Atranes: New Examples with Unexpected Properties

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We have discovered three curious features about the football-shaped molecules of the type below which make these aesthetically attractive species exceedingly interesting to study. One such feature is that the distance

$$Z–E \ (YCH_2CH_2)_3N$$

Z = lone pair; E = group 15 element

Z = O, NR; E = group 5, 15 element

Z = R, SR, OR, NR$_2$; E = group 4, 14 element } Y = O, NR

Z = nothing; E = group 13 element

Z = N; E = group 6 element

between the ends of the football portion of these molecules can vary smoothly from the sum of the van der Waals radii of the atoms E and N, depicted as **A**, through intermediate distances, represented by **B**, to full transannular bonds, as shown in **C**. As will be

pro-atrane   quasi-atrane   atrane
   A   **B**   **C**
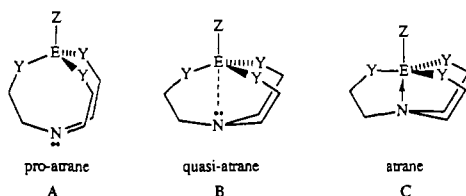
shown, the degree of delocalization of the bridgehead nitrogen lone pair into a three-center, four-electron bond system along the molecular axis can be stereoelectronically controlled. A second feature is that the partial (**B**) or complete (**C**) donation of electron density from the axial nitrogen enhances the electron density on E and Z. As we shall see, these two attributes combine to confer unusual basicity and reactivity properties, including catalysis, on E and Z. A third feature is that in some cases the tripodal ligands in structures of type **C**, wherein Y = NR, can be exchanged from another E atom (Y = NR' or O) and in others it can be transferred onto a different E atom.

To differentiate qualitatively among structures **A–C**, it is proposed that we refer to these configurations by the trivial names given, since five-coordinate species of

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type **C**, wherein E = Si and Y = O, have been referred to as "silatranes" for over a decade before our entry into this area. It is further proposed that when Y = NR, the prefix "aza" be inserted before "elementaatrane" (e.g., "proazaphosphatrane"). While this nomenclature is admittedly somewhat crude in terms of precisely identifying structures not quite at the bonding extremes characterized by **A** and **C**, it is helpful in focusing our attention on the flexibility of these compounds with respect to partial transannulation.

Contributions by others in this chemistry[1] address mainly atrane systems (i.e., Y = O in **C**) of group 14 elements,[1a,b] with a few reports dealing with Bi(III),[1c] Ti(IV),[1d–g] V(V),[1h,i] B(III),[1j] Al(III),[1k] and Fe(III).[1l] As we shall see, azatranes provide greater structural and chemical versatility than atranes, partially because the size of the R group on Y can be varied. However, only five compounds of this class had been reported previous to our work, all of which were of the type E = Si, Z = R, Y = NH.[1m] Prior to our investigations, no publications on proatranes, proazatranes, and quasiazatranes had appeared. However, two structures of quasisilatranes determined by X-ray means had been published,[1n,o] and reports have very recently appeared on several azatitanatranes,[1p] azavanadatranes,[1p] and a chiral zirconatrane.[1q]

The intriguing question we have been attempting to address in our research is the following: What steric and electronic factors govern the diverse reactivities and structural properties of these versatile ZE(YCH$_2$CH$_2$)$_3$N compounds? To help answer this question, we will briefly explore some of the wide-ranging reactions of these molecules and the structural consequences of these transformations. As an organizational theme, we will sequentially examine in the succeeding sections reactions occurring at E, Z, Y, and N and structural changes that accompany them.

Chemistry at E

The unusual basicity of the phosphorus in prophosphatranes first came to light in an attempt to make an

(1) See, for example: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* 1986, *131*, 99. (b) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* 1982, *233*, 1. (c) Miller, W. T. *J. Am. Chem. Soc.* 1940, *62*, 2707. (d) Voronkov, M. G.; Faitel'son, F. D. *Khim. Geterotsikl. Soedin.* 1967, 39; *Chem. Abstr.* 1967, *67*, 64321w. (e) Cohen, H. J. *J. Organomet. Chem.* 1967, *9*, 177. (f) Harlow, R. L. *Acta Crystallogr.* 1983, *C39*, 1344. (g) Taube, R.; Knoth, P. *Z. Anorg. Allg. Chem.* 1990, *581*, 89. (h) Mittal, R. K. *Z. Anorg. Allg. Chem.* 1967, *351*, 309. (i) Shestakov, E. E.; Voronkov, M. G.; Frolov, Y. L.; Baryshok, V. P. *J. Gen. Chem. USSR* 1983, *53*, 1161. (j) Müller, E.; Burgi, H.-B. *Helv. Chim. Acta* 1987, *70*, 499, 511. (k) Mehrotra, R. C.; Mehrotra, R. K. *J. Indian Chem. Soc.* 1962, *39*, 677. (l) Starke, K. *J. Inorg. Nucl. Chem.* 1959, *11*, 77. (m) Jurkschat, K.; Muegge, C.; Schmidt, J.; Tzschach, A. *J. Organomet. Chem.* 1985, *287*, C1. (n) Jurkschat, K.; Tzchach, A.; Meunier-Piret, J.; Van Meersche, M. *J. Organomet. Chem.* 1986, *317*, 145. (o) Eaborn, C.; Odele, K. J.; Pidcock, A.; Scollary, G. *J. Chem. Soc., Chem. Commun.* 1976, 317. (p) Cummings, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* 1992, *11*, 1452. (q) Nugent, W. A. *J. Am. Chem. Soc.* 1992, *114*, 2768.
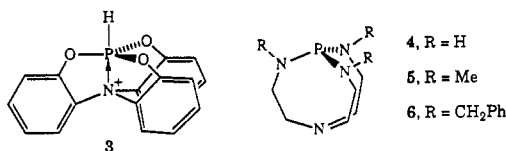
Scheme I
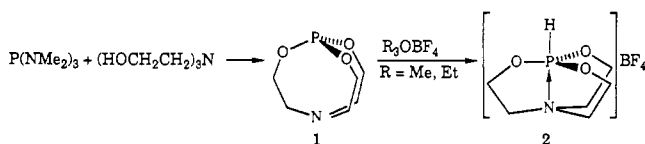
Scheme II
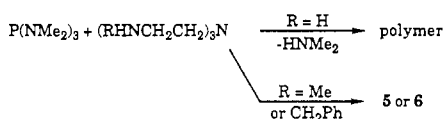
alkylated derivative of unstable 1, shown in Scheme I, since 1 eluded isolation by forming an intractable polymer for reasons that are not clear.[2,3] Instead of alkylating the nitrogen or phosphorus of 1, 2(BF₄) was formed. The R₃OBF₄ in the reaction was shown to have alkylated unreacted triol in the mixture,[4] and the protons subsequently liberated attacked 1, forming cation 2. The real surprises are that the phosphorus (rather than the more basic nitrogen) is protonated (as shown by its ³¹P-H NMR coupling and X-ray crystal structure)[5] and that the phosphorus possesses a transannular bond (1.986 Å[5]), as was also indicated by its upfield ³¹P chemical shift (-20.9 ppm).[2] The extraordinarily weak acidity of cation 2 was demonstrated by its stability in the presence of NaOMe and the strong base 1,8-bis(dimethylamino)naphthalene (Proton Sponge). The stability of this cation to protonation of its quaternary nitrogen was shown by its unchanged ³¹P NMR spectrum when it was dissolved in magic acid solution (HSO₃F·SbF₃ in liquid SO₂).[2] Although the CH₂CH₂ bridges in 1 are sufficiently flexible to allow transannulation upon phosphorus protonation, the utilization of rigid benzo rings in their place has been found to provide only solution NMR evidence for 3.[6]

