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# Facile Dissociation of B—S Coordination Bonds in [2,6-Bis(ethylthiomethyl)phenyl]diethylborane by an $S_N2$-Type Mechanism

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ABSTRACT: *The title organoboron complex undergoes dissociation of the intramolecular B–S coordination bond much faster than the corresponding mono ethylthiomethyl complex as revealed by the dynamic NMR study. The facile dissociation is attributable to an $S_N2$-type mechanism, where the uncoordinated ligand assists the dissociation of the coordinated ligand in the transition state. This mechanism is supported by the* ab initio *calculations of a model reaction system.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:241–245, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20005

## INTRODUCTION

We have demonstrated that the dissociation of the B—N coordination bonds in [2,6-bis(dimethylaminomethyl)phenyl]borane **1** took place faster by a factor of ca. $10^5$ than that in the corresponding mono dimethylaminomethyl compound **2** (Fig. 1) [1]. The facile dissociation in **1** is explained by a contribution of the $S_N2$-type mechanism [2], in which the uncoordinated ligand assists the dissociation of the coordinated ligand through a trigonal-bipyramidal (TBP) transition state, on the basis of experimental and theoretical data (Scheme 1). This result aroused our interest in viewing the scope of this mechanism in the same series of organoboron compounds carrying two intramolecular ligands. Therefore, we studied the case of sulfide-sulfur ligands by using compounds **3** and **4** with two and one ethylthiomethyl group(s), respectively: the 2,6-bis(alkylthiomethyl)phenyl ligand system in the former compound has been used as a novel pincer-type S,C,S tridentate ligand mainly in the transition metal chemistry [3]. We report herein the kinetic data of the dissociation of the B–S coordination bonds in the intramolecular borane complexes. The strength of the coordination bond in **4** is compared with those in similar complexes **5** and **6** reported previously [4,5] to get further insight into the substituent effects on the Lewis acidity of boron atoms toward intramolecular sulfur ligands.

## RESULTS AND DISCUSSION

Compounds **3** and **4** were prepared by the reaction of the corresponding organolithium compounds with $B(OMe)Et_2$ in a similar manner as the preparation of **1** and **2** [1]. These compounds are stable toward water and air because of the stabilization by the intramolecular coordination. $^{11}B$ NMR signals were observed at ca. 16 ppm ($BF_3:OEt_2$ at 0 ppm) for both the compounds, this chemical shift indicating that the boron atoms are tetracoordinated with one sulfur ligand coordinating [6].

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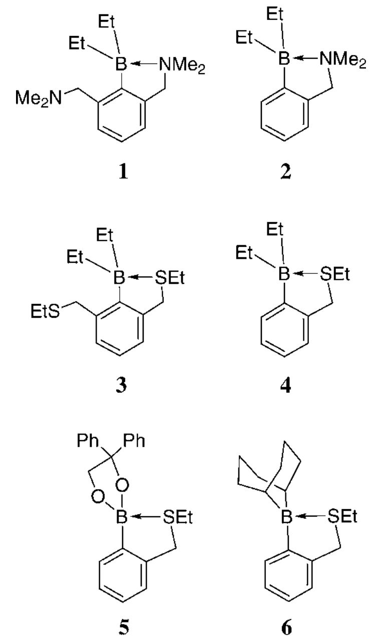


**FIGURE 1** Intramolecular borane complexes.

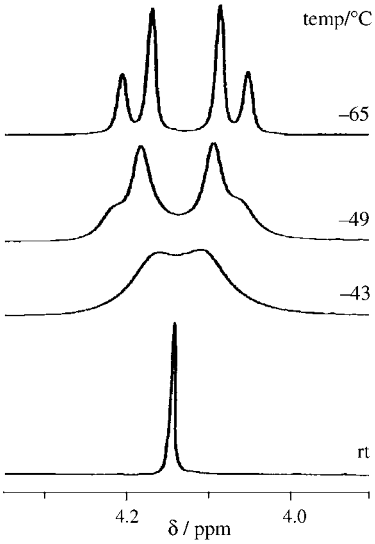
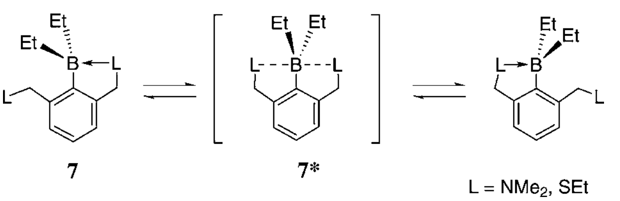


