2Cl_2 (15 ml), 70% aqueous *t*-butyl hydroperoxide solution (20 ml) and 1,2,3,5,6,7-hexahydro-1,1,5,5-tetramethyl-*s*-indacene (**8**) 1.50 g (7.00 mmol) in CH_2Cl_2 (15 ml) were added at room temperature. The mixture was stirred for 12 h. The reaction was quenched by bubbling of H_2S. After filtration through Celite, the resulting solution was washed twice with saturated aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the crude product was purified by silica-gel column chromatography (hexane/ethyl acetate, 4 : 1) to give **9** (1.36 g, 80% yield). Colorless crystals (from petroleum ether); mp 182—183 °C; IR (KBr) 1707, 1430, 1320, 1225, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.37 (12H, s), 2.59 (4H, s), 7.73 (2H, s). Found: C, 79.11; H, 7.46%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

Preparation of 1,5-Dihydro-1,1,5,5-tetramethyl-*s*-indacene (10): To an ethanol (50 ml) solution of **9** (250 mg) was added $NaBH_4$ (50 mg) at room temperature and the mixture was stirred for 12 h. After addition of a drop of 1 M aqueous HCl, the solvent was evaporated in vacuo. The residue was treated with *p*-toluenesulfonic acid (1 g) in mixed solution of THF (5 ml) and CH_2Cl_2 (5 ml) at room temperature; then the mixture was stirred for 6 h. The reaction was quenched with pH 7 phosphate buffer. The organic materials were extracted with CH_2Cl_2, and the combined extracts were dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by silica-gel column chromatography (hexane) to give **10** (191 mg, 88% yield). Colorless crystals (from petroleum ether); mp 87°C ; IR (KBr) 1460, 1350, 880, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.15 (12H, s), 6.20 (2H, d, J=6.1 Hz), 6.50 (2H, d, J=6.1 Hz), 7.19 (2H, s). Found: C, 91.12; H, 8.54%. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63%.

Preparation of (1*RS*, 2*SR*, 5*RS*, 6*SR*)-1,2,3,5,6,7-Hexahydro-3,3,7,7-tetramethyl-*s*-indacene-1,2,5,6-tetrayl 1,2 : 5,6-Bis(phenylboronate) (*cis* Bis(boronate) 1) and (1*RS*, 2*SR*, 5*SR*, 6*RS*)-1,2,3,5,6,7-Hexahydro-3,3,7,7-tetramethyl-*s*-indacene-1,2,5,6-tetrayl 1,2:5,6-bis(phenylboronate) (*trans* Bis(boronate) 5): To a solution of dihydroxyphenylborane (550 mg, 4.5 mmol), NMO (550 mg, 4.7 mmol), and **10** (270 mg, 1.3 mmol) in CH_2Cl_2 (20 ml) was added OsO_4 (4 mg) at room temperature, and the mixture was stirred for 3h. The reaction was quenched by bubbling of H_2S. After filtration through Celite, the filtrate was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/CH_2Cl_2, 1 : 1), to give a mixture of **1** and **5**. Yield 330 mg (58% yield). Each isomer was separated by

recrystallization (hexane/AcOEt).

1: Mp 260 °C (decomp); IR (KBr) 1600, 1360, 1240, 1095, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.28 (6H, s), 1.45 (6H, s), 4.84 (2H, d, J=6.1 Hz), 5.87 (2H, d, J=6.1 Hz), 7.28 (4H, t, J=7.2 Hz), 7.32 (2H, s), 7.38 (2H, t, J=7.2 Hz), 7.75 (4H, d, J=7.2 Hz). Found: C, 74.85; H, 6.15%. Calcd for $C_{28}H_{28}B_2O_4$: C, 74.71; H, 6.27%.

5: Mp 260 °C (decomp); IR (KBr) 1600, 1360, 1240, 1095, 860 cm^{-1}; ^1H NMR δ=1.26 (6H, s), 1.47 (6H, s), 4.83 (2H, d, J=6.1 Hz), 5.86 (2H, d, J=6.1 Hz), 7.32 (2H, s), 7.33 (4H, t, J=7.2 Hz), 7.43 (2H, t, J=7.2 Hz), 7.79 (4H, d, J=7.2 Hz). Found: C, 74.75; H, 6.22%. Calcd for $C_{28}H_{28}B_2O_4$: C, 74.71; H, 6.27%.

