# ORGANOMETALLICS

# Synthesis of Silaoxazolinium Salts Bearing Weakly Coordinating Anions: Structures and Catalytic Activities in the Aldol Reaction

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Supporting Information

ABSTRACT: The synthesis and structures of silaoxazolinium salts 2 and their application to the catalytic Mukaiyama aldol reaction are described. The reaction of (N-amidomethyl)dimethylchlorosilane (1a) or (N-amidomethyl)bis(trimethylsilyl)chlorosilane (1b) with metal salts of weakly coordinating anions such as Na[TFPB] (TFPB = B[3,5- $(CF_3)_2C_6H_3]_4$  and  $Cs[CB_{11}H_{12}]$   $(CB_{11}H_{12}^- = carba-closo-dodecaborate)$  gave the R=Me, TMS; X = weakly coordinating anior corresponding five-membered-ring silaoxazolinium salts 2 in high yields (93-97%). The



structures of a series of silaoxazolinium salts 2 were determined by X-ray crystal analysis as well as <sup>29</sup>Si NMR spectra. It was proved that the silicon atoms of silaoxazolinium salts 2a,b are nearly completely free from the coordination of anions, and the geometries of the silicon centers are distorted tetrahedra. The <sup>29</sup>Si chemical shifts of salts 2 appeared in the range +31 to +49 ppm, revealing the appreciable silylium cation character of the silicon. The silaoxazolinium salt of TFPB anion 2a exhibited effective catalytic activity for the Mukaiyama aldol reaction of low reactive unactivated ketones such as cyclohexanone and acetophenone, giving the corresponding aldol products in high yields. The catalytic activity is highly dependent on the nature of the counteranions and the substituents on the silicon. DFT calculations of silaoxazolinium cation have disclosed that positive charges of silaoxazolinium cations are mainly located at the silicon atoms, while the nitrogen atoms and oxygen atoms are negatively charged.

# INTRODUCTION

The synthesis of highly reactive tetracoodinate silvlium cations  $[R_3SiL]^+$  (L = coordinating solvent or donor atoms) and trivalent silvlium cations is currently one of the most challenging topics in the fields of inorganic and organometallic chemistry.<sup>1</sup> Tetracoordinate silvlium cations have also attracted much attention from synthetic chemists, because extremely electrophilic silvlium cations can promote a number of unique reactions as reagents.<sup>2</sup> Moreover, tetracoordinate silylium cations exhibit effective catalytic activity for organic reactions such as Diels-Alder reactions and Friedel-Crafts alkylations.<sup>3</sup>

In contrast, very little attention has been paid to the chemistry of five-membered-ring cationic silicon compounds such as silaoxazolinium salts 2 and (N-amidomethyl)dimethyl-(X)silanes 3-6 (X = I, TfO), although these compounds can be easily prepared from commercially available materials (Scheme 1). The synthesis and the crystal structures of fivemembered-ring (N-amidomethyl)dimethyl(X)silanes 3-6 have been reported in the mechanistic studies of nucleophilic substitution at a pentacoordinate silicon atom (Scheme 1).<sup>4</sup> For compounds 3-6, the positive charge has been thought to be distributed among oxygen and nitrogen, but most of the positive charge is located around nitrogen.<sup>4a,c,e,f</sup> The silicon atoms of (N-amidomethyl)dimethyl(X)silanes 3-6 are coordinated by iodide or triflate, and the geometries of the silicon centers gradually vary from trigonal bipyramidal (TBP) to distorted tetrahedral with weakening coordination of anions.<sup>4</sup> Accordingly, completely coordination-free (N-amidomethyl)-

Scheme 1



dimethyl(X)silanes are regarded to be silaoxazolinium salts 2. It seems reasonable to assume that the geometry of the silicon as well as the extent of  $X \rightarrow Si$  coordination would strongly influence the charge distribution, the electronic properties of silaoxazolinium salts, and the Lewis acidity of the silicon.<sup>1j,k,5</sup> We have carried out DFT calculations to shed light on the factors which influence the charge distribution of silaoxazolinium cations. Our calculations have strongly suggested that the positive charge of silaoxazolinium cations 2 is mainly located at the silicon, indicating an appreciable Lewis acidity of the silicon.

We report herein the synthesis and X-ray crystal structures of silaoxazolinium salts 2 having weakly coordinating anions such as  $B[3,5-(CF_3)_2C_6H_3]_4$  (TFPB anion) and  $CB_{11}H_{12}^-$  (carbacloso-dodecaborate anion) (Scheme 2).6a 29Si NMR spectros-

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copy demonstrated that the tetramethylsilaoxazolinium salt of TFPB **2a** and tetramethylsilaoxazolinium salt of  $CB_{11}H_{12}$  **2b** are almost free from the coordination of anions in solution. Furthermore, we have found silaoxazolinium salt **2a** to be a highly effective catalyst for the Mukaiyama aldol reaction of low reactive unactivated ketones such as cyclohexanone and acetophenone.<sup>3b</sup> A detailed comparison of the structures of silaoxazolinium salts **2** with those of (*N*-amidomethyl)-dimethyl(X)silanes **3**–**6** revealed that the counteranions and the substituents on the silicon play a decisive role in the catalytic activity for the Mukaiyama aldol reaction.

