Pentacoordinate Silicon Compounds. V.[1a] Novel Silatrane Chemistry

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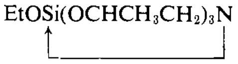
Abstract: Silatranes are pentacoordinate silicon derivatives formed from the reaction of trialkanolamines such as triethanolamine with trifunctional silanes such as $RSi(OMe)_3$. This paper describes the synthesis of a number of unusual silatranes bearing halo, acyloxy, siloxy, and hydroxy substituents at the apical silicon site. An effort is made to rationalize the sometimes exceptional chemistry of silatranes and to account for some of the apparent structural requisites for stable transannular dative bonding of nitrogen to silicon. The convenient preparation of polymeric modifications from epoxy functional precursors is also described.

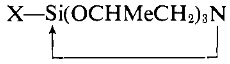
Triethanolamine and other trialkanolamines of suitable structure react with trifunctional silicon substrates to yield highly crystalline, monomeric silanes to which, in view of assorted physical and chemical evidence, a pentacoordinate structure was assigned.[1b] This assignment has recently been amply confirmed by the detailed X-ray crystallographic studies of Boer, Turley, and coworkers.[2] Although these compounds were originally[1b] referred to as triptych-siloxazolidines by analogy to earlier borate nomenclature, Voronkov[3] subsequently suggested that these species having transannular nitrogen–metal dative bonds be described as boratranes, silatranes, etc., and we will in most cases employ this simpler "-atrane" terminology. In the present paper we describe the preparation and chemistry of a somewhat miscellaneous but unusual collection of novel silatranes including examples with halogen, hydroxy, and siloxy apical substituents.[4]

Enhanced Solvolytic Stability of Silatranes. Since the formation of a N→Si dative bond results in a negatively charged silicon atom, it was anticipated that retarded rates would be observed for reactions involving nucleophilic displacement on the silatrane silicon center. A number of qualitative observations have indeed confirmed this expectation. For instance



$EtOSi(OCHCH_3CH_2)_3N$

was recovered in 66% yield by boiling its aqueous solution free of water. Another aqueous solution of this material was evacuated free of water at room temperature, affording a quantitative recovery of the unreacted crystalline ethoxysilatrane; such solvolytic stability is unprecedented for conventional orthosilicates. Further qualitative information of this type is the resistance of such derivatives to solvolytic decomposition in glacial acetic acid. In order to fully titrate these triisopropanolamine derivatives, it was necessary to expose them to the titrant (0.1 *N* perchloric acid in glacial acetic acid) for prolonged periods (30 min) at elevated temperatures (100°). Still another example of this greatly enhanced solvolytic stability is the successful recovery of the 1-halosilatranes

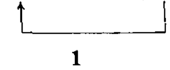


$X{-}Si(OCHMeCH_2)_3N$

from alcoholic solution.

Several other factors presumably also contribute to the observed decreased reactivity. (1) The bridgehead nature of the silicon precludes backside attack, and flank attack is not expected to be particularly facile; *i.e.*, in constrast to the very reactive bridgehead halides described by Sommer and Bennett,[5] the silatrane structures are believed to be essentially free of strain which might otherwise have enhanced the ease of flank attack. (2) When the silatrane cage is alkyl substituted (as in the triisopropanolamine derivatives), the peripheral groups may tend to impede the attack of an approaching nucleophile. Also, it is well known that alkyl decoration often retards ring-opening reactions. (3) As a result of the transannular dative bond, the silicon 3d orbitals are already partially occupied and hence less available to an incoming nucleophile; this may just be another way of saying that the resultant negative charge will electrostatically discourage attack by a nucleophile.

While the rates of displacement reactions are obviously sharply retarded, 1-alkoxysilatranes can nevertheless be induced to undergo synthetically useful displacement reactions if sufficiently forcing conditions are employed. Thus, the ethoxy group of **1** can be



$EtOSi(OCH_2CH_2)_3N$

1

displaced by a variety of hydroxylic reagents[4] including alcohols, phenols, carboxylic acids, and silanols. These displacements appeared to be facilitated by increased acidity in the hydroxylic reagent, and in the case of silanolysis (with Ph_3SiOH), a Lewis acid [$Zn(OAc)_2$] was employed to shorten reaction times. We will not dwell on the alkoxy and aryloxy derivatives at this point, since such structures have subsequently been prepared by closely related methods and discussed at some length by Voronkov.[3] Voronkov has noted,[3]

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[1] (a) Paper IV: C. L. Frye, *J. Amer. Chem. Soc.*, **92**, 1205 (1970); (b) C. L. Frye, G. E. Vogel, and J. A. Hall, *ibid.*, **83**, 996 (1961).

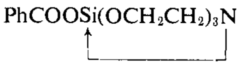
[2] (a) J. W. Turley and F. P. Boer, *ibid.*, **90**, 4026, (1968); (b) F. P. Boer, J. W. Turley, and J. J. Flynn, *ibid.*, **90**, 5102 (1968); (c) J. W. Turley and F. P. Boer, *ibid.*, **91**, 4129 (1969); (d) F. P. Boer and J. W. Turley, *ibid.*, **91**, 4134 (1969);

[3] For a review of his extensive silatrane studies, see M. G. Voronkov, *Pure Appl. Chem.*, **13**, 35 (1966).

[4] Some of the work described herein was presented previously: C. L. Frye and G. A. Vincent, Abstracts of Papers, 141st National Meeting of the American Chemical Society, Washington, D. C., Mar 1962, p 6-O.

[5] (a) L. H. Sommer and O. F. Bennett, *J. Amer. Chem. Soc.*, **79**, 1008 (1957); (b) L. H. Sommer and O. F. Bennett, *ibid.*, **81**, 251 (1959).

