20 mL of dichloromethane. The reaction mixture was allowed to reach ambient temperature, and stirring was continued overnight. The decolorized reaction mixture was slowly added to a solution of 15 g of sodium carbonate in 30 mL of water while steam was being passed through the solution. The steam distillate was collected, and the organic phase was separated. The aqueous solution extracted with ether, and the combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to yield an oil, which was distilled from anhydrous sodium carbonate to yield 2.58 g (52%) of product: bp 68 °C (15 mmHg); $[\alpha]^{20}$ +13.06° (*c* 1.1, ethanol).

(*R*)-(−)-(4-Methylcyclohexylidene)fluoromethane. To a solution of 7.76 g (0.0375 mol) of (*S*)-(+)-(4-methylcyclohexylidene)bromofluoromethane, $[\alpha]^{20}$ +13.06° (*c* 1.1, ethanol), and 1.08 mL (0.012 mol) of 1,2-dibromoethane in 130 mL of methanol was added 18 g (0.75 mol) of magnesium. CO_2 was continuously passed through the reaction mixture during the course of the reaction. After an induction period, a very vigorous exothermic reaction ensued. The resultant slurry was stirred at 65 °C for 1.5 h, and the unreacted magnesium was separated by centrifugation and washed with 20 mL of methanol and then pentane (2 × 50 mL). The combined organic extract was acidified with 6 N HCl at 0 °C and extracted with pentane (5 × 100 mL). The combined extracts were washed with water and dried over $MgSO_4$. The solvent was removed by distillation through a spinning-band distillation column (pot temperature, 50 °C; column temperature, 45 °C). Distillation of the residue gave 3.2 g (68%) of pure product: bp 115–116 °C; $[\alpha]^{20}$ −38.6° (*c* 1.1, ethanol); UV (*c* $1.6 \cdot 10^{-4}$, cyclohexane) ($\lambda_{196\text{nm}}$) ϵ 6250; CD (*c* 1.6×10^{-4}, cyclohexane) $\Delta\epsilon_{200}$ +2.44; IR (film) 1670 cm^{-1}; ^{1}H NMR δ 0.90 (d, *J* = 7 Hz, 3 H), 0.92–1.95 (m, 7 H), 2.00–2.11 (m, 1 H), 2.71–2.82 (m, 1 H), 6.38 (d, *J* = 88 Hz, 1 H); ^{19}F NMR δ ($CF_3C_6H_5$ ref = 0 ppm) −78.17 (d, *J* = 87 Hz). Anal. Calcd for $C_8H_{13}F$: C, 74.96; H, 10.22. Found: C, 74.87; H, 10.19.

(*S*)-(+)-(4-Methylcyclohexylidene)fluorodeuteriomethane. To a solution of 5.18 g (0.025 mol) of (*R*)-(−)-(4-methylcyclohexylidene)bromofluoromethane, $[\alpha]^{20}$ −12.7° (*c* 1.1, ethanol), and 0.72 mL (0.008 mol) 1,2-dibromoethane in 85 mL of methanol-*O-d* was added 12.1 g (0.5 mol) of magnesium. CO_2 was passed continuously through the reaction mixture during the course of the reaction. After an induction period, a very vigorous exothermic reaction ensued. The resultant slurry was stirred at 65 °C for 1.5 h, and the unreacted magnesium was separated by centrifugation and washed with 20 mL of methanol and then pentane (2 × 50 mL). The combined organic extract was acidified with 6 N HCl at 0 °C and then extracted with pentane (5 × 100 mL). The combined extracts were washed with water and dried over $MgSO_4$. The solvent was removed by distillation through a spinning-band distillation column (pot temperature, 50 °C; column temperature, 45 °C). Distillation of the residue gave 2.2 g (69%) of pure product: bp 115–116 °C; $[\alpha]_{Hg}$ +39.6° (*c* 1.1, ethanol); UV (*c* 1.43×10^{-4}, cyclohexane) (λ_{194}) ϵ 6700; CD (*c* 1.43×10^{-4}, cyclohexane) $\Delta\epsilon_{201}$ −1.56; IR (film) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (d, *J* = 7 Hz, 3 H), 0.92–1.95 (m, 7 H), 2.00–2.11 (m, 1 H), 2.71–2.82 (m, 1 H). Anal. Calcd for $C_8H_{12}DF$: C, 74.38; HD, 10.90. Found: C, 74.14; HD, 10.57.

