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Intramolecular C=O···B Interactions in *o*-Boron Substituted Benzaldehyde, Acetophenone, and Benzophenone

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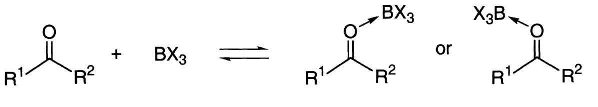
The title carbonyl compounds bearing a 4,4-diphenyl-1,3,2-dioxaborolan-2-yl group at the *ortho* position were prepared to compare the Lewis basicity of carbonyl-oxygen atoms. In the benzoyl and formyl compounds, the intramolecular C=O···B interactions are so weak that no significant changes were observed in the ^{13}C and ^{11}B NMR and IR spectra compared with the reference compounds. For the acetyl compound, the C=O stretching absorption was shifted to lower wavenumber by 18 cm^{-1} in the IR spectrum because of the coordination. The interaction energy could be estimated to be ca. 27 kJ mol^{-1} by the variable temperature ^{1}H NMR measurement. These substituent effects are discussed from the viewpoints of Lewis basicity and the conformational stability of the carbonyl moieties with the assistance of the DFT calculations.

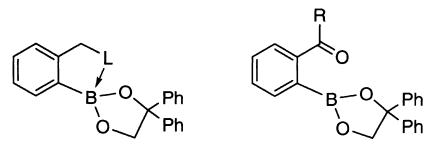
The complex formation of carbonyl compounds with Lewis acids plays an important role in activating carbonyl moieties in the organic synthesis.[1] Borane reagents are frequently used for the purposes:[2] structures, electronic properties, and complexation energies have been experimentally and theoretically studied for several kinds of borane complexes with carbonyl compounds to get insights into such Lewis acid catalyzed reactions (Scheme 1).[3–14]

We have been studying the coordination of boron atoms with various Lewis bases, amines, ethers, and thioethers, by using 2-(substituted methyl)phenylboranes **1** (Chart 1).[15–19] The intramolecular system allows us to disclose the nature of coordination by the X-ray analysis and the dynamic NMR method, even though the coordination is not so strong.[20] Similarly, phenylborane derivatives with a carbonyl substituent at the *ortho* position can be applied to the investigation of the intramolecular C=O···B interactions.[21] An important feature is that the coordination site, namely *E* or *Z* about the C=O bond, as well as pairs of interacting atoms, is always fixed in this structural system, contrary to the case for intermolecular complexes. As an example of this type of compound, we synthesized 2-phenyl-1,3,2-dioxaborolanes (**2**) with formyl, acetyl, or benzoyl group at the *ortho* position, which can form a 5-membered coordination. The intramolecular coordination and the related phenomena are presented in this paper on the basis of spectroscopic data and theoretical calculations.



R^1, R^2 = alkyl, H etc.

Scheme 1.



1

L = NMe_2, SEt, OEt

2

a R = H
b R = Me
c R = Ph

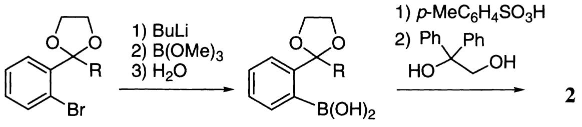
These notations are valid throughout this paper.

Chart 1.

Results and Discussion

Synthesis. Compounds **2** were prepared from 2-(2-bromophenyl)-1,3-dioxolane derivatives **3** according to the route shown in Scheme 2. The bromide **3** was converted to the corresponding dihydroxy(2-substituted phenyl)borane **4** in an ordinary manner via the organolithium compound.[22,23] Deprotection of the carbonyl group under an acidic condition and the subsequent esterification with 1,1-diphenyl-1,2-ethanediol gave the 1,3,2-dioxaborolane compounds **2** in good overall yields. **2a–c** are colorless oils and are stable under ordinary conditions.

