Cage-Shaped Borate Esters with Tris(2-oxyphenyl)methane or -silane System Frameworks Bearing Multiple Tuning Factors: Geometric and Substituent Effects on Their Lewis Acid Properties

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Abstract: Boron complexes that contain new tridentate ligands, tris(o-oxyaryl)methanes and -silanes, were prepared. These complexes had a cageshaped structure around a boron center and showed higher Lewis acidity and catalytic activity than open-shaped boron compounds. The cage-shaped ligands determined the properties of the borates by altering the geometry and were consistently bound to the metal center by chelation. The synthesized compounds were $L \cdot B(OC_6H_4)_3CH$, $L \cdot B(OC_6H_4)_3$ SiMe, and its derivatives (L=THF or pyridine as an external ligand). Theoretical calculations suggested that the cage-shaped borates had a large dihedral angle (C_{ipso}-O-B-O) compared with open-shaped bo-

rates. The geometric effect due to the dihedral angle means that compared with open-shaped, the cage-shaped borates have a greater Lewis acidity. The introduction of electron-withdrawing groups on the aryl moieties in the cage-shaped framework increased the Lewis acidity. Substitution of a bridgehead Si for a bridgehead C decreased the Lewis acidity of the boron complexes because the large silicon atom reduces the dihedral angle of C_{ipso}-O-B-O. The ligand-exchange rates of the *para*-fluoro-substituted compound B-

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(OC₆H₃F)₃CH and the ortho-phenylsubstituted compound B(OC₆H₃Ph)₃-CH were less than that of the unsubstituted borate $B(OC_6H_4)_3CH$. The ligand-exchange rate of B(OC₆H₄)₃-SiMe was much faster than that of B-(OC₆H₄)₃CH. A hetero Diels-Alder reaction and Mukaiyama-type aldol reactions were more effectively catalyzed by cage-shaped borates than by the open-shaped borate $B(OPh)_3$ or by the strong Lewis acid BF₃·OEt₂. The cageshaped borates with the bulky substituents at the ortho-positions selectively catalyzed the reaction with less sterically hindered substrates, while the unsubstituted borate showed no selectivity.

Introduction

Group 13 elements are very important to Lewis acid chemistry.^[1] Among them, boron-containing compounds have been widely studied as typical Lewis acids, and have been applied to various types of organic transformations.^[2] One of the most commonly available compounds is the boron trihalide BX₃ **A**, as shown in Scheme 1a. In this compound, a Lewis basic substrate (*Sub*) interacts with a strong Lewis acid **A** to form the adduct **B**. The activated substrate may react with an external reagent to give the product complex **C** that includes a B–*Pro* bond (*Pro*=product). Usually, the metal center releases the original ligand X due to a stronger B– *Pro* bond.^[3] In this pathway, an equimolar amount of the Lewis acid **A** is consumed to complete the reaction. Consequently, high Lewis acidity and high catalytic turnovers are

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b) B(OR)3 as a weak Lewis acid

a) BX3 as a strong Lewis acid



c) This work: Cage-shaped borate



Scheme 1. Working hypothesis for conceptually new Lewis acid.

incompatible. In contrast, the borate ester $B(OR)_3 A'$ has low Lewis acidity due to the overlap between lone pairs on oxygen atoms with a vacant p orbital on boron (Scheme 1b).^[4,5] Unfortunately, the Lewis acidity of the borate ester $B(OR)_3 A'$ is too low to react with the substrate. To overcome the problems associated with A and A', we have designed a new type of Lewis acid, A", with a cageshaped ligand system, as shown in Scheme 1c. We used the "cage" to generate the appropriate Lewis acidity, as conformational changes in the frame of the cage could be used to activate the substrate and to keep the original oxy ligands on boron due to the chelating effect of the cage frame. Therefore, if designed appropriately, both high Lewis acidity and high catalytic turnovers would be compatible in the new type of Lewis acid \mathbf{A}'' , if it has labile boron–ligand bonds. Various types of metal complexes can be controlled by changing the geometry around the metal using special ligands,^[6] but this approach often causes relatively large alterations in the metal complex properties, which interfere with its catalytic activity. The proposed cage-shaped borate \mathbf{A}'' could be a suitable Lewis acid catalyst and finely tuned by many factors, such as the size of the cage or steric and electronic effects, based on the ligand design.

In this paper, we report on borate compounds with cageshaped frameworks and their application to the catalysis of organic transformations.^[7,8] We synthesized new borate compounds **1**B with a triaryloxy ligand **1** that combined with bridgehead atom X, as shown in Scheme 2. The properties of these compounds were effectively controlled by varying R and X; that is, R provided substituent control due to electronic and steric factors,^[9] while the bridgehead atom X allowed control of the geometric control.



Scheme 2. Cage-shaped borate esters 1B with triaryloxy ligand 1.

Results and Discussion

Synthesis of various ligands of tris(o-oxyphenyl)methanes or -silanes 1H₃: Based on the novel concept presented in Scheme 1c, we prepared borate 1B as a structurally strained Lewis acid. Reportedly, organic components that include preorganized phenoxy moieties are effective ligand systems for metal complexes.^[10,11] Scheme 3 shows the synthetic routes to ligands 1a-hH₃ that were used for the formation of the various compounds 1B.^[12] Tris(2-hydroxyphenyl)methane (1aH₃) was synthesized as follows. ortho-Lithiation of anisole (2a) followed by treatment with ethyl chloroformate gave the triarylmethanol 3a. The treatment of 3a with p-toluenesulfonic acid in THF/MeCN directly gave the reduced compound 4a. The in situ-generated carbenium cation, which was stabilized by electron-donating groups,^[13] was reduced by THF probably by means of either an ionic or a single-electron transfer (SET) mechanism.^[14] The desired compound 1aH₃ was obtained after deprotection of 4a by BBr₃. Bromination of **1a**H₃ in AcOH/CCl₄ gave the *o*- and p-brominated compound 1bH₃. Bromination of 4a afforded *p*-brominated 4c, which was deprotected by BBr₃ to give 1cH₃.^[15] The fluorinated compound 1dH₃ was prepared from 2-bromo-4-fluoroanisole (2d) in a manner similar to that used to prepare $1aH_3$. The phenyl- and naphthyl-substituted compounds $1eH_3$ and $1fH_3$ were prepared from the substituted anisole derivatives 2e and 2f, respectively.