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Pentacoordinate Allylsilicates: Characterization and Highly Stereoselective Reaction with Aldehydes[1]

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Abstract: Lithium and bis(triphenylphosphoranylidene)ammonium salts of bis(1,2-benzenediolato)allylsilicates, which were prepared via the reactions of allyl-, prenyl-, and (*E*)- and (*Z*)-crotyltrichlorosilanes with dilithium catecholate, were found to react with aromatic aldehydes chemoselectively to give the corresponding homoallyl alcohols in a regiospecific and highly diastereoselective manner in high yields. The unique reaction modes including the diastereoselectivity are interpreted by a six-membered cyclic transition state, which is favored by the enhanced nucleophilicity of the γ-carbon of the allylsilicates as well as by the significant Lewis acidity giving hexacoordinate silicates. In contrast, however, allylsilicates with α,α-bis(trifluoromethyl)benzenemethanolato(2−)-C^2,*O* ligands did not react with the aldehydes. The inertness may be attributable to the rather rigid trigonal-bipyramidal structure with low Lewis acidity.

Although allylation of carbonyl compounds with allyltrimethylsilanes promoted by fluoride ions has been well established as a useful synthetic method for homoallyl alcohols,[2,3] the reaction mechanism is still unclear. In our previous paper,[2] we suggested that an allylic carbon–silicon bond is cleaved by fluoride ions to generate an allyl anion that adds to carbonyl compounds on the basis of the substantial difference in the values of Si–C and Si–F bond strength as well as the low regiospecificity of the reaction. More recently, Majetich et al.[3] proposed pentacoordinate allylsilicate intermediates formed from fluoride ion addition to silicon as an ambient nucleophilic species. However, nothing had been known about pentacoordinate allylsilicates before we initiated the present study,[4] whereas a number of pentacoordinate organosilicates have been well characterized.[7] After completion of this work,[8] we became aware of the closely related studies on the pentacoordinate allylsilicates by Corriu et al.[9] and by Hosomi et al.[10] We report here the characterization of several pentacoordinate allylsilicates and their unique reactivity toward carbonyl compounds. In contrast to allyl anions, pentacoordinate allylsilicates were found to react with aldehydes chemoselectively to give the corresponding homoallyl alcohols in regiosepecific and highly stereoselective manner. The reaction modes of penta-

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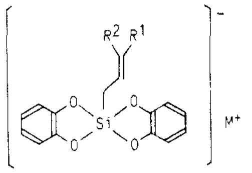
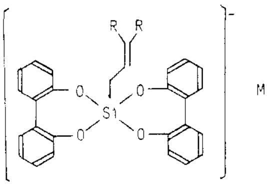
coordinate allylsilicates were also found to be quite different from that of allyltrimethylsilanes in the presence of Lewis acids.[11] This conceptually novel reactivity of pentacoordinate allylsilicates has lead us to the development of the useful synthetic method for the highly stereoselective allylation of aldehydes by the use of allyltrifluorosilane–cesium fluoride systems.[12]

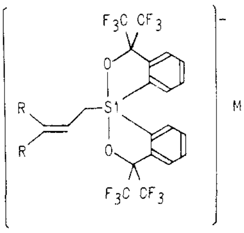
Results and Discussion



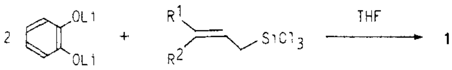
1a, $R^1 = R^2 =$ H, M = Li;
1b, $R^1 = R^2 = CH_3$, M = Li;
1c, $R^1 = CH_3$, $R^2 =$ H, M = Li;
1d, $R^1 =$ H, $R^2 = CH_3$, M = Li;
3a, $R^1 = R^2 =$ H, M = PPN;
3b, $R^1 = R^2 = CH_3$, M = PPN.



