New Azasilatranes: Synthesis and Substitution Reactions

Dietrich Gudat and John G. Verkade*

Gilman Hall, Iowa State University, Ames, Iowa 50011

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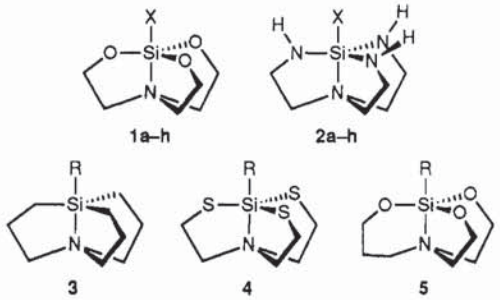
The syntheses of new azasilatranes of the type $XSi(NRCH_2CH_2)_3N$ (R = H, X = OEt (**2f**), OPh (**2g**); R = Me, X = H (**8a**), OEt (**8b**); R = $SiMe_3$, X = H (**9a**)) via condensation reactions of tetraamines $N(CH_2CH_2NHR)_3$ and substituted tris(dimethylamino)silanes, $XSi(NMe_2)_3$, are described. In the case of **2g**, the required silane $PhOSi(NMe_2)_3$ was generated in situ from the reaction of PhOH and $Si(NMe_2)_4$. The chloroazasilatrane, **2h** (R = H, X = Cl), whose synthesis was not feasible by the above method, was obtained by reaction of hydroazasilatrane, **2a** (R = H, X = H), with CCl_4 in the presence of a platinum or palladium catalyst. Reaction of azasilatranes **2a** and **2f** with $ClSiMe_2R'$ (R' = H, Me, Ph) in the presence of triethylamine affords the silyl-substituted azasilatranes $XSi(N(SiMe_2R')CH_2CH_2)_3N$ (X = H, R' = H (**9b**), Me (**9a**), Ph (**9c**); X = OEt, R' = H (**14a**)) and $XSi(N(SiMe_2R')CH_2CH_2)_2NHCH_2CH_2N$ (X = OEt; R' = Me (**14b**), Ph (**14d**)), respectively, while no reaction was observed between either **2a** or **2f** and $ClSiMe_2$-*t*-Bu. The new azasilatranes are characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, by high-resolution mass spectroscopy, and by an X-ray crystal structure determination in the case of **8b**.

Introduction

Silatranes of type **1**[1] are one of the most extensively and systematically studied classes of compounds featuring hypervalent main-group elements. Hypercoordination in this case stems from the existence of a transannular donor–acceptor bond between silicon and nitrogen, resulting in an approximately tbp coordination of silicon and formal quaternization at nitrogen. The expanded coordination of silicon here leads to the unique chemical and physical properties of silatranes, which in many respects differ remarkably from derivatives of four-coordinate silicon. Systematic studies of silatranes, using a variety of physicochemical techniques, have provided considerable detailed insight into their electronic structure and bonding.[1] On the basis of these results, the observed changes in physical properties and chemical reactivity have successfully been correlated with variations in the strength of the transannular Si–N bond.



1a–h **2a–h**

3 **4** **5**

a, X = H; **b**, X = Me; **c**, X = Vi; **d**, X = Ph; **e**, X = Et; **f**, X = OEt; **g**, X = OPh; **h**, X = Cl

Silatrane analogues featuring a modified tricyclic skeleton, such as triaza-[2] (**2**), tricarba-[3] (**3**), trithia-[4] (**4**), or homosilatranes[5] (**5**) are also known, but they have so far garnered rather limited interest. Although hydro- and hydrocarbon-substituted azasilatranes[6] **2a–e**, which are isoelectronic with **1**, were prepared more than a decade ago,[2] a systematic multinuclear NMR spectroscopic study was published only recently.[7] The results of a recent X-ray crystal structure determination of the phenyl derivative **2d** have also been reported,[8] providing for the first time a set of molecular structure parameters for an azasilatrane. These data suggest a close similarity of these derivatives to silatranes, with an even stronger transannular interaction between silicon and the axial nitrogen.

Bearing these similarities in mind, it was of interest to expand the comparison between silatranes and their aza analogues to derivatives with axial functional groups featuring a silicon bond to atoms other than carbon or hydrogen. Moreover, since the polarity of the equatorial bonds seems to influence the strength of the transannular bond,[2,7] azasilatranes appeared to be excellent model compounds for varying the equatorial bond polarity by substituting one or more of the exocyclic NH hydrogens with groups of different electronegativity. Such a study is, of course, precluded in silatranes because of the two-coordinate nature of the equatorial oxygens.

As will be demonstrated, N-substituted azasilatranes can be realized either via substitution reactions of NH functionalities of azasilatranes or by direct synthesis starting from N-substituted tris (2-aminoethyl)amines. Also presented is a method for substituting the axial Si–H bond in azasilatranes. The systematic investigation of the reactivity of hydro- and the new ethoxyazasilatrane at their equatorial N–H groups in the presence of di- and trisubstituted chlorosilanes reveals the dominating influence of steric interactions. Characterization of the new compounds by means of multinuclear NMR and mass spectroscopy is reported, as is the crystal structure of the new 1-ethoxy-*N*,*N*′,*N*″-trimethylazasilatrane (**8b**). A more detailed interpretation of the ^{29}Si NMR data for the azasilatranes presented here will be given elswhere.[9]

(1) For a comprehensive review of the chemical and physical properties of silatranes see: Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1 and references cited therein.
(2) Lukevics, E.; Zelchan, G. I.; Solomennikova, I. I.; Liepin'sh, E. E.; Yankovska, I. S.; Mazheika, I. B. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1977**, *47*, 98.
(3) Jurkschat, K.; Muegge, C.; Schmidt, J.; Tzschach, A. *J. Organomet. Chem.* **1985**, *287*, C1.
(4) Zelchan, G. I.; Solomennikova, I. I.; Lukevics, E.; Yankovska, I. S.; Mazheika, I. B. IVth Internat. Symp. Organosilicon Chem., Abstracts of Papers, Moscow 1975, 198, Vol. I, part 1.
(5) Lukevics, E.; Solomennikova, I. I.; Zelchan, G. I. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1976**, *46*, 133.
(6) The term "azasilatrane" is used throughout this paper to denote molecules containing the 1-sila-2,5,8,9-tetraazatricyclo[3.3.0]undecane skeleton, in which all three oxygen atoms of silatranes are formally replaced by NR groups.
(7) Kupce, E.; Liepin'sh, E. E.; Lapsina, A.; Zelchan, G. I.; Lukevics, E. E. *J. Organomet. Chem.* **1987**, *333*, 1.
(8) Macharashvili, A.; Shklover, V. E.; Struckhov, Yu. T.; Lapsina, A.; Zelchan, G.; Lukevic, E. *J. Organomet. Chem.* **1988**, *349*, 23.
(9) Gudat, D.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, in press.