Preparation of (1*RS*, 2*SR*)-3,3-Dimethylindan-1,2-diyl Phenylboronate (Monoboronate 6): Compound **6** was prepared from 1,1-dimethylindene according to the same procedure as preparation of **1** and **5**. Yield 78%. Colorless crystals (from hexane/AcOEt); mp 94 °C; IR (KBr) 1600, 1360, 1310, 1090, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (3H, s), 1.44 (3H, s), 4.83 (1H, d, J=6.1 Hz), 5.90 (1H, d, J=6.1 Hz), 7.19 (1H, d, J=7.5 Hz), 7.26 (1H, t, J=7.5 Hz), 7.32 (3H, m), 7.42 (1H, t, J=7.5 Hz), 7.51 (1H, d, J=7.5 Hz), 7.78 (2H, d, J=7.1 Hz). Found: C, 77.07; H, 6.74%. Calcd for $C_{17}H_{17}BO_2$: C, 77.31; H, 6.49%.

Preparation of (1*RS*, 2*SR*, 5*RS*, 6*SR*)-1,2,3,5,6,7-Hexahydro-3,3,7,7-tetramethyl-*s*-indacene-1,2,5,6-tetrayl 1,2 : 5,6-Bis[(2-fluorophenyl)boronate)] (11): To a mixture of NMO (4.20 g, 35.8 mmol) and **10** (3.40 g, 16.1 mmol) in acetone (120 ml)–H_2O (30 ml) was added OsO_4 (40 mg) at room temperature. The mixture was stirred for 48 h. The reaction was quenched by bubbling of H_2S. After filtration through Celite, the filtrate was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (CH_2Cl_2/MeOH, 10 : 1), to give *cis*-tetrol **13** (1.57 g, 35% yield), and *trans*-tetrol **14** (1.08 g, 24% yield).

13: IR (KBr) 3370, 1715, 1255, 1085 cm^{-1}; ^1H NMR (CD_3OD) δ=1.26 (6H, s), 1.31 (6H, s), 3.92 (2H, d, J=5.1 Hz), 4.89 (4H, br), 4.99 (2H, d, J=5.1 Hz), 7.27 (2H, s). HRMS Found: *m/z* 278.1554. Calcd for $C_{16}H_{22}O_4$: M, 278.1518.

14: IR(KBr) 3380, 1320, 1070 cm^{-1}; ^1H NMR(CD_3OD) δ=1.28 (6H, s), 1.31 (6H, s), 3.93 (2H, d, J=5.1 Hz), 4.89 (4H, br), 5.00 (2H, d, J=5.1 Hz), 7.27 (2H, s).

To a CH_2Cl_2 (5 ml) solution of (2-fluorophenyl)dihydroxyborane (202 mg, 1.4 mmol) was added **13** (184 mg, 0.66 mmol), and the mixture was stirred for 30 min. The solvent was evaporated in vacuo. The residue was purified by preparative TLC (hexane/CH_2Cl_2, 1 : 1) to give **11** quantitatively (321 mg). Colorless crystals (from hexane/CH_2Cl_2); mp 260 °C (decomp); IR (KBr) 1615, 1360, 1210, 1030, 775, cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (6H, s), 1.44 (6H, s), 4.83 (2H, d, J=6.1 Hz), 5.87 (2H, d, J=6.1 Hz), 6.94 (2H, t, J_{HF}=8.9 Hz), 7.05 (2H, t, J=7.3 Hz), 7.34 (2H, s), 7.37 (2H, m), 7.54 (2H, m). HRMS Found: *m/z* 486.1981. Calcd for $C_{28}H_{26}B_2F_2O_4$: M, 486.1985.

Preparation of (1*RS*, 2*SR*, 5*RS*, 6*SR*)-1,2,3,5,6,7-Hexahydro-3,3,7,7-tetramethyl-*s*-indacene-1,2,5,6-tetrayl 1,2 : 5,6-Bis[(2,4,6-trifluorophenyl)boronate)] (12): Compound **12** was prepared from **10** and (2,4,6-trifluorophenyl)dihydroxyborane according to the same procedure as employed in the preparation of **11**. Colorless crystals (from hexane/CH_2Cl_2); mp 260 °C (decomp); IR (KBr) 1640, 1615, 1360, 1300, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (6H, s), 1.47 (6H, s), 4.88 (2H, d, J=6.3 Hz), 5.92 (2H, d, J=6.3 Hz), 6.59 (2H, t, J=8.3 Hz), 7.38 (2H, s). HRMS Found: *m/z* 558.1639. Calcd for $C_{28}H_{22}B_2F_6O_4$: M, 558.1608.

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