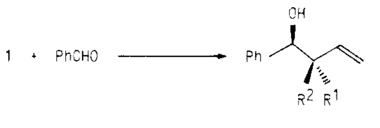
4a, R = H, M = Li;
4b, R = CH_3, M = Li.



5a, R = H, M = Li;
5b, R = CH_3, M = Li;
6a, R = H, M = PPN;
6b, R = CH_3, M = PPN.



(1)

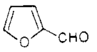
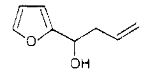


(2)

2a, $R^1 = R^2 =$ H; 2b, $R^1 = R^2 = CH_3$;
2c, $R^1 = CH_3$, $R^2 =$ H; 2d, $R^1 =$ H, $R^2 = CH_3$.

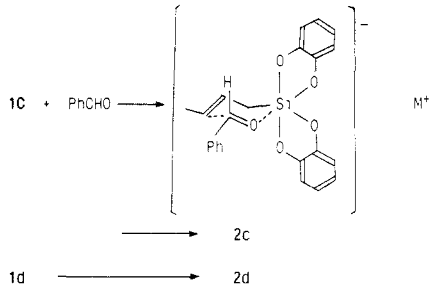
We recently reported the preparation and reactions of novel pentacoordinate hydridosilicates prepared by the reactions of trichlorosilane and dilithium catecholate in THF.[13] A similar method was applied to the preparation of the lithium salts of pentacoordinate allylsilicates **1a–d** and their use for the allylation of aldehydes (eq 1 and 2). As a typical example, allyltrichlorosilane in THF was added to 2 mol of dilithium catecholate in THF–hexane at room temperature, and the mixture was stirred for 1 h. Whereas all attempts to isolate dilithium bis(1,2-benzenediolato)allylsilicate (**1a**) failed, the resultant solution reacted with benzaldehyde without any catalyst to produce 1-phenylbut-3-en-1-ol (**2a**) in 91% yield. Furfural afforded the corresponding homoallyl alcohol in high yield, but alkanals did not give the expected products. Ketones and esters did not react under similar conditions. Besides 1,2-benzenediolate, 2,2′-biphenolate was also utilized as a ligand to produce an allylsilicate that afforded the corresponding homoallyl alcohols in the reaction with benzaldehyde. The reaction was regiospecific where the C–C bond formation occurred exclusively at the γ-carbon of the allylsilanes. Thus, prenyltrichlorosilane gave 2,2-dimethyl-1-phenylbut-3-en-1-ol (**2b**) as a sole regioisomer in 87% yield via the reactions of eq 1 and 2. The results are summarized in Table I.

Table I. Allylation of Aldehydes with Allylsilicates[a]

allylsilicates	aldehyde	product	yield,[b] %
1a	PhCHO (**7**)	**2a**	91
1a			86
1b	**7**	**2b**	87
1c/**1d** (88/12)[c]	**7**	**2c**/**2d** (88/12)[d]	82
1c/**1d** (21/79)[c]	**7**	**2c**/**2d** (22/78)[d]	91
3a	**7**	**2a**	90
3b	**7**	**2b**	80
4a	**7**	**2a**	85
4b	**7**	**2b**	80

[a] All reactions were carried out under reflux in THF for 90 h. [b] Yield determined after isolation by preparative TLC. [c] *E*/*Z* ratio of the crotylsiliconates is shown in parentheses. [d] Threo to erythro ratio of 2-methyl-1-phenylbut-3-en-1-ol is shown in parentheses.

