

Articles

Synthesis and Structural Characterization of Functional Bicyclic Intramolecularly Coordinated Aminoarylsilanes in a Series of Dibenzyl(1,5)azasilocines

Francis H. Carré, Robert J. P. Corriu,* Gérard F. Lanneau,* Philippe Merle, Florence Soulairol, and Jiachang Yao

Laboratoire des Précurseurs Organométalliques de Matériaux, UMR 044 Université Montpellier II, Case 007, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France

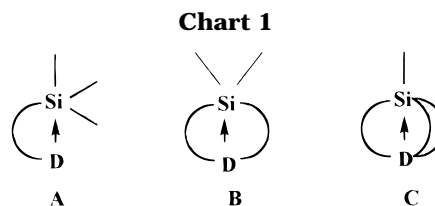
Received April 28, 1997[®]

A new synthetic approach to functional eight-membered silicon-containing heterocycles has been developed. The intramolecular coordination of chelated aminoaryl ligands, $-o\text{-C}_6\text{H}_4\text{-CH}_2\text{-N(R)-CH}_2\text{-C}_6\text{H}_4\text{-}o\text{-}$, with $\text{R} = \text{t-Bu, i-Pr, PhCH}_2$, results in rigid molecules of the type $\text{R-NCH}_2\text{C}_6\text{H}_4\text{Si(XY)C}_6\text{H}_4\text{CH}_2$, ($\text{X} = \text{Y} = \text{H, OMe, F}$ and $\text{X} = \text{H, Y} = \text{F, Cl, Br, I, OMe, OTf}$). Two types of molecules are characterized in the refined structure of $\text{t-BuNCH}_2\text{C}_6\text{H}_4\text{-Si(F)}_2\text{C}_6\text{H}_4\text{CH}_2$. Pentacoordination of the silicon atom is observed, with the donor atom and one fluorine atom occupying axial sites in an overall trigonal bipyramidal geometry (N-Si average distance of 2.43 Å). Stereodynamic rearrangements in solution are deduced from the NMR spectral data. Equivalence of the CH_2 benzylic protons (an AB system at low temperature) implies an inversion at the nitrogen atom. The activation parameters for a dissociative mechanism have been calculated, following variable-temperature NMR measurements with different probes. The activation energy barriers of the isomerization process are strongly dependent on the functional ligands X_2 attached to the silicon atom and decrease in the order for various X ligands $\text{F} > \text{H} > \text{OMe}$. A similar decrease of ΔG^\ddagger is observed by changing the R group attached to the nitrogen atom, $\text{t-Bu} > \text{i-Pr} > \text{PhCH}_2$.

Introduction

In recent investigations of the molecular structures of organosilicon or other group 14 molecules, much attention has been paid to interactions between heteroatoms which are intermediates between covalent bonds and van der Waals associations.¹ These dative bonds have been involved in Lewis-base-catalyzed nucleophilic substitutions at the silicon atom.² Examples of intramolecular coordination presented in the literature were essentially concerned with monocyclic A, bicyclic B, or tricyclic C systems (Chart 1).

Silatrane or its analogues (C) have been studied in detail, and the influence of the coordinated ligand upon the reactivity of these systems has been exploited.³ Monocyclic derivatives (A) have been investigated more



recently, and both amino ligands, developed by van Koten in the case of tin compounds,⁴ and carbonyl functionalities have been shown to be highly efficient

[®] Abstract published in *Advance ACS Abstracts*, August 1, 1997.

(1) (a) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119. (b) Tandura, S. N.; Voronkov, N. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99. (c) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; Chapter 20. (d) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (e) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17.

(2) (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; Chapter 4. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (c) Corriu, R. J. P. *Pure Appl. Chem.* **1988**, *60*, 99. (d) For a recent compilation on penta- and hexacoordinate silicon compounds as reaction intermediates, see: Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371

(3) (a) Voronkov, M. G. *Top. Curr. Chem.* **1979**, *84*, 77. (b) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483. For examples, see: (c) Frye, C. L.; Vincent, G. A.; Finzel, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 6805. (d) Attar-Bashi, M. T.; Eaborn, C.; Vencl, J.; Walton, D. R. M. *J. Organomet. Chem.* **1976**, *117*, C87. (e) Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reyé, C. *J. Organomet. Chem.* **1987**, *328*, C17. (f) Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Nayyar, N. K.; Reyé, C. *J. Organomet. Chem.* **1990**, *389*, 159.

(4) (a) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5393. (b) Jastrzebski, J. T. B. H.; Knaap, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287. (c) Corriu, R. J. P.; Royo, G.; de Saxcé, A. *J. Chem. Soc., Chem. Commun.* **1980**, 892. (d) Klebe, G.; Hensen, K.; Fuess, H. *Chem. Ber.* **1983**, *116*, 3125. (e) Onan, K. D.; McPhail, A. T.; Yoder, C. H.; Hillyard, R. W. *J. Chem. Soc., Chem. Commun.* **1978**, 209. (f) Voronkov, M. G.; Frolov, Y.-L.; D'yakov, V. M.; Chipanina, N. N.; Gubanova, L. I.; Gavrilova, G. A.; Klyba, L. V.; Aksamentova, T. N. *J. Organomet. Chem.* **1980**, *201*, 165. (g) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Y.-T.; Oleneva, G. I.; Kramarova, E. P.; Shipov, A. G.; Baukov, Y.-I. *J. Chem. Soc., Chem. Commun.* **1988**, 683.

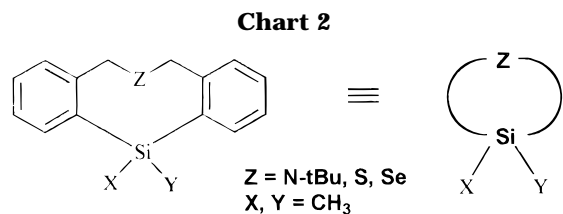


Table 1. Numbering Scheme of the Symmetrical Difunctional Silanes

| X | R | | |
|-------------------|-----------|-----------|-------------------|
| | t-Bu | i-Pr | PhCH ₂ |
| OMe | 5a | 5b | 5c |
| H | 6a | 6b | 6c |
| F | 7a | 7b | 7c |
| | 8a | | |
| SiMe ₂ | 9a | | |

for intramolecular coordination.⁵ In the case of B systems, some X-ray structural data are available with eight-membered silicon-containing heterocycles⁶ (Chart 2).

In the dibenzosilazocine ($Z = t\text{-BuN}$), described by Joyce and Eugene Corey,^{6b} the N–Si distance is 2.948–(3) Å, which indicates only a minor intramolecular interaction between the nitrogen and the silicon atom (by comparison, the sum of their van der Waals radii^{7c} is 3.4 Å). In similar sulfur- and selenium-containing derivatives, these distances X–Si are 4.159(7) and 4.271(8) Å, respectively, even larger than the sum of the respective van der Waals radii (3.90 and 4.04 Å).^{7c}

Functional organosilanes of type A containing electronegative substituents (halogens, carboxylates, ...) are generally more highly coordinated than tetraorganosilicon compounds.^{4,5} We have, therefore, decided to study functional eight-membered silicon-containing heterocycles of the dibenzosilazocine series, $R\text{-}\overline{\text{NCH}_2\text{C}_6\text{H}_4\text{-Si(X)(Y)C}_6\text{H}_4\text{CH}_2}$, that contain electronegative substituents, with the idea in mind that coordination of the nitrogen atom will be favored when the silicon atom is more electrophilic. The following notation will be used: series a for $R = t\text{-Bu}$, series b for $R = i\text{-Pr}$, and series c for $R = \text{PhCH}_2$ (Bz). The symmetrical species, **5–9**, are described in Table 1. Compounds **10c–15c**

correspond to the benzylic derivatives (series c), with $X = \text{H}$ and $Y = \text{OMe, F, Cl, Br, I, and OTf}$, respectively.

Experimental Section

All reactions were carried out under an atmosphere of dry argon. Air-sensitive products and reagents were handled by standard Schlenk techniques. Tetrahydrofuran was dried and distilled from a purple solution of sodium/benzophenone ketyl. Toluene was distilled from sodium under nitrogen. Chloroform and dichloromethane were dried with CaH_2 and distilled under nitrogen. The glassware was dried in an oven at 110–120 °C prior to use. Commercially available chemicals were used as such without any further purification. ²⁹Si, ¹³C, ¹H, and ¹⁹F NMR spectra were recorded on a Bruker WP 200 SY, AC 250, or AW 80 spectrometer. ¹H and ¹³C chemical shifts were measured against Me_4Si using the solvent resonance as a standard lock. ²⁹Si chemical shifts were referenced to external Me_4Si in the same solvent. ¹⁹F chemical shifts were referenced to CFCl_3 . IR spectra were recorded on a Perkin-Elmer 1600 FT as KBr pellets, Nujol suspension, or solutions in CaF_2 cells. The mass spectra were obtained on a JEOL JMS D100 apparatus by EI ionization at 30 or 70 eV. In some cases, positive FAB mass spectra in *m*-nitrobenzyl alcohol (NBA) were also recorded. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS in Lyon or in the ENSC Montpellier.

Preparation of the Silanes $R\text{-}\overline{\text{NCH}_2\text{C}_6\text{H}_4\text{Si(X)(Y)-C}_6\text{H}_4\text{CH}_2}$

Bromination of Bromotoluene 1. 2-Bromotoluene (60 g, 0.35 mol), benzoyl peroxide (1 g, 0.004 mol), and 200 mL of CCl_4 were added to a 500 mL three-necked flask equipped with a water-cooled reflux condenser. A solution of *N*-bromosuccinimide (62.4 g, 0.35 mol) in CCl_4 was added dropwise, and the reaction mixture was heated at reflux until the reaction started (appearance of a white cloudy precipitate of succinimide), then it was left for 2 h. The insoluble succinimide was filtered and the solution concentrated to afford **2** as a yellow oil (78.8 g, 0.315 mol, 90% yield). ¹H NMR (CDCl_3): δ 4.5 (s, 2H, CH_2Br), 7.8 (m, 4H, Ar).

Compounds of Series a, t-BuN, Derived from tert-Butylamine. Different syntheses of compounds **3–9** of series a, $R = t\text{-BuN}$ derived from *tert*-butylamine will be described in detail as being typical of the procedures used.

Preparation of *N,N*-Bis(2-bromobenzyl)*tert*-butylamine, 3a. A solution of *tert*-butylamine (11.47 g, 0.155 mol) in 100 mL of dimethylformamide (DMF) was added dropwise to a mixture of **2** (90 g, 0.36 mol) and K_2CO_3 (56.6 g, 0.4 mol). After the reaction mixture had been heated at reflux for 2 h and stirred for 12 h at room temperature, the product was extracted with ether, washed with a little water, dried over MgSO_4 , and concentrated under vacuum. The product was crystallized from a mixture of hexane/ether (80/20), mp 117 °C (37.5 g, 62% yield). ¹H NMR (CDCl_3): δ 1.17 (s, t-Bu, 9H), 3.83 (s, 4H, CH_2N), 6.80 to 7.80 (m, 8H, Ar). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NBr}_2$: C, 52.81; H, 5.17; N, 3.42. Found C, 52.74; H, 5.19; N, 3.48.

