Main group atranes: chemical and structural features

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CONTENTS

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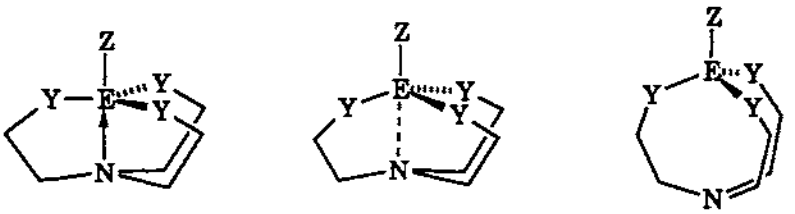
ABSTRACT

Atranes are comprised of two bridgehead atoms bridged by three three-atom moieties. When the bridgehead atoms interact, a [3.3.3.0]tricyclic system is produced; when they do not, a [3.3.3]bicyclic structure is evident. Quasi-tricyclic structures are also known in which the bridgehead–bridgehead bond length lies between the sum of the van der Waals radii and a normal transannular bond. Because of this and additional factors, atranes give rise to interesting new and useful chemistry as well as novel molecular architectures. In this review the chemical reactivities and structural properties of main group atrane systems are surveyed.

1. INTRODUCTION

Since the 1960s the term "atrane" has been primarily used to refer to structures of type **A**. The first well-substantiated reports of such examples dealt with silatranes

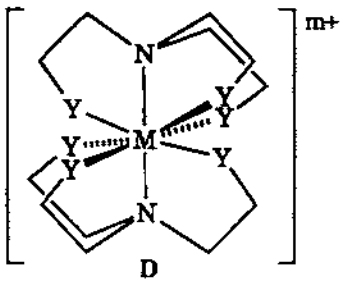


atrane **A** **quasi-atrane** **B** **pro-atrane** **C**

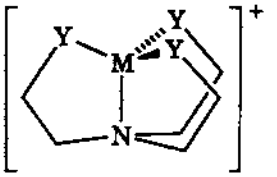
wherein E≡Si, Y≡O and Z is an organic substituent (see later). More recently it has become apparent that the transannular coordinate bond in atranes (**A**) can be considerably stretched (providing novel quasi-atranes, **B**) and even broken (giving pro-atranes, **C**) by imposing stereoelectronic constraints on the Y and Z substituents for several main group elements E.

The focus of the present review is on the variegated coordination chemistry displayed by atranes wherein E is a main group element. Thus the cleavage of the transannular coordinate bond in **A** liberates the bridgehead nitrogen for coordination with Lewis acids in **C**. Moreover, a lone pair on Y (e.g. Y≡O or NR) can ligate, as is also the case for a lone pair on Z (which can be an atom or a group) or when Z itself is a lone pair on E.

The non-metallic elements of groups 13–15 form atranes that are characterized by covalent bonding between Y and the group element E as depicted above. For the more metallic elements of groups 13–15, however, cationic atranes of type **D** are



D



E

observed in which the Y heteroatom of an HO, RNH or H_2N function is coordinatively bound to the metal. "Double atranes" of type **D** extend into the group 12 metals and also into the alkaline earth metal ions in group 2. For the proton and the alkali metal ions of group 1, coordinatively bound atrane structures of type **E** are found in which anions may also coordinate axially to the metal. As we shall see, this chemistry contains many surprises that have interesting and valuable implications for synthesis and catalysis.

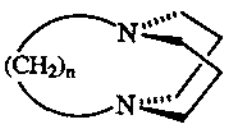
Atrane chemistry presently extends from group 1 to group 15. Because the emphasis in this review is on main group elements, groups 3–11 will not be addressed.

2. GROUP 15 ATRANES

Two elements in this group, namely nitrogen and phosphorus, appear thus far to exhibit a well-defined atrane chemistry. Antimony and bismuth atrane compounds are quite rare.

2.1. Pro-carbaazatranes and carbaazatranes

Bicyclic compounds of type **1** ($n=2$–4) are pro-carbaazatranes possessing interesting chemical and structural properties [1]. For example, the nearly planar nitrogen



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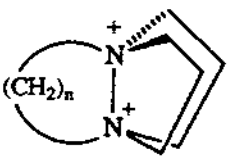
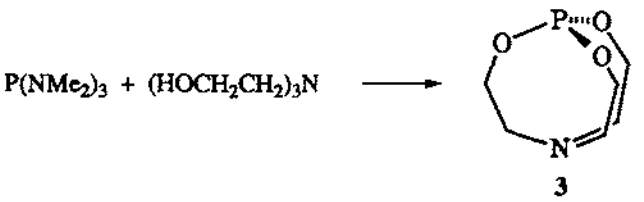


2

stereochemistry in **1** ($n=3$), whose origin lies in van der Waals interactions among $N(CH_2)_3$ hydrogen atoms, is believed to be responsible for the relatively low $\Delta H^{\ddagger}$ of bridge carbon conformational flipping. This conformational flexibility is reduced by quaternizing both nitrogen atoms with protons or methyl carbocations [1]. Dications of type **2** ($n=2$–4) have also been synthesized [1].

2.2. Phosphatranes, quasi-phosphatranes and pro-phosphatranes

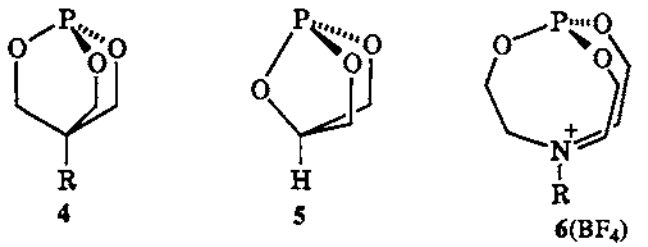
The atrane chemistry of phosphorus is extensive [2–32]. It was already apparent during our discovery of this class of compounds in 1976 that they were quite unusual [2]. Attempts to isolate **3** from reaction (1) by evaporation of the solvent produced an intractable material which decomposed violently upon attempted vac-



(1)

3

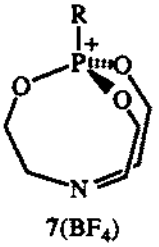
cuum sublimation. Although we have no direct proof of the prophosphatrane structure shown for **3**, it is a reasonable one based on indirect evidence brought out in later subsections. The polymeric nature of the residue from reaction (1) may at first glance appear surprising, since ring strain might not be expected to inhibit the formation of the bicyclic structure of **3**. Thus, for example, **4** [33] and **5** [34],



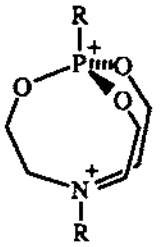
4 **5** **6**(BF_4)

which are highly constrained bicyclic structures have been isolated and characterized. Indeed, **5** hydrolyzes violently, suggesting the presence of considerable strain in this molecule. It is apparent, however, that [3.3.3]bicyclo compounds also experience some strain, since they are composed entirely of eight-membered rings [1]. Attempts to alkylate **3** *in situ* with Et_3OBF_4 or Me_3OBF_4 did not produce a product of alkylation such as **6–8** as expected, but instead gave only **9**(BF_4) according to its high field ^{31}P nuclear magnetic resonance (NMR) shift (−20.9 ppm), its one-bond P–H coupling constant (790 Hz) and its configuration determined by X-ray crystallography (P–N bond length 1.986 Å) [2]. The R_3OBF_4 in this reaction was shown to have alkylated unreacted $(HOCH_2CH_2)_3N$, releasing protons that surprisingly gave rise to a transannulated structure wherein the proton (a poorly apicophilic substituent) resides in such a position [13].

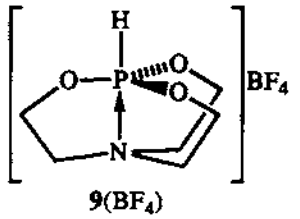
Although coordination of the bridgehead nitrogen of **3** to a proton is expected on basicity grounds, any such kinetically formed cation must rearrange to cation **9** owing to stabilization by the three chelating five-membered rings formed upon transannulation. Relief of strain in the formation of additional bonds to the bridge-



7(BF_4)

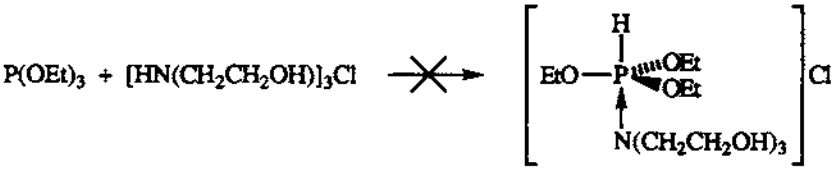


8(BF_4)$_2$



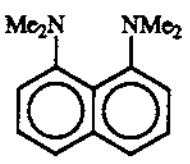
9(BF_4)

head atoms in going from **3** to **9** probably also plays a role [1b]. That chelation plays an important role here was shown by the failure of reaction (2) in which a



(2)

one-bond P–H coupling would have been expected for the product salt [5]. Further evidence for the stability of the phosphorus coordination compound **9**(BF_4)$_2$ is its survival in the presence of NaOMe, Proton Sponge (**10**) and "magic acid" solution ($HSO_3F \cdot SbF_5$/liquid SO_2) in which no protonation of the quaternary nitrogen was observed [5].



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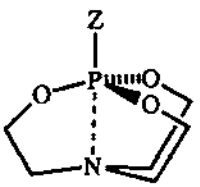
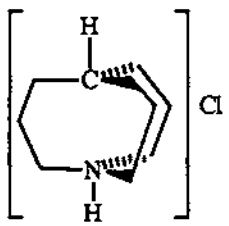


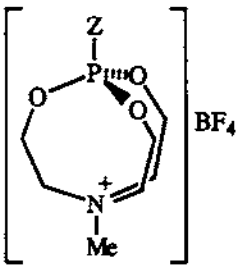
Z		Z	
11	O	**14**	BH_3
12	S	**15**	$W(CO)_5$
13	Se	**16**	$Mo(CO)_5$



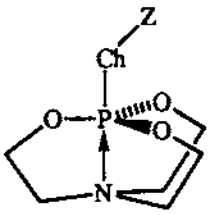
17(Cl)

In situ derivatization of **3** was also accomplished upon oxidation with peroxide or elemental sulfur or selenium to give stable **11–13** respectively and by coordination as shown in **14–16**. An X-ray study of **12** revealed a planar bridgehead nitrogen (average C–N–C angle 119.2°) and a P–N distance of 3.132 Å [3]. Here the planarity of the nitrogen is at least partially steric in origin owing to van der Waals interactions among the hydrogen atoms on the methylene carbon atoms α to the bridgehead nitrogen, as was shown earlier to be the case for manxine hydrochloride **17**(Cl) wherein the C–N–C angles (average 115.5°) are abnormally large compared with the tetrahedral angle [35]. The P–N distance in **12** is about 6% shorter than the sum of the van der Waals radii of these atoms (3.34 Å [36]) as a consequence of the

planarity of the bridgehead nitrogen. To the extent that any measurable shortening of the P–N distance over the sum of the van der Waals radii qualifies a compound as a quasi-atrane, **12** is a quasi-phosphatrane. Partial transannulation also occurs for **14** in which the P–N_{ax} distance is 3.098 Å [4]. Coordination of the bridgehead nitrogen in **11–13**, **15** and **16** to a methyl carbocation (**18–22** respectively) has also been observed [5], although no X-ray structural studies were carried out to determine P–N distances.

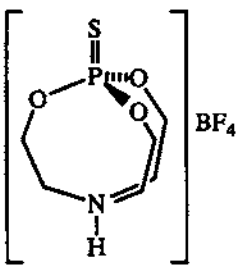


	Z
18	O
19	S
20	Se
21	$Mo(CO)_5$
22	$W(CO)_5$

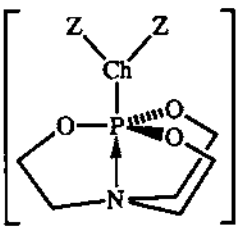


	Ch	Z
23	O	BF_3
24	O	H^+
25	S	H^+
26	O	Et^+
27	S	Et^+
28	O	$SiEt_3^+$

Interestingly, the chalcogens in **11** and **12** are also capable of coordinating to main group elements as was shown from NMR spectral evidence (which included the high field ^{31}P NMR shifts expected for five-coordinate phosphorus) for **23–28** [8,11,12,18,21]. In the case of cation **27** an X-ray study confirmed the trigonal bipyramidal geometry of the phosphorus [8]. The protonation of **12** is apparently solvent dependent, since **25** is observed in CF_3CO_2H whereas **29**(BF_4) can be isolated from aqueous HBF_4 [12]. Solution NMR evidence was also reported for cations **30** [11] and **31–35** [12] in which the chalcogen is sufficiently basic (presumably from transannulation of the nitrogen lone pair) to coordinate to two Lewis acids.

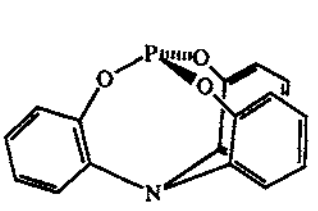


29(BF_4)



	Ch	Z
30	O	$SiEt_3^+$
31	O	H^+
32	S	H^+
33	O	Et^+
34	S	Et^+
35	S	Me^+

Unlike **3**, **36** [15,37a] does not easily form transannulated structures, probably owing to the reduced flexibility of the C_2 bridges imposed by the benzo rings. Acidification of **36** leads to an upfield ^{31}P chemical shift consistent with the formation of cation **37**, but it appears to be too fragile to isolate [37a]. The structure of **36**, however, does feature a transannular distance of 3.136 Å [37a] which is 6.3% shorter than the van der Waals sum of the phosphorus and nitrogen radii. The BH_3 adduct



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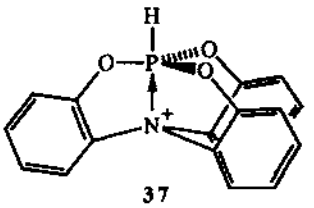

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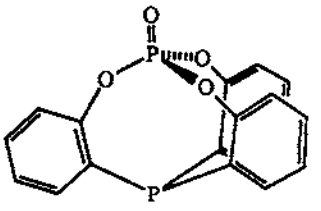
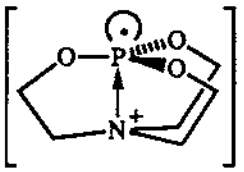


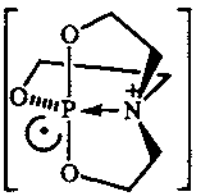
38

and the oxide of **36** have also been reported [15]. Compound **38**, which contains a phosphorus atom at both bridgeheads, shows no evidence of transannular bonding on the basis of its solid state structure determined by X-ray crystallography [37b].

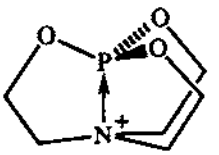
X-Ray irradiation of a single crystal of **9**(BF_4) was reported to give a free radical of structure **39** according to its electron spin resonance (ESR) spectrum, while low temperature UV excitation followed by X-ray irradiation gave ESR spectra



39(BF_4)



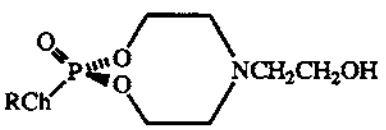
40(BF_4)



41

consistent with the structure shown as **40** [38]. The evidence for the structure of cation **39** has also been interpreted to be consistent with that of **41** with the odd electron localized in a P–N σ^* molecular orbital (MO) [10].

The bonding in phosphatranes has been studied using the minimum neglect of differential overlap (MNDO) approximation on model compounds of the type $ZPF_3 \cdot NH_3$ where Z is a lone pair, H^+, O or OH^+ [14,39]. The presence and absence of P–N bonding in $HPF_3^+ \cdot NH_3$ and $O{=}PF_3 \cdot NH_3$ respectively were rationalized on the decrease in acceptor ability of the lowest unoccupied molecular orbital (LUMO) on phosphorus. It may be observed at this point that cations such as **26** and **27** are subject to nucleophilic attack at the OCH_2 carbon by OH^- to give monocyclic **42** [8,40].



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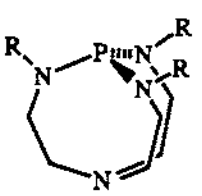
2.3. Pro-azaphosphatranes, quasi-azaphosphatranes and azaphosphatranes

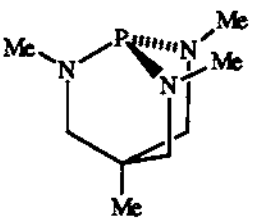
In this review the trivial nomenclature "aza-elementa-atranes" will be used to denote structures **A**–**C** in which Y ≡ NR.

