

Structural Effect on the Stability of Acetophenone–B(OMe)₂ Complexes in the Gas Phase. The Nature of the Bond between the Boron Cation and Neutral Molecules

Shuhei Itoh,[†] Md. Mizanur Rahman Badal,[†] and Masaaki Mishima^{*,†,‡}

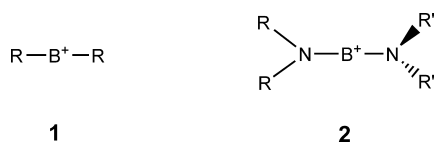
Department of Chemistry and Physics of Condensed Matter, Graduate School of Sciences, and Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan

Received: May 5, 2009; Revised Manuscript Received: July 22, 2009

The free energy changes (ΔG , boron cation basicity; BCB) for the reaction $[(\text{MeO})_2\text{B}]\text{L}^+ = (\text{MeO})_2\text{B}^+ + \text{L}$ (L = acetophenones) were determined in the gas phase by measuring ligand exchange equilibria using an FT-ICR mass spectrometer. On the basis of the correlation analysis by the Yukawa–Tsuno equation, $\Delta G = \rho(\sigma^\circ + r^+\Delta\sigma_{\text{R}}^+)$, the substituent effect on ΔBCB of acetophenone was characterized by a ρ value (in $\text{kJ mol}^{-1} \sigma^{-1}$ unit) of -43.2 and an r^+ value of 0.89 . Both the ρ and r^+ values were found to be similar to the corresponding values for protonation, indicating that the bond between $(\text{MeO})_2\text{B}^+$ and the oxygen atom of the carbonyl group has a high covalent character similar to the $\text{H}^+ - \text{O}=\text{C}$ bond. This conclusion was consistent with the geometrical features and the charge distribution calculated at DFT-B3LYP/6-311+G(d,p) level of theory. A comparison with the results for a series of Lewis cation basicity of the acetophenone system showed that the r^+ value decreases in the order of $\text{H}^+ = (\text{MeO})_2\text{B}^+ > \text{Me}_3\text{Si}^+ > \text{Me}_3\text{Ge}^+ > \text{Cu}^+ > \text{Li}^+$. This decreasing order is related to increasing ionic (ion–dipole interaction) nature of the bonding interaction between Lewis cations and the carbonyl oxygen atom. This was also supported by the theoretical calculations.

Introduction

Disubstituted boron cations **1** are of particular interest as possible intermediates in the reactions of substituted boranes in solution.^{1–7} In the condensed phase, studies of boron cations have been limited to species with strongly π -back bonding and bulky substituents that provide electronic stabilization through π -interaction and steric inhibition of nucleophilic attack at the boron cation center **2**.^{8–10} Contrary to solution phase studies, in the gas phase it is relatively easy to generate and to examine the highly reactive ionic species which are unknown in solution. Hence, the reactivity of disubstituted boron cations has been studied by means of mass spectrometry.^{11–21}



Simple disubstituted boron cations have been found to be highly reactive toward oxygen-containing organic molecules. For example, $\text{CH}_3\text{BCH}_3^+$ and $\text{CH}_3\text{OBOCH}_3^+$ rapidly abstract water from alcohols and ethers and also attack carbonyl compounds to result in C=O and C–C bond cleavages.^{19,20} Besides these results, the reactions of $\text{CH}_3\text{OBOCH}_3^+$ with ketones such as acetone and ethylmethyl ketone were found to form exclusively the corresponding adduct ions, $(\text{MeO})_2\text{B}:\text{O}=\text{C}(\text{Me})_2^+$ and $(\text{MeO})_2\text{B}:\text{O}=\text{C}(\text{Me})\text{Et}^+$, instead of their C=O and C–C bond cleavage reactions.²¹ This result allows us to study the nature of the binding interaction between disubstituted boron cations and neutral ligands. Recently, we have investigated the gas-phase basicity of organic molecules toward metal ions such as Me_3Si^+ ,²² Me_3Ge^+ ,²³ Li^+ ,²⁴ and Cu^+ .^{25,26} The structural effects on these cation basicities were found to change significantly

with a Lewis cation, and these results were interpreted in relation to the nature of the binding interaction between a Lewis cation and a neutral ligand. In particular, the analysis of the substituent effect on the acetophenone system in which the binding site can be kept constant without the change in the steric environment has been proved to give valuable information on the nature of the metal ion–ligand bond. In this paper, we report the substituent effect on the bond strength of $(\text{MeO})_2\text{B}^+$ with acetophenone.