# RESULTS AND DISCUSSION

**Synthesis of Silaoxazolinium Salts 2.** Chloride abstraction from pentacoordinate chlorosilanes  $1^7$  by sodium or cesium salts of weakly coordinating anions such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB anion) and CB<sub>11</sub>H<sub>12</sub><sup>-</sup> (1-carba-*closo*-dodecaborate anion) proceeded smoothly in dichloromethane, giving tetracoordinate silaoxazolinium salts **2** in nearly quantitative yields (Scheme 2). A





series of pentacoordinate chlorosilanes 1 can be easily prepared from commercially available *N*-methyl-*N*-(trimethylsilyl)acetamide and (chloromethyl)chlorosilanes  $R_2(ClCH_2)SiCl$ (1a, R = Me; 1b, R = SiMe<sub>3</sub>). The resulting silaoxazolinium salts 2 are colorless crystals and fairly stable in air at room temperature. Layering the solution of 2 in dichloromethane with hexane or pentane yielded crystals suitable for X-ray diffraction. The structural determination by X-ray crystallography revealed that the electronic nature and steric bulk of the substituents on the silicon centers. The key structural parameters of 2a-d are given in Table 1.

Silaoxazolinium salts 2 are structurally similar to (*N*-amidomethyl)dimethyl(X)silanes (X = I, TfO), which differ in the extent of the coordination of the anion to the silicon. The structural changes from pentacoordinate (*N*amidomethyl)dimethyl(X)silanes to tetracoordinate silaoxazolinium salts are shown by several structural parameters, as summarized in Scheme 3. For example, the O–Si bond lengths of these silicon compounds reflect faithfully the geometries of the silicon.<sup>8</sup> The ratio of Si…X distances to the sum of van der Waals radii, Si…X/ $\sum$ vdW, displays the extent of coordination of the anion to the silicon. When Si…X/ $\sum$ vdW is larger than 1.0, the silicon center is completely free from the coordination of the anion. In Scheme 3,  $\Delta$ Si shows the perpendicular distance of the silicon center from the planes formed by two substituents R on the silicon and the carbon atom bonded to



the silicon; the  $\Delta$ Si value indicates the displacement of the silicon atoms toward the oxygen atoms. Thus,  $\Delta$ Si increases with increasing tetrahedral character of the silicon centers.

For a comparison with the structures of 2, the Si–O bond lengths and the Si···X (X = I, OTf) atomic distances of representative (*N*-amidomethyl)dimethyl(X)silanes 3,<sup>4e</sup> 4,<sup>4a</sup> 5,<sup>4d</sup> and 6,<sup>4d</sup> whose silicon centers are relatively close to tetrahedral geometry among a number of (*N*-amidomethyl)dimethyl(X)silanes, are shown in Scheme 4.

X-ray Crystal Structures of 2a,b. The crystals of 2a consist of asymmetric cell a containing crystallographically two independent structures, 2a(A) and 2a(B). The X-ray crystal structure of 2a(A) is shown in Figure 1, and the key structural data of 2a(A) and 2a(B) are shown in Table 1. The structural

Scheme 4. Structural Data of Representative (*N*-Amidomethyl)dimethyl(X)silanes (X = I, OTf)





Figure 1. ORTEP representation of 2a. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level.

parameters of 2a(A), including bond lengths, atomic distances, and bond angles, are nearly identical with those of 2a(B).

Table 1. Key Bond Lengths (Å) and Bond Angles (deg) of 2a-d in X-ray Crystal Structures

	2a	2b	2c	2d
O–Si	1.723(3) (A)	1.734(2)	1.766(5)	1.770(3)
	1.721(3) (B)			
F-Si <sup>a</sup>	3.365 (A)		3.353	
H–Si <sup>b</sup>		3.175		2.756
С-О	1.292(5) (A)	1.308(4)	1.292(7)	1.310(4)
	1.299(5)(B)			
$O-Si-C^{c}$	89.7(2) (A)	90.3(1)	88.6(3)	88.6(1)
	89.7(2) (B)			
N-C-Si	102.0(3) (A)	102.0(2)	103.2(4)	104.0(2)
	102.7(3) (B)			
$\sum A-Si-B^d$	347.3(7) (A)	347.5(5)	352.6(3)	352.3(4)
	345.9(3) (B)			
∑Si	0.3892(3) (A)	0.3826(5)	0.349(5)	0.3527(3)
	0.3897(3) (B)			

<sup>*a*</sup>The shortest atomic distance between the central silicon atoms and the fluorine atoms on the TFPB anion. <sup>*b*</sup>The shortest atomic distance between the central silicon atoms and the hydrogen atoms on the CB<sub>11</sub>H<sub>12</sub> anion. <sup>*c*</sup>Ring carbon. <sup>*d*</sup>Sum of the three bond angles C–Si–C (**2a,b**); sum of the bond angles Si–Si–Si and two C–Si–Si (**2c,d**).