In order to explore the chemistry of the prophosphatrane structure 1 with isolable analogues, we sought to synthesize 4–6. Whereas the transamination reaction in Scheme II for R = H gave rise to intractable polymer, 5 and 6 could be obtained in ~20–50% yield over a period of weeks.[7] The slowness of this reaction and the mediocre yields surprised us, since we found that the more constrained cage P(MeNCH₂)₃CMe is formed in a few hours in 90% yield in the analogous reaction with (MeHNCH₂)₃CMe.[8] The unusual basicity of proazaphosphatranes 4–6 emerged when we endeavored to

(2) Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 6607.

(3) Ring strain would not appear to be a problem in 1 since more constrained phosphite esters such as P(OCH₂)₃CR (Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1) and P(OCH₂)₂C(H)O (Denney, D. B.; Varga, S. C. *Phosphorus* **1973**, *2*, 245) have been reported.

(4) Carpenter, L. E.; Verkade, J. G. *J. Org. Chem.* **1986**, *51*, 4287.

(5) Clardy, J. C.; Milbrath, D. S.; Springer, J. P.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 623.

(6) Müller, E.; Bürgi, H.-B. *Helv. Chim. Acta* **1987**, *70*, 1063.

(7) Lensink, C.; Xi, S.-K.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478.

(8) Laube, B. L.; Bertrand, R. D.; Casedy, G. A.; Compton, R. D.; Verkade, J. G. *Inorg. Chem.* **1967**, *6*, 173.

improve the synthesis of 5 by employing the more reactive phosphorus reagent in Scheme III. In spite of the presence of Et₃N, 7–9 were formed in nearly quantitative yields at room temperature in about 1 h.[9] These compounds are also formed in the absence of base, and in fact cation 7 has been made in 99% yield as the triflate salt by reacting an equimolar mixture of P(NMe₂)₃, (H₂NCH₂CH₂)₃N, and HOSO₂CF₃ in CH₂Cl₂ for 15 min at room temperature.[9]

Scheme III
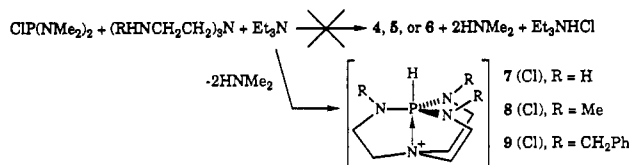
Scheme IV
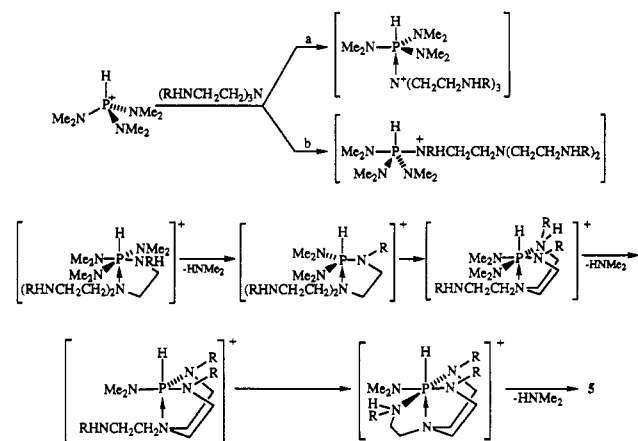
It is plausible to suppose that protonation of the phosphorus of P(NMe₂)₃ in the latter reaction facilitates nucleophilic attack by the tetramine via its tertiary nitrogen (path a in Scheme IV) or by one of its amine arms (path b), followed by successive chelation and HNMe₂ elimination steps. The formation of a transannular bond at an early stage in Scheme IV is suggested by *ab initio* calculations on models of silatranes RSi(OCH₂CH₂)₃N. Thus the Si←N bond length in MeSi(OCH₂CH₂)₃₋ₙNHₙ(OH)ₙ *increases* by ca. 0.1 Å each time one of the silicon's OH groups is replaced by a bridging OCH₂CH₂ moiety,[10] indicating that successive chelate ring formation actually inhibits the Si←N interaction, probably because of strain associated with the five-membered ring. The importance of chelation in stabilizing species such as 2 and 5–9 is illustrated by our failure to detect NMR evidence[2] either for an analogue of the first intermediate of path a in Scheme IV in an equimolar mixture of H⁺, P(NMe₂)₃, and Et₃N or for an analogous [H(EtO)₃P←N(CH₂CH₂OH)₃]Cl species upon attempting to react an equimolar mixture of P(OEt)₃ and [HN(CH₂CH₂OH)₃]Cl.[2] The decrease in entropy required for the (intermolecular) formation of such monodentate adducts may well be prohibitively greater than for (intramolecular) transannulation.