2.3.1. Pro-azaphosphatranes: synthesis and basicity

Our hope in synthesizing pro-azaphosphatranes was to be able to isolate pro-atrane structures such as **43**–**45** which are analogues of unstable **3**. Reaction (3)



	R
43	H
44	Me
45	CH_2Ph



46

failed for the preparation of **43**, but **44** and **45** could be obtained in reaction (4) in about 20%–50% yield after several weeks [17]. While the product of reaction (3)

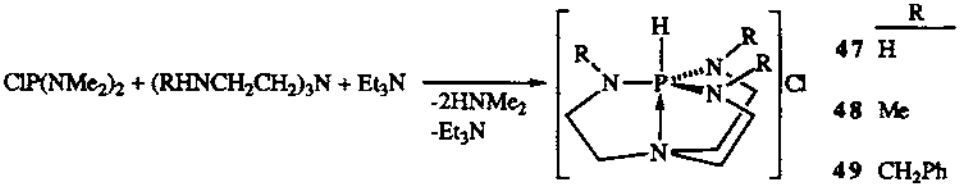
$$P(NMe_2)_3 + (H_2NCH_2CH_2)_3N \xrightarrow[-HNMe_2]{} \text{polymer} \quad (3)$$

$$P(NMe_2)_3 + (RNHCH_2CH_2)_3N \xrightarrow[-HNMe_2]{} \mathbf{44} \text{ or } \mathbf{45} \quad (4)$$

was not too surprising in view of the availability of two reactive hydrogen atoms on each primary amine of the tetramine, we were initially astonished at the sluggishness of reaction (4). The slow rate of reaction (4) is associated with strain in the eight-membered ring bicyclic products. Interestingly, the more rigid molecule **46** forms in 90% yield within a few hours in the analogous reaction with $(MeHNCH_2)_3CMe$ [41]. Here, however, relatively strainless six-membered rings comprise the cage structure. In an effort to enhance the rate of formation of **43**–**45**, the more reactive phosphorus reagent in reaction (5) was employed. To our surprise, however, this

$$ClP(NMe_2)_2 + (RHNCH_2CH_2)_3N + Et_3N \not\longrightarrow \mathbf{43}, \mathbf{44} \text{ or } \mathbf{45} + 2HNMe_2 + Et_3NHCl \quad (5)$$

reaction took a different course, producing nearly quantitative yields of **47**–**49** within about 1 h at room temperature [24]. The preparations of these salts do not require the presence of base, and indeed, cation **47** forms in 99% yield as the triflate in reaction (7) [24]. It is reasonable to suggest that protonation of the phosphorus in $P(NMe_2)_3$ in reaction (7) facilitates nucleophilic attack by a tertiary nitrogen (path "a" in Scheme 1) or by a primary nitrogen (path "b") of the tetramine, followed by successive chelation and elimination steps.



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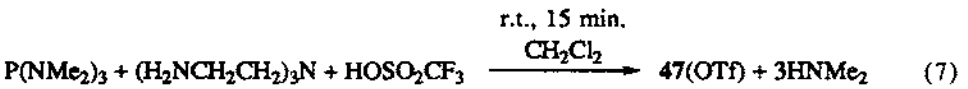
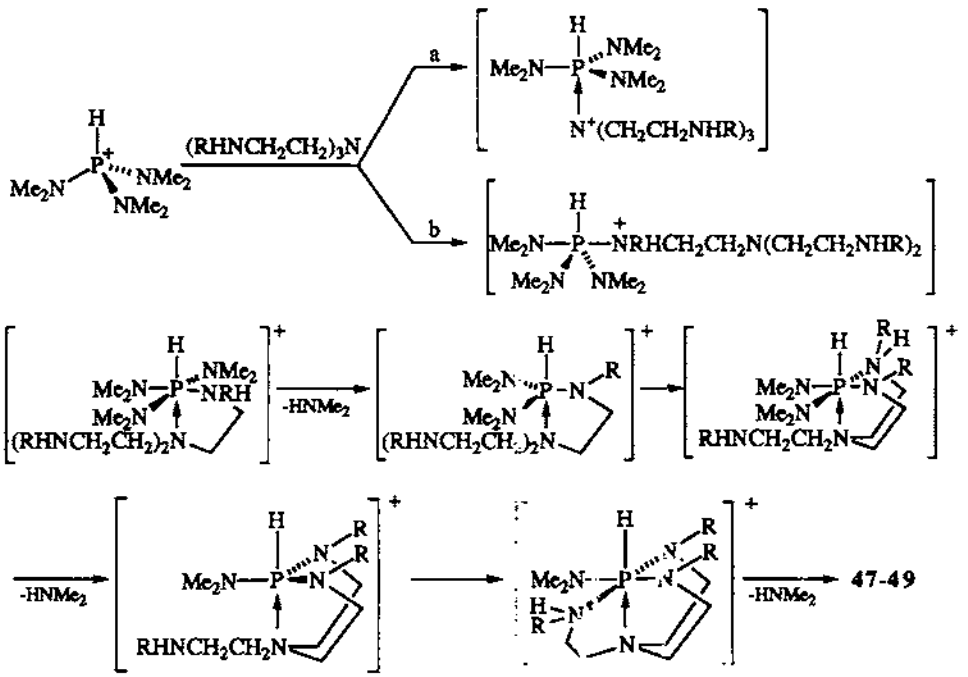


(7)

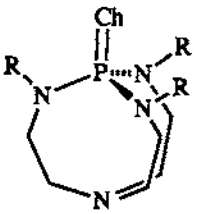
Scheme I



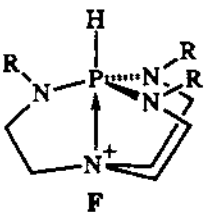
As in the formation of the phosphatrane cation **9**, coordination is also important to the stabilization of the azaphosphatrane cations **47–49** wherein the phosphorus also coordinates to a proton. Thus in parallel with the failure of reaction (2), reaction (8) was also unsuccessful. It may be that the drop in entropy associated with the intermolecular adduct formation in these reactions is prohibitively large compared with intramolecular transannulation in **9** and **47–49**. Further facilitating transannulation in **47–49** could be relief of strain experienced by their respective pro-atrane precursors **43–45** upon forming additional bonds to the bridgehead atoms [1b].

$$P(NMe_2)_3 + Et_3N + H^+ \not\longrightarrow Me_2N{-}P^{+}(H)(NMe_2)_2(NEt_3) \quad (8)$$

This process is counteracted to some extent, however, by the formation of three somewhat strained five-membered rings in **47–49**. Like **9**, cations **47–49** are very stable. For example, **47–49** fail to exchange their P–H proton in $DOC(O)CF_3$ and require the strong ionic base KO–^{t}Bu to liberate the corresponding pro-azaphosphatranes **43–45** quantitatively at room temperature. Compound **43** survives in solution long enough to derivatize with O_2 and Se so that the phosphorus can coordinate to oxygen and selenium as shown in **50** and **51** respectively [18,19,24]. On the other hand, **44** and **45** can be isolated as sublimable solids.



	R	Ch
50	H	O
51	H	Se
52	Me	Se
53	CH_2Ph	Se



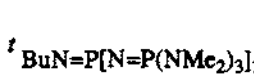
F

In competitive deprotonation experiments in KO–^{t}Bu/DMSO the relative acidities of cations **47–49** fell in the unexpected order **49** > **48** > **47** [23]. On electron induction grounds the order expected was **49** > **47** > **48**. The observed acidity order is supported by the parallel decrease in $^1J_{PH}$ coupling (506, 491 and 453 Hz respectively) as well as the decrease in $^1J_{PSe}$ coupling in the selenides **51–53** in the order **53** > **52** > **51** (774, 754 and 590 Hz respectively) [5,11,18,19]. One-bond couplings generally decrease as the s-character in the linkage diminishes and/or as the positive charge on one of the atoms decreases [42]. Moreover, there is ample evidence in the literature that, for bases of similar structure, rising solution and gas phase basicity can be linearly correlated with decreasing $^1J_{PSe}$ values of their selenium adducts and with decreasing $^1J_{PH}$ couplings of their protonated forms [42,43].

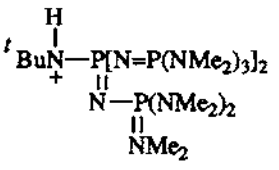
The $^1J_{PH}$ values for **47** and **48**, though consistent with their relative acidities, are opposite in order to that expected on the basis of their structural parameters. Thus **47** is more distorted toward a tetrahedral $HP(N_{eq})_3$ stereochemistry (structure **F**) than is **48** in that the N_{eq}–P–N_{ax} bond angles in **47** (84.01(3)°) are smaller than in **48** (85.9(4)°, 86.5(2)°) and the P–N_{ax} bond length in **47** (2.0778(4) Å) is slightly longer than in **48** (1.976(8) Å) [23]. The larger distortion in **47** should place more s-character in the P–H bond and a larger positive charge on phosphorus. Despite this, $^1J_{PH}$ in **47** is smaller. The decrease in steric interactions between the substituents on the equatorial nitrogen atoms and the P–H proton in the order **49** > **48** > **47** (and hence decreasing sterically assisted proton departure) may be a dominating factor

accounting for the corresponding acidity order of these cations. It is also possible that electronic stabilization by delocalization in the three-center, four-electron bond of **47** is particularly advantageous for some as yet unknown reason.

The pK_a value in DMSO estimated for **47** by competitive deprotonation reactions monitored by ^{31}P NMR spectroscopy is 29.6 [23]. An estimate of 26.8 as an upper limit for the pK_a values of **48** and **49** was made on the assumption that the pK_a of HO–^{t}Bu in DMSO is 28.6 [44]. It should be noted that the phosphorus atoms in **43–45** are the most basic by many orders of magnitude of any phosphine



54

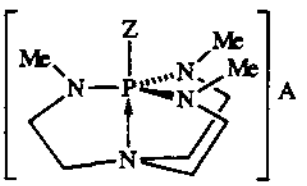


55

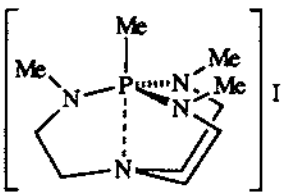
compound known. On the other hand, there are phosphazenes such as **54** which are even more basic [45]. However, their basicity derives not from phosphorus protonation, but from the nine resonance structures that can be drawn for species such as **55** in which the terminal imido nitrogen is protonated.

Advantage can be taken of the extraordinary basicity of pro-azaphosphatranes in a variety of organic syntheses. We have shown, for example, that routes to pyrroles, dipyrromethanes, oxazoles and porphyrins which require a strong non-ionic base such as 1-diazabicyclo[5.4.0]undec-7-ene (DBU) can be greatly improved in speed and yield by using **44** instead [31,46–49].

It may be anticipated that **44** could also coordinate carbocations and halonium ions. This was confirmed by the isolation of **56–60** for which solution upfield ^{31}P chemical shifts are consistent with transannulation of the bridgehead nitrogen



	Z	A
56	CH_2Br	Br
57	CH_2I	I
58	Cl	Cl
59	Br	Br
60	I	I



61

[19,25]. Curiously, CH_3^+ does not induce full transannulation in **61** according to its ^{31}P chemical shift (48.6 ppm) [16]. This cation is probably a quasi-azaphosphatrane as will become clear in the next subsection.

2.3.2. Quasi-azaphosphatranes: structural features

An operational definition we employ of a quasi-atrane structure is that the E–N transannular distance is less than the sum of the van der Waals radii of the E

and N atoms but greater than the shortest distance seen in transannulated structures. In the present instance the van der Waals sum for the P and N atoms is 3.35 Å [36] and the fully transannulated P–N distance is about the 2.0 Å distance found in the protonated species **47** (2.0778(4) Å) and **48** (1.976(8) Å) [23]. Although ^{31}P NMR spectroscopy usually allows us to assign a fully transannulated phosphatrane structure to a compound, it does not allow us to differentiate between a pro-atrane and a quasi-atrane and we must therefore rely on X-ray crystallography. Summarized in Table 1 are pertinent structural metrics for quasi-azaphosphatranes we have collected thus far, all of which are derived from pro-azaphosphatrane **44**. At first glance the percentage shortening of the P–N distance over the sum of the van der Waals radii may not seem very remarkable, especially for compounds in the upper half of the table. However, it must be recognized that the full transannular coordinate covalent P–N bond in the trigonal bipyramidal structure of cations **47** and **48** represents only a 40% shortening over the van der Waals sum. By contrast, the covalent P–NMe distances in the compounds in Table 1 (about 1.6 Å) are approximately 50% shorter than the van der Waals sum. The somewhat greater length of a full transannular coordinate P–N bond can be attributed to its participation in a three-center four-electron MO system.

The metrics in Table 1 are plotted in Fig. 1, wherein it can be seen that the correlation of the P–N distance with the MeN–P–NMe angle is quite linear (r^2 = 0.97). In this plot the point at the upper extreme represents the fully transannulated atrane **48**, while the platinum compound at the lower extreme denotes a pro-atrane structure for which the percentage shortening of the transannular distance over the sum of the van der Waals radii is negligible (about 1%) [22].

The progressive closing of the transannular distance over a range of about 1 Å is remarkable. The bond angle changes during the collapse of the oblate cage of the

TABLE 1

Transannular P–N distances and MeN–P–NMe angles in quasi-azaphosphatranes derived from **44**

Compound	P–N (Å)	P–N interaction[a] (%)	MeN–P–NMe (°)	Reference
cis-Br(OC)$_4$Re(**44**), **62**	3.307	1.3	105.5	[26]
S=(**44**), **63**	3.250	3.0	106.8	[22]
P=(**44**), **64**	3.137	6.3	107.6	[47]
Cl$_2$Hg(**44**), **65**	3.143	6.2	108.3	[26]
S$_2$C(**44**), **66**	3.008	10.2	110.3	[22]
MeS(S)C(**44**)$^+$, **67**	2.771	17.3	113.4	[26]
HPhN(**44**)$^+$, **68**	2.551	23.8	115.1	[30]
MeSC(NPh)(**44**)$^+$, **69**	2.190	34.6	118.6	[26]

[a] Percentage shortening of the P–N distance relative to the sum of the van der Waals radii.

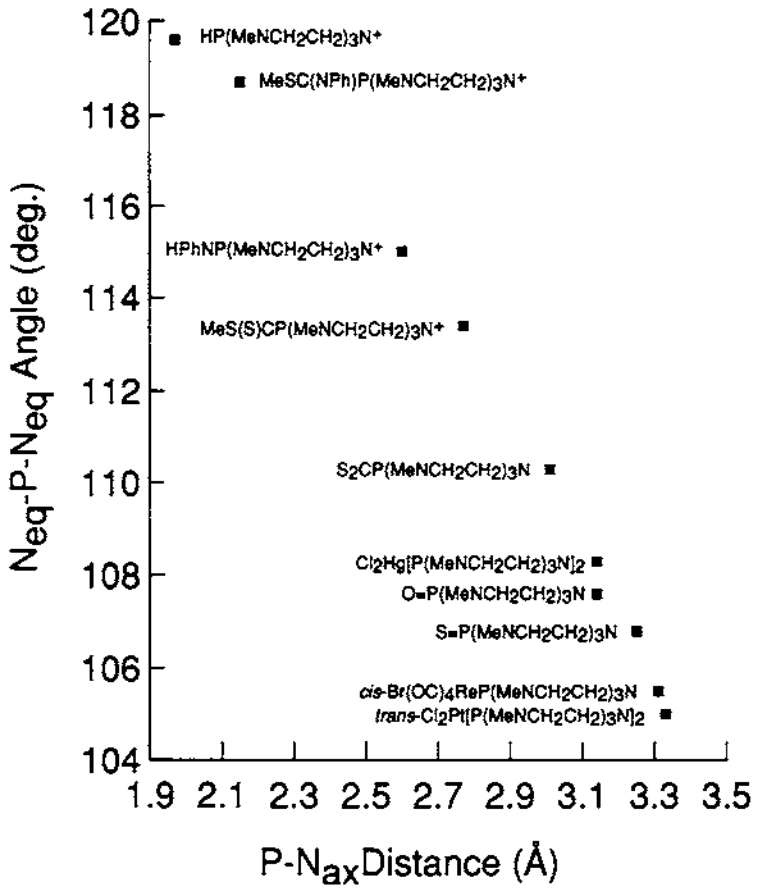


Fig. 1. Plot of P–N distances against the MeN–P–NMe angle in quasi-azaphosphatranes derived from $P(MeNCH_2CH_2)_3N$ (44).

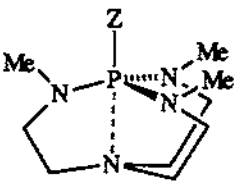
pro-azaphosphatrane to the azaphosphatrane structure are most strongly registered in the MeN–P–NMe angles. This observation may be associated with the lower hybridizational reorganization energy of phosphorus compared with other atoms in the bridges of the molecule. This process perhaps also reflects the increasing strain and decreasing entropy associated with the formation of the three five-membered rings, which counterbalance the electron withdrawal of the Z substituent. Since there is no trend in the degree of collapse of the cage moiety with the size of Z, electronic and strain factors probably dominate the process of strengthening the transannular bond.

It could be suggested that the structures observed by X-ray crystallography do not persist in solution and that perhaps crystal forces are somehow responsible for the variation in the solid state transannular distances. Since the ^{31}P chemical shift is very sensitive to bond angle changes around phosphorus, we compared these

values in both the solid and solution states for a few of these compounds [27]. The ^{31}P shift values in the two states lie within 0.4 ppm of one another.

2.3.3. Quasi-azaphosphatranes: basicity

In view of the extraordinary basicity of pro-azaphosphatrane **44** stemming from transannulation in the conjugate acid **48** (Section 2.3.2), it was of interest to determine whether transannulation could be accentuated upon adding a Lewis acid to a Z group in a quasi-azaphosphatrane. In this subsection we therefore consider the coordinating ability of the Z group in the quasi-azaphosphatranes **63**, **64**, **66**, **70**



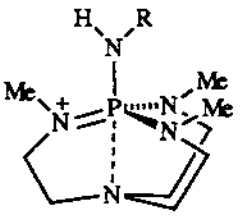
	Z
63	S
64	O
66	CS_2
70	NMe
71	NPh

$MeN{=}P(NMe_2)_3$ **72**

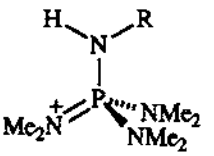
$PhN{=}P(NMe_2)_3$ **73**

and **71** to some Lewis acids. Although Table 1 tells us that **64** and **66** are indeed quasi-azaphosphatranes, we can only assume by analogy at this point that **70** and **71** are also partially transannulated.