The structural data of (*N*-amidomethyl)dimethyl(X)silanes shown in Scheme 4 illustrate that the Si–O bond lengths of **3** (1.831(2) Å), **4** (1.749 Å), **5** (1.75 Å), and **6** (1.745(3) Å) are longer than that of **2a** (1.723(3) Å). The Si–O bond of **2a** is apparently covalent, which is very close to the Si–O covalent bond length of 1-oxa-3-aza-5-silacyclopentane (1.722 Å),<sup>8</sup> proving the tetrahedral geometry of the silicon of **2a** (Scheme 3). The Si…I atomic distances of **3** (3.510(2) Å) and **4** (3.734 Å) are significantly shorter than the sum of van der Waals radii ( $\sum$ vdW for Si…I = 4.08 Å)<sup>9</sup> to indicate that the silicon atoms are appreciably coordinated by I<sup>-</sup>. The Si…O<sub>Tf</sub> atomic distances of **5** (2.79 Å) and **6** (2.762(3) Å) are also considerably shorter than the sum of van der Waals radii ( $\sum$ vdW for Si…O = 3.62 Å),<sup>9</sup> implying that the silicon atoms are strongly coordinated by "OTf.

In the case of **2a**, the shortest atomic distance between the silicon atom and the fluorine atom on TFPB<sup>-</sup> (Si…F = 3.365 Å) is also shorter than the sum of the van der Waals radii ( $\sum$ vdW for Si…F = 3.57 Å),<sup>9</sup> whereas the Si…F/ $\sum$ vdW ratio (0.97) is fairly close to 1.0, indicating that silicon is very weakly coordinated by the fluorine atom of TFPB<sup>-</sup>. The geometry of the silicon atom of **2a** is distorted tetrahedral, since the sum of

C4A–Si1A–C3A, C3A-Si1A–C2A, and C4A–Si1A–C2A bond angles of 2a(A) is  $347.3(7)^{\circ}$  and that of 2a(B) is  $345.9(3)^{\circ}$ , which are noticeably smaller than the sum of the three angles for a regular TBP geometry ( $360^{\circ}$ ) (Table 1). In addition, the out-of-plane distances of the central silicon atom from the C2A–C3A–C4A plane ( $\sum Si$ ) of 2a are fairly large (0.3892 Å for 2a(A), 0.3897 Å for 2a(B)) in comparison to those of 3-6, agreeing with the tetrahedral geometry of the silicon of 2a. Thus, the weak coordination of the TFPB anion apparently leads to the tetrahedral geometry of the silicon of 2a.

The X-ray crystallographical analysis of **2b** (Figure 2) having a  $CB_{11}H_{12}$  anion revealed that the shortest distance between



Figure 2. ORTEP representation of 2b. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level.

the silicon atom and the hydrogen atom on  $CB_{11}H_{12}^{-}$  (3.175 Å) is slightly shorter than the sum of the van der Waals radii ( $\sum$ vdW for Si…H = 3.20 Å).<sup>9</sup> Other structural parameters of **2b** are almost identical with those of **2a** (Table 1). Thus, the silicon atom of **2b** was proved to be nearly completely free from the coordination of the anion.

<sup>29</sup>Si NMR Spectroscopic Analysis of 2a,b. The <sup>29</sup>Si NMR chemical shifts are highly sensitive to the degree of silylium cation character, the coordination numbers of silicon, and the coordination frameworks of silicon.<sup>10,11</sup> In general, <sup>29</sup>Si chemical shifts of neutral tetracoordinate silicon compounds with the coordination framework of SiCCCO (C = alkyl, O = alkoxy) appear in the range +13 to +19 ppm in CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub>.<sup>11a</sup> As shown in Table 2,  $\delta$ (<sup>29</sup>Si) of 2a, which has an

Table 2. <sup>29</sup>Si NMR Chemical Shifts of Silaoxazolinium Salts  $2a-d^{a}$ 

entry	compd	<sup>29</sup> Si chem shift, ppm
1	2a	46.1
2	$2a^b$	-78.4
3	2b	49.6
4	2c	-12.0 (terminal Si), 31.0 (central Si)
5	2d	-13.2 (terminal Si), 27.3 (central Si)
<sup><i>a</i></sup> Measured ТНЕ	in $CD_2Cl_2$	otherwise noted. <sup>b</sup> Measured in deuterated

identical coordination framework, appears at +46.1 ppm in  $CD_2Cl_2$ , which is shifted significantly downfield from those of the neutral tetracoordinate silicon atoms by ca. +30 ppm (entry 1). It is known that ring strain of cyclic silicon compounds exerts a pronounced effect on the <sup>29</sup>Si chemical shifts; however, in the case of 1-oxa-2-silacyclic compounds such as **2**, this effect is negligible.<sup>11a</sup> Thus, the observed downfield shift of  $\delta$ (<sup>29</sup>Si) of **2a** can be attributed to silylium cation character.<sup>5</sup> Bassindale and Borbaruah have predicted that the <sup>29</sup>Si chemical shifts of coordination-free silaoxazolinium cations will appear at about +40 ppm in CDCl<sub>3</sub> or CD<sub>3</sub>CN on the basis of experimental results, strongly supporting our assumption.<sup>4c</sup>