For synthesis of the silane derivatives $1gH_3$ and $1hH_3$, a different protecting group was required. Although we obtained (*o*-MeOC₆H₄)₃SiMe by the reaction of *o*-lithioanisole with MeSiCl₃, deprotection with BBr₃ failed and gave an undesired product due to weak Si–aryl bonds. Among the protecting groups examined, a dimethylcarbamoyl group



Scheme 3. Synthesis of triphenolic methanes and silanes 1H₃.

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worked very well for $1gH_3$, as shown in Scheme 3.^[16] Protection of 2-bromophenol with dimethylcarbamoyl chloride and its subsequent lithiation followed by treatment with MeSiCl₃ gave the triarylmethylsilane 4g. Deprotection of 4g by LiAlH₄ effectively afforded 1gH₃. In a similar manner, the isobutyl derivative 1hH₃ was obtained.

Generation of cage-shaped borates: The treatment of $1H_3$ with BH_3 ·THF readily generated the cage-shaped borates 1B·THF (Scheme 4). These compounds were thermally



Scheme 4. Generation of cage-shaped borates $1 \ensuremath{B\mathchar`L}$ with various substituents.

stable, but decomposed in air (O₂ and/or water), and, thus, purification and recrystallization were performed in a nitrogen-filled glove box and NMR spectroscopy measurements were performed under nitrogen. The THF-free **1**B was not observed under these conditions, which suggests that cageshaped borate had a higher Lewis acidity than that of planar borates, such as B(OPh)₃. The generated cage-shaped borates **1a–hB**·L with various substituents and bridgehead atoms are shown in Scheme 4. The pyridine complexes **1B**·Py were formed by addition of pyridine to the generated **1B**·THF, and were thoroughly analyzed by X-ray crystallography (described later).

NMR data for cage-shaped borates 1B·L: Selected NMR signals for the cage-shaped borates 1B·L and their ligands $1H_3$ are shown in Table 1. The NMR data of the generated THF-ligated cage-shaped borates (1B·THF) showed characteristic signals. For 1aB·THF, the significant upfield shift of

	Ar	$_{3}CH$		Ar ₃ SiC		
	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{29}\text{Si})$	$\delta({}^{1}\mathrm{H})$	$\delta(^{13}C)$	$\delta(^{11}\text{B})$
1 a H ₃	6.07	38.4				
1 b H ₃	6.31	39.7				
1cH ₃	6.03	37.9				
$1 dH_3$	6.06	38.1				
1eH ₃	6.46	38.3				
1 f H ₃	6.51	38.8				
1gH ₃			-18.2	0.95	-3.0	
$1 h H_3$			-19.8	1.50	22.2	
1 aB∙THF	5.13	57.4				5.52
1bB·THF	4.94	56.5				4.32
1cB∙THF	4.88	55.8				5.13
1dB·THF	4.88	56.6				5.27
1eB∙THF	5.37	58.2				5.04
1 fB THF	5.51	58.2				4.40
1gB∙THF			-21.3	1.06	-6.7	7.11
1hB·THF			-24.4	1.73	18.8	5.87
1aB·Py	5.19	57.9				4.45
1bB·Py	5.01	57.0				4.12
1cB·Py	4.95	56.3				4.06
1dB·Py	4.95	57.1				4.19
1eB·Py	5.44	58.8				4.46
1 f B∙Py	5.58	58.8				3.54
1gB·Py			-21.1	1.08	-6.4	4.32
1hB·Py			-24.0	1.77	20.8	3.99
B(OPh) ₃						16.52

Table 1. NMR chemical shifts of the cage-shaped borates.

the methine hydrogen was confirmed relative to that of $1aH_3$ (6.07 \rightarrow 5.13 ppm). This shift has been observed for similar cage-shaped compounds.^[17] The chemical shift δ (¹³C) of the methine carbon of 1aB·THF was observed at 57.4 ppm (38.4 ppm for $1aH_3$).^[17] The ligated THF showed broadening and downfield-shifted signals at $\delta({}^{1}\text{H}) = 4.46$ and 2.13 ppm (free THF: $\delta(^{1}\text{H}) = 3.73$ and 1.84 ppm). The boron NMR signals appeared at $\delta(^{11}B) = 5.52 \text{ ppm}$ for **1a**B·THF, while the open-shaped borate B(OPh)₃ appeared at 16.52 ppm.^[18] Similar NMR chemical shifts were observed for the cage-shaped pyridine complex 1aB·Py. The chemical shifts for the methine moiety were $\delta({}^{1}\text{H}) = 5.19 \text{ ppm}, \delta$ - $(^{13}C) = 57.9$ ppm, and $\delta(^{11}B) = 4.45$ ppm. The ligated pyridine showed downfield-shifted signals around $\delta({}^{1}\text{H}) = 9.24, 8.20,$ and 7.78 ppm (free pyridine: $\delta(^{1}H) = 8.61$, 7.61, and 7.28 ppm). Other cage-shaped complexes 1b-fB·L showed analogous chemical shifts for their ¹H, ¹³C, and ¹¹B NMR spectra, as shown in Table 1. The order of the downfield shifts $\Delta \delta({}^{1}\text{H})$ of the ligated THF on **1a-dB** as compared to free THF was as follows: 1bB·THF (4.85 and 2.35 ppm)> 1cB·THF (4.53 and 2.28 ppm)>1dB·THF (4.52 and 2.26 ppm > 1 aB·THF (4.46 and 2.13 ppm). The sharper signals of the ligated THF were observed in the same order.^[19] These results were probably due to the Lewis acidity of the cage-shaped borates. The number and type of halogen atoms precisely controlled the Lewis acidity; the magnitude of the effect on the enhancement of Lewis acidity was dibromo>monobromo>monofluoro>unsubstituted compounds on one phenyl group in the cage-shaped borates.^[20] For the ortho-phenyl substituted compound 1eB·THF, the ligand THF showed a broadening and upfield-shifted signals