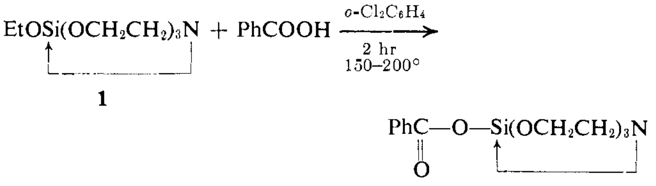
however, that derivatives of carboxylic acids are extremely unstable. While we experienced some difficulty in preparing an acetoxy derivative, the synthesis of **2**



$$\mathrm{PhCOOSi(OCH_2CH_2)_3N}$$

2

from benzoic acid and the ethoxy precursor appeared to proceed without complication;[4] *i.e.*

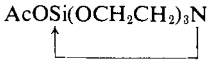


$$\mathrm{EtOSi(OCH_2CH_2)_3N + PhCOOH \xrightarrow[\text{2 hr, 150–200°}]{o\text{-}Cl_2C_6H_4} PhC(=O)\text{—}O\text{—}Si(OCH_2CH_2)_3N}$$

1

2, mp 240°, 90%

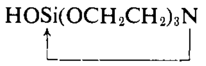
The acetoxy analog **3** was obtained by two methods. It



$$\mathrm{AcOSi(OCH_2CH_2)_3N}$$

3

was suspected that our initial attempts might have been thwarted by unwanted esterification of the by-produced ethanol with the glacial acetic acid, producing water which could then lead to siloxane formation, etc. In any event, we successfully prepared **3** by including an equivalent quantity of acetic anhydride in the reactants (*i.e.*, **1** and acetic acid). We were subsequently also able to prepare this compound by the facile condensation of acetyl chloride with the novel pentaccordinate silanol **4** in the presence of Et_3N as an HCl acceptor. In

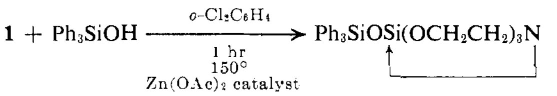


$$\mathrm{HOSi(OCH_2CH_2)_3N}$$

4

marked contrast to the aromatic derivative **2**, the simple aliphatic derivative **3** appeared to undergo relatively facile hydrolytic decomposition.

The relatively high-temperature displacement reactions can also be employed for the preparation of certain mixed siloxane structures containing both tetra- and pentacoordinate silicon components as shown below by the synthesis of the Ph_3SiOH derivative **5**.

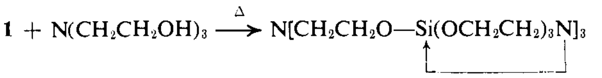


$$\mathrm{1 + Ph_3SiOH \xrightarrow[\text{1 hr, 150°, Zn(OAc)}_2\text{ catalyst}]{o\text{-}Cl_2C_6H_4} Ph_3SiOSi(OCH_2CH_2)_3N}$$

5

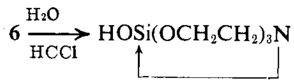
This type of high-temperature 5-ethoxysilatrane solvolysis can obviously only be exmployed for relatively stable silanols such as Ph_3SiOH; however, as will be seen below, the availability of the pentacoordinate silanol **4** allows the straightforward synthesis of a variety of siloxane structures by mild condensation methods.

1-Hydroxysilatrane (4). This uniquely structured silanol was prepared by the high-temperature alcoholysis of the 1-ethoxysilatrane **1** with triethanolamine, followed by a strikingly selective hydrolysis of the resulting derivative, **6**.



$$\mathrm{1 + N(CH_2CH_2OH)_3 \xrightarrow{\Delta} N[CH_2CH_2O\text{—}Si(OCH_2CH_2)_3N]_3}$$

6



$$\mathrm{6 \xrightarrow[HCCl]{H_2O} HOSi(OCH_2CH_2)_3N}$$

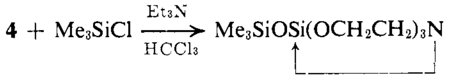
4

The "tris[silatranoxyethyl]amine" **6** can also be prepared directly from triethanolamine (TEA) and ethyl silicate; *i.e.*

$$\mathrm{3(EtO)_4Si + 4TEA \xrightarrow{\Delta} 6 + 12EtOH}$$

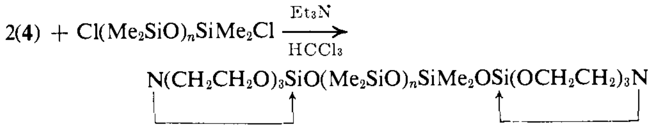
While **6** is only sparingly soluble in $HCCl_3$, it dissolves quite readily in the presence of moisture (presumably through formation of a $HCCl_3$-soluble hydrate) and subsequently is hydrolyzed to the silanol which deposits from the solution as a crystalline solid (mp 210°) in approximately 50% yield. Such selective displacement of the apical groups is remarkable in view of the other three alkoxy ligands on each silatrane silicon. Hydrolytic selectivity was *not* observed in our attempts to prepare **4** *via* the direct hydrolysis of **1**, which led to siliceous deposits and, at best, only trace amounts of **4**. The lability of the apical ligands of compound **6** may be a consequence of the strategically located basic nitrogen site at the β-carbon atoms of these groups; *i.e.*, partial protonation of this nitrogen should enhance the nucleophilicity of the incoming water molecule and inductively weaken the apical SiOC bond as well. Alternatively, the formation of a strong hydrogen bond to this nitrogen may simply result in the water being held in a very favorable position for selective displacement of the apical ligand.

1-Hydroxysilatrane is a very convenient reagent for preparing silatrane modifications of conventional siloxanes. Thus, unsymmetrical disiloxane hybrids containing both penta- and tetracoordinate silicon sites (**7**) as well as symmetrical polysiloxanes containing the silatrane moiety at both ends (**8**) were prepared by the following facile condensations.



$$\mathrm{4 + Me_3SiCl \xrightarrow[HCCl_3]{Et_3N} Me_3SiOSi(OCH_2CH_2)_3N}$$

7

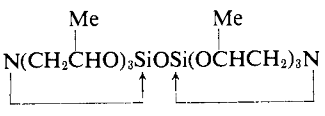


$$\mathrm{2(4) + Cl(Me_2SiO)_{\mathit{n}}SiMe_2Cl \xrightarrow[HCCl_3]{Et_3N} N(CH_2CH_2O)_3SiO(Me_2SiO)_{\mathit{n}}SiMe_2OSi(OCH_2CH_2)_3N}$$

8

As noted above, **4** can also react in a similar way with acetyl chloride (or acetic anhydride) to yield the previously unreported 1-acetoxysilatrane (**3**).

A Doubly Pentacoordinate Disiloxane. A novel structure



$$\mathrm{N(CH_2CH(Me)O)_3SiOSi(OCH(Me)CH_2)_3N}$$

9

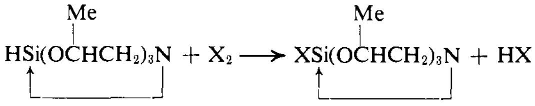
containing two silatrane cages joined by an intervening oxygen atom was prepared by the KOH-catalyzed high-temperature alcoholysis of hexaethoxydisiloxane with triisopropanolamine (TIPA); *i.e.*

$$\mathrm{[(EtO)_3Si]_2O + 2TIPA \xrightarrow[240°]{KOH} 9}$$

This product is especially interesting because it contains two closely situated silicon atoms which are both negatively charged as a consequence of the transannular N→Si dative bonding. Prior to this successful synthesis, we had feared that this feature of closely juxtapositioned like charges might result in a structure so unstable as to preclude its preparation and isolation. In actual fact, however, this unusual disiloxane was sufficiently robust to survive solution in water and recovery therefrom. The nmr spectrum of the aqueous solution was very similar to that obtained in CCl_4. Furthermore, upon evacuation of the water, the infrared spectrum of the residue was identical with that of the starting disiloxane; hydrolysis does occur, however, under more forcing conditions.