When the <sup>29</sup>Si NMR spectrum of 2a was measured in deuterated THF, the <sup>29</sup>Si chemical shift of 2a was shifted markedly upfield to -78.4 ppm (Table 2, entry 2). Generally, coordination expansion of silicon atoms accompanies upfield shift of  $\delta(^{29}\text{Si})$ .<sup>10,11b</sup> The observed upfield shift in THF indicates the formation of hypervalent silicon species. In addition, <sup>29</sup>Si chemical shifts of cationic pentacoordinate silicon compounds, whose structures have been unequivocally determined by spectral methods or X-ray crystallographic analysis, appear in a wide range from +6.9 to -120 ppm.<sup>12</sup> The large upfield shift of  $\delta$ <sup>(29</sup>Si) of **2a** ( $\Delta\delta$  = -124.5 ppm) observed in deuterated THF, therefore, can be ascribed to the formation of cationic pentacoordinate silicon species, formed by coordination of the THF molecule to the silicon of 2a  $([(CD_2)_4O \rightarrow SiL_4]^+)$ . This observation demonstrates the appreciable Lewis acidity of the silicon of 2a.

The <sup>29</sup>Si chemical shift of **2b** appeared at +49.6 ppm in  $CD_2Cl_2$ , which is shifted somewhat downfield in comparison with **2a**, revealing that **2b** has the same degree of silylium cation character as that of **2a** (Table 2, entry 3). The similarities of the geometric parameters as well as the <sup>29</sup>Si chemical shifts of **2a**,b demonstrate the extremely weak coordination by anions and the fairly large degree of silylium cation character.

**Crystal Structures of 2c,d.** Crystallization of compounds **2c,d** from  $CH_2Cl_2$ /hexane yielded colorless crystals suitable for X-ray crystallographic analysis. The X-ray structures of **2c,d** are shown in Figures 3 and Figure 4, respectively, displaying that



Figure 3. ORTEP representation of 2c. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level.



Figure 4. ORTEP representation of 2d. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level.

two sterically demanding trimethylsilyl groups on the central silicon exert a considerable influence on the geometries of the silicon centers. As can be seen from Table 1, the shortest atomic distance between the silicon of 2c and the fluorine on TFPB<sup>-</sup> is 3.353 Å, which is considerably shorter than the sum of van der Waals radii ( $\sum vdW = 3.57$  Å).<sup>9</sup> The sum of Si1–Si2–Si3, Si3–Si2–C1, and Si1–Si2–C1 bond angles of 2c is 352.6°, which is close to 360°, indicating the appreciable

flatness of the plane formed by the three silicon atoms and the C1 atom. Moreover, the Si1–Si2–Si3 bond angle  $(125.0(1)^{\circ})$  is very close to that of a regular trigonal bipyramid  $(120^{\circ})$ . Consequently, the geometry of the central silicon atom of **2c** is ascertained to be TBP. It is reasonable to consider that the two sterically demanding trimethylsilyl groups of **2c** are oriented toward the equatorial positions in the TBP structure to avoid steric repulsion; the axial position is occupied by the small fluorine atom on TFPB<sup>-</sup>. The structural parameters of silaoxazolinium salt **2d** are nearly identical with those of **2c** (Table 1), indicative of the TBP structure of **2d**.

<sup>29</sup>Si NMR Spectroscopic Analysis of 2c,d. The <sup>29</sup>Si NMR chemical shifts of the central silicon atoms of 2c,d appeared at +31.0 and +27.3 ppm, respectively, while the terminal silicon atoms of 2c,d exhibited chemical shifts at -12.3 and -13.2 ppm, respectively (Table 2, entries 4 and 5). In view of the similar geometric parameters as well as the nearly identical <sup>29</sup>Si chemical shifts of 2c,d, the geometries of the silicon and the electronic environments around the silicon are affected little by the counteranions.

Mukaiyama Aldol Reaction of Poorly Reactive Ketones Catalyzed by Silaoxazolinium Salts 2. The usefulness of new silaoxazolinium salts 2 in organic synthesis can be best appreciated by reference to the limitations in synthetically important reactions. The effectiveness of 2 as a Lewis acid catalyst was evaluated by the Mukaiyama aldol reaction of poorly reactive unactivated ketones such as acetophenone and cyclohexanone with silyl enol ethers, which are less reactive than silvl ketene acetals. Numerous applications of Lewis acid catalysts to the Mukaiyama aldol reactions of highly reactive activated ketones such as  $\alpha$ -keto esters and  $\alpha$ -diketones are known in the literature.<sup>13</sup> In contrast, only a limited number of effective catalysts have been reported for the Mukaiyama aldol reaction between sterically congested unactivated ketones and less reactive silvl enol ethers.<sup>3b,13a,14</sup> Unfortunately, these catalysts are highly sensitive to moisture, and the preparations of the catalysts are tedious.