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around $\delta({}^{1}\text{H}) = 3.18$ and 1.24 ppm. These results indicate that the ligated THF was surrounded by ortho-substituted phenyl rings and was affected by an anisotropic effect. Similar changes in the NMR chemical shifts were observed for the cage-shaped pyridine complex 1eB·Py. The ligated pyridine showed upfield-shifted signals at $\delta({}^{1}\text{H}) = 7.77$, 7.67 and 6.84 ppm. The ortho-naphthyl-substituted, cage-shaped borate 1 fB·L exists as a mixture of conformational isomers owing to bulky substituents, and showed large upfield shifts for ligated THF (1.56 and 0.03 ppm) and pyridine (6.53 and 5.84 ppm; 6.20 and 5.49 ppm for 2- and 3-H, respectively).^[21] For the silicon-bridging compound 1gB·THF, the NMR data showed a characteristic shift for the Me group on Si. A downfield shift of $\delta({}^{1}\text{H})$ of the Me group (0.95 \rightarrow 1.06 ppm) and an upfield shift of $\delta(^{13}C)$ (-3.0 \rightarrow -6.7 ppm) were confirmed relative to those of the ligand 1gH₃. The ²⁹Si NMR spectrum showed an upfield chemical shift $(-18.2 \rightarrow$ -21.3 ppm) relative to $1gH_3$. The ligated THF signals appeared in lower fields with a broadening (δ (¹H)=3.91 and 2.14 ppm) relative to those of free THF. The pyridine complex 1gB·Py showed similar spectral changes with downfield-shifted pyridine signals (δ (¹H) = 9.26, 8.16, and 7.75 ppm). Similar spectral data were obtained for the isobutyl derivatives 1hB·THF and 1hB·Py.

X-ray crystallographic analysis of cage-shaped borates: The pyridine complexes of cage-shaped borates 1a-hB·Py produced crystals of sufficient quality to be analyzed as singlecrystal structures.^[22] Selected crystal data and structural refinement parameters are shown in Table 2. The ORTEP drawings are shown in Figure 1. The selected bond lengths, angles, and tetrahedral character (THC)^[23] of the boron atom are shown in Table 3. For 1aB·Py, boron has a distorted tetrahedral coordination sphere with average bond angles of O-B-O, 114.2° and N-B-O, 104.2°. This compound is the first example of a triphenolic methane-based mononuclear complex that acts as a Lewis acid.^[24,25] The top view of **1aB**·Py (Figure 2) clearly shows a nearly C_3 -symmetric propeller shape. The aromatic rings deviate from a plane perpendicular to that of the three oxygen atoms (B-C_{bridge}-C- $C=19.2^{\circ}$), and, thus, the complex has a chirality that is

Table 2. X-ray data for all crystallographically characterized complexes.



Figure 1. ORTEP drawings of cage-shaped borates 1B·Py (some hydrogen atoms are omitted for clarity).

	1 a B·Py	1 b B∙Py	1 cB·Py	1dB·Py	1eB·Py	1 fB·Py	1gB·Py	1 hB·Py
formula	C ₂₄ H ₁₈ BNO ₃	C24H12BBr6NO3	C ₂₄ H ₁₅ BBr ₃ NO ₃	C ₂₄ H ₁₅ BF ₃ NO ₃	C ₄₂ H ₃₀ BNO ₃	C54H36BNO3	C24H20BNO3Si	C ₂₇ H ₂₆ BNO ₃ Si
$M_{\rm r}$	379.22	852.60	615.91	433.19	607.51	757.69	409.32	451.40
space group	Pbca	Pbca	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_{1}2_{1}2_{1}$	$P2_1/n$	Pbca
$\mu(Mo_{K\alpha}) [mm^{-1}]$	0.087	9.290	5.436	0.116	0.082	0.619	0.142	0.126
a [Å]	14.8638(6)	9.2617(3)	10.4648(10)	8.5360(4)	10.0002(10)	13.2269(2)	9.19210	9.1369(3)
<i>b</i> [Å]	15.4624(6)	22.1780(6)	10.6734(12)	10.5824(4)	10.2302(9)	13.3959(3)	15.3839(2)	20.4629(5)
c [Å]	16.3768(6)	25.3996(7)	20.055(2)	12.5929(5)	16.9575(16)	21.9181(12)	14.4803(4)	25.7290(6)
α [°]	-	-	-	64.1478(12)	100.935(3)	-	-	-
β [°]	-	_	92.540(3)	71.7351(13)	106.528(3)	_	98.4086(15)	_
γ [°]	-	-	-	83.6755(13)	107.048(3)	_	-	-
$V[Å^3]$	3763.9(2)	5217.2(3)	2237.8(4)	971.65(7)	1517.8(2)	3883.59(12)	2025.65(6)	4810.5(2)
Z	8	8	4	2	2	4	4	8
<i>R</i> 1	0.0677	0.0828	0.0414	0.0402	0.0335	0.0732	0.0803	0.0462
wR2	0.1602	0.0859	0.0988	0.0636	0.0689	0.1177	0.0906	0.0553