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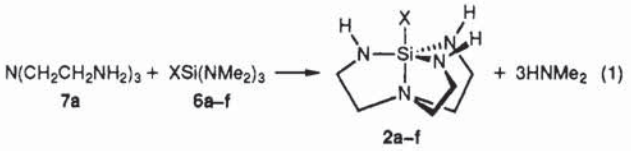
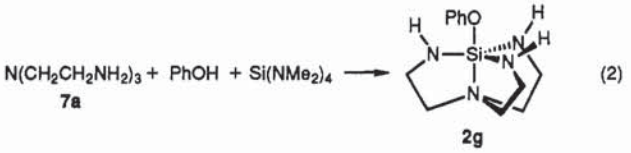
Results and Discussion

Reactions of Tris(2-aminoethyl)amines ($N(CH_2CH_2NHR)_3$) with Tris(dimethylamino)silanes ($XSi(NMe_2)_3$). As lukevics et al. reported in 1977,[2] heating of tris(dimethylamino)silanes **6a–e** with tris(2-aminoethyl)amine (**7a**, tren) to 100–120 °C results in the formation of dimethylamine and azasilatranes **2a–e** (reaction 1). We find that the reaction is effectively catalyzed by



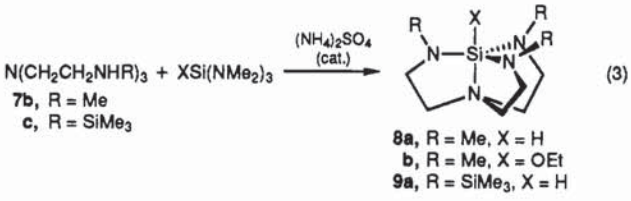
a, X = H; **b**, X = Me; **c**, X = Vi; **d**, X = Ph; **e**, X = Et; **f**, X = OEt

trimethylchlorosilane, resulting in a lower reaction temperature and improved purity of the product. The synthesis of **2a** was thereby readily achieved at 80 °C, and the melting point of the purified product (77–79 °C) was considerably higher than the literature value (51–55 °C[2]). Similarly, 1-ethoxyazasilatrane (**2f**) was obtained from tren and ethoxytris(dimethylamino)silane at 135 °C, the higher reaction temperature in this case reflecting the poorer reactivity of the alkoxysilane compared with its hydro or alkyl analogues. Furthermore, a catalytic amount of ammonium sulfate proved to be superior to trimethylchlorosilane, which may be explained by the lower volatility of the ammonium salt. In analogy to the synthesis of aryloxysilatranes,[10] we find that in situ generation of tris(dimethylamino)(aryloxy)silanes by the alcoholysis of tetrakis(dimethylamino)silane can be utilized as an alternate procedure to simplify the synthesis of aryloxy-substituted azasilatranes (reaction 2). Here, 1-phenoxy-



azasilatrane (**2g**) is obtained directly from the reaction of an equimolar mixture of phenol, tetrakis(dimethylamino)silane, and tren, without the necessity of isolating the intermediate phenoxytris(dimethylamino)silane.

The synthesis of equatorial N-trisubstituted azasilatranes **8a,b** and **9a** in the ammonium sulfate-catalyzed reaction 3 was accomplished by employing the appropriate



substituted tren compounds **7b** (R = CH_3; Me-tren) and **7c** (R = $Si(CH_3)_3$; Tms-tren). Compared with the preparation of azasilatranes **2a** and **2f** in reaction 1, higher temperatures and longer reaction times are required, probably reflecting the increased steric crowding around the pentacoordinate silicon atom. A remarkable regioselectivity is displayed in the reaction of tris(dimethylamino)silane with Tms-tren. The crude product, according to ^1H NMR spectroscopic analysis, consists of an approximately 90:10 mixture of two components, which may be assigned as *N,N',N''*-tris(trimethylsilyl)azasilatrane (**9a**) (major product) and *N,N'*-bis(trimethylsilyl)azasilatrane, respectively. The latter is assumed to arise at some point in the reaction from elimination of (dimethylamino)trimethylsilane, which competes with the elimination of dimethylamine (Scheme I). The relative ratio of the products obtained by the alternative pathways a and b indicates that the reactivity of the N–H bond exceeds that of the N–Si bond in this reaction.

Scheme I

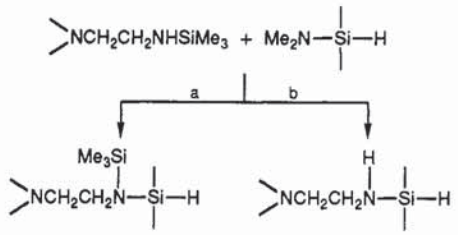


Table I. Reaction of Hydroazasilatrane 2a with CCl_4 in $CDCl_3$

catalyst	temp, °C	reactn time, h	product ratio **2a:2h**
	70	3.5	80:20
cis-$(Me_2PhP)_2PtCl_2$ (**10a**)	70	3.5	25:75
$(Me_2PhP)_2PdCl_2$ (**10b**)	28	0.2	<1:99
cis-$(Me_2PhP)_2PtCl_2$/pyridine-d_5	70	3.5	50:50

Attempts to synthesize 1-(dimethylamino)- or 1-chloroazasilatrane by reacting tren with tetrakis(dimethylamino)silane or chlorotris(dimethylamino)silane, respectively, failed, whether or not ammonium sulfate was present as a catalyst. Although the preparation of 1-(dimethylamino)azasilatrane by the former route has been claimed in the patent literature,[11] our attempts produced only nonvolatile, oligomeric/polymeric materials.

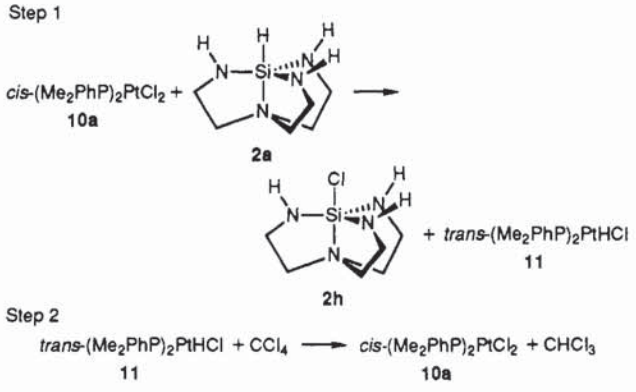
Substitution Reactions at the Si–H Bond of 1-Hydroazasilatrane. Because direct synthesis of 1-chloroazasilatrane from acyclic precursors was not successful, an approach involving substitution at the silicon atom of an appropriate azasilatrane precursor was developed. Since the preparation of halogenated silatranes by oxidation of 1-hydrosilatrane (**1a**) using organic halides has been reported,[1] we decided to investigate the analogous reaction of azasilatrane.

