# Fine-Tuning of Boron Complexes with Cage-Shaped Ligand Geometry: Rational Design of Triphenolic Ligand as a Template for Structure Control

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ABSTRACT
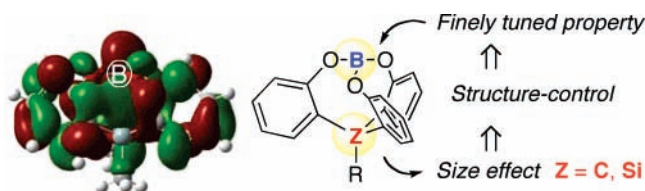
Boron complexes surrounded with organic cages were controlled precisely by a remote atom placed at the bottom of the cage. A replacement of the bottom tether atom (carbon or silicon) changed the characteristics (kinetic and thermodynamic factors) of boron complexes by geometric effects. A theoretical study shows that the bottom atoms also control eigenvalues of MO. This cage complex will provide a systematic template for fine-tuning of metal complexes to create various properties.

The properties of metal complexes undoubtedly depend on the metal centers and ligands. Numerous studies have been performed to alter various properties of the complexes by varying the metal centers and ligands. However, replacing a metal center and/or its ligands often causes changes in the properties of the metal–ligand complex that are too large. Changing the geometry around the metal can alter the properties of metal complexes, but this approach may cause relatively large alterations in the metal complex properties.[1] Character changes of metal complexes have been extensively studied when the metals or ligands are replaced; however,

no attention has been focused on systematic study of fine-tuning of metal complexes in spite of the importance of finely tuned catalysts or materials. One reason for the undeveloped situation is the lack of suitable templates to investigate. In this context, the purpose of this study was to create a new ligand system that changes neither chemical connectivity nor geometry around the metal but instead alters the steric structure of the ligand apart from the metal. Recently, our research group reported cage-shaped borate esters, such as $B(OC_6H_4)_3CH$ (**1B**), that have higher Lewis acidity and catalytic activity than the ordinal open-shaped borate ester $B(OPh)_3$ (**2**).[2,3] The cage shape forces a larger dihedral angle (C–O–B–O) than the open-shaped borate ester.[2] The characters of open- and cage-shaped borates still have large

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(1) Some examples are shown: (a) Denmark, S. E.; Griedel, B. D.; Coe, D. M.; Schnute, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 7026–7043. (b) Nelson, S. G.; Kim, B.-K.; Peelen, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 9318–9319. (c) Kobayashi, J.; Kawaguchi, K.; Kawashima, T. *J. Am. Chem. Soc.* **2004**, *126*, 16318–16319. (d) Wagner, C. E.; Kim, J.-S.; Shea, K. J. *J. Am. Chem. Soc.* **2003**, *125*, 12179–12195.

(2) Although we previously proposed the concept to explain the different characters between open- and cage-shaped borates, theoretical discussion had not been employed: Yasuda, M.; Yoshioka, S.; Yamasaki, S.; Somyo, T.; Chiba, K.; Baba, A. *Org. Lett.* **2006**, *8*, 761–764.

differences between them and are not finely tuned despite bearing the same planar geometries around the boron centers. However, the cage-shaped borates led to us to consider the cage−ligand as a suitable template for investigating a systematic fine-tuning system. Accordingly, a sila derivative of the cage-shaped borate, B(OC$_6$H$_4$)$_3$SiR (**3B**), with a larger tether introduced into the cage, was thought to be worthwhile to examine. We report here on *a systematic fine-tuning protocol of metal complexes with precisely designed ligands* that does not directly affect on the boron center but control the character by slight change of the ligand structure. A gradual and useful character change has been accomplished using the triphenolic cage−ligand system with different tethers.
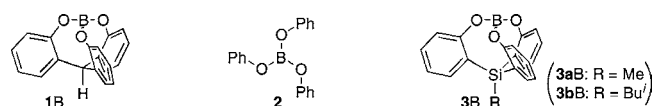
The structural change of the cage−ligand is related to dihedral angle of (C−O−B−O) that determines the character of metal complexes.[2] Therefore, B(OH)$_3$ was chosen as a model compound to perceive any change of its character: The relationship between the dihedral angle (H−O−B−O) θ and the lowest unoccupied MO contributing to the Lewis acid was theoretically calculated,[4] keeping connectivity and geometry around the boron center (planar structure in sp^2 hybridization) constant as shown in Scheme 1. The angle (θ