Silaoxazolinium salt 2a exhibited high catalytic activity for the Mukaiyama aldol reaction of unactivated ketones with silyl enol ethers and silvl ketene acetals in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, giving high yields of the corresponding aldol products. Table 3 summarizes the results of the aldol reaction of unactivated ketones with silvl enol ethers catalyzed by 2a. The reaction of sterically congested acetophenone with 1-(trimethylsilyloxy)styrene (7a) proceeded smoothly in the presence of 5 mol % of **2a**, giving the corresponding  $\beta$ -hydroxy ketone in 82% yield after acidic workup (entry 1). Moreover, the catalytic Mukaiyama aldol reaction between the cyclohexanone and 3a furnished the desired aldol product in 98% yield (entry 2). Aldol reactions of silyl enol ethers with aliphatic aldehyde and sterically congested aldehyde were also effectively catalyzed by **2a** to give the  $\beta$ -hydroxy ketones in good yields (entries 3 and 4). To avoid the possibility of a proton-promoted reaction, the reaction of cyclohexanone and 7a was carried out in the presence of 2a (5 mol %) and the proton scavenger 2,6-di-tertbutyl-4-methylpyridine (10 mol %). As shown in entry 6, the addition of proton scavenger did not affect the yield, excluding the possibility of proton-promoted aldol reaction.

The catalytic activities of silaoxazolinium salts 2 depend completely upon the substituents on the silicon and the counteranions. The reaction profile of the Mukaiyama aldol reaction of cyclohexanone and silyl enol ehter 7a catalyzed by 2a-c is shown in Figure 5. The observed reaction profile





<sup>*a*</sup>Conditions: carbonyl compound (0.60 mmol), **2a** (0.03 mmol), dichloromethane (2 mL) at room temperature. <sup>*b*</sup>Isolated. <sup>*c*</sup>7a (0.66 mmol) was used. <sup>*a*</sup>7a or 7b (1.2 mmol) was used. <sup>*c*</sup>The syn/anti ratio of product **11** determined by <sup>1</sup>H NMR spectroscopy was 91/9. <sup>*f*</sup>The reaction was carried out in the presence of **2a** (5 mol %) and 2,6-*tert*-butyl-4-methylpyridine (10 mol %) in dichloromethane. <sup>*g*</sup>When the reaction was carried out at -10 °C, the reaction did not proceed.



Figure 5. Reaction profile of the aldol reaction between cyclohexanone (10 mmol) and silyl enol ether 7a (10 mmol) catalyzed by 2 (0.5 mmol) in dichloromethane (20 mL) at room temperature.

apparently indicates that 2a, having a TFPB anion, is the most catalytically active. The reaction catalyzed by 2c was not completed under the same conditions, indicating the deactivation of catalytically active species before the reaction completion. Although the precise mechanism of the present reaction is unclear, the highest catalytic activity of 2a can be correlated to the stronger Lewis acidity of 2a (see DFT Calculations).<sup>15</sup>

To our surprise, the aldol reaction catalyzed by salt **2b**, having a  $CB_{11}H_{12}$  anion, was not successful under the same conditions, although the structure of the silaoxazolinium cation of **2b** is almost identical with that of **2a**; just after the start of the reaction catalyzed by **2b**, the reaction abruptly stopped. This result is evidently due to the rapid deactivation of catalytically active species. No simple explanation for the rapid deactivation of catalyst **2b** can be offered at the present time. The most acceptable explanation for the deactivation of catalyst **2b** is that the decomposition of the  $CB_{11}H_{12}$  anion took place via hydride abstraction by an electrophilic species in the reaction solution, leading to the deactivation of catalytically active species.

For further investigation as to the influence of the counteranions on the catalytic activity of the silaoxazolinium cations, we attempted the aldol reaction between cyclohexanone and silyl enol ether 7a by using (N-amidomethyl)dimethyliodosilanes 4 as a catalyst (5–10 mol %) (Scheme 5).<sup>4a</sup> Since the structure of compound 4 (e.g., O–Si bond

#### Scheme 5



length,  $\sum$ Si, and Si…I/ $\sum$ vdW ratio) is close to that of 2a (Table 1 and Scheme 4), a comparison of catalytic activities between 4 and 2a in the same reaction gives detailed information about the counteranion effect on the catalytic activity. Unexpectedly, compounds 4 failed to catalyze the reaction under the same reaction conditions (in CH<sub>2</sub>Cl<sub>2</sub>, room temperature for 30 h). An increase in the amount of 4 (10 mol %) did not improve the yield of the aldol product. An <sup>1</sup>H NMR analysis of the reaction mixture showed that both substrates and catalyst 4 remained unchanged. Although the reason for the low catalytic activity of 4 is unclear, the possible explanation is that the strong coordination of I<sup>-</sup> to the silicon occupies the coordination site of the silicon; hence, the cyclohexanone cannot be activated by coordination to the silicon. This result strongly suggests that a weakly coordinating anion such as TFPB<sup>-</sup> of 2a plays an essential role in promoting the ketonealdol reaction.

**DFT Calculations.** The present work has stemmed from the DFT calculations of coordination-free silaoxazolinium cation **A** (a model compound of silaoxazolinium cations **2c**,**d**) and **B** (a model compound of silaoxazolinium cations **2a**,**b**). The MOs (LUMO and LUMO+1) of **A** and **B** calculated at the B3LYP/ 6-31G(d) level are illustrated in Figure 6.