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Table 3. Selected bond lengths and angles [°]	, and THCs for the cage-shaped borates
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		1 aB·Py	1bB·Py	1 cB·Py	1 dB·Py	1eB·Py	1 fB·Py	1gB-Py	1 hB·Py
bond lengths [Å]	В-О	1.432(4)	1.392(12)	1.439(7)	1.436(2)	1.417(5)	1.438(7)	1.426(5)	1.432(5)
5 ()	В-О	1.440(5)	1.450(11)	1.443(8)	1.452(2)	1.441(5)	1.440(8)	1.437(5)	1.437(4)
	B-O	1.457(5)	1.451(11)	1.452(8)	1.453(2)	1.462(6)	1.456(8)	1.445(6)	1.447(4)
	average	1.443	1.431	1.445	1.447	1.440	1.445	1.436	1.439
	B-N	1.628(5)	1.619(13)	1.611(9)	1.626(2)	1.647(6)	1.631(8)	1.655(5)	1.645(5)
	B-C _{bridge}	2.979(5)	2.992(13)	3.025(9)	3.010(2)	2.984(7)	2.990(8)	_	_ ``
	B-Si _{bridge}	_		_	_	-	_	3.158(5)	3.159(4)
	Ar ₃ C-H	0.95(3)	0.950(8)	0.951(5)	0.898(1)	0.950(4)	0.950(5)	_	_ ``
	Ar ₃ Si–C	_	_	_	_	_	_	1.857(6)	1.879(3)
	Ar–C	1.515(4)	1.477(12)	1.521(8)	1.530(2)	1.528(4)	1.508(8)	_	_ ()
	Ar–C	1.517(5)	1.503(11)	1.526(8)	1.530(3)	1.536(6)	1.535(7)	_	_
	Ar–C	1.525(4)	1.514(11)	1.529(8)	1.531(2)	1.546(5)	1.538(7)	_	_
	average	1.519	1.498	1.525	1.530	1.537	1.527	_	_
	Ar-Si	_	_	_	_	_	_	1.864(3)	1.873(3)
	Ar-Si	_	_	_	_	_	_	1.872(4)	1.882(3)
	Ar-Si	_	_	_	_	_	_	1.874(3)	1.882(3)
	average	-	-	-	-	-	-	1.870	1.879
bond angles [°]	O-B-O	113.4(3)	113.2(7)	112.2(5)	112.3(1)	112.1(4)	113.0(5)	114.2(3)	113.6(3)
8 - E I	O-B-O	113.7(3)	114.2(7)	113.8(5)	113.1(1)	115.0(4)	113.2(5)	114.4(3)	114.4(3)
	O-B-O	115.6(3)	114.3(7)	114.0(5)	115.1(1)	115.7(4)	115.0(5)	114.5(3)	114.5(3)
	total	342.7	341.7	340.0	340.5	342.8	341.2	343.1	342.5
	N-B-O	102.3(3)	103.4(7)	104.4(5)	104.2(1)	103.0(4)	104.2(4)	102.7(3)	102.7(3)
	N-B-O	104.4(3)	104.5(7)	105.3(5)	105.1(1)	103.9(4)	104.7(4)	104.1(3)	104.6(3)
	N-B-O	105.9(3)	105.7(7)	106.1(5)	106.0(1)	105.3(4)	105.4(4)	105.0(3)	105.3(3)
	total	312.6	313.6	315.8	315.3	312.2	314.3	311.8	312.6
torsion angles [°]	B-Christer-C-C	16.7(3)	17.3(7)	19.2(5)	19.3(1)	14.8(4)	17.5(5)	_	_
	B-Christer-C-C	19.5(3)	17.7(8)	19.8(6)	19.8(1)	16.9(4)	17.5(5)	_	_
	B-C	21.6(3)	20.4(7)	22.6(5)	22.2(1)	17.3(4)	20.0(5)	_	_
	average	19.3	18.5	20.5	20.4	16.3	18.3	_	_
	B-Si -C-C	_	_	_	_	_	_	16.4(3)	19.9(2)
	B-Si	_	_	_	_	_	_	17.3(3)	21.5(2)
	B-Si	_	_	_	_	_	_	17.8(3)	22.1(2)
	average	-	-	-	-	-	-	17.2	21.2
THC [%]	boron	67	69	73	72	66	70	65	67



Figure 2. ORTEP drawing of $1aB\cdot Py$. Top view (pyridine is omitted for clarity).

