Organometallics **2001,** *20,* 2331−2337

Synthesis of Silatranes with All Six-Membered Rings. Influence of Steric Effect on Structure and NMR Behavior[1a,b]

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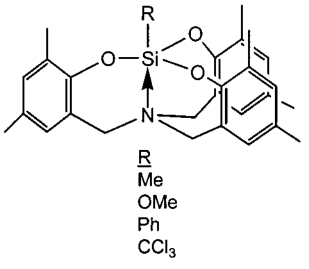
Received November 30, 2000

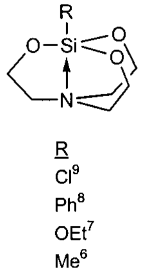
New silatranes containing all six-membered rings, $N[CH_2(Bu^tMeC_6H_2)O]_3SiR$, where R = CH_2Cl (**1**), Cl (**2**), Ph (**3**), OH (**4**), Me (**5**), and CCl_3 (**6**), were synthesized starting with tris(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)amine (**7**) as the encapsulating agent. The silatranes other than **4** were prepared by the reaction of the triphenol **7** with an appropriate chlorosilane, whereas **4** resulted from the hydrolysis of **2**. Their structures were established by X-ray analyses and ^{29}Si NMR data. VT ^1H NMR spectra revealed fluxional behavior for **3** and **4**. Activation energies for the enantiomeric conversion of the clockwise and anticlockwise orientations of the propeller-like silatranes correlated with increased structural rigidity associated with the ring system. The presence of *tert*-butyl groups on the aryl ring system located adjacent to the axial R groups introduces a steric effect that is largely responsible in restricting the donor−acceptor interaction to a narrow range of Si−N distances. The latter range is comparable to that found in previous studies which invariably concentrated on silatranes possessing five-membered rings. The present study confirms that unencumbered silatranes with six-membered rings provide the most effective way to study the influence of substituent effects on nitrogen−silicon donor−acceptor interactions.

Introduction

Recently we prepared a new class of silatranes[2] containing all six-membered rings by making use of tris(2-hydroxy-3,5-dimethylbenzyl)amine as the encapsulating agent. All previous work[3−5] had centered on silatranes containing five-membered rings. It was shown that the silatrane systems[1b,2] with the larger rings allowed substituent effects associated with the axial position of the resulting trigonal bipyramidal structures (TBP) to be reflected in dramatically altering the Si−N bond interactions as well as in changes of the ^{29}Si chemical shifts, e.g., **A**.[2] By contrast, corresponding substitutions in five-membered ring silatranes, e.g., **B**,[6−9] produced Si−N distances that were confined to a narrow range and thus limited the extent of Si−N interaction that could be studied by substituent variations.



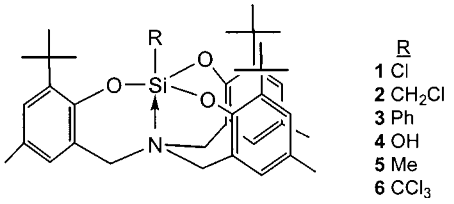
A



B

On comparison of the series of silatranes **A** having six-membered rings,[2] X-ray analysis showed a variation of over 0.8 Å in the Si−N distance, while the analogous series **B**, with five-membered rings[6−9] ranged only over 0.15 Å. It was concluded[2] that the greater rigidity imposed by the presence of five-membered rings in all previously studied silatranes[3−5] limited the extent of Si−N interaction that could be studied by substituent variations.

In the present study, we have modified the triaryl encapsulating agent to contain *tert*-butyl groups. In this way, a steric interaction arises between the axial groups in newly formed silatranes, **1**−**6**, and the neighboring



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10.1021/om001024h CCC: $20.00

tert-butyl groups. Like our previous studies,[1b,2] the new silatranes have all six-membered rings.

Their syntheses, dynamic NMR behavior in solution, and solid state structures from X-ray analyses are reported. The results are compared with our previous studies[1b,2] to demonstrate the consequences of steric effects in reducing ring flexibility as reflected in Si−N donor action controlled by substituent variations.

Experimental Section

2-*tert*-Butyl-4-methylphenol, hexamethylenetetramine, chloromethyltrichlorosilane, tetrachlorosilane, methyltrichlorosilane, and phenyltrichlorosilane (Aldrich) were used as supplied. Triethylamine (Aldrich) was distilled over KOH pellets. Solvents were purified according to standard procedures.[10] All reactions were carried out in a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC200-FT-NMR spectrometer in $CDCl_3$. Silicon-29 NMR spectra were recorded on a Bruker AMX500 FT-NMR spectrometer (in CH_2Cl_2). Chemical shifts are reported in ppm, downfield positive relative to tetramethylsilane. All were recorded at around 20 °C. Variable-temperature ^1H NMR data were obtained in $C_6D_5CD_3$ solution. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. 1-Chloromethylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′-methyl, 6′-*tert*-butylbenzo)[4.4.4.0^{1,6}]-tricyclotetradecane, $N[CH_2(Bu^tMeC_6H_2)O]_3SiCH_2Cl$ (1). A solution of chloromethyltrichlorosilane (0.250 mL, 2.00 mmol) in dichloromethane (40 mL) was added to a solution of **7** (1.10 g, 2.01 mmol) and triethylamine (0.850 mL, 6.10 mmol) in dichloromethane (100 mL) with stirring at room temperature over a period of 30 min. The reaction mixture was stirred for a further 48 h. The resulting solution was washed with water (3 × 100 mL), then heptane was added (50 mL). The solution was dried over anhydrous magnesium sulfate and filtered. Afterward it was left under a flow of nitrogen to obtain good quality crystals: mp > 240 °C (yield 0.80 g, 64%). ^1H NMR: 1.41 (s, 27H, *tert*-butyl), 2.26 (s, 9H, aryl-*Me*), 3.21 (s, 2H,CH_2Cl), 2.94 (d, 14.4 Hz, 3H, N*CH_2*), 4.37 (d, 14.1 Hz, 3H, N*CH_2*), 6.62 (s, 3H, aryl), 7.08(s, 2H, aryl). ^1H NMR($C_6D_5CD_3$, 300 K): 1.53 (s, 27H, *tert*-butyl), 2.20 (s, 9H, aryl-*Me*), 2.36 (d, 14.5 Hz, 3H, N*CH_2*), 3.58 (s, 2H, CH_2Cl), 4.27 (d, 14.1 Hz, 3H, N*CH_2*), 6.26 (s, 3H, aryl), 7.09 (s, 2H, aryl). ^1H NMR($C_6D_5CD_3$, 370 K): 1.53 (s, 27H, *tert*-butyl), 2.18 (s, 9H, aryl-*Me*), 2.5 (br, 3H, N*CH_2*), 3.52 (s, 2H, CH_2Cl), 4.3 (br, 3H, N*CH_2*), 6.33 (s, 3H, aryl), 7.12 (s, 2H, aryl). ^{29}Si NMR: −132.5. Anal. Calcd for $C_{37}H_{50}ClNO_3Si$: C, 71.64; H, 8.12; N, 2.26. Found: C, 71.12; H, 8.25; N, 2.20.