The Mulliken charges of A and B are given in Table 4. As can be seen from Figure 6, the MOs, which accept the electron pair of Lewis bases, are LUMO+1 for A and B, whereas the LUMOs of **A** and **B** are  $\pi^*$  MOs of [-OC=N-] moieties. The charge distribution in A and B is intriguing (Table 4). The positive charges of (N-amidomethyl)dimethyl(X)silanes 3-6 have been considered to be located around oxygen and nitrogen (Scheme 6, C and C').<sup>4a,c,e</sup> Examination of Table 4, however, reveals the striking features of the charge distribution in A and B: (a) the quaternary iminium nitrogen atoms, which have a formal positive charge, are negatively charged; (b) despite the formal positive charge on the oxygen, the oxygen atoms are negatively charged; (c) appreciable positive charge is located on the silicon; (d) the silicon of **B**, which is a model for **2a**,**b**, carries a larger positive charge than the silicon of A, which is a model for 2c.d.

The results of Mulliken charge analysis are entirely consistent with the <sup>29</sup>Si NMR analysis of a series of silaoxazolinium salts **2** as well as the observed strong Lewis acidity of silaoxazolinium salt **2a**. The formal positive charge on the nitrogen would be neutralized by electron release from the five neighboring hydrogen atoms in geminal positions relative to the nitrogen.<sup>17</sup> All of the results obtained from the experimental observations



**Figure 6.** Molecular orbitals of model compounds **A** and **B** calculated at the B3LYP/6-31G(d) level.

Table 4. Mulliken Charges for Model Compounds A and B at the B3LYP/6-31G(d) Level

Α		В	
Si(central)	0.559	Si	1.039
Si(terminal)	0.705	methyl carbon bonded to Si	-0.714
Si(terminal)	0.714	methyl carbon bonded to Si	-0.715
0	-0.572	0	-0.585
Ν	-0.485	Ν	-0.495
amido C	0.593	amido C	0.615

#### Scheme 6



and the DFT calculations, which fully explain the Lewis acidities of silaoxazolinium cations, indicate the substantial contribution of resonance structure C'' (Scheme 6), in which the charge distributions are totally different from the formal charge distribution.

DFT calculations throw light on the substituent effect on the Lewis acid strength of the silicon. The highest catalytic activity for **2a** among a series of silaoxazolium salts can be explained by the largest positive charge on the silicon (1.039), leading to the strong Lewis acidity. In addition, the weakly coordinating

TFPB anion of 2a opens a coordination site on the silicon, which permits the strong electrophilic activation of carbonyl compounds by coordination. In the case of trimethylsilylsubstituted silaoxazolinium cations 2c,d, two electron-releasing TMS groups on the central silicon neutralize the positive charge of the central silicon (0.559) to reduce the Lewis acidity. Moreover, sterically demanding TMS groups would hinder the approach of carbonyl compounds to the silicon, thereby disturbing the activation of carbonyl compounds by coordination to the silicon.

# CONCLUSION

DFT calculations of a coordination-free silaoxazolinium cation predicted the significant Lewis acidity of the silicon atom. In order to demonstrate the results of the calculation, a series of silaoxazolinium salts with weakly coordinating anions such as TFPB<sup>-</sup> and  $CB_{11}H_{12}^{-}$  were synthesized. X-ray crystal analysis of the silaoxazolinium salts has revealed that dimethyl-substituted silaoxazolinium salts **2a**,**b** are nearly completely free from the coordination of counteranions, whereas the silaoxazolinium salts **2b**,**c**, in which the silicon atoms are substituted with two trimethylsilyl groups, are weakly coordinated by counteranions.

Silaoxazolinium salt **2a**, with a TFPB anion, exhibits effective catalytic activity for the Mukaiyama aldol reaction of poorly reactive ketones with low reactive silyl enol ethers, giving the corresponding aldol products in high yields. The counteranions as well as the substituents on the silicon exert a strong influence on the catalytic activities of silaoxazolinium salts.

In comparison with widely used strong silicon Lewis acids such as TMSOTf, TMSNTf<sub>2</sub>, and TMSI, the Lewis acid strength of **2a** is evidently lower.<sup>18</sup> For example, the catalytic Mukaiyama aldol reaction between Ph(CH<sub>2</sub>)<sub>2</sub>CHO and **7a** catalyzed by **2a** did not proceed at -10 °C (Table 3, entry 4), while the same reaction catalyzed by TMSOTf, TMSNTf<sub>2</sub>, and TMSI smoothly proceeds at -78 °C.<sup>18</sup> However, despite the higher Lewis acid strength, these conventional silicon Lewis acids failed to promote the Mukaiyama aldol reaction of unactivated ketones in spite of the optimization of the reaction conditions,<sup>3b,19</sup> though the same reaction is smoothly catalyzed by **2a**. The discrepancy between the catalytic efficiency and the Lewis acid strength is highly suggestive of a different reaction mechanism of the aldol reaction catalyzed by **2a**.

As a catalyst, silaoxazolinium salt **2a** possesses several advantages over other metal Lewis acids: (a) **2a** is air stable and can be handled in air, whereas metal Lewis acids are usually highly sensitive to moisture;<sup>18</sup> (b) the aldol reaction catalyzed by **2a** takes place smoothly at room temperature without use of low-temperature conditions; (c) more importantly, the silaoxazolinium-catalyzed aldol reaction shows wider substrate scope, including not only aldehydes but also unactivated ketones. Further investigations focused on the application of the silaoxazolinium catalysts to other organic reactions are underway.