Spectroscopic Measurements. Selected spectroscopic data of **2a–c** are listed in Table 1. ^{11}B NMR signals were observed at 32 ppm (ref. $BF_3{:}OEt_2$ at $\delta = 0$) as very broad bands for all the compounds. This chemical shift is typical for neutral tricoordinate boron atoms with one C and two O ligands, for example 2-phenyl-1,3,2-dioxaborolane at δ = 31.2.[26,27]



3

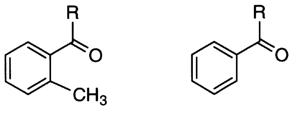
4

Scheme 2.

Table 1. Selected NMR and IR Data of Compounds **2** and the Reference Compounds **5**[a]

Compound	**2a**	**2b**	**2c**
^{11}B NMR δ[b]	32.8	31.6	32.3
^{13}C NMR $\delta_{C=O}$	194.3	200.5	198.3
5[c]	192.4	201.5	198.5
Δ	+1.9	−1.0	−0.2
IR $\nu_{C=O}$/cm^{-1}	1694	1668	1670
5[d]	1697	1686	1665
Δ	−3	−18	+5

a) NMR: in $CDCl_3$. IR: Neat. Δ: difference between **2** and **5**. b) External reference BF_3:OEt_2 at $\delta = 0$. *Cf.* 2-phenyl-1,3,2-dioxaborolane: $\delta = 31.2$. c) Ref. 24. d) Ref. 25.



5 **6**

Chart 2.

Table 2. Compilation of Various Data of Complexes of **6** with BF_3 and $B(C_6F_5)_3$[a]

	6a	**6b**	**6c**
BF_3 Complex			
$-\Delta H°$/kcal mol^{-1} [b]	17.9	17.8	15.0
^{13}C NMR $\delta_{C=O}$[c]	199.8	214.7	—
Free	191.8	197.9	
Δ	+8.0	+16.8	
IR $\nu_{C=O}$/cm^{-1} [d]	1632	1568	1552
Free	1703	1683	1658
Δ	−71	−116	−106
$B(C_6F_5)_3$ Complex[e]			
O···B distance/Å[f]	1.610	1.576	—
^{11}B NMR δ	5.0	2.3	—
^{13}C NMR $\delta_{C=O}$	199.4	212.8	—
Free	192.1	197.0	
Δ	+7.3	+15.8	
IR $\nu_{C=O}$/cm^{-1}	1620	1603	—
Free	1702	1686	
Δ	−82	−83	

a) Δ: difference between free and complexed compounds. b) Heat of complex formation in CH_2Cl_2. Ref. 3 and 4. c) Refs. 5 and 9. d) Refs. 28–30. e) Ref. 10. f) X-ray structure.

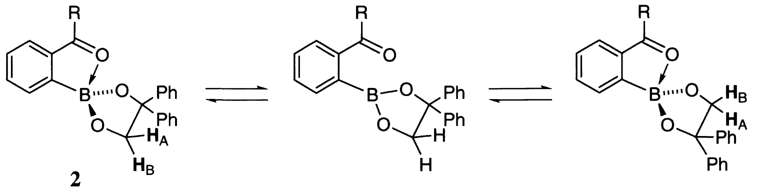
The signals are generally shifted toward upfield by the coordination, typical chemical shifts being δ 5–15 for tetracoordinate compounds.

The data of carbonyl moieties are compared with those of the boron-free compound: 2-methyl substituted compounds **5** rather than the parent compounds **6** are chosen as the reference compounds to allow us to consider the steric effect (Chart 2). ^{13}C NMR signals due to the carbonyl carbons in **2** and **5** are within ±2 ppm for each pair, and no deshielding effect due to the coordination was observed. This is in contrast to the intermolecular complex of **6** with BF_3, of which signals are shifted to downfield by more than 8 ppm (Table 2).[5,9] As for the IR spectra, a significant shift of C=O stretching band to lower wavenumber was observed only in **2b**. This indicates that the C=O bond in **2b** is weakened by the interaction with the boron atom, although the shift of 18 cm^{-1} was smaller than any shifts observed for strongly coordinated complexes.[28–30]