**FIGURE 2** VT $^1$H NMR signals due to the benzylic methylene protons in **4** in DMF-$d_7$.

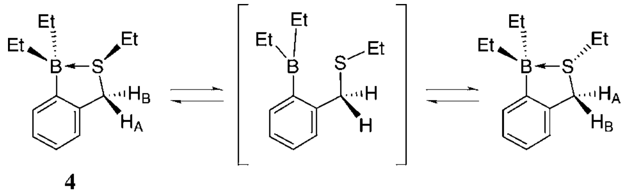
$^1$H NMR spectra of **3** and **4** were measured at various temperatures to observe the dynamic processes involving the dissociation of the B–S coordination bonds. **4** showed lineshape changes at the signal due to the benzylic methylene protons at low temperatures: a singlet observed at room temperature decoalesced at ca. −40°C, and finally became an AB quartet at −65°C (Fig. 2). This dynamic process is illustrated in Scheme 2. The benzylic methylene protons, which are diastereotopic in the coordinated form, exchange their magnetic sites, $H_A$ and $H_B$, with each other after the dissociation of the coordination bond followed by the recombination at another site. The total lineshape analysis gave the kinetic parameters for the dissociation of the B–S coordination bond (Table 1). The kinetic data were obtained in four organic solvents with various polarities. By contrast, no lineshape changes were observed in the $^1$H and $^{13}$C NMR signals for **3** during the temperature change from room temperature to −90°C: the two ethylthiomethyl groups were magnetically equivalent throughout the temperature change. This finding means that the exchange between the coordinated and uncoordinated ligands as shown in Scheme 1 takes place much faster than the NMR timescale even at −90°C. The barrier to dissociation is estimated to be less than 8 kcal/mol for **3**.

As shown in Table 1, the barrier to dissociation of the B–S bond in **3** is lower by at least 3 kcal/mol than that in **4**, this suggesting the switching of the dissociation mechanism by the introduction of an extra ligand to **4**. The facile dissociation in **3** is explained by the $S_N2$-type mechanism via a trigonal bipyramidal transition state (**7*** in Scheme 1, L = SEt), as proposed for the corresponding amine analog **1** previously [1].

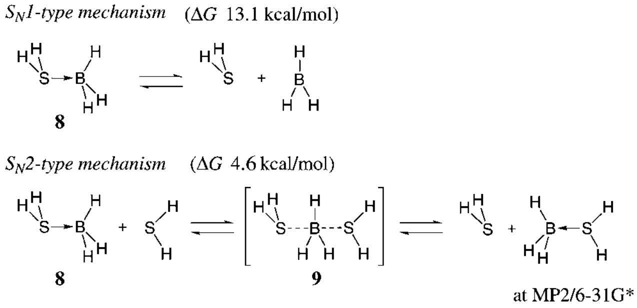
To verify the mechanism, the ab initio calculations were performed for the model reactions consisting of $BH_3$ and $SH_2$ molecules (Scheme 3). The structures were optimized at the MP2/6-31G* level: the structures and thermodynamic data of Lewis acid-base complexes are reproduced reasonably on applying the electron correlation. The calculated structures of the 1:1 complex (**8**) and 1:2