By monitoring the reaction of 1-hydroazasilatrane (**2a**) with excess CCl_4 in $CDCl_3$ at 70 °C with ^1H NMR spectroscopy, we found that **2a** was slowly converted into a new product. Together with the disappearance of the Si–H resonance of **2a**, formation of chloroform was detected, indicating the expected transformation of **2a** into 1-chloroazasilatrane (**2h**). The reaction rate was found to be considerably increased by the addition of catalytic amounts of a bis(phosphine)platinum or -palladium dichloride (Table I). Thus, addition of 2–5 mol % of *cis*-$(Me_2Ph)_2PtCl_2$ (**10a**) accelerates by a factor of 12 the conversion of **2a** into **2h**, as measured by the relative ratio of products in the ^1H NMR spectrum. Surprisingly, addition of pyridine to a mixture of **2a**/CCl_4/**10a** resulted in a decrease of the rate compared with that of the same reaction in the absence of base. Upon addition of the palladium analogue **10b**, no starting material could be detected after 10 min at room temperature. The only

(10) Voronkov, M. G.; Zelchan, G. I. *Chem. Heterocycl. Compd.* **1965**, *1*, 137.

(11) LeGrow, G. E. U.S. Patent 3,576,026, 1971.

Scheme II



soluble byproduct detectable by ^1H NMR spectroscopy was a trace of $CHDCl_2$ resulting from reduction of the solvent. In all these reactions, various quantities of an insoluble byproduct were also obtained, whose nature is still obscure. Purification and isolation of 1-chloroazasilatrane was successfully achieved after separation of the insoluble material, and its constitution was unequivocally proved by NMR and high-resolution mass spectrometry (vide infra).

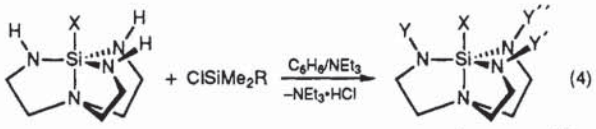
Formation of a Pt–Si bond has been reported in the reaction of 1a with **10a**,[12] yielding a transition-metal-substituted silatrane. Further investigation of the metal-catalyzed reaction of **2a** and CCl_4 was therefore of interest in order to detect possible formation of a platinum-substituted azasilatrane as an intermediate. For this purpose, the reaction of **2a** and a stoichiometric amount of **10a** was monitored by ^1H and ^{31}P NMR spectroscopy. Upon addition of **10a** to a solution of **2a** in $CDCl_3$, the ^{31}P resonance of **10a** ($\delta(^{31}P)$ −15.4 ppm ($^1J_{P-Pt}$ = 3546 Hz)) was immediately replaced by a new signal at −3.1 ppm ($^1J_{P-Pt}$ = 2770 Hz). The smaller value of the phosphorus–platinum coupling in the product suggests a trans configuration of the phosphine ligands. In the ^1H spectrum, a second product in addition to **2h** was observed, which was identified as *trans*-$(Me_2PhP)_2PtHCl$ (**11**) by the appearance of a multiplet at $\delta(^1H)$ −16.7 ppm ($^2J_{H-P}$ = 15 Hz, $^1J_{H-Pt}$ = 1271 Hz) as expected for a hydrogen bound directly to platinum. The identity of **11** was confirmed by comparison of the spectroscopic data with those of an authentic sample. Further, no intermediate featuring a silicon–platinum bond was detectable by means of NMR spectroscopy.

Since the reaction of **11** with CCl_4 is known from the literature to give **10a** and chloroform[13] over a period of several days, the following two-step pathway for the formation of **2h** can be proposed (Scheme II). First, metathesis of the Cl and H substituents of **2a** and **10a**, respectively, gives **2h** and the platinum hydride **11**. It can be assumed that this reaction proceeds via an oxidative addition/reductive elimination mechanism, which involves a species containing an azasilatranyl ligand bound to a Pt(IV) center as an intermediate. Similar intermediates and their decomposition into halosilanes and platinum halo complexes have been previously discussed in reactions of silylplatinum complexes with halogens.[14] In the second step of Scheme II, oxidation of **11** by CCl_4 regenerates **10a**. Since our NMR studies show that the first step is rapid, the oxidation of **11** can be considered as rate determining.

The observed inhibition of the overall reaction upon addition of pyridine may be explained by an equilibrium between **11** and $[(Me_2PhP)_2PtH(py)]^+Cl^-$ under these conditions,[15] which is apparently less prone to undergo oxidation by CCl_4.

Attempts to utilize the Si–H bond in **2a** in order to introduce dialkylamino groups were unsuccessful. Whereas formation of Si–N bonds by the amide-catalyzed reaction of silanes with amines is well-known,[16] no reaction occurred between **2a** and excess diethylamine in the presence of lithium diethylamide, and unreacted **2a** was recovered in almost quantitative yield.

Substitution Reaction at Equatorial N–H Bonds of Azasilatranes. Silylation reactions of **2a** and **2f** were studied with silanes of the type $ClSiMe_2R$ (**13a–d**) in the presence of a base (reaction 4). The results demonstrate



(4)

	X		R		X	Y	Y′	Y″
2a	H	**13a**	Me	**9a**	H	$SiMe_3$	$SiMe_3$	$SiMe_3$
2a	H	**13b**	H	**9b**	H	$SiMe_2H$	$SiMe_2H$	$SiMe_2H$
2a	H	**13c**	Ph	**9c**	H	$SiMe_2Ph$	$SiMe_2Ph$	$SiMe_2Ph$
2a	H	**13d**	*t*-Bu	no reaction				
2f	OEt	**13b**	H	**14a**	OEt	$SiMe_2H$	$SiMe_2H$	$SiMe_2H$
2f	OEt	**13a**	Me	**14b,(c)**	OEt	$SiMe_3$	$SiMe_3$ (H)	H
2f	OEt	**13c**	Ph	**14d,(e)**	OEt	$SiMe_2Ph$	$SiMe_2Ph$ (H)	H
2f	OEt	**13d**	*t*-Bu	no reaction				

the ability of azasilatranes to undergo substitution reactions at the equatorial N–H functional groups with retention of the atrane structure. Typically the reactions were carried out by addition of excess triethylamine and the appropriate chlorosilane to benzene solutions of the azasilatranes. Workup of the reaction mixtures consisted of filtering off the ammonium salt formed, removing the volatiles in vacuo, followed by sublimation or distillation of the residue. Characterization of the products was carried out by NMR and mass spectroscopies (vide infra).

Reaction of **2a** with chlorosilanes **13a–c** afforded substitution of all three amino groups, giving **9a–c**. Also, a tris-silylated 1-ethoxyazasilatrane (**14a**) was obtained from **2f** and dimethylchlorosilane. With **2f** and the more bulky trimethyl- and dimethylphenylchlorosilane, respectively, the reaction stopped with disubstitution, and bis-silylated azasilatranes **14b,d** were isolated. Compound **14d** was contaminated by a small amount of monosubstitution product **14e**, which could not be removed by distillation. Pure *N*-(trimethylsilyl)-1-ethoxyazasilatrane (**14c**), featuring substitution of only one equatorial N–H group, was obtained from **2f** and trimethylchlorosilane, by appropriately adjusting the reaction conditions (see Experimental Section). No reaction was observed with either **2a** or **2f** and *tert*-butyldimethylchlorosilane.