Results

Measurements of Gas-Phase $(\text{MeO})_2\text{B}$ Cation Basicity.

Gas-phase boron cation basicities (BCB) were determined by measuring the equilibrium constants of the reversible ligand-transfer reactions on an FT-ICR spectrometer. When two acetophenone derivatives L^1 and L^2 were present in the ICR cell, $\text{L}^1\text{B}(\text{OMe})_2^+$ and $\text{L}^2\text{B}(\text{OMe})_2^+$ formed as initial reaction products (eqs 2 and 3), being consistent with the literature data.²¹ These reactions were followed by ligand-exchange reaction (eq 4). The free energy change (ΔG_4) for the equilibrium is given by eq 5.



$$K = \frac{[\text{L}^2\text{B}(\text{OMe})_2^+][\text{L}^1]}{[\text{L}^1\text{B}(\text{OMe})_2^+][\text{L}^2]} \quad \Delta G_4 = -RT \ln K \quad (5)$$

Figure 1 shows a typical time profile for the ligand exchange reaction. From the free energy changes, ΔG_4 , for the respective ligand-exchange equilibria indicated by arrows, a ladder of the BCB was constructed as shown in Table 1.

* Corresponding author. E-mail: mishima@ms.ifoc.kyushu-u.ac.jp. Fax: +81-92-642-2715.

[†] Graduate School of Sciences.

[‡] Institute for Materials Chemistry and Engineering.

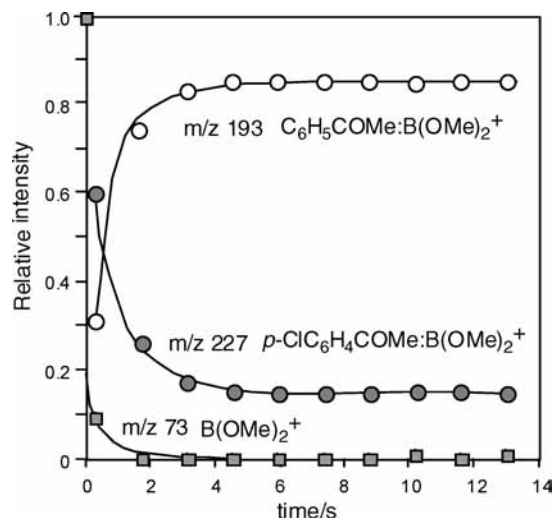


Figure 1. Time profile of $(\text{MeO})_2\text{B}^+$ complexes formed from a binary mixture of *p*-chloroacetophenone (3.7×10^{-7} Torr) and acetophenone (0.96×10^{-7} Torr). Closed squares, m/z 73 $\text{B}(\text{OMe})_2^+$; open circles, m/z 193 $\text{C}_6\text{H}_5\text{C}(\text{Me})\text{OB}(\text{OMe})_2^+$; closed circles, m/z 227 $p\text{-ClC}_6\text{H}_4\text{C}(\text{Me})\text{OB}(\text{OMe})_2^+$.

Theoretical Calculations. Since the present experimental method can determine only relative BCB values between two compounds, it is needed to convert these relative values to

absolute scales for a comparison with gas-phase basicities toward a proton and other Lewis cations. The $(\text{MeO})_2\text{B}^+$ cation affinity (BCA) of $165.2 \text{ kJ mol}^{-1}$ was estimated for methanol based on a thermochemical cycle using heats of formation for $(\text{MeO})_2\text{B}^+$ and $\text{MeO}(\text{H})\text{B}(\text{OMe})_2^+$ which were determined by means of collision-induced dissociation threshold measurements in combination with proton affinity bracketing.¹⁷ However, a direct measurement of $(\text{MeO})_2\text{B}^+$ transfer equilibrium between methanol and acetophenone is not possible because of no formation of an adduct ion of $\text{MeOHB}(\text{OMe})_2^+$ under the present ICR experimental conditions. Hence, the theoretical calculation would be a practical method to convert the relative BCB values to absolute scales. At first, the BCB value has been calculated for methanol to examine reliability of the calculated value. The calculations at B3LYP/6-311+G(d,p), mPW1K/6-311+G(d,p), and MP2/6-311+G(d,p) using the optimized structure at the respective levels of theory provided BCA of 180.6, 208.8, and 204.5 kJ mol^{-1} for methanol, respectively. Since the B3LYP/6-311+G(d,p) seems to be somewhat better fit for the estimated value of $165.2 \text{ kJ mol}^{-1}$ from a thermochemical cycle, the BCB of $180.7 \text{ kJ mol}^{-1}$ for acetophenone calculated at this level of theory was used as an anchor to convert the relative experimental values to absolute scales.²² These converted values are given in Table 1. The BCB value of $180.7 \text{ kJ mol}^{-1}$ for acetophenone was found to be similar to the corresponding values for Li^+ and Cu^+ rather than the GB value