**SCHEME 1**



**SCHEME 2**



SCHEME 3

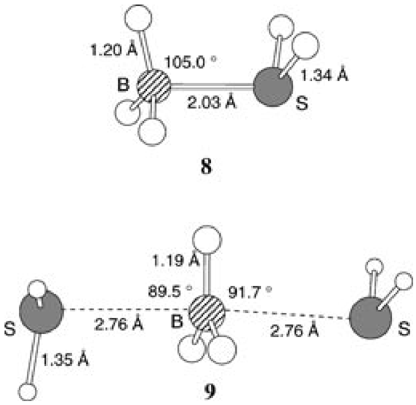


**FIGURE 3** Structures of **8** and **9** optimized at MP2/6-31G*.

complex (**9**) are shown in Fig. 3 together with selected structural parameters. Compound **9** was obtained as a transition state of the $S_N2$-type mechanism, in which the B· · ·S interatomic distances of 2.76 Å are larger than that in **8** (2.03 Å) [7]. The activation energies of the $S_N1$- and $S_N2$-type mechanisms are 13.1 and 4.7 kcal/mol, respectively, this large difference supporting the preference of the latter mechanism under ideal conditions. We consider that this conclusion can be extended to the observed dynamic behavior of **3** in solutions [11]. The energy gap between the two mechanisms (8.4 kcal/mol) is smaller than that for the corresponding $NH_3$ complexes (20.8 kcal/mol) calculated at the same level [1].

The kinetic data of **4** are discussed in more detail. The entropy of activation ($\Delta S^{\neq}$) is large and positive in any solvent. This is a typical feature for the dissociation of coordination bonds in this type of complexes, being attributed to the effective solvation toward the polar initial state relative to the less polar transition state. The solvent effect on the kinetic parameters is negligible even though the solvent polarity is changed from toluene-$d_8$ to DMF-$d_7$. The free energy of activation of **4** is comparable to that of the 9-BBN complex **6** (11.6 kcal/mol at 233 K) [5]. Therefore, the kinetic acidity of boron atoms is insensitive to the steric size of the attaching alkyl groups in the [2-(ethylthiomethyl)phenyl]borane system. The low barrier to dissociation in the boronate complex **5** (<8 kcal/mol) [4] is in accord with a general order of the strength of Lewis acidity of boron atoms, trialkylborane > dialkoxyalkylborane.

## *EXPERIMENTAL*

### *General*

$^1H$ and $^{13}C$ NMR spectra were measured on a Bruker AMX-R400 at 400.1 and 100.6 MHz, respectively. $^{11}B$ NMR spectra were measured on the same machine at 128.3 MHz with external reference of $BF_3$:$OEt_2$ at 0 ppm. Melting points are uncorrected. High-resolution mass spectra were measured on a JEOL JMS-700 MStation spectrometer. Elemental analyses were performed by a Perkin-Elmer 2400-type analyzer. Preparative HPLC was carried out with a HITACHI L-6250 pump using a Chemcosolb Si column (5 μ, 10 mmϕ × 300 mm).

### *[2,6-Bis(ethylthiomethyl)phenyl]diethylborane (3)*

A precursor of the organolithium compound, 1-bromo-2,6-bis(ethylthiomethyl)benzene, was prepared as follows. A solution of sodium ethylthiolate was prepared by the treatment of 5.0 ml

**TABLE 1** Kinetic Parameters for Dissociation of B—S Coordination Bond in **3** and **4**

| *Compound* | *Solvent (ε)*[a] | *$\Delta H^{\neq}$ (kcal/mol)* | *$\Delta S^{\neq}$ (cal/mol K)* | *$\Delta G^{\neq}_{233}$ (kcal/mol)* |
|---|---|---|---|---|
| **4** | Toluene-$d_8$ (2.38) | 14.8 ± 0.5 | 15.2 ± 2.3 | 11.3 |
| **4** | $CD_2Cl_2$ (8.93) | 15.8 ± 0.5 | 19.2 ± 2.1 | 11.3 |
| **4** | Acetone-$d_6$ (20.6) | 16.0 ± 0.6 | 20.0 ± 2.5 | 11.3 |
| **4** | DMF-$d_7$ (36.7) | 16.0 ± 0.5 | 20.0 ± 2.3 | 11.4 |
| **3** | | | | <8 |

[a]Dielectric constants of solvents.