Attempts to prepare **9** in the absence of a strongly basic catalyst such as KOH were unsuccessful. The KOH is believed to contribute to the successful outcome in two ways: (a) by causing more complete alcoholysis of the ethoxy groups (in the absence of KOH, only about 85% of the expected ethanol could be obtained); (b) by facilitating redistribution of the alkoxy and siloxy substituents at more moderate temperatures, thereby minimizing thermal degradation of the nitrilotrialkoxy moieties; thus the product [bp 215° (0.1 mm)] distilled readily from a reaction mixture whose temperature was about 240°, whereas, in the absence of KOH, the reaction flask temperature soared to 280–320°, leading to appreciable pyrolytic decomposition with resultant contamination of the product.

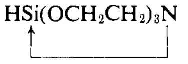
1-Halosilatranes The 1-halosilatranes[4] are perhaps the most interesting members of this family of pentacoordinate silicon compounds, in view of the chemistry leading to their isolation, their extremely high melting points and low solubilities, and their remarkable solvolytic stability. The first preparation to be attempted involved the direct halogenation of 3,7,10-trimethylsilatrane (**10**).



$$\mathrm{HSi(O\overset{Me}{C}HCH_2)_3N} + X_2 \longrightarrow \mathrm{XSi(O\overset{Me}{C}HCH_2)_3N} + HX$$

10 **11a**, X = Br; **b**, X = Cl

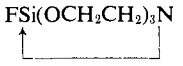
Although the reaction was expected to yield 1-halo-3,7,10-trimethylsilatrane and HX, it was noted that the Si–H content was exhausted upon the addition of only one-half the stoichiometric amount of halogen, strongly suggesting that HX itself was reacting rapidly with the starting hydride (*i.e.*, **10** + HBr → **11a** + H_2). This suspicion was easily confirmed by adding a chloroform solution of HBr or HCl to a chloroform solution of **10**, whereupon H_2 was *immediately* evolved and the expected halosilatrane separated from solution as a crystalline deposit. This remarkable reaction is not observed with tetracoordinate silanes such as Et_3SiH or $(EtO)_3SiH$. Such reactivity is, however, eminently consistent with the enhanced hydridic character of the silicon-bonded hydrogen moiety implicit in the silatrane structure.[1] The chloro- and bromosilatranes can also be prepared by halogenating the hydride with the appropriate *N*-halosuccinimide. Similar attempts to prepare the iodo derivative with *N*-iodosuccinimide were unsuccessful. Although the hydride derived from triethanolamine, *i.e.*, **12**, is not as easily prepared as is **10**, and for this reason was not used for these halogenations, there can be little doubt that entirely analogous results would have been obtained.



$$\mathrm{HSi(OCH_2CH_2)_3N}$$

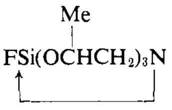
12

Although, as initially prepared, **10** is a mixture of isomers (because of the asymmetric nature of the 3, 7, and 10 sites of the silatrane cage derived from TIPA), a less soluble higher melting fraction (mp 175–183°) was used for these halogenations. The resulting bromides and chlorides were even higher melting (237 and 306°, respectively). This is probably at least partially a consequence of a shorter N→Si bond afforded by the more electronegative halo ligands whose increased polarity should be reflected in greater crystal stability. It was possible to recrystallize these halides from alcoholic solvents with little or no loss of product from solvolysis of the Si–X bond. This unprecedented stability has been rationalized elsewhere herein. Fluoro derivatives, **13** and **14**, were prepared by the addition of concentrated HF to 2-propanolic solutions of the appropriate ethoxysilatranes (*i.e.*, **1** and **15**, respectively).



$$\mathrm{FSi(OCH_2CH_2)_3N}$$

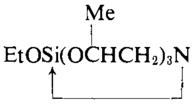
13



$$\mathrm{FSi(O\overset{Me}{C}HCH_2)_3N}$$

14

The halosilatranes are believed to possess structures in which the silicon–halogen bond is essentially covalent.



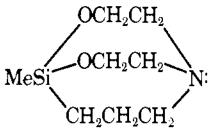
$$\mathrm{EtOSi(O\overset{Me}{C}HCH_2)_3N}$$

15

This view is consistent with their infrared spectra (KBr pellets), which are very similar to those of the corresponding Si–H analogs except for (a) the absence of the Si–H absorptions at approximately 2120 and 930 cm^{-1} and (b) the presence of the additional Si–X stretching absorptions at 392 cm^{-1} for the chloro derivative **11b**, at 360 cm^{-1} for the bromo derivative **11a**, at 765 cm^{-1} for fluoro derivative **14**, and a pair at 780 and 800 cm^{-1} for fluoro derivative **13**. The Si–F frequencies are substantially lower than normal, presumably in consequence of the longer bond length resulting from rehybridization (as was observed previously for the Si–H bond[1b]).

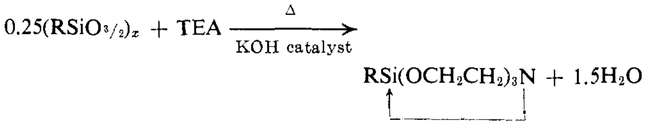
Structural Requirements for Silatrane Stability. The strength of the transannular N→Si dative bond is enhanced by increased electron-withdrawing ability of the apical substituent. This is presumably the basis for the pronounced differences in the ease of silatrane formation from the reaction of triethanolamine with a series of aryltrialkoxysilanes; thus $m\text{-}NO_2(C_6H_4)Si(OEt)_3$ reacted exothermally and rapidly at room temperature, $C_6H_5Si(OMe)_3$ required the application of heat for reasonable reaction rate, and $p\text{-}Me_2N\text{-}C_6H_4Si(OMe)_3$ required even more forcing conditions for comparable yields. Consistent with these qualitative observations, the N→Si bond lengths for *m*-nitrophenylsilatrane and phenylsilatrane were found to be 2.116 and 2.193 Å, respectively,[2a,c] confirming the anticipated bond-shortening effect of the nitro substituent. In addition to inductive effects of the above type, there are other even more stringent structural requirements for silatrane stability. For instance, the obviously cross-linked macromolecular nature of the product resulting from the attempted preparation of $PhSi(OCH_2CH_2CH_2)_3N$ underscored the importance of having only two carbons between the oxygen and nitrogen sites; gelation resulted even when attempts were made to displace the ring–chain equilibria in favor of the desired cage structure by well-known dilution effects.