An explanation of the observed differences in reactivity in the reactions of **2a,f** with chlorosilanes **13a–d**, respectively, becomes feasible by taking into account steric strain in the products formed. Thus, the failure of bis-silyl-substituted products **14b,d** to undergo complete silylation with excess reagent may be attributed to steric overcrowding stemming from repulsive interactions of the ethoxy substituent on silicon and the two bulky tri-

(12) Eaborn, C.; Odell, K. J.; Pidcock, A.; Scollary, G. *J. Chem. Soc., Chem. Commun.* **1976**, 317.
(13) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.
(14) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343.
(15) Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. L. *J. Chem. Soc.* **1961**, 2207.
(16) Pawlenko, S. In *Houben-Weyl, Bd XIII/5*; Georg Thieme Verlag: Stuttgart, 1980; S. 227f.
(17) Bellama, J. M.; Nies, J. D.; Ben Zvi, N. *Magn. Reson. Chem.* **1986**, *24*, 748.

Table II. High-Resolution Mass Spectral Data

	mol formula	m/e- (calcd), amu	m/e- (found), amu	error, mamu
2f	$C_8H_{20}N_4OSi$	216.14065	216.14037	−0.28
2g	$C_{12}H_{20}N_4OSi$	264.14065	264.14063	−0.02
2h	$C_6H_{15}ClN_4Si$	206.07546[b]	206.07589[b]	0.43
8a	$C_9H_{21}N_4Si$[a]	213.15356	213.15379	0.23
8b	$C_{11}H_{26}N_4OSi$	258.18758	258.18733	−0.25
9a	$C_{15}H_{39}N_4Si_4$[a]	387.22519	387.22550	0.31
9b	$C_{12}H_{33}N_4Si_4$[a]	345.17823	345.17884	0.61
9c	$C_{30}H_{45}N_4Si_4$[a]	573.27214	573.27241	0.27
14a	$C_{14}H_{37}N_4OSi_4$[a]	389.20445	389.20484	0.39
14b	$C_{14}H_{36}N_4OSi_3$	360.21971	360.22059	0.88
14c	$C_{11}H_{28}N_4OSi_2$	288.18018	288.17096	−0.22
14d	$C_{24}H_{40}H_4OSi_3$	484.25101	484.24978	−1.23

[a] $(M - H)^+$; M^+ was not observed with sufficient intensity to ensure discrimination from ^{13}C and ^{29}Si satellites of $(M - H)^+$. [b] ^{37}Cl isotope: calcd. 208.072 50, found 208.073 01.

methylsilyl or dimethylphenylsilyl substituents on adjacent nitrogen atoms with another incoming silyl substituent. In monosilylated azasilatranes **14c,e**, the same type of steric hindrance consistently explains the slower rate of subsequent substitution steps which allows the isolation of **14c** in the reaction of **2f** and trimethylchlorosilane (**13b**). A release of strain is provided by decreasing the bulk of either the silicon- or nitrogen-bound substituents, thus allowing the formation of tris-silyl-substituted azasilatranes **9a–c** and **14a**, respectively. The failure of both **2a** and **2f** to react with *tert*-butyldimethylchlorosilane may be attributed to overcrowding of the tetracoordinate silicon center, which is unable to accommodate both the bulky *tert*-butyl and the azasilatranyl substituents.

Spectroscopic Properties. The identity and purity of the compounds synthesized were verified by high-resolution mass spectroscopy (Table II) and by ^1H (Table III) and ^{13}C and ^{29}Si NMR spectroscopy (Table IV). For symmetrically substituted compounds, the AA′XX′ spectrum of the methylene protons of the silatrane cage usually appears as two sets of virtual triplets, as has been observed for a variety of silatranes[1,18] and azasilatranes **2a–e**.[2] Only in the case of **8a** was a more complex AA′BB′ pattern observed, owing to a smaller chemical shift difference. Unsymmetrically substituted **14b–d** displayed two sets of resonances that are assigned as AA′XX′ and ABXY spectra, respectively. Although complete analysis of these spectra should in principle be possible, only the average of the two different values of $^3J_{HH}$, and one of the geminal couplings could be extracted from the data because of chemical shift degeneracy in one of the AB subspectra.

In both the ^{13}C and the ^1H spectra, the presence of different axial substituents on silicon gave rise to relatively small changes in chemical shifts, and the data obtained for derivatives **2f–h** are almost identical with those reported for **2a–e**.[2,7] The larger chemical shift differences induced by variation of substituents on the equatorial nitrogens are comparable to those observed among tren derivatives **7a–c**. For monosubstituted **14c**, chemical shifts assignable to the nuclei of the unsubstituted five-membered rings are comparable to those in **2f**, while the corresponding signals in **14b,d** experience a less pronounced shift in the same direction compared with that observed for the N-silylated rings.

The ^{29}Si chemical shifts of all the new azasilatranes are found in the high-field region characteristic for the five-coordinate atrane structure,[1,18] thus confirming the presence of a transannular Si–N interaction in all cases. For the substituted azasilatranes **2f–h**, comparison of the ^{29}Si chemical shifts with those of the corresponding tris(dimethylamino)silanes reveals a coordination shift, $\Delta\delta = [\delta_{RSi(NMe_2)_3} - \delta_{RSi(NHCH_2CH_2)_3N}]$, of 54.5 ppm in the case of **2h**, which falls into the range of 52–57 ppm obtained for alkyl-substituted azasilatranes **2a–d**.[7] In contrast, significantly lower values for $\Delta\delta$ of 39.6 and 40.9 ppm, respectively, are found for alkoxy-substituted azasilatranes **2f,g**. Similar variations of $\Delta\delta$ as a consequence of different substitution on silicon have been reported for silatranes[1,18] and were attributed to differences in the strength of the transannular Si–N bond.[18] Our findings indicate that a similar dependence of $\delta(^{29}Si)$ on the degree of transannular interaction exists for azasilatranes, although because of the complex nature of this correlation,[1] no quantitative interpretation of the data is presently possible.

N-Substitution in azasilatranes generally causes marked downfield movements of ^{29}Si chemical shifts, the only exception being **8b**, where a less pronounced effect is observed in the opposite direction. For **8a** and silylated derivatives **9a–c**, the downfield chemical shift movements are accompanied by an increase of the value of $^1J_{H-Si}$ with respect to **2a**, although the observed values are still significantly smaller than those known for analogues featuring tetracoordinate silicon.[7] Since it is known that coupling through the axial bond in metallatranes depends strongly on the strength of the axial N–M bond,[19] our data suggest that N-silylation of azasilatranes exerts a weakening effect on the axial Si–N interaction, leading to an increase in s character in the axial Si–H bond. A rationale for these observations may be provided by two mechanisms. The first is distortion of the coordination sphere around silicon toward tetrahedral (with simultaneous weakening of the transannular Si–N bond) arising from steric interaction between bulky groups on the equatorial nitrogens and the axial silicon substituent. A second alternative or concomitant influence may arise from subtle differences in electronegativity effects among the equatorial ligands. Presently, the data are insufficient to establish the importance of either effect and a more detailed investigation of these phenomena is currently in progress.