1-Chlorosila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′-methyl, 6′-*tert*-butylbenzo)[4.4.4.0^{1,6}]tricyclotetradecane, $N[CH_2(Bu^tMeC_6H_2)O]_3SiCl$ (2), and 1-Hydroxysila-2,10,-11-trioxa-6-aza-3,4;8,9;12,13-tris(4′-methyl,6′-*tert*-butylbenzo)[4.4.4.0^{1,6}]tricyclotetradecane, $N[CH_2(Bu^tMeC_6H_2)O]_3SiOH$ (4). A solution of tetrachlorosilane (0.200 mL, 1.75 mmol) in dichloromethane (50 mL) was added to a solution of **7** (0.950 g, 1.74 mmol) and triethylamine (0.800 mL, 5.74 mmol) in dichloromethane (100 mL) with stirring at room temperature over a period of 30 min. The reaction mixture was stirred for a further 24 h. The solvent was removed and the residue extracted with ether. Solvent was removed from the extract, and the residue was recrystallized from dichloromethane−heptane (2:1, 80 mL) to give a crystalline product that was very sensitive to moisture: mp 238−241 °C (dec) (yield 0.15 g, 15%). The compound was found to have half a molar equivalent of a heptane molecule. Single crystals suitable for an X-ray study were obtained from diethyl ether. ^1H NMR: 1.45 (s, 27H, *tert*-butyl), 2.25 (s, 9H, aryl-*Me*), 3.01 (d, 14.2 Hz, 3H, N*CH_2*), 4.36 (d, 14.0 Hz, N*CH_2*), 6.65 (s, 3H, aryl), 7.10 (s, 3H, aryl). ^1H NMR ($C_6D_5CD_3$, 293 K): 1.62 (s, 27H, *tert*-butyl), 2.20 (s, 9H, aryl-*Me*), 2.31 (d, 14.1 Hz, 3H, N*CH_2*), 4.16 (d, 13.8 Hz, N*CH_2*), 6.26 (s, 3H, aryl), 7.11 (s, 3H, aryl). ^1H NMR ($C_6D_5CD_3$, 370 K): 1.59 (s, 27H, *tert*-butyl), 2.19 (s, 9H, aryl-*Me*), 2.5 (br, 3H, N*CH_2*), 4.2 (br, N*CH_2*), 6.34 (s, 3H, aryl), 7.12 (s, 3H, aryl). Due to extreme sensitivity toward decomposition, satisfactory elemental analyses could not be obtained. As a result, ready formation of **4** took place as discussed in the following paragraph.

The mother liquor on evaporation gave a powdery solid (0.50 g, 50%), which was found to be the hydroxy silatrane **4**. Single crystals suitable for an X-ray study were obtained from heptane−dichloromethane, mp 224−227 °C. ^1H NMR: 1.42 (s, 27H, *tert*-butyl), 2.26 (s, 9H, aryl-*Me*), 2.87 (d, 14.2 Hz, 3H, N*CH_2*), 4.27 (d, 14.0 Hz, N*CH_2*), 6.65 (s, 3H, aryl), 7.06 (s, 3H, aryl). ^1H NMR($C_6D_5CD_3$, 295 K): 1.56 (s, 27H, *tert*-butyl), 2.21 (s, 9H, aryl-*Me*), 2.35 (br, 3H, N*CH_2*), 4.15 (br, N*CH_2*), 6.37 (s, 3H, aryl), 7.09 (s, 3H, aryl). ^1H NMR ($C_6D_5CD_3$, 370 K): 1.54 (s, 27H, *tert*-butyl), 2.20 (s, 9H, aryl-*Me*), 3.35 (br, 6H, N*CH_2*), 6.44 (s, 3H, aryl), 7.11 (s, 3H, aryl). ^{29}Si: −141.8. Anal. Calcd for $C_{36}H_{49}NO_4Si{\cdot}1/4C_7H_{16}$: C, 73.97; H, 8.71; N, 2.28. Found: C, 73.33; H, 9.11; N, 2.07.