In view of the above apical substituent inductive effects, future attempts to prepare such unfavored structures should probably be performed on a *m*-nitrophenyl substrate. It is very doubtful, however, that this would change the result, since increasing the length of only one of the three hydroxyalkyl moieties led to destabilization; *i.e.*, attempts to prepare a stable cage structure from $PhSi(OMe)_3$ and $HOCH_2CH_2CH_2N(CH_2CH_2OH)_2$ also yielded obviously gelled macromolecular products. Gels also resulted when the hydroxyalkyl moieties were not distinctly separate nitrogen substituents, *e.g.*, $HOCH_2CH_2NHCH(CH_2OH)_2$ yielded a gelled product. In fact, the structural requirements are so stringent that the typical silatrane characteristics are drastically diminished when only one of the oxygen atoms is replaced by a methylene moiety. Thus $Me(EtO)_2SiCH_2CH_2CH_2NH_2$ reacts readily with ethylene oxide to yield the anticipated monomeric cage compound[6]



which is low melting (60–61°), soluble in pentane, not exceptionally high boiling [94° (0.3 mm)], and immediately titratable as a nitrogen base. Although there appears to be some transannular coordination of nitrogen to silicon in this species,[2d] it is certainly minor compared to that evident in methylsilatrane, which is much higher melting (151–153°), soluble only in polar solvents, higher boiling, and exhibits the "delayed neutralization"[1b] phenomenon. One might argue that the silicon atom in the former material is less likely to coordinate since it bears *two* hydrocarbon substituents and is hence less electrophilic. To check this point we prepared a derivative bearing an apical ethoxy substituent (*i.e.*, the reaction product of $H_2N(CH_2)_3Si(OEt)_3$ and propylene oxide); however, the resulting cage species again showed none of the characteristics typical of the stable silatranes. Were a slightly distorted trigonal-bipyramidal structure not so clearly evidenced by the aforementioned X-ray crystallographic studies, it would be tempting to suggest a pseudorotational explanation for the diminished stability; *i.e.*, it might be argued that pseudorotation is inhibited by the reluctance of an equatorial methylene to become axial. Perhaps the explanation lies simply in the less flexible nature of the $(CH_2)_3$ linkage relative to the $O(CH_2)_2$ linkage.

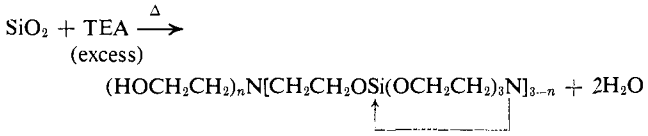
Direct Conversion of Silica and Silsesquioxanes to Silatranes. It is known that siloxane bonds are susceptible to alcoholysis under suitable conditions.[7] When this reaction is performed on organosilsesquioxane substrates with triethanolamine as the alcoholic reactant, silatranes are formed in high yield. Thus both ethyl- and phenylsilatrane were formed in high yield by this method.



$$0.25(RSiO_{3/2})_x + TEA \xrightarrow[\text{KOH catalyst}]{\Delta} RSi(OCH_2CH_2)_3N + 1.5H_2O$$

It was observed qualitatively that electron-withdrawing groups on the silicon facilitated the reaction. Although KOH was employed as a catalyst in the preparation of the ethyl derivative, it may not have been necessary since the corresponding phenyl- and *m*-nitrophenylsilatranes were obtained in the absence of any added inorganic base.

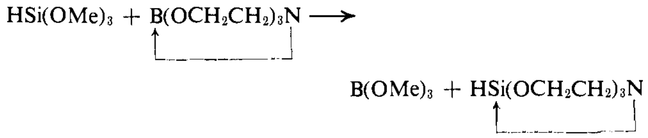
In related work, even silicic acid was observed to dissolve in excess TEA at temperatures of 200–250°; *i.e.*



$$SiO_2 + \underset{\text{(excess)}}{TEA} \xrightarrow{\Delta} (HOCH_2CH_2)_nN[CH_2CH_2OSi(OCH_2CH_2)_3N]_{3-n} + 2H_2O$$

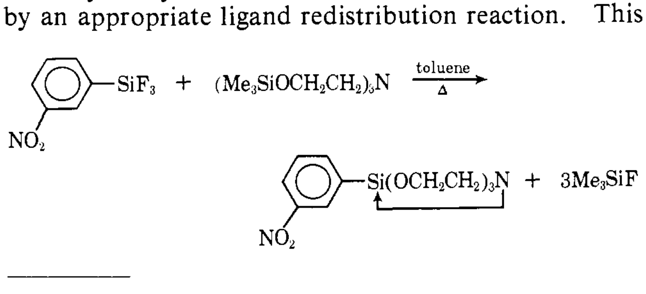
A parallel attempt with triisopropanolamine was unsuccessful, *i.e.*, the silica did not dissolve and very little water was evolved even at 290°. Voronkov has described similar silatrane syntheses utilizing $(RHSiO_{2/2})_x$ substrates.[3] Silatranes could presumably also be obtained from the reaction of trialkanolamines with appropriate polysilanes (*i.e.*, $Me(MeO)_2SiSi(OMe)_2Me$) and possibly from elemental silicon itself.

Preparation of Silatranes under Aprotic Conditions. Voronkov[8] has reported the elegant preparation of $HSi(OCH_2CH_2)_3N$[1b] from the following alkoxy ligand redistribution



$$HSi(OMe)_3 + B(OCH_2CH_2)_3N \longrightarrow B(OMe)_3 + HSi(OCH_2CH_2)_3N$$

The aprotic conditions preclude unwanted Si–H solvolysis. In view of the ready availability of trimethylsiloxylating agents such as $(Me_3Si)_2NH$, we have devised an alternative aprotic approach to atranes involving trimethylsiloxylation of the trialkanolamine followed by an appropriate ligand redistribution reaction. This



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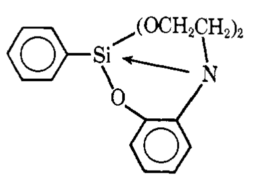
[6] Although a tetracoordinate silicon structure was claimed for this compound [E. L. Morehouse, Canadian Patent 625,353 (1961)], X-ray crystallographic data[2d] would appear to indicate at least some transannular interaction.