TABLE 1: Measured Free-Energy Changes for Ligand-Exchange Equilibria and $(\text{MeO})_2\text{B}^+$ Cation Basicities [BCB] in kJ mol^{-1}

Subst. in acetophenone	Measured ΔG°_4	BCB	ΔBCB	GB ^a	ΔGB
<i>p</i> -OMe		212.2	31.5	863.2	33.9
<i>p</i> -SMe	5.2	207.6	26.9	856.5	27.2
<i>p</i> -OH	9.5	204.0	23.3	851.9	22.6
3',4'-Me ₂	1.5	202.5	21.8	850.6	21.3
3'-Cl-4'-OMe	1.3	201.1	20.4	851.9	22.6
<i>p</i> - <i>t</i> -Bu	1.1	200.5	19.8	850.2	20.9
3'-Cl-4'-SMe	6.7	197.2	16.5	848.1	18.8
<i>p</i> -Me	3.8	193.6	12.9	846.0	16.7
3',5'-Me ₂	0.6	193.1	12.4	845.6	16.3
<i>m</i> -OMe	5.0	188.1	7.4	840.6	11.3
<i>m</i> -Me	2.4	185.6	4.9	836.4	7.1
H	4.8	180.7^b	0.0	829.3	0.0
<i>p</i> -F	6.2	174.5	-6.2	826.8	-2.5
<i>p</i> -Cl	1.3	173.4	-7.3	826.8	-2.5
<i>m</i> -Cl	7.5	166.7	-14.0	815.5	-13.8
<i>m</i> -F	0.6	166.1	-14.6	813.8	-15.5
<i>m</i> -CF ₃	7.1	158.6	-22.1	807.1	-22.2
<i>p</i> -CF ₃	9.9	156.1	-24.6	805.0	-24.3

^a Ref 27. ^b Calculated value at B3LYP/6-311+G(d,p)/B3LYP/6-311+G(d,p), used as an anchor to convert relative values to absolute scales.

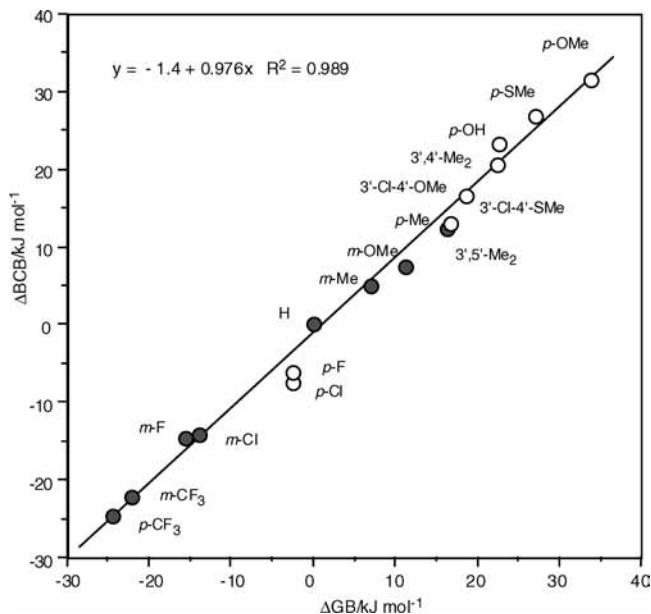


Figure 2. Correlation of ΔBCB with ΔGB for substituted acetophenones.

of $829.3 \text{ kJ mol}^{-1}$, indicating that $(\text{MeO})_2\text{B}^+$ binds with the oxygen of the carbonyl group with an energy similar to other Lewis cations. Although the accuracy of the absolute scales is insufficient, there is a good linear relationship between experimental relative basicity (ΔBCB) values and the calculated ones with a slope of unity.

$$\Delta\text{BCB}_{\text{calc}} = 1.08\Delta\text{BCB}_{\text{exp}} \quad (R^2 = 0.987) \quad (6)$$

Hence, the calculation at the present level of theory will be used for discussions about the substituent effect on BCB and optimized structures of the complex ions. The calculated BCBs, selected bond distances, and the group natural charges of the complexes derived using the natural population analysis (NPA) scheme are summarized in Tables S1, S2, S4, and S5 in the Supporting Information.