Scheme 1. Relationship between Dihedral Angle θ and Energy Level of the Lowest Unoccupied MO Concerning to Lewis Acid
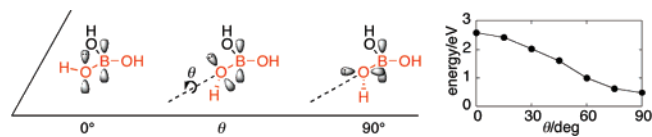
= 0°) gives the highest MO energy level because of effective conjugation between the *p*-orbitals on O and B. Gradual change in the MO level can be realized by varying θ, even with three B−O bonds, keeping the structure in-plane.[2] This result shows our concept is promising for precise control.

Next, the structures of two types of **3B** (R = Me, **3aB**; R = ^{i}Bu, **3bB**) were estimated from theoretical calculations (Table 1 and Scheme 2). The boron had three oxygens in-plane (sum of the three OBO angles: **3aB**, 360.0°; **3bB**, 359.9°). The dihedral angles (C−O−B−O) θ were 45.4° and 43.6° for **3aB** and **3bB**, respectively. These values were intermediate to those of carbon-tethered cage-shaped borate **1B** (48.4°) and the open-shaped configuration **2** (2.0°).[2] **3aB** had a slightly larger angle than **3bB**. As expected from this

Table 1. Theoretical Calculation of **3B**, **1**B, and **2**

entry	borate		dihedral angle θ (C−O−B−O) (deg)	eigenvalue (kcal/mol)	ΔE in pyridine com-plexation (kcal/mol)
1^a	B(OC$_6$H$_4$)$_3$CH	**1**B	48.4	−18.26	−19.2
2	B(OC$_6$H$_4$)$_3$SiMe	**3a**B	45.4	−16.81	−13.2
3	B(OC$_6$H$_4$)$_3$Si^{i}Bu	**3b**B	43.6	−16.46	−13.1
4^a	B(OPh)$_3$	**2**	2.0	−12.46	−5.0

^{a} Reference 2.

result, the energy levels of the lowest unoccupied MO[4] concerning Lewis acids also were intermediate to the values obtained for **1B** and **2**, as follows: **1B** < **3aB** < **3bB** < **2**. The MO diagrams show accessible lobes on the borons, which are suitable for accepting a Lewis base (Scheme 2). The pyridine-complexation energies, ΔE, also showed the order **1B** < **3aB** < **3bB** < **2**. The theoretically calculated results prompted the comparison of silicon-tethered cage-shaped borate esters with carbon-tethered esters because fine-tuning of the Lewis acidity of the boron complexes may be possible by ligand structure control.

Scheme 2. Optimum Structures and MO Diagrams of **3a**B/**3b**B
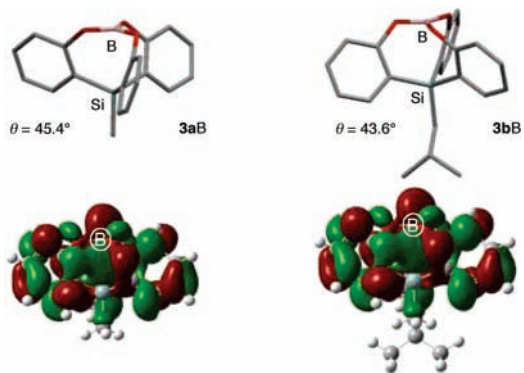
An interesting theoretical result in Table 1 and Scheme 2 prompted us to synthesize triphenolic silanes **3H$_3$** (R = Me, **3aH$_3$**; R = ^{i}Bu, **3bH$_3$**) which are precursors of sila-cage-shaped complexes **3B**. Although we obtained (*o*-MeOC$_6$H$_4$)$_3$-SiMe by the reaction of *o*-lithioanisol with MeSiCl$_3$ according to our previously reported procedure for **1B**,[2] its deprotection by BBr$_3$ failed and gave the undesired product owing to weak Si−aryl bonds. Among many protecting groups examined, dimethylcarbamate worked well for **3aH$_3$** as shown in Scheme 3. Protection of 2-bromophenol **4** and its subsequent lithiation[5] followed by treatment with MeSiCl$_3$ gave the triarylmethylsilane **6a**. Deprotection of **6a** by LiAlH$_4$ effectively afforded **3aH$_3$** without cleavage of Si−aryl bonds. Once the general and reliable synthetic procedure for **3H$_3$** was established, the derivatives were obtained to