Preparation of Dimethoxysilane **5a**, $t\text{-BuNCH}_2\text{C}_6\text{H}_4\text{Si-}(\text{OCH}_3)_2\text{C}_6\text{H}_4\text{CH}_2$

A solution of *n*-BuLi (2.5 M) in hexane (0.078 mol, 31.3 mL) was added dropwise to a solution of *N,N*-bis(2-bromobenzyl)*tert*-butylamine, **3a** (16.1 g, 0.039 mol), in 100 mL of ether at –30 °C. The solution, which became red with the first drops added, was stirred at that temperature for 6 h and then allowed to warm to room temperature for an additional 2 h. The mixture was again cooled to –30 °C, and a cold solution of tetramethoxysilane (5.93 g, 39 mmol) in 90 mL of ether was added dropwise with a static-pressure dropping funnel. The solution became yellow, and a precipitate formed. The reaction mixture was maintained at –30 °C overnight and stirred for an additional 2 h at room temperature. Removal of the solvent left an oil, which was partially

(5) (a) Tzschach, A.; Jurkschat, K. *Pure Appl. Chem.* **1986**, *58*, 647. (b) Lukevics, E.; Pudova, O.; Sturkovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis Horwood: Chichester, 1989; p 10. (c) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; Chapter 3, p 227.

(6) (a) Corey, J. Y.; Janoski, H. M.; Vermount, D. F.; Paton, J. P.; Chang, V. H. T. *J. Organomet. Chem.* **1980**, *194*, 15. (b) Paton, W. F.; Corey, E. R.; Corey, J. Y.; Glick, M. D. *Acta Crystallogr.* **1977**, *33B*, 3322. (c) Larsen, W.; Corey, J. Y. *J. Am. Chem. Soc.* **1977**, *99*, 1740.

(7) (a) Soltz, B. L.; Corey, J. Y. *J. Organomet. Chem.* **1979**, *171*, 291. (b) Shklover, V. E.; Struchkov, Y.-T.; Rodin, O. G.; Traven', V. F.; Stepanov, B. I. *J. Organomet. Chem.* **1984**, *266*, 117. See also: Shklover, V. E.; Struchkov, Y.-T.; Traven', V. F.; Rodin, O. G.; Rockickaya, V. I.; Aismont, M. Y.; Stepanov, B. I. *VII International Symposium on Organosilicon Chemistry*, Kyoto, 1984, 121. (c) Bondi, A. *J. Phys. Chem.* **1966**, *70*, 3006.

redissolved in 50 mL of CH_2Cl_2 /pentane (80/20). Filtration and concentration of the filtrate gave **5a** as an oil, which was purified by distillation (155–160 °C at 0.01 mmHg) (6.52 g, 70% yield). ^1H NMR (CDCl_3): δ 1.05 (s, 9H, t-Bu), 3.68 (s, 6H, OCH_3), 3.75 (s, 4H, CH_2Ph), 6.98–8.03 (m, 8H, Ar). ^{13}C NMR (CDCl_3): δ_{C} 27.2 ($\text{C}(\text{CH}_3)_3$), 50.9 (OCH_3), 54.7 ($\text{CH}_2\text{C}_6\text{H}_4$), 57.4 ($\text{C}(\text{CH}_3)_3$), 126.5, 127.2, 130.4, 137.3, 150.6 (Ar). ^{29}Si NMR (CDCl_3): δ_{Si} –33.01 (s). MS (EI, 70 eV, m/e): 341 (M^+), 314, 284, 326, 310, 252. Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_2\text{Si}$: C, 70.33; H, 7.97; N, 4.10; Si, 8.22. Found: C, 70.68; H, 7.90; N, 4.15; Si, 8.11.

Preparation of Dihydrosilane **6a**, $\text{t-BuNCH}_2\text{C}_6\text{H}_4\text{Si}$

(H) $_2$ C $_6$ H $_4$ CH $_2$. A solution of dimethoxysilane **5a** (1.36 g, 4 mmol) in 100 mL of ether was added from a static-pressure dropping funnel to a solution of LiAlH_4 (0.11 g, 3 mmol) in 100 mL of ether at 0 °C. The reaction mixture was left at room temperature for 48 h. After filtration of the salts, the solution was hydrolyzed with crushed ice, dried over MgSO_4 , and filtered again. The solvent was evaporated under vacuum. Distillation (115–125 °C, 0.01 mmHg) gave **6a** (0.82 g, 73% yield). ^1H NMR (CDCl_3): δ 1.05 (s, 9H, t-Bu), 3.79 (br s, 4H, CH_2N), 5.28 (s, 2H, SiH_2), 6.82–7.92 (m, 8H, Ar). ^{13}C NMR (CDCl_3): δ_{C} 27.3 ($\text{C}(\text{CH}_3)_3$), 55.3 (CH_2N), 58.1 ($\text{C}(\text{CH}_3)_3$), 125.8, 127.1, 130.4, 138.4, 148.5 (Ar). ^{29}Si NMR (CDCl_3): δ_{Si} –41.76 (dd, $J_{\text{SiH}} = 185, 187$ Hz). IR (CCl_4): ν_{SiH} 2157, 2056 cm^{-1} . MS (FAB): 281 (M^+), 280 ($\text{M}^+ - 1$), 266 ($\text{M}^+ - \text{CH}_3$). Anal. Calcd for $\text{C}_{18}\text{H}_{23}\text{NSi}$: C, 76.81; H, 8.24; N, 4.98. Found C, 77.03; H, 8.50; N, 4.72.

Preparation of Difluorosilane **7a**, $\text{t-BuNCH}_2\text{C}_6\text{H}_4\text{Si}$

(F) $_2$ C $_6$ H $_4$ CH $_2$, from Dimethoxysilane **5a**. Dimethoxysilane **5a** (2.2 g, 6.45 mmol) was diluted with 20 mL of hexane, and the solution was cooled to 0 °C. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.55 mL, 4.5 mmol) was added dropwise, and the reaction mixture was stirred for 3 h at room temperature. The solvent was evaporated, and 20 mL each of dichloromethane and hexane were added. The mixture was filtered, and the solvents were removed under vacuum. Difluorosilane **7a** was distilled (120–130 °C at 0.1 mmHg) (2.03 g, 98% yield). ^1H NMR (CDCl_3): δ 1.06 (s, 9H, t-Bu), 3.46 and 4.08 (AB system, $^2J_{\text{HH}} = 47$ Hz), 6.90–7.43 (6H, Ar), 7.88–8.12 (2H, Ar). ^{19}F NMR (CDCl_3): δ_{F} –142.3 (d), –132.7 (d), $J_{\text{FF}} = 19$ Hz. ^{29}Si NMR (CDCl_3): δ_{Si} –48.75 (dd, $J_{\text{SiF}1} = 269$ Hz, $J_{\text{SiF}2} = 257$ Hz). MS (EI): 317 (M^+), 316 ($\text{M}^+ - 1$), 301 ($\text{M}^+ - \text{CH}_4$). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NSiF}_2$: C, 68.10; H, 6.69; N, 4.43; Si, 8.84. Found C, 68.20; H, 6.79; N, 4.48; Si, 8.69.

Preparation of Silane **8a**, $\text{t-BuNCH}_2\text{C}_6\text{H}_4\text{Si}[\text{CH}_2\text{C}$

(CH $_3$)=C(CH $_3$)CH $_2$] $_2$ C $_6$ H $_4$ CH $_2$. Difluorosilane **7a** (1.5 g, 4.73 mmol), 2,3-dimethyl-1,3-butadiene (0.58 g, 6.93 mmol), and lithium wire (0.067 g, 9.5 mmol) in 10 mL of THF were stirred at room temperature under nitrogen for 20 h. The initial brown color of the mixture disappeared after the lithium was consumed. The solvent was removed under vacuum; 20 mL of hexane was added, and the suspension was filtered. The solvent was evaporated. Kugelrohr distillation (160 °C, 0.2 mmHg) gave **8a** (0.86 g, 50% yield). ^1H NMR (CDCl_3): δ 1.05 (s, t-Bu), 1.75 (CH_2), 1.91 (CH_3), 3.80 (br s, 4H, CH_2N), 6.90–7.26, 7.51–7.73 (Ar). ^{13}C NMR (CDCl_3): δ_{C} 19.70 ($\text{CH}_3\text{C}=\text{C}$), 27.17 ($\text{C}(\text{CH}_3)_3$), 27.31 ($\text{SiCH}_2\text{C}=\text{C}$), 57.25 ($\text{C}(\text{CH}_3)_3$), 54.70 (NCH_2Ph), 125.0–150.0 (C sp^2). ^{29}Si NMR (CDCl_3): δ_{Si} –4.01. MS (EI): 361 (M^+), 360 ($\text{M}^+ - 1$), 278, 222. Redistillation of the oil which had been washed with water and extracted with ether failed to produce an analytical sample.

Preparation of Silane **9a**,^{6a} $\text{t-BuNCH}_2\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_2$

C $_6$ H $_4$ CH $_2$. A solution of methyllithium (7.9 mL, 11.8 mmol, 1.5 M in ether) was added dropwise to dimethoxysilane **5a** (2.0 g, 5.9 mmol) and dissolved in 50 mL of ethyl ether, and the mixture was stirred at room temperature for 1 day. After hydrolysis with saturated NH_4Cl , the ether layer was sepa-

rated, washed with water, dried over MgSO_4 , and concentrated. The crude product was purified by Kugelrohr distillation (120 °C, 0.01 mmHg) to give **9a** (1.5 g, 82% yield), from which the ^1H NMR spectrum was identical with that of authentic sample.^{6a} ^1H NMR (CDCl_3): δ 0.68 (s, 6H, Me_2Si), 1.14 (s, 9H, t-Bu), 3.92 (s, 4H, NCH_2Ph), 7.0–7.42, 7.70–7.85 (Ar). ^{13}C NMR (CDCl_3): δ_{C} 3.1 (SiMe_2), 26.9 ($\text{C}(\text{CH}_3)_3$), 57.1 ($\text{C}(\text{CH}_3)_3$), 54.5 (NCH_2Ph), 149.7, 136.1, 129.7, 128.1, 126.9 (C sp^2). ^{29}Si NMR (CDCl_3): δ_{Si} –13.49.

Preparation of 4,4,5,5-Tetramethyl-1,3-dioxo-2-silacyclopentane Derivative **16a**. Dihydrosilane **6a** (4.27 g, 15.2 mmol) and pinacol (1.8 g, 15.2 mmol) were mixed in 50 mL of CCl_4 and stirred at 60 °C for 15 days. Removal of the solvent under vacuum left a solid residue, which was recrystallized from a mixture of dichloromethane and hexane (20/80), giving **16a** (4.2 g, 10.5 mmol, 70% yield), mp 170–171 °C. ^1H NMR (CDCl_3): δ 1.16 (s, 6H, $(\text{CH}_3)_A$), 1.22 (9H, t-Bu), 1.27 (s, 6H, $(\text{CH}_3)_B$), 3.46–4.15 (4H, AB system, $^2J_{\text{HH}} = 47$ Hz), 6.80–7.38, 7.87–8.13 (Ar). ^{13}C NMR (CDCl_3): δ_{C} 26.45, 26.64, 27.13 ($(\text{C}(\text{CH}_3)_3$), 55.03 (NCH_2Ph), 59.37 ($\text{C}(\text{CH}_3)_3$), 79.64 ($\text{C}(\text{CH}_3)_2$), 80.16 ($\text{C}(\text{CH}_3)_2$), 125.03, 126.73, 129.92, 134.81, 136.75, 148.11 (C sp^2). ^{29}Si NMR (CDCl_3): δ_{Si} –33.22. MS (EI): 396 ($\text{M}^+ + 1$), 380 ($\text{M}^+ - \text{CH}_3$), 338 ($\text{M}^+ - \text{t-Bu}$), 280, 238, 222. Anal. Calcd for $\text{C}_{24}\text{H}_{33}\text{NO}_2\text{Si}$: C, 72.91; H, 8.35; N, 3.57. Found: C, 72.97; H, 8.51; N, 3.43.