1-Phenylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′-methyl, 6′-*tert*-butylbenzo)[4.4.4.0^{1,6}]tricyclotetradecane, $N[CH_2(Bu^tMeC_6H_2)O]_3SiPh$ (3). A procedure similar to that for **2** was used. The quantities were as follows: **7** (1.70 g, 3.11 mmol), triethylamine (1.30 mL, 9.33 mmol), and phenyltrichlorosilane (0.500 mL, 3.12 mmol). Single crystals suitable for an X-ray study were obtained from acetone: mp > 250 °C (yield 1.00 g, 50%). ^1H NMR: 1.24 (s, 27H, *t*-butyl), 2.26 (s, 9H, aryl-*Me*), 2.98 (d, 14.4 Hz, 3H, N*CH_2*), 4.51 (d, 14.1 Hz, N*CH_2*), 6.64 (s, 3H, aryl), 7.08 (s, 3H, aryl), 7.26 (m, 3H, SiPh), 8.15 (m, 2H, SiPh). ^1H NMR ($C_6D_5CD_3$, 303 K): 1.38 (s, 27H, *t*-butyl), 2.21 (s, 9H, aryl-*Me*), 2.46 (d, 14.3 Hz, 3H, N*CH_2*), 4.47 (d, 14.3 Hz, N*CH_2*), 6.31 (s,3H,aryl), 7.12 (s, 3H, aryl), 7.33 (m, 1H, SiPh), 7.48 (m, 2H, SiPh), 8.49 (dd, 8.2, 1.4 Hz, 2H, SiPh). ^1H NMR ($C_6D_5CD_3$, 373 K): 1.36 (s, 27H, *t*-butyl), 2.19 (s, 9H, aryl-*Me*), 3.6 (br, 6H, N*CH_2*), 6.38 (s, 3H, aryl), 7.12 (s, 3H, aryl), 7.28 (m, 1H, SiPh), 7.41 (m, 2H, SiPh), 8.42 (d, 7.6 Hz, 2H, SiPh). ^{29}Si: −133.1. Anal. Calcd for $C_{42}H_{53}O_3NSi$: C, 77.85; H, 8.24; N, 2.16. Found: C, 77.52; H, 8.39; N, 2.06.

1-Methylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′-methyl, 6′-*tert*-butylbenzo)[4.4.4.0^{1,6}]tricyclotetradecane, $N[CH_2(Bu^tMeC_6H_2)O]_3SiMe$ (5). A procedure similar to that for **2** was used. The quantities were as follows: **7** (1.20 g, 2.13 mmol), triethylamine (0.900 mL, 6.45 mmol), and methyltrichlorosilane (0.250 mL, 2.13 mmol). The crystals obtained from diethyl ether had two molecules per asymmetric unit. Another set of crystals was obtained from dichloromethane−heptane (2:1, 80 mL), and crystals were found to have a half molar equivalent of a hexane molecule in all the data: mp 248−250 °C (yield 1.00 g, 81%). ^1H NMR: 0.54 (s, 3H, Si-*Me*), 1.38 (s, 27H, *tert*-butyl), 2.25 (s, 9H, aryl-*Me*), 2.85 (d, 13.7 Hz, 3H, N*CH_2*), 4.27 (d, 14.0 Hz, N*CH_2*), 6.63 (s,3H,aryl), 7.05 (s, 3H, aryl). ^1H NMR ($C_6D_5CD_3$, 293 K): 1.02 (s, 3H, Si-Me), 1.51 (s, 27H, *t*-butyl), 2.21 (s, 9H, aryl-*Me*), 2.36 (d, 13.9 Hz, 3H, N*CH_2*), 4.23 (d, 13.9 Hz, N*CH_2*), 6.34 (s, 3H, aryl), 7.10 (s, 3H, aryl). ^1H NMR ($C_6D_5CD_3$, 373 K): 0.94 (s, 3H, Si-Me), 1.50 (s, 27H, *t*-butyl), 2.20 (s, 9H, aryl-*Me*), 2.6 (br, 3H, N*CH_2*), 4.2 (br, 3H, N*CH_2*), 6.41 (s, 3H, aryl), 7.10 (s, 3H, aryl). ^{29}Si: −119.8. Anal. Calcd for $C_{37}H_{51}O_3NSi{\cdot}C_3H_7$: C, 76.38; H, 9.29; N, 2.23. Found: C, 76.51; H, 9.96; N, 2.19.

1-Trichloromethylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,-13-tris(4′-methyl,6′-*tert*-butylbenzo)[4.4.4.0^{1,6}]tricyclotetradecane, $N[CH_2(Bu^tMeC_6H_2)O]_3SiCCl_3$ (6). A procedure similar to that for **2** was used. The quantities were as follows: **7** (1.10 g, 2.01 mmol), triethylamine (0.80 mL, 5.7 mmol), and trichloromethyltrichlorosilane (0.50 g, 1.98 mmol). The reaction was only about 20% complete after 3 days. The residue

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Table 1. Crystallographic Data for Compounds 1−5

	1	**2**	**3**	**4**	**5**
formula	$C_{37}H_{50}ClNO_3Si$	$C_{36}H_{48}ClNO_3Si{\cdot}C_4H_{10}O$	$C_{42}H_{53}NO_3Si$	$C_{36}H_{49}NO_4Si{\cdot}1/4C_7H_{16}$	$C_{37}H_{51}NO_3Si{\cdot}1/2C_6H_{14}$
fw	620.3	680.4	647.9	612.9	629.0
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$Pbca$	$P1$	$P2_1/c$	$P\bar{1}$
cryst size, mm	0.25 × 0.2 × 0.05	0.4 × 0.35 × 0.15	0.7 × 0.5 × 0.1	0.5 × 0.4 × 0.05	0.6 × 0.3 × 0.2
a (Å)	11.2357(3)	20.9334(2)	9.9237(3)	13.9943(6)	9.2828(3)
b (Å)	16.1066(3)	16.8328(2)	10.9142(3)	16.3708(6)	13.9380(4)
c (Å)	19.2187(6)	23.1209(3)	17.7380(6)	17.1492(4)	16.2227(4)
α (deg)	90	90	89.561(2)	90	75.693(2)
β (deg)	92.605(2)	90	88.715(2)	98.026(2)	82.420(2)
γ (deg)	90	90	79.228(2)	90	74.166(2)
V (Å^3)	3474.4(2)	8147.1(2)	1886.8(1)	3890.4(2)	1952.0(1)
Z	4	8	2	4	2
D_{calc} (g/cm^3)	1.186	1.109	1.140	1.046	1.070
$\mu_{Mo\ K\alpha}$ (cm^{-1})	1.80	1.60	1.00	0.95	0.95
total no. of reflns	6050	7153	6608	6852	6846
no. of reflns with $I > 2\sigma_I$	4326	4226	5305	4231	5372
R^a	0.0478	0.0546	0.0473	0.0707	0.0568
$R_w{}^b$	0.1349	0.1266	0.1277	0.1909	0.1518