(3) Similar cage-shaped compounds were reported as follows. As a Lewis base: Dinger, M. B.; Scott, M. J. *Inorg. Chem.* **2001**, *40*, 856−864. As a titanium complex: Akagi, F.; Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2005**, *127*, 11936−11937.

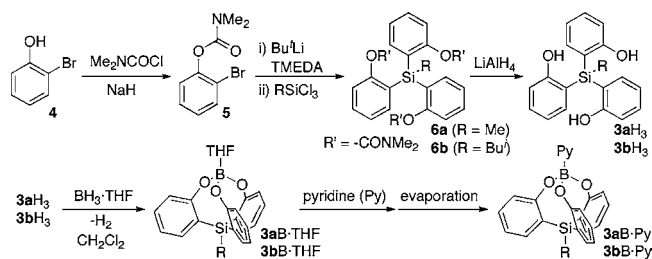(4) The described MOs are the lowest unoccupied orbitals with suitable lobes on boron as a Lewis acid.

(5) Godard, A.; Robin, Y.; Queguiner, G. *J. Organomet. Chem.* **1987**, *336*, 1−12.

Scheme 3. Triphenolic Silane $3H_3$ and Cage-Shaped Borate $3B$

finely tune the metal complexes. In fact, synthesis of $3bH_3$ was successful in the similar procedure. The reaction of $3aH_3$ with $BH_3 \cdot THF$ gave the desired cage-shaped silicon-tethered borate $3aB$ as a THF complex, which was confirmed by NMR spectra.[6,7] The pyridine complex $3aB \cdot Py$ was obtained by ligand-exchange. NMR of $3aB \cdot Py$ showed a characteristic shift in the Me group on Si. A downfield-shift of $\delta(^1H)$ of the Me group (0.95 → 1.08 ppm) and an upfield-shift of $\delta(^{13}C)$ (−3.0 → −6.4 ppm) were confirmed relative to the spectra of the original organic ligand $3aH_3$. A ^{29}Si NMR shift was observed at the upper field (−18.2 → −21.1 ppm). The pyridine signals, which appeared in lower fields relative to those of free pyridine, indicated strong coordination of the pyridine to the boron in $3aB$. Analogous results for synthesis and spectral analyses were obtained for $3bB$.

The pyridine-complex $3aB \cdot Py$ was analyzed by X-ray crystallography (Figure 1a).[8] Boron has a distorted tetrahedral
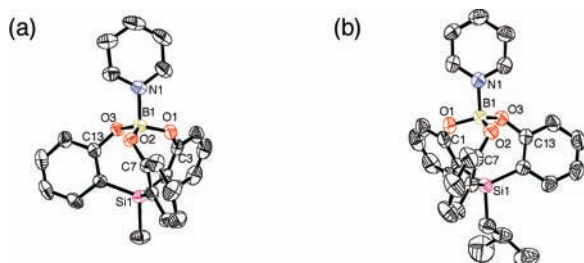
Figure 1. ORTEP drawings of (a) $3aB \cdot Py$ and (b) $3bB \cdot Py$ (some hydrogens are omitted for clarity).

coordination sphere with the sum of the bond angles as follows: O−B−O, 343.1° and N−B−O, 311.8° ($1B \cdot Py$ has the corresponding angles[2] as follows: O−B−O, 342.9° and N−B−O, 312.2°). The geometries around B in $3aB \cdot Py$ and $1B \cdot Py$ were nearly identical. The larger silicon tether results in longer Si-aryl bonds (average 1.871 Å) in $3aB \cdot Py$ than

(6) Recent review of ligands bearing phenoxy moieties: Matsuo, T.; Kawaguchi, H. *Chem. Lett.* **2004**, *33*, 640−645.