Compounds of Series b, i-PrN, Derived from Isopropylamine. Preparation of *N,N*-Bis(2-bromobenzyl)isopropylamine, **3b**. The reaction of isopropylamine (5.6 g, 0.096 mol) in 100 mL of DMF with *o*-bromobenzyl bromide (47.9 g, 0.19 mol) and K_2CO_3 (65.6 g, 0.47 mol) was performed under the same conditions described above for **3a**. After that usual work-up, the syrupy material was purified by distillation (160–170 °C, 0.01 mmHg) to give **3b** as a yellow viscous oil (27.6 g, 72% yield). ^1H NMR (CDCl_3): δ 1.0 (d, 6H, $^2J_{\text{HH}} = 6.5$ Hz), 2.9 (m, 1H), 3.6 (s, 4H), 6.6–7.6 (m, 8H, Ar). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NBr}_2$: C, 51.41; H, 4.82; N, 3.53. Found C, 51.52; H, 4.79; N, 3.48.

Preparation of Dimethoxysilane **5b**, $\text{i-PrNCH}_2\text{C}_6\text{H}_4\text{Si}$

(OCH $_3$) $_2$ C $_6$ H $_4$ CH $_2$. The method was the same as that for compound **5a**. A solution of *n*-BuLi in hexane (0.175 mol, 75 mL) was added dropwise to a solution of **3b** (27.5 g, 0.07 mol) in 100 mL of ether at –30 °C. A cold solution of tetramethoxysilane (10.6 g, 0.07 mol) in 90 mL of ether was added dropwise. The reaction mixture was left at –30 °C for 12 h and 2 h at room temperature. Evaporation of the solvents under vacuum left an oil, which was Kugelrohr distilled (150–170 °C, 0.01 mmHg) before crystallization in a mixture of CH_2Cl_2 /pentane (80/20) to give white crystals of **5b** (10.1 g, 45% yield), mp 107 °C. ^1H NMR (CDCl_3): δ 1.1 (d, 6H, $^2J_{\text{HH}} = 6.5$ Hz), 3.4 (m, 1H), 3.8 (s, 10H, OCH_3 , CH_2Ph), 7.1–7.4, 8.1 (m, 8H, Ar). ^{13}C NMR (CDCl_3): δ_{C} 18 (OCH_3), 23 (i-Pr), 45–55 (CH_2Ph , i-Pr), 120–150 (Ar). ^{29}Si NMR (CDCl_3): δ_{Si} –43 (s). MS (EI, 70 eV, m/e): 327 (M^+ , 20), 312 (60), 284 (100). For analytical purposes, **5b** was recrystallized from hexane, mp 107.5 °C. Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2\text{Si}$: C, 69.68; H, 7.69. Found: C, 69.72; H, 7.71.

Preparation of Dihydrosilane **6b**, $\text{i-PrNCH}_2\text{C}_6\text{H}_4\text{Si}$

(H) $_2$ C $_6$ H $_4$ CH $_2$. Reduction of dimethoxysilane **5b** (1.2 g, 6 mmol) with LiAlH_4 (1.27 g, 33 mmol) in 200 mL of ether at 25 °C after the usual work-up gave 1.4 g of **6b** (84% yield). The crude solid material was recrystallized twice from cyclohexane, mp 123–124 °C. ^1H NMR (CDCl_3): δ 1.0 (d, 6H, $^2J_{\text{HH}} = 6.5$ Hz), 3.1 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.7 (s, 4H, CH_2N), 5.4 (br s, 2H, SiH_2), 6.8–7.9 (m, 8H, Ar). ^{29}Si NMR (CDCl_3): δ_{Si} –45.2 (t, $J_{\text{SiH}} = 181$ Hz). IR (CCl_4): ν_{SiH} 2100, 2034 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NSi}$: C, 76.35; H, 7.91. Found: C, 76.52; H, 7.89.

Preparation of Difluorosilane **7b**, $\text{i-PrNCH}_2\text{C}_6\text{H}_4\text{Si}$

(F) $_2$ C $_6$ H $_4$ CH $_2$. Using the same experimental conditions as those for the preparation of **7a**, dimethoxysilane **5b** (2.5 g, 7

mmol) was reacted with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.1 mL, 9 mmol) for 4 h at room temperature. Then 10 mL of water was added, the mixture was extracted three times by 20 mL of ether and dried over magnesium sulfate, and the solvent was removed under vacuum. Trituration of the crude material with hexane left **7b** as a solid residue, which was recrystallized from hexane (1.8 g, 80% yield), mp 149–152 °C. ^1H NMR (CD_2Cl_2): δ 1.05 (d, 6H, $\text{CH}(\text{CF}_3)_2$, $^2J_{\text{HH}} = 6.5$ Hz), 3.15 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.74, 4.16 (AB system, $^2J_{\text{HH}} = 16$ Hz), 7.10–7.50 (6H, Ar), 8.00 (2H, Ar). ^{13}C NMR (CDCl_3): δ_{C} 16.7, 18.4, 55.5, 56.7, 124.3, 127.2, 131.8, 135.9, 146. ^{19}F NMR (CDCl_3): δ_{F} –138.2 (d), –153.0 (d), $J_{\text{FF}} = 20$ Hz. ^{29}Si NMR (CDCl_3): δ_{Si} –61.5 (dd, $J_{\text{SiF}_1} = 260$ Hz and $J_{\text{SiF}_2} = 256$ Hz). MS (EI): 303 (15), 288 (100). For analytical purposes, **7b** was recrystallized from hexane, mp 152 °C. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NSiF}_2$: C, 67.29; H, 6.31. Found: C, 67.55; H, 6.11.

Compounds of Series c, N-Bz, Derived from Benzylamine. Preparation of 3c. A solution of benzylamine (15.82 g, 0.145 mol) in 50 mL of DMF was added dropwise to a mixture of **2** (73.87 g, 0.29 mol) and K_2CO_3 (51 g, 0.36 mol). After the reaction mixture had been heated at reflux for 2 h and stirred for 12 h at room temperature, the product was extracted with ether, washed with water, dried over MgSO_4 , and concentrated under vacuum to give an oil. Distillation at 170 °C, 0.01 mmHg, of the crude product gave **3c** (45 g, 70% yield). ^1H NMR (CDCl_3): δ 3.6 (s, 2H, CH_2Ph), 3.7 (s, 4H, CH_2N), 6.8–7.8 (m, 13H, Ar).

Preparation of Dimethoxysilane 5c, Bz–NCH₂C₆H₄Si–

(OCH₃)₂C₆H₄CH₂. The method was the same as that for compound **5a**, using *n*-BuLi in hexane (0.2 mol, 101 mL) and **3c** (45 g, 0.1 mol), followed by addition of tetramethoxysilane (15.3 g, 0.1 mol). After work-up, Kugelrohr distillation afforded 20.6 g of **5c** (190 °C, 0.01 mmHg, 55% yield). ^1H NMR (CDCl_3): δ 3.62 (s, 4H, CH_2N), 3.71 (s, 8H, OCH₃, CH_2Ph), 6.98–8.03 (m, 13H, Ar). ^{13}C (CDCl_3): δ_{C} 51.43 (OCH₃), 54.78 (CH_2Ph), 55.96 (CH_2N), 126.54, and 146.94 (Ar). ^{29}Si (CDCl_3): δ_{Si} –46.3 (s). For analytical purposes, **5c** was recrystallized from a toluene/hexane mixture (10/90), mp 67–69 °C. Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{NSiO}_2$: C, 73.56; H, 6.71. Found: C, 73.47; H, 6.68.

Preparation of Dihydrosilane 6c, Bz–NCH₂C₆H₄Si–

(H)₂C₆H₄CH₂. Reduction of dimethoxysilane **5c** (15 g, 40 mmol) with LiAlH_4 (3.8 g, 0.1 mol) in 100 mL of ether at 0 °C was conducted as for **6a**. After work-up, crystallization from CH_2Cl_2 /hexane afforded **6c** as a yellow powder (7.57 g, 60% yield), mp 96–99 °C. ^1H NMR (CDCl_3): δ 3.65 (br s, 6H, CH_2N , CH_2Ph), 5.00 (s, 2H, SiH₂), 6.88–8.03 (m, 13H, Ar). ^{13}C NMR (CDCl_3): δ_{C} 55.24 (CH_2N), 55.76 (CH_2Ph), 126.17, 145.36 (Ar). ^{29}Si NMR (CDCl_3): δ_{Si} –48.92 (dd, $J_{\text{SiH}_1} = 210$ Hz, $J_{\text{SiH}_2} = 212$ Hz). IR (CCl_4): ν_{SiH} 2109, 2030 cm^{-1} . For analytical purposes, **5c** was recrystallized from hexane, mp 106.5 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{NSi}$: C, 79.95; H, 6.71. Found: C, 80.02; H, 6.73.

Preparation of Difluorosilane 7c, Bz–NCH₂C₆H₄Si–

(F)₂C₆H₄CH₂. (a) **From Dimethoxysilane 5c.** Dimethoxysilane **5c** (10 g, 26.7 mmol) was diluted in 50 mL of ether, and the solution was cooled to 0 °C. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (3.94 mL, 26.7 mmol) was added dropwise, and the reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated under reduced pressure, yielding the difluorosilane **7c** as a white powder, which was recrystallized from CH_2Cl_2 /hexane (20/80), mp 137–143 °C (7 g, 75% yield). ^1H NMR (CDCl_3): δ 3.44, 3.96 (AB system, $^2J_{\text{HH}} = 14.7$ Hz, 4H, CH_2N), 3.85 (s, 2H, CH_2Ph), 6.86–8.22 (m, 13H, Ar). ^{13}C NMR (CDCl_3): δ_{C} 55.44 (CH_2N), 56.37 (CH_2Ph), 125.49, 144.98 (Ar). ^{29}Si NMR (CDCl_3): δ_{Si} –63.54 (dd, $J_{\text{SiF}_1} = 254.5$ Hz, $J_{\text{SiF}_2} = 266.3$ Hz). ^{19}F NMR (CDCl_3): δ_{F} –133.0 (d, $J_{\text{FF}} = 20.2$ Hz), –152.9 (d, $J_{\text{FF}} = 20.2$ Hz). For analytical purposes, **5c** was recrystallized from a toluene/hexane mixture (10/90), mp 143–

144 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{NSiF}_2$: C, 71.76; H, 5.45. Found: C, 71.67; H, 5.41.

