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Photoswitching of the Lewis Acidity of a Catecholborane Bearing an Azo Group Based on the Change in Coordination Number of Boron

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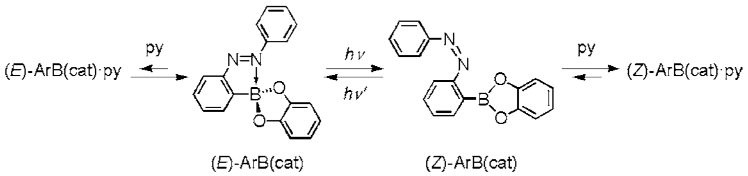
ABSTRACT



Photoisomerization of a catecholborane bearing a 2-(phenylazo)phenyl group with an N−B dative bond caused photoswitching of the coordination number of boron between 3 and 4. The Lewis acidity of the catecholborane was switched by photoirradiation, and the complexation ability of the (*E*)- and the (*Z*)-isomers of the catecholborane with pyridine differs by more than a factor of 300.

Tricoordinate organoboron compounds are known to be useful Lewis acids in organic synthesis.[1] Their Lewis acidity is attributable to the existence of the vacant 2p orbital of boron. In several organoboron compounds bearing a heteroatom tether in the vicinity of the boron atom, the 2p orbital is filled by coordination with the lone pair of a heteroatom such as nitrogen or oxygen.[2] Although these tetracoordinate species do not have Lewis acidity, most of them are in equilibrium with the tricoordinate species that are not coordinated with the heteroatom, which show high Lewis acid characteristics. Usually, the coordination number of boron is switched by the addition of external reagents or solvents with high Lewis basicity. There have been several reports on the switching of some functions of organoboron compounds by taking advantage of the change in coordination number of boron caused by the addition of external reagents.[3] If the coordination number of boron could be changed by external stimuli such as light and magnetism, the structure, reactivities, and Lewis acidity of the organoboron compounds could be controlled without addition of any external reagent. However, there has been no report on such control of the coordination number of boron by photoirradiation.

Azobenzene moieties, which have been widely utilized as switches as a result of their geometrical change caused by photoirradiation,[4] are expected to coordinate to a boron center and work as a photoswitching unit of the coordination

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(1) (a) Ishihara, K. In *Lewis Acid Reagents*; Yamamoto, H., Ed.; Oxford University Press: Oxford, 1999; Chapter 3, pp 31−63. (b) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, 527. (c) Ishihara, K. In *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: New York, 2000; Vol. 1, Chapter 4, pp 89−133.

(2) (a) Lauer, M.; Wulff, G. *J. Organomet. Chem.* **1983**, *256*, 1. (b) Lauer, M.; Böhnke, H.; Grotstollen, R.; Salehnia, M.; Wulff, G. *Chem. Ber.* **1985**, *118*, 246. (c) Kirby, A. J.; Percy, J. M. *Tetrahedron* **1988**, *44*, 6903. (d) Liu, X.-C.; Hubbard, J. L.; Scouten, W. H. *J. Organomet. Chem.* **1995**, *493*, 91. (e) Brown, D. S.; Carmalt, C. J.; Cowley, A. H.; Decken, A.; Isom, H. S. *Heteroat. Chem.* **1998**, *9*, 79. (f) Toyota, S.; Asakura, M.; Futawaka, T.; Oki, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1879. (g) Vedejs, E.; Chapman, R. W.; Lin, S.; Müller, M.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3047. (h) Wiskur, S. L.; Lavigne, J. J.; Ait-Haddou, H.; Lynch, V.; Chiu, Y. H.; Canary, J. W.; Anslyn, E. V. *Org. Lett.* **2001**, *3*, 1311. (i) Yamashita, M.; Kamura, K.; Yamamoto, Y.; Akiba, K.-y. *Chem. Eur. J.* **2002**, *8*, 2976. (j) Norman, D. W.; Edwards, J. P.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Can. J. Chem.* **2002**, *80*, 31. (k) Norrild, J. C.; Sotofte, I. *J. Chem. Soc., Perkin Trans. 2* **2002**, 303. (l) Giles, R. L.; Howard, J. A. K.; Patrick, L. G. F.; Probert, M. R.; Smith, G. E.; Whiting, A. *J. Organomet. Chem.* **2003**, *680*, 257. (m) Toyota, S.; Ito, F.; Nitta, N.; Hakamata, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2081.