(9) Laramay, M. A. H.; Verkade, J. G. *Z. Anorg. Allg. Chem.* **1991**, *605*, 163.

(10) Gordon, M. S.; Carroll, M. T.; Jensen, J. H.; Davis, L. P.; Burgraff, L. W.; Guidry, R. M. *Organometallics* **1991**, *10*, 2657.

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Further evidence of the weakly acidic nature of cations 7–9 is the failure of each to exchange its proton with DOC(O)CF$_3$ and the necessity to use an exceedingly strong ionic base to liberate 4–6:

$$\text{7, 8, or 9} \xrightarrow{\text{}^-\text{O-}t\text{-Bu}} \text{4, 5, or 6, respectively} \qquad (1)$$
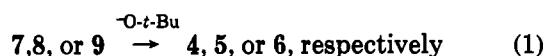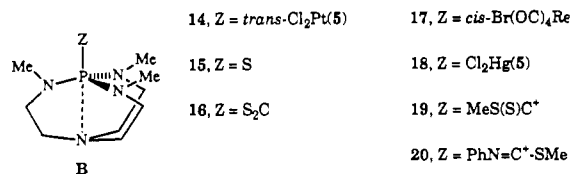
While 4 polymerizes on attempted isolation, 5 and 6 are stable sublimable solids. Strong evidence for the formation of 4 in reaction 1, however, is its reaction with O$_2$ to form isolable 10.[9]

10, Ch = O, R = H
11, Ch = Se, R = H
12, Ch = Se, R = Me
13, Ch = Se, R = CH$_2$Ph
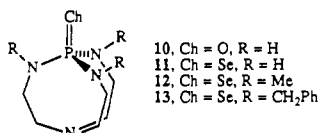
The relative acidities of 7–9 were determined by ^{31}P NMR spectroscopy in competitive deprotonation experiments using KO-t-Bu in DMSO.[11] Contrary to expectation on electron induction grounds, the acidity order is 9 > 8 > 7 rather than 9 > 7 > 8. The observed acidity order of these cations is corroborated by the decrease in $^1J_{PH}$ coupling they display (506, 491, and 453 Hz) and the increasing order of $^1J_{PSe}$ coupling in the selenides 11–13 (590, 754, and 774 Hz) of the corresponding proazaphosphatranes 4–6.[2,12–15] Decreasing steric interactions between the axial proton and the NR groups in the order CH$_2$Ph > Me > H in 9, 8, and 7, respectively, may dominate in accounting for the observed acidity order. From the competitive deprotonation data with KO-t-Bu, it is possible to calculate a pK_a of 29.6 for cation 7 in DMSO and an estimate of 26.8 as an upper limit for the pK_a values of 8 and 9, assuming a pK_a of 28.6 for HO-t-Bu in this solvent.[11] It should be noted that prophosphatrane 1 and proazaphosphatranes 4–6 derive their basicity from the stability of the five-coordinate structures of their chelated conjugate acids 2 and 7–9, respectively. In this configuration, transannulation of the nitrogen lone pair makes the phosphorus unusually electron rich, and it confers electronic stability on the cation by formation of a delocalized 4-electron, 3-center bond along the three-fold axis.[9,11,13]

When proazaphosphatrane 5 is reacted with substrates providing less-electron-withdrawing Z substituents, partially transannulated structures of type B can be realized. The structures of 14–20 determined by X-ray analysis reveal a stepwise closing of the transannular distance from 3.33 down to 2.190 Å, terminating at 1.967 Å for 8 (Z = H$^+$).[16] This distance for 14 is near the sum of the van der Waals radii for P

14, Z = trans-Cl$_2$Pt(5)
15, Z = S
16, Z = S$_2$C
17, Z = cis-Br(OC)$_4$Re
18, Z = Cl$_2$Hg(5)
19, Z = MeS(S)C$^+$
20, Z = PhN=C$^+$-SMe

B

and N (3.34 Å), while in 20 it is 34% shorter and in 8 it is 40% shorter than this sum.[17] The widening of the MeN–P–NMe angle from 104.5° in 14 to 118.6° in 20 and finally to 119.6° in 8 is virtually linear ($r^2 = 0.98$) with the closing transannular bond distance. This substantial angle change at phosphorus may be associated with a lower reorganization energy associated with phosphorus rehybridization than for other atoms in the bridges tethering the P to the tertiary N.[16,18] This process may also reflect increasing strain and decreasing entropy associated with formation of the three five-membered rings in 8, which counterbalance the electron-withdrawing power of the Z substituent. The lack of a trend in the size of Z with the transannular distance in 14–20 and 8 strongly indicates the dominance of an electronic effect in this series.