Discussion

Correlation of ΔBCB with ΔGB . Figure 2 shows a plot of ΔBCB s of substituted acetophenones against the corresponding ΔGB s. There is a good linear relationship with a slope of 0.98, indicating that the polar effect of the substituent contributes to the stability of the $(\text{MeO})_2\text{B}^+$ complex in a manner similar to the protonated species.

To analyze more quantitatively the substituent effect, the Yukawa–Tsuno (Y–T) equation (eq 7)²⁹ is useful.^{23–26} Indeed, it has been applied successfully not only to GB²⁸ but also to Me_3Si^+ ,²³ Me_3Ge^+ ,²⁴ Li^+ ,²⁵ and Cu^+ ²⁶ basicities of acetophenones in the gas phase, and the correlation results obtained for these Lewis cations have helped our understanding of the nature of the bond between Lewis acids and neutral ligands.

$$\Delta G = \rho(\sigma^\circ + r^+\Delta\bar{\sigma}_R^+) \quad (7)$$

where σ° and $\Delta\bar{\sigma}_R^+$ are the normal substituent constant and the resonance substituent constant, respectively, and r^+ is the resonance demand parameter representing a degree of the π -delocalization of the positive charge into the aryl π -system. Application of the Y–T equation (eq 7) to ΔBCB provides a ρ value of -43.2 (in $\text{kJ mol}^{-1} \bar{\sigma}^{-1}$ unit) and an r^+ value of 0.89

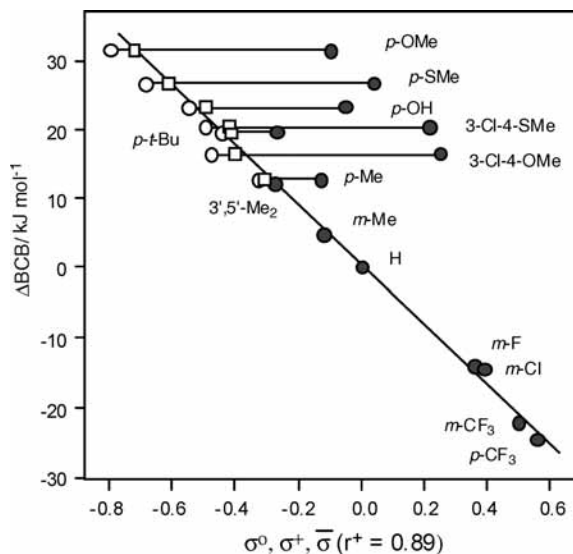


Figure 3. Y–T analysis of ΔBCB of acetophenone. Closed circles, σ° ; open circles, σ^+ ; open squares, $\bar{\sigma}$ ($r^+ = 0.89$).

TABLE 2: Correlation Results of Y–T Analysis for Lewis Cation Basicities of Acetophenones

Lewis cation	$-\rho^a$	r^+	gas-phase basicity ^b
H^+ ^c	46.6	0.87	829.3 (838.8)
$(\text{MeO})_2\text{B}^+$	43.2	0.89	(180.7)
Me_3Si^+ ^d	46.0	0.75	158.2 (159.9)
Me_3Ge^+ ^e	40.6	0.71	(122.0)
Cu^+ ^f	37.5	0.60	205.6 (216.5)
Li^+ ^g	34.7	0.49	(185.0)

^a In $\text{kJ mol}^{-1} \bar{\sigma}^{-1}$ unit. ^b Lewis cation basicity of unsubstituted acetophenone in kJ mol^{-1} . The values in parentheses are calculated at B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p). ^c Refs 27, 31. ^d Ref 23. ^e Ref 24. ^f Ref 25. ^g Ref 26.

with satisfactory precision ($R^2 = 0.998$) as shown in Figure 3.³⁰ The results of the Y–T analysis for a series of Lewis cation basicities of acetophenones (H^+ , Me_3Si^+ , Me_3Ge^+ , Cu^+ , and Li^+) are summarized in Table 2.