(7) (a) Livant, P. D.; Northcott, J. D.; Shen, Y.; Webb, T. R. *J. Org. Chem.* **2004**, *69*, 6564−6571. (b) Verkerk, U.; Fujita, M.; Dzwiniel, T. L.; McDonald, R.; Stryker, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 9988−9989. (c) Fujita, M.; Qi, G.; Verkerk, U. H.; Dzwiniel, T. L.; McDonald, R.; Stryker, J. M. *Org. Lett.* **2004**, *6*, 2653−2656.

(8) The X-ray crystallographic data of $3aB \cdot Py$, $3bB \cdot Py$, $1B \cdot 8$, and $3aB \cdot 8$ are given in the Supporting Information.

the C−aryl bonds (average 1.519 Å) in $1B \cdot Py$. It is worth noting that the silicon in $3aB \cdot Py$ has an almost tetrahedral structure (sum of Ar−Si−Ar; 330.3°), while the carbon in $1B \cdot Py$ has a distorted structure with the sum of the bond angles equal to 343.3°. The ^iBuSi-tethered borate $3bB \cdot Py$ was also analyzed by X-ray crystallography (Figure 1b). It had a framework similar to that of $3aB \cdot Py$. The sums of the bond angles for $3bB \cdot Py$ were as follows: O−B−O, 342.5°; N−B−O, 312.6°; Ar−Si−Ar, 328.0°. The average Si−aryl bond length was 1.879 Å.

Complexation of the borate esters with 2,6-dimethyl γ-pyron **8** was examined by NMR to estimate their Lewis acidity.[9] A chemical shift $\delta(^{13}C)$ of C3 in **8** clearly shows the degree of Lewis acidity (Table 2). For comparison with

Table 2. Complexation of Boron Compounds with Carbonyl Compound **8**

entry	B compound	$\Delta\delta(^{13}C)$ of C3/ppm
1	$1B \cdot THF$	6.8
2	$3aB \cdot THF$	5.8
3	$3bB \cdot THF$	4.5
4	**2**	2.5
5	$BF_3 \cdot OEt_2$	8.7

other Lewis acids, the planar borate $B(OPh)_3$ **2** and a typical strong Lewis acid $BF_3 \cdot OEt_2$ were employed. In fact, the complexation of **8** with $BF_3 \cdot OEt_2$ showed the largest downfield shift ($\Delta\delta(^{13}C) = 8.7$ ppm) in C3. Interestingly, silacage compounds $3aB$ and $3bB$ were shifted downfield by 5.8 and 4.5 ppm, respectively, an effect intermediate to those of $1B$ and **2**. This result is consistent with the Lewis acidity expected based on the theoretical results in Table 1.

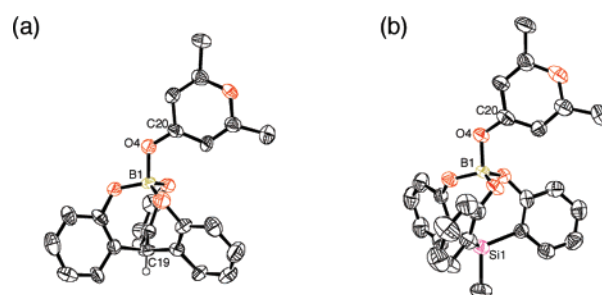The carbonyl complexes of $1B$ and $3aB$ with **8** were isolated and analyzed by X-ray crystallography (Figure 2).[8]

Figure 2. ORTEP drawings of (a) $1B \cdot 8$ and (b) $3aB \cdot 8$ (some hydrogens and solvents are omitted for clarity). Selected bond lengths (Å): (a) O(4)−C(20) 1.294(8), (b) O(4)−C(20) 1.280(5).