(68 mmol) of ethanethiol with 3.4 g (85 mmol) of sodium hydroxide in 70 ml of methanol. To the solution was added 9.6 g (28 mmol) of 1-bromo-2,6-bis(bromomethyl)benzene [12] with small portions at room temperature. After the stirring for 2 h, the mixture was extracted with 100 ml of ether. The ethereal solution was washed with aqueous NaOH and then with aqueous NaCl, and the solution was dried over $MgSO_4$. The solvent was evaporated and the residue was recrystallized from hexane to give pure material as colorless crystals. 1-Bromo-2,6-bis(ethylthiomethyl)benzene, Yield 4.51 g (53%); mp 37–38°C; $^1H$ NMR ($CDCl_3$)$\delta = 1.27$ (t, $J = 7.4$ Hz, 6H), 2.52 (q, $J = 7.4$ Hz, 4H), 3.90 (s, 4H), 7.22–7.28 (m, 3H); MS (FAB) found 305.0067, calcd for $C_{12}H_{17}{}^{79}BrS_2$: 305.0033 [$MH^+$]; Anal Found: C, 47.29; H, 5.62%. Calcd for $C_{12}H_{17}BrS_2$: C, 47.21; H, 5.61%. A solution of 1.00 g (3.28 mmol) of the bromide in 10 ml of dry ether was cooled to −78°C under a nitrogen atmosphere. To the solution was slowly added 2.4 ml (3.9 mmol) of 15% butyllithium solution in hexane. The reaction mixture was allowed to warm up to −30°C, and this temperature was kept for 30 min. After the mixture was cooled to −78°C, 4.9 ml (4.9 mmol) of 1.0 mol/l solution of $B(OMe)Et_2$ in THF (Aldrich Chemical Co.) was added. The reaction mixture was allowed to stand at room temperature and stirred overnight. The volatile materials were removed by evaporation under a reduced pressure, and the residue was extracted with dichloromethane. The crude material was purified by HPLC with hexane–ethyl acetate 50:1 eluent to give the desired compound as colorless oil. Yield 402 mg (42%); $^1H$ NMR ($CDCl_3$)$\delta = 0.80$–$0.92$ (m, 10H), 1.29 (t, $J = 7.6$ Hz, 6H), 2.50 (q, $J = 7.6$ Hz, 4H), 3.84 (s, 2H), 7.06–7.15 (m, 3H); $^{13}C$ NMR ($CD_2Cl_2$)$\delta = 11.5$, 13.7, 14.3 (br), 26.9, 37.8, 125.9, 126.2, 140.5, 152.4 (br); $^{11}B$ NMR ($CDCl_3$)$\delta = 16.4$ (half band width, 109 Hz); MS (FAB) found 294.1728, calcd for $C_{16}H_{27}{}^{11}BS_2$: 294.1762 [$MH^+$]; Anal Found: C, 65.16; H, 9.40%. Calcd for $C_{16}H_{27}BS_2$: C, 65.29; H, 9.25%.

### *Diethyl[2-(ethylthiomethyl)phenyl]borane (**4**)*

A solution of 2.00 g (8.66 mmol) of 1-bromo-2-(ethylthiomethyl)benzene [13] in 30 ml of dry ether was cooled to −78°C under a nitrogen atmosphere. To the solution was slowly added 6.4 ml (10 mmol) of 15% butyllithium solution in hexane. The reaction mixture was allowed to warm up to room temperature, and stirred for 2 h. To the solution was added, 17.2 ml (17.2 mmol) of 1.0 mol/l solution of $B(OMe)Et_2$ in THF, and the whole was stirred overnight. The volatile materials were removed by evaporation under a reduced pressure, and the residue was extracted with dichloromethane. After the removal of the solvent, the oily residue was distilled with a glass-tube oven under a reduced pressure. A fraction at 140–141°C (0.7 mmHg) was collected. The analytical material was obtained by further purification by HPLC with hexane–ether 100:1 eluent. The pure material crystallized upon standing. Yield 662 mg (35%); mp 51–53°C; $^1H$ NMR ($CDCl_3$)$\delta = 0.72$–$0.77$ (m, 4H), 0.82–0.87 (m, 6H), 1.29 (t, $J = 7.4$ Hz, 3H), 2.41 (q, $J = 7.4$ Hz, 2H), 3.95 (s, 2H), 7.09–7.25 (m, 4H); $^{11}B$ NMR ($CDCl_3$)$\delta = 16.1$ (half band width, 103 Hz); MS (FAB) found 220.1594, calcd for $C_{13}H_{21}{}^{11}BS$: 220.1571 [$MH^+$]; Anal Found: C, 70.60; H, 9.72%. Calcd for $C_{13}H_{21}BS$: C, 70.91; H, 9.61%.