Scheme I



The intermediacy of the pentacoordinate allylsilicates was proved as follows. After allyltrichlorosilane was treated with dilithium catecholate in THF followed by evaporation of the solvent, a CH_2Cl_2 solution of bis(triphenylphosphoranylidene)ammonium chloride [(PPN)Cl] was added and the mixture was stirred for 12 h at room temperature. Removal of LiCl by filtration under argon followed by evaporation of the solvent afforded the PPN salt of allylsilicate (**3a**), which was very unstable to air and moisture. The structure was confirmed by NMR and negative-ion FAB MS. Similarly, a PPN salt of prenylsilicate (**3b**) was obtained. The isolated allylsilicates **3a** and **3b** yielded **2a** and **2b** in 90% and 80% yields, respectively, when refluxed with benzaldehyde in THF for 90 h.

Stereochemical control in the addition of crotylmetals to aldehydes has been extensively investigated from both mechanistic and synthetic viewpoints.[14] Recently, reactions of crotyltrimethylsilanes with aldehydes in the presence of Lewis acids have been found to proceed via acyclic transition states to give erythro products regardless of the stereochemistry of the starting crotylsilanes.[15] The characteristic reactivity of the pentacoordinate allylsilicates was also shown by the diastereoselection of crotylation. Thus, when a mixture of crotyltrichlorosilanes with an *E*/*Z* ratio of 88/12 was used as a starting allyltrichlorosilane in eq 1 and 2, a mixture of the threo (**2c**) and erythro (**2d**) homoallyl alcohols was obtained in 82% yield with an threo/erythro ratio of 88/12. Another mixture of crotyltrichlorosilanes (*E*/*Z* = 21/79) afforded the alcohols in 91% yield (**2c**/**2d** = 22/78). The results indicate that the present reaction is essentially stereospecific, giving *threo*- and *erythro*-homoallyl alcohols from (*E*)- and (*Z*)-crotylsilanes, respectively.

The reaction modes of pentacoordinate allylsilicates including the diastereoselection are very similar to those of the allyl boro-

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(11) (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (b) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1.

(12) We have recently found that allyltrifluorosilanes react with various aldehydes in the presence of fluoride ions under much milder conditions than those reported here, affording the corresponding homoallyl alcohols in high yields. Since the reaction proceeds also in regiospecific and highly stereoselective manner, pentacoordinate allyltetrafluorosilicates are proposed as the important intermediates: Kira, M.; Kobayashi, M.; Sakurai, H. *Tetrahedron Lett.* **1987**, *28*, 4081.

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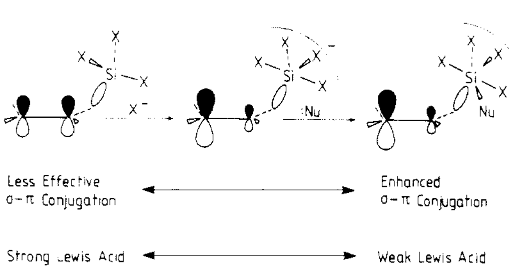

Figure 1. Schematic Presentation of the Effects of Extracoordination on the Allylsilane HOMO and the Lewis Acidity.

nates.[16] The stereoselectivity of allylation is thus interpreted by the six-membered cyclic transition state having a chair conformation as shown in Scheme I.[17]

The higher reactivity of the allylsilicates than that of the tetracoordinate silicon analogues may be caused by the significant Lewis acidity giving hexacoordinate silicates[18] and the enhanced nucleophilicity of the γ-carbon of the allylsilicates due to σ–π conjugation (Figure 1). The highly coordinate silicon may be even more electron-donating to the allyl π systems due to σ–π conjugation than the trialkylsilyl group, whereas electronegative substituents on tetracoordinate silicon usually reduce the electron-donating ability.[19] Actually, the increased electron density at the γ-carbon of **3a** was evidenced by the lower field resonance of the ^{13}C NMR chemical shift in $CDCl_3$ (δ 110.6) than those of allyltrimethylsilane (δ 112.5) and other tetracoordinate allylsilanes.[20] The cyclic transition state may be favored since the hexacoordination at silicon may further increase the electron-donating ability of the silyl group and, in turn, the nucleophilicity of the allylic γ-carbon due to σ–π conjugation.