(b) **From Dihydrosilane 6c.** Under similar conditions as those used above, boron trifluoride diethyl etherate (0.2 mL, 3.17 mmol) was added dropwise to dihydrosilane **6c** (1 g, 3.17 mmol) in 20 mL of ether at room temperature. Evaporation of the solvent under reduced pressure left **7c** as a white solid, mp 140–143 °C (1 g, yield 90%), identified by comparison of its NMR spectra (^1H , ^{19}F , and ^{29}Si) with those of an authentic sample (*vide supra*).

(c) **Via Ph₃C⁺BF₄[–].** A solution of $\text{Ph}_3\text{C}^+\text{BF}_4^-$ (1.57 g, 4.76 mmol) in 10 mL of CH_2Cl_2 was added with a cannula to a solution of dihydrosilane **6c** (1.5 g, 4.76 mmol) in 20 mL of CH_2Cl_2 . The reaction mixture was stirred for 1 h, and the solution was concentrated under vacuum to give the difluorosilane **7c** (1.45 g, 87% yield), identified as described above.

(d) **Via Silver Tetrafluoroborate.** A solution of AgBF_4 (0.48 g, 2.5 mmol) in 10 mL of CH_2Cl_2 was added with a cannula to a solution of dihydrosilane **6c** (0.78 g, 2.5 mmol) in 10 mL of CH_2Cl_2 at room temperature and left for 1 h. After filtration, the solvent was eliminated under vacuum to give a white powder, which was washed with a little ether and dried under vacuum to afford pure difluorosilane **7c**, mp 142–144 °C (0.84 g, yield 96%). Again, the NMR spectra (^1H , ^{19}F and ^{29}Si) were similar to those of an authentic sample (method a).

(e) **From Hydrochlorosilane 12c.** A solution of hydrochlorosilane **12c** (0.5 g, 1.58 mmol) in 20 mL of CCl_4 was added to cesium fluoride (0.73 g, 4.8 mmol), previously dried by heating at 200 °C, 10^{-2} mmHg, under a flow of dry argon. The reaction mixture was heated at reflux for 3 h, and after filtration, the solvent was evaporated under vacuum to afford difluorosilane **7c** as a white solid, mp 142–144 °C (0.54 g, 96% yield), identified by comparison of its NMR spectra (^1H , ^{19}F and ^{29}Si) with those of an authentic sample.

Preparation of Silanes 10c–15c, Bz–NCH₂C₆H₄Si(H)–

(X)C₆H₄CH₂. Preparation of Hydromethoxysilane 10c,

Bz–NCH₂C₆H₄Si(H)(OMe)C₆H₄CH₂. The method was the same as that for the preparation of dimethoxysilane **5c**, with trimethoxysilane, $\text{HSi}(\text{OMe})_3$, as the starting material. The hydromethoxysilane **10c** was obtained as a yellow powder in 65% yield after recrystallization from CH_2Cl_2 /hexane (10/90). ^1H NMR (CD_2Cl_2): δ 3.86, 3.50 (AB system, $^2J_{\text{HH}} = 15.2$ Hz, 4H, CH_2N), 3.80 (s, 3H, OCH₃), 3.69 (s, 2H, CH_2Ph), 5.23 (s, 1H, SiH), 6.8–8.0 (m, 13H, Ar). ^{13}C NMR (CD_2Cl_2): δ_{C} 55.3 (CH_2N), 56.2 (CH_2Ph), 58.3 (OCH₃), 122.9–140.6 (Ar). ^{29}Si NMR (CD_2Cl_2): δ_{Si} –45.4 (d, $J_{\text{SiH}} = 242$ Hz). Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{NSiO}$: C, 76.48; H, 6.71. Found: C, 76.64; H, 6.63.

Preparation of Hydrofluorosilane 11c, Bz–NCH₂C₆H₄Si–

(H)(F)C₆H₄CH₂. (a) **From Cesium Fluoride and Hydrochlorosilane 12c.** A solution of hydrochlorosilane **12c** (0.5 g, 1.43 mmol) in 10 mL of CCl_4 was added by cannula to 0.22 g of cesium fluoride in 10 mL of CCl_4 . After 12 h, filtration of the salts and evaporation of the solvent gave **11c** as a white powder, mp 155–157 °C, (0.29 g, yield 61%), identified by comparison of its NMR spectra (^{19}F and ^{29}Si) with those of an authentic sample, described in the next paragraph.

(b) **From BF₃·Et₂O with 6c.** $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.1 mL, 0.81 mmol) was added by syringe to dihydrosilane **6c** (0.51 g, 1.62 mmol) in 10 mL of ether. The reaction was immediate, with the formation of a yellow precipitate, which was filtered, washed with ether, and dried under vacuum (0.44 g, yield 81%), mp 156–158 °C. ^1H NMR (CD_2Cl_2): δ 3.52, 3.92 (AB system, $^2J_{\text{HH}} = 14.4$ Hz, 4H, CH_2N), 3.78 (s, 2H, CH_2Ph), 5.12 (d, $J_{\text{HF}} = 80$ Hz, 1H, SiH), 6.97–8.00 (m, 13H, Ar). ^{13}C NMR (CD_2Cl_2): δ_{C} 55.93 (CH_2N), 56.77 (CH_2Ph), 125–144.4 (Ar). ^{29}Si NMR (CD_2Cl_2): δ_{Si} –55.2 (dd, $J_{\text{SiF}} = 275$ Hz, $J_{\text{SiH}} = 255$ Hz). ^{19}F NMR (CD_2Cl_2): δ_{F} –145 (d, $J_{\text{HF}} = 80$ Hz). IR (KBr): ν_{SiH} 2124 cm^{-1} . MS (EI, 70 eV, *m/e* (relative intensity)): 333 (M^+ , 4), 260 (46), 242 (10), 91 (100). For analytical purposes,

11c was recrystallized from hexane, mp 163 °C. Anal. Calcd for $C_{21}H_{20}NSiF$: C, 75.64; H, 6.04. Found: C, 75.67; H, 6.11.

Preparation of Hydrochlorosilane **12c**, $Bz-NCH_2-$

$C_6H_4Si(H)(Cl)C_6H_4CH_2$. (a) From Chlorotrimethylsilane and **6c.** Chlorotrimethylsilane (0.25 mL, 2 mmol) was added by syringe to a solution of dihydrosilane **6c** (0.63 g, 2 mmol) in 20 mL of CCl_4 at room temperature, and the reaction mixture was left for 24 h. The solvent was evaporated under vacuum to give **12c** as a white powder (0.59 g, yield 84%), which was recrystallized from a mixture of CH_2Cl_2 and hexane (10/90), mp 201–203 °C. ^{29}Si NMR ($CDCl_3$): δ -61.17 (d, J_{SiH} = 278.5 Hz). IR (KBr): ν_{SiH} 2144 cm^{-1} . Anal. Calcd for $C_{21}H_{20}NSiCl$: C, 72.10; H, 5.72. Found: C, 71.94; H, 5.71.

(b) From *N*-Chlorosuccinimide and **6c.** A solution of *N*-chlorosuccinimide (0.84 g, 6.34 mmol) was added to a solution of dihydrosilane **6c** (2 g, 6.34 mmol) in 20 mL of CCl_4 at room temperature. After 15 min, the succinimide was filtered and the solvent was evaporated under vacuum to give 2 g of a white powder, mp 200–202 °C, which was identified as **12c** (90% yield) by comparison of its NMR spectra (1H and ^{29}Si) with those of an authentic compound (next paragraph).

(b) From PCl_5 and **6c.** A solution of PCl_5 (0.67 g, 6.5 mmol) in 20 mL of THF was added by cannula to a solution of dihydrosilane **6c** (2.05 g, 6.5 mmol) in 20 mL of THF at room temperature. The reaction was immediate, and the solvent was evaporated under vacuum to give the product as a white powder, which was washed with ether and recrystallized in CH_2Cl_2 /hexane (20/80) (1.7 g, yield 75%), mp 203 °C. 1H NMR (CD_2Cl_2): δ 3.6, 4.0 (AB system, $^2J_{HH}$ = 16 Hz, 4H, CH_2N) 3.9 (s, 2H, CH_2Ph), 5.73 (s, 1H, SiH), 6.8–8.6 (m, 13H, Ar). ^{13}C NMR (CD_2Cl_2): δ 55.7 (CH_2N), 56.4 (CH_2Ph), 124.9–143.4 (Ar). ^{29}Si NMR (CD_2Cl_2): δ -61.05 (d, J_{SiH} = 278 Hz). IR (KBr): ν_{SiH} 2145 cm^{-1} . MS (EI, 70 eV, *m/e* (relative intensity)): 348 (M^+ , 12), 314 (23), 270 (24), 258 (72), 91 (100). Anal. Calcd for $C_{21}H_{20}NSiCl$: C, 72.10; H, 5.72; N, 4.01. Found: C, 71.94; H, 5.71; N, 4.08.

Preparation of Hydrobromosilane **13c**, $Bz-NCH_2-$

$C_6H_4Si(H)(Br)C_6H_4CH_2$. (a) From Bromotrimethylsilane and **6c.** The method was the same as that for chlorotrimethylsilane giving **12c**. Bromotrimethylsilane (0.27 mL, 2 mmol) was added to dihydrosilane **6c** (0.63 g, 2 mmol) in 20 mL of CCl_4 . After work-up, **13c** (0.63 g, 80% yield) was recrystallized from a mixture of dichloromethane and hexane (50/50), mp 191–193 °C (dec). The ^{29}Si NMR (CD_2Cl_2) spectrum of **13c** obtained here is identical with that of the compound described in the next paragraph. Anal. Calcd for $C_{21}H_{20}NSiBr$: C, 63.95; H, 5.11. Found: C, 63.78; H, 5.16.

(b) From *N*-Bromosuccinimide and **6c.** The method was the same as that for the preparation of **12c** from *N*-chlorosuccinimide. *N*-Bromosuccinimide (1.13 g, 6.34 mmol) was added to dihydrosilane **6c** (2 g, 6.34 mmol) in 20 mL of CCl_4 . Hydrobromosilane **13c** was obtained in 75% yield (1.88 g), mp 186–189 °C (dec). 1H NMR (CD_2Cl_2): δ 3.56, 3.97 (AB system, $^2J_{HH}$ = 15 Hz, 4H, CH_2N), 3.78 (s, 2H, CH_2Ph), 6.06 (s, 1H, SiH), 7–8.34 (m, 13H, Ar). ^{13}C NMR (CD_2Cl_2): δ 55.74 (CH_2N), 56.33 (CH_2Ph), 124.90–143.20 (Ar). ^{29}Si NMR (CD_2Cl_2): δ Si -62.07 (d, J_{SiH} = 282 Hz). IR (KBr): ν_{SiH} 2148 cm^{-1} . MS (EI, 70 eV, *m/e* (relative intensity)): 395 (M^+ , 5), 314 (85), 302 (20), 222 (50), 91 (100).

Preparation of Hydroiodosilane **14c**, $Bz-NCH_2C_6H_4Si-$

$(H)(I)C_6H_4CH_2$. (a) From Iodotrimethylsilane and **6c.** The method was the same as that for chlorotrimethylsilane giving **12c**. Iodotrimethylsilane (0.4 g, 2 mmol) was added to dihydrosilane **6c** (0.63 g, 2 mmol) in 20 mL of CCl_4 . After work-up, hydroiodosilane **14c** was obtained as a white powder (0.53 g, yield 61%), mp 198–201 °C (dec). For analytical purposes, **14c** was recrystallized from a CH_2Cl_2 /hexane mixture (50/50), mp 203 °C (dec). Anal. Calcd for $C_{21}H_{20}NSiI$: C, 57.14; H, 4.57. Found: C, 56.97; H, 4.54.