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = \{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2}$.

was washed with water and stored over ethanolic potassium hydroxide overnight to remove the unreacted materials. Afterward, it was filtered, washed with water, and air-dried. Several attempts to grow single crystals suitable for X-ray study using different solvents were not successful. Mp > 240 °C (yield 0.10 g, 7.2%). The low yield is directly related to the slowness of the reaction. Altering the conditions, including boiling toluene, did not improve the yield. ^{1}H NMR: 1.45 (s, 27H, *tert*-butyl), 2.26 (s, 9H, aryl-*Me*), 3.04 (d, 14.8 Hz, 3H, N*CH₂*), 4.61 (d, 14.4 Hz, N*CH₂*), 6.61 (s, 3H, aryl), 7.15 (s, 3H, aryl). ^{29}Si: −142.3. Anal. Calcd for $C_{37}H_{48}Cl_3NO_3Si$: C, 64.48; H, 7.02; N, 2.03. Found: C, 65.31; H, 7.02; N, 1.98.

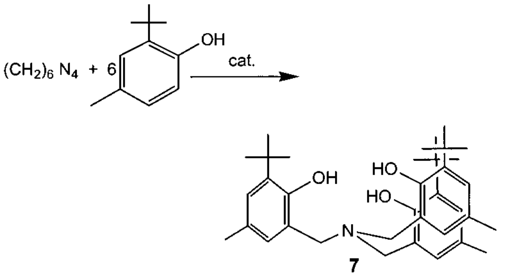
Tris(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)amine, N-[CH$_2$(Bu^{t}MeC$_6$H$_2$)OH]$_3$ (7). A mixture of hexamethylenetetramine (2.50 g, 17.8 mmol, 53.4 eq), 2-*tert*-butyl-4-methylphenol (20.00 g, 122.0 mmol, 40.7 equiv), and *p*-toluenesulfonic acid hydrate (1.00 g) in 1-propanol (5 mL) was stirred for 2 h at about 20 °C and then heated with an oil bath at 100−110 °C for 2 weeks. Commercial ethanol (95%, 100 mL) was added to the mixture and stirred until all the pasty material dissolved, leaving only the powdery material. This mixture was left in a freezer (−20 °C) for 2 days and the precipitate filtered, washed with ethanol (20 mL), and air-dried, mp 191−193 °C (yield 9.0 g, 40%). ^{1}H NMR: 1.37 (s, 27H, *tert*-butyl), 2.24 (s, 9H, aryl-*Me*), 3.57 (s, 6H, NCH2), 6.77 (d, 1.8 Hz, 3H, aryl), 7.01 (d, 1.8 Hz, 3H, aryl). Anal. Calcd for $C_{36}H_{51}O_3N$: C, 79.22; H, 9.42; N, 2.57. Found: C, 78.92; H, 9.14; N, 2.52.

X-ray Studies. The X-ray crystallographic studies were performed using a Nonius KappaCCD diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal of **2** was coated with epoxy to protect it from the atmosphere. Data were collected at 23 ± 2 °C for $\theta_{MoK\alpha} \leq 25°$. All of the data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares. Refinements were based on F^2, and computations were performed on a 600 MHz Pentium III computer using SHELXS-86 for solution[11] and SHELXL-93 for refinement.[12] All of the nonhydrogen atoms, except those of solvents, were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded atoms. For **2** and **3**, the hydrogens on the methyl groups para to the oxygen were staggered in two sets of positions with equal occupancy. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table 1.

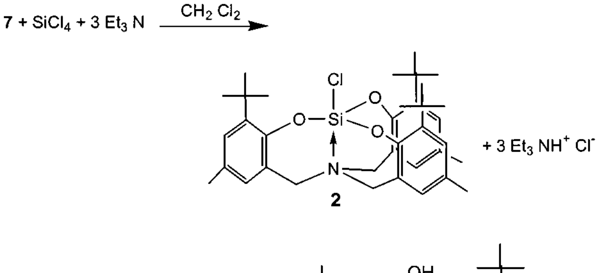
There was an ether molecule in the lattice of **2**, heptane in one-quarter mole ratio in **4**, and hexane in half molar ratio in **5**. All these atoms were refined isotropically, and hydrogens on the solvent atoms were not included in the calculations.

Results and Discussion

Syntheses. The silatranes **1**, **3**, **5**, and **6** were synthesized by the reaction of the triphenol **7** with the appropriate trichlorosilane in the presence of triethylamine. For the synthesis of **2**, $SiCl_4$ was used in a similar reaction. Due to the reactivity of 2, hydrolysis occurred to give the hydroxysilatrane **4**. These reactions are illustrated in the case of the formation of **2** and **4** in eqs 1−3.



(1)



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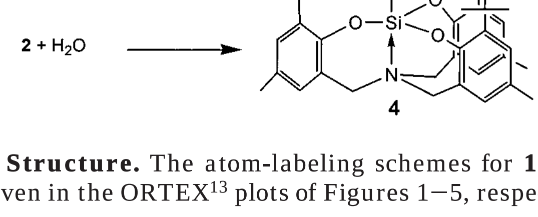

(3)

Structure. The atom-labeling schemes for **1−5** are given in the ORTEX[13] plots of Figures 1−5, respectively.