In order to investigate the effects of ligands on the reactivity of pentacoordinate allylsilicates, we prepared lithium (**5a,b**) and PPN salts (**6a,b**) of the allyl- and prenylsilicates with two α,α-bis(trifluoromethyl)benzenemethanolato(2−)-C^2,*O* ligands[21] and investigated the reactivity toward aldehydes. Interestingly, both **5** and **6** did not react with benzaldehyde under refluxing in THF. The ^{13}C NMR chemical shift of the γ-carbon of **6a** was lower than that of **3a**, suggesting even higher nucleophilicity of the γ-carbon of **6a**. The inertness may be thus attributed to the rather rigid trigonal-bipyramidal structure of silicates like **5** and **6** and the poor electron-accepting ability of the ligands.[22] These silicates may be too weak as Lewis acids to produce the hexacoordinate transition states during the reaction with aldehydes. In contrast to this, bis(1,2-benzenediolato)silicates like **1** and **3** would be stronger Lewis acids due to the nonrigid structure with four electron-accepting ligands on silicon.[7b]

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded on a Varian EM-390, Varian XL-200, or JEOL FX-90Q spectrometer. ^{13}C and ^{29}Si NMR spectra were recorded on JEOL FX-90Q spectrometer. Mass spectra were obtained on a JEOL JMS-D300 mass spectrometer. Negative-ion FAB mass spectra were recorded on a JEOL JMS-DX303HF mass spectrometer.[23] Analytical gas chromatography was performed on a Hitachi 163 or Shimadzu 8A gas chromatograph with thermal conductivity detector on a 1.5 m × 4 mm (i.d.) glass column of 15% SE-30 or 25% PEG-20M on Celite 545.

Catechol, bis(triphenylphosphoranylidene)ammonium chloride [(PPN)Cl], trichlorosilane, and 1.5 M *n*-hexane solution of *n*-butyllithium were commercially available. 1,1,1,3,3,3-Hexafluoro-2-phenyl-2-propanol was synthesized with the reported procedure[24] (bp 159 °C, 96% yield). Crotyltrichlorosilane (E/Z = 88/12) and prenyltrichlorosilane were prepared by the reactions of the corresponding allyl chlorides with trichlorosilane in the presence of triethylamine and catalytic amounts of $Cu^{I}Cl$,[25] in yields of 89% and 83%, respectively. Crotyltrichlorosilane (E/Z = 21/79) was prepared by the hydrosilation of 1,3-butadiene with trichlorosilane catalyzed by $Pd^{II}(PhCN)_2Cl_2$.[26] The E/Z ratios of crotyltrichlorosilanes were determined by GLC as the E/Z ratios of trimethylcrotylsilanes after methylation of the chlorosilanes by excess methyllithium.

Dilithium Catecholate. Typically, *n*-butyllithium (2 mmol) in hexane (1.3 mL) was added to a THF (0.2-mL) solution of catechol (1 mmol) at −78 °C in a 30-mL two-neck flask, and the mixture was stirred for 2 h at room temperature. The dilithiation was monitored with 2,2′-bipyridyl as an indicator and found to be achieved similarly in DME but only incompletely in diethyl ether.

Dilithium 2,2′-Biphenolate. A similar procedure as above was successfully applied to the preparation of dilithium biphenolate in THF–hexane.

Allylation of Benzaldehyde with Allyltrichlorosilane–Dilithium Catecholate System. To a THF–hexane solution of dilithium catecholate (8.0 mmol) prepared with the procedure as described above were added allyltrichlorosilane (702 mg, 4.00 mmol) and THF (10 mL) at room temperature under argon. After the resultant mixture was stirred for 1 h, benzaldehyde (212 mg, 2.00 mmol) in THF (10 mL) was added dropwise. After being refluxed for 90 h, the reaction mixture was hydrolyzed. After the usual workup, preparative TLC afforded 1-phenylbut-3-en-1-ol in 91% yield. The product was identified by comparing the GLC retention times, ^{1}H NMR spectrum, and MS spectrum with the authentic sample prepared with the reaction of allyllithium and benzaldehyde: ^{1}H NMR (CCl_4) δ 7.33 (s, 5), 6.1–5.4 (m, 1), 5.10 (d, J = 10 Hz, 1), 5.05 (d, J = 18 Hz, 1), 4.63 (t, J = 7 Hz, 1), 2.43 (t, J = 7 Hz, 2), 2.05 (br s, 1); MS m/z (relative intensity) 130 (M^+ − 18, 100), 129 (92.9), 107 (59).