(b) From Iodine and **6c.** A solution of iodine (0.49 g, 1.92 mmol) in 10 mL of CCl_4 was added by cannula to a solution of dihydrosilane **6c** (1.21 g, 3.84 mmol) in 20 mL of CCl_4 . After 1 h, filtration, evaporation of the solvent, and washing with CCl_4 afforded the product **14c** as a white powder in 89% yield, mp 201–204 °C (dec). **14c** was identified by comparison of its NMR spectra (1H and ^{29}Si) with those of an authentic compound (next paragraph).

(c) From Methyl Iodide and **6c.** Methyl iodide (0.2 mL, 3.17 mmol) was added to dihydrosilane **6c** (1 g, 3.17 mmol) in 20 mL of CCl_4 . After the usual work-up, **14c** was isolated in 65% yield (0.9 g), mp 204–206 °C. 1H NMR (CD_2Cl_2): δ 3.62, 4.08 (AB system, $^2J_{HH}$ = 14.4 Hz, 4H, CH_2N), 3.87 (s, 2H, CH_2Ph), 5.26 (s, 1H, SiH), 6.80–8.60 (m, 13H, Ar). ^{13}C NMR (CD_2Cl_2): δ 53.9 (CH_2N), 54.4 (CH_2Ph), 122.9–140.6 (Ar). ^{29}Si NMR (CD_2Cl_2): δ Si -62.07 (d, J_{SiH} = 282 Hz). IR (KBr): ν_{SiH} 2150 cm^{-1} . MS (EI, 70 eV, *m/e* (relative intensity)): 440 (M^+ , 4), 314 (20), 222 (18), 91 (100). Anal. Calcd for $C_{21}H_{20}NSiI$: C, 57.14; H, 4.57; N, 3.17. Found: C, 57.38; H, 4.59; N, 3.27.

Preparation of Silane **15c**, $Bz-NCH_2C_6H_4Si(H)(OTf)-$

$C_6H_4CH_2$. (a) From Dihydrosilane **6c.** Trimethylsilyl trifluoromethanesulfonate (0.44 g, 2 mmol) was added to dihydrosilane **6c** (0.63 g, 2 mmol) in 20 mL of CCl_4 . After 1 h, the solvent was evaporated under vacuum to give the product as a white powder, mp 220 °C (dec), identified as **15c** (0.77 g, 83% yield) by comparison of its NMR spectra (1H and ^{29}Si) with those of an authentic compound (next paragraph). For analytical purposes, **15c** was recrystallized from a CH_2Cl_2 /hexane mixture (50/50), mp 225 °C. Anal. Calcd for $C_{22}H_{20}NSiF_3SO_3$: C, 57.0; H, 4.35. Found: C, 57.15; H, 4.31.

(b) From Hydrochlorosilane **12c.** A mixture of hydrochlorosilane **12c** (1.99 g, 5.7 mmol) and trimethylsilyl trifluoromethanesulfonate (1.26 g, 5.7 mmol) was treated using the same procedure as above to give product **15c** as a white powder (1.7 g, 65% yield), mp 224 °C. 1H NMR (CD_2Cl_2): δ 3.60, 4.09 (AB, $^2J_{HH}$ = 14.9 Hz, 4H, CH_2N), 3.88 (s, 2H, CH_2Ph), 5.29 (s, 1H, SiH), 7.09–7.91 (m, 13H, Ar). ^{13}C NMR (CD_2Cl_2): δ 56.8 (CH_2N), 57.4 (CH_2Ph), 117.3–143.7 (Ar). ^{29}Si NMR (CD_2Cl_2): δ Si -61.5 (d, J_{SiH} = 286 Hz). IR (KBr): ν_{SiH} 2192 cm^{-1} . MS (EI, 70 eV, *m/e* (relative intensity)): 462 (M^+ , 4), 385 (6), 372 (20), 314 (22), 235 (30), 222 (20), 91 (100). Anal. Calcd for $C_{22}H_{20}NSiF_3SO_3$: C, 57.0; H, 4.35; N, 3.02; F, 12.29. Found: C, 57.5; H, 4.35; N, 3.08; F, 12.73.

Crystal Structure of Compound **7a. Crystal Preparation.** Crystals of compound **7a** were grown by cooling a saturated hexane solution. Colorless needles were produced. A block cut from a needle was sealed inside a Lindeman glass capillary and mounted on a Weissenberg camera. An orthorhombic unit cell was determined, having the [001] direction parallel to the *f* axis of the diffractometer. The systematic absences uniquely defined the space group *Pbca*.

X-ray Data Collection. Data were collected at 22 °C on a CAD-4 automated diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.710 69 Å).

Lattice constants (Table 2) came from a least-squares refinement of 25 well-defined reflections in the range $18^\circ < 2\theta < 25^\circ$. The intensities of three standard reflections were monitored at 60 min intervals; a 2.6% decrease in these check reflections was observed. Structure amplitudes were obtained after decay correction and the usual Lorentz and polarization reductions. Only the reflections having $\sigma(F)/F < 0.36$ were considered to be observed. No absorption corrections were applied.

Structure Determination and Refinement. Direct methods (1980 version of the MULTAN program) were used to solve the structure⁸ and to give the positions of the 2 silicon atoms,

(8) Main, P.; Germain, G.; Woolfson, M. M. *MULTAN-80, a system for computer programs for the automatic solution of crystal structures for the X-ray diffraction data*; Universities of York, England and Louvain, Belgium, 1980.

Table 2. Summary of the Crystal Data, Intensity Measurements, and Refinement of Compound 7aA,B

| | |
|--|--|
| formula | C ₁₈ H ₂₁ F ₂ NSi |
| cryst syst | orthorhombic |
| space group | <i>Pbca</i> |
| <i>a</i> , Å | 24.671(5) |
| <i>b</i> , Å | 15.159(3) |
| <i>c</i> , Å | 17.818(4) |
| vol, Å ³ | 6663.6 |
| mol wt | 317.46 |
| <i>Z</i> | 16 |
| <i>d</i> _{calcd} , g cm ⁻³ | 1.265 |
| <i>d</i> _{measd} , g cm ⁻³ | 1.256(8) |
| cryst size, mm ³ | 0.30 × 0.45 × 0.70 |
| cryst color | colorless |
| recryst solvent | hexane |
| mp, °C | 98–99 |
| method of data collection | ω/θ |
| radiation (graphite monochromatoed) | Mo K α |
| μ , cm ⁻¹ | 1.50 |
| 2 θ limits, deg | 4–42 |
| no. of unique reflns | 3036 |
| no. of obsd reflns | 1321 |
| final no. of variables | 190 |
| <i>R</i> | 0.048 |
| <i>R</i> _w | 0.049 |
| residual electron density | 0.304 |

3 fluorine atoms, and 10 carbon atoms. Subsequent Fourier maps and difference Fourier syntheses revealed all the remaining non-hydrogen atoms. The conventional *R* factor was 0.092. The hydrogen atoms were positioned by calculation (SHELX-76 program),⁹ and silicon, fluorine, and nitrogen atoms were refined anisotropically. Convergence occurred for the *R* (*R*_w) values of 0.048 (0.049). The labeling scheme is given in Figure 1.

Bond lengths are listed in Table 3, and important bond angles are given in Table 4. A full table of bond angles, the final atomic coordinates, a list of the anisotropic thermal parameters for Si, F, and N atoms, and a list of the calculated hydrogen atom positions are available as Supporting Information.

Dynamic NMR Investigations. Variable-temperature ¹H NMR spectra were recorded in CDCl₃ or toluene-*d*₆ unless otherwise specified. Computed-generated spectra were obtained using the program DNMR 4¹⁰ and compared to the experimental data in order to evaluate the rate constants for the exchange process at the different temperatures. Putting the rate constants obtained by simulation into the Eyring equation¹¹ yielded the activation parameters. *K*_{coal} was obtained from eq 1 for separated signals, such as the methoxy groups directly attached to the silicon atom. In the case of AB systems, *K*_{coal} was deduced from eq 2.

$$K_{\text{coal}} = \Pi(\nu_A - \nu_B)/\sqrt{2} \quad (1)$$

$$K_{\text{coal}} = \Pi\sqrt{[(\nu_A - \nu_B)^2 + 6(J_{AB})^2]}/\sqrt{2} \quad (2)$$

Results and Discussion

Synthesis of Symmetrical Difunctional Silanes

R–NCH₂C₆H₄Si(X)(Y)C₆H₄CH₂, X = Y. Dibenzyl-1,5-azasilocines were initially prepared from the condensation of primary amines with bis(*o*-bromomethylphenyl)-dimethylsilane.⁶ In order to obtain compounds with functional groups at silicon, we describe here a somewhat different, more general, approach. The first

member of the series, dimethoxysilane **5a**, was obtained in four steps from commercially available *o*-bromotoluene, **1**, after bromination with NBS in CCl₄ (90% yield), amination of **2** with 0.5 equiv of *tert*-butylamine in DMF/K₂CO₃ (70% yield), dimetalation with *n*-BuLi/hexane in Et₂O at –30 °C, giving **4a**, and reaction of **4a** with tetramethoxysilane to give **5a** with an overall yield of 31% (Scheme 1).

Reduction of **5a** with LiAlH₄ gave the silicon dihydride **6a** (60% yield). The difluorosilane **7a** was isolated (75% yield) on reaction of **5a** with BF₃·Et₂O (Scheme 2). The silacyclopentenyl derivative **8a** was obtained from **7a**, via halodemetalation with Li metal, in the presence of 2,3-dimethylbutadiene (Scheme 3). Secondary products were not observed, suggesting the relative stability of the assumed transient silylene through intramolecular coordination of the nitrogen atom.¹² Reaction of **7a** with an excess of methylolithium afforded compound **9a** (Scheme 4), identified by comparison with an authentic sample,^{6a} prepared as shown in Scheme 4. Two other series were prepared using different primary amines RNH₂ (R = *i*-Pr, PhCH₂) in place of *t*-BuNH₂.

Characterizations. Compounds **5–8**, and all other new compounds **9–16** prepared in this study were characterized by multinuclear NMR spectroscopy (¹H, ¹³C, ²⁹Si), mass spectrometry, and elemental analysis. All data are given in the Experimental Section.

The ²⁹Si chemical shifts of these aminoarylsilanes are significantly upfield from those for tetracoordinated diarylsilanes, a typical behavior which has been noted in a wide range of compounds showing coordination of intramolecular nitrogen atoms to the silicon center. Two types of benzylic protons are generally observed at room temperature, affording AB systems with two doublets of equal coupling constant. When X and Y are different, the AB system is not changed whatever the temperature, since the chirality is maintained around the silicon atom. When X and Y are the same, the NMR spectra are temperature dependent. Fluxional behavior results in equivalence of the benzylic protons. This aspect will be discussed later (*vide infra*).