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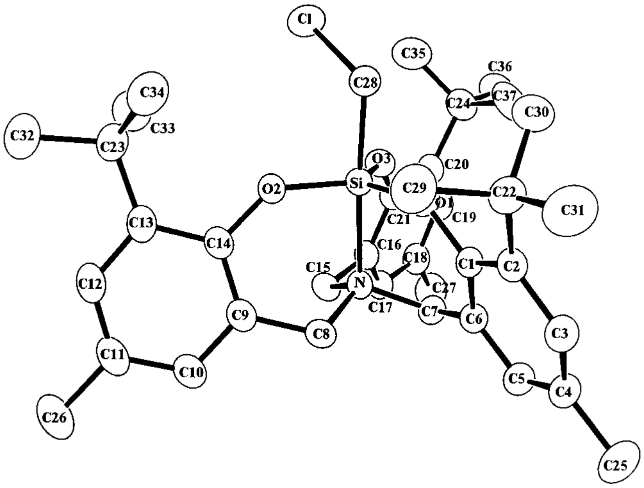

Figure 1. ORTEX diagram of **1**.

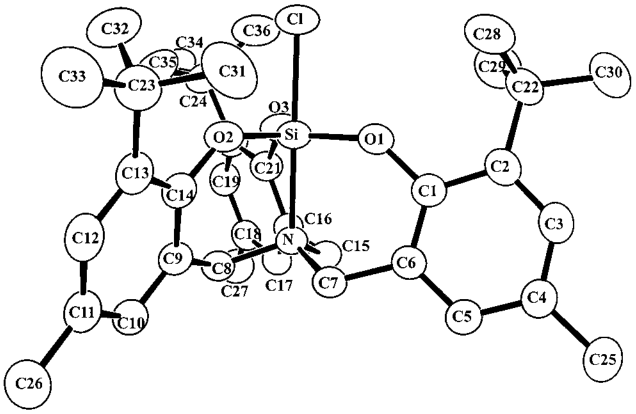

Figure 2. ORTEX diagram of **2**.

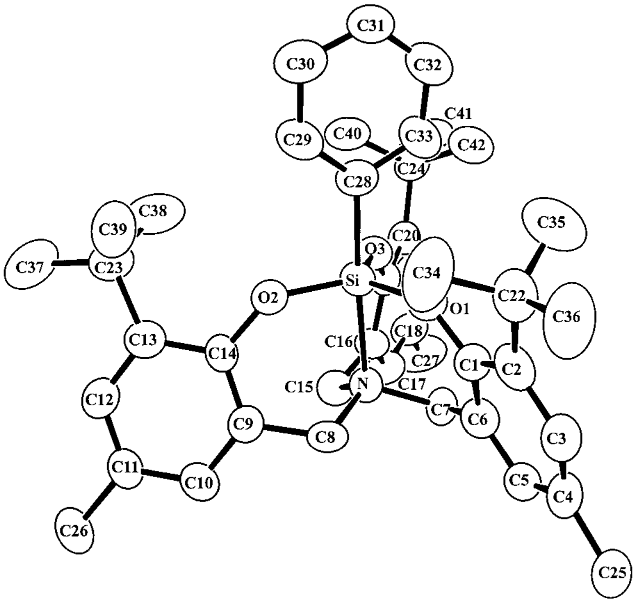

Figure 3. ORTEX diagram of **3**.

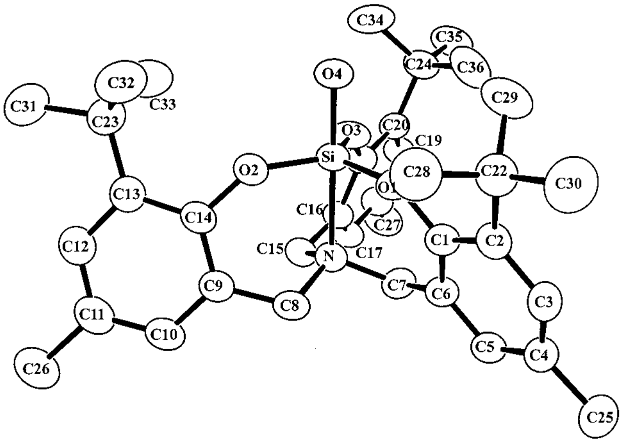

Figure 4. ORTEX diagram of **4**.

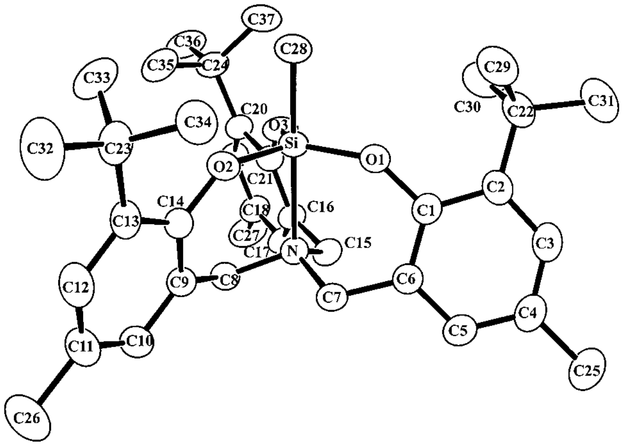

Figure 5. ORTEX diagram of **5**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Si–O(1)	1.673(2)	Si–O(2)	1.660(2)
Si–O(3)	1.669(2)	Si–C(28)	1.906(2)
Si–N	2.045(2)		
O(1)–Si–O(2)	118.8(1)	O(1)–Si–O(3)	120.5(1)
O(2)–Si–O(3)	120.6(1)	O(1)–Si–C(28)	88.1(1)
O(2)–Si–C(28)	93.4(1)	O(3)–Si–C(28)	92.3(1)
O(1)–Si–N	88.11(8)	O(2)–Si–N	89.67(8)
O(3)–Si–N	88.52(8)	C(28)–Si–N	175.9(1)
C(1)–O(1)–Si	139.6(1)	C(14)–O(2)–Si	139.2(2)
C(21)–O(3)–Si	138.4(2)	C(7)–N–C(8)	108.2(2)
C(7)–N–C(15)	109.3(2)	C(8)–N–C(15)	108.9(2)
C(7)–N–Si	110.4(1)	C(8)–N–Si	111.0(1)
C(15)–N–Si	109.1(1)		

The thermal ellipsoids are shown at the 40% probability level, and all hydrogen atoms are omitted for clarity. Selected bond parameters are given in Tables 2–6. X-ray analysis shows that silatranes **1**–**5** have structures that are pentacoordinate and vary in their degree of trigonal bipyramidal character due to the extent of Si–N coordination. The degree of silatrane TBP character is estimated from the approach of the Si–N distance to the sum of the silicon and nitrogen covalent radii of 1.93 Å [14] relative to that for the sum of the van der Waals radii of 3.65 Å.[15] Table 7 lists these values and the Si–N distances from which they were derived.