[7] (a) J. F. Hyde, U. S. Patent 2,746,982 (1956); (b) M. M. Sprung and F. O. Guenther, *J. Org. Chem.*, **26**, 562 (1961).

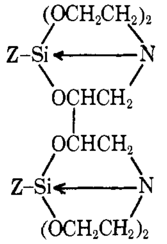
[8] G. I. Zelchan and M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, **2**, 371 (1967).

type of reaction can be used for the direct conversion of metal halides to their atrane derivatives without generating hydrogen halide acids, as in the example shown above.

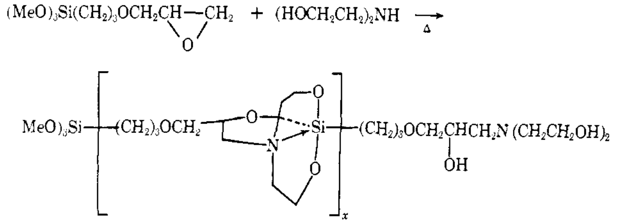
Preparation of Silatranes from Epoxy Reactants. Perhaps not unexpectedly, silatranes can be conveniently prepared directly in one step from alkoxysilanes, alkanolamines, and epoxides by a procedure which involves the *in situ* generation of a trialkanolamine. Thus diethanolamine, phenyltrimethoxysilane, and styrene oxide react to give the expected 1,3-diphenylsilatrane (mp 165°) in good yield (a small amount of the isomeric 1,4-diphenylsilatrane (mp 270°) resulting from ring-opening attack at the benzylic site was also isolated in this instance). In similar fashion, an arylolamine such as *o*-aminophenol reacts with ethylene oxide and silanes such as phenyltrimethoxysilane to also yield the expected pentacoordinate silane (mp 145°)



The delayed neutralization of an acidic titrant observed for this last compound illustrates that demonstrable transannular dative bonding occurs despite the unusual nature of this peripheral modification; in subsequent work, a triol having three such aromatic moieties (*i.e.*, *O,O′,O″*-nitrilotriphenol) was prepared and converted to pentacoordinate silicon derivatives.[9] Polyfunctional epoxides can also be used; thus butadiene dioxide and diethanolamine reacted with either phenyltrimethoxysilane or ethyl silicate to give good yields of the expected crystalline dimeric phenyl- (mp 268°) and ethoxy- (mp 254°) silatranes

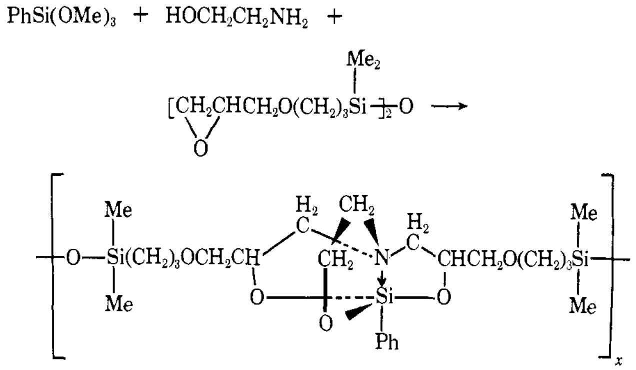


Polymeric Modifications. A number of interesting polymeric structures were prepared *via* chemistry illustrated in the above examples. Thus, a suitably polyfunctional substrate such as glycidyloxypropyltrimethoxysilane reacts with dialkanolamines to yield the novel crystalline polymer as shown below.



The product of the above condensation was a crystalline substance of regularly "tiered-terraced" morphology so often observed with crystalline polymers; the melting point depended on the solvent from which the crystallization took place (143–150° from methyl ethyl ketone, 85–90° from benzene).

In the example given earlier involving the diepoxide butadiene dioxide, it is obvious that linear polymers could have arisen if bis(trialkoxysilyl)alkanes or -arenes had been employed, although there is the possibility that oligomeric cyclic formation could preclude the formation of linear polymeric structures. There is a less obvious means by which linear polymers can be prepared from simple monomeric tri- or tetraalkoxysilanes which involves the use of a primary amino compound such as ethanolamine or *o*-aminophenol. The feasibility of this general approach was established by the following specific example.



Experimental Section

Halosilatranes. (A) **1-Bromo-3,7,10-trimethylsilatranes (11a).** *N*-Bromosuccinimide (21.0 g, 0.118 mol) was added to a solution of 3,7,10-trimethylsilatrane (25.6 g, 0.118 mol) in $HCCl_3$ (621 g); this addition was quite exothermic. Subsequent cooling yielded a crystalline deposit which was collected by filtration, triturated with hexane, and evacuated briefly to remove residual hexane. The resulting solid is a 1:1 chloroform solvate of the desired product. Lengthy evacuation at 100° produced the expected weight loss (28.8%) and afforded 23 g (65% yield) of 1-bromo-3,7,10-trimethylsilatrane, mp 233–237°. The infrared spectrum is quite similar to that of the hydride precursor, the major differences being the absence of the intense Si–H stretching absorption at 4.7 μ and the presence of a rather broad band at 27.8 μ believed to be attributable to Si–Br stretching.

Anal. Calcd for $SiC_9H_{18}NO_3Br$: C, 36.5; H, 6.12; Si, 9.47; N, 4.43; Br, 27.0. Found: C, 36.1; H, 6.5; Si, 9.53; N, 4.73; Br, 26.1.

Samples of this product were found capable of being recrystallized from 2-propanol, ethanol, or methanol without undergoing alcoholysis.

(B) 1-Chloro-3,7,10-trimethylsilatrane (11b). *N*-Chlorosuccinimide (13.4 g, 0.100 mol) was added all at once to a solution of 3,7,10-trimethylsilatrane (21.7 g, 0.100 mol) in $HCCl_3$ (400 g). Within 60 sec, the temperature of the solution rose to 62° (reflux), illustrating the marked exothermicity of this reaction. In order to remove the needlelike crystals which formed very rapidly, the reaction product was filtered hot and squeezed free of adhering solution by use of a rubber dam and reduced pressure. This crystalline material appears to be essentially a 1:1 $HCCl_3$ solvate of the desired compound, undergoing a weight loss of 29.2% upon heating for 2 hr at 150°, comparing favorably with the expected 32.2% weight loss for the solvate. The chloroform-free solid amounted to 17.2 g (68% yield), mp 305–306°.