We begin with a comparison of the coordination behavior of **70** and **71** to a proton with that of their acyclic analogues **72** and **73**. The two questions here were whether transannulation could enhance the basicity of the cage species and whether resonance structures depicted by **G** might be sufficiently configurationally disfavored

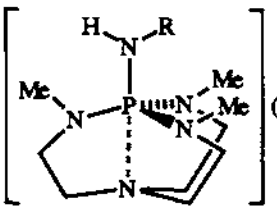


G

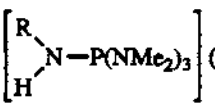


H

over those for the acyclic structure **H** that **70** and **71** would be less basic than their acyclic counterparts regardless of possible transannulation in **G**. Recently we isolated the protonated salts **74**–**77** and compared the relative basicities of their conjugate



	R
74	Me
75	Ph



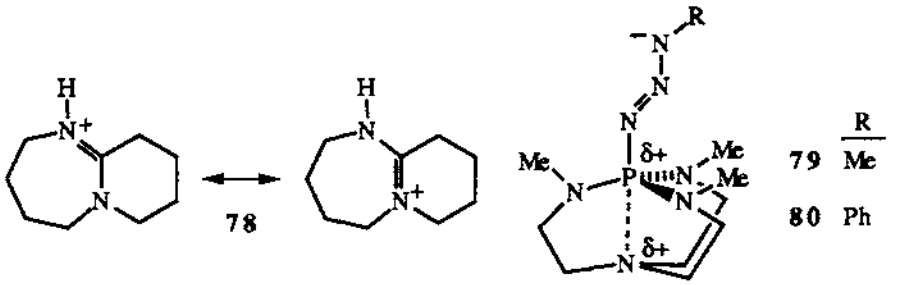
	R
76	Me
77	Ph

bases **70–73** [30]. In this study we also isolated the salt of **54**, namely **55**(O_2CCF_3), for inclusion in the ranking of base **54** among our compounds. Using ^{31}P NMR spectroscopy, we measured equilibria from both directions between pairs of bases and their conjugate acids. From the data we deduced the order of basicity to be

$$^{t}\text{BuN=P[N=P(NMe}_2)_3]_3 \;>\; \mathbf{44} \;>\; \mathbf{70} \;>\; \mathbf{72} \;>\; \text{DBU} \;>\; \mathbf{71} \;>\; \mathbf{73}$$

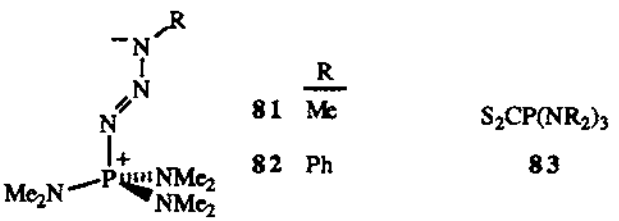
54

Since nine resonance structures can be drawn for the conjugate acid to **54** (i.e. **55**) and only three for **74–77**, it is easily rationalized that **54** is the strongest base. That **70** and **72** are stronger bases than DBU can be rationalized on the basis of the three resonance structures that can be drawn for them, while there are only two for



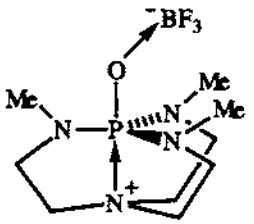
the conjugate acid **78** of DBU. On the other hand, DBU outranks **71** and **73** as a base owing to the presence of electron-withdrawing phenyl groups on the imido nitrogen. Most intriguing are the stronger basicities of **70** and **71** relative to their respective acyclic analogues **72** and **73**. We attribute this result to partial transannulation in **70** and **71**. This conclusion is borne out by the crystal structure determination of **68**(O_2CCF_3) (Table 1) which features 23.8% transannulation. The placement of the imido proton (which was located in the structure) on the imido nitrogen results in the lengthening of the N=P bond (as found in structural determinations of model compounds) by about 0.1 Å [30].

Another conclusion of these studies was that the relative stability of the new compounds **79** and **80** to N_2 elimination compared with their acyclic analogues **81**

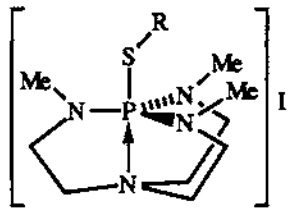


and **82** and the relative stability of **66** to its analogues **83** may be associated with partial transannulation in **79**, **80** and **66** [27,30].

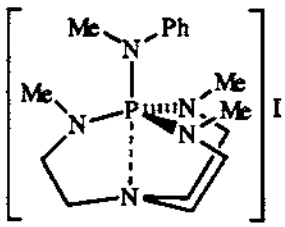
Lewis acids coordinated by the Z substituent in quasi-azaphosphatranes include BF_3 and R^+ as in **84–93**. The upfield ^{31}P chemical shifts of **84** [19] and **85–87** [27]



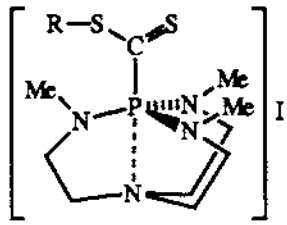
84



	R
85	Me
86	Et
87	n-Bu



88

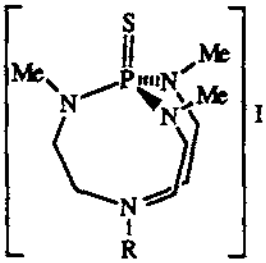


	R		R
67	Me	**92**	n-Bu
89	allyl	**93**	i-Pr
90	Et		
91	n-Pr		

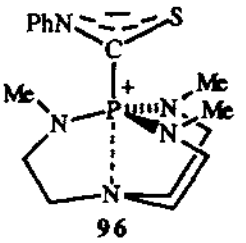
by 78 and about 25 ppm respectively over the corresponding parent quasi-azaphosphatranes suggest the transannulated structures shown, although no crystal structures for these compounds have yet been determined. Since upfield shifts are not observed in the alkylated derivatives **88**, **67** and **89–93**, they probably all have quasi-azaphosphatrane structures. This tentative conclusion is corroborated by the structural data in Table 1 for **68** (the proton analogue of **88**) and **67** (an analogue of **89–93**). It is note worthy, in fact, that the transannular distance in **66** shortens significantly upon alkylation to **67**.

If it is assumed that the transannular distance in the imide **71** is at least as long as in **64** in Table 1, which contains the more electronegative oxygen on phosphorus, protonation of the imide gives rise to an approximately 0.5 Å decrease in the P–N distance. Alkylation of the sulfur in **66** to give **67** leads to only an approximately 0.2 Å decrease in this distance, since the point of derivatization is two atoms removed from the phosphorus. Derivatization of the phosphorus of **44** by a directly adjacent positive charge to give **48**, for example, leads as expected to the largest shrinkage in the P–N distance (about 1.3 Å) if the reasonable assumption is made that this distance in **44** is at least close to the sum of the van der Waals radii. The relative rates of alkylation of **66** to **67** and **89–93** follow the order MeI > CH_2=$CHCH_2$I > EtI > ^{n}PrI ≈ ^{i}PrI [27] which is consistent with S_N2 attack by the partially negatively charged sulfur in zwitterionic **66**.

Methylation and ethylation of the sulfur in **63** do not give exclusively **85** and **86** respectively but also the pro-atrane regioisomers **94** and **95** in which the bridgehead nitrogen coordinates to the carbocation. No such regioisomers were detected



R
94 Me
95 Et



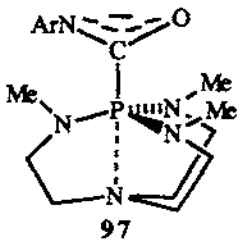
96

in mixtures of **63** with ^{n}BuI (which gave only **87**) or ^{i}PrI (which did not react). These results accord with the idea that the bridgehead nitrogen in **63** is more sensitive to the steric properties of the alkylating group than the sulfur. That these regioisomers are kinetically rather than thermodynamically established in solution was shown by heating isolated **85** and **94** in separate solutions of MeCN to 40–45°C for 10 h and observing no detectable interconversion by ^{31}P NMR spectroscopy [27].

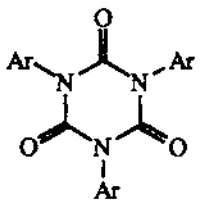
In closing this subsection, one last example of a probable quasi-azaphosphatrane will be mentioned, namely **96**, which is formed from **44** and phenylisothiocyanate [26]. Like the adduct S_2C(**44**) (**66**), **96** is a stable isolable compound.

2.3.4. Pro-azaphosphatranes and quasi-azaphosphatranes: catalysis

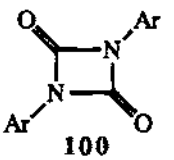
In surprising contrast with the stability of **96**, its analogue **97** (Ar ≡ Ph) could not be isolated [28]. Although its probable presence was indicated by a ^{31}P NMR



97



Ar
98 Ph
99 *p*-MeOC$_6$H$_4$



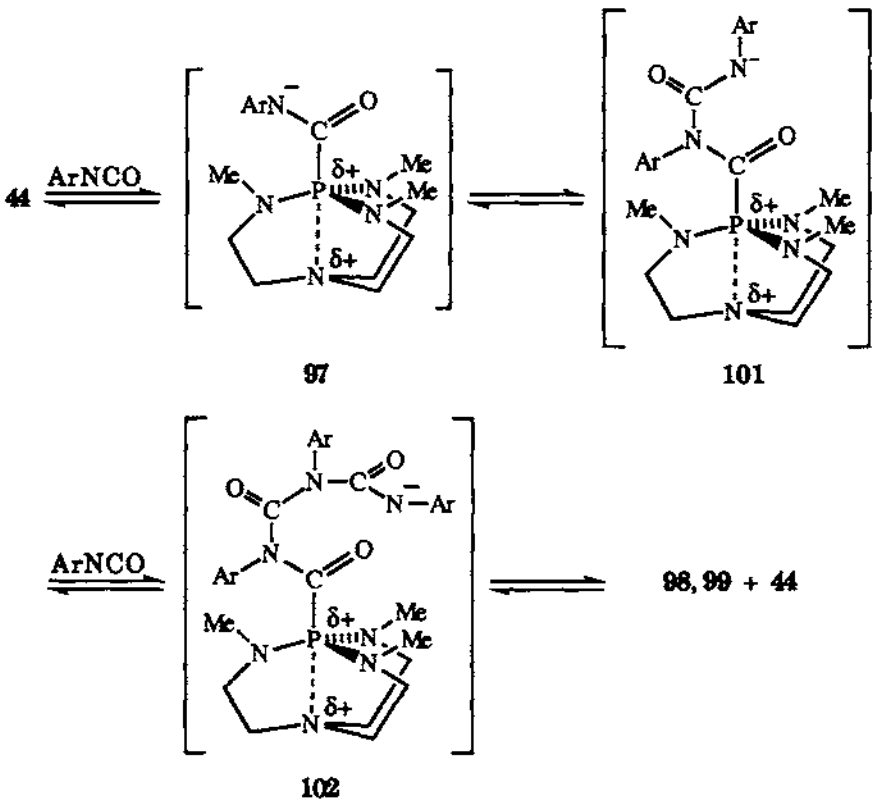
100

resonance at 29.5 ppm and a fast atom bombardment mass spectrometry (FAB-MS) peak for M + H in a mixture, this species disappears as another reaction progresses. Finally, only **44** and the trimer of PhNCO, namely **98**, remain. This exothermic catalytic reaction can be run very efficiently without solvent with as little as 0.33 mol% of **44** in about 3 min at room temperature. The corresponding isocyanurate **98** is formed in 97% yield in high purity as judged by a single TLC spot [28,50]. Similarly the *p*-methoxyphenyl isocyanurate **99** is formed in 8 min in 99% yield [28,51].

Triarylisocyanurates are commercially valuable as activators for the continuous anionic polymerization and post-polymerization of ε-caprolactam to nylon-6 possessing a highly stable melt viscosity and a low unreacted monomer content [52]. The excellent thermal properties and hydrolytic stability of isocyanurate-based foams

and plastics have generated considerable interest in the development of efficient isocyanurate trimerization catalysts [53]. Catalyst **44** is superior to other catalysts described previously in terms of the mild reaction conditions that can be employed with **44** and the yield and purity of the trimer formed [50]. In view of the difficulty encountered with previous catalysts in trimerizing electron-rich aryl isocyanates such as *p*-MeC_6H_4NCO [54], it is astonishing that **44** so easily catalyzes the trimerization of the even more electron-rich *p*-$MeOC_6H_4NCO$ to **99** [28] and also of alkyl isocyanates [55]. It should be mentioned that $P(NMe_2)_3$, an acyclic analogue of **44**, produces only a small amount of cyclic dimer **100**, even over an extended time period.

Scheme 2



A pathway for the trimerizations with **44** is shown in Scheme 2. The contrasting stability of adduct **96** to further reaction with PhNCS can be attributed to the reduced nucleophilicity of the PhN nitrogen and the diminished electrophilicity of the PhNC carbon induced by the less electronegative sulfur atom. The much stronger catalytic activity of **44** compared with $P(NMe_2)_3$ may have its origin in a substantial stabilizing influence of transannulation (i.e. electron delocalization) on adducts **101** and **102** (and particularly on **102**) which facilitates its nucleophilic attack on a third ArNCO molecule. It is reasonable to suggest that when intermediate **102** undergoes

ring closure to form the trimer, the resulting augmentation in electron density on the PC carbon weakens the transannular interaction. This facilitates departure of the trimer molecule and regeneration of catalyst **44** in which transannulation is presumably the weakest (Section 2.3.2.). This advantageous flexibility of the transannular interaction in Scheme 2 is strongly supported by the data in Table 1 and Fig. 1.

Although not as catalytically active as **44**, its phenyl imide derivative **71** is quite a strong catalyst for the trimerization of isocyanates, giving a 100% yield of **98** in 25 min at room temperature in the presence of 0.33 mol% of the catalyst [55].

In contrast with **71**, the sulfide and oxide of **44**, namely **63** and **64** respectively, are catalysts for the conversion of isocyanates to carbodiimides rather than isocyanurates. Thus **64** is substantially more effective in converting alkyl and aryl isocyanates to the corresponding carbodiimides than its acyclic analogue $OP(NMe_2)_3$. Perhaps not surprisingly, **63** is nearly as catalytically active as **64**, since both are quasi-azaphosphatranes (Table 1 and Fig. 1) and hence enjoy flexible transannulation possibilities. It is also possible that they share a common reaction pathway in the catalysis cycle as shown in Scheme 3. Unlike the pathway suggested for other catalysts containing an O=P bond [56], the phosphorimide **104** is not expected as an intermediate in our reactions because its presence would catalyze the reaction of isocyanates to isocyanate trimers (isocyanurates) as discussed previously. It seems reasonable to suggest then that transition state **105** is operative rather than **103**, since **105** precludes formation of **104**. Transition state **105** is also favored sterically and by the presence of a six- instead of a four-membered ring. That **63** and **64** share the same reaction pathway was shown by the exclusive presence of **64** at the end of the reaction in both cases [55].

2.4. *Stibatrane*

Stibatrane, **106** was reported as a sublimable product from reaction (9), although no evidence for a transannular bond was put forth [57a].

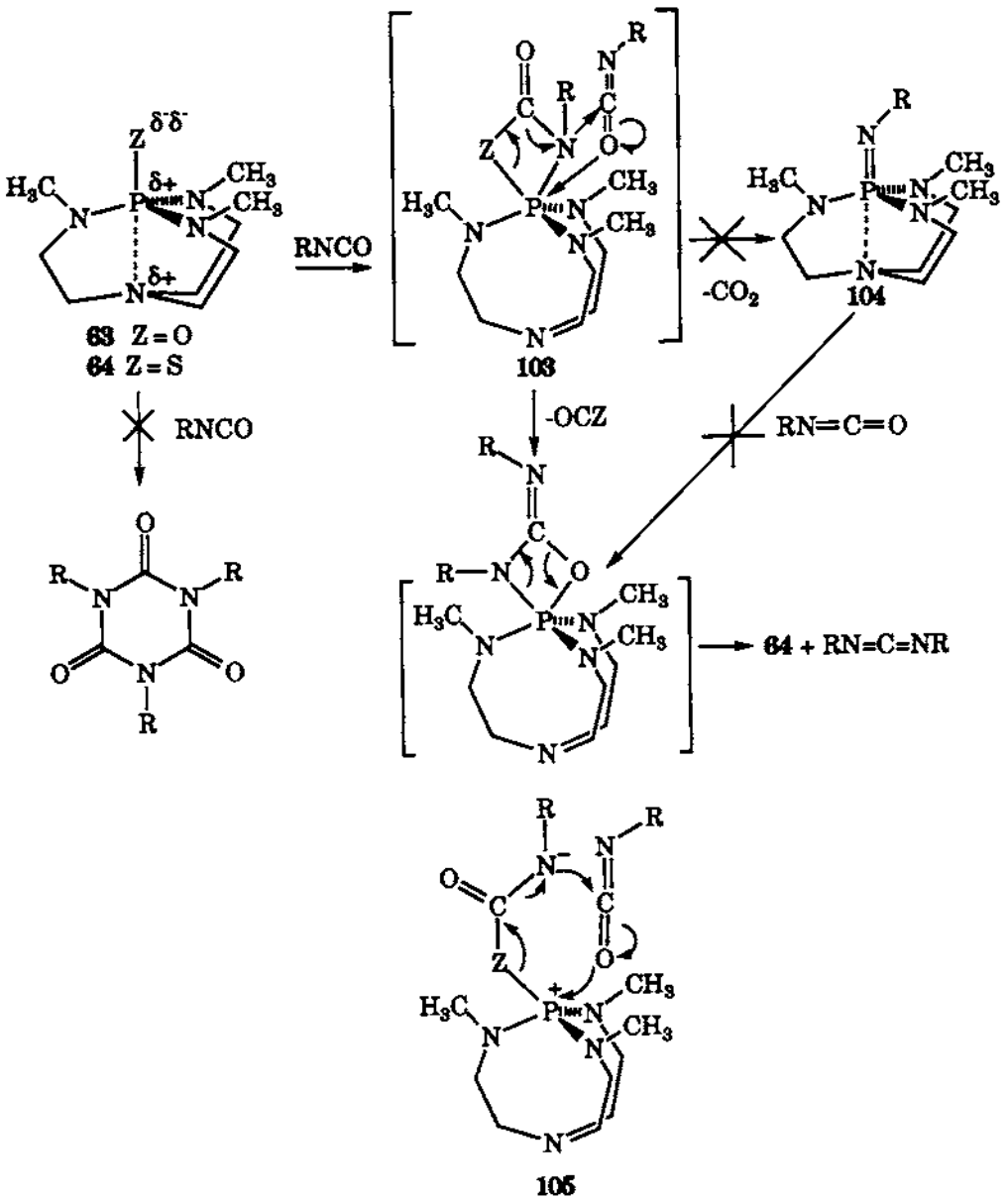
2.5. *Pro-bismatrane and a bismatrane complex*

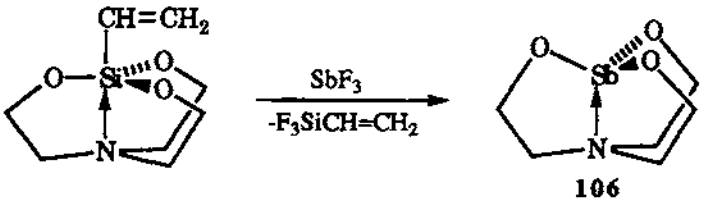
A compound formulated as **107** was reported to form in reaction (10) [57b]. The only evidence given for its formulation was a favorable elemental analysis. Preliminary evidence for a complex of the type $Bi[(HOCH_2CH_2)_3N]_2Cl_3$ has been observed [58]. It is, however, quite insoluble in most solvents and recrystallization has not as yet been successful.