Asymmetrical Difunctional Silanes. We have replaced the hydrogen atom in **6c** by different leaving groups (Scheme 5). The monofluorosilane **11c** was obtained by addition of 0.5 equiv of BF₃·Et₂O on the dihydrosilane **6c** (80% yield). The compound **11c**, which is insoluble in anhydrous ether, is stable at room temperature and can be handled in air. An excess of boron trifluoride etherate afforded the difluorosilane **7c** (90% yield). The hydrochlorosilane **12c** was obtained by quantitative halogenation of **6c** with Me₃SiCl, PCl₅, or *N*-chlorosuccinimide. An excess of reactant was not sufficient to exchange both hydrogen atoms of **6c**. Exchange reactions of **6c** with *N*-bromosuccinimide or bromotrimethylsilane (1 equiv or an excess) afforded **13c** in 75 and 80% yield, respectively. The reaction stopped at monosubstitution. Similarly, addition of iodotrimethylsilane gave the iodosilane **14c** (61% yield). The same compound was obtained when iodine (0.5 equiv) was added to **6c** in CCl₄. Hydrogen was evolved

(9) Sheldrick, G. M. *SHELX-76, a program for crystal structure determination*; University of Cambridge: Cambridge, England, 1976.

(10) Program DNMR4/QCPE 466.

(11) Gunther, H. *La spectroscopie de RMN*; Masson, Ed., Paris, 1993.

(12) Corriu, R. J. P.; Lanneau, G. F.; Priou, C.; Soulaire, F.; Auner, N.; Probst, R.; Conlin, R.; Tan, C. *J. Organomet. Chem.* **1994**, *466*, 55.

(13) Marsmann, H. ²⁹Si-NMR Spectroscopic Results in *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R. Eds.; Springer-Verlag: Berlin, 1981; Vol. 17, pp 65–235.

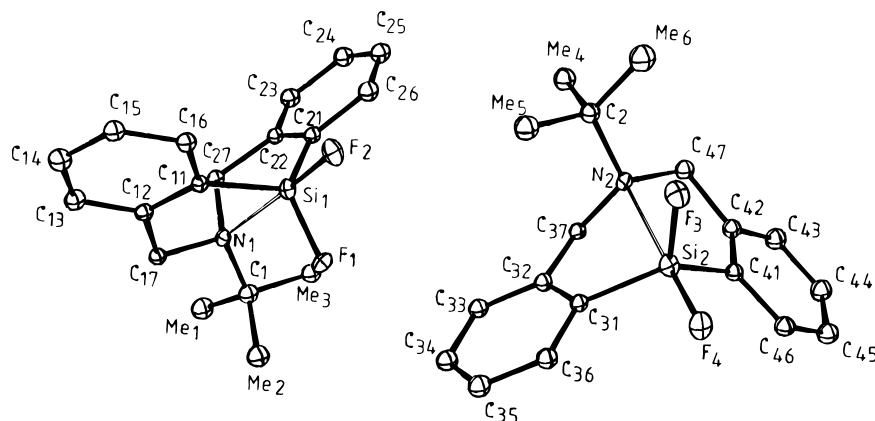


Figure 1. ORTEP representation of the two independent molecules A and B of compound 7, showing their relative positions within the asymmetric unit. The ellipsoids and spheres are at the 10% probability level. Important bond lengths (Å): Si–F1,F3 (mean) 1.592(5), Si–F2,F4 (mean) 1.616(5), Si1···N1 2.400(7), Si2···N2 2.459(7). The mean bond angle value for N1···Si1–F2 and N2···Si2–F4 is 178.8(3)°.

Table 3. Bond Distances (Å) in the Two Molecules of Compound 7a,B (Esd's in Parentheses)

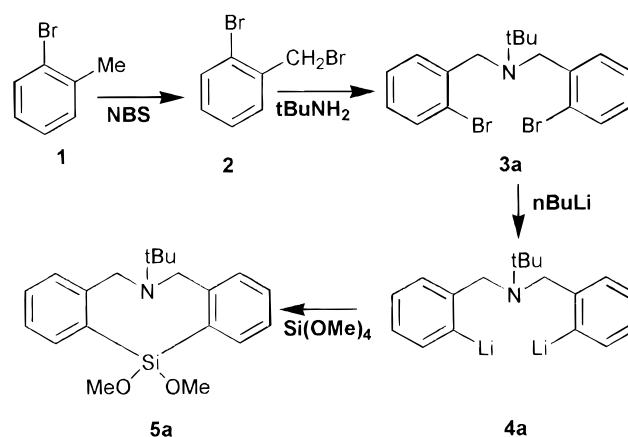
| | | | |
|---------|-----------|---------|-----------|
| Si1–F1 | 1.591(5) | Si2–F3 | 1.592(6) |
| Si1–F2 | 1.618(5) | Si2–F4 | 1.614(5) |
| Si1–C11 | 1.852(8) | Si2–C31 | 1.835(8) |
| Si1–C21 | 1.850(9) | Si2–C41 | 1.841(9) |
| Si1–N1 | 2.400(7) | Si2–N2 | 2.459(7) |
| C11–C12 | 1.391(11) | C31–C32 | 1.387(11) |
| C12–C13 | 1.398(13) | C32–C33 | 1.400(12) |
| C13–C14 | 1.385(13) | C33–C34 | 1.401(13) |
| C14–C15 | 1.337(13) | C34–C35 | 1.362(13) |
| C15–C16 | 1.392(13) | C35–C36 | 1.394(13) |
| C16–C11 | 1.407(12) | C36–C31 | 1.414(12) |
| C12–C17 | 1.502(12) | C32–C37 | 1.507(12) |
| C17–N1 | 1.490(10) | C37–N2 | 1.474(10) |
| C21–C22 | 1.375(11) | C41–C42 | 1.395(12) |
| C22–C23 | 1.401(12) | C42–C43 | 1.409(13) |
| C23–C24 | 1.411(14) | C43–C44 | 1.369(13) |
| C24–C25 | 1.339(13) | C44–C45 | 1.372(13) |
| C25–C26 | 1.377(13) | C45–C46 | 1.390(13) |
| C26–C21 | 1.428(12) | C46–C41 | 1.413(12) |
| C22–C27 | 1.500(11) | C42–C47 | 1.489(12) |
| C27–N1 | 1.478(10) | C47–N2 | 1.485(11) |
| N1–C1 | 1.537(11) | N2–C2 | 1.518(11) |
| C1–Me1 | 1.529(14) | C2–Me4 | 1.527(13) |
| C1–Me2 | 1.523(13) | C2–Me5 | 1.539(14) |
| C1–Me3 | 1.533(13) | C2–Me6 | 1.528(14) |

Table 4. Selected Bond Angles (deg) in 7a,B (Esd's in Parentheses)

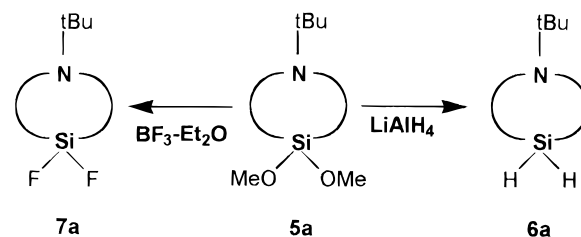
| | | | |
|-------------|----------|-------------|----------|
| N1–Si1–F2 | 178.3(3) | N2–Si2–F4 | 179.2(3) |
| F2–Si1–F1 | 96.2(3) | F4–Si2–F3 | 96.4(3) |
| F2–Si1–C11 | 99.7(3) | F4–Si2–C31 | 100.0(3) |
| F2–Si1–C21 | 99.4(3) | F4–Si2–C41 | 100.7(3) |
| N1–Si1–F1 | 85.6(3) | N2–Si2–F3 | 84.4(3) |
| N1–Si1–C11 | 79.5(3) | N2–Si2–C31 | 79.6(3) |
| N1–Si1–C21 | 79.7(3) | N2–Si2–C41 | 78.9(3) |
| F1–Si1–C11 | 116.5(3) | F3–Si2–C31 | 116.3(3) |
| C11–Si1–C21 | 120.2(4) | C31–Si2–C41 | 119.8(4) |
| C21–Si1–F1 | 117.0(3) | C41–Si2–F3 | 116.6(4) |
| Si1–C11–C12 | 121.0(6) | Si2–C31–C32 | 119.6(6) |
| C11–C12–C17 | 120.1(7) | C31–C32–C37 | 118.6(7) |
| C12–C17–N1 | 108.9(7) | C32–C37–N2 | 110.8(6) |
| C17–N1–Si1 | 104.1(4) | C37–N2–Si2 | 97.5(4) |
| Si1–C21–C22 | 119.7(6) | Si2–C41–C42 | 122.0(6) |
| C21–C22–C27 | 117.6(7) | C41–C42–C47 | 120.0(8) |
| C22–C27–N1 | 110.7(6) | C42–C47–N2 | 110.8(7) |
| C27–N1–Si1 | 98.6(4) | C47–N2–Si2 | 102.3(4) |
| C17–N1–C27 | 108.9(6) | C37–N2–C47 | 108.7(6) |
| C1–N1–Si1 | 121.5(5) | C2–N2–Si2 | 124.2(5) |
| C1–N1–C17 | 110.2(6) | C2–N2–C37 | 112.2(6) |
| C1–N1–C27 | 112.5(6) | C2–N2–C47 | 110.5(6) |

immediately with decolorization of the solution (89% yield). Compound 14c also is accessible via reaction of 6c with methyl iodide in excess (yield 65%) with

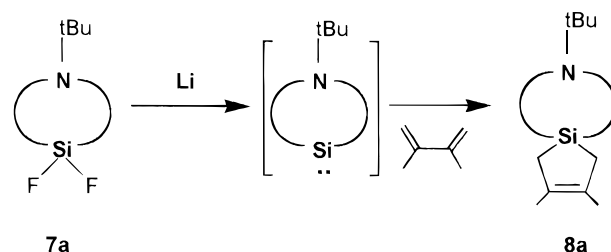
Scheme 1



Scheme 2



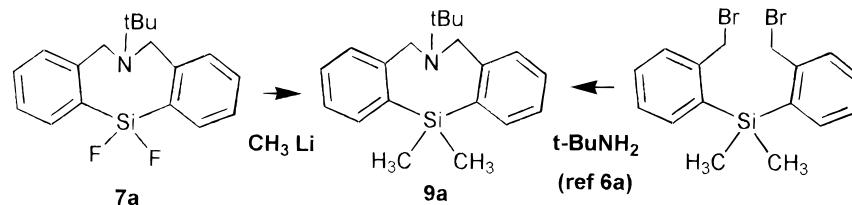
Scheme 3



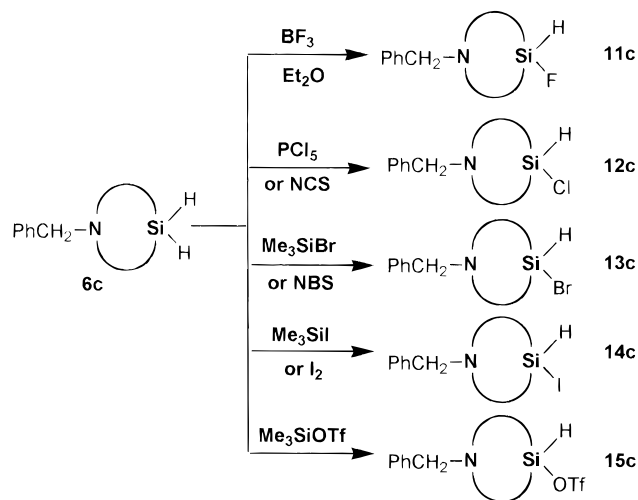
elimination of methane. The reaction of 6c and Me₃SiOTf (CCl₄, 25 °C) gave the solid silyl monotriflate, 15c, in 83% yield, even when an excess of trimethylsilyl trifluoromethanesulfonate was used. A fast exchange of the functional groups –Cl and –OTf was observed between the monochlorosilane 12c and Me₃SiOTf (Scheme 6).