A marked feature of structure **2**, as well as **1**, is that the strength of intramolecular interaction is measurable by the dynamic NMR method as the lineshape change of the signals due to the methylene protons in the dioxaborolane ring. These nuclei are diastereotopic in the rigid coordinated form, and the site exchange results from the dissociation-recombination of the coordination bond after the facile rotation of the dioxaborolane ring (Scheme 3). This process was actually observed for **2b** by the VT NMR measurements (Fig. 1). While the signal due to the methylene protons appeared as a sharp singlet at room temperature and even at −76 °C, it almost decoalesced at −134 °C, the lowest attainable temperature. The rate of exchange is determined to be approximately 27 kJ mol^{-1}. The other compounds did not show significant broadening even at the low temperature.

Molecular Structure. Molecular structures of the carbonyl-borane compounds were calculated by the hybrid DFT method (B3LYP). We used this method because the electron correlation is often important in reproducing the experimental structures of coordination compounds.[6,7] The calculations were carried out for simplified model compounds **7** (Chart 3), which lack geminal phenyl groups in **2**.

The coordinated forms were obtained as energy minimum structures for **7a–c** at the B3LYP/6-31G* level of theory (Fig. 2).[31] The distance between the O and B atoms (2.4–2.6 Å) are within the sum of van der Waals radii of B (ca. 1.8 Å) and O (1.52 Å) atoms, but these are much longer than those observed in similar compounds, e.g. **8** (1.817 Å).[21] The O···B distance increases in the order of **7b** < **7c** < **7a**. In the optimized struc-



2

Scheme 3.

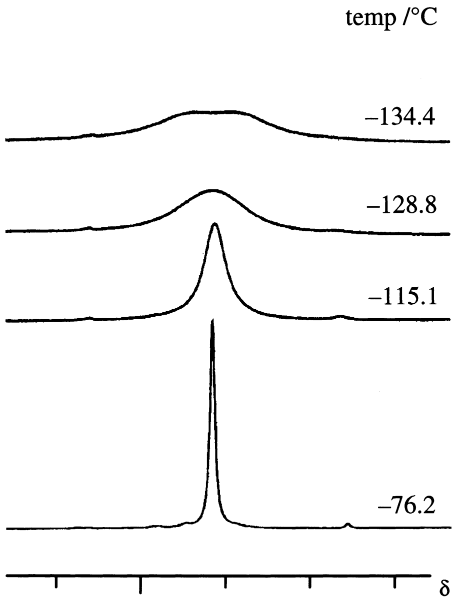
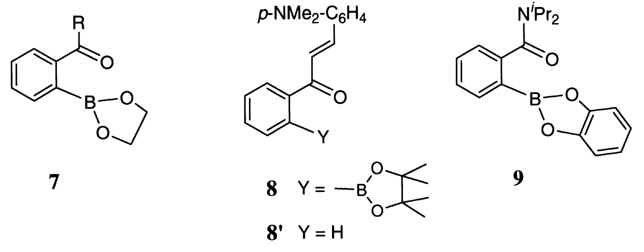


Fig. 1. VT ^{1}H NMR spectra of the signal due to the methylene protons in the 1,3,2-dioxaborolane group in **2b** in CD_2Cl_2/CS_2.