Prenylation of Benzaldehyde with Prenyltrichlorosilane–Dilithium Catecholate System. With the similar procedure as above but by the use of prenyltrichlorosilane instead of allyltrichlorosilane 2,2-dimethyl-1-phenylbut-3-en-1-ol was obtained in the yield of 87%. Analysis of the product by GLC and ^{1}H NMR and MS spectra revealed the absence of the any regioisomers: ^{1}H NMR (CCl_4) δ 7.30 (s, 5), 5.95 (dd, J = 16.1 Hz, 1), 5.2–4.8 (m, 2), 4.33 (s, 1), 3.33 (br s, 1), 1.00 (s, 3), 0.95 (s, 3); MS m/z (relative intensity) 107 (100), 105 (31.6), 79 (54.1). The spectral data were completely in accord with those of the product from allylation of benzaldehyde with allyltrimethylsilane in the presence of titanium chloride.[11]

Crotylation of Benzaldehyde with Crotyltrichlorosilane (E/Z = 88/12)–Dilithium Catecholate. 2-Methyl-1-phenylbut-3-en-1-ol was obtained in the yield of 82%. No regioisomers were found in the products analyzed by GLC and ^{1}H NMR and MS spectra. The ratio of threo to erythro alcohols was determined to be 88/12 by comparing the ^{1}H NMR data with that reported.[27] Threo isomer: ^{1}H NMR (CCl_4) δ 7.14 (s, 5), 5.9–5.5 (m, 1), 5.1–4.8 (m, 2), 4.22 (d, J = 6 Hz, 1), 2.6–2.1 (m, 1), 2.40 (br s, 1), 0.83 (d, J = 6 Hz, 3). Erythro isomer: ^{1}H NMR (CCl_4) δ 7.14 (s, 5), 5.9–5.5 (m, 1), 5.1–4.8 (m, 2), 4.36 (d, J = 6 Hz, 1), 2.6–2.1 (m, 1), 2.40 (br s, 1), 0.94 (d, J = 6 Hz, 3). Similarly, when crotyltrichlorosilane with the E/Z ratio of 21/79 was used, 2-methyl-1-phenylbut-3-en-1-ol was obtained in 91% yield with the threo to erythro ratio of 22/78.

Allylation of Furfural with Allyltrichlorosilane–Dilithium Catecholate. 1-(2-Furyl)but-3-en-1-ol was obtained in 86% yield: ^{1}H NMR (CCl_4) δ 7.3–7.1 (m, 1), 6.4–6.0 (m, 2), 6.0–5.4 (m, 1), 5.01 (d, J = 15 Hz, 1), 4.97 (d, J = 11 Hz, 1), 4.57 (t, J = 6 Hz 1), 3.27 (br s, 1), 2.50 (dd, J = 6, 5.3 Hz, 2); MS m/z (relative intensity) 138 (M^+, 0.2), 120 (98), 91 (100).

Allylation of Benzaldehyde with Allyltrichlorosilane–Dilithium 2,2′-Biphenolate System. To a THF–hexane solution of dilithium 2,2′-biphenolate (8.0 mmol) prepared with the procedure as described above were added allyltrichlorosilane (702 mg, 4.00 mmol) and THF (10 mL) at room temperature under argon. After the resultant mixture was

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stirred for 1 h, benzaldehyde (212 mg, 2.00 mmol) in THF (10 mL) was added dropwise. After being refluxed for 90 h, the reaction mixture was hydrolyzed. After the usual workup, preparative TLC afforded 1-phenylbut-3-en-1-ol in 85% yield.