The reactions of dihydrosilane 6c with AgBF₄ or Ph₃C⁺BF₄[–] both gave directly the difluorosilane 7c in

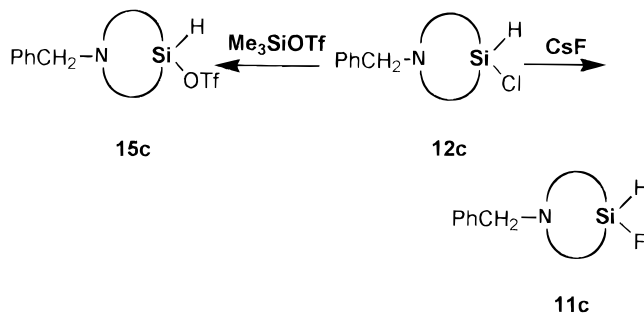
Scheme 4



Scheme 5



Scheme 6



Scheme 7

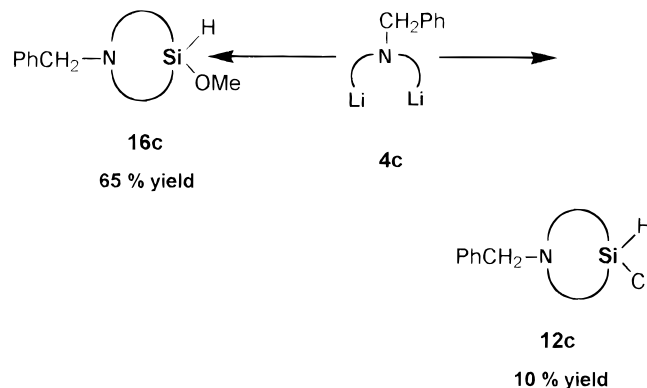


Chart 3

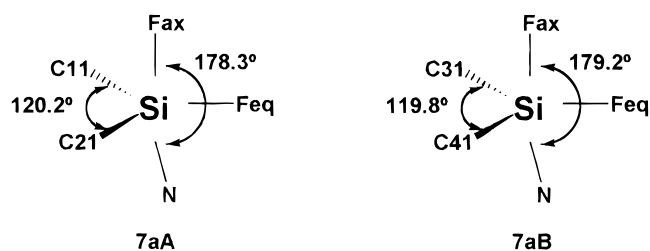


Chart 4



excellent yield (96 and 87%, respectively). The monofluorosilane **11c** was obtained by the exchange reaction of the chlorosilane **12c** with 1 equiv of CsF (Scheme 6). Use of an excess of CsF afforded **7c**.

The direct formation of **12c** by the reaction of the dilithio derivative **4c** with HSiCl_3 gave only a low yield (10%). The monomethoxy derivative **16c**, which was not accessible from **6c** by the reaction with methanol or tributylmethoxytin, could be obtained directly by reaction of the dilithium derivative **4c** with $\text{HSi}(\text{OMe})_3$ at low temperature (65% yield; Scheme 7).

Molecular Structure of 7a. Thus far, all pentacoordinated silicon species with an intramolecular donor atom bound to silicon have exhibited a trigonal bipyramidal geometry, with the donor–Si bond in the apical position.^{1–5} The bicyclic difluorosilane, $t\text{-BuNCH}_2\text{C}_6\text{H}_4\text{-Si}(\text{F})_2\text{C}_6\text{H}_4\text{CH}_2$ **7a**, was chosen for a crystal structural determination (space group $Pbca$, orthorhombic crystal-line system, $Z = 16$). Two types of molecules, **7aA** and **7aB**, have been characterized in the refined structure. The atom labeling schemes of **7a** are given in the ORTEP plot in Figure 1. Bond lengths and angles for **7aA** and **7aB** are given in Tables 3 and 4. Atomic

coordinates, anisotropic thermal parameters, and least-squares planes are provided as Supporting Information.

The two fluorine atoms are differentiated in the solid state. The silicon atom possesses a somewhat distorted trigonal bipyramidal coordination (Chart 3), with the chelated nitrogen atom in an apical position. The N–Si bond length (2.400(7) Å for **A**, 2.459(7) Å for **B**, average 2.430 Å) is shorter than the value^{1b} generally observed with aminoarylfluorosilanes, such as 2-((dimethylamino)methyl)phenyl-8-(dimethylamino)naphthyldifluorosilane (average N–Si bond length, 2.7 Å). Both molecules **7aA** and **7aB** possess a near trigonal bipyramidal geometry which is exemplified by the value of 120.2(4)° for the angle C(11)–Si–C(21) in **A** and of 119.8(4)° for C(31)–Si–C(41) in **B**, which are close to the expected theoretical value of 120°.

The silicon atom is not exactly in the equatorial plane defined by the equatorial fluorine and the two aryl carbon atoms, F(1)C(11)C(21) (**A**) and F(3)C(31)C(41) (**B**), but is displaced toward the axial fluorine atom (the F(1)–Si(1)–F(2) angle is equal to 96.2(3)° (**A**) and the

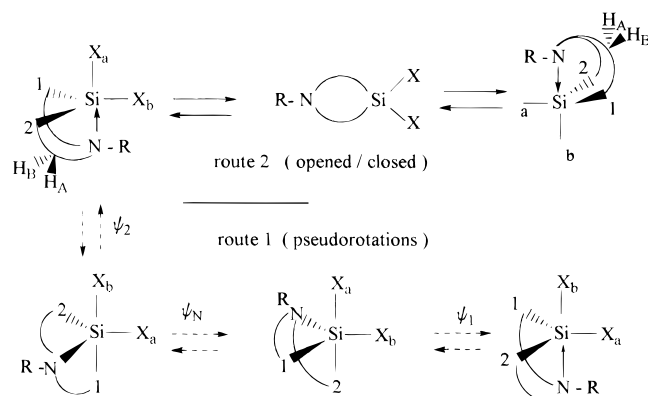


Figure 2.

Table 5. ^{29}Si NMR Chemical Shifts and Coupling Constants $J(\text{Si}-\text{X})$ ($\text{X} = \text{F}, \text{H}$) for Axial and/or Equatorial Ligands

| | ^{29}Si (ppm) | $J_{\text{Si}-\text{F}}$ (Hz) | ^{29}Si (ppm) | $J_{\text{Si}-\text{H}}$ (Hz) |
|---------------------------|---------------------------|----------------------------------|---------------------------|----------------------------------|
| 7c | -63.5 | 255 (eq) 266 (ax) | 6c | -48.9 210 (eq) 212 (ax) |
| | -57.0 | 295 | | -44.6 210 |
| Ph_2SiF_2 | -30.5 | 303 | Ph_2SiH_2 | -34.5 200 |

F(3)–Si(2)–F(4) angle is $96.4(3)^\circ$ (**B**). One of the two five-membered rings created by the coordination of the nitrogen atom is almost semiplanar, with torsion angles of 1.1° for Si(1)C(21)C(22)C(27) (**A**) and 0.7° for Si(2)C(31)C(32)C(37) (**B**), while the second ring is in a twisted envelope form in which no four consecutive atoms are coplanar (8.56° for Si(1)C(11)C(12)C(17) (**A**) and 7.5° for Si(2)C(41)C(42)C(47) (**B**)). Another presentation of that deformation in the solid state is shown in Figure 2 with a view along the N(1)–SiF(2) axis, with the dihedral angle between the silicon–equatorial fluorine bond and the N–t-Bu bond, respectively, being -24.8° for F(1)–Si(1)N(1)C(1) (**A**) and -24.6° for F(3)Si(2)N(2)C(2) (**B**).

Intramolecular Coordination in Solution. The ^{29}Si NMR chemical shifts of the symmetrical difunctional silanes **5–7** are found in the high-field region, showing that pentacoordination around the silicon atom is maintained in solution, except for the alkoxy derivatives. A shielding effect of the fluorine atoms is observed, as already noted in the case of other similar systems,^{14,15} with a differentiation of the coupling constants $J_{\text{Si}-\text{X}}$ ($\text{X} = \text{F}, \text{H}$) for axial and/or equatorial ligands (Table 5).

Comparison of the ^{29}Si NMR chemical shifts of unsymmetrical silanes $\text{Bz}-\text{NCH}_2\text{C}_6\text{H}_4\text{Si}(\text{H})(\text{X})\text{C}_6\text{H}_4\text{CH}_2$, **10c–15c**, with those of the parent **6c**, $\text{Bz}-\text{NCH}_2\text{C}_6\text{H}_4\text{Si}(\text{H})_2\text{C}_6\text{H}_4\text{CH}_2$, shows that except for the methoxysilane, **10c**, all of the compounds are shifted upfield, whereas the opposite effect was observed in the case of

Table 6. ^{29}Si NMR Variable-Temperature Data for **11c**

| T ($^\circ\text{C}$) | δ_{Si} (ppm) | $J_{\text{Si}-\text{F}}$ (Hz) | $J_{\text{Si}-\text{H}}$ (Hz) |
|--------------------------|----------------------------|-------------------------------|-------------------------------|
| +25 | -55.2 | 275 | 255 |
| 0 | -55.7 | 274 | 255 |
| -40 | -56.7 | 273 | 255 |

Table 7. ^{19}F NMR Variable-Temperature Data for **7c**

| | -70 $^\circ\text{C}$ | -40 $^\circ\text{C}$ | -10 $^\circ\text{C}$ | +50 $^\circ\text{C}$ | +80 $^\circ\text{C}$ |
|----------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| δ_{F_1} (ppm) | -130.7 | -131.5 | -132.2 | -133.4 | -134.1 |
| δ_{F_2} (ppm) | +152.90 | +152.95 | +152.92 | +152.90 | +152.85 |
| $J_{\text{F}_1-\text{F}_2}$ (Hz) | 19.3 | 20.0 | 20.7 | 19.5 | 18.5 |

Table 8. ^{19}F NMR Variable-Temperature Data for **11c**

| | -70 $^\circ\text{C}$ | +20 $^\circ\text{C}$ | +80 $^\circ\text{C}$ |
|--------------------------------|----------------------|----------------------|----------------------|
| δ_{F} (ppm) | -141 | -145 | -146 |
| $^2J_{\text{H}-\text{F}}$ (Hz) | 81.4 | 80.0 | 78.6 |

tetracoordinated silanes.¹⁴ A similar order which established a parallel between the apicophilicity of the ligands and their polarizability already was noted:¹⁵ $\text{OCH}_3, \text{H} < \text{F} < \text{Cl} < \text{OTf} < \text{Br} < \text{I}$.