7

8 Y =

8' Y = H

9

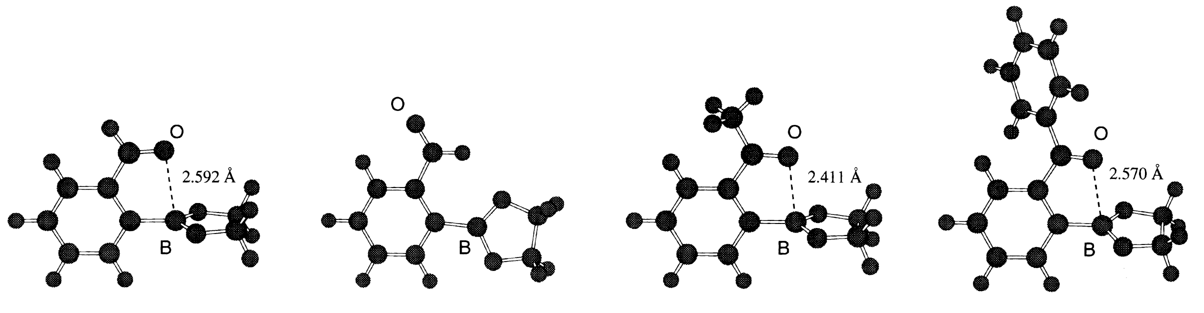
Chart 3.

ture, the carbonyl group and the boron atom are almost perfectly coplanar with the benzene ring. This means that one of the lone pairs on the carbonyl oxygen coordinates to the boron atom, which lies on the nodal plane of the C=O π electrons. The boron atom is only slightly deformed from planar to tetrahedral structure, as indicated by small values of the tetrahedral character[32] in Fig. 2.

Only **7a** gave another optimized structure, in which the carbonyl oxygen atom was also coplanar with the benzene ring but away from the boron atom. This structure (*E*)-**7a** is more stable by 2.1 kJ mol^{-1} than the coordinated form. The former is sterically favorable and this factor is superior to the attractive O···B interaction. Similar uncoordinated forms are unstable for **7b** and **7c** because the methyl or phenyl group should strongly interact with the boron moiety.

C=O···B Interactions. The affinity of carbonyl compounds toward Lewis acids has been investigated by several methods in connection with the nucleophilic addition to carbonyl carbons. Table 2 lists selected literature data that are useful for discussing the Lewis basicity of **6**. One of the convenient scales of the Lewis basicity is the heat of complex formation with Lewis acids. For the complexes of BF_3, the Lewis basicity increases in the order of **6c** < **6b** ≈ **6a** (Table 2), where both the steric and electronic effects influence the basicity.[3,4,33] In contrast, the effects of the complexation on the IR and ^{13}C NMR signals are larger in **6b** and **6c** than those in **6a**. When the Lewis acid is bulky $B(C_6F_5)_3$, an equilibrium experiment reveals that **6a** coordinates to the boron atom more tightly than **6b**, because the steric effect becomes important. However, the structural and spectroscopic data in Table 2 are not always correlated with the thermodynamic result: for example the O···B distance in **6b** is shorter than that in **6a**. The above findings mean that the basicity of these carbonyl compounds is influenced by various factors; this result prevents the establishment of a universal scale of Lewis basicity, especially for intermolecular complexes.

We here reconsider the results of compounds **2**. In the intramolecular system, the factors influencing the coordination are simpler than those in the intermolecular system: for example, the entropy contribution is much less important in the former. This advantage allows us to explore the intrinsic properties of Lewis acids and bases. The IR and VT NMR data unambiguously show the presence of C=O···B interaction in **2b**, and do not show such interaction in **2a** and **2c**. The difference between **2b** and **2c** can mainly be attributed to the electronic demand on the carbonyl-oxygen itself, because both the compounds prefer to take the coordinated forms as predicted by the DFT calculation. The weak interaction in **2a** relative to **2b** is partly due to the electronic effect (the inductive effect of H and Me), but the conformational effect also becomes significant: most of molecules take the uncoordinated form rather than the coordinated form. The observed spectra are averaged or over-



(*Z*)-**7a** [1.9%] (*E*)-**7a** [0.0 %] **7b** [3.8%] **7c** [1.9%]

Fig. 2. Optimized structures of **7** calculated at the B3LYP/6-31G* level. (Values in blakets indicate the tetrahedral character of the boron atoms.)

lapped signals due to the two species, and this makes it difficult to detect the coordination effect of the spectroscopic data if it is significant.