#### EXPERIMENTAL SECTION

**General Remarks.** All manipulations were carried out under a nitrogen atmosphere using Schlenk tube techniques. <sup>1</sup>H (500 MHz), <sup>13</sup>C (125.4 MHz), and <sup>29</sup>Si (99.0 MHz) NMR spectra were recorded on a JEOL LA-500 spectrometer. Chemical shifts were referenced to CH<sub>2</sub>Cl<sub>2</sub> (5.31 ppm) for <sup>1</sup>H NMR, CD<sub>2</sub>Cl<sub>2</sub> (53.62 ppm) for <sup>13</sup>C NMR, and Me<sub>4</sub>Si (0 ppm) for <sup>29</sup>Si NMR. Infrared spectra were measured on a JASCO FT/IR-5000 instrument in Nujol mulls prepared under inert

atmosphere. Solvents were purified as follows: hexane by distillation from benzophenone ketyl under nitrogen and dichloromethane by distillation from calcium hydride. All the above solvents were distilled just prior to use. Silyl enol ethers and silyl ketene acetals were prepared by literature procedures.<sup>20</sup> Sodium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (Na[TFPB]) was obtained from Wako Chemical Co. Cs[CB<sub>11</sub>H<sub>12</sub>] was prepared by the literature procedure.<sup>6a</sup> Compound **1a** was prepared by the literature procedure,<sup>7a</sup> and compound **1b** was prepared from commercially available chloro(chloromethyl)-dimethylsilane (Aldrich) and *N*-methyl-*N*-(trimethylsilyl)acetamide (Tokyo kasei) according to the literature procedure.<sup>21</sup>

2,3,5,5-Tetramethyl-5-silaoxazolinium Tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (2a). A 20 mL Schlenk tube was charged with 1a (0.054 g, 0.300 mmol) and sodium tetrakis[3,5bis(trifluoromethyl)phenyl]borate (Na[TFPB]; 0.290 g, 0.315 mmol) under nitrogen. To this mixture was added anhydrous dichloromethane (2 mL), and the reaction mixture was further stirred at room temperature for 2 h. The precipitated sodium chloride was separated by transfer of the dichloromethane solution into another flask using cannula. The solution was condensed under reduced pressure to afford a colorless solid, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane at -30 °C to give 2a as colorless crystals (0.290 g, 0.287 mmol, 96%). Mp: 110-113 °C. IR (Nujol): 2750, 1635, 1355, 1276, 1116, 887, 860, 809, 779, 711, 682, 671 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 0.63 (s, 6 H), 2.34 (s, 3 H), 3.12 (s, 2 H), 3.30 (s, 3 H), 7.67 (s, 4 H), 7.83 (s, 8 H). <sup>13</sup>C NMR-DEPT (CD<sub>2</sub>Cl<sub>2</sub>): δ -1.5 (CH<sub>3</sub>), 16.9 (CH<sub>3</sub>), 39.6 (CH<sub>2</sub>), 42.9 (CH<sub>3</sub>), 118.0 (TFPB-C4), 125.1 (q,  ${}^{1}J_{FC} = 271.7$  Hz, CF<sub>3</sub>), 129.4  $(q, {}^{2}J_{FC} = 31.0 \text{ Hz}, \text{TFPB-C3,5}), 135.3 \text{ (TFPB-C2,6)}, 162.1 (q, {}^{1}J_{BC} =$  $(1-1)^{2}$  (1)  $(1-1)^{2}$  ( for C<sub>38</sub>H<sub>26</sub>BF<sub>24</sub>NOSi: C, 45.30; H, 2.60; N, 1.39. Found: C, 45.06; H, 2.46: N. 1.20.

2,3,5,5-Tetramethyl-5-silaoxazolinium 1-Carba-closo-dodecaborate (2b). A 20 mL Schlenk tube was charged with 1a (0.054 g, 0.300 mmol) and cesium 1-carba-closo-dodecaborate (0.087 g, 0.315 mmol) under nitrogen. To this mixture was added anhydrous dichloromethane (2 mL), and the reaction mixture was further stirred at room temperature for 12 h. The precipitated cesium chloride was separated by transfer of the dichloromethane solution into another flask using cannula. The solution was condensed under reduced pressure to afford a colorless solid, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane at room temperature to give 2b as colorless crystals (0.081 g, 0.281 mmol, 93%). Mp: 112-114 °C. IR (Nujol): 2601, 1637, 1540, 1305, 1153, 1022, 850, 771, 721, 592 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 0.66 (s, 6 H), 1.00–2.34 (m, 12 H), 2.45 (s, 3 H), 3.24 (s, 2 H), 3.41 (s, 3 H). <sup>13</sup>C NMR-DEPT (CD<sub>2</sub>Cl<sub>2</sub>): δ -0.4 (CH<sub>3</sub>), 17.9 (CH<sub>3</sub>), 40.2 (CH<sub>3</sub>), 43.3 (CH<sub>2</sub>), 52.1 (carborane-C), 177.7 (CO). <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 49.6. Anal. Calcd for C<sub>7</sub>H<sub>26</sub>B<sub>11</sub>NOSi: C, 29.26; H, 9.12; N, 4.87. Found: C, 29.05; H, 8.88; N, 4.66.