(3) (a) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1994**, 477. (b) James, T. D.; Sandanayake, K. R. A. S.; Iguchi, R.; Shinkai, S. *J. Am. Chem. Soc.* **1995**, *117*, 8982. (c) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Nature* **1995**, *374*, 345.

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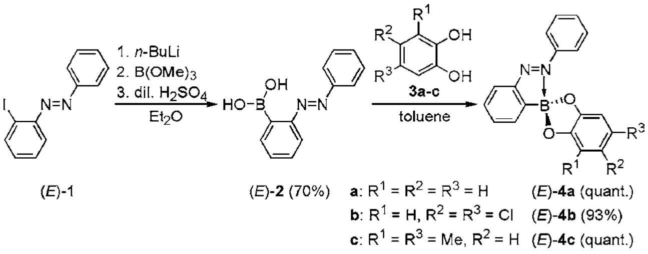
number of the central boron atom.[5] We report here the change of the Lewis acidity of a catecholborane bearing an azo group based on the change in coordination number of the boron atom induced by photoirradiation.

(*E*)-2-Iodoazobenzene ((*E*)-**1**) in ether was allowed to react successively with *n*-BuLi (1.10 equiv), trimethyl borate (1.1 equiv) at −112 °C, and diluted sulfuric acid at 0 °C to give boronic acid (*E*)-**2** (70%) (Scheme 1). The dehydration reaction of (*E*)-**2** and catechols **3a**−**c** (1.0 equiv) at 100 °C in toluene afforded catecholboranes (*E*)-**4a**−**c** in good yields. In the ^{11}B NMR spectra, all of the catecholboranes (*E*)-**4a**−**c** showed a broad peak at higher fields [(*E*)-**4a**, δ_B 21.8; (*E*)-**4b**, δ_B 18.6; (*E*)-**4c**, δ_B 23.6] than phenylcatecholborane [δ_B 32.0] in C_6D_6. They are considered to have tetrahedral structures around the boron atom in the solution state. The structure of (*E*)-**4b** was finally determined by X-ray crystallographic analysis.[6] Figure 1 shows the ORTEP drawing of one of the two independent molecules of (*E*)-**4b** in the unit cell. The N2 atom of the azobenzene unit is directed to the B1 atom [N2−B1, 1.721(6) Å (1.734(6) Å)[7]]. Considering the bond angles [94.1(3)−118.3(4)°] around the B1 atom and the sum of bond angles of O1−B1−O2, O1−B1−C1, and O2−B1−C1 (343°), (*E*)-**4b** presented a distorted tetrahedral structure around the tetracoordinate boron atom with the N2−B1 dative bond. The N1−N2 bond length [1.280(5) Å (1.264(5) Å)[7]] exhibited only slight elongation compared to the mean value (1.25 Å)[8] of the previously reported (*E*)-azobenzenes, suggesting no formation of a zwitterionic inner borate-amido complex, but rather retention of the double-bond character of the N−N bond despite the formation of the N−B dative bond. This is the first example of organoboron compounds with the coordination of an azo group to the boron atom.

Scheme 1



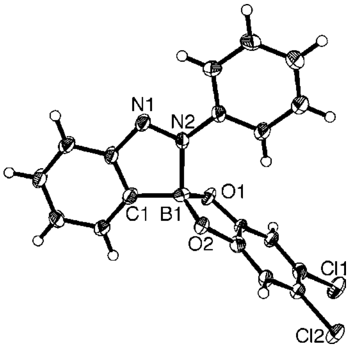
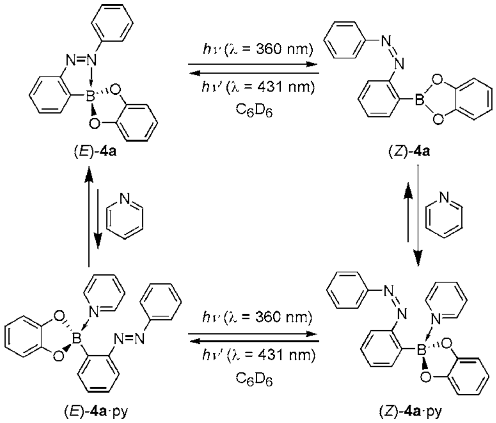