3. GROUP 14 ATRANE SYSTEMS

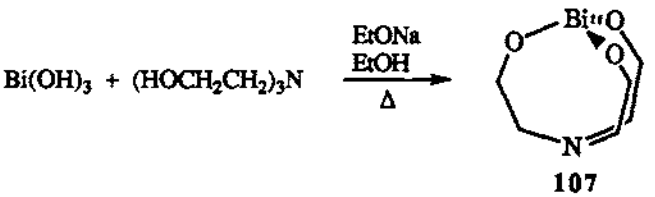
The first four elements of this group display atrane structures, and as we shall see, lead(II) forms a coordination complex with $(HOCH_2CH_2)_3N$.

Scheme 3





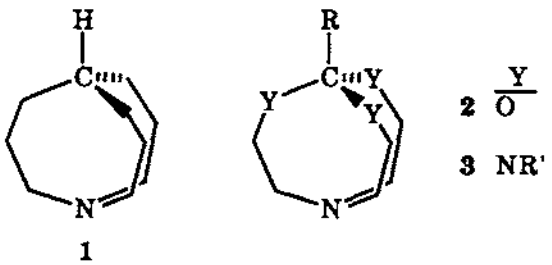
106 (9)



107 (10)

3.1. A pro-carbacarbatrane

The parent amine of 17(Cl) in section 2.1, namely 1, is a pro-carbacarbatrane better known as manxine [35]. Efforts in our laboratories to synthesize the analogues



1

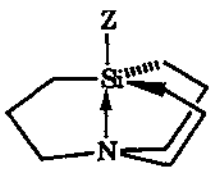
2 Y = O

3 NR'

of types 2 and 3 have thus far not been successful. Apparently previous efforts to synthesize 2 have also failed [59].

3.2. Carbasilatranes

Compounds of types 4, 5 [60,61], 6 [62] and 7 [62] are known and the structures of 6 [60] and 7 [61], determined by X-ray crystallography, confirm the

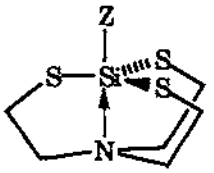


	Z
4	Me
5	Cl
6	1/2 O
7	*p*-MeC_6H_4

presence of a transannular interaction. In the presence of Me_2SnCl_2, 4 is transformed to 5 [61b].

3.3. Thiasilatranes

A report of an example, **8**, of the title compound from the reaction of $PhSi(NMe_2)_3$ with $(HSCH_2CH_2)_3N$ appeared in the patent literature [63]. We were



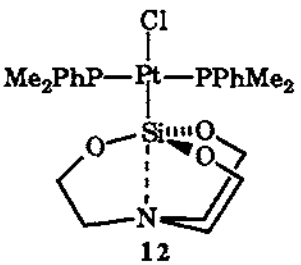
	Z
8	Ph
9	H
10	Me
11	OEt

able to synthesize **9** and **10** as well as **8** by this route, although these compounds are difficult to purify owing to their poor solubility in organic solvents [64]. An attempt to synthesize the ethoxy derivative **11** led to decomposition [64]. The upfield ^{29}Si NMR chemical shifts of **9** and **10** (−68.5 and −41.7 ppm respectively) are consistent with a five-coordinate structure, although these resonances are at somewhat lower field than for their silatrane analogues (−83.0 and −65.1 ppm respectively) [64]. This result is not unexpected, however, since the shifts of the acyclic analogues $MeSi(SMe)_3$ (−41.4 ppm) are similarly related [65a]. A series of compounds formulated as $RNHCH_2CH_2SSi(CHR_2CH_2)_3N \cdot HCl$ were reported and their toxicities and radioprotective properties determined [65b].

3.4. Quasi-silatranes and silatranes

Silatranes were the first examples of atrane structures to be reported and are the compounds on which the trivial but useful "atrane" nomenclature is based [66].

Transannular distances in $Z–Si(OCH_2CH_2)_3N$ compounds (where Z can also be a very electronegative substituent such as fluorine or chlorine) could presumably range between 1.87 Å (the sum of the covalent radii of silicon and nitrogen) and 3.65 Å (the sum of the van der Waals radii of these atoms [36,67]). The longest



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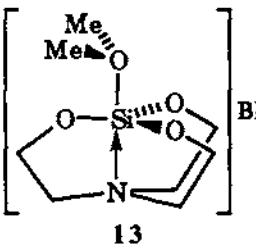

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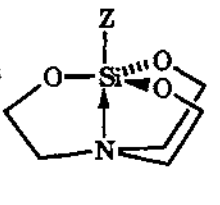
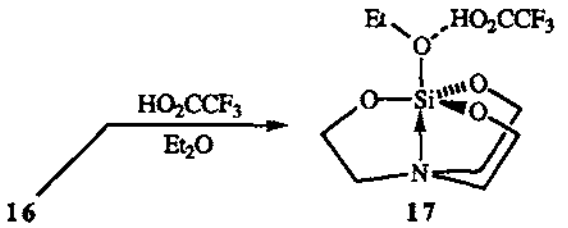
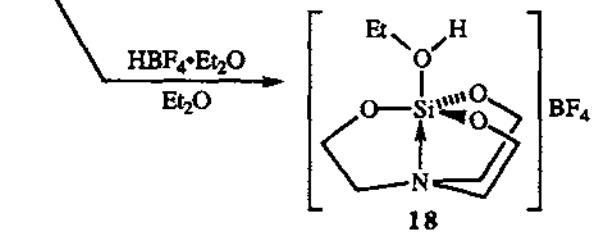


	Z
14	OMe
15	Cl
16	OEt

recorded transannular distance is in **12** (2.89(1) Å [68]), which represents a 21% shortening over the sum of the van der Waals radii. The shortest $Si–N_{ax}$ distance was recently measured in our laboratories for cation **13** (1.965(5) Å), which was synthesized by reacting **14** with Me_3OBF_4 [69]. The next shortest silatrane transan-



(11)



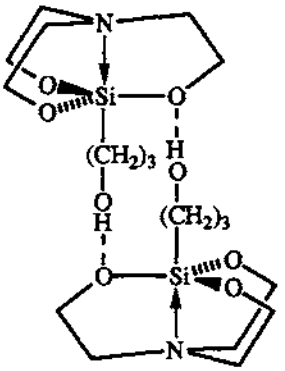
(12)

nular bond was recorded for **15** (2.02 Å) [59]. The shrinkage of the transannular bond in **13** over that in **15** and **16** (2.152(13) Å [69]) attests to the high effective electronegativity of the Me_2O^+ group which is created by the coordination of the axial ether oxygen of **14** to a carbocation.

Reactions aimed at coordinating the axial ether oxygen of **16** to a proton provided two interesting isolable compounds as shown in reactions (11) and (12). Of the two compounds, only **17** grew crystals suitable for X-ray studies, which revealed a transannular bond of 2.050(3) Å and an unusually short distance (2.489 Å) between the oxygen atoms containing the hydrogen which is engaged in hydrogen bonding [69]. The latter distance is comparable with those in hydrogen-bonded acid salts of carboxylic acids [70], in tetramesityl-1,3-difluorohydrogen bisulfonate (2.43 Å [71]) and in 1,2,3-benzotriazolium dihydrogen phosphate (2.48 Å [72]). Whereas these examples are known to be symmetrically bonded around the hydrogen, **17** is unsymmetrically hydrogen bonded. As a representative of the latter type of hydrogen bonding, **17** contains the shortest O(H)O distance reported so far. Not surprisingly, the dimeric structure **19** contains a considerably longer O(H)O distance (2.81 Å [73]) and the analogous thiol compound exhibits no hydrogen bonding [74].

Evidence for full protonation in the case of cation **18** consisted of greater downfield ^1H NMR chemical shifts compared with **16**, these shifts being similar to those observed in the isolated alkylated salts **13**(BF_4) and **20**(BF_4) [69].

From a linear plot of the Si–N_{ax} distance vs. the distance from the silicon to the plane of the equatorial oxygen atoms in a series of silatranes, it was concluded from the value of the intercept that the Si–N_{ax} distance would be 1.83 Å if the silicon were coplanar with the equatorial oxygen atoms [59]. The virtually ideal trigonal bipyramidal geometry of cation **13**, which features an Si–N_{ax} bond distance that is



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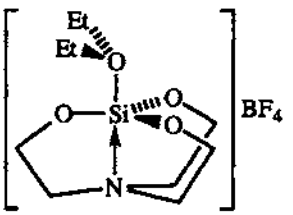

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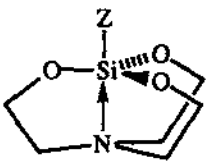


	Z
21	Me
22	H
23	*p*-F-C_6H_4
24	*p*-F-$C_6H_4CH_2$

at least 0.1 Å longer than 1.83 Å, suggests that the aforementioned linear plot is not reliable at short $Si-N_{ax}$ distances.

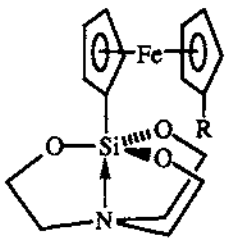
A measure of the basicity of a series of similar bases can be determined from the OH stretching frequency shift of phenol [75]. Using this technique, the basicity order $(Me_3Si)_2O < (RO)_3SiOR < \mathbf{14} < \mathbf{16} \approx Me_3SiOMe < Et_2O$ was obtained [69]. This order is consistent with the order $(H_3Si)_2O < H_3SiOCH_3 < H_3COCH_3$, with the additional feature that a silatranyl moiety bound to an OR group is more basic than an analogously bound $(RO)_3Si$ moiety (presumably owing to transannulation) whereas it is less basic than an Me_3Si or Et group linked to OR.

X-Ray studies of a wide variety of silatranes have been extensively reported (see e.g. ref. 76). It appears that the transannular distance is linearly related to the distance of the silicon above the plane formed by the three oxygen atoms [77] and also to the benzene-induced shift of the CH_2N protons [78].

Bond moment and complete neglect of differential overlap (CNDO/2) calculations have shown that the average value of the overall dipole moment in a series of silatranes is independent of the Si–N distance, with the nitrogen atom donating 10% of its electron density to the silicon 3d orbitals [79a]. The molecular dipole moments of a group of alkyl and alkoxy silatranes range from 5.7 to 7.1 D and calculated moments of the Si–N bond and the silatranyl group are 8.6 and 5.2 D respectively [79b]. In a series of alkyl silatranes the molecular dipole moment has been found to be quite constant and rather independent of the temperature [80].

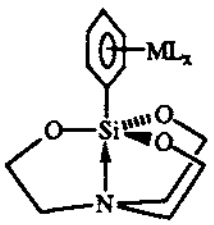
Benzene-induced NMR shifts of the CH_2N protons in a series of silatranes were linear with the dipole moments [78]. From ionization potential data the Si–N bond strength was determined to be 54.0, 73.3 and 92.7 kJ mol^{-1} in **21**, **22** and **16** respectively [81], reflecting a progression with increasing electron-withdrawing power of Z. Oxidation potentials for a series of silatranes including **21** and **22** ranged from 1.42 to 1.85 V [82]. Correlations with Taft σ^* constants, ^{15}N NMR chemical shifts and ^{15}N–^{29}Si couplings indicated that the reaction center in the formation of cation radicals is the nitrogen [82].

Electron induction effects on the Z group resulting from transannulation have been observed from the ^{19}F NMR chemical shifts of **23** and **24** [83] and the



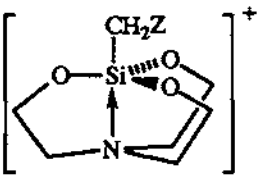
25

electrochemical redox potentials of **25** (R ≡ H) and **25** (R ≡ $Si(OCH_2CH_2)_3N$) [84]. A Taft σ^* constant of −3.49 has been obtained for the silatranyl moiety from an IR



26 $Cr(CO)_3$

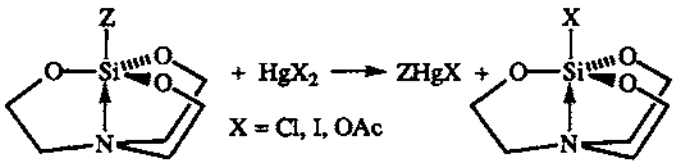
27 $Mn^+(CO)_2P(OMe)_3$



28

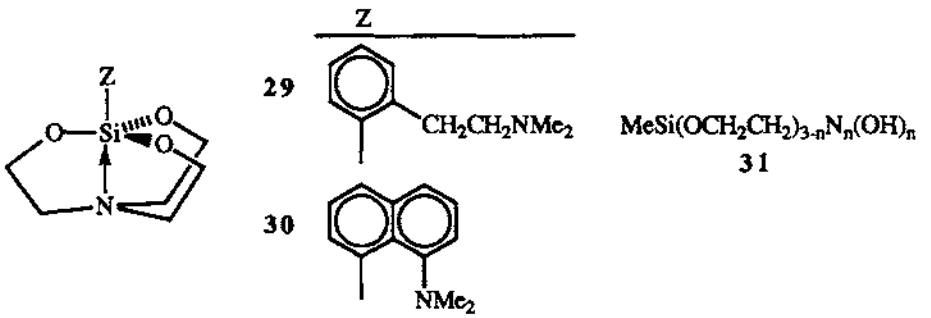
method [85]. Complexes **26** [86] and **27** [87] have recently been reported. In **26** the transannular distance (2.105(5) Å) is slightly shorter than in the parent phenyl silatrane [86]. The parent $Mn(CO)_3^+$ derivative of **27** undergoes reactions with a variety of nucleophilic anions to give neutral compounds ortho and para substituted on the resultant η^5-C_6H_5 ligand [87b,c]. Electron induction effects in the alkyl silatrane cations of type **28** (Z ≡ PPh_3, Me_3N and Me_2S) are expected to be stronger than in **26**, and indeed the transannular distances are shorter (2.098 [88a], 2.08(1) [88b] and 2.046(2) Å [88b] respectively). These distances are close to that for the Si–N bond in diphenyl thiophosphinoxy silatrane (2.060(3) Å [88c]) and *m*-chlorophenoxy silatrane (2.079(2) Å [87b]), which for electron induction reasons is somewhat shorter than that in *tert*-butoxy silatrane (2.189(4) Å [87b]) and ethoxy silatrane (2.152(13) Å [69]).

Another consequence of electron induction via transannulation is the substantially increased electrophilic character of the apical carbon of silatranes in reaction

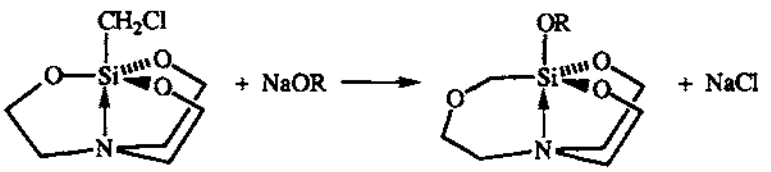


(13)

(13), wherein the reaction rate order for the Z groups is vinyl ≈ Ph ≈ *p*-ClC_6H_4 > Me > Et ≈ Pr > *c*-hexyl ≈ $ClCH_2$ ≈ OEt [89]. Under the same conditions $ZSi(OR)_3$ compounds are inert. Nucleophilic attack at silicon is still possible in these electron-rich compounds, however, as was shown in hydrolytic rate studies of 26 aryloxy silatranes which revealed an S_N2 mechanism to be operating [90]. Although the structure of **29** determined by X-ray means exhibited no chelation of the NMe_2

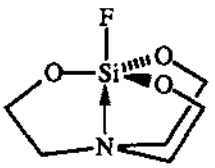


group, that of **30** indicated a weak interaction between the silicon and its NMe_2 function, further demonstrating the acidic character of the silicon despite coordination of the bridgehead nitrogen [91]. Nucleophilic attack of silicon by OR^- may also be implicated in the novel ring expansion in reaction (14) [92].