2,3-Dimethyl-5,5-bis(trimethylsilyl)-5-silaoxazolinium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (2c). A 20 mL Schlenk tube was charged with 1b (0.088 g, 0.300 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na[TFPB]; 0.290 g, 0.315 mmol) under nitrogen. To this mixture was added anhydrous dichloromethane (2 mL), and the reaction mixture was further stirred at room temperature for 2 h. The precipitated sodium chloride was separated by transfer of the dichloromethane solution into another flask using cannula. The solution was condensed under reduced pressure to afford a colorless solid, which was recrystallized from  $CH_2Cl_2$ /hexane at -30 °C to give 2c as colorless crystals (0.327 g, 0.291 mmol, 97%). Mp: 103-107 °C. IR (Nujol): 2724, 2362, 1631, 1276, 968, 935, 887, 775, 669, 603, 568 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 0.25 (s, 18 H), 2.33 (s, 3 H), 3.32 (s, 3 H), 3.38 (s, 2 H), 7.57 (s, 4 H), 7.72 (s, 8 H). <sup>13</sup>C NMR-DEPT (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –2.5 (CH<sub>3</sub>), 17.3 (CH<sub>3</sub>), 39.6 (CH<sub>3</sub>), 41.3 (CH<sub>2</sub>), 117.9 (TFPB-C4), 125.0 (q, <sup>1</sup>J<sub>FC</sub> = 272.5 Hz,  $CF_3$ ), 129.5 (q,  ${}^2J_{FC}$  = 31.7 Hz, TFPB-C3,5), 135.2 (TFPB-C2,6), 162.15 (q,  ${}^{1}J_{BC}$  = 49.8 Hz, B-C1), 178.5 (CO). <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ -12.3 (terminal Si), 31.3 (central Si). Anal. Calcd for C42H38BF24NOSi3: C, 44.89; H, 3.41; N, 1.24. Found: C, 44.67; H, 3.25; N, 1.39.

2,3-Dimethyl-5,5-bis(trimethylsilyl)-5-silaoxazolinium 1-Carba-closo-dodecaborate (2d). A 20 mL Schlenk tube was charged with 1b (0.088 g, 0.300 mmol) and cesium 1-carba-closododecaborate (0.087 g, 0.315 mmol) under nitrogen. To this mixture was added anhydrous dichloromethane (2 mL), and the reaction mixture was further stirred at room temperature for 12 h. The precipitated cesium chloride was separated by transfer of the dichloromethane solution into another flask using cannula. The solution was condensed under reduced pressure to afford a colorless solid, which was recrystallized from  $CH_2Cl_2$ /hexane at -30 °C to give 2d as colorless crystals (0.113 g, 0.280 mmol, 94%). Mp: 132-134 °C. IR (Nujol): 2518, 1625, 1455, 1247, 1018, 844, 757, 501 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 0.31 (s, 18 H), 1.04–2.35 (m, 12 H), 2.44 (s, 3 H), 3.46 (s, 3 H), 3.55 (s, 2 H). <sup>13</sup>C NMR-DEPT (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -2.0 (CH<sub>3</sub>), 17.6 (CH<sub>3</sub>), 39.8 (CH<sub>3</sub>), 41.8 (CH<sub>2</sub>), 52.1 (carborane-C), 178.1 (CO). <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –13.2 (terminal Si), 27.3 (central Si). Anal. Calcd for C<sub>11</sub>H<sub>38</sub>B<sub>11</sub>NOSi<sub>3</sub>: C, 32.74; H, 9.49; N, 3.47. Found: C, 32.98; H, 9.30; N, 3.45.

General Procedure for the Catalytic Aldol Addition. To a solution of 2a (0.030 g, 0.030 mmol) in anhydrous dichloromethane (2 mL) were added silyl enol ether or silyl ketene acetal (0.66–1.2 mmol) and ketone or aldehyde (0.60 mmol) dropwise at room temperature. After stirring for an additional 10 h at room temperature, the reaction mixture was poured into a saturated NH<sub>4</sub>Cl solution (6 mL) and stirred for a few minutes and then extracted with ether (20 mL  $\times$  2). The extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by preparative thin -layer chromatography using hexane/ethyl acetate (9/1) as eluent to furnish an aldol adduct in the yields shown in Table 3. The isomeric ratio was determined by 500 MHz  $^1\rm H$  NMR spectroscopy.

All compounds in Table 3 have been previously isolated and characterized. Their *Chemical Abstracts* registry numbers are as follows: **8**, 6397-70-2; **9**, 57213-26-0; **10**, 60669-64-9; *syn*-**11**, 103108-36-7; *anti*-**11**, 103108-37-8; **12**, 33026-24-3.

# ASSOCIATED CONTENT

#### **Supporting Information**

CIF files giving crystallographic data for **2a**–**d**, figures giving <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra of new compounds, and a table giving crystallographic data and experimental parameters for the structure analysis of **2a**–**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

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