Whereas 5 forms the isolable adduct 21 with PhNCS,[16] the analogous adduct with PhNCO (22) was, to our surprise, short-lived. An adduct in this reaction was

21 S
22 O

23
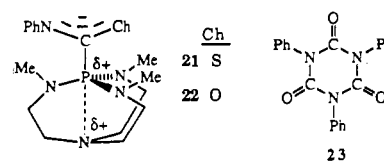
observed by ^{31}P NMR to react further with PhNCO to give the isocyanurate 23 over a period of minutes. This catalytically formed trimer precipitates in virtually quantitative yield and in TLC purity from a benzene solution containing as little as 0.33 mol% of 5.[19,20] Aryl isocyanurates are useful as activators for the continuous anionic polymerization and postpolymerization of ε-caprolactam to nylon-6 possessing a low unreacted monomer content and a highly stable melt viscosity.[21] They also contribute to the superior thermal properties and hydrolytic stability of isocyanate-based foams and plastics.[22] In our superior catalytic process, the variable basicity of 5 (owing to its flexible transannular bond) is believed to play an important role.[20]

Although compound 24 might conceivably be expected to react with strong Lewis bases such as F$^-$ or t-BuO$^-$ (with concomitant weakening or cleavage of the transannular bond), no evidence for this process was detected.[23] On the other hand, the aluminum congener 25 is a dimer whose central ring stereochemistry is still

(11) Laramay, M. A. H.; Verkade, J. G. *J. Am. Chem. Soc.* 1990, *112*, 9421.

(12) In recent years, several phosphorus compounds (e.g., t-BuN=P-[N=P(NMe$_2$)$_3$]$_3$ (P$_4$-t-Bu)) have been synthesized (Schwesinger, R. *Nachr. Chem., Tech. Lab.* 1990, *38*, 1214 and references therein), some of which are somewhat more basic than our systems. These phosphazenes are quite different from our compounds, however, in that they derive their basicity from π resonance stabilization, which can occur when the imide *nitrogen* is protonated.

(13) Schmidt, H.; Xi, S.-K.; Lensink, C.; Verkade, J. G. *Phosphorus, Sulfur Silicon* 1990, *49/50*, 163.

(14) Schmidt, H.; Lensink, C.; Xi, S.-K.; Verkade, J. G. *Z. Anorg. Allg. Chem.* 1989, *578*, 75.

(15) Carpenter, L. E.; Verkade, J. G. *J. Am. Chem. Soc.* 1985, *107*, 7084.

(16) Tang, J. S.; Laramay, M. A. H.; Young, V.; Ringrose, S.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* 1992, *114*, 3129.

(17) While the P–NMe bond distances (~1.6 Å) in these compounds are ~50% shorter than the van der Waals radii sum, it should be recalled that the transannular bond is lengthened somewhat by its 3-center, 4-electron nature.

(18) Gudat, D.; Verkade, J. G. *Organometallics* 1989, *8*, 2772.

(19) Tang, J.-S.; Verkade, J. G. U.S. Patent Appl. 08/005,231, Sept 21, 1992.

(20) Tang, J.-S.; Verkade, J. G. *Angew. Chem., Int. Ed. Engl.* 1993, *32*, 896.

(21) (a) Bukac, Z.; Sebenda, J. *Czech. CS* 227,247, 1985; *Chem. Abstr.* 1986, *105*, 173224r. (b) Bukac, Z.; Sebenda, J. *Chem. Prum.* 1985, *35*, 361; *Chem. Abstr.* 1984, *103*, 123978c. (c) Horsky, J.; Kubanek, U.; Marick, J.; Kralicek, J. *Chem. Prum.* 1982, *32*, 599; *Chem. Abstr.* 1983, *98*, 5459q.

(22) (a) Ulrich, H. *J. Cell. Plast.* 1981, *17*, 31. (b) Kordemenas, P. I.; Kresta, J. E. *Macromolecules* 1981, *14*, 1434. (c) Hoffman, D. K. *J. Cell. Plast.* 1984, *20*, 129.

(23) Pinkas, J.; Gaul, B.; Verkade, J. G. *J. Am. Chem. Soc.* 1993, *115*, 3925.

24   25   26
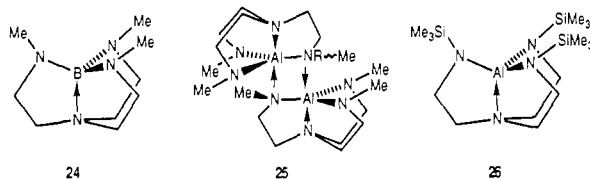
under investigation. The bulkier Me₃Si analogue of this compound, however, is a monomer (26).[23]

Chemistry at Z

The tendency for 1 and 5 to transannulate extends to their chalconides 27–31 in the presence of electrophiles El, as indicated by strong upfield shifts in the ³¹P NMR spectra of their corresponding products 32–39 (Scheme V).[13-15,24] In one case (cation 36), the five-coordinate structure was confirmed by X-ray means.[25] Salts of 38 and 39 have been isolated recently, and the structure of 38(BF₄) determined by X-ray analysis revealed a transannular distance of 2.559 Å,[26] which is only 25% shorter than the sum of the van der Waals radii and which contrasts with the considerably shorter distance found in 8 (1.967 Å[16]), wherein the proton is directly attached to the phosphorus. Equilibration studies followed by ³¹P NMR spectroscopy reveal the sequence of basicities:[26]

$$P_4\text{-}t\text{-Bu}^{12} > 5 > 31 > (Me_2N)_3P{=}NMe > DBU >$$
$$30 > (Me_2N)_3P{=}NPh$$
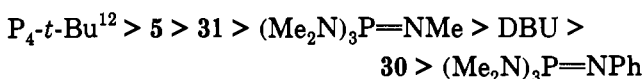
The stronger basicities of 31 and 30 than their corresponding acyclic analogues are attributed to partial transannulation in the conjugate acids 38 and 39, respectively, which was demonstrated in the case of 38 by the aforementioned X-ray structure determination.