Anal. Calcd for $SiC_9H_{18}NO_3Cl$: C, 43.0; H, 7.15; Si, 11.13; N, 5.56; Cl, 14.1. Found: C, 42.5; H, 6.9; Si, 11.3; N, 5.2; Cl, 13.3.

Additional material was obtained from the first filtrate, but it was less pure and presumably contained some succinimide. In a companion experiment, it was determined that anhydrous HCl reacted immediately with a $HCCl_3$ solution of the hydride precursor to form H_2 and the desired chloro derivative. The infrared spectra of the bromo and chloro derivatives are almost superposable over the

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[9] C. L. Frye, G. A. Vincent, and G. L. Hauschildt, *J. Amer. Chem. Soc.*, **88**, 2727 (1966).

2–15-μ range; the latter exhibits an absorption at 25.5 μ believed to arise from the SiCl stretching vibration.

(C) 1-Fluoro-3,7,10-trimethylsilatrane (14). Concentrated aqueous HF (7.70 g, containing 0.20 mol of HF) was added to a solution of 1-ethoxy-3,7,10-trimethylsilatrane (**15**)[4,10] (56 g, 0.2 mol) in methanol (70 g). After standing overnight the resulting slurry was triturated with additional hot methanol in order to dissolve the crystalline product, and the siliceous by-product was removed by filtration after adding diatomaceous earth (Johns Manville, Super Cel) to prevent plugging. The filtrate was then "azeotroped" free of methanol by adding CCl_4 and boiling until the fluorosilatrane precipitated and the supernatant liquid boiled at 77° (*i.e.*, the boiling point of CCl_4). Filtration of the thusly precipitated product followed by evacuation to free of clinging CCl_4 afforded 34.3 g (73% yield) of **14**, mp 212–214°; a related run yielded a product melting at 217–220°. Variations of this type could arise from differences in the diastereomeric composition (*i.e.*, there are three asymmetric carbon sites). About 5 g of unreacted **15** was recovered from the filtrate; the yield based on unrecovered **15** is therefore 78%.

Anal. Calcd for $C_9H_{18}NO_3FSi$: C, 45.9; H, 7.66; neut equiv, 235. Found: C, 45.5; H, 7.74; neut equiv, 239.

(D) 1-Fluorosilatrane (13). Concentrated aqueous HF (3.85 g of 52% HF; *i.e.*, 0.10 mol of contained HF) diluted with 2-propanol (100 g) was added to a solution of 1-ethoxysilatrane (**1**) (2.19 g, 0.100 mol) in 2-propanol (100 ml), producing a considerable evolution of heat. The bulky precipitate which formed after about 4–5 hr at room temperature was then filtered, employing diatomaceous earth to avoid plugging by the amorphous siliceous by-product. The dried cake was then extracted with hot methanol to yield 4.8 g (25% yield) of **13**; the melting point of this crystalline material is high but has not been determined because of its sublimable character.

Anal. Calcd for $C_6H_{12}NO_3FSi$: C, 37.3; Si, 14.55; F, 9.84; neut equiv, 193. Found: C, 37.7; Si, 14.5; F, 9.76; neut equiv, 194.

Silatrane Hydrides. (A) Silatrane (12). A solution of 24 g (0.16 mol) of triethanolamine in 20 ml of methyl ethyl ketone was added (all at once, with swirling) to a solution of 16.8 g (0.14 mol) of $HSi(OMe)_3$ in 100 g of methyl ethyl ketone. This resulted in a slight evolution of heat and the formation of a moderate amount of gas (H_2). After a moment or so a precipitate formed and was filtered out; a rubber dam was used to press the solid free of adhering liquid; this solid (A) weighed 8.1 g (upon evacuation), mp 200–223°. The filtrate was diluted with 500 ml of pentane causing the immediate deposition of additional solid which was filtered out and then redissolved in a little boiling methyl ethyl ketone; upon cooling, this ketone solution yielded 1.60 g of white solid (B), mp 220–240°. Recrystallization of combined crops A and B from chloroform yielded 5.4 g (22% yield) of pure $HSi(OCH_2CH_2)_3N$, mp 252–256°.

Anal. Calcd: Si, 16.02; C, 41.4; H, 7.43; H(Si), 0.576; neut equiv, 175. Found: Si, 16.23; C, 40.7; H, 7.59; H(Si), 0.586; neut equiv, 177.

(B) 3,7,10-Trimethylsilatrane (10). Solutions of triisopropanolamine (271 g, 1.42 mol, in 193 g of benzene) and trimethoxysilane (173 g, 1.42 mol, in 257 g of benzene) were poured rapidly together. This resulted in the evolution of heat, and within a moment considerable evolution of H_2 commenced. The reaction flask (a 4-l. erlenmeyer) was then immersed in a pail of ice water to somewhat control the vigor of the reaction. After about 10 min an aliquot of the reaction mixture (10.34 g) was withdrawn and diluted with two volumes of pentane, causing the precipitation of a crystalline solid which, after isolation, weighed 2.13 g and corresponds to 62% of the theoretical amount anticipated for this aliquot. The bulk of the benzene solution was then treated similarly. Dilution with approximately two volumes of pentane caused the formation of a crystalline deposit and two liquid phases. The crystalline solid was collected by filtration, and recrystallization from CCl_4 afforded 100.4 g (33.9% yield) of the desired $HSi(OC(Me)HCH_2)_3N$. The melting point of this material (175–183)°) is broad as a consequence of its diastereomeric composition (*i.e.*, it is made up of two racemic structural pairs because of the presence of the three asymmetric carbon sites). A related preparation involving the reaction of triisopropanolamine with $(Et_2N)_3SiH$ offered little advantage over the above procedure.

(C) Oxybis[3,7,10-trimethylsilatrane] (9). Hexaethoxydisiloxane (68.4 g, 0.200 mol), triisopropanolamine (76.4, 0.400 mol), and KOH (0.24 g) were heated together under a short distillation column. The reaction flask was heated to 270° over a 2-hr period, during which time 52.5 g (95% theoretical) of ethanol was distilled from the system. Subsequent distillation of the residue afforded the desired product in 59% yield (52.8 g): bp 215° (0.10 mm), mp (from toluene) 185–190°.

Anal. Calcd for $Si_2C_{18}H_{36}O_7N_2$: Si, 12.54; neut equiv, 224. Found: Si, 12.55; neut equiv, 229. The absence of ethoxy groups was confirmed by the infrared spectrum (no absorption at 10.55 μ) and also by the nmr spectrum (only those lines expected for $OC(Me)HCH_2$ moiety were observed). The infrared spectrum shows strong lines at 8.7, 8.9, 9.25, 10.2, and 11.3 μ.