For comparison, Si–N distances and extent of displacement toward a trigonal bipyramid (% TBP) are listed for silatranes[1b,2] that possess the same R group and have only methyl substituents on the aryl components of the encapsulating agent instead of methyl and *tert*-butyl groups as used in the present study.

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(13) McArdle, P. *ORTEX 5e*; Crystallography Centre, Chemistry Department, University College Galway: Galway, Ireland, 1996.

(14) Sutton, L. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Special Publication Nos. 11 and 18; The Chemical Society: London, 1958 and 1965.

(15) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

Si−O(1)	1.630(2)	Si−O(2)	1.628(2)
Si−O(3)	1.629(2)	Si−N	2.046(2)
Si−Cl	2.1794(8)		
O(1)−Si−O(2)	120.7(1)	O(1)−Si−O(3)	120.5(1)
O(2)−Si−O(3)	118.8(1)	O(1)−Si−N	90.38(7)
O(2)−Si−N	90.85(7)	O(3)−Si−N	90.08(7)
O(1)−Si−Cl	89.43(6)	O(2)−Si−Cl	89.86(6)
O(3)−Si−Cl	89.40(6)	N−Si−Cl	179.26(7)
C(1)−O(1)−Si	139.9(1)	C(14)−O(2)−Si	137.7(1)
C(21)−O(3)−Si	137.9(1)	C(7)−N−C(8)	107.2(2)
C(7)−N−C(15)	108.7(2)	C(8)−N−C(15)	109.2(2)
C(7)−N−Si	111.3(1)	C(8)−N−Si	110.4(1)
C(15)−N−Si	110.0(1)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3

Si−O(1)	1.678(1)	Si−O(2)	1.673(1)
Si−O(3)	1.674(1)	Si−C(28)	1.909(2)
Si−N	2.120(1)		
O(1)−Si−O(2)	121.31(6)	O(1)−Si−O(3)	121.08(7)
O(2)−Si−O(3)	116.83(6)	O(1)−Si−C(28)	90.31(7)
O(2)−Si−C(28)	96.13(7)	O(3)−Si−C(28)	92.41(6)
O(1)−Si−N	85.94(6)	O(2)−Si−N	87.36(5)
O(3)−Si−N	88.00(5)	C(28)−Si−N	175.85(7)
C(1)−O(1)−Si	141.6(1)	C(14)−O(2)−Si	138.6(1)
C(21)−O(3)−Si	141.2(1)	C(7)−N−C(15)	107.6(1)
C(8)−N−C(15)	109.2(1)	C(7)−N−C(8)	109.1(1)
C(7)−N−Si	110.8(1)	C(8)−N−Si	108.7(1)
C(15)−N−Si	111.4(1)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 4

Si−O(1)	1.638(2)	Si−O(2)	1.645(2)
Si−O(3)	1.640(2)	Si−O(4)	1.677(2)
Si−N	2.163(3)		
O(1)−Si−O(2)	118.1(1)	O(1)−Si−O(3)	120.3(1)
O(2)−Si−O(3)	120.6(1)	O(1)−Si−O(4)	94.0(1)
O(2)−Si−O(4)	93.5(1)	O(3)−Si−O(4)	92.3(1)
O(1)−Si−N	87.0(1)	O(2)−Si−N	86.5(1)
O(3)−Si−N	86.7(1)	O(4)−Si−N	178.8(1)
C(1)−O(1)−Si	142.3(2)	C(14)−O(2)−Si	141.0(2)
C(21)−O(3)−Si	141.7(2)	C(7)−N−C(8)	108.6(2)
C(7)−N−C(15)	108.8(2)	C(8)−N−C(15)	109.7(2)
C(7)−N−Si	111.1(2)	C(8)−N−Si	109.4(2)
C(15)−N−Si	109.3(2)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 5

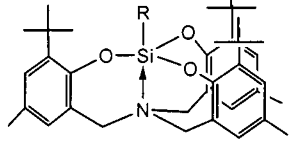
Si−O(1)	1.657(2)	Si−O(2)	1.662(2)
Si−O(3)	1.650(2)	Si−C(28)	1.878(2)
Si−N	2.211(2)		
O(1)−Si−O(2)	120.8(1)	O(1)−Si−O(3)	119.3(1)
O(2)−Si−O(3)	117.9(1)	O(1)−Si−C(28)	94.3(1)
O(2)−Si−C(28)	94.4(1)	O(3)−Si−C(28)	95.0(1)
O(1)−Si−N	85.20(7)	O(2)−Si−N	85.51(7)
O(3)−Si−N	85.58(7)	C(28)−Si−N	179.4(1)
C(1)−O(1)−Si	142.6(1)	C(14)−O(2)−Si	143.6(1)
C(21)−O(3)−Si	142.5(1)	C(7)−N−C(8)	108.8(2)
C(7)−N−C(15)	109.4(2)	C(8)−N−C(15)	108.6(2)
C(7)−N−Si	109.8(1)	C(8)−N−Si	110.7(1)
C(15)−N-Si	109.4(1)		

The data listed in column 5 are shown in decending order of increasing Si−N distance, which parallels an approximate decrease in the electronegativity of the axial R groups. It is apparent that there is a much more limited overall change in the Si−N distances (0.166 Å) for the present series **1**−**5** compared to that in our studies of related series[1b,2] lacking any *tert*-butyl substituents (0.813 Å). The former change in the Si−N distance is nearly the same as that found in a series of silatranes **B**[6−9] (depicted in the Introduction) with comparable axial R groups. These contain only five-membered rings. The overall change in Si−N distances over this series is 0.149 Å.