(14)

Theorists, intrigued by the nature of the transannular bond in silatranes, have drawn some interesting conclusions. In ab initio calculations the Si–N bond length in the model system **31** *increases* by about 0.1 Å after each replacement of an OH group with a bridging OCH_2CH_2 moiety [93], suggesting that strain energy is present in the rings. Gas phase structures for silatranes typically feature longer Si–N bond distances than are found in the solid phase. For example, this decrease from the gas to the solid phase in **32** is 0.28 Å [94]. This has been confirmed theoretically in two calculational studies [93,95]. Ab initio calculations show that despite this significant change



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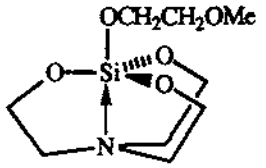


33

in length, there is very little change in the Mulliken charges [96]. However, there is a bond critical point found between the two atoms, suggesting the existence of an Si–N bond [93]. Crystal forces may be responsible for the diminished distances of this bond in the solid state, since the energy required for the additional constraint is calculated to be less than 6 kcal mol^{-1} [93]. It is interesting in this regard that the solid state Si–N distance in **32** (2.042(1) Å) is longer than in the corresponding chloro derivative **15** (2.02 Å) [59], contrary to predictions based on the inductive Taft σ^* constant and Sanderson electronegativity considerations [88b]. CNDO/2, incomplete neglect of differential overlap (INDO) and MNDO calculations on the silatrane fragments $RSi(OR)_3$, NR_3 and $Me_2NSi(OR)_3$ show that transannular three-center C–Si–N bond formation is weaker than the conventional Si–N bond in $Me_2NSi(OMe)_3$ [97]. MNDO calculations on $XSiF_3 \cdot NH_3$ as models for **15** and **32** indicate that the Si–N bond strengths depend upon the structure chosen for the model [14].

A variety of mass spectral techniques have recently been applied to the study of the transannular bond [98,99]. Apparently, weakening of the Si–N bond due to π donor effects of the Z group has a significant influence on the fragmentation pattern of silatranes [98].

NMR investigations reveal that transannulation in silatranes produces an approximately 20 ppm upfield shift in the ^{29}Si resonance compared with acyclic $ZSi(OR)_3$ compounds [100]. These high field shifts in silatranes relative to their acyclic counterparts are of diamagnetic origin, arising predominantly from the transannular bond [101]. As increasingly electronegative Z substituents are introduced, the transannular bond strengthens and the absolute value of the difference in the paramagnetic terms in silatranes and their acyclic analogues increases more strongly than that in the diamagnetic terms. The result is that the difference in the ^{29}Si chemical shifts of the corresponding four- and five-coordinate silicon systems is reduced as the electronegativity of Z increases [101]. In a solid state NMR study of **32** the principal axis of the δ_{33} element is collinear with the F–Si–N nuclei [102].

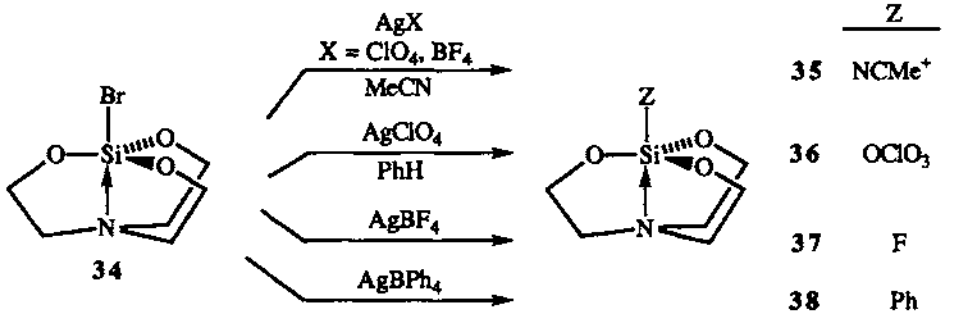
^{29}Si–^{15}N coupling constants obtained from a study involving 50 silatranes ranged from 6 to 47.6 Hz. These constants, whose values are interpreted in terms of the Fermi contact interaction, have been quantitatively correlated with nitrogen hybridization [103] and also with the Si–N bond order and length [104,105]. Based on ^{15}N and ^{29}Si NMR data, it was concluded that the Si–N interaction is weaker in solution than in the solid state and that solvents of low polarity and weak proton donor ability exert a greater weakening effect [105b]. ^{15}N NMR data have also been correlated with the Taft polar substituent constant σ^* in a series of silatranes

[106]. Compared with tetracoordinated silicon analogues, $^3J_{SiOCH}$ couplings involving the cage methylene protons are larger while those involving the axial Z groups are smaller [107]. From an examination of the ^{1}H NMR behavior of **33** in various solvents it was concluded that there was enhanced electrostatic repulsion between the vicinal oxygen atoms (producing a trans conformation around the C–C bond) stemming from electron induction from the transannular bond [108]. This effect was apparently smaller than in phosphatranes.

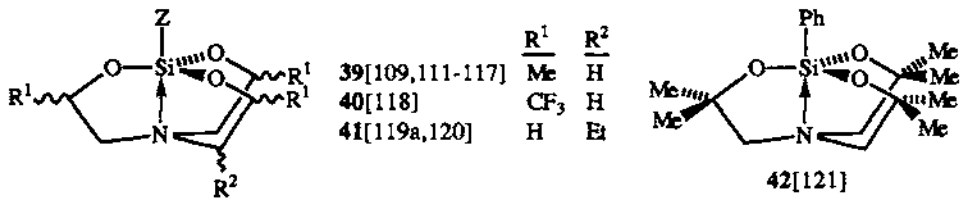
Silatranes are, in contrast with four-coordinate analogues, remarkably stable to hydrolysis and alcoholysis, presumably owing to the negative charge on the silicon from the nitrogen lone pair and also because of some degree of steric protection by the five-coordinate structure [109]. Even in the presence of 0.1 N $HClO_4$ in glacial acetic acid, elevated temperatures and prolonged time periods are required to hydrolyze some of these derivatives. Selective displacement of the EtO substituent in **16** can be effected by phenols, carboxylic acids and HF for example. These reactions seem to be aided by increased acidity of the hydroxylic reagent [109], suggesting prior protonation of the EtO oxygen.

As with carbon substituents in the apical position of silatranes (reaction (13)) and the ethoxy substituent in **16** just discussed, the bromide in **34** is subject to electrophilic displacement, giving the novel cation **35** and the covalent compounds **36–38** in Scheme 4 [110].

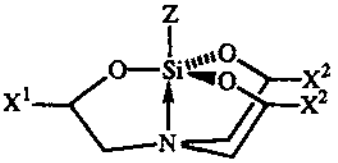
Scheme 4



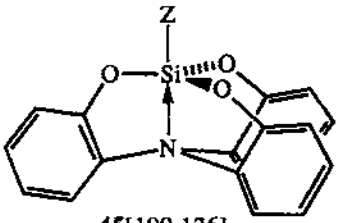
Silatranes of the type **39–45** that are substituted on the cage carbon atoms



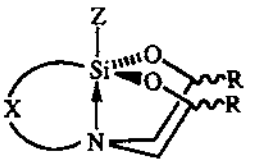
have been described. Also reported are the related unsymmetrical compounds **46–51**. X-Ray diffraction studies of **7**, **39** ($Z \equiv p$-MeC_6H_4) and **52** show a decrease in the



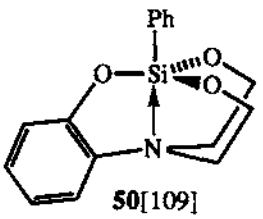
	X^1	X^2
43[122]	H_2	=O
44[123-125]	=O	=O



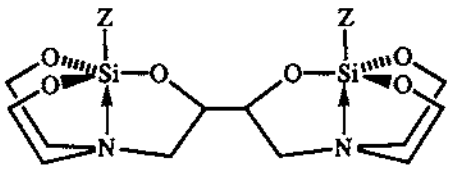
45[109,126]



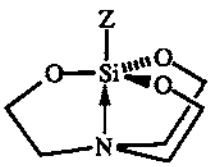
	R	X
46[127]	H	$OC(O)CH_2$
47[109,127]	H	$(CH_2)_3$
48[127]	H	$O(CH_2)_3$
49[128]	Me	$O(CH_2)_3$



50[109]



51[109]



	Z
52	*p*-MeC_6H_4
53	C_6H_5
54	*p*-ClC_6H_4

Si–N bond distance in the order **7** (2.290(2) Å), **39** (the unsymmetrical isomer, 2.236(3) Å), **52** (2.169(2) Å) [88b,112,113], as expected on the basis of steric grounds, the greater hybridizational flexibility of oxygen vs. methylene and the more electronegative silicon in **39** and **52** than in carbasilatrane **7**. Whereas this distance in **7** is the same as in its phenyl derivative [112], it is larger in **39** (Z ≡ *p*-MeC_6H_4, 2.236(3) Å [113]) than in the latter's phenyl derivative (2.175(6) Å [112]), presumably owing to the greater inductive effect of the para-methyl group. Similar comparisons can be made between the phenyl derivative of **39** and **53** and between **52** and **54**. The transannular bond in **47** (Z ≡ Ph, 2.291(1) Å) is about 0.1 Å longer than that found in **53** (2.193(5) Å [127b]) and a weakened transannular bond is also found in **47** (Z ≡ Me, 2.336(4) Å [129]). The weakening of the transannular bond by cage substitution of the type shown in **39** and **45** (Z ≡ Ph) is corroborated by mass spectral studies [115] and X-ray studies (**45** Z ≡ Ph, 2.344(4) Å [126a]).

Several hydrolysis studies of variously substituted silatranes have turned up interesting trends as well as some contrasting results [119,130–132]. Whereas alkyl and aryl tribenzosilatranes of type **45** were concluded to undergo acid hydrolysis via cleavage of an Si–OH^+ bond involving an equatorial oxygen [130a], cage-unsubstituted silatranes were believed to hydrolyze after concerted protonation of the nitrogen and breakage of a transannular bond [131]. In one study [131], substitution of the cage with methyl groups on the three OC carbon atoms was found to enhance the rate of hydrolysis, whereas in more recent experiments, increasing methyl substitution was observed to significantly retard the rate, with that for **42** being by far the slowest [132]. These attenuations were attributed not only to steric effects, but in dominating measure to rigidity of the cage rings (and hence the stereochemistry around silicon) imposed by the methyl substituents [132]. The substantial difference in hydrolysis rates of the symmetrical and unsymmetrical diastereomers of **39** (Z ≡ Ph) allowed the purification of the symmetrical diastereomers by partial hydrolysis [132]. It may be noted here that the diastereomers of **40** (Z ≡ Me) have been separated by chromatography [118]. In yet another recent study [119], cage-unsubstituted and cage-substituted silatranes of type **39** were suggested to undergo acid hydrolysis by means of a four-center intermediate involving an $SiOH^+$ moiety and a water molecule. Evidence that the chloro derivative of **45** hydrolyzes via a silatranium–chloride ion pair has been put forth [130]. It is speculated that since the analogous germatrane does not hydrolyze by such a pathway, (p→d)π O→Si stabilization of the silatranium cation is responsible for its stability. An Si–N distance of 1.885 Å has been calculated by MNDO/PM3 for the analogous cation derived from **15** [88c].

The Si–N distance in **41** (Z ≡ *S*–(+)–1-*p*-ClC_6H_4) was measured by X-ray means (2.146(5) Å) and its absolute configuration was determined by the anomalous scattering of the Si and Cl atoms [122]. From NMR studies it was concluded that there is little conformational mobility in the silatrane skeleton of molecules of this type [119].

Introduction of carbonyl groups into the silatrane framework (**43**, **44**) has been shown by X-ray studies and CNDO/2 calculations to shorten the Si–N distance compared with parent silatrane analogues [123–125]. It seems that despite the wider angle at the carbonyl carbon than at a methylene carbon, electronegativity effects dominate. X-Ray diffraction studies of benzosilatranes of type **45** [126] have shown that although the Z ≡ Ph derivative possesses a longer Si–N bond distance (2.344(5) Å [126a]) than is present in phenyl silatrane (2.193(5) Å [133]), the electronegative Z substituent *m*-O_2NPh on **45** shortens this distance to 2.116(8) Å [126b].

In contrast with the reaction of ethoxy silatrane **16** with CF_3CO_2H, which gives the isolable hydrogen-bonded adduct **17** (reaction (11)), **45** (Z ≡ OEt) under the same conditions intermolecularly eliminates a water molecule and CF_3CO_2Et to give the disiloxane **45** (Z ≡ ½O) [64]. The longer and weaker transannular bond expected for **45** (Z ≡ OEt) compared with **16** increases the susceptibility of the CH_2

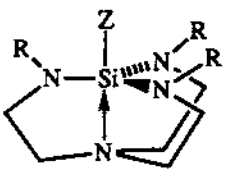
carbon of the ethyl group to nucleophilic attack by $CF_3CO_2^-$, favoring condensation of **45** (Z≡OEt) rather than formation of a hydrogen-bonded adduct. A strong indication of reduced transannular bonding in **45** (Z≡OEt) is the shift (241 cm^{-1}) in the phenol stretching frequency (3371 cm^{-1}) in CCl_4 which suggests that the hydrogen bonding interaction with the axial oxygen is measurably weaker than for **16** (273 cm^{-1}, 3339 cm^{-1}) [64]. Both **45** (Z≡OEt) and **45** (Z≡½O) display ^{29}Si NMR chemical shifts in the five-coordinate region in solution (−91.3 and −96.1 ppm respectively) [64].

Analysis of spin–spin coupling constant and nuclear Overhauser spectroscopy (NOESY) data of **46–48** permitted the suggestion that conformational interconversion of the five-membered rings in their cage frameworks takes place by a multistep rather than a concerted mechanism [128].

Silatranes have long been known to possess a wide range of biological activities [79b]. Although some of them are quite toxic (e.g. **54**) [79b], pilotropic and growth-regenerative [134], ulcerostatic [135,136], anticoagulant [137], hypercoagulant [138], anti-atherosclerotic [137], wound-healing [139], cholesterol-reducing [140,141], anticancer [142–144] and radioprotective [145] properties have been reported.

3.5. *Azasilatranes, quasi-azasilatranes and pro-azasilatranes*

Although the hydro and hydrocarbon azasilatranes **55–59** had been described [146,147] more than a decade before our excursion into the title area, we believed



	R	Z		R	Z		R	Z
55	H	H	**60**	H	H	**65**	H	Cl
56	H	Me	**61**	H	OPh	**66**	$SiMe_3$	H
57	H	$CH{=}CH_2$	**62**	Me	H	**67**	$SiMe_2H$	H
58	H	Ph	**63**	Me	OEt	**68**	$SiMe_2Ph$	H
59	H	Et	**64**	$SiMe_3$	H	**69**	$SiMe_2H$	OEt

that the possibility of functionalizing the equatorial nitrogen atoms with more bulky groups offered an interesting opportunity to sterically influence the strength and length of the transannular interaction. An improved route to azasilatranes **55–64** reported from our laboratories is summarized in reaction (15) [148]. The catalyst

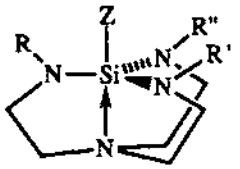
$$ZSi(NMe_2)_3 + (RHNCH_2CH_2)_3N \xrightarrow{\text{catalyst}} \textbf{55-64} \qquad (15)$$

for the preparation of **55–60** is Me_3SiCl, whereas for **61–64** $(NH_4)_2SO_4$ proved to be more efficacious, probably owing to its lesser volatility at the higher temperature required [148]. Compound **65** was made via the catalyzed substitution reaction (16) [148].

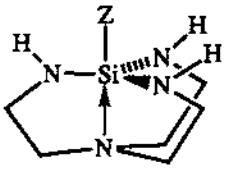
Substitution of the equatorial NH hydrogen atoms in preformed azasilatranes

$$\mathbf{55} + CCl_4 \xrightarrow{cis\text{-}(Me_2PhP)_2PtCl_2} \mathbf{65} + CHCl_3 \qquad (16)$$

to give **66–72** [148], **73**, **74** [149] and **75** [150] is also possible, as summarized in

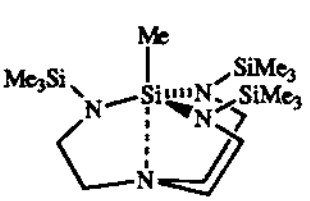


	R	R'	R''	Z
70	H	$SiMe_3$	$SiMe_3$	OEt
71	H	$SiMe_2Ph$	$SiMe_2Ph$	OEt
72	H	$SiMe_3$	$SiMe_3$	H
73	H	H	$SiMe_3$	Me
74	H	$SiMe_3$	$SiMe_3$	Me
75	H	PPh_2	PPh_2	OEt
76	Li	$SiMe_3$	$SiMe_3$	Me
77	Me	$SiMe_3$	$SiMe_3$	Me

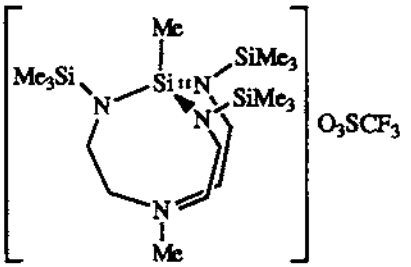


$$+ \quad \begin{matrix} ClSiR_3 \\ or \\ ClPPh_2 \end{matrix} \xrightarrow{NEt_3} \mathbf{66\text{-}75} \qquad (17)$$

reaction (17). The ^{29}Si NMR chemical shifts for compounds **66–75** are in the high field region (−60 to −90 ppm) which is typical of five-coordinate silicon, except for **74** (−36.2 ppm [149]) wherein there may be sterically induced weakening of the transannular bond. An X-ray crystallographic investigation of **63** showed a transannular bond distance (2.135(2) Å [148]) which is within experimental error of that for **58** (2.132(4) Å [151]). The coordination geometry around the equatorial nitrogen atoms of **63** is essentially planar (sum of bond angles equal to 356°), as found for azatranes in general. By forcing further substitution of **74**, it is possible to realize **76–78** [149]. Stretching of the transannular bond in structures **76–78** is suggested

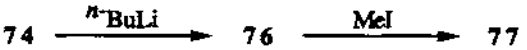


78



79(O_3SCF_3)

by their relatively downfield ^{29}Si NMR chemical shifts (−36, −26 and −26 ppm respectively [149]) and this phenomenon was confirmed by an X-ray study of **78**. The structure of **78** features a virtually planar axial nitrogen and a transannular



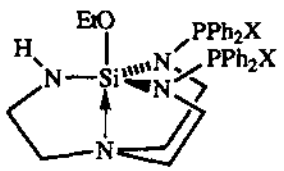
(18)

(19)

distance of 2.775(7) Å [149]. This distance is 24% shorter than the sum of the relevant atomic radii and is the longest ever recorded in an azasilatrane. Compounds **76–78** can therefore be considered quasi-azasilatranes.