### *Dynamic NMR Measurement*

Samples for the variable temperature NMR were prepared by the dissolution of ca. 10 mg of a compound in 0.6 ml of a deuterated solvent. The temperatures of the sample were read from a thermocouple after the calibration with chemical shift differences of the methanol signals. The total lineshape analysis was carried out by the DNMR3K program [14]. The lineshapes of the signals due to the benzylic methylene protons were analyzed as a mutual exchange of AB system for **4**. Chemical shift differences and coupling constants of the AB signals were measured at several temperatures, where the exchange was negligibly slow. The chemical shift differences ($\Delta\nu$) were assumed to be correlated with the temperature linearly, and the coupling constants were constant at –16.4 Hz at any temperature. Spin-spin relaxation times ($T_2$) were estimated from the lineshapes at the slow exchange limit. The correlation of the chemical shift difference with the temperature [temp (°C)] and the $T_2$ values in each solvent are as follows. Toluene-$d_8$: $\Delta\nu = -0.12\,t + 227.4$ Hz, $T_2 = 0.10$ s. $CD_2Cl_2$: $\Delta\nu = 0.32\ t + 155.3$ Hz, $T_2 = 0.07$ s. Acetone-$d_6$: $\Delta\nu = 0.44\ t + 94.4$ Hz, $T_2 = 0.08$ s. DMF-$d_7$: $\Delta\nu = 0.34\ t + 72.1$ Hz, $T_2 = 0.08$ s. The rate constants are listed in Table 2. The rate constant of **3** was assumed to be $>1000\ s^{-1}$ at −90°C on the basis of the NMR lineshapes and timescale, the upper limit of the free energy of activation being 8 kcal/mol.

### *Ab Initio Calculation*

The ab initio calculations were carried out by the Gaussian98 program [15] with a DEC work-station. The structures were fully optimized with 6-31G* basis set at the MP2 level. The total energies were

**TABLE 2** Rate Constants of Dissociation of B—S Coordination Bonds in **4**

| *Solvent* | *k* (s$^{-1}$) [temp (°C)]$^{a}$ |
|---|---|
| Toluene-$d_8$ | 26 (–50.6), 46 (–47.6), 80 (–44.1), 120 (–41.1), 180 (–38.2), 260 (–35.2), 380 (–32.2), 560 (–29.3), 860 (–26.3) |
| $CD_2Cl_2$ | 16.0 (–52.5), 30 (–49.5), 48 (–46.6), 76 (–43.0), 130 (–40.2), 200 (–37.1), 320 (–34.1), 440 (–31.3), 660 (–28.3), 1240 (–23.5) |
| Acetone-$d_6$ | 10.0 (–54.6), 18.0 (–51.6), 30 (–48.7), 46 (–45.8), 74 (–42.2), 200 (–36.3), 300 (–33.4), 620 (–23.5) |
| DMF-$d_7$ | 6.0 (–57.5), 10.0 (–54.6), 18.0 (–51.6), 30 (–48.7), 48 (–45.8), 80 (–42.2), 120 (–39.2), 190 (–36.2) |

$^{a}$The values given in parenthesis represent temperature (°C).

−26.46424 ($BH_3$), −398.78841 ($H_2S$), −425.27350 (**8**), and −824.05450 (**9**) Hartree. The frequency analysis was carried out for the optimized structure of **9** to give one imaginary value in wavenumbers.

## ACKNOWLEDGMENT

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