Although the C=O···B interaction in **2b** is the strongest, it is so weak that there are little changes in the chemical shifts of ^{13}C and ^{11}B NMR, which seem to be less sensitive to the coordination than IR. The weak interaction in **2b** (ca. 27 kJ mol^{-1}) is explained by the lowered Lewis acidity of dihydroxyborane derivatives compared with those of trihalo- or trialkylboranes. Relatively strong C=O···B interactions were observed in the intramolecular ethylene dioxyborane-carbonyl complexes **8** (^{11}B NMR $\delta = 25.5$, O···B 1.817 Å, $\Delta\nu_{C=O}$ -47 cm^{-1} from **8′**)[21] and **9** (^{11}B NMR $\delta = 13.5$, O···B 1.556 Å),[34] where the coordinated form was stabilized by the resonance effect. Therefore, the Lewis basicity of carbonyl oxygen atoms increases in the following order: acetyl < (*E*)-3-(4-dimethylaminophenyl)-2-propenoyl < *N*,*N*-dialkylcarbamoyl.

In conclusion, the spectroscopic measurements convince us of the presence of the intramolecular C=O···B interactions in **2b**. The observation of such a weak interaction, especially the determination of its energy, becomes possible by using the intramolecular structure. The fact that no experimental evidence of coordination was observed in **2a** and **2c** is elucidated by the electronic and conformational effects.

Experimental

^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX-400 spectrometer at 400 and 100 MHz, respectively. ^{11}B NMR spectra were measured on the same instrument at 128 MHz with $BF_3{:}OEt_2$ as external reference at $\delta = 0$. IR spectra were measured on a Nicolet Avatar 320 FT-IR spectrometer. High-resolution mass spectra were measured on a JEOL MStation-700 spectrometer by the FAB method. Melting points are uncorrected. Elemental analyses were performed by a Perkin-Elmer 2400 series analyzer. GPC was carried out on a Japan Analytical Industry Co. LC-908 recycling preparative HPLC system with 20 mm $\phi \times 600$ mm JAIGEL-1H, 2H columns eluted with chloroform.

2-(2-Formylphenyl)-4,4-diphenyl-1,3,2-dioxaborolane (2a). A solution of 2-(1,3-dioxolan-2-yl)phenyllithium in ca. 10 mL of ether was prepared from 1.00 g (4.37 mmol) of 2-(2-bromophenyl)-1,3-dioxolane[35] and 4.4 mmol of butyllithium by a known method.[22,23] To the solution was added 1.0 mL (8.8 mmol) of trimethyl borate at once at −78 °C. The reaction mixture was stirred for 1 h at the temperature, and then allowed to warm up to room temperature. After being kept for 12 h, the reaction mixture was treated with 5 mL of water for 10 min. The contents were extracted with ether several times (total ca. 100 mL), and then the combined organic solution was evaporated. The residue was treated with 20 mg (0.11 mmol) of *p*-toluenesulfonic acid monohydrate in 50 mL of acetone for 1 h at room temperature. About 500 mg of powdered sodium hydrogencarbonate was added to the solution, and the whole was stirred for 10 min. Insoluble materials were removed by filtration. The filtrate was concentrated by evaporation. The residue was heated in 50 mL of toluene with 935 mg (4.37 mmol) of 1,1-diphenyl-1,2-ethanediol[36] in a flask equipped with a Dean–Stark apparatus for 3 h. After the evaporation of the solvent, the crude material was purified by GPC. The desired compound was obtained as a colorless oil. The overall yield was 1.22 g (85%). HRMS (FAB, MH$^+$) Found: *m*/*z* 328.1270. Calcd for $C_{21}H_{17}O_3{}^{11}B$: MH 328.1275. ^{1}H NMR ($CDCl_3$) δ 4.99 (2H, s), 7.22–7.39 (7H, m), 7.44–7.48 (3H, m), 7.56–7.65 (2H, m), 7.99–8.02 (2H, m), 10.65 (1H, s). ^{13}C NMR ($CDCl_3$) δ 78.4, 87.6, 125.6, 127.7, 128.0, 128.3, 128.5, 131.8, 133.1, 135.9, 141.4, 144.4, 194.3. ^{11}B NMR ($CDCl_3$) δ 32.8 (line width $h_{1/2} = 584$ Hz). IR (neat) 1694.0 cm^{-1} (C=O). The synthesis was carried out without isolating the intermediate dihydroxyboranes, which existed in a mixture of several species such as boroxin.