Crystal Structure of *N,N′,N″*-Trimethyl-1-ethoxyazasilatrane (8b). An X-ray crystallographic study of *N,N′,N″*-trimethyl-1-ethoxyazasilatrane (**8b**) revealed the presence of two molecules related by symmetry in the unit cell, with no significant intermolecular interactions. The positional coordinates are given in Table VI, and an ORTEP drawing is shown in Figure 1. The silicon atom possesses a somewhat distorted trigonal-bipyramidal coordination sphere similar to that in silatranes[1] and azasilatrane **2d**.[8] The transannular Si–N(1) bond length of 2.135 (2) Å is identical within experimental error with that reported for **2d** (2.132 (4) Å).[8] Moreover, both the axial Si–N and the Si–O distances (1.669 (3) Å) in **8b** are very similar to the values found for this bond in one of the two independent molecules in 1-ethoxysilatrane (Si–N = 2.138 (15) Å; Si–O = 1.6396 (11) Å).[20] The axial N(1)–Si–O bond angle of 179.12 (8)° in **8b** almost matches the ideal value of 180° as does the axial angle for **1f** (176.9 (5)°).[20]

The equatorial N–Si bond distances in **8b** (1.746 (2)–1.766 (2) Å, average 1.755 Å) are elongated with respect to those in **2d** (1.731 (4)–1.753 (4), average 1.739 Å) and the N–Si distances in the tetrahedral silicon derivative H_3SiNMe_2[21] (1.715 (4) Å). The N(ax)–Si–N(eq) angles

(18) Sidorkin, V. F.; Pestunovich, V. A.; Voronkov, M. G. *Magn. Reson. Chem.* **1985**, *23*, 491.

(19) Kupce, E.; Liepin'sh, E.; Lapsina, A.; Urtane, I.; Zelchan, G. I.; Lukevics, E. *J. Organomet. Chem.* **1985**, *279*, 343.

(20) Das, S. K.; Verkade, J. G., to be submitted for publication.

Table III. ^{1}H NMR Data for Azasilatranes $XSi(NHCH_2CH_2)_{3-m}(RNCH_2CH_2)_mN$[a]

compd	m	δ(RNCH_2–CH_2)$_m$N)	$^3J_{HH}$	X	δ(^{1}H)	$^3J_{HH}$ or $^1J_{SiH}$	R	δ(^{1}H)
2f	3	3.00 t, 2.64 t	5.9	OEt	3.53 q, 1.06 t	7.0	H	0.90 s
2g	3	3.05 t, 2.72 t	5.9	OPh	7.12 m, 6.87 m, 6.76 m[b]		H	1.46 s, 6.76 m[b]
2h	3	2.49 t, 2.72 t	5.9	Cl			H	1.33 s
8a	3	2.77 m, 2.70 m	5.8	H	3.70	194	Me	2.53 s
8b	3	2.82 t, 2.62 t	6.0	OEt	3.69 q, 1.16 t	6.9	Me	2.62 s
9a	3	2.69 t, 2.40 t	5.6	H	4.62	198	$SiMe_3$	0.03 s
9b	3	2.82 t, 2.57 t	5.8	H	4.50	184	$SiHMe_2$	0.10 d, 4.38 sept[c]
9c	3	2.78 t, 2.43 t	5.7	H	4.76	198	$SiPhMe_2$	7.57 m, 7.29 m,[d] 0.33 s[e]
14a	3	2.71 t, 2.36 t	5.3	OEt	3.80 q, 1.12 t	6.9	$SiHMe_2$	0.12 d, 4.38 sept[f]
14b	2	2.78 dt, 2.31 t 2.72 dt[g]	5.1	OEt	3.57 q, 1.12 t	7.0	$SiMe_3$	0.04 s
	1	2.79 dt,[h] 2.57 t	5.8	OEt	3.57 q, 1.12 t	7.0	H	0.79 s
14c	2	2.95 t, 2.63 t	5.9	OEt	3.56 q, 1.08 t	6.9	H	0.84 s
	1	2.94 t, 2.47 t	5.6			6.9	$SiMe_3$	0.04 s
14d	2	2.76 m, 2.23 dt 2.19 dt	5.2	OEt	3.45 q, 0.98 t	7.0	$SiPhMe_2$	7.55 m, 7.27 m[d] 0.39 s, 0.34 s[e]
	1	2.87 t, 2.58 t	5.8	OEt	3.45 q, 0.98 t	7.0	H	0.89 s

[a] In $CDCl_3$ at 20 °C. [b] Meta, ortho, and para hydrogens, respectively. [c] $^3J_{HH}$ = 3.3 Hz. [d] C_6H_5 resonances. [e] CH_3 resonances. [f] $^3J_{HH}$ = 3.2 Hz. [g] $^2J_{HH}$ = −12.9 Hz. [h] $^3J_{HCNH}$ = 2.1 Hz. [i] $^2J_{HH}$ = −11.7 Hz.

Table IV. ^{29}Si and ^{13}C NMR Data for Azasilatranes $XSi(HNCH_2CH_2)_{3-m}(RNCH_2CH_2)_mN$[a]

compd	m	δ(^{29}Si) $XSiN_3$	δ(^{29}Si) R_3SiN	δ(^{13}C) Si(RNCH_2–CH_2)$_m$N	X	δ(^{13}C)	R	δ(^{13}C)
2f	3	−82.9	...	36.9, 50.2	OEt	57.0, 19.0	H	...
2g	3	−87.8	...	37.0, 50.8	OPh	157.7, 128.1 119.9, 119.1	H	...
2h	3	−83.2	...	37.0, 51.0	Cl	...	H	...
8a	3	−62.2[b]	...	45.4, 49.1	H	...	Me	36.1
8b	3	−87.7	...	48.0, 48.4	OEt	56.8, 18.3	Me	38.4
9a	3	−70.1[c]	3.2	39.1, 55.0	H	...	$SiMe_3$	1.9
9b	3	−78.0[d]	−8.8[e]	39.1, 52.1	H	...	$SiHMe_2$	−0.5
9c	3	−78.3[b]	−1.9	39.3, 58.1	H	...	$SiPhMe_2$	142.2, 133.6, 127.5, 128.3[g] 0.25[h]
14a	3	−58.7	−9.0[f]	43.0, 56.9	OEt	58.8, 18.2	$SiHMe_2$	−0.2
14b	2	−65.6	3.4	41.0, 57.3	OEt	56.3, 18.4	$SiMe_3$	1.8
	1		...	38.5, 54.7			H	...
14c	2	−79.4	2.5	37.2, 51.6	OEt	57.1, 18.9	$SiMe_3$	2.6
	1		...	40.6, 58.5			H	...
14d	2	−67.9	−1.7	41.4, 56.5	OEt	57.0, 18.1	$SiPhMe_2$	142.4, 133.6, 128.2, 127.3[g] 0.6[h]
	1		...	38.2, 54.4			H	...

[a] In $CDCl_3$ at 20 °C. [b] $^1J_{SiH}$ = 194 Hz. [c] $^1J_{SiH}$ = 197 Hz. [d] $^1J_{SiH}$ = 188 Hz. [e] $^1J_{SiH}$ = 195 Hz. [f] $^1J_{SiH}$ = 198 Hz. [g] SiC_6H_5. [h] $SiCH_3$.