Figure 1. ORTEP drawing of (*E*)-**4b** with thermal ellipsoid plot (50% probability). One of two independent molecules in the cell was omitted. Selected bond lengths (Å) and bond angles (deg): B1−O1, 1.459(6); B1−O2, 1.445(6); B1−C1, 1.570(6); B1−N2, 1.721(6); N1−N2, 1.280(5); O1−B1−O2, 107.0(4); O1−B1−C1, 117.7(4); O1−B1−N2, 108.4(3); O2−B1−C1, 118.3(4); O2−B1−N2, 110.3(4); C1−B1−N2, 94.1(3).

In the UV−vis spectrum in cyclohexane, (*E*)-**4a** showed its absorption maximum at 339 nm, assignable to the $\pi-\pi^*$ transition of the azo group. Irradiation (λ = 360 nm) of (*E*)-**4a** in C_6D_6 for 2 h caused its photoisomerization to give (*Z*)-**4a** in 35% yield (Scheme 2). Irradiation of (*E*)-**4a** in cyclohexane gave a better yield of (*Z*)-**4a** (51%).[9] Upon irradiation of a cyclohexane solution of (*E*)-**4a**, a decrease in the absorption maximum at 339 nm and a corresponding increase in a new maximum at 460 nm were observed. The absorption maximum at 460 nm is assigned to the $n-\pi^*$ transition of the azo group of (*Z*)-**4a**. Irradiation (λ = 431 nm) of (*Z*)-**4a** caused recovery of (*E*)-**4a** in 98% yield.

Scheme 2



In the ^{11}B NMR spectra of (*Z*)-**4a**, the signal was observed at δ_B 30.8 in C_6D_6, which is almost the same value as that

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(4) In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001.

(5) For photoswitching of the coordination number of silicon in organosilicon compounds, see: (a) Kano, N.; Komatsu, F.; Kawashima, T. *J. Am. Chem. Soc.* **2001**, *123*, 10778. (b) Kano, N.; Yamamura, M.; Komatsu, F.; Kawashima, T. *J. Organomet. Chem.* **2003**, *686*, 192. (c) Kano, N.; Yamamura, M.; Kawashima, T. *J. Am. Chem. Soc.* **2004**, *126*, 6250.

(6) Crystallographic data. (*E*)-**4b**: $C_{18}H_{11}BCl_2N_2O_2$, monoclinic, $P2_1$, $a = 8.809(4)$, $b = 18.028(8)$, $c = 10.368(5)$ Å, $\beta = 96.8388(19)$°, $V = 1634.8(13)$ Å^3, $Z = 4$, MW = 369.00, $T = 120$ K, $R1(I > 2\sigma(I)) = 0.045$, $wR2$(all data) = 0.0939, GOF = 0.898. The unit cell contains two independent molecules of (*E*)-**4b**, which have a similar conformation around the boron atom.

(7) Data in parentheses are those for another independent molecule.

(8) Allmann, R. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; John Wiley & Sons: London, 1975; Chapter 2, p 43.

(9) The yields of photoisomerization of **4a** and **4c** were determined by the integral of the ^{1}H NMR spectra.

of phenylcatecholborane (δ_B 32.0). The downfield shift indicates the tricoordination state of (*Z*)-**4a** in the solution state. The coordination number of the boron atom in catecholborane **4a** is switched between 3 in the (*Z*)-isomer and 4 in the (*E*)-isomer by photoirradiation, because the azobenzene moiety isomerizes reversibly between the (*E*)- and (*Z*)-isomers. Catecholborane (*E*)-**4c** similarly isomerized to give (*Z*)-**4c** (δ_B 30.8) in 31% yield in C_6D_6, whereas (*E*)-**4b** did not isomerize under similar conditions.[9]