Another interesting comparison is the variation observed with various organochlorosilanes R_2SiHCl . A downfield shift variation^{13,14} is observed in tetracoordinated silicon compounds R_2SiHCl compared with R_2SiH_2 , whereas all of the silanes which have an aminoaryl ligand show an upfield modification of their ^{29}Si NMR value. The greater difference is observed with cyclic **12c** and (((dimethylamino)methyl)naphthyl)phenylchlorosilane,¹⁶ which has been shown to be strongly coordinated. An exception is the bischelating 2,6-bis((dimethylamino)methyl)phenyl ligand, which induces the formation of a cationic pentacoordinated silicon species.¹⁷ For this system, a downfield shift is observed in the ^{29}Si NMR spectrum with a constant value of $\delta -29.7$ ppm for $\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{BF}_4^-, \text{or } \text{CF}_3\text{SO}_3^-$.

The upfield-shift variation with increased coordination is also observed in the case of monofluorosilanes. Methylphenylfluorosilane is shifted downfield in comparison with methylphenylsilane with a variation of more than +45 ppm, whereas the bicyclic system **11c** is shifted upfield when compared to **6c**, $\Delta\delta -6.3$ ppm.

Examination of the ^{29}Si NMR signal at variable temperatures showed that the environment around the silicon atom is only slightly modified when the temperature of the solution is decreased. No change was observed in the coupling constants $^1J_{\text{Si}-\text{F}}$ and/or $^1J_{\text{Si}-\text{H}}$ (Table 6).

^{19}F NMR spectroscopy is another technique which has been widely used to characterize pentacoordinated structures at silicon.¹⁸ Axial fluorine atoms generally are observed at lower field than equatorial atoms in tbp (trigonal bipyramidal) geometry. Compounds **7c** and **15c** have been analyzed by ^{19}F NMR spectroscopy (Tables 7 and 8). Two doublets are observed for **7c** at room temperature. The lower signal, which is reason-

(14) (a) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; Chapter 8, p 511. (b) Bassindale, A. R.; Jiang, J. *J. Organomet. Chem.* **1993**, *446*, C3.

(15) Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; De Saxe, A.; Young, J. C. *J. Organomet. Chem.* **1990**, *395*, 1–26 and references cited therein.

(16) Boyer, J.; Breliere, C.; Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C. *J. Chem. Soc., Dalton Trans* **1989**, 43.

(17) (a) Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1311. (b) Carre, F. H.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1097.

(18) See for example: Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155.

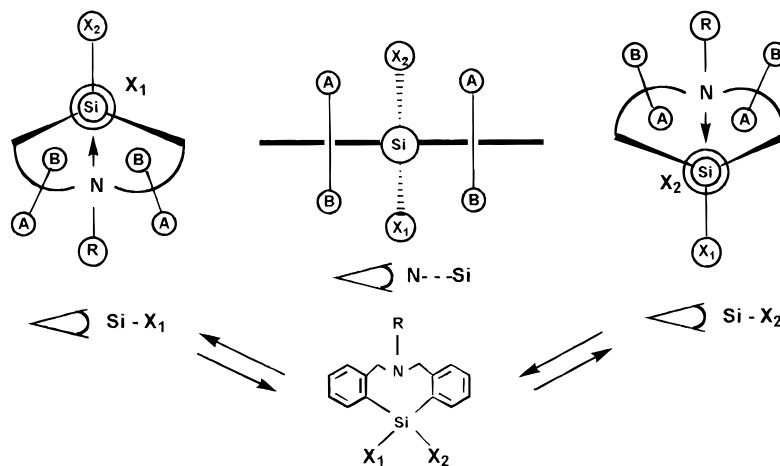


Figure 3. Different pathways explaining the isomerization of the tbp geometry.

ably attributed to the axial fluorine atom, is shifted slightly upfield when the temperature is changed from -70 to $+80$ °C, while no change is observed for the upfield signal attributed to the equatorial fluorine atom. The coupling constant J_{F1-F2} is not affected by the temperature changes. The ^{19}F NMR spectrum of monofluorosilane **11c** presents similar variations with temperature, the signal shifting from -141 at -70 °C to -146 at $+80$ °C, which is in accord with the reasonable hypothesis that the fluorine atom is in an apical position of the tbp whereas the hydrogen atom is equatorial.² A small decrease of the coupling constant J_{H-F} is observed when the temperature increases (Table 8).

Molecular Dynamics. ^1H , ^{19}F , and ^{13}C NMR spectra indicate that the intramolecular coordination which has been evidenced in the solid-state structure of difluorosilane **7a** can be reasonably retained for the other systems in solution. For example, the two doublets which are observed in the ^{19}F NMR spectra of **7a**, **7b**, and **7c** ($^2J_{F1-F2} = 18\text{--}20$ Hz) are characteristic of two differentiated fluorine atoms in the same molecule. These signals coalesce at high temperature to afford one broad signal above $+95$ °C. The same observation is noted for **5** and **6** but at lower temperatures. The two hydrogen atoms directly attached to the silicon atom in **6a–c** or the methoxy groups in **5a–c**, which give rise to only singlets in the ^1H NMR spectra at room temperature, change when the temperature is decreased. At low temperature, the dimethoxysilanes **5a–c** show two different signals for the methoxy groups whereas dihydrosilanes **6a–c** give AB systems. Such data indicate that reorganization processes are occurring reversibly with these molecules, dependent on the conditions under which the measurements are performed. ^1H NMR coalescence temperatures when used in the Eyring equation¹¹ allowed calculation of the values of the free energy of activation (ΔG^\ddagger) for these site-exchange processes (Table 9). In some cases, two determinations of the ΔG^\ddagger values were possible with different probes in the molecule. This is the case, for example, for the dihydrosilanes **6a–c**, which present two AB systems in the ^1H NMR spectra, one for the two hydrogen atoms directly attached to the silicon atom and the other for the benzylic $-\text{CH}_2-$ groups. Since similar values are obtained with the different systems, we can assume that the two coalescences are associated with the same dynamic process.

A priori, there are two processes that could account

Table 9. Comparison of the Activation Energy Barriers, ΔG^\ddagger (kcal mol⁻¹), at the Coalescence Temperature for NMR Exchange Processes in 5–7

| Derivatives, $\text{RNCH}_2\text{C}_6\text{H}_4\text{Si}(\text{X})_2\text{C}_6\text{H}_4\text{CH}_2$ | ΔG^\ddagger (kcal mol ⁻¹) | | | |
|--|---|-----------------------|--------------------|-------------------|
| | R | X = O-CH ₃ | X = H ^a | X = F |
| (CH ₃) ₃ C- | | 11.5 ± 0.2 (11.4) | 13.6 ± 0.2 (13.5) | 16.6 ± 0.3 (16.5) |
| (CH ₃) ₂ CH- | | 12.6 ± 0.2 (12.6) | 14.1 ± 0.2 (14.0) | 17.6 ± 0.3 (17.3) |
| (C ₆ H ₅)CH ₂ - | | 13.2 ± 0.2 (13.3) | 14.7 ± 0.2 (14.5) | 18.8 ± 0.3 (19.0) |

^a Determined with the ^1H signals of the benzylic protons; values in brackets correspond to ^1H or ^{19}F signals of the Si-X groups.

for this behavior (Figure 3). The coalescences could be the result of intramolecular rearrangements involving a simultaneous exchange of ligands in the bipyramidal structure, either via pseudorotations or through turnstile isomerizations (route 1). Another possibility is coalescence resulting from Si-N dative bond dissociation, followed by pyramidal inversion of the nitrogen atom, rotation around the aryl C-N bonds, and recoordination of the nitrogen atom to silicon (route 2). Where it is observed, the site-exchange process of the two functional ligands directly attached to the silicon atom could be explained by either one of these routes. Consequently, a simple examination of this phenomenon is unable to distinguish between routes 1 and 2.

The permutational isomerization process (route 1) can definitely be eliminated, considering the behavior of the benzylic protons, since "the site exchange of the intracyclic CH_2 protons is only possible through route 2, which involves an inversion at the nitrogen atom" (Figure 3, the protons H_A and H_B become equivalent). Moreover, the ΔG^\ddagger values reported in Table 9 decrease with the steric hindrance of the R ligands attached to the nitrogen ($\Delta G^\ddagger_{t-\text{Bu}} > \Delta G^\ddagger_{i-\text{Pr}} > \Delta G^\ddagger_{\text{PhCH}_2}$). It is thus reasonable to assume that the coordination is of lower energy because of the steric repulsion with the equatorial X_e group.

A confirmation of the influence of steric effects is found from the comparison of experimental variable-temperature studies with simulated spectra, which allowed us to obtain the activation parameters. For a given molecule, calculations obtained independently onto different probes afford the same values for ΔH^\ddagger and ΔS^\ddagger , which means that only one process is occurring (Table 10). If we compare the ΔG^\ddagger values obtained for the bicyclic system with those for other difunctional

Table 10. Activation Parameters^{10,11} for ¹H NMR Exchange Processes in 5a–c^{a,b}

| | ΔG^\ddagger (kcal mol ⁻¹) | ΔH^\ddagger (kcal mol ⁻¹) | ΔS^\ddagger (cal K ⁻¹ mol ⁻¹) |
|------------------------------------|--|--|---|
| 5a (R = t-Bu) | 11.5 (±0.2) ^a | 8.3 (±0.2) ^a | -13 (±1) ^a |
| | 11.4 (±0.3) ^b | 8.1 (±0.2) ^b | -15 (±1) ^b |
| 5b (R = i-Pr) | 12.6 (±0.2) ^a | 9.2 (±0.2) ^a | -14 (±1) ^a |
| | 12.6 (±0.2) ^b | 9.1 (±0.3) ^b | -14 (±1) ^b |
| 5c (R = PhCH ₂) | 13.2 (±0.2) ^a | 11.6 (±0.4) ^a | -7 (±2) ^a |
| | 13.3 (±0.3) ^b | 11.3 (±0.3) ^b | -8 (±1) ^b |

^a Calculated from benzylic protons data. ^b Calculated from methoxyl protons data.

compounds,^{2,15,19} the higher efficiency of the bicyclic model for intramolecular coordination of aminoaryl ligand is evident.

Conclusion

In the present paper, we have described the potential of a fused bicyclic ligand to prepare Lewis-base-coordinated functional organosilanes. Intramolecular coordination of the aminoaryl ligand enhances the

(19) Carre, F. H.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C.; Belin, C. *J. Organomet. Chem.* **1994**, *470*, 43–57.

reactivity of at least one of the two functionalities at the silicon atom. The rigid bicyclic molecules which have been isolated occupy trigonal bipyramidal geometries which allow one to differentiate axial and equatorial ligands of the same nature. Further development of the chemistry encountered with this particular system will be published shortly.

Acknowledgment. We are grateful to R. Astier of the Laboratoire de Mesures Physiques (Université Montpellier II) for assistance with the X-ray data collection on a Nonius CAD-4 diffractometer. G.F.L. thanks A. Fruchier and S. Bourg for help in obtaining the NMR-simulated spectra.

Supporting Information Available: Tables of bond angles, atomic coordinates, anisotropic thermal parameters for the silicon, fluorine, and nitrogen atoms, and calculated hydrogen atom coordinates and NMR spectra (¹H, ¹³C, ²⁹Si) of compound **8a**, t-BuNCH₂C₆H₄Si[CH₂C(CH₃)=C(CH₃)CH₂]-C₆H₄CH₂ (14 pages). Ordering information is given on any current masthead page.

OM970361W