Both ρ and r^+ values for ΔBCB were found to be similar to the corresponding values for protonation as expected from a good linear relationship in Figure 2, indicating similarities in the nature of the bond between $\text{C}=\text{O}-\text{B}^+$ and $\text{C}=\text{O}-\text{H}^+$. The optimized geometries of the $(\text{MeO})_2\text{B}^+$ –acetophenone complex, the protonated acetophenone, and the neutral are shown in Figure 4 along with the selected bond distances. The C7O9 distance lengthens by 0.073 \AA upon the binding with $(\text{MeO})_2\text{B}^+$, and contrary to this, the C1C7 shortens by 0.067 \AA . The C2C3 and C5C6 shorten, and the C1C2 and C1C6 lengthen. Similar changes in bond distance upon protonation are observed. These changes in bond distance are consistent with the concept of the π -delocalization of a positive charge developed at C7 by binding with $(\text{MeO})_2\text{B}^+$ or H^+ into the phenyl group. Indeed, the group natural charge of the phenyl moiety of 0.281 was obtained for the $(\text{MeO})_2\text{B}^+$ –acetophenone complex based on the natural population analysis at B3LYP/6-311+G(d,p), indicating the existence of a large charge transfer from boron cation to an acetophenone molecule though its magnitude is somewhat smaller than $\Sigma q_{[\text{Ph}]}$ of 0.327 for protonation.

All these results lead to a conclusion that the bond of $(\text{MeO})_2\text{B}^+$ with the oxygen atom of the carbonyl group has a high covalent character similar to the $\text{C}=\text{O}-\text{H}^+$ bond. This

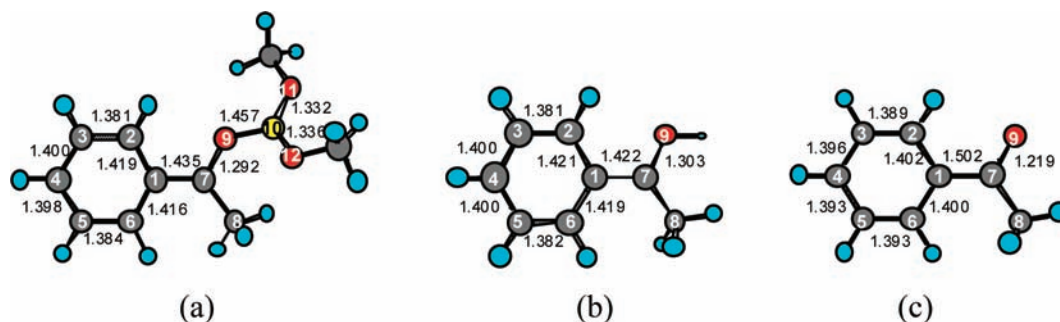


Figure 4. Optimized geometries of acetophenone complexes, (a) $(\text{MeO})_2\text{B}^+$ and (b) H^+ , and neutral acetophenone (c) at B3LYP/6-311+G(d,p). Values given are bond distances in Å.

is further supported by the similarities of substituent effects on the geometrical features and the charges between the $(\text{MeO})_2\text{B}^+$ complex and the protonated one. For example, when the substituent changes from *p*- CF_3 to *p*- NMe_2 , the C1C7 distance shortens by 0.040 Å for the $(\text{MeO})_2\text{B}^+$ complex and 0.035 Å for the protonated species, respectively, and C7O9 lengthens by 0.032 Å for the former and 0.028 Å for the latter. These substituent effects on the bond distance are identical for both complexes.

$$R_{\text{C1C7}}(\text{B}^+) = 1.10R_{\text{C1C7}}(\text{H}^+) - 0.13 \quad (R^2 = 0.995) \quad (8)$$

$$R_{\text{C7O9}}(\text{B}^+) = 1.07R_{\text{C7O9}}(\text{H}^+) - 0.10 \quad (R^2 = 0.995) \quad (9)$$

It is also found that the group natural charge of the phenyl moiety increases with the change of the substituent from *p*- CF_3 to *p*- NMe_2 in the same manner for both systems.

$$\Sigma q_{[\text{Ph}]}(\text{B}^+) = 1.01\Sigma q_{[\text{Ph}]}(\text{H}^+) - 0.05 \quad (R^2 = 0.997) \quad (10)$$