Reaction of Benzaldehyde with Prenyltrichlorosilane–Dilithium α,α-Bis(trifluoromethyl)benzenemethanolato(2–)-C^2,O System. To a dilithium compound prepared from hexafluorocumyl alcohol (1.490 g, 8.00 mmol) in THF–hexane (ref 21, method B) were added allyltrichlorosilane (702 mg, 4.00 mmol) and THF (10 mL) at room temperature. After the resultant mixture was stirred for 1 h, benzaldehyde (212 mg, 2.00 mmol) in THF (10 mL) was added to the mixture. No allylation products of benzaldehyde were found in the reaction mixture by GLC analysis even after refluxing for 90 h.

Isolation of Bis(triphenylphosphoranylidene)ammonium Bis(1,2-benzenediolato)allylsilicate (3a). To dilithium catecholate (8.0 mmol) in THF–hexane was added allyltrichlorosilane (4.00 mmol) in THF (20 mL), and the mixture was stirred for 12 h at room temperature. After removal of the solvent under vacuum followed by the addition of PPN(Cl) (2.296 g, 4.00 mmol) in CH_2Cl_2 (40 mL), the mixture was stirred for 12 h at room temperature. Filtration of the produced LiCl under argon followed by removal of the solvent under vacuum afforded a solid of the title compound quantitatively. The salt was very unstable in air and moisture, preventing further purification, but it afforded satisfactory spectral data: ^{1}H NMR ($CDCl_3$) δ 7.7–7.2 (m, 30), 6.9–6.2 (m, 8), 6.2–5.5 (m, 1), 4.60 (d, $J = 7$ Hz, 1), 4.45 (d, $J = 9$ Hz, 1), 1.72 (d, $J = 7.2$ Hz, 2); ^{13}C NMR ($CDCl_3$) δ 149.0 (s), 136.5 (d), 133.1, 131.5, 131.2, 131.0, 129.1, 128.8, 128.5, 123.7, 117.2 (d), 110.6 (t), 110.3 (d), 24.1 (t); ^{29}Si NMR ($CDCl_3$) δ –78.8; negative-ion FAB MS m/e –285 (anion).

Bis(triphenylphosphoranylidene)ammonium Bis(1,2-benzenediolato)prenylsilicate (3b): ^{1}H NMR ($CDCl_3$) δ 7.7–7.2 (m, 30), 6.9–6.2 (m, 8), 5.37 (d, $J = 8$ Hz, 1), 1.61 (d, $J = 8$ Hz, 2), 1.40 (s, 3), 1.31 (s, 3); ^{13}C NMR ($CDCl_3$) δ 150.1 (s), 133.8, 132.2, 131.9, 131.7, 129.8, 129.4, 129.2, 124.4, 118.4 (d), 117.4 (s), 115.6 (d), 110.6 (d), 26.4 (t), 25.7 (q), 17.5 (q); ^{29}Si NMR ($CDCl_3$) δ –77.3; negative-ion FAB MS m/e –313 (anion).

Bis(triphenylphosphoranylidene)ammonium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2–)-C^2,O]allylsilicate (6a). To a dilithium compound of hexafluorocumyl alcohol in THF–hexane prepared with the literature method[21] by using hexafluorocumyl alcohol (1.952 g, 8.00 mmol) were added allyltrichlorosilane (4.00 mmol) and THF (20 mL) at room temperature, and then the mixture was stirred for 12 h. After filtration of LiCl salts, the organic layer was washed with water and dried over anhydrous Na_2SO_4 and the solvent was evaporated. The crude product was purified by reprecipitation from acetone–diethyl ether: 85% yield; white crystals; mp 145–148 °C; ^{1}H NMR ($CDCl_3$) δ 8.3–8.1 (m, 2), 7.7–7.0 (m, 36), 6.13 (ddd, $J = 16.5, 9.0, 8.3$ Hz, 1), 4.52 (dd, $J = 16.5, 3.0$ Hz, 1), 4.35 (dd, $J = 9.0, 3.0$ Hz, 1), 1.93 (d, $J = 8.3$ Hz, 2); ^{13}C NMR ($CDCl_3$) δ 144.6 (s), 141.2 (s), 141.0 (d), 137.9 (d), 133.8, 132.1, 132.0, 131.9, 129.6, 129.5, 129.4, 128.0 (d), 127.8 (d), 125.8, 123.3 (d), 108.9 (t), 81.9 (sep), 31.5 (t); ^{29}Si NMR ($CDCl_3$) δ –66.6; negative-ion FAB MS m/e –553 (anion).