Upon addition of excess acid to 33 or 34 or of ethylating agent to 35, new species displaying further upfield ³¹P chemical shifts were detected. These shifts were concluded to arise from binding of a second proton or ethyl carbenium ion to the apical chalcogen.[15,24] These observations attest to the formidable basicity enhancement of the Z atom by the transannular bond. The apical oxygen in silatrane 40 is also sufficiently basic to form the stable species 41 and 42.[27] Their structures

40, R = Et, El = nothing

41, R = Et, El = HOC(O)CF₃

42, R = Me, El = Me⁺

43
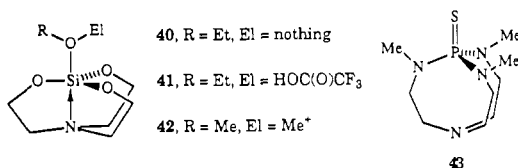
(determined by X-ray means) revealed that the Si←N distances decreased substantially from 40 (2.152 Å) to 41 (2.050 Å) and 42 (1.965 Å), with the latter being even shorter than in ClSi(OCH₂CH₂)₃N (2.02 Å[28]), which previously represented the shortest transnnular dis-

(24) Carpenter, L. E.; van Aken, D.; Buck, H. M.; Verkade, J. G. *J. Am. Chem. Soc.* 1986, *108*, 4918.
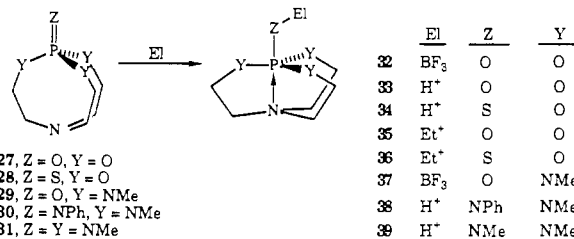
(25) van Aken, D.; Merkelbach, I. I.; Koster, A. S.; Buck, H. M. *J. Chem. Soc., Chem. Commun.* 1980, 1045.

(26) Tang, J.-S.; Dopke, J.; Verkade, J. G. *J. Am. Chem. soc.* 1993, *115*, 5015.

(27) Garant, R. J.; Daniels, L. M.; Das, S. K.; Janakiraman, M. N.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* 1991, *113*, 5728.

(28) Sidorkin, S. F.; Pestunovich, V. A.; Voronkov, M. G. *Russ. Chem. Rev. (Engl. Transl.)* 1980, *49*, 414.

Scheme V

	El	Z	Y
32	BF₃	O	O
33	H⁺	O	O
34	H⁺	S	O
35	Et⁺	O	O
36	Et⁺	S	O
37	BF₃	O	NMe
38	H⁺	NPh	NMe
39	H⁺	NMe	NMe

27, Z = O, Y = O
28, Z = S, Y = O
29, Z = O, Y = NMe
30, Z = NPh, Y = NMe
31, Z = Y = NMe

tance reported for a silatrane. Interestingly, the El group in 41 is unsymmetrically hydrogen bonded to the oxygen, and the distance of the latter atom to the OH oxygen of the acid (2.489 Å) is the shortest reported for this type of hydrogen bond. Phenol OH infrared shift measurements rank the electron-releasing ability of the silicon of 40 ahead of that in (RO)₃Si but below that of an Et group.[27]

Compound 16 is a particularly interesting example of a phosphine–CS₂ adduct. It is quite stable and can be isolated, whereas acyclic analogues (spectroscopically observed only at –20 °C) readily rearrange at room temperature:[29]

$$(R_2N)_3PCS_2 \rightarrow (R_2N)_2PS(S)CNR_2 \qquad (2)$$
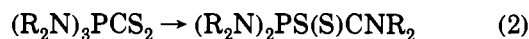
The relative stability of 16 can be attributed to its partially transannulated structure (3.250 Å[16]). Over a period of weeks in MeCN solution, however, 16 decomposes to its corresponding sulfide 43.[26] This reaction can be effectively prevented by alkylating 16 to salts (e.g., 19) with a variety of alkyl groups. The rates of these alkylations are in the expected order for S_N2 attack by the sulfur of 16 on RX, namely, MeI > EtI > *n*-PrI ≫ *i*-PrI.[26] The greater solution stability of these alkylated salts compared with 16 is at least in part ascribed to a shorter transannular bond, as in 19 (2.771 Å,[16] see above).

The rate of displacement of Z = NR₂ in titanatranes 44–46 is in the order R = Et ≫ Me ≅ *i*-Pr for a variety of ROH, ArOH RSH, and ArSH.[30] This sequence is

44	Me
45	Et
46	*i*-Pr

| 48 | F |
| 49 | OSiPh₃ |

47
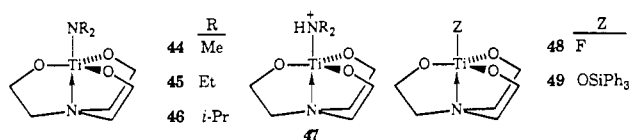
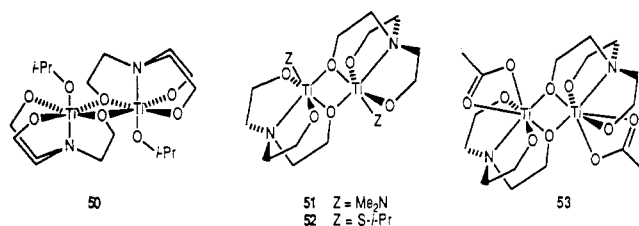unexpected if the rate is dominated by nucleophilic attack of the Ti center by the chalcogen, since the order Me > Et > *i*-Pr would then be expected on steric grounds. Consistent with the observed order, however, is the prior formation of the protonated intermediate 47, which is stabilized by electron donation from the nitrogen in the transannular bond before nucleophilic attack by the anion. The concentration of 47 is expected to be highest for R = Et and *i*-Pr, for which the basicities of the corresponding amines R₂NH are strongest (pK_a = 11.090 and 11.13, respectively), and lowest for R = Me, since Me₂NH is a weaker base (pK_a = 10.992). The slow rate of displacement of N(*i*-Pr)₂ in 46 is attributed to the increased steric inhibition of nucleophilic attack by the *i*-Pr groups.[30] Evidence for the intermediacy of

(29) Pudovik, M. A.; Kibardina, L. K.; Aleksandrova, I. A.; Khairullin, V. K.; Pudovik, A. N. *Zh. Obshch. Khim.* 1981, *51*, 530.