caused by the cage shape.^[26] A similar borate structure, with its phenolic rings connected to nitrogen, was reported, but its coordination to boron resulted in nearly perpendicular aromatic rings.^[27] The bond length of B–N in **1a**B·Py is 1.628(5) Å, and the sum of the angles for O-B-O and N-B-O around boron are 342.7 and 312.6°, respectively. The Br-sub-

stituted compounds 1b,cB·Py and F-substituted compound 1dB·Py have structures that are similar to 1aB·Py and their THCs also are very similar, as shown in Table 3. The phenyl-substituted borate 1eB·Py has a longer B-N bond length (1.647(6) Å) with a larger Σ (O-B-O) angle (342.8°) and a smaller Σ (N-B-O) angle (312.2°) around boron, probably because of the steric hindrance of the ortho-phenyl groups. In the bulkier naphthyl-substituted borate 1 fB·Py, the B-N bond length (1.631(8) Å) is less than that of 1eB·Py, presumably due to crystal-packing effects and/or a π - π interaction between the pyridine and naphthyl rings. A silicon-based compound with a pyridine-ligand 1gB·Py was also analyzed by X-ray crystallography. The larger size of the bridging Si atom resulted in longer Si-aryl bonds (average 1.870 Å) in **1g**B·Py than the C-aryl bonds (average 1.519 Å) in **1a**B·Py, and, therefore, it directly affected the geometry of the cage. The boron has a distorted tetrahedral coordination sphere and the Σ (O-B-O) and Σ (N-B-O) bond angles are 343.1 and 311.8°, respectively, while the angles of 1aB·Py are 342.7 and 312.6°, respectively. The geometries around boron in 1gB Py and 1aB Py were nearly identical, but that of 1gB·Py was more planar. The B-N bond length

in **1g**B·Py is 1.655(5) Å, which is longer than that in **1a**B·Py. This geometry suggests that **1g**B·Py has a lower Lewis acidity than **1a**B·Py. It is worth noting that the silicon atom in **1g**B·Py has an almost tetrahedral structure (sum of Ar-Si-Ar; 330.3°), while the carbon atom at the bottom of **1a**B·Py has a distorted structure with bond angles that equaled 343.7°. The *i*BuSi-bridging borate **1h**B·Py was also analyzed by X-ray crystallography, and has a framework similar to that of **1g**B·Py. The sum of the bond angles for **1g**B·Py are as follows: Σ (O-B-O), 342.5°; Σ (N-B-O), 312.6°; Σ (Ar-Si-Ar), 328.0°. The average Si–aryl bond length for **1g**B·Py is 1.879 Å.

Lewis acidity of the cage-shaped borates: To investigate the ability of the cage-shaped borates 1B to activate carbonyl compounds, we synthesized their complexes with the 2,6-dimethyl- γ -pyrone 5. A $\Delta\delta$ (¹³C) shift of C3 in 5 clearly shows the degree of Lewis acidity. These data provide an estimate of the Lewis acidity that is more precise than the chemical shift of ligated THF coordinated to boron, as discussed above in the section on NMR data for cage-shaped borates. The $\Delta\delta(^{13}C)$ shifts of C3 in 5 are shown in Table 4 for various borates. For comparison with other Lewis acids, the planar borate B(OPh)₃ and the strong Lewis acid BF₃·OEt₂ were also employed. In fact, the complexation of 5 with BF₃·OEt₂ showed the largest downfield shift $(\Delta \delta)^{(13)} =$ +8.708 ppm) in C3 (entry 10), and B(OPh)₃ showed only a small chemical shift ($\Delta\delta$ (¹³C)=+0.774 ppm) (entry 9). It is worth noting that all cage-shaped borates 1B showed a Lewis acidity that lay between that of B(OPh)₃ and $BF_3 \cdot OEt_2$. The unsubstituted borate **1a**B showed a downfield shift of +6.782 ppm (entry 1). The introduction of an electron-withdrawing group onto the aryl rings in cageshaped borates allowed for precise control of the Lewis acidity. Introduction of F onto the aryl rings of the cageshaped borate 1dB resulted in a higher Lewis acidity than that observed for the unsubstituted borate 1aB (entry 4). The p-Br-substituted compound 1cB had a higher Lewis acidity (entry 3) than 1dB, and the highest Lewis acidity

Table 4. Complexation of boron compounds with the carbonyl compound **5**. [B] = complexed boron compound

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	Boron compound + $\begin{pmatrix} 2 & 3 \\ 1 & 1 \\ 0 & 5 \end{pmatrix}$			
Entry	Boron compound	$\Delta\delta(^{13}\text{C})$ of C3 [ppm]		
1	1 aB·THF	+6.782		
2	1bB·THF	+7.630		
3	1cB·THF	+7.605		
4	1dB·THF	+7.243		
5	1eB·THF	+5.564		
6	1 fB·THF	+3.877		
7	1gB·THF	+5.844		
8	1hB·THF	+4.519		
9	$B(OPh)_3$	+0.774		
10	$BF_3 \cdot OEt_2$	+8.708		

among the cage-shaped borates 1B was observed for the oand p-Br-substituted compound 1bB (entry 2). This shift corresponds to the chemical shifts observed for the ligated THF discussed above. Interestingly, replacement of the bridgehead C with a bridgehead Si decreased the Lewis acidity. The silicon-bridging compounds 1gB and 1hB showed smaller downfield shifts of the pyrone, +5.844 and +4.519 ppm (entries 7 and 8), respectively, than that of the carbon-bridging compound 1aB (+6.782 ppm). The strength of the Lewis acidity based on the measurement of $\Delta \delta$ ⁽¹³C) was: $BF_3 > 1bB > 1cB > 1dB > 1aB > 1gB > 1hB > B(OPh)_3$. The Lewis acidities of 1eB and 1fB could not be estimated by using this $\Delta\delta(^{13}C)$ measurement method, because the ortho-aryl groups had a significant anisotropic effect on the chemical shifts of ligated 5. Table 4 describes the fine-tuning of Lewis acidity using the new cage-shaped template over a range of moderate Lewis acidity that would be useful for catalysts.