2-(2-Acetylphenyl)-4,4-diphenyl-1,3,2-dioxaborolane (2b). This compound was similarly prepared from 2-(2-bromophenyl)-2-methyl-1,3-dioxolane.[35] Colorless oil. Yield 90%. HRMS (FAB, MH$^+$) Found: *m*/*z* 342.1446. Calcd for $C_{22}H_{19}O_3{}^{11}B$: MH 342.1431. ^{1}H NMR ($CDCl_3$) δ 2.63 (3H, s), 4.96 (2H, s), 7.24–7.30 (2H, m), 7.35–7.39 (4H, m), 7.44–7.56 (7H, m), 7.86 (1H, d, $J = 7.7$ Hz). ^{13}C NMR ($CDCl_3$) δ 24.8, 78.5, 87.0, 126.2, 127.4, 128.2, 128.3, 129.0, 132.1, 132.9, 130.8, 145.0, 200.5. ^{11}B NMR ($CDCl_3$) δ 31.6 (line width $h_{1/2} = 610$ Hz). IR (neat) 1668.0 cm^{-1} (C=O).

2-(2-Benzoylphenyl)-4,4-diphenyl-1,3,2-dioxaborolane (2c). This compound was similarly prepared from 2-(2-bromophenyl)-2-phenyl-1,3-dioxolane.[37] Colorless oil. Yield 76%. HRMS (FAB, MH$^+$) Found: *m*/*z* 405.1693. Calcd for $C_{27}H_{21}O_3{}^{11}B$: MH 405.1667. ^{1}H NMR ($CDCl_3$) δ 4.77 (2H, s), 7.20–7.31 (10H, m), 7.40–7.45 (2H, m), 7.51–7.58 (4H, m), 7.83–7.88 (3H, m). ^{13}C NMR ($CDCl_3$) δ 78.4, 87.3, 125.6, 127.3, 128.3, 128.4, 130.0, 130.1, 130.3, 132.7, 134.4, 137.4, 144.3, 144.7, 198.3. ^{11}B NMR ($CDCl_3$) δ 32.3 (line width $h_{1/2} = 837$ Hz). IR (neat) 1670.0 cm^{-1} (C=O).

VT NMR Measurement. ^{1}H NMR spectra at low temperatures were measured for a dichloromethane-d_2/CS_2 (ca. 5 : 1) solution. The temperatures of the sample were read from a thermocouple equipped with the instrument after the calibration with chemical shift differences of the methanol signals. For **2b**, the signals due to the ring methylene protons and some aromatic protons became broad at low temperature: the former nearly decoalesced at −134 °C. Assuming that the chemical shift difference and coupling constant between the diastereotopic methylene protons were 100 Hz and 12 Hz, respectively, one could estimate the rate of site exchange to be 230 s^{-1} at the temperature, corresponding to the free energy of activation of ca. 27 kJ mol^{-1}.[38] No significant lineshape changes were observed for **2a** and **2c** at −130 °C; this suggests that the barriers should be lower than 25 kJ mol^{-1}.

DFT Calculation. The calculations were performed by the Gaussian 98 program[39] on a Tempest-3 workstation. The structures of **7** were optimized at the B3LYP/6-31G* level. The vibration analyses were carried out for each optimized structure to check whether it was an energy minimum or not.

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