The change in coordination number induced by photoirradiation resulted in a change in the Lewis acidity of catecholborane **4a**. Reactions of the (*E*)- and (*Z*)-isomers of **4a** with pyridine were examined to estimate the Lewis acidity of these two isomers of **4a**. Catecholborane (*E*)-**4a** was treated with 1 equiv of pyridine in C_6D_6, and the chemical shift (δ_B 21.8) in the ^{11}B NMR spectrum showed no change from that in the absence of pyridine. Irradiation ($\lambda = 360$ nm) of a mixed solution of (*E*)-**4a** and pyridine (1 equiv) for 2 h caused a large upfield shift (δ_B 13.8) at ^{11}B NMR spectrum. This chemical shift is at higher field than those of (*E*)-**4a** and (*Z*)-**4a**. These results show that the equilibrium in eq 1 favors (*E*)-**4a** rather than its pyridine complex (*E*)-**4a**·py, in which pyridine coordinates to the boron atom instead of the nitrogen atom of the azobenzene moiety, as shown in Scheme 2. In contrast, the upfield shift after irradiation indicates that (*Z*)-**4a** generated by photoisomerization and pyridine form the complex (*Z*)-**4a**·py, and that the equilibrium in eq 2 lies to the right:

$$(E)\text{-}\mathbf{4a} + \text{py} \rightleftarrows (E)\text{-}\mathbf{4a}\cdot\text{py} \qquad (1)$$

$$(Z)\text{-}\mathbf{4a} + \text{py} \rightleftarrows (Z)\text{-}\mathbf{4a}\cdot\text{py} \qquad (2)$$

Changes of the ^{11}B NMR chemical shifts upon addition of 1−10 equiv of pyridine to a solution of (*E*)-**4a** are shown in Figure 2, in which ■ and ◇ denote the values with and without irradiation, respectively. The signal of (*E*)-**4a** was gradually shifted upfield with an increase in the ratio of pyridine to (*E*)-**4a** and reached δ_B 18.0, which is far from that (δ_B 11.7) in pyridine. By contrast, the signal of (*Z*)-**4a** formed under irradiation showed a large upfield shift by addition of 1 equiv of pyridine from δ_B 30.8 to 13.8, which is almost the same as that (δ_B 11.2) of (*Z*)-**4a** in pyridine.

The equilibrium constants of eqs 1 and 2, K_1 and K_2, were calculated by curve fitting to be $(1.45 \pm 0.08) \times 10$ and $(5.3 \pm 0.9) \times 10^3$ M^{-1}, respectively (Figure 2). These values show that irradiation of catecholborane **4a** changed its Lewis acidity by a factor of 300. Furthermore, irradiation ($\lambda = 431$ nm) of the mixture of (*Z*)-**4a** and 1 equiv of pyridine in C_6D_6 changed the ^{11}B chemical shift from δ_B 13.8 to 21.4, which is the same as that of the mixture of (*E*)-**4a** and pyridine, indicating the complete photoisomerization to (*E*)-**4a**. These results demonstrate that the complexation ability of a catecholborane with pyridine can be reversibly changed by photoirradiation.

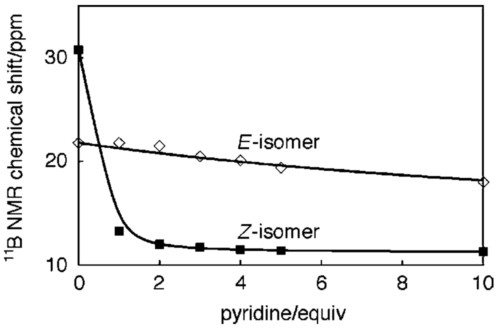

Figure 2. Changes of the ^{11}B NMR chemical shifts upon addition of pyridine to a solution of (*E*)- and (*Z*)-**4a**.

In summary, we have succeeded in photoswitching the coordination number of boron in a catecholborane and changing the Lewis acidity toward pyridine induced by irradiation. This concept of switching the Lewis acidity based on the photoinduced change in coordination number will enable photocontrol in the future of some reaction processes catalyzed by a Lewis acid.

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Supporting Information Available: Synthetic procedures and spectral data for (*E*)-**2**, (*E*)-**4a**−**c**, and (*Z*)-**4a** and the X-ray crystallographic data in CIF format for (*E*)-**4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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