Theoretical calculations: The characteristic properties of cage-shaped borates 1B were investigated by theoretical calculations. Optimized structures and unoccupied molecular orbitals contributing to the Lewis acidity of the cage-shaped borates 1B and the open-shaped borate B(OPh)₃ are shown in Figure 3. Some of the calculated data are shown in Table 5. The optimized structures of the cage-shaped borates 1B show that the geometries around the boron centers are nearly planar, and the sums of the three O-B-O angles are nearly 360° in each case (Figure 3 and Table 5). Figure 3 also shows the molecular orbital (MO) diagram of unoccupied MOs^[28] of the cage-shaped borates 1a-dB, 1gB, and 1hB, and the open-shaped borate B(OPh)₃. The cageshaped borates include a large and accessible lobe on boron, while the corresponding lobe in B(OPh)₃ (LUMO in this case) is small and buried. From the optimized borate structures, we observe that the bridgehead atom significantly affects the cage structure-for example, the dihedral angle (C_{inso}-O-B-O) θ (Table 5). The bridgehead atoms, either carbon or silicon, control the dihedral angles (C_{ipso}-O-B-O) θ (1aB 48.4°; 1gB 45.4°; 1hB 43.6°; entries 1, 5 and 6). As the angles become smaller, the cage-shaped borates showed the lower energy levels of the unoccupied MOs^[29] of Lewis acids. Their eigenvalues are on the order of 1aB < 1gB <**1h**B. In fact, the open-shaped borate $B(OPh)_3$ has a nearly planar structure (small dihedral angle, $\theta = 2.0^{\circ}$) and a high eigenvalue (entry 7). To examine the correlation between the dihedral angle and the eigenvalue of the corresponding MO, a series of theoretical calculations were carried out. The change of the eigenvalue could be traced by changing the dihedral angle (H-O-B-O) θ under the constraints on the geometry around the boron center (planar structure in sp² hybridization) (Scheme 5). The angle of $\theta = 0^{\circ}$ gave the highest MO energy level because of the effective conjugation between the p orbitals on O and B. Gradual changes in the MO level can be realized by varying θ , even with three B-O bonds, by keeping the structure in-plane. These results show that the dihedral angle θ controls the overlap between

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Figure 3. Optimized structures and unoccupied MO diagrams of cageshaped and open-shaped borates.

Table 5. Theoretical calculations for borates.

Entry	Borate	Σ(O-B-O) [°]	Dihedral angle (C-O-B-O) [°]	Eigenvalue [eV] ^[a]	ΔE [kcal mol ⁻¹] ^[b]
1	1 aB	359.7	48.4	-0.79	-19.2
2	1 b B	359.4	46.6	-1.67	-31.4
3	1cB	359.6	48.1	-1.31	-22.5
4	1 d B	359.6	47.5	-1.12	-20.8
5	1gB	360.0	45.4	-0.73	-13.2
6	1 hB	359.9	43.6	-0.71	-13.1
7	$B(OPh)_3$	360.0	2.0	-0.54	-5.0

[a] Eigenvalues of MOs depicted in Figure 3. [b] For pyridine complexation.

the p orbitals on O and B, which allows fine-tuning of the MO energy level. While the differences among the carbonbridging borates **1a–dB** are minimal ($\theta \approx 47-48^\circ$; entries 1–



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Scheme 5. Relationship between the dihedral angle θ and the energy level of the lowest unoccupied MO relative to a Lewis acid.

4), the energy levels of the unoccupied MOs^[29] that contribute to the Lewis acids are controlled by the electronic factors of the substituents on the aryl rings. The eigenvalues are on the order of 1bB < 1cB < 1dB < 1aB. It is understandable that electron-withdrawing groups lead to favorable interactions between the borates and the Lewis basic substrates. In total, the order of the eigenvalues is $1bB < 1cB < 1dB < 1aB < 1gB < 1hB < B(OPh)_3$. The pyridine complexation energies, ΔE , also showed the same order. Thus, we were able to fine-tune the Lewis acidity of the borates by structural and electronic controls. The Lewis acidity data were highly consistent with the experimental NMR data for pyrone 5.

Ligand exchange rate of cage-shaped borates: The ligand exchange rate of the cage-shaped borates 1B was investigated to obtain information on the kinetics of the ligand association–dissociation process that controls a Lewis acid catalyst reaction. Dimethylaminopyridine (DMAP) complexes of 1B were dissolved in [D₅]pyridine, and the ligand dissociation rate was measured during ligand exchange from DMAP to pyridine. The results are shown in Table 6. The unsubstituted cage-shaped borate 1aB has a dissociation rate constant of $k=2.32 \times 10^{-9} \text{ s}^{-1}$, whereas that for the fluoro-substituted compound 1dB is smaller ($k=8.37 \times 10^{-12}$; entries 1 and 2). The activation enthalpy ΔH^{\pm} of 1dB is much larger than that of 1aB, because the electron-withdrawing effect of fluorine increased the Lewis acidity of the boron center by stabilization of the negative charge generated during complex-

Table 6. Kinetic parameters for ligand dissociation of the cage-shaped borates 1B.



Entry	Borate	ΔH^+	ΔS^+	ΔG^+	ĸ
		$[kcal mol^{-1}]$	$\left[calK^{-1}mol^{-1}\right]$	$[\text{kcal mol}^{-1}]^{[a]}$	$[s^{-1}]^{[a]}$
1	1 aB·L	35.1	22.3	28.6	2.32×10^{-9}
2	1 dB·L	43.6	40.0	31.9	8.37×10^{-12}
3	1eB·L	31.2	7.5	29.0	1.16×10^{-9}
4	1gB·L	26.4	14.2	22.3	1.28×10^{-4}

[a] ΔG^{\dagger} and k are calculated at T = 20 °C.