(30) Naiini, A. A.; Ringrose, S. L.; Su, Y.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* 1993, *32*, 1290.

47 includes (a) the faster rates observed for alcohols of greater acidity but similar steric size (e.g., CF_3CH_2OH vs EtOH), (b) the immediate displacement of NR_2 by HBF_4 to give **48** but the lack of any detectable reaction with $NaBF_4$, (c) the detection of peaks consistent with **47** wherein H = Et when **45** is reacted with Et_3OBF_4, (d) the quantitative displacement of NEt_2 in **46** by Cl when NH_4Cl is added but the lack of reaction with Me_4-NCl, and (e) the similarity in substitution rates of **44** and **45** in the presence of the strong nonnucleophilic base **5**. It should be mentioned here that unless Z is bulky (e.g., Ph_3SiO, **49**, or t-Bu), titanatranes display NMR evidence of forming fluxional dimers in solution.[31] The existence of a monomer (**49**) and several types of dimers (**50–53**) in the solid state has also been confirmed by X-ray crystallography.[1f,30–32] Interestingly, the elec-


tronegative alkoxy Z group is trans to an electron-donating nitrogen in **50**, whereas in **51** and **52** the more-electron-donating Z groups are each trans to a more electronegative bridging oxygen. In **53**, electron pair donation from both oxygens in the bidentate acetato Z group also imposes a transoid relationship of this group to a more electronegative bridging oxygen.

It is possible that the reactions in Scheme VI proceed by a mechanism similar to that of titanatranes **44–46**.[33]

Scheme VI
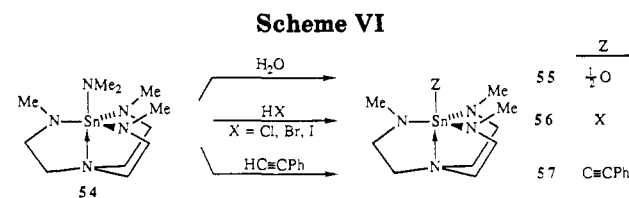
That compounds **55–57** are monomeric is confirmed by the structure of **58** determined by X-ray means and the
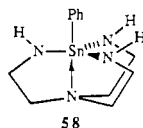
similarity of the solid-state and solution ^{119}Sn chemical shifts of **55–58**.[33] Silatranes undergo similar substitutions of the Z group, as illustrated in Scheme VII for **59**.

Chemistry at the Y Substituents

An azasilatrane can be converted to a quasiazasilatrane by introducing sterically bulky NR nitrogens, as shown in Scheme VIII.[34] Stretching of the transannular

Scheme VII

	Z
6 0	NCMe⁺
6 1	OClO₃
6 2	F
6 3	Ph

Scheme VIII
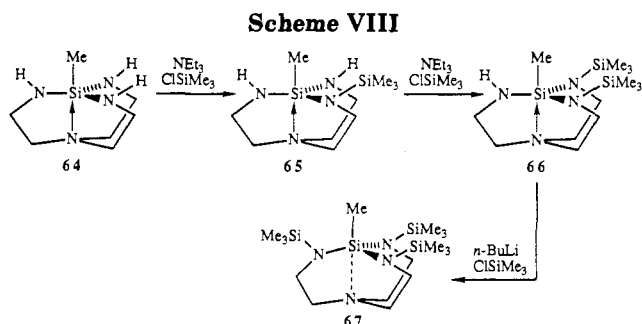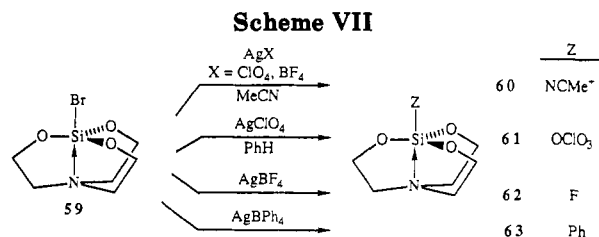
bond in **65** and **66** is indicated by the downfield ^{29}Si chemical shifts (−56.7 and −36.2 ppm, respectively) from **64** (−68.3 ppm). The further drop in $\delta\ ^{29}Si$ to −25.7 ppm for **67**, coupled with its 2.775-Å transannular distance (which is 24% shorter than the sum of the van der Waals radii), establishes this compound as the first quasiazasilatrane.[34] In this structure the tertiary nitrogen is nearly trigonal planar, though protruding slightly upward (average H_2C–N–CH_2 angle, 118.7°), and the Me_3SiN–Si–$NSiMe_3$ angles are larger than those for a tetrahedral structure (average 112.1°). Long transannular bonds have also been reported in **68** (2.477 Å[1n]) and **69** (2.89 Å[1o]). While steric factors probably play a dominant role in determining the conformation of **69**, electronic factors are probably of greater importance in **68**.