By reacting **78** with $MeOSO_2CF_3$, the pro-azasilatrane cation **79** is formed [149]. The structure depicted for cation **79** is supported by a further downfield movement in ^{29}Si NMR shift to −10 ppm [149] and an X-ray crystallographic study [152].

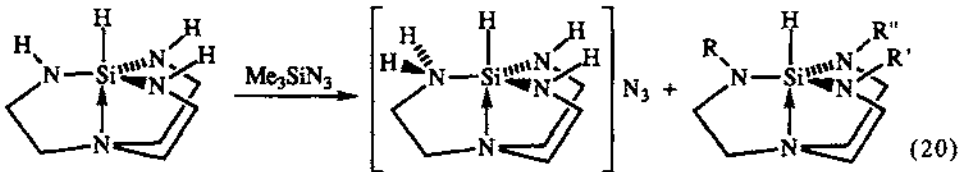
Compound **75** apparently possesses a transannular bond judging from its



	X
80	S
81	Me^+
82	$1/2PtCl_2$
83	$1/2Ni(CO)_2$
84	$1/2Mo(CO)_4$
85	$1/2W(CO)_4$

upfield ^{29}Si chemical shift (−89 ppm [150]). This is also true of its derivatives **80–85** for which this value ranges from −78 to −95 ppm [150]. This conclusion is confirmed by the structural metrics obtained for **80** derived by X-ray crystallography (2.214(3) Å [150]).

An attempt to remove the axial proton from **55** gave an unexpected set of

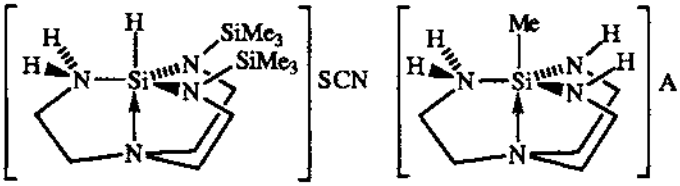


55 **86**(N_3) (20)

	R	R'	R"
87	Me_3Si	Me_3Si	Me_3Si
88	H	Me_3Si	Me_3Si
89	H	H	Me_3Si

products [153]: Single crystals isolated from the reaction mixture were shown by X-ray crystallography to contain **86** (N_3) and unreacted **55** in a 1:1 ratio with transannular bond lengths of 2.087(6) and 2.080(6) Å respectively and magic angle

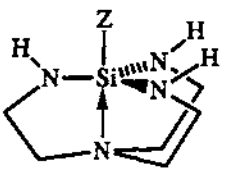
spinning (MAS) ^{29}Si NMR chemical shifts of −86 and −83 ppm respectively [153]. A transformation analogous to reaction (20) involving **88** and Me_3SiNCS gave cation



90(SCN)

A	
91	N_3
92	SCN

90 whose X-ray crystallographic data permitted the location of the hydrogen atoms as shown and revealed an elongated H_2N–Si bond and a transannular distance of 2.062(2) Å [154]. Its MAS ^{29}Si NMR chemical shift of −85 ppm is also indicative of five-coordinate silicon [154]. The reaction of **56** with Me_3SiN_3 and Me_3SiNCS gave **91** and **92** respectively, which unlike the product of reaction (20) is a cocrystallized mixture with **56** only in the case of the SCN^- salt **92** [155].

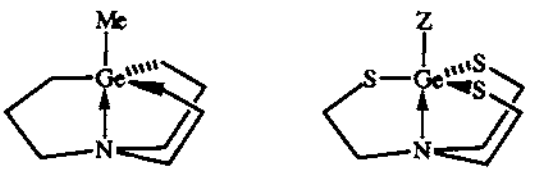


Z	
93	N_3
94a	-SCN
94b	-NCS

Thermolysis of crystals of **86**(N_3)/**55** and **90**(SCN) gives **93** and isomeric **94a** and **94b** respectively [155], with the elimination of hydrogen gas. Presumably **90**(SCN) also disproportionates to replace its Me_3Si substituents with hydrogen atoms.

3.6. *Carbagermatrane and thiagermatranes*

In the structure of **95** the exceptionally long Ge–N distance of 2.436(4) Å was attributed to the relative inflexibility of the CH_2 group compared with the oxygen

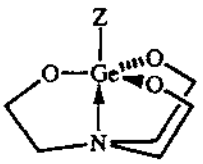


95 **96**

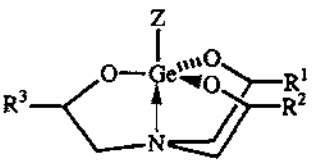
atoms [156]. A general route to compounds of the type **96** has been reported [157,158]. Thiagermatranes have been found to relieve pain [158], to inhibit neoplasms [159] and to exert a radioprotective effect [65b].

3.7. Germatranes and azagermatranes

Germatranes of the type **97–101** (X≡F, Cl, Br, I in **101**) have been synthesized [160–173], as have cage-substituted systems such as **102–106** (X≡F, Cl, Br, I in

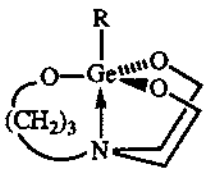


	Z
97	R
98	OR
99	OH
100	H
101	X

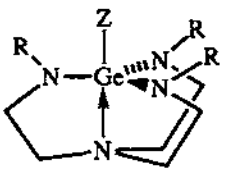


	Z	R^1	R^2	R^3
102	H	Me	H	H
103	H	Me	Me	H
104	H	Me	Me	Me
105	OH	Me	Me	Me
106	X	Me	Me	Me
107	R	=O	=O	=O
108	Cl	=O	=O	=O
109	Ph	=O	H	H

106) [169–172,174] and **107–109** [175,176]. The expanded germatrane **110** has also been reported [173].



110



	Z	R
111	R'	H
112	R'	Me
113	NMe_2	Me

X-Ray diffraction experiments on **97** revealed Ge–N distances of 2.238(6) Å for Z≡^{t}Bu [177], 2.24 [176] and 2.25 Å [178] for Z≡Et, 2.20 Å for **109** [176] and 2.44 Å for **110** [176]. When Z≡CH_2I, Br and (−)-1-menthoxy in **97**, the transannular distances appeared to decrease (2.19 [176], 2.09 [176] and 2.150(7) Å respectively [179]).

Calculated energies for the transannular bond in several germatranes exceed those in corresponding silatranes [165]. ^{15}N chemical shifts in these compounds correlated linearly with the Taft σ^* constant and from the data the conclusion is again made that the Ge–N bond strength exceeds that in silatranes [180]. Moreover, the Ge–N bond strength also increases with increasing electronegativity of the Z substituent [180]. Also correlated with increasing Ge–N bond strength are ^1H–^{15}N and ^1H–^{13}C NMR coupling constants in ^{15}N-enriched germatranes, which paralleled increasing N pyramidality [104]. Interestingly, it was concluded on the basis of ^{13}C, ^{15}N and ^{73}Ge NMR data collected on germatranes and homogermatranes of type **110** that the transannular interaction in **110** exceeded that in germatranes [173]. A variety of other techniques, including electron impact and FAB-MS [98,99,181a], one-bond ^{13}C–^{15}N NMR coupling constant measurements [104] and chromatographic retention time studies [181b], have been employed to elucidate the transannular bonding in germatranes. Benzene-induced ^1H NMR shifts have been observed to be linearly correlated with the dipole moments of these compounds [78].

Hydroxy-germatranes **99** and **105** were found to react with NH_4F to give the corresponding fluorogermatranes and with NH_4Cl to give the analogous chloro derivatives [174]. Hydroxy-germatranes **99** and **105** also react with alcohols to give the corresponding alkoxy-germatranes [172], while ethoxy-germatrane transesterifies with benzyl alcohol to give benzyloxy-germatranes [182]. It may be that these reactions are facilitated by prior protonation of the electron-rich axial oxygen.

Germatranes have been examined for their neurotropic [163,183] and antitumor activities [183]. They also possess radioprotective properties [146]. Phenyl germatrane is about two orders of magnitude less toxic than its silicon analogue [79b].

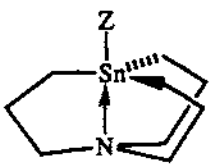
The first examples of azagermatranes (**111–113**) were recently reported from our laboratories [184], but the nature of the transannular interaction awaits the results of crystal structure studies presently under way. Azagermatranes undergo reversible exchange with smaller ligands, presumably owing to a decrease in steric hindrance (reaction (21)) or the formation of stronger Ge–O bonds (reaction (22)) [184].

112 (R' = Me, ^{t}Bu) + $(H_2NCH_2CH_2)_3N$ → **111** (R' = Me, ^{t}Bu) + $(MeHNCH_2CH_2)_3N$ (21)

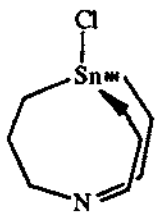
111, 112 (R' = Me, ^{t}Bu) + $(HOCH_2CH_2)_3N$ → **97** (R = Me, ^{t}Bu) + $(RHNCH_2CH_2)_3N$ (22)
R = H, Me

3.8. Carbastannatranes, pro-carbastannatranes and thiastannatranes

Syntheses of the carbastannatranes **114** and **115** have been reported [61b,185,186] and their solid state structures reveal transannular distances of

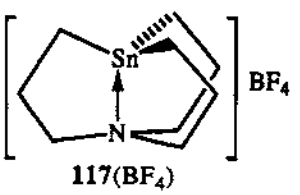


	Z
114	Cl
115	Me

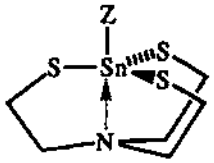


116

2.372(29) [186] and 2.624(8) Å respectively [187]. Variable-temperature ^1H NMR studies suggested that **114** is in equilibrium with its conformationally extended pro-carbastannatrane form **116** ($\Delta H^{\ddagger} = 70$ kJ mol^{-1}) [61b]. Furthermore, a $\Delta G^{\ddagger}$ for racemization of the rings in **114** and **115** has been calculated to be about 37 kJ mol^{-1} [61c]. Although no X-ray studies have been carried out on carbastannatranes, IR and Raman studies in conjunction with group theoretical calculations suggest the presence of a transannular bond [188]. By reacting **114** with $AgBF_4$, **117**(BF_4) is



117(BF_4)



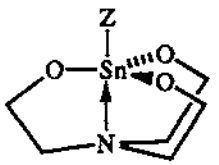
	Z
118	Me
119	^{t}Bu

formed which exhibits a ^{119}Sn NMR chemical shift in the tetracoordinate tin region (103 ppm) [61b].

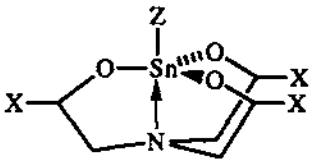
Thiastannatranes **118** and **119** have been synthesized and unlike stannatranes (see below) they are monomeric in solution [189–191].

3.9. Stannatranes

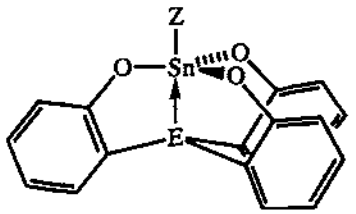
Examples of the title class of compounds that have been reported include those of the types **120–122a** [188–200], **124**, **125** [190,201,202], **126–128** [190,191,203], and **129** and **130** [191]. A $^1J_{PSn}$ coupling of 874 Hz was reported for **129** [191].



	Z
120	R
121	Ar
122	OR
122a	X

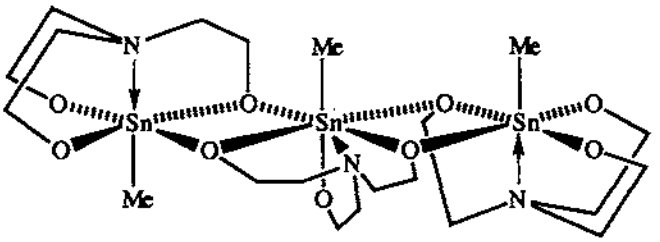


	Z	X
123	Ar	Me
124	Me	=O
125	^{t}Bu	=O



	Z	E
126	^{n}Bu	N
127	^{t}Bu	N
128	Ph	N
129	^{n}Bu	P
130	^{t}Bu	P

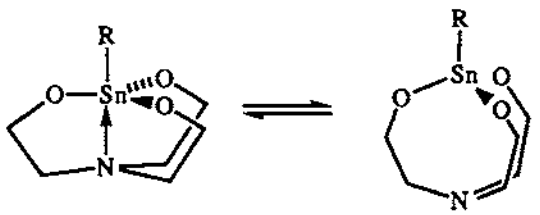
Although **120** (R ≡ ^{t}-Bu) and **121** (Ar ≡ *o*-tolyl) are monomeric at room temperature in non-polar solvents [189], **120** for less bulky R groups (Me, Et, ^{n}Bu) and **121** for R ≡ Ph are trimeric under such conditions. The latter result is contrasted by the earlier finding that such compounds are monomeric [193]. In this regard it should be noted that NMR measurements indicate dissociation of **120** (R ≡ Me) at higher temperatures to give a single methyl signal [190] and ebullioscopic molecular weight measurements are consistent with monomers for **120** (R ≡ Me, Et, ^{n}Bu) and **121** (R ≡ Ph) [194,204]. In the case of **120** (R ≡ ^{t}Bu) a monomeric structure was confirmed (Sn–N distance 2.32 Å [191]) and a trimeric structure was determined for **120** (R ≡ Me [205]) by X-ray crystallography. Here the central tin stereochemistry is roughly pentagonal bipyramidal (Sn–N distance 2.33(2) Å) and the terminal tin atoms are approximately octahedral (Sn–N distance 2.28(1) Å), with a strong associ-



120 (R = Me)

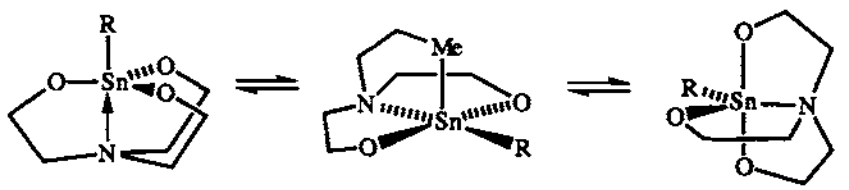
ation of the three units as indicated by relatively short bridging Sn–O bonds [205]. The presence of three chemically inequivalent tin atoms in this structure as well as in **120** (R ≡ Et, ^{n}Bu) and **121** (R ≡ Ph) is consistent with the observation of three ^{119}Sn NMR resonances at −50°C (−532.9 ppm for the central tin and −356.4 and −352.3 ppm for the terminal tin atoms) [206]. Consistent with the usual downfield shift of an atom with increasing coordination number is the observation that five-coordinate **120** (R ≡ ^{t}Bu) displays a ^{119}Sn chemical shift at −245.5 ppm [206]. Mössbauer data also support five-coordinate tin in stannatranes [207].

The nature of the fluxionality of trimeric **120** (R ≡ Me) indicated by its NMR behavior is not entirely straightforward. To rationalize the equivalence of two of the three ^{119}Sn atoms at $T_c = 6.7$°C, a dissociation rotation mechanism has been put forward which converts the trimer to its enantiomer [190]. Earlier variable-temperature NMR results had been interpreted in terms of an equilibrium involving



(23)

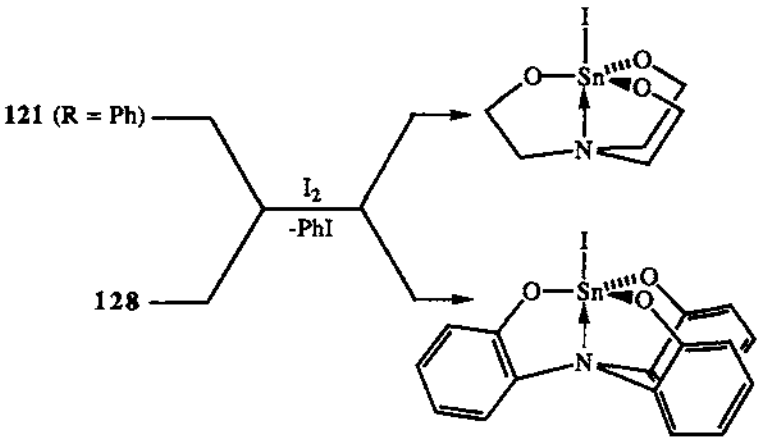
cleavage of the transannular bond as depicted in reaction (23) [193] and in terms of intramolecular processes involving Berry pseudorotation and ring flipping in



(24)

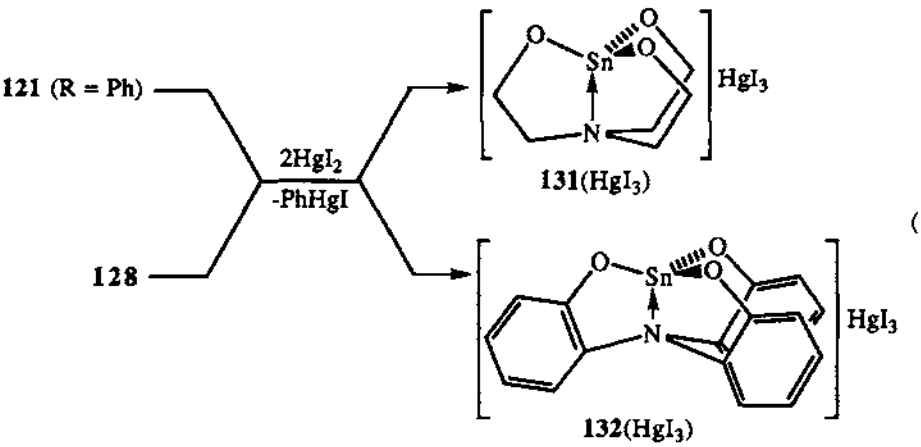
monomeric species as illustrated in equilibria (24) [208]. Equilibria of these types undoubtedly render untrustworthy the dipole moments reported for **120** (R ≡ Et, 4.59 D; R ≡ ^{n}Bu, 4.53 D) as presumed monomers [194].