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ation. For **1eB**, which has sterically demanding *ortho*-phenyl substituents, a decrease in the rate constant $(k=1.16 \times 10^{-9} \text{ s}^{-1})$ is also observed (entry 3). The activation entropy ΔS^{+} of **1eB** is much lower than that of **1aB**, although the activation enthalpy is nearly identical. The steric repulsion caused by the bulky *ortho*-substituents during ligand dissociation controls the entropic effect. The electronic factor controls the ligand exchange rate by changing ΔH^{+} , and the steric factor influences the rate with different ΔS^{+} . It is worth noting that the silicon-bridging compound **1gB** has a low ΔG^{+} , mainly due to a lower $\Delta H^{+} = 26.4 \text{ kcalmol}^{-1}$ (entry 4). This result shows that the geometry of the cage shape is an important determinant of the character of a Lewis acid catalyst.

Catalytic activity of cage-shaped borates of organic transformation: The cage-shaped borates were applied as catalysts in the hetero Diels–Alder reaction of the Danishefsky diene 6 with benzaldehyde (7a); the results are shown in Table 7.^[30] For a Lewis acid catalyst, the balance between

Table 7. Hetero Diels-Alder reaction catalyzed by various borates.

	Me ₃ SiO	≠ 0 +Ph	borate (10 mol %) CH ₂ Cl ₂ , RT, 18 h	0 O Ph
	6	7a		8a
Entry		Bora	te	Yield [%]
1		1aB∙	THF	77
2	1bB·THF			14
3		1 cB-'	THF	25
4		1 d B∙	THF	29
5		1e B·	THF	77
6		1 f B '	THF	65
7		1g B·	THF	85
8	B(OPh) ₃			7
9		BF ₃ ·	DEt ₂	<5

the Lewis acidity and the ability to exchange ligands is important.^[31] In fact, both the weak Lewis acid B(OPh)₃ and the strong Lewis acid BF₃·OEt₂ gave low yields (entries 8 and 9). The cage-shaped borates 1B afforded higher yields (entries 1-7), because of their moderate Lewis acidity. The unsubstituted cage-shaped borate 1aB.THF gave the cycloaddition product 8a in 77% yield. The halogen-substituted cage-shaped borates yielded the product on the order of 1dB > 1cB > 1bB. This result suggests that a Lewis acidity that is too high leads to a strong affinity between the boron center and the product, which reduces the catalytic turnover. The silicon-bridging borate 1gB THF was the best catalyst for the hetero Diels-Alder reaction, giving the product in 85% yield (entry 7). In this case, the Lewis acidity of the borate 1gB was slightly lowered by bridgehead-control, which promotes release of the product, contributing to an increase in catalytic activity. The phenyl-substituted borate 1eB gave the product in satisfactory yield (entry 5).

The Mukaiyama aldol reaction^[32,33] was also examined using the ketene silyl acetal **9** substituted with methyls at the terminal olefinic moiety, as shown in Table 8. In contrast

Table 8. Mukaiyama aldol reaction using aldehyde catalyzed by various borates.

	OSi R ¹ OMe R ² 9 or 10 9, 11: R ¹ , R ¹ 10, 12: R ¹ , F	7a $\frac{\text{borate}()}{CH_2}$ ² , Si = Me, Me, R ² , Si = H, H, tE	(10 mol %) Cl ₂ , RT Me ₃ Si BuMe ₂ Si	Ph R^1 R^2 11 or 12	DMe
Entry	Nucleophile	Time [h]	Borate	Product	Yield [%]
1	9	6	1aB·THF	11	<5
2	9	6	1bB·THF	11	98
3	9	6	1cB·THF	11	17
4	9	6	1dB·THF	11	<5
5	9	6	1eB·THF	11	69
6	9	6	1 fB THF	11	90
7	9	6	1gB∙THF	11	20
8	9	6	$B(OPh)_3$	11	<5
9	9	6	BF ₃ ·OEt ₂	11	9
10	10	4	1aB∙THF	12	30
11	10	4	1bB·THF	12	91
12	10	4	1cB·THF	12	50
13	10	4	1dB·THF	12	43
14	10	4	1eB·THF	12	67
15	10	4	1 fB THF	12	54
16	10	4	1gB∙THF	12	31
17	10	4	B(OPh) ₂	12	26

to the results of a hetero Diels–Alder reaction, the appropriate Lewis acid was the dibromo-substituted cage-shaped borate **1b**B, while the unsubstituted borate **1a**B was ineffective (entries 1 and 2). In this case, the activation step, rather than the catalyst-regeneration process (releasing step), was more important in the catalytic cycle. Interestingly, a relatively high yield of the product **11** was obtained by using the phenyl-substituted borate **1e**B (entry 5). The open-shaped borate catalyst showed no catalytic activity (entry 8), and the strong Lewis acid afforded very low yields (entry 9). When the unsubstituted silyl nucleophile **10** was used, **1b**B also afforded the product **12** in high yield (entry 11), and the cage-shaped borates also worked well. It should be noted that different reactions had different suitable catalysts, even among the cage-shaped borate catalysts.

BF3·OEt2

12

8

In the case of the Mukaiyama aldol reaction that used the acetal **13** as an electrophile,^[34] the dibromo- and monobromo-substituted borates **1bB** and **1cB** gave high yields among the series of cage-shaped borate catalysts (Table 9, entries 2 and 3). The phenyl- and naphthyl-substituted borates **1eB** and **1fB** did not give the product, probably because steric hindrance prevented the approach of the bulky electrophile **13** (entries 5 and 6). Based on these results, we thought that the *ortho*-aryl substituted cage-shaped borates **1eB** and **1fB** recognized the bulkiness of the substrates.