(D) Tris(nitrilo-2,2′,2′′-triethoxysiloxyethyl)amine (6). Triethanolamine (596 g, 4.0 mol) was heated with ethyl silicate (624 g, 3.0 mol), removing ethanol as formed from the alcoholysis reaction. As the reaction flask was heated beyond 200°, deposition of the crystalline product **6** commenced. The system was then heated to 250° while evacuating to assist in the complete removal of ethanol. Recrystallization of this material from acetonitrile afforded the desired product in 54% yield (360 g), mp 260°.

Anal. Calcd for $Si_3C_{24}H_{48}O_{12}N_4$: C, 43.2, H, 7.23; Si, 12.6; N, 8.38. Found: C, 43.0; H, 7.43; Si, 12.5; N, 8.0.

(E) 1-Hydroxysilatrane (4). This compound was obtained from the selective hydrolysis of **6** (360 g, 0.54 mol) in 2 l. of chloroform containing a stoichiometric amount of water (29 g, 1.6 mol). The reactants were maintained at reflux temperature for 1 hr; however, deposition of the crystalline silanol commenced after only a few minutes. Subsequent filtration of the resulting product afforded **4** in 57% yield (170 g), mp 205–210°.

Anal. Calcd for $SiC_6H_{13}O_4N$: C, 37.7, H, 6.85; Si, 14.68; N, 7.32; neut equiv, 191. Found: C, 37.6; H, 7.0; Si, 14.5; N, 7.0; neut equiv, 192. Infrared spectroscopy confirmed the presence of silanol (absorption at 3460 cm^{-1}) and the absence of water (no absorption at 6.0 μ).

The silanol was condensed with a variety of chlorosilanes using triethylamine as an HCl acceptor. Chloroform was used as the solvent in these reactions. To obtain good yields it was found necessary to use $HCCl_3$ which had been extracted with concentrated H_2SO_4 to remove the 0.75% ethanol (present as a preservative) which would otherwise have competed with the silanol for the chlorosilane. (In retrospect, use of ethanol-free $HCCl_3$ in the hydrolysis of **6** would probably have considerably improved the yield of **4** itself.) The following $ZOSi(OCH_2CH_2)_3N$'s were prepared and characterized (Z, % yield, melting point, °C): Me_3Si, 92, 156; $PhMe_2Si$, 89, 83; Ph_2MeSi, 81, 130; Ph_3Si, 89, 256; Me_2HSi, 77, 98; PhMeHSi, 79, 108; $ViMe_2Si$, 99, 127. In the same fashion, **4** was condensed with chlorine end-blocked linear polydimethylsiloxanes to give the following $N(CH_2CH_2O)_3SiO(Me_2SiO)_nSi(OCH_2CH_2)_3N$'s ($n$, % yield, mp °C): 1, 44, 240; 2, 53, 193; 3, 32, 140; 4, 35, 122; 5, 45, 68. The chloroform used in this latter series had not been freed of ethanol, hence the lower yields. Use of purified $HCCl_3$ in the example where $n = 3$ increased the yield from 32 to 63%. Actual yields were no doubt higher than the given yields of isolated purified products. In all cases, acceptable elemental analyses were obtained.

Formation of Silatranes *via* Alcoholysis of Siloxane Precursors with Triethanolamine. A. Ethylsilatrane. Triethanolamine (76 g, 0.51 mol) and 81 g of a neutral toluene solution of ethyltrichlorosilane hydrolysate (40 g, 0.49 mol) were placed in a 300-ml distillation flask. After adding 0.3 g of powdered KOH, these reactants were heated to 250° under a small distillation assembly. Upon removal of the toluene, the silsesquioxane resin gradually reacted with the triethanolamine to form the desired product which was collected by distillation at reduced pressure, affording an 85% yield (87 g), bp 170–180° (20 mm). This material was identical in all respects with that prepared by other means.[3]

(B) Phenylsilatrane. Triethanolamine was heated with $(PhSiO_{3/2})_8$ at 250° for 30 min. Although no KOH was added, alcoholysis of this crystalline silsesquioxane was rapid and an almost quantitative yield of phenylsilatrane[1,3] was crystallized (mp 209–211°) from the resulting reaction product.

(C) "Triethanolamine Silicate." This more or less nondescript silatrane material was prepared by heating Mallinckrodt analytical reagent grade silicic acid (30 g, 0.50 mol) with an excess of triethanolamine (149 g, 1.0 mol) to 260° under a N_2 purge for 3.5 hr, during which time the silica "dissolved" and approximately 27 g of H_2O was distilled from the reaction flask. Titration of the resulting viscous liquid confirmed the presence of an appreciable amount of silatrane type nitrogen base (*i.e.*, the delayed neutralization characteristic of silatranes[1b] was observed). This material may be rep-

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(10) C. M. Samour, U. S. Patent 3,118,921 (Jan 21, 1964).

resented by the somewhat idealized structure, $(HOCH_2CH_2)_2NCH_2CH_2OSi(OCH_2CH_2)_3N$.

m-Nitrophenylsilatrane. Triethanolamine can be trimethylsilylated by reaction with $(Me_3Si)_2NH$ to give $N(CH_2CH_2OSiMe_3)_3$: bp 126° (2.7 mm); $n^{25}D$ 1.4269; neut equiv 366 (calcd value 365). This product (3.7 g, 0.010 mol) was placed in a 1-oz vial with *m*-nitrophenyltrifluorosilane (2.1 g, 0.010 mol) and 5.0 g of *o*-xylene. After heating the xylene solution for 30 min at about 110°, during which time Me_3SiF was allowed to escape, the vial was removed from the hot plate and, upon cooling, crystallization occurred to give 2.83 g of the desired product (95% yield) whose infrared spectrum, neutralization equivalent, and other characteristics were identical with those of authentic material prepared by the more conventional method utilizing triethanolamine and the triethoxyarylsilane.

$N(CH_2CH_2CH_2OH)_3$, Preparation and Reaction with $PhSi(OMe)_3$. The 3,3′,3′′-nitrilotripropanol was prepared by heating 3-amino-1-propanol with 3-bromo-1-propanol and K_2CO_3 at reflux in absolute ethanol as per the instructions of Tishler,[11] *et al.*, for a similar synthesis. Distillation afforded a 65% yield of the desired triol: bp 180° (0.2 mm); $n^{25.2}D$ 1.4862. Subsequent condensation of this material (5.09 g, 0.0266 mol) with $PhSi(OMe)_3$ (5.30 g, 0.0268 mol) in the presence of 26 g of *o*-xylene as a diluent led to gelation; *i.e.*, there does not appear to be any tendency to form the monomeric cage structure.