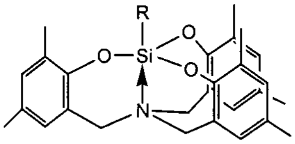
Table 7. Comparison of Si−N Distances and Displacements toward TBP Geometries for Silatranes with Six-Memebered Rings

compd	R	Si−N[a,b] (Å)	% TBP[a,b]	Si−N[c,d] (Å)	% TBP[c,d]
6	CCl_3			2.025(4)	95
2	Cl	2.046(2)	93		
1	CH_2Cl	2.045(2)	93	2.112(4)	89
				2.130(5)	88
3	Ph	2.120(1)	89	2.193(3)	85
				2.283(3)	79
4	OH	2.163(3)	86		
5	Me	2.211(2)	84	2.745(5)	53

[a] The silatranes **1**−**6** listed in columns 3 and 4 have the formula



[b] This work. [c] The silatranes listed in columns 5 and 6 have the formula



[d] The values tabulated in these two columns are taken from ref 2 except that for R = CH_2Cl, which is from ref 1b.

We had reasoned[2] that due to ring constraints in silatranes that contain all five-membered rings, the Si−N donor−acceptor interaction is confined to a narrow range. In fact, all previous studies have centered on silatranes with five-membered rings.[3−9] In over 60 of these systems,[3−5] the Si−N distances found in the crystalline state are confined to a narrow range (0.275 Å) extending from 1.965(5) to 2.240(9) Å.

In the present study of **1**−**5**, we can anticipate a similar ring restriction. In this case, we postulate the restriction is a result of a repulsion effect between the bulky *tert*-butyl groups positioned on the aryl components and the neighboring axial group in each of the silatranes. This is somewhat evident from the ORTEX plots in Figures 1−5, where the aryl rings are displaced away from the axial R groups. A comparison in Figure 6 makes this effect more evident where an ORTEX plot of silatrane **5** is shown relative to one of the related silatranes having the same methyl axial substituent but composed of all six-membered rings, which are less restrictive.[2] As a consequence of the steric interactions in **1**−**5**, the tilting of the aryl components away from the axial groups is relieved by a steric compression of the weak Si−N bond.

A further detail of the silatranes **1**−**5** from the X-ray analysis reveals that they all are chiral and have centrosymmetric space groups. A propeller arrangement for the rings when viewed down the HO−Si−N axis is illustrated in the ORTEX diagram for **4** in Figure 7. This information will prove useful in the discussion of their dynamic NMR behavior in the following section.

NMR Spectroscopy. ^1H NMR spectra at ambient temperature show that the signals of NCH_2 protons comprise two doublets of equal intensity. Table 8 lists

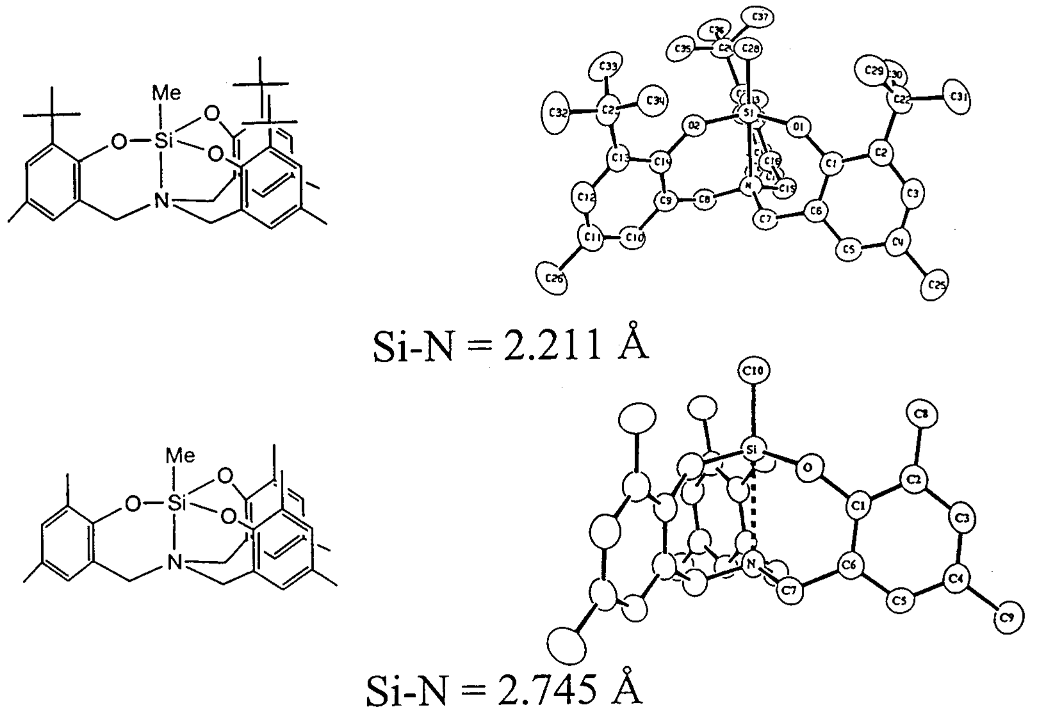


Figure 6. ORTEX representation of steric compression of the Si−N distance typified by silatrane **5** by *tert*-butyl groups relative to the similarly constituted silatrane without *tert*-butyl groups. Both have axial methyl substituents. For labeling of **5**, see Figure 5. For labeling of the lower silatrane, see Figure 1 of ref 2.

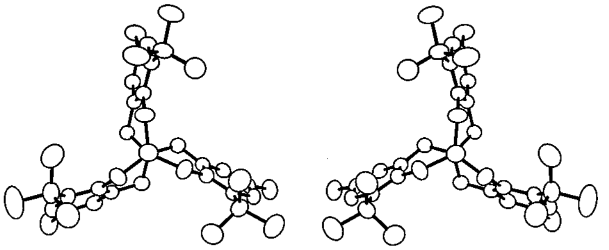


Figure 7. ORTEX diagram showing the propeller arrangements of the clockwise and anticlockwise orientations of the centrosymmetric related molecules of **4**. Both are viewed along the HO−Si−N axis with OH at the top.