	X
7 1	lp
7 2	S
7 3	Me⁺
7 4	½ PtCl₂
7 5	½ Ni(CO)₄
7 6	½ Mo(CO)₄
7 7	½ W(CO)₄
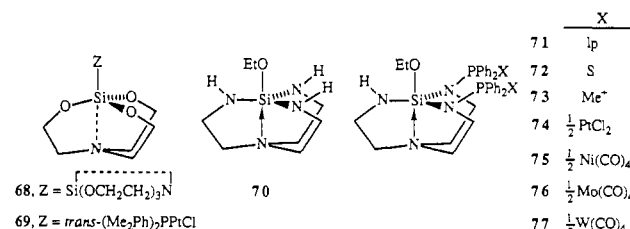
Placement of two bulky PPh_2 groups on ethoxyazasilatrane **70** gives ligand **71**, which readily forms derivatives **72** (whose structure has been determined by X-ray crystallography), dication **73**, and also the chelated complexes **74–77**, of which **74** has been structured by X-ray means.[35] Photolysis of **76** and **77** causes ejection of a CO molecule to give the corresponding tris-chelated analogues, wherein the silyl ether oxygen binds the metal. This bond is reversibly broken in the presence of excess CO.[35]

Protonation of azasilatranes on one of the equatorial nitrogens was discovered by accident in reaction 3, which was aimed at removing H_{ax} as a hydride from **78** in the form of Me_3SiH and replacing H_{ax} with the azide group.[36] Instead, the mixture of compounds shown
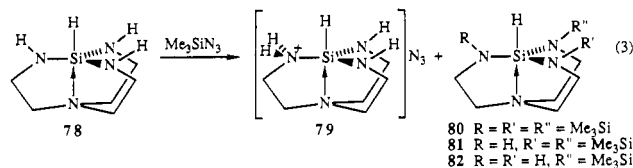
(31) Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 4628.

(32) Naiini, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 5009.

(33) Plass, W.; Verkade, J. G., manuscript in preparation.

(34) Gudat, D.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 8520.

(35) Gudat, D.; Daniels, L. M.; Verkade, J. G. *Organometallics* **1990**, *9*, 1464.

(36) Woning, J.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 4601.

resulted, including single crystals which contain **79** and unreacted **78** in a 1:1 ratio, as revealed by X-ray crystallography. The crystallographically determined structure of analogue **83** (formed in the reaction of **78** with Me₃SiNCS) revealed the location of the hydrogens as shown, as well as an elongated H_2N^+–Si bond, thus
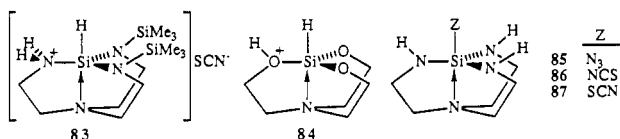
lending support to the postulate of a protonated intermediate of type **84** in the hydrolysis of silatranes.[36,37] Thermolysis of **79** caused an interesting hydrogen elimination, giving **85**. Heating of **83** gave rise to linkage isomers **86** and **87**.[37]
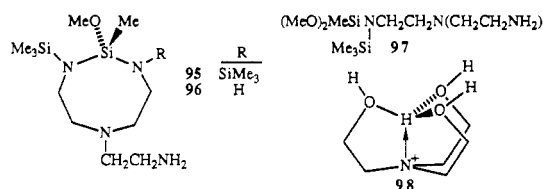
Azasilatranes react with $R'O_3SCF_3$ to form isolable salts such as **88–93**;[38] the last compound is the first reported stable example of an $(R_3Si)_3NR^+$ ion. Notable
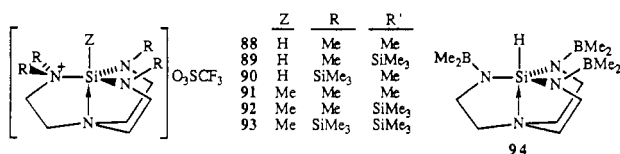
is the lack of a Z = H analogue for **93**, which is attributed to the shorter transannular bond in the less congested parent compound **80**. Thus, the more compact structure of **80** sterically protects it from attack of the Me₃Si⁺ ion. A comparison of the ²⁹Si chemical shifts of **80** (–70.1 ppm) and **67** (–25.7 ppm), whose structures possess an unusually long transannular bond (see above), supports this hypothesis. As expected, δ ²⁹Si for **93** is even further downfield (19.0 ppm) than that of **67**, since **93** is likely to lack significant transannular interaction. Similar reasoning applies to the reluctance of azasilatrane **70** to undergo electrophilic silylation of all three equatorial nitrogens compared with its less congested analogue **78**.[38]

Because azasilatranes are hydrolytically more unstable than silatranes, it was of interest to examine by ¹H and ²⁹Si NMR spectroscopy the course of solvolysis of the former compounds using the relatively mild solvent MeOH.[39] In the case of **80**, cleavage of the endocyclic N_{eq}–Si bonds by methanol was shown to follow sequential methanolysis of the three Me₃Si groups, whereas **94** quantitatively yielded N(CH₂CH₂-NHBMe₂)₃, wherein the B–N bonds survived owing presumably to robust BN π as well as σ interaction. The quasiazasilatrane **67** upon methanolysis gave ¹H and ²⁹Si NMR and GC/MS evidence for the formation of intermediates **95–97**. The greatly weakened transannular bond in **67** apparently renders the endocyclic

(37) Woning, J.; Verkade, J. G. *Organometallics* **1991**, *10*, 2259.
(38) Woning, J.; Verkade, J. G. *J. Am. Chem.* **1991**, *113*, 944.
(39) Gudat, D.; Verkade, J. G. *Organometallics* **1990**, *9*, 2172.

and exocyclic N_{eq}–Si bonds quite comparable in solvolytic reactivity.[39]

The sensitivity of azasilatranes to water was dramatically illustrated in an attempt to recrystallize to salt **60**.[33] Adventitious moisture in the solvent caused formation of the novel cation **98**, the parent of all atranes! In this structure, all of the hydrogens were located, and the central proton is hydrogen-bonded to the three oxygens.