Syntheses Involving Displacement Reactions on Ethoxysilatrane Substrate. (A) Acetoxysilatrane (3). Ethoxysilatrane **1** (21.8 g, 0.100 mol), acetic acid (6.0 g, 0.10 mol), and acetic anhydride (10.2 g, 0.10 mol) were heated at 160° for 16 hr. Recrystallization of the resulting product from a chloroform–heptane mixture afforded 60% (14 g) of the desired product, mp 172–175°; the infrared spectrum had the anticipated strong absorption at 5.9 μ.

Anal. Calcd for $SiC_8H_{15}O_5N$: C, 41.2; H, 6.44; Si, 12.0, neut equiv, 233. Found: C, 40.8: H, 6.24; Si, 12.1; neut equiv, 238.

(B) Triphenylsiloxysilatrane (5). When triphenylsilanol (27.5 g, 0.10 mol) was heated with ethoxysilatrane **1** (22 g, 0.10 mol) and 0.2 g of $Zn(OAc)_2$ in *o*-dichlorobenzene (50 g) at 150° for 2 hr, the desired compound **5** formed, and upon cooling it was isolated in 70% yield, mp 256°; this material had a neutralization equivalent of 450 (calcd 449) and was identical with that described elsewhere herein.

Anal. Calcd for $Si_2C_{18}H_{27}O_4N$: C, 64.1; H, 6.01; Si, 12.5; N, 3.11. Found: C, 63.8; H, 6.3; Si, 12.4; N, 3.10.

If a mixture of Ph_3SiOH and **1** is recrystallized without being heated long enough to permit reaction to occur, a 1:1 complex of the two compounds may be isolated; mp 135–138°; neut equiv, 500 (calcd 495).

Synthesis of Polymers with Silatrane Backbone Units. (A) Reaction of 3-Glycidyloxypropyltrimethoxysilane with Diethanolamine. Diethanolamine (10.5 g, 0.10 mol) and 3-glycidyloxypropyltrimethoxysilane (23.6 g, 0.100 mol) were heated under a Vigreux–Claisen assembly which was suitably protected from atmospheric moisture. Upon heating to 70°, the pot contents were pale yellow, but still immiscible. At about 80° miscibility resulted and an exotherm caused the temperature to increase very rapidly to 130°, whereupon the flask contents gelled. Gentle refluxing of the gel for several hours caused the gel to pass back into solution; the resulting solution was diluted with 25–30 ml of dry methyl ethyl ketone. This solution exhibits the delayed neutralization characteristic of silatrane structures.[1b,2] The methyl ethyl ketone solution deposited a crystalline product melting at 143–150°. Recrystallization of this solid from benzene yielded what appeared to be a polymorphic form melting at 85–90°. In both cases the crystalline solids melted to yield extremely viscous liquids and were merely polymorphs, as evidenced by their essentially identical infrared spectra.

Anal. Calcd for $SiC_{10}H_{19}O_4N$: C, 48.9; H, 7.81; N, 5.71. Found: C, 48.6; H, 7.62; N, 5.96.

(B) Preparation of a Novel Polymer From $PhSi(OMe)_3$, $HOCH_2CH_2NH_2$, and *sym*-Bis(3-glycidyloxypropyl)tetramethyldisiloxane. $PhSi(OMe)_3$ (99 g, 0.50 mol), ethanolamine (30.8 g, 0.50 mol), and the diepoxide (181 g 0.500 mol) were heated in a 1-l. three-necked flask fitted with an agitator, dropping funnel, condenser *via* a Dean Stark trap, and N_2 purge. After about 15 min at 90°, the contents were becoming quite viscous, so 400 ml of *o*-xylene was added. During the following 2-hr period, approximately 150 g of volatiles was distilled from the system. These volatiles presumably included the anticipated 48 g of methanol produced by the reaction. The viscosity of the resulting resin solution did not undergo further change upon additional heating. Weight loss measurement confirmed that the solution was approximately 52.8% nonvolatile material, and titration of the solution confirmed the presence of silatrane-type amine (*i.e.*, delayed neutralization effect). Evaporation of a small portion of this polymer solution in an aluminum foil cup yielded a tacky film.

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(11) E. Wilson and M. Tishler, *J. Amer. Chem. Soc.*, 73, 3635 (1951).

Reaction of Triphenylmethylamines with Boron Trihalides

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Abstract: Triphenylmethylamines react with boron trifluoride to form stable 1:1 adducts, $(C_6H_5)_3C^+R_2NBF_3^-$ (R = CH_3 or H). A similar reaction which produces $(C_6H_5)_3C^+(CH_3)_2NBCl_3^-$ occurs between triphenylmethyldimethylamine and boron trichloride. Tensimetric titrations at −78° demonstrate the existence of an unstable $(C_6H_5)_3C^+(CH_3)_2N(BF_3)_2^-$. No further coordination of either BF_3 or BCl_3 to $(C_6H_5)_3C^+(CH_3)_2NBCl_3^-$ could be detected. The basicity of $(CH_3)_2NBF_3^-$ and $(CH_3)_2NBCl_3^-$ is discussed.

The difunctional Lewis acid 1,2-bis(difluoroboryl)ethane, $F_2BCH_2CH_2BF_2$, reacts with triphenylmethyl ethers[2,3] and triphenylmethylamines[4] to form "chelated" 1:1 adducts. For example

$$(C_6H_5)_3CN(CH_3)_2 + F_2BCH_2CH_2BF_2 \longrightarrow (C_6H_5)_3C^+ + [(CH_3)_2N(F_2B\text{–}CH_2)_2]^-$$

Similarly, boron trifluoride reacts with triphenylmethyl methyl ether[3] to form $(C_6H_5)_3C^+CH_3O(BF_3)_2^-$. Since complexes in which two boron Lewis acids are coordinated to a single donor atom are relatively rare, the reactions of boron trihalides with triphenylmethyl-

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(1) NASA Trainee, 1968–1969; NSF Trainee, 1970.

(2) M. J. Biallas and D. F. Shriver, *J. Amer. Chem. Soc.*, **88**, 375 (1966).

(3) D. F. Shriver and M. J. Biallas, *ibid.*, **89**, 1078 (1967).

(4) M. J. Biallas, *ibid.*, **91**, 7290 (1969).