(81.7 (1), 83.5 (1), 83.8 (1)°, average 83.0°) compare favorably with those observed for **2d** (81.3 (2)°, 82.9 (2)°, 82.2 (2)° average 82.1°) and with the N(ax)–Si–O(eq) angles in **1f** (average 83.8°). For the tricoordinate nitrogen atoms in **8b**, an essentially planar coordination geometry is observed in case of N(3) (sum of bond angles 355.9°). The more distorted geometries observed for N(3) and N(4) (sums of the angles = 353.9° and 347.9°, respectively) may be related to stronger intramolecular interactions between the adjacent methyl groups and the methylene group of the ethoxy substituent (see Figure 1). As was found for **2d**, the tricyclic skeleton of **8b** shows virtual C_3 symmetry, with an envelope conformation for each of the five-membered rings. Overall, the crystal structure parameters are consistent with the results of the solution NMR spectroscopic investigations, and they further confirm that the similarity between silatranes and isoelectronic NH-substituted azasilatranes encompasses N-substituted azasilatranes.

Conclusions

It has been shown that the synthetic approach to the few azasilatranes known provides access to 1-alkoxy as well as N-substituted azasilatranes. Additional derivatives,

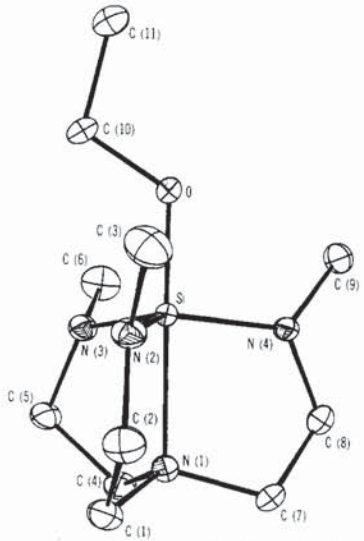


Figure 1. ORTEP drawing of **8b**, with ellipsoids drawn at the 50% probability level.

(21) Glidewell, C.; Rankin, D. W. N.; Robielle, A. C.; Sheldrick, G. M. *J. Mol. Struct.* **1970**, *6*, 231.

Table V. Crystal Data for $EtOSi(MeNCH_2CH_2)_3N$ (8b)

formula	$SiON_4C_{11}H_{26}$
fw	258.44
space group	$P2_1$ (No. 4)
a, Å	7.341 (2)
b, Å	12.208 (4)
c, Å	8.000 (2)
β, deg	104.61 (2)
V, Å^3	694.0 (7)
Z	2
d_{calc}, g/cm^3	1.237
cryst size, mm	0.3 × 0.4 × 0.4
μ(Mo Kα), cm^{-1}	1.563
data collectn instrument	Enraf–Nonius CAD4
radiatn (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientatn reflctns, no. range (2θ)	23, 18 < 2θ < 36
temp, °C	−140
data collectn range 2θ, deg	0–55
no. of unique data total	1481
with $F_o^2 > 3\sigma(F_o^2)$	1389
no. of parameters refined	155
R^a	0.0357
R_w^b	0.0481
quality-of-fit indicator[c]	1.05
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	0.430

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(|F_o|) + 0.001|F_o|^2]$. [c] Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Table VI. Positional Parameters for $EtOSi(MeNCH_2CH_2)_3N$ (8b) and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Si	0.36104 (8)	0.316	0.16635 (8)	0.96 (1)
O	0.2330 (2)	0.3937 (2)	0.2716 (3)	1.31 (4)
N(1)	0.5182 (3)	0.2176 (2)	0.0323 (3)	1.16 (4)
N(2)	0.2577 (3)	0.3621 (2)	−0.0439 (3)	1.34 (4)
N(3)	0.5853 (3)	0.3662 (2)	0.2752 (3)	1.38 (4)
N(4)	0.2929 (3)	0.1901 (2)	0.2338 (3)	1.25 (4)
C(1)	0.4981 (4)	0.2655 (3)	−0.1407 (4)	1.72 (5)
C(2)	0.3006 (3)	0.3124 (3)	−0.1950 (3)	1.71 (5)
C(3)	0.0692 (4)	0.4097 (3)	−0.0940 (4)	2.06 (6)
C(4)	0.7151 (3)	0.2209 (3)	0.1356 (4)	1.60 (5)
C(5)	0.7444 (3)	0.3372 (2)	0.2061 (4)	1.77 (6)
C(6)	0.6351 (4)	0.3662 (3)	0.4629 (4)	2.30 (6)
C(7)	0.4335 (4)	0.1074 (2)	0.0241 (4)	1.60 (5)
C(8)	0.3773 (4)	0.0900 (2)	0.1926 (4)	1.68 (6)
C(9)	0.2127 (4)	0.1750 (2)	0.3807 (3)	1.54 (5)
C(10)	0.2545 (4)	0.5087 (2)	0.2889 (4)	1.68 (6)
C(11)	0.1128 (4)	0.5527 (3)	0.3801 (4)	2.25 (7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

bearing functionalities on either the silicon or nitrogen atoms, can be obtained via substitution reactions of azasilatranes with retention of the tricyclic atrane structure. Spectroscopic and structural studies give evidence of a strong transannular Si–N interaction in NH- and NMe-substituted azasilatranes.

Experimental Section

All reactions were carried out with strict exclusion of moisture. Solvents were dried by standard methods and distilled before use. Commercial tris- and tetrakis(dimethylamino)silane (Petrarch) were used without purification. Me-tren was prepared from tren by using a standard procedure.[22a] Ethoxytris(dimethylamino)-silane was prepared from ethoxytrichlorosilane and excess dimethylamine.[22b] Bis(dimethylphenylphosphine)palladium and -platinum dichloride were obtained by reaction of (1,5-cycloctadiene)platinum dichloride and bis(dimethyl sulfoxido)-palladium dichloride, respectively, with 2 equiv of dimethylphenylphosphine. NMR spectra were recorded on a Nicolet NT300 (^{1}H, ^{13}C) or Bruker WM200 (^{29}Si), using $CDCl_3$ as an internal lock and TMS as the external reference. ^{29}Si NMR spectra of compounds containing Si–H bonds were obtained with the DEPT technique.[23a] The remaining ^{29}Si spectra were recorded with inverse gated decoupling and addition of 2–5% by weight (with respect to the sample) of $Cr(acac)_3$ as a relaxation agent. High-resolution mass spectra were obtained on a Kratos MS-50 mass spectrometer using electron-impact ionization (70 eV).

Warning: Some silatranes are toxic[23b] and should be handled with caution.

Tris[2-(trimethylsilylamino)ethyl]amine (Tms-tren, 7c). A solution of 2.00 g (13.7 mmol) of tren in 35 mL of THF was cooled to −50 °C, and 20.5 mL of a 2 M solution of *n*-butyllithium in hexanes was added slowly. The mixture was allowed to warm to room temperature and stirred for an additional hour. After the reaction mixture was cooled to −30 °C, 5.50 mL (43.4 mmol) of trimethylchlorosilane was added and the resulting mixture warmed to room temperature and stirred for an additional hour. The mixture was evaporated to dryness, suspended in 50 mL of ether, and stirred for 30 min. After filtration and evaporation of the solvent, the residue was distilled affording 2.66 g of a colorless liquid (bp 80–92 °C; yield 54%).