It has been observed that stannatranes **121** (Ar ≡ Ph) and **128** react seven times



(25)

faster in reaction (25) than $PhSn(OMe)_3$. This was interpreted as an indication of the presence of a transannular bond in the transition state [203a]. Using HgI_2 as a

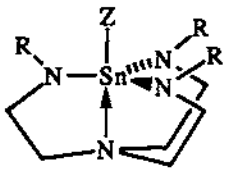


(26)

reagent in reaction (26), these workers reported that cations **131** and **132** were formed. The reactivity order [203b] **121** (R ≡ Ph) = **128** ≫ $PhSn(OMe)_3$ was rationalized by invoking the role of transannulation in stabilizing the developing positive charge on tin.

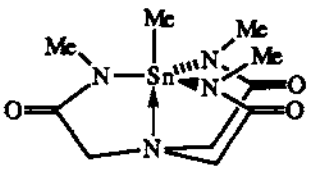
3.10. Azastannatranes

Compounds in this class include **133–144** recently reported from our laboratories [209] and **145** described by previous workers [191,202]. Five-coordinate tin in **135** was demonstrated by an X-ray crystallography study which revealed the presence of two crystallographically independent molecules with trigonal bipyramidal config-



	Z	R
133	R'	H
134	R'	Me
135	Ph	H
136	Ph	Me
137	Me_2N	Me
138	1/2O	Me

	Z	R
139	F	Me
140	Cl	Me
141	Br	Me
142	I	Me
143	1/2C≡C	Me
144	C≡CPh	Me



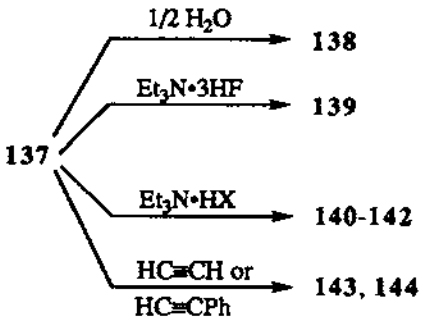
145

urations [209]. The only significant differences between the molecules are the two transannular bond lengths (2.380(2) and 2.453(2) Å) and the angle between the phenyl ring plane and the Sn–*ipso*-C bond vector (179.1(2)° and 173.2(2)°). Both transannular bond distances in **135** are in the lower part of the range for Sn–N interactions in five-coordinate organotin compounds (2.32–2.66 Å [210]) but exceed the Sn–N_{eq} distances in this compound (average 2.058(2) Å [209]). The latter value is comparable with that found in the normal Sn–N single bond, however (2.06(4) Å [211]). The transannular distance in **137** determined by X-ray means (2.368(3) Å [212]) is within experimental error of that for one of the independent molecules of **135** in the unit cell but smaller than that for the other. This is curious in view of the greater steric interactions expected in **137** compared with **135**, which could be expected to lengthen the transannular bond. It is also interesting that the Me_2N–Sn bond length in **137** is within experimental error of the Sn–N_{eq} distances (average 2.038(4) Å) whereas the transannular bond is about 0.3 Å longer.

Comparable solution and solid state ^{119}Sn and ^{13}C NMR spectral shifts in azastannatranes **133–144** suggest the preservation of the five-coordinate geometry in these compounds in both states [209,212]. Data obtained in Mössbauer studies also corroborate a trigonal bipyramidal coordination geometry for **145** [207]. Variable-temperature ^{1}H NMR solution spectral studies show that a $\Delta G_T^{\ddagger}$ of about 34 kJ mol^{-1} is associated with the racemization of the five-membered rings in these systems [209,212], a value which is somewhat lower than in carbastannatranes (about 37 kJ mol^{-1} [61c]). We have also concluded from a comparison of ^{119}Sn NMR chemical shifts of azastannatranes **133–137** [209] that these shifts are more sensitive to Z than in carbastannatranes [61c] and stannatranes [189]. The solution ^{119}Sn NMR chemical shift of **145** (−236.8 ppm [202]) is considerably upfield from that of **134** wherein R ≡ Me or "Bu (−90.0 and −117.1 ppm respectively [209]). The

increased electronegativity of the carbonyl groups in **145** may account for this and this suggestion is supported by the upfield shift observed for **138** (−255.2 ppm [209]).

Compounds **138–144** were obtained by displacement of the Me_2N group in



(27)

(28)

(29)

(30)

137 as shown in reactions (27)–(30) [209,212]. Exclusive substitution at the apical position of **137** in these reactions clearly demonstrates the substantial difference in reactivity of the axial and equatorial amido bonds in these compounds. This could be accounted for by greater basicity of the axial nitrogen (owing to the sharing of its bond to the tin with a trans tertiary nitrogen lone pair) with the consequence that displacement is facilitated by preferential protonation of the axial nitrogen by the reagent.

In contrast with stannatranes, which were observed to bridge intermolecularly via their equatorial oxygen atoms (Section 2.9.), **145** is apparently monomeric [202]. That **133–144** are also monomeric is indicated by the solid state structures of **135** and **137** and by the similarity of their solution and solid state ^{119}Sn NMR chemical shifts [209,212].

3.11. A plumbatrane complex

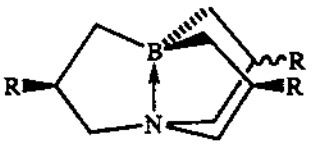
The reaction of $Pb(OAc)_2$ with $(HOCH_2CH_2)_3N$ in methanol gives a nearly quantitative yield of $Pb[HOCH_2CH_2)_3N]_2(OAc)_2$ [58]. Whether or not all the potentially ligating atoms are bound to the metal is difficult to ascertain in the current absence of suitable crystals for an X-ray study.

4. GROUP 13 ATRANE SYSTEMS

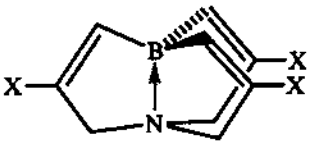
The first three elements of this group have been found to form atrane compounds. Aluminum appears thus far to possess the most extensive structural and chemical diversity, however.

4.1. Carbaboratranes, thiaboratrane, boratranes and azaboratranes

Carbaboratranes **1** [213,214], **2** [213] and **3** (X≡Cl, Br) [215] have been reported. The ^{11}B NMR chemical shifts of **1** (9.40 ppm [214]) and **3** (X≡Cl, 14.6;



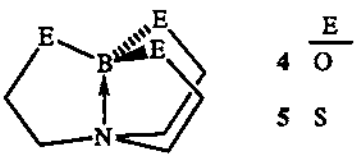
	R
1	H
2	Me



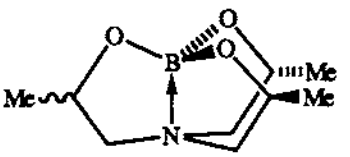
3

X≡Br, 12.1 ppm [215]) are consistent with four-coordinate boron. Photoelectron spectroscopy studies of **1** reveal that its B–N bond strength is stronger than in **4** owing to strong π back donation from the oxygen atoms to the boron. An adduct of **1** with $SbCl_5$ was also reported [213]. The diastereomers of **2** were separated by high pressure liquid chromatography (HPLC) and gas chromatography (GC) [213]. The B–N distance in **3** (X≡Cl) has been determined by X-ray diffraction to be 1.63 Å [215]. The thiaboratrane **5** has been reported [216].

Boratrane **4** has been known since 1951 [217] and its structure, determined by X-ray means, has been reported no fewer than five times in the period 1971–1983 [218–222]. An error analysis on X-ray data in the literature was also described



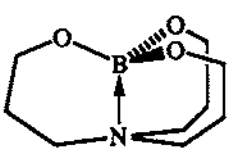
	E
4	O
5	S



6

[223]. The best value for the B–N distance appears to be 1.677(6) Å [220]. The presence of a transannular bond has also been inferred from gas chromatographic retention times [181b] and the high dipole moment for **4** (8.8 D [224]).

Other symmetrically substituted boratranes including **6** [225], **7**, **8** [226] and **9** [15,227,228] have been characterized. Adducts **10** [15] and **11**–**14** [227,228] have



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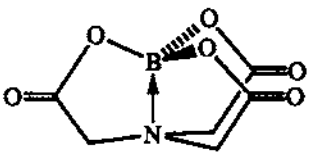
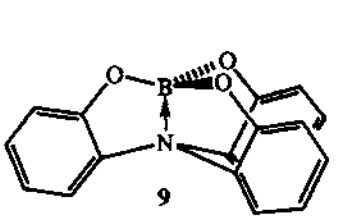


8

also been reported as well as the weak BH_3 adduct of **9** in which the nitrogen presumably inverts and binds to the BH_3 group [15].

The transannular B–N distance in **9** is 1.681(5) Å whereas in **11** and **12** it



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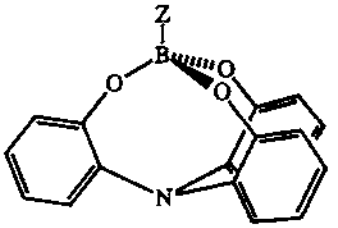
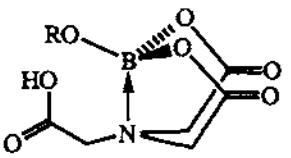
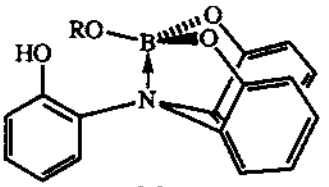


	Z
10	H_2NPh
11	C_5H_5N
12	$N(CH_2CH_2)_3CH$
13	$N(CH_2CH_2)_3N$
14	p-Me_2N-C_5H_4N

opens up to 2.816(4) and 2.845(5) Å respectively as the boron and nitrogen atoms in **9** invert to accommodate the new B–N adduct bond [228]. From variable-temperature ^1H NMR experiments it was concluded that the reaction of **9** with pyridine progresses through an associative transition state, thereby implicating an S_N2-type mechanism for the nucleophilic substitution [227]. NMR evidence has also been put forth for intermediates of type **15** and **16** in the formation of **8** [226] and

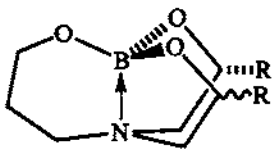


15

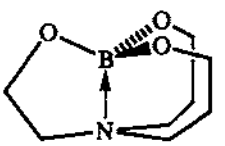


16

9 [227] respectively from $(RO)_3B$ and the corresponding trihydroxy nitrilo compound.



	R
17	H
18	Me



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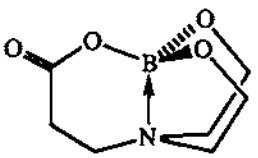

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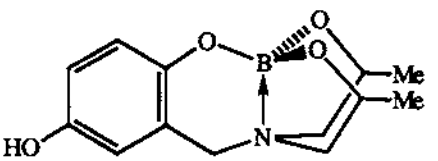
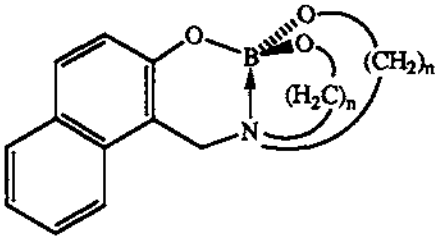


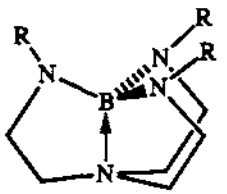
21

Unsymmetrical boratranes of types **17**, **18** [229] and **19–23** [225] have been reported. In ^{11}B NMR chemical shift studies the roles of stereochemical constraint and the degree of B–N interaction were examined [225]. Thus for the series of boratranes **4**, **6**, **7**, **17**, **19–23**, increasingly upfield shift ranges were observed from [4.4.4] (**7**, **23**, −1 to −2 ppm) to [3.4.4] (**19**, −4 ppm) to [3.3.4] (**17**, **20–22**,

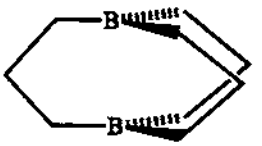


	n
22	2
23	3

approximately −10 ppm) to [3.3.3] (**4**, **5**, approximately −14 ppm) tricyclic systems. Although stereochemical constraint increases with the upfield movement of $\delta^{11}B$, it also appears that the B–N shielding interaction is augmented.



	R
24	Me
25	$SiMe_3$



26

Azaboratranes **24** and **25** were reported recently from our laboratories [230]. Compound **25**, in contrast with **24**, exists as a pair of rigid enantiomers that interconvert slowly at room temperature on the NMR time scale owing to steric repulsion of the $SiMe_3$ groups. Variable-temperature ^1H and ^{11}B NMR studies provide evidence for a concerted rather than a stepwise racemization mechanism. Thus $\Delta S^{\ddagger}$ is -36 ± 13 J mol^{-1} K^{-1}, suggesting a symmetric C_{3v} transition state (as depicted in Fig. 2) that preserves the transannular bond [230]. The rigidity of **25** on the NMR time scale undoubtedly arises from steric repulsions of the $SiMe_3$ groups, which distort the structure from the nearly eclipsed conformation (as viewed down the B–N axis in Fig. 2(a)) encountered in the crystallographically determined structure of **4** to a more staggered one (Fig. 2(b)). This process reduces the crowding among the $SiMe_3$ groups by increasing the distance between each pair.

The ^{11}B NMR chemical shifts of these cage compounds are rather similar (**1**, 9.40 ppm [214]; **3**, X≡Cl, 14.6 ppm [215]; **3**, X≡Br, 12.1 ppm [215]; **4**, 10.7–14.2 ppm depending on the solvent [225,231]; **6**, 14.2 ppm [231]; **10**, 14.2 ppm [15]; **16**, 10.1 ppm [230]; **17**, 16.1 ppm [230]). A substantial upfield shift was observed for **11** (+4.4 ppm [15]), perhaps reflecting a stronger B–N bond than the ring-strained transannular bond in **10**. Compounds **5** and **6** apparently have some activity as a chemosterilant for screw-worm flies [232]. For completeness, it is worthy of note that a compound related to carbaboratrane **1**, namely the diboron cage **26**, has been reported [214].

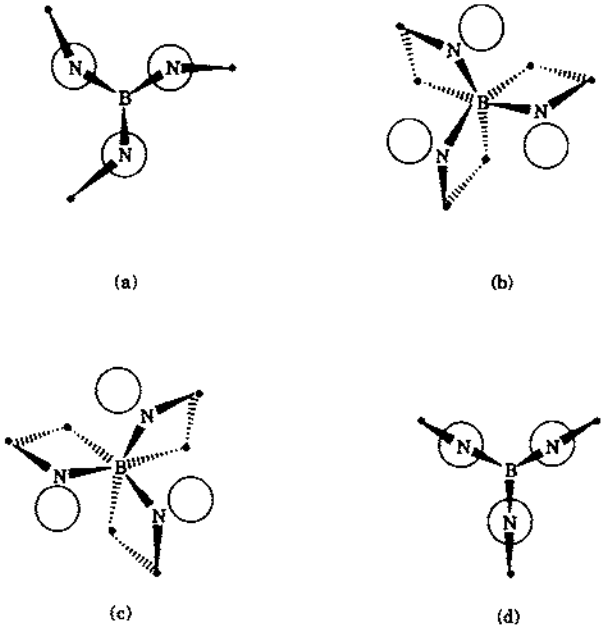
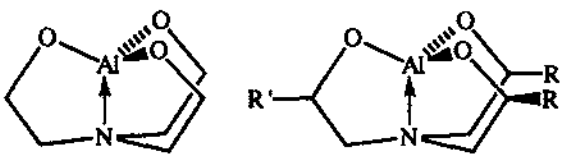


Fig. 2. View down the B–N transannular bond axis of 4 showing an eclipsed conformation of the bonds on these atoms (a), enantiomeric staggered conformations (b) and (c), and a proposed transition state in which all the atoms in the framework of the five-membered rings are coplanar (d). The circles represent the Me_3Si groups bonded to the adjacent trigonal nitrogen.

4.2. *Alumatranes, pro-alumatranes and azaalumatranes*

Alumatrane, depicted as the monomer **27**, is actually a tetramer in the solid state as shown by X-ray crystallography [233], for which a sketch is shown in Fig. 3.



27

	R	R'
28	Me	H
29	Me	Me

The Al–N distance in the pro-alumatrane unit is 3.239(3) Å, while that in the three alumatrane moieties averages 2.069(5) Å [233]. In our laboratories we have shown that the solid state X-ray photoelectron spectrum is consistent with this structure [234].