We next investigated the generality of the aldehydes in the hetero Diels-Alder reaction using the cage-shaped bo-

18

10

4

Table 9. Mukaiyama aldol reaction using acetal catalyzed by various borates.

	OSiMe ₃ MeO OMe borate (10 mol %) OMe + H Ph CH ₂ Cl ₂ , RT, 6 h 9 13	MeO O Ph OMe 14
Entry	Borate	Yield [%]
1	1aB·THF	8
2	1bB·THF	62
3	1cB·THF	61
4	1dB·THF	17
5	1eB·THF	<5
6	1 fB·THF	<5
7	1gB·THF	<5
8	B(OPh) ₃	<5
9	$BF_3 \cdot OEt_2$	31

rates **1a**B and **1e**B at room temperature for 4 h (Table 10). The reaction of **6** with benzaldehyde **7a** gave the product **8a** in 72% yield in the presence of a catalytic amount of **1a**B

Table 10. Hetero Diels–Alder reaction catalyzed by two types of borates: **1a**B·THF and **1e**B·THF. OMe

	Me ₃ SiO	+ C	B CH ₂ Cl ₂ , I	0 mol %) RT, 4 h	∕⊂0 ∕── [−] B
	6	7	,		8
Entry	Aldehyd	le	Borate	Product	Yield of 8 [%]
1	0		1aB·THF	8a	72
2	Н	7a	1eB·THF	8a	74
3	O Me		1aB·THF	8b	64
4	Н	7b	1eB·THF	8b	64
5	O Ph		1aB·THF	8 c	53
6	Н	7 c	1eB·THF	8c	67
7	O II		1aB·THF	8 d	54
8	н	7 d	1eB·THF	8 d	61
9	O II		1aB·THF	8 e	56
10	Н	7e	1eB·THF	8e	63
11	0		1aB·THF	8 f	76
12	Н	7 f	1eB·THF	8 f	65
13	O II		1aB∙THF	8 g	38
14	н	7 g	1eB·THF	8g	42

(entry 1). The substituted aldehydes **7b** and **7c** also gave the products, although a small decrease in yields was observed because of the steric effects of the *ortho*-substituents (entries 3 and 5). The aliphatic aldehydes **7d–g** were also applied to this catalytic reaction system to give the corresponding products **8d–g** (entries 7, 9, 11, and 13). Unexpectedly, the use of phenyl-substituted borate **1e**B showed almost the same results in the hetero Diels–Alder reaction as use of **1a**B, in spite of the bulky *ortho*-phenyl groups in **1e**B.

A careful comparison between 1aB and 1eB was performed by competitive reaction using a mixture of the benzaldehyde (7a) and *o*-phenylbenzaldehyde (7c) (Table 11).

Table 11. Competitive reaction of the Danishefsky diene with two types
of aldehyde 7a and 7c catalyzed by the borates 1aB·THF, 1eB·THF, or
1 fB·THF. ^[a]

Me ₃ SiO	OMe + 6 7 7 7 7 7 7 7	Ph	$\frac{\text{te}}{4 \text{ h}} \begin{cases} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0$	O H Ba O Ph Bc
Entry	Borate	Solvent	Yield [%]	Ratio 8a/8c
1	1 aB·THF	CH_2Cl_2	86	1.1
2	1 eB·THF	CH_2Cl_2	87	3.6
3	1 aB·THF	acetonitrile	67	0.97
4	1 eB·THF	acetonitrile	73	6.3
5	1 fB·THF	acetonitrile	69	12.8

[a] The reactions were carried out using **6** (1.0 mmol), **7a** (1.0 mmol), **7c** (1.0 mmol), and borate catalyst (0.1 mmol).

When the unsubstituted borate 1aB in dichloromethane was used as the catalyst for the competitive reaction, the product ratio of 8a/8c was 1.1 (=52:48; entry 1). In contrast, when the phenyl-substituted borate 1eB was used, the product ratio was 3.6 (= 78:22), and, therefore, the selectivity was increased 3.27-fold (entry 2). This result can be explained by the steric effects of the ortho-phenyl substituent that prevented access of the bulky substrate to the metal center.^[35,36] The use of 1eB with acetonitrile as the solvent showed a 6.49-fold increase compared to 1aB (entries 3 and 4). The coordinative solvent somewhat retarded complexation with the substrate aldehyde, and, hence, the selectivity was enhanced. Notably, the naphthyl-substituted borate 1 fB gave a much higher value of 12.8 (13.2-fold greater than 1aB) due to effective steric hindrance for substrate-selectivity (entries 3 and 5). The cage-shaped borates provide steric hindrance due to their inflexible structure; therefore, they effectively controlled the substrate-selective reaction system, as shown in Table 11.

Conclusion

We have synthesized cage-shaped borates with a tris(*o*-oxyphenyl)methane or -silane moiety, with various substituents. The cage shape resulted in a novel boron center, which is a unique Lewis acid. Both the Lewis acidity and the catalytic activity of organic transformation were successfully enhanced. A moderate Lewis acidity was attained by tuning factors such as the substituents (electronic and steric control) and the bridgehead atoms (geometric control). Theoretical calculations suggested that the energy levels of the unoccupied molecular orbitals, which greatly contributed to activation of the substrate, are finely tuned by the substituent effect and the cage geometry. The *ortho*-aryl substituent on the cage-shaped borate controlled the selectivity of the competitive reaction between sterically different aldehydes. The cage-shaped template can be modified in many ways by altering either the geometry^[37] or the substituents, and it is a promising template for other metal complexes to be used in catalysts, new metal complexes, or materials.

Experimental Section

Full experimental details and the structural data for borates 1b--fB-Py are given in the Supporting Information. $^{[38]}$

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