Reaction of Tris(2-aminoethyl)amines ($N(CH_2CH_2NHR)_3$) with Tris(dimethylamino)silanes ($XSi(NMe_2)_3$). As a general procedure, a mixture of 5.0 mmol of tren, Me-tren, or Tms-tren, 5.5 mmol of the aminosilane, and a catalytic amount of trimethylchlorosilane or ammonium sulfate was heated under a dry argon atmosphere to 80–135 °C. The reaction was monitored by observing the escape of dimethylamine through a bubbler, and heating was stopped when no more gas evolved. After the reaction mixture was cooled to room temperature, a colorless solid was obtained, which was purified by evaporating excess aminosilane under reduced pressure at room temperature followed by vacuum sublimation of the residue.

The following compounds were obtained by this route: 1-hydroazasilatrane (**2a**), reaction temperature 80 °C, yield 72–84%, mp 77–79 °C; 1-ethoxyazasilatrane (**2f**), reaction temperature 135 °C, yield 84%, mp 60–62 °C; 1-hydro-*N*,*N*′,*N*″-trimethylazasilatrane (**8a**), reaction temperature 100 °C, yield 54%, mp 86–88 °C; 1-ethoxy-*N*,*N*′,*N*″-trimethylazasilatrane (**8b**), reaction temperature 135 °C, yield 58%, mp 79–80 °C; 1-hydro-*N*,*N*′,*N*″-tris(trimethylsilyl)azasilatrane (**9a**), reaction temperature 100 °C. After distillation of the crude product, a colorless liquid (bp. 95–99 °C (0.1 Torr)) was obtained, which contained ca. 10% of a compound assigned as the disubstituted product (yield 61%). Since **9a** could not be obtained pure by this method, another approach was developed (vide infra).

1-Phenoxyazasilatrane (2g). A mixture of 2.06 g (10.1 mmol) of $Si(NMe_2)_4$, 0.93 g (9.9 mmol) of phenol, and a few grains of ammonium sulfate was heated with stirring at 100 °C for 1 h. After the reaction mixture was cooled to room temperature, 1.46 g (10.0 mmol) of tren was added and the mixture heated to 130 °C for 4 h, until evolution of $HNMe_2$ ceased. After the mixture was cooled to room temperature, the solid residue was subjected to sublimation at 0.1 Torr. The small fraction of liquid collected at a bath temperature of 100 °C was discarded. After the bath temperature was gradually raised to 180 °C, a colorless solid slowly sublimed. The crude product was dissolved in 40 mL of CH_2Cl_2, the solution filtered, and the solvent evaporated in vacuo. Sublimation of the residue gave 890 mg (34%) of pure product as a colorless solid (mp 108–112 °C).

Reaction of 1-Hydroazasilatrane with CCl_4. Approximately 50 mg of **2a** was dissolved in 2 mL of a 1:4 mixture of CCl_4 and $CDCl_3$. The mixture was then heated to 70 °C for 3.5 h without catalyst or after adding 1–2 mg of **10a**, **10b**, or **10a** plus 0.1 mL of pyridine-d_5. After the reaction mixture was cooled to room

(22) (a) Dannley, M. L.; Lukin, M.; Shapiro, J. *J. Org. Chem.* **1955**, *20*, 92. (b) Breederveld, H.; Waterman, H. J. *Research* **1952**, *5*, 537.

(23) (a) Blinka, T. A.; Helmer, B. J.; West. R. *Adv. Organomet. Chem.* **1984**, *23*, 193. (b) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1.

Table VII. Selected Bond Distances and Angles in $EtOSi(MeNCH_2CH_2)_3N$ (8b)

	Bond Distances (Å)		
Si–O	1.699 (2)	Si–N(3)	1.766 (2)
Si–N(1)	2.135 (2)	Si–N(4)	1.746 (2)
Si–N(2)	1.753 (2)	O–C(10)	1.416 (4)
	Bond Angles (deg)		
O–Si–N(1)	179.12 (8)	Si–O–C(10)	122.5 (2)
O–Si–N(2)	98.0 (1)	Si–N(2)–C(2)	122.1 (2)
O–Si–N(3)	97.4 (1)	Si–N(2)–C(3)	122.7 (2)
O–Si–N(4)	95.7 (1)	Si–N(3)–C(5)	117.8 (2)
N(2)–Si–N(3)	119.1 (1)	Si–N(3)–C(6)	118.0 (2)
N(2)–Si–N(4)	119.3 (1)	Si–N(4)–C(8)	120.1 (2)
N(3)–Si–N(4)	117.2 (1)	Si–N(4)–C(9)	124.6 (2)

temperature, the white precipitate that formed was removed by centrifugation. The clear supernatant liquid was analyzed by ^1H NMR spectroscopy, and the ratio of products **2a** and **2h**, respectively, was determined by integration (see Table I).

1-Chloroazasilatrane (2h). To a stirred solution of 1.2 g (7 mmol) of **2a** in 11 mL of CH_2Cl_2 was added 4 mL of CCl_4, followed by a solution of 10 mg of **10b** in 1 mL of CH_2Cl_2. The solution became warm, and a white solid precipitated. After being stirred for 1 h, the mixture was filtered and the residue washed twice with a 10:1 mixture of benzene/CH_2Cl_2. The combined filtrates were evaporated to dryness, and the residue was extracted twice with a 10:1 mixture of benzene/CH_2Cl_2. The extract was slowly concentrated affording a colorless solid precipitate that was collected by filtration and dried in vacuo to give 440 mg (30% yield) of **2h** (decomp >185 °C).

Reaction of 2a with Diethylamine. To 10 mL of freshly destilled diethylamine was added 0.2 mL of a 2 M solution of *n*-butyllithium in hexanes, followed by a solution of 100 mg (0.58 mmol) of **2a** in 2 mL of THF. The mixture was refluxed for 3 h, but no gas evolution was observed. After the reaction mixture was cooled to room temperature and the volatiles were removed in vacuo, a colorless solid remained consisting of pure **2a** whose ^1H NMR spectrum matched published NMR data.[2]