The solid-state structure of **1B·8** showed a longer carbonyl bond than that of **3a**B**·8**, reflecting the expected Lewis acidity in the order **1B** > **3a**B, although the difference was not large. The precise tuning of Lewis acidity was realized by size-control of ligand.

The ligand-exchange rate, which is based on the complexation stability and the energy level of the unoccupied MO discussed in Table 1, illustrates another aspect of cage-shaped complexes. The mixture of the complex **1B·pyridine-**d_5 (or **3a**B**·pyridine-**d_5) with unlabeled pyridine was observed by NMR during ligand-scrambling. Kinetic study of the mixtures revealed a faster rate of ligand-exchange in the case of **3a**B compared with **1B** (see the Supporting Information). Activation parameters for ligand dissociation were shown in Table 3. Almost the same entropies $\Delta S^{\ddagger}$ for **3a**B and **1B**

Table 3. Kinetic Parameters for Ligand (Pyridine) Dissociation of Cage Borates **1B** and **3a**B
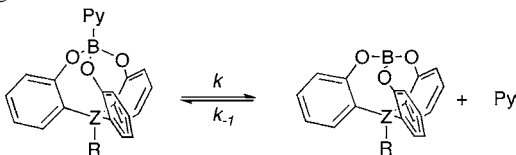
entry	Z–R		$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/K·mol)	$\Delta G^{\ddagger,a}$ (kcal/mol)	k^a (s^{-1})
1	C–H	**1B**	26.6	12.8	22.8	5.84×10^{-5}
2	Si-Me	**3a**B	20.9	12.7	17.1	1.01×10^{1}

^{a} $\Delta G^{\ddagger}$ and k are calculated at $t = 20$ °C.

indicated similar transition states in both cases. The free energy of activation $\Delta G^{\ddagger}$ mainly depended on $\Delta H^{\ddagger}$. The smaller $\Delta H^{\ddagger}$ of **3a**B than **1B** can be expected from the result of the ΔE values in Table 1. Surprisingly, a much higher

rate constant k (~10^6 times larger at 20 °C) was shown for **3a**B compared with **1B**. The size of the cage is found to be quite sensitive to ligand-exchange rate. This result suggests that the precise tuning is very important for design of metal complex. For Lewis acid catalysts, balance between thermodynamic factor (Lewis acidity) and kinetic factor (rate of ligand-exchange) is important.[10] This controlling methodology by cage-size is promising for precise design of the catalyst.[11]

In summary, the cage-shaped borates with different tethers were synthesized and investigated as Lewis acids based on thermodynamic and kinetic points of view in the present study. The general synthetic procedure of the cage-ligands was established. Cage-size/geometry precisely controlled Lewis acidity. The rate of ligand-exchange unexpectedly showed relatively large difference. Other elements to be used as tethers or to functionalize organic cage moieties to control the properties of metal complexes will be investigated in future studies.

Supporting Information Available: Experimental procedures, listing of absolute energies and geometries for calculated species, and X-ray data for **3a**B**·Py**, **3b**B**·Py**, **1B·8**, and **3a**B**·8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

(9) Although pyridine shifts were observed, the anisotropic effect due to phenyl rings would confuse the estimates by NMR shifts.

(10) (a) Yasuda, M.; Yamasaki, S.; Onishi, Y.; Baba, A. *J. Am. Chem. Soc.* **2004**, *126*, 7186−7187. (b) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1414−1416. (c) Onishi, Y.; Ogawa, D.; Yasuda, M.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 13690−13691.

(11) We preliminary examined a catalytic hetero-Diels−Alder reaction. The use of the silicon-tethered borate **3a**B**·THF** gave higher yield (85%) than carbon-tethered borate **1B·THF** (77% ref 2). We are now investigating catalytic activities of them based on reaction rates.