Table 8. ^{1}H and ^{29}Si NMR Data for Silatranes with Six-Membered Rings

compd	R	δ(NCH$_2$)^{a,b} (ppm)	δ(^{29}Si)^{a,c} (ppm)	$\Delta G^{\ddagger\, a,d}$ (kcal/mol)	δ(^{29}Si)^{e} (ppm)	$\Delta G^{\ddagger\, e}$ (kcal/mol)
6	CCl$_3$	3.04, 4.61	−142.3	≥18	−140.8	>16.6
2	Cl	3.01, 4.36				
1	CH$_2$Cl	2.94, 4.37	−132.5	≥18	−123.8	11.8
3	Ph	2.98, 4.51	−133.1	16.0	−110.7	9.7
4	OH	2.87, 4.27	−141.8	15.1		
5	Me	2.85, 4.27	−119.8	≥18	−74.5	10.3

[a] See footnotes *a* and *b* to Table 7. [b] In CHCl$_3$ solution. [c] In CH$_2$Cl$_2$ solution. [d] Calculated from VT ^{1}H NMR data obtained from C$_6$D$_5$CD$_3$ solutions. [e] See footnotes *c* and *d* to Table 7.

these chemical shifts. On warming to 370 K, coalescence is observed for silatranes **3** and **4** with a T_c of 358 and 325 K, respectively. Thus, the signals of each of the methylene protons, which are different at low temperature and couple with each other, coalesce and time average. The process that makes the methylene protons become equivalent is most likely associated with the presence of a racemic mixture of the chiral silatranes which are rapidly intraconverting at room temperature. The silatranes **1**, **2**, **5**, and **6** are rigid even at 370 K. As shown in Figure 7 for **4**, the three rings most likely flip or pseudorotate simultaneously to cause the clockwise and counterclockwise propeller orientations to interchange with one another. The activation energies $\Delta G^{\ddagger}$ are computed from eq 4.[16]

$$\Delta G^{\ddagger} = 1.987 \times T_c \times (23 + \log_e(T_c/\Delta\nu)) \qquad (4)$$

For **3** and **4** the activation energies are 16 and 15 ± 1 kcal/mol, respectively. It is expected to be ≥18 kcal/mol for the other silatranes. These values are noticeably large compared to that displayed in Table 8 (columns 7 and 8) for silatranes with the same axial ligands studied earlier[1b,2] that contained a more flexible six-membered ring system. For these and related silatranes having the latter ring system[1b,2] the range of $\Delta G^{\ddagger}$ was 9.1−11.8 kcal/mol except for the trichloromethyl silatrane,[2] which had a value of >16.6 kcal/mol. Part of the reason for this increase in **1**−**6** is reasonably associated with the steric effect introduced by the presence of the *tert*-butyl groups as part of the encapsulating amine. It is imagined that this effect acts to inhibit the ring pseudorotational process proposed in the enantiomeric conversion. However, it is not clear why the silatranes **3** and **4** have a lower activation energy than that for silatrane **5**.

Also in Table 8, ^{29}Si chemical shifts for **1**−**6** are compared to those for analogous silatranes[1b,2] that have the same axial ligand but have methyl groups in place of *tert*-butyl groups attached to the ring system. The ^{29}Si shifts for **1**−**6** are confined to a narrow range of about 22 ppm and show values that only loosely follow electronegativity associated with the axial ligand other

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(16) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill: New York, 1989; p 103. The expression in eq 4 is a variation of the one reported in this reference.

than R = OH. By contrast, the series with the more flexible ring system,[1b,2] as already explained, shows a large variation in ^{29}Si shift, covering a range that extends over 66 ppm.[1b] It was demonstrated that these shifts show an increase in shielding that parallels a decrease in the Si−N distance and which correlates with an increase in the axial ligand electronegativity.[1b,2] The present series of silatranes **1**−**6** behaves more like the analogous series of silatranes with five-membered rings, e.g., series **B**[6−9] in the Introduction. In series **B**, the range of ^{29}Si shifts extends over 30 ppm and exhibits no trend with axial ligand electronegativity.

Summary and Conclusions. The present study demonstrates that the introduction of a steric effect via *tert*-butyl groups on the six-membered ring system that interacts with the axial ligand of the silatrane results in restricting the Si−N donor−acceptor interaction. The steric effect reduces the range of Si−N distances to 0.166 Å, i.e., from 2.045(2) to 2.211(2) Å, in a series of silatranes with axial ligands that vary in electronegativity where the most electronegative ligand produces the shortest Si−N distance. By contrast, an entirely analogous series of silatranes[1b,2] containing six-membered rings but lacking a steric effect shows a range of Si−N distances that is over 4 times as great, 0.813 Å, i.e., from 2.025(4) to 2.838(4) Å.

The steric restriction in limiting the Si−N interaction in the present study of silatranes containing six-membered rings is comparable to the range found in an analogous series of silatranes with five-membered rings.[6−9] Here the Si−N distance ranged over 0.15 Å.

It is concluded that the greater rigidity imposed by the presence of a sufficient steric effect in silatranes containing six-membered rings is comparable to that found in all previous studies of silatranes[3−9] composed of five-membered rings and that this ring restriction limits the extent of Si−N interaction that could be studied by substituent variations. In the less restricted silatranes studied earlier[1b,2] with six-membered rings, the degree of nitrogen donor interaction is found to depend primarily on electronegativity effects induced at silicon by the exocyclic ligand. In the present study, this is not so.

Further, for silatranes with a six-membered ring system, increased activation energies for enantiomeric conversion of the propeller-like silatranes correlate in general with increased structural rigidity associated with the ring system.

Acknowledgment. The support of this research by the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM001024H