In solution a cryoscopic determination of the molecular weight suggested an octameric constitution [235], while an ebullioscopic measurement indicated hexameric behavior [236]. Mass spectroscopic studies led to the conclusion that oligomers no higher than dimers existed in the gas phase [237]. Mild chemical ionization

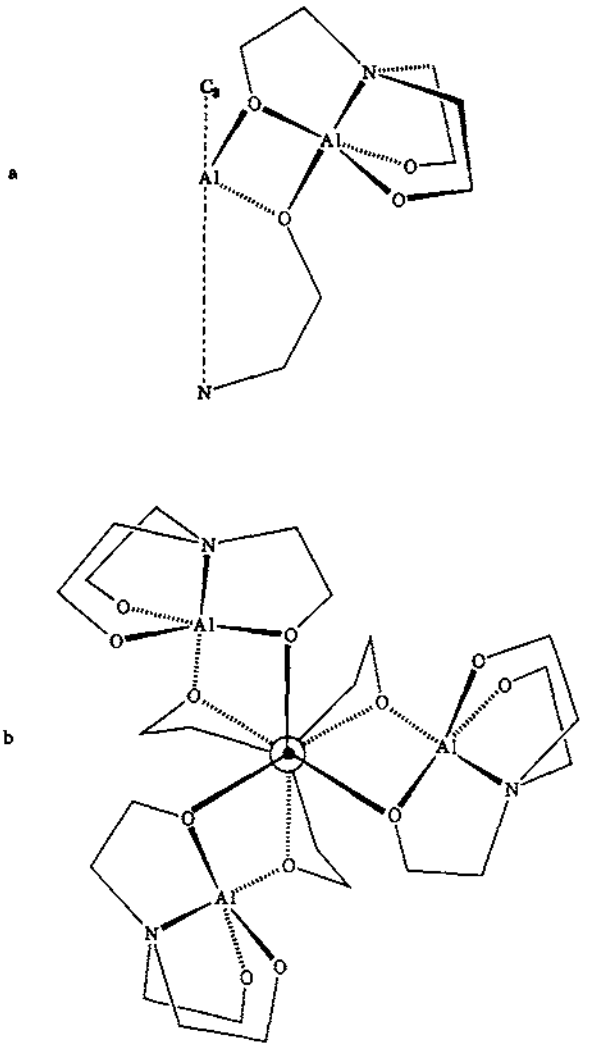
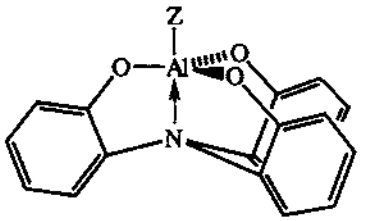


Fig. 3. Side view of an equivalent one-third of tetrameric alumatrane $(\mathbf{27})_4$ (a) and a view down the C_3 axis of tetramer $(\mathbf{27})_4$ (b).

in the presence of NH_3 gas, however, allowed us to observe both dimers and tetramers in the gas phase by mass spectroscopy [234].

Two papers on the ^{27}Al NMR spectra of **27–29** reported monomeric behavior as the suggested result of a tetrahedral aluminum environment [238,239]. Our ^{27}Al NMR experiments revealed two chemical shifts for **27** in the solution and solid states: one in the six-coordinate aluminum region (about 5 ppm) and the other in the five-coordinate range (about 67 ppm) in the ratio of 1:3, consistent with the tetrameric structure $(\mathbf{27})_4$ [234]. Variable-temperature ^{13}C NMR studies on $(\mathbf{27})_4$ revealed that racemization of the five-membered rings occurs. Further increasing the

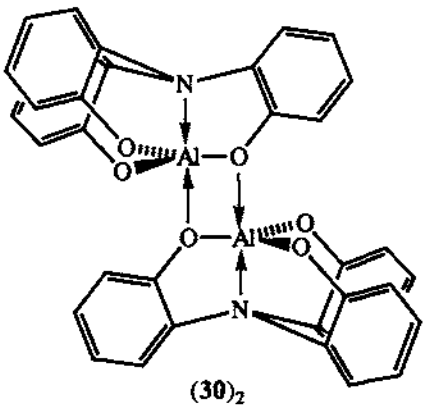
temperature results in rotation of the five-coordinate alumatrane units around their C_3 axes [234].



	Z
30	nothing
31	H_2NCH_2Ph
32	HO-^{i}Pr

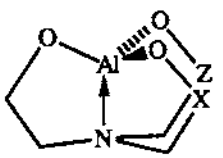
	Z
33	C_5H_5N
34	HO^-

Although alumatrane **30** and its adduct **31** were reported as monomers [15,240], the solution ^{27}Al NMR spectrum of the adduct revealed two resonances (about 4 and 66 ppm [15]) which could be interpreted as a dissociation of **31** to form tetrameric $(\mathbf{30})_4$ analogous to tetrameric $(\mathbf{27})_4$ (Fig. 3).



$(\mathbf{30})_2$

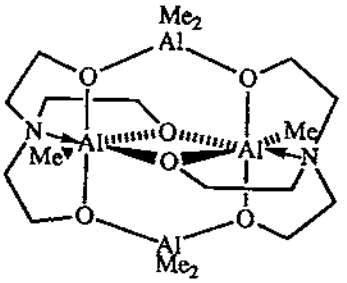
The solid state structure of **30** is dimeric with an Al–N distance of 2.094(18) Å [241]. This distance is within experimental error of that found in **33** (2.153(6) Å) but shorter than that observed in anion **34** (2.278(3) Å) [241]. As expected, the external Al–N distance in **33** (1.992(6) Å) is shorter than the internal (transannular) Al–N distance, probably owing to ring strain.



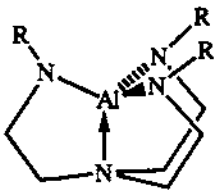
	X	Z
35	CH_2	C=O
36	C=O	C=O

Alumatranes **35** and **36** have been reported to be monomeric with tetracoordinate aluminum atoms on the basis of their solution ^{27}Al NMR spectra [242]. Compound **37** possesses an octahedral coordination geometry around each aluminum [243]. Here the Al–N distance is 2.058(9) Å [243].

The only known examples of azaalumatranes, namely **38–40**, were reported

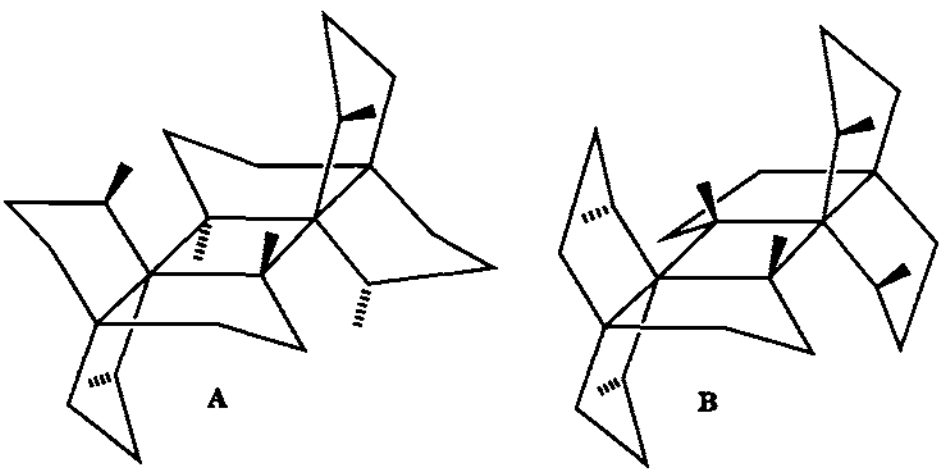


37



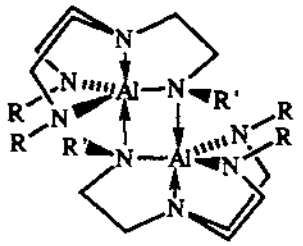
	R
38	Me
39	$SiMe_3$
40	$SiMe_2$-^{t}Bu

from our laboratories [230,244]. ^1H, ^{13}C and ^{27}Al NMR studies indicate that **38** is dimeric (analogous to $(\mathbf{30})_2$) while the more sterically hindered **39** and **40** are monomeric in solution [230,244]. Because the solution NMR data for $(\mathbf{38})_2$ are consistent with either a trans or a cis relationship of the *N*-methyl groups on the central four-membered ring as depicted in **A** and **B**, an X-ray crystallographic investigation was carried out, which confirmed the cis configuration for this molecule.

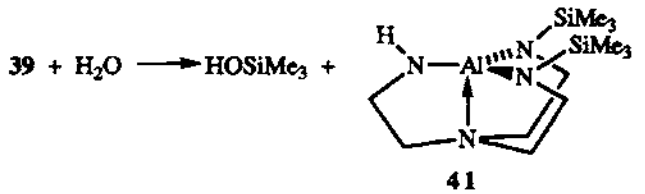


A **B**

The Al–N distance in $(\mathbf{38})_2$ (2.161(2) Å) is longer than that observed in monomeric **39** (1.983(6) Å) which features a trigonal monopyramidal aluminum geometry owing to steric intereference among the Me_3Si groups [244]. Upon exposure to moisture,



	R	R'
$(38)_2$	Me	Me
$(41)_2$	$SiMe_3$	H



41

(31)

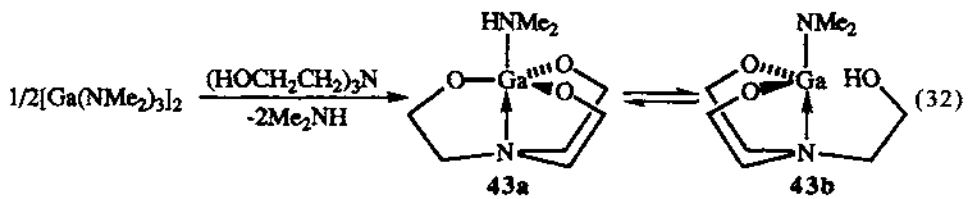
39 apparently reacts according to eqn. (31) to give 41 which then dimerizes to $(41)_2$ [244].

4.3. Carbagallatranes, gallatranes and azagallatranes

The carbagallatrane 42 is reported to be a very stable and sublimable solid [245]. The Ga–N bond distance of 2.095(2) Å reflects some strain in the rings, since

42

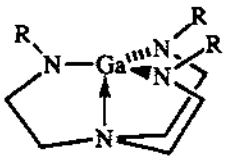
the sum of the corresponding covalent radii is 1.95 Å [245]. Interestingly, the Ga stereochemistry is quite trigonal monopyramidal with C–Ga–C angles of 120°.



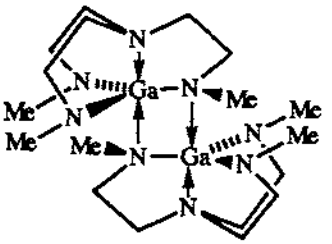
43a 43b

(32)

Reaction (32) was recently shown by us in proton NMR studies to give rise to an equilibrium between 43a and 43b [246]. Azagallatranes 44 and 45 have been recently synthesized in our laboratories, but an attempt to make 46 gave the dimer $(46)_2$ [246], as was the case for the aluminum analogue $(38)_2$.



	R
44	$SiMe_2$-^{t}Bu
45	$SiMe_3$
46	Me



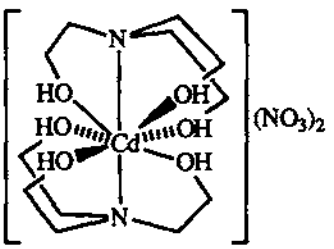
$(46)_2$

5. GROUP 12 ATRANE COMPLEXES

Thus far zinc and cadmium are the metals in this group for which atrane systems have been characterized.

5.1. *Cadmatrane and zincatrane complexes*

Complexes of the type $Zn[(HOCH_2CH_2)_3N]_2A_2$ (A ≡ Br, NO_3) and $Cd[(HOCH_2CH_2)_3N]_2A_2$ (A ≡ Cl, NO_3) have recently been characterized in our



$1(NO_3)_2$

laboratories [58]. The crystal structure of the cadmium nitrate complex **1** reveals eight coordination, a relatively rare coordination number for cadmium. The Cd–N distance of 2.460(2) Å is slightly longer than the Cd–O distances (2.417(3) Å). There is extensive hydrogen bonding in the structure involving the nitrate anions.

5.2. *Azazincatrane complexes*

The title compounds include **2** [247,248] and **3** [249,250], of which the structures of **2** (A ≡ SCN [248] and **3** (A ≡ Br [251]) have been verified by X-ray studies. The structure of **2** (A ≡ SCN) features five-coordinate zinc, in which the transannular Zn–N bond is 2.27 Å and the average Zn–N_{eq} distance is 2.07 Å [248]. In **3** (A ≡ Br) these distances are 2.19(2) and 2.11(2) Å respectively in the five-coordinate monocation [251]. A Mössbauer study of **3** (A ≡ I) indicated that both

$Zn(H_2NCH_2CH_2)_3NA_2$

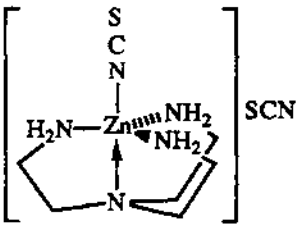
A = CF_3SO_3, SCN

2

$Zn(Me_2NCH_2CH_2)_3NA_2$

A = Cl, Br, I, NO_3, ClO_4, SCN

3



2(SCN)

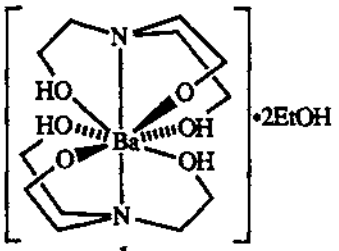
iodine atoms are ionic, suggesting that zinc is four coordinate and not five coordinate [252] as in the corresponding bromide.

6. GROUP 2 ATRANE SYSTEMS

In group 2, reports of atrane-type compounds include those of magnesium, calcium, strontium and barium.

6.1. Magnesatrane, calcatrane, strontatrane and baratrane systems

Thus far structural information on alkoxide compounds with triethanolamine (TEA) has been restricted to one report, namely that of **1** [253]. Here the Ba–N distance is 3.009(3) Å and the octacoordinate charge-neutral monomeric units are connected in a two-dimensional network by hydrogen bonding involving the ethanol molecules. The hydrogen atoms could not be located in this structure. Cationic coordination of group 2 metals with TEA is also characterized by extensive hydrogen bonding via the anions. In some cases the anions also coordinate to the metal as in nine-coordinate **2** [254], ten-coordinate **3** [255], nine-coordinate **4** [256] and ten-coordinate **5** [257], while in others they do not (i.e. eight-coordinate **6** [258], **7** [258] and **8** [259]). Except for **5** in which eight of the ten oxygen atoms are coordinated to two Ba^{2+} ions (giving rise to a complicated two-dimensional network



1

$[Ba(TEA)_2\ (2,4\text{-}(O_2N)_2C_6H_3O](2,4\text{-}(O_2N)_2C_6H_3O)$

2

$[Ba(TEA)_2(picrate)](picrate)$

3

$[Ba(TEA)_2(OAc)]OAc$

4

$[Ba(TEA)_2(OC_6H_4\text{-}o\text{-}NO_2)_2]$

5

$[Ca(TEA)_2](N_3)_2$

6

$[Sr(TEA)_2](N_3)_2$

7

$[Sr(TEA)_2](NO_3)_2$

8

$[Sr(TEA)_2](ClO_4)_2$

9

$[Ba(TEA)_2](ClO_4)_2$

10

$Mg(TEA)_2Cl_2$

11

of Ba–O interactions), the OH groups of ligating TEA have been found to coordinate to a single M^{2+} ion.

Complexes **9–11** have been characterized in our laboratories [260,261]. A novel feature of the solid state structure of **8** is that it is dimeric with bridging perchlorate anions, thus rendering each barium ten coordinate [262]. The average Ba–N distance in this structure is 3.055(4) Å and there is extensive hydrogen bonding.

6.2. Azabaratranes

Complexes **12** and **13** were recently synthesized by us [262]. The structure of the latter compound is currently being determined by X-ray means.

$\{Ba[(H_2NCH_2CH_2)_3N]_2\}(ClO_4)_2$

12

$\{Ba[(MeHNCH_2CH_2)_3N]_2\}(ClO_4)_2$

13

7. GROUP 1 ATRANE COMPLEXES

Examples of atrane complexes including H^+ to Rb^+ in this group have been characterized.

7.1. Protatrane, lithatrane and sodatrane complexes

Compounds in this category include the TEA complexes **1** [260,263–265], **2** [260], **3** [260], **4** [266], **5** [261] and **6** [261]. Cation **1**, the parent of all atranes,

$[H(TEA)]^+$ **1**

$[Na(TEA)ClO_4]$ **3**

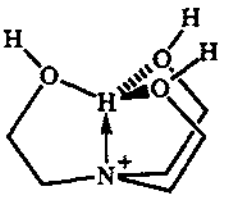
K(TEA)Cl **5**

$[Li(TEA)]ClO_4$ **2**

[Na(TEA)I] **4**

Rb(TEA)Cl **6**

has been structured by X-ray means as its $PhOCH_2CO_2^-$ [263], *p*-Cl-$C_6H_4SCH_2CO_2^-$ [264], NO_3^- [265] and ClO_4^- [260] salts. The most precise measurement of the transannular H–N distance appears to be our determination of 0.972(4) Å [260].



1

Cation **1** contains a rare example of trifurcated hydrogen bonding and it seems to be the only example of such bonding that possesses threefold symmetry.

Both **3** and **4** possess coordinated anions in the solid state. In **3** we observed that the seven-coordinate sodium is bonded to the four heteratoms of a TEA molecule, an oxygen of a perchlorate and the oxygen of an OH group from each of two neighboring cations [260]. The Na–N distance here is 2.611(2) Å. The structure of **3** differs from that of **4** in that in the latter two OH groups from each molecule bridge two seven-coordinate sodium ions [266]. In **4** the Na–N distance is 2.610(5) Å. Both structures are extensively hydrogen bridged.

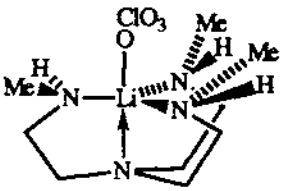
7.2. Azalithatrane complexes

Compounds **7** and **8** have recently been synthesized in our laboratories and their structures have been determined by X-ray crystallography [262]. The lithium in **8** is five coordinate with an Li–N_{ax} distance of 2.20(1) Å and an Li–N_{eq} distance

$Li(H_2NCH_2CH_2)_3NClO_4$ **7**

$Li(MeHNCH_2CH_2)_3NClO_4$ **8**

of 2.120(3) Å. The structure of **7** is analogous, displaying Li–N_{ax} and Li–N_{eq} distance of 2.18(1) and 2.12(3) Å respectively.



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