Bis(triphenylphosphoranylidene)ammonium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2–)-C^2,O]prenylsilicate (6b): 81% yield, white crystals; mp 151–151.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.3–8.1 (m, 2), 7.7–7.0 (m, 36), 5.42 (t, $J = 8$ Hz, 1), 1.78 (d, $J = 8$ Hz, 2), 1.45 (s, 3), 1.38 (s, 3); ^{13}C NMR ($CDCl_3$) δ 145.1 (s), 141.1 (s), 137.7 (d), 133.8, 132.2, 131.9, 131.7, 129.8, 129.4, 129.2, 127.6 (d), 127.4 (d), 125.3 (d), 124.5, 123.0 (d), 119.2 (s), 26.0 (t), 24.5 (q), 17.4 (q); ^{29}Si NMR ($CDCl_3$) δ –65.4.

Reaction of 3a with Benzaldehyde. A mixture of **3a** (1.648 g, 2 mmol), benzaldehyde (110 mg, 1.00 mmol), and THF (10 mL) was refluxed for 90 h under argon. The usual workup afforded 2,2-dimethyl-1-phenylbut-3-en-1-ol in 90% yield, which was determined by GLC.

Reaction of 3b with Benzaldehyde. A mixture of **3b** (1.704 g, 2.00 mmol), benzaldehyde (110 mg, 1.00 mmol), and THF (10 mL) was refluxed under argon for 90 h. The usual workup afforded 2,2-dimethyl-1-phenylbut-3-en-1-ol in 80% yield. No other regioisomers were detected by GLC and ^{1}H NMR spectra.

Reaction of 6b with Benzaldehyde. A mixture of **6b** (2.184 g, 2.00 mmol), benzaldehyde (110 mg, 1.00 mmol), and THF (10 mL) was refluxed for 90 h. No allylation products were found in the reaction mixture. A similar experiment in the presence of excess CsF did not give the desired products.

Modeling Chemical Reactivity. 9. The Role of the Metal in Controlling the Stereochemistry of Nucleophilic Additions of Organometallic Reagents

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Abstract: The stereochemistry of nucleophilic addition of organometallic reagents to unsaturated organic substrates depends on at least three factors: (1) the accessibility of the metal, (2) the degree of reagent ion pairing in solution, and (3) the ability of the substrate to discriminate between the nucleophilic and electrophilic character of the reagent. Reagents such as $LiAl(CH_3)_4$ behave as if they were fully separated ion pairs; the lithium cation plays little if any role in the selectivity of tetramethylaluminate anion. A similar situation prevails for reagents such as methyltitanium triisopropoxide, the metal that is shielded from the substrate by its ancillary ligands. On the other hand, Grignard, dialkylmagnesium, and alkyllithium compounds incorporate accessible and highly electrophilic metal centers, which are able to interact with the substrate and influence the stereochemical outcome of the addition process. It is suggested that nucleophiles that are associated with an accessible electrophilic metal will show opposite stereochemical preferences from "free" nucleophiles or compounds where the metal center is shielded from the substrate. Available experimental data on stereoselectivities of Michael additions to chiral vinylic sulfoxides with different reagents provide support for such a classification of nucleophilic reagents. The effects of solvent upon asymmetric additions involving nucleophilic reagents are addressed. It is argued that solvation is of relatively minor importance in determining reaction asymmetries in this class of additions.

Few classes of compounds have contributed to selective carbon–carbon bond forming reactions as significantly as have metalated organic reagents.[1] The variety of organic substrates known to undergo facile transformations upon treatment with organometallic compounds has prompted development of reagents for novel synthetic applications and has spurred efforts toward

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