A comparison of the ρ values for a series of Lewis cation basicities in the acetophenone system shows that a ρ value decreases in the order of $\text{H}^+ \geq \text{Me}_3\text{Si}^+ > (\text{MeO})_2\text{B}^+ > \text{Me}_3\text{Ge}^+ > \text{Cu}^+ > \text{Li}^+$. A ρ value is generally considered a measure of the magnitude of the charge developed at the benzylic carbon and/or of distance between the charge center and the substituent. Accordingly, the decrease of the ρ value suggests that the charge at the benzylic carbon decreases along this series, i.e., more positive charge is localized at the Lewis cation moiety of the adduct ions compared with that for protonation because an adduct complex bears unity charge in the species. This order seems to be qualitatively consistent with the decreasing covalent character of the $\text{C}=\text{O}-\text{M}^+$ bond. Contrary to a ρ value, the r^+ value may represent more directly the degree of π -delocalization of the charge into the aromatic π -system.²⁹ The r^+ value varies with the Lewis cation in a similar manner to the ρ value, and the r^+ value of 0.89 for the $\text{B}(\text{OMe})_2^+$ is practically identical to that for protonation. The large r^+ value for the ΔBCB reveals clearly the existence of a large π -delocalization of the positive charge into the aryl group, being consistent with a large group natural charge of the phenyl moiety mentioned above.

The selected bond distances and the natural group charges for a series of Lewis cation–acetophenone complexes are given in Table S5 (Supporting Information). The natural charge of the phenyl moiety ($\Sigma q_{[\text{Ph}]}$) decreases in the order of $\text{H}^+ > (\text{MeO})_2\text{B}^+ > \text{Me}_3\text{Si}^+ > \text{Me}_3\text{Ge}^+ > \text{Cu}^+ > \text{Li}^+$, and

that of the Lewis cation moiety ($\Sigma q_{[\text{M}^+]}$) increases in this order. That is, both natural charges change inversely with the change of a Lewis cation, $\Sigma q_{[\text{M}^+]} = 1.383 - 2.74\Sigma q_{[\text{Ph}]}$ ($R^2 = 0.927$). In addition, the C1C7 and C7O9 bond distances also change inversely, and both distances are linearly correlated with the $\Sigma q_{[\text{Ph}]}$ (Figure S1, Supporting Information), $R_{\text{C1C7}} = 1.499 - 0.23\Sigma q_{[\text{Ph}]}$ ($R^2 = 0.994$), and $R_{\text{C7O9}} = 1.201 + 0.31\Sigma q_{[\text{Ph}]}$ ($R^2 = 0.989$). These changes in bond distance and in the group charges with the variation of the Lewis acid are consistent with the change of the π -delocalization of the positive charge described by an r^+ value. Indeed, it is found that the change in r^+ value is roughly related to these changes in the bond distance and the group natural charge (eqs 11 and 12). In conclusion, a covalent bond character of the $\text{C}=\text{O}-\text{M}^+$ bond decreases, and an ionic character increases in this order when a Lewis cation changes.

$$R_{\text{C1C7}} = -0.0866r^+ + 1.507 \quad (R^2 = 0.830) \quad (11)$$

$$\Sigma q_{[\text{Ph}]} = 0.384r^+ - 0.043 \quad (R^2 = 0.877) \quad (12)$$

Finally, it should be noted that the ρ value for $(\text{MeO})_2\text{B}^+$ is similar to that for protonation despite a significantly small binding energy. With respect to this, we found previously the constant ρ values of -50 for the GBs of a series of benzoyl compounds, ArCOR , of which the GB varies significantly with *R*, e.g., an increase in GB by 134.3 kJ mol^{-1} from α,α,α -trifluoroacetophenone to *N,N*-dimethylbenzamide.²⁶ Thus, the ρ value is less sensitive to the change in thermodynamic stability of the adduct ion as far as a covalent bond is formed with an extensive charge transfer.

Conclusion

The free energy changes (ΔG , boron cation basicity; BCB) for the reaction $[(\text{MeO})_2\text{B}]^+\text{L} = (\text{MeO})_2\text{B}^+ + \text{L}$ ($\text{L} = \text{acetophenones}$) were determined in the gas phase by measuring ligand exchange equilibria using an FT-ICR mass spectrometer. The substituent effect on ΔBCB of acetophenone which was determined in the gas phase by measuring ligand exchange equilibria using an FT-ICR mass spectrometer was characterized by a ρ value (in $\text{kJ mol}^{-1} \bar{\sigma}^{-1}$ unit) of -43.2 and an r^+ value of 0.89 based on the correlation analysis by the Yukawa–Tsunoo equation. Both the ρ and r^+ values were found to be similar to the corresponding values for protonation, indicating that the bond between $(\text{MeO})_2\text{B}^+$ and the oxygen atom of the carbonyl group has a high covalent character similar to the $\text{H}^+-\text{O}=\text{C}$ bond. This conclusion was consistent with the geometrical