Reaction of Azasilatranes ($XSi(NHCH_2CH_2)_3N$, 2a,f) with Chlorosilanes ($ClSiRMe_2$). To a stirred solution of 7 mmol of azasilatranes **2a** or **2f** in 15 mL of a mixture of benzene and triethylamine (2:1) was added excess chlorosilane (5 mL in the cases of **13a** and **13b**, 4.5 equiv of **13c**, and 1.5 equiv of **13d**). Formation of a colorless precipitate began immediately. The reaction mixture was stirred at room temperature for 24 h in the case of reactions involving **2a** and for 4 days for reactions with **2f**. The mixture was then filtered, and the volatiles were removed in vacuo. The colorless or light yellow oil or solid reamining was purified by vacuum destillation. In this manner, the following compounds were prepared: 1-hydro-*N*,*N*′,*N*″-tris(dimethylsilyl)azasilatrane (**9b**), bp 94–95 °C (0.01 Torr), yield 63%; 1-hydro-*N*,*N*′,*N*″-tris(trimethylsilyl)azasilatrane (**9a**), bp 98 °C (0.01 Torr), mp 43–45 °C, yield 76% (Anal. Calcd (Found): C, 46.72 (46.33); H, 11.16 (10.37); N, 14.97 (14.53); Si, 28.02 (28.89); 1-hydro-*N*,*N*′,*N*″-tris(phenyldimethylsilyl)azasilatrane (**9c**), bp 190–210 °C (0.01 Torr), yield 51%; 1-ethoxy-*N*,*N*′,*N*″-tris(dimethylsilyl)azasilatrane (**14a**), bp 90–96 °C (0.01 Torr), yield 75% (according to the ^1H and ^{29}Si NMR spectra, the product also contained ca. 5–8% of a product assigned as the N,N′-disubstituted azasilatrane[9]); 1-ethoxy-*N*,*N*′-bis(trimethylsilyl)azasilatrane (**14b**), bp. 96 °C (0.01 Torr), mp 63–65 °C, yield 74% (Anal. Calcd (Found): C, 47.19 (46.62); H, 10.71 (10.06); N, 16.08 (15.53); Si, 23.45 (23.35)); 1-ethoxy-*N*,*N*′-bisdimethylphenylsilyl)azasilatrane (**14d**), bp. 165–180 °C (0.01 Torr), mp 86–88 °C, yield 45% (according to the ^1H and ^{29}Si NMR spectra, the mixture contained ca. 8% of a product assigned as the N-monosubstituted azasilatrane[9]).

1-Ethoxy-*N*-(trimethylsilyl)azasilatrane (14c). A solution of 610 mg (2.82 mmol) of **2f** in 12 mL of benzene–triethylamine (2:1) was prepared and cooled to 0 °C, and a solution of 380 mg (3.5 mmol) of chlorotrimethylsilane in 2 mL of benzene was slowly added. A precipitate formed immediately, and the mixture was allowed to warm to room temperature and stirred overnight. After filtration and removal of solvents in vacuo, the residue was distilled. The distillate was redissolved in 12 mL of benzene–triethylamine and treated again with 380 mg of chlorotrimethylsilane and the procedure repeated. The crude product obtained after the second distillation was found to be an approximately 2:1 mixture of **14b** and **14c**, containing traces of unreacted **2f**. Further purification was conducted by slow vacuum sublimation in a glass tube, which was heated to 80 °C in an oil bath at the lower end. Colorless crystals formed on the wall of the tube, whose surface was covered with a viscous oil. After collection, carefully washing with chloroform and drying in vacuo, pure crystalline **14c** was obtained in 30% yield (mp 95–98 °C).

Crystal Structure Determination of 8b. A colorless crystal of **8b** of dimensions 0.3 × 0.3 × 0.4 mm grown by vacuum sublimation was taken from an argon-filled flask, quickly mounted on the end of a glass fiber, and immediately placed in the cold nitrogen stream of the crystal cooling device on the diffractometer. The crystal temperature was maintained at −140 ± 1 °C. The monoclinic cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table V.

The systematic absences indicated the space group to be either $P2_1$ (No. 4) or $P2_1/m$ (No. 11). Although intensity statistics indicated an acentric group, the centric group was initially assigned. However, neither direct methods nor a Patterson map gave reasonable solutions in space group $P2_1/m$. The space group $P2_1$ was then adopted, and direct method[24] immediately produced the positions of all 17 non-hydrogen atoms. Following isotropic least-squares refinement, a difference Fourier map produced peaks corresponding to every expected hydrogen atom. In the final cycles of full-matrix refinement, hydrogen atoms were placed in idealized positions (C–H distance fixed at 1.08 Å). One common isotropic thermal parameter was refined for the primary hyrogen atoms and another for the secondary hydrogen atoms. No significant differences in the structure or the refinement were observed when the enantiomorph was refined.

The final cycle of refinement included 155 variable parameters and converged with unweighted and weighted agreement factors of[25] $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.0357$ and $R_2 = [\sum w(|F_o| - |F_c|)^2)]^{1/2} = 0.0481$, respectively.

X-ray data collection and the structure solution were carried out at the Iowa State Molecular Structure Laboratory. All calculations were performed on a Digital Equipment Corp. MicroVAX II computer. The refinement was carried out with the SHELX-76 package.[26] Positional parameters and selected bond distances and angles are listed in Tables VI and VII, respectively.

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Registry No. **2a** (silane entry), 31701-34-5; **2a** (coordination compound entry), 63344-72-9; **2f** (silane entry), 123290-92-6; **2f** (coordination compound entry), 123308-08-7; **2g** (silane entry), 123290-96-0; **2g** (coordination compound entry), 123308-12-3; **2h** (silane entry), 123290-97-1; **2h** (coordination compound entry), 123308-13-4; **6a**, 15112-89-7; **6f**, 25440-34-0; **7a**, 4097-89-6; **7b**, 65604-89-9; **7c**, 117748-25-1; **8a** (silane entry), 123290-93-7; **8a** (coordination compound entry), 123308-09-8; **8b** (silane entry), 123290-94-8; **8b** (coordination compound entry), 123308-10-1; **9a** (silane entry), 123290-95-9; **9a** (coordination compound entry), 123308-11-2; **9b** (silane entry), 123290-98-2; **9b** (coordination compound entry), 123330-16-5; **9c** (silane entry), 123290-99-3; **9c** (coordination compound entry), 123308-14-5; **13a**, 75-77-4; **13b**, 1066-35-9; **13c**, 768-33-2; **14a** (silane entry), 123291-00-9; **14a** (coordination compound entry), 123308-15-6; **14b** (silane entry),

(24) SHELXS-86: Sheldrick, G. M. Institut fuer Anorganische Chemie der Universität, Goettingen, FRG.

(25) Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallagraphy*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(26) SHELX-76: Sheldrick, G. M. In *Computing in Crystallography*; H. Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University: Delft, 1978.

123291-01-0; **14c** (silane entry), 123291-03-2; **14c** (coordination compound entry), 123330-17-6; **14d** (silane entry), 123291-02-1; **14e** (silane entry), 123291-06-5; **14e** (coordination compound entry), 123308-20-3; $Si(NMe_2)_4$, 1624-01-7; phenol, 108-95-2; 1-ethoxy-*N*,*N*′-bis(dimethylsilyl)azasilatrane (silane entry), 123291-04-3; 1-ethoxy-*N*,*N*′-bis(dimethylsilyl)azasilatrane (coordination compound entry), 123308-16-7; 1-hydro-*N*,*N*′-bis(trimethylsilyl)azasilatrane (silane entry), 123291-05-4; 1-hydro-*N*,*N*′-bis(trimethylsilyl)azasilatrane (coordination compound entry), 123308-19-0.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond lengths, least-squares planes, and bond angles (10 pages); a table of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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