Azametallatranes can be used as synthons for other azametallatranes. Thus reaction 4 in toluene at 70 °C gives high yields of **100** (which was structured by X-ray means) and **101**.[40] Although it would appear that
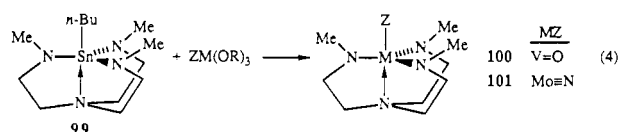

transamidation of ZM(NMe₂)₃ with (HMeNCH₂CH₂)₃N would be more direct, this approach in our hands led only to polymer in both cases. $\Delta G_{Tc}^{\ddagger}$ values for ring inversion in **100** and **101** (ca. 40 kJ/mol) calculated from their ¹H NMR spectra are somewhat higher than for azastannatranes (~33–36 kJ/mol). This is reasonable, assuming that N → M π bonding in the equatorial plane of **100** and **101** enhances the rigidity of the chelate rings.[40] In view of its highly congested structure, it is surprising that the dimeric alumaazatrane **25** can be substituted for **99** in reaction 4! These reactions are primarily thermodynamically driven and represent unusually massive yet orderly molecular reorganizations that somehow avoid polymer formation.

Reaction 4 can be viewed as the exchange of a tetracoordinated azatranyl moiety for three alkoxides. This could be construed to imply that a four-coordinate azatranyl group could be exchanged for an atranyl group (say, from (HOCH₂CH₂)₃N) since M–O bonds tend to be stronger than M–N bonds and since the atranyl group engenders less steric hindrance. We have shown recently that the reactions in Scheme IX are very efficient.[41] Strain relief is also evident in the reactions in Scheme X, wherein less sterically encumbered
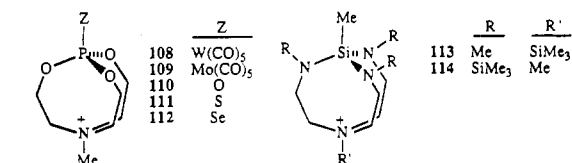
Scheme IX
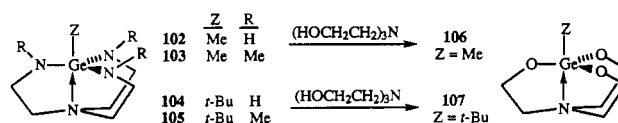
Scheme X
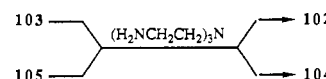
(40) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.
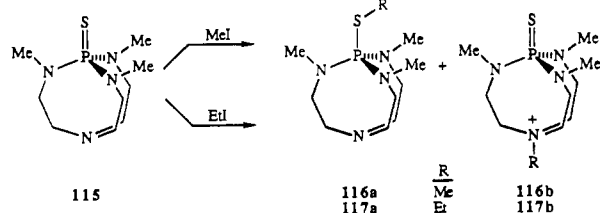(41) Wan, Y.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 79.

azatranes are formed from more sterically congested ones.

Chemistry at the Bridgehead Nitrogen

Atranes and azatranes of the pro (**A**) and quasi (**B**) types might be expected to possess a bridgehead nitrogen sufficiently basic that its quaternization becomes feasible. This is indeed the case, and cations 108–114 have been characterized,[2,34] of which the last was structured by X-ray analysis.[42] As Scheme XI

Scheme XI

reveals, however, regioisomers can also be encountered, and in both instances shown they were separated and characterized.[26] That these regioisomers are kinetically rather than thermodynamically formed was demonstrated by a lack of interconversion of **116a** and **116b** upon heating in MeCN at 40–45 °C for 10 h. This is not true of 114, however, which occurred as a mixture with its regioisomer 92, depending on the solvent and temperature.[38] Thus 92 is the more stable form in CDCl₃, whereas 114 dominates in hot hexane. Isolation attempts always resulted in mixtures of 92 and 114.

The protonated regioisomers 118a,b were observed (Scheme XII) when 28 was protonated in different solvent systems.[2] Although 118b could be isolated, attempts to isolate 118a failed, and its presence could be detected only by ³¹P and ¹H NMR spectroscopy. The formation of 118b in an aqueous medium may be

(42) Gudat, D.; Verkade, J. G., to be published.
(43) Verkade, J. G. U.S. Patent 5,051,533, Sept 24, 1991. Aldrich Chemical Company has negotiated a license with ISU Research Foundation to market this compound.
(44) Verkade, J. G. U.S. Patent Appl. 07/911,923, July 8, 1993.

Scheme XII

related to the stabilization of the ammonium cation by solvation effects in H₂O.

Conclusions

The transannular bond length in these systems is apparently quite variable, depending in part upon the electron-withdrawing power of the Z substituent and upon the steric properties of the E substituents. In cases where steric effects are minimal or absent, this bond length variability probably stems from an accommodation between a tendency to transannulate and resistance to this process caused by strain in the three five-membered rings that are formed. It will be interesting to determine from calculations currently in progress the degree of bond formation occurring at the various stages of transannulation and how such bonding might influence the NMR chemical shifts of the bridgehead atoms. In experiments underway, it will be exciting to explore further the use of proazaphosphatranes such as 5 as catalysts for other base-catalyzed reactions (e.g., the acylation of sterically hindered alcohols) and also to test its efficacy as a base[43] in reactions such as dehydrohalogenation. Azatranes such as those discussed herein are generally volatile, and they are currently being evaluated as MOCVD precursors to nonmetallic, metalloidal, and metallic nitride films.[44]

We believe that we have barely scratched the surface of the chemistry of these versatile and aesthetically pleasing molecules. Further synthetic, mechanistic, and theoretical explorations will undoubtedly turn up additional exciting and informative surprises.