features and the charge distribution calculated at the DFT-B3LYP/6-311+G(d,p) level of theory. A comparison with the results for a series of Lewis cation basicity of the acetophenone system showed that the r^+ value decreases in the order of $H^+ = (MeO)_2B^+ > Me_3Si^+ > Me_3Ge^+ > Cu^+ > Li^+$. This indicates that a covalent bond character of the C=O–M⁺ bond decreases and an ionic character increases in this order when a Lewis cation changes.

Experimental Section

ICR Measurements. Ligand-exchange equilibrium measurements in the gas phase were performed on an Extrel FTMS 2001 spectrometer. Most of the experimental techniques used for these measurements are the same as the procedures reported previously.^{23,26} Only significant changes and/or additional procedures are given here. All measurements were performed in the temperature range of 50–70 °C at a constant magnetic field strength of 3.0 T. The pressures of the neutral reactants were measured by means of a Bayard–Alpert type ionization gauge with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of various compounds.³² The overall pressures of the neutrals were maintained at 3 to 10×10^{-7} Torr (1 Torr = 133.3 Pa) by controlled rates through leak valves (Anelva) from a parallel inlet manifold into the reaction cell in the vacuum chamber. (MeO)₂B⁺ was generated by electron ionization of (MeO)₃B. The desired reactant ions were isolated by ejecting all the unwanted ions from the ICR cell. The isolated ions were allowed to react with a neutral reagent for a variable period of time. After an appropriate reaction period of 6–20 s, depending upon the reactant and pressures, equilibrium was attained, and the relative abundances of (MeO)₂BL⁺ were measured based on the signal intensities in the ICR spectra. Each experiment was performed at several ratios of partial pressures and at different overall pressures. The arithmetic-mean values of equilibrium constants were used to calculate ΔG at 343 K with an average uncertainty of ± 1 kJ mol⁻¹ in most of these cases. The reversibility of the ligand-transfer reaction was confirmed by an ion-eject experiment.

Substituted acetophenones used in this study were available from commercial sources and/or our previous studies. Trimethyl borate was purchased from Aldrich (>99.999%). All the materials were degassed prior to use by several freeze–pump–thaw cycles on the sample-inlet system of the ICR. Their purities were verified by GC and/or an FT-ICR mass spectrometer.

Calculations. Theoretical calculations were carried out using the Gaussian 03 program suite.³³ The geometries were fully optimized at the DFT-B3LYP/6-311+G(d,p) level of theory. Vibrational normal-mode analyses were performed at the same level to ensure that each optimized structure was a true minimum on the potential energy surface. Unscaled B3LYP/6-311+G(d,p) frequencies were used to obtain thermochemical quantities, the thermal enthalpy, and free energy corrections.

Acknowledgment. This work was supported by a Grant-in-Aid from the Ministry of Education, Culture, Sport, Science and Technology, Japan, and by Joint Project of Chemical Synthesis Core Research Institutes.

Supporting Information Available: The calculated BCBs, selected bond distances, and the group natural charges of the

complexes derived using the natural population analysis (NPA) scheme are available (Tables S1–S5 and Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: Weinheim, 2000. (b) Sanrelli, N.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC Press: Boca Raton, 1996.
- (2) (a) Davidson, J. M.; French, C. M. *J. Chem. Soc.* **1958**, 114–117. (b) Davidson, J. M.; French, C. M. *J. Chem. Soc.* **1962**, 3364.
- (3) (a) Nöth, H.; Staudigl, R.; Wagner, H.-U. *Inorg. Chem.* **1982**, *21*, 706. (b) Kölle, P.; Nöth, H. *Chem. Rev.* **1985**, *85*, 399–418. (c) Schneider, W. F.; Narula, C. K.; Nöth, H.; Bursten, B. E. *Inorg. Chem.* **1991**, *30*, 3919.
- (4) Higashi, J.; Eastman, A. D.; Parry, R. W. *Inorg. Chem.* **1982**, *21*, 716.
- (5) Köster, R.; Willemsen, H. G. *Justus Liebigs Ann. Chem.* **1974**, 1843.
- (6) Kiyooka, S.-i.; Fujiyama, R.; Kawai, T.; Fujimoto, H.; Goh, K. *Tetrahedron Lett.* **2001**, *42*, 41513.
- (7) Uddin, M. K.; Fujiyama, R.; Kiyooka, S.-i.; Fujio, M.; Tsuno, Y. *Tetrahedron Lett.* **2004**, *45*, 3913.
- (8) (a) Nöth, H.; Staudigl, R.; Wagner, H.-U. *Inorg. Chem.* **1982**, *21*, 706. (b) Kölle, P.; Nöth, H. *Chem. Rev.* **1985**, *85*, 399. (c) Schneider, W. F.; Narula, C. K.; Nöth, H.; Bursten, B. E. *Inorg. Chem.* **1991**, *30*, 3919.
- (9) Higashi, J.; Eastman, A. D.; Parry, R. W. *Inorg. Chem.* **1982**, *21*, 7160.
- (10) Köster, R.; Willemsen, H. G. *Justus Liebigs Ann. Chem.* **1974**, 1843.
- (11) (a) Law, R. W.; Margrave, J. L. *J. Chem. Phys.* **1956**, *25*, 1086. (b) Wada, Y.; Kiser, R. W. *J. Phys. Chem.* **1964**, *68*, 1580. (c) Fallon, P. J.; Kelly, P.; Lockhart, J. C. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1*, 133.
- (12) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1433.
- (13) Kappes, M. M.; Uppal, J. S.; Staley, R. H. *Organometallics* **1982**, *1*, 1303.
- (14) Forte, L.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1990**, *68*, 1629.
- (15) (a) Depuy, C. H.; Gareyev, R.; Hankin, J.; Davico, G. E.; Krempf, M.; Damrauer, R. *J. Am. Chem. Soc.* **1998**, *120*, 5086. (b) Gareyev, R.; DePuy, T. J.; Bierbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrom.* **1998**, *179/180*, 55.
- (16) Hettich, R. L.; Cole, T.; Freiser, B. *Int. J. Mass Spectrom. Ion Processes* **1985**, *81*, 203.
- (17) Ranatunga, T. D.; Poutsma, J. C.; Squires, R. R.; Kenttämaa, H. I. *Int. J. Mass Spectrom. Ion Processes* **1993**, *128*, L1.
- (18) Leeck, D. T.; Ranatunga, T. D.; Smith, R. S.; Partanen, T.; Vainiotalo, P.; Kenttämaa, P. *Int. J. Mass Spectrom. Ion Processes* **1995**, *141*, 229.
- (19) Ranatunga, T. D.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 8600.
- (20) Ranatunga, T. D.; Kenttämaa, H. I. *Inorg. Chem.* **1995**, *34*, 18.
- (21) Ranatunga, T. D.; Kennady, J. M.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1997**, *119*, 5200.
- (22) The calculation at MP2/6-311+G(d,p)//MP2/6-311+G(d,p) gave the BCB of 189.1 kJ mol⁻¹ for acetophenone.
- (23) Mustanir; Shimada, K.; Ohta, F.; Mishima, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1845.
- (24) Mustanir; Mishima, M. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 798.
- (25) Maeda, H.; Irie, M.; Than, S.; Kikukawa, K.; Mishima, M. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 195.
- (26) Than, S.; Maeda, H.; Irie, M.; Kikukawa, K.; Mishima, M. *Int. J. Mass Spectrom.* **2007**, *267*, 205.
- (27) Than, S.; Maeda, H.; Itoh, S.; Irie, M.; Kikukawa, K.; Mishima, M. *J. Phys. Chem. A* **2007**, *111*, 5988.
- (28) Mishima, M.; Mustanir, M.; Fujio, Y. T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2009.
- (29) (a) Tsuno, Y.; Fujio, M. *Adv. Phys. Org. Chem.* **1999**, *31*, 267. (b) Tsuno, Y.; Fujio, M. *Chem. Soc. Rev.* **1996**, *25*, 129. (c) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 965. (d) Yukawa, Y.; Tsuno, Y.; Sawada, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2274.
- (30) The gas-phase substituent constant values used for the correlation were taken from ref 28. *p*-Cl and *p*-F were excluded from the correlation analysis because their gas phase σ^o values are not confirmed well.
- (31) Recalculated in this study excluding *p*-Cl and *p*-F.
- (32) (a) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149. (b) Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8533.
- (33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.;

Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.;

Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.

JP904159U