

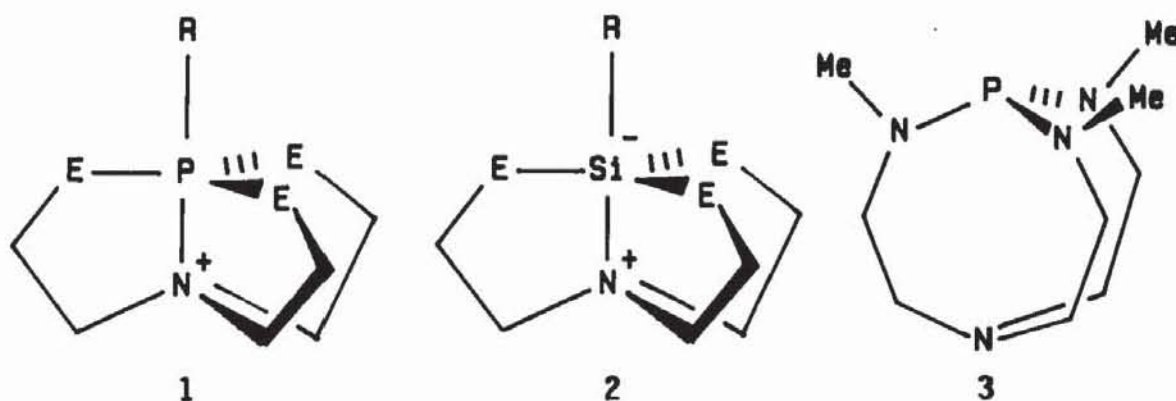
NOVEL PROPERTIES OF NEW PHOSPHATRANES AND SILATRANES

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Abstract The synthesis of the new pro-phosphatranes $YP(\overline{\text{MeNCH}_2\text{CH}_2})_3\text{N}$ ($Y = \text{lone pair, O, S, Se, BH}_3 \text{ and CH}_3^+$) containing four-coordinate phosphorus, and the tbp phosphatranes $YP(\overline{\text{MeNCH}_2\text{CH}_2})_3\text{N}$ ($Y = \text{H}^+, \text{BrCH}_2^+ \text{ and Cl}^+$) are reported. New azasilatranes of the type $YSi(\overline{\text{RNCH}_2\text{CH}_2})_3\text{N}$ ($R = \text{H, Me, SiMe}_3; Y = \text{H, OMe, OEt}$) are also reported and the results of nucleophilic substitution studies of the labile hydrogen on the equatorial nitrogens are given.

INTRODUCTION

Phosphatranes¹ (1) and silatranes² (2) are examples of trigonal-bipyramidally chelated non-metals ($E = \text{oxygen}$) that are also iso-electronic. Azasilatranes³ ($E = \text{NR}$) have thus far not

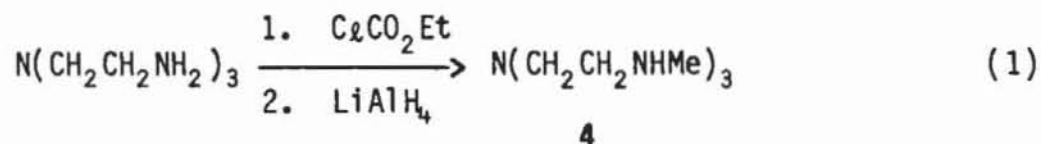


received nearly the attention accorded silatranes, and azaphosphatranes have heretofore been unreported. In the

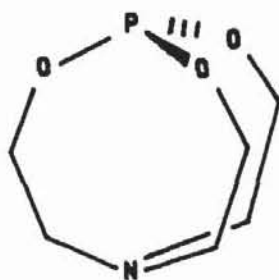
literature, the "atrane" nomenclature has traditionally been associated with structures possessing the transannular axial $N \rightarrow Si$ bond. Because we report here the synthesis and reactions of the azaphosphatrane precursor **3**, such untransannulated structures will be referred to as pro-azaphosphatranes. Also reported are reactions of azasilatranes of type **2** ($E = NH$) to form new azasilatranes in which the equatorial nitrogens are sequentially substituted by Me and PPh_2 groups.

PRO-AZAPHOSPHATRANES AND AZAPHOSPHATRANES

The new tren derivative **4** is prepared in a standard manner⁴ in two steps according to reaction 1. Upon transaminating **4**

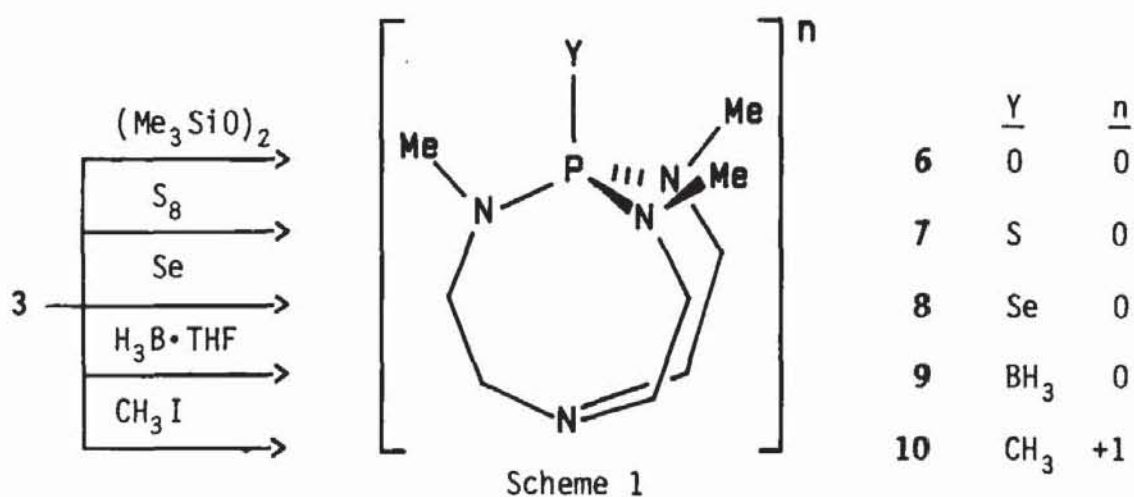


with $P(NMe_2)_3$ by heating in xylene, new ^{31}P nmr resonances at 113.8, 115.2 and 120.8 ppm slowly form. When the latter peak, associated with **3**, ceases to grow perceptibly (ca. 20 days) the reaction mixture is worked up. The peaks at 113.8 and 115.2 ppm may be associated with the mono and disubstituted intermediates. In contrast with pro-phosphatrane **5**, which polymerizes unless it is quickly derivatized in situ¹, **3** is a stable sublimable solid which can be stored indefinitely in the absence of moisture.



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In Scheme 1 are shown transformations of **3** leading to several four-coordinate pro-azaphosphatranes. The four-coordinate nature of phosphorus in all of these isolable



compounds is strongly suggested by the crystallographically determined structure of **7**,⁵ and the ³¹P chemical shifts (Table 1) which are typical for acyclic tris-aminophosphine derivatives of this type.

TABLE I ^{31}P nmr chemical shifts of pro-phosphatranes and phosphatranes.^a

Compound	$\delta^{31}\text{P}$	Solvent	Compound	$\delta^{31}\text{P}$	Solvent
3	120.8	C_6D_6	10	48.6	CDCl_3
6	20.3	C_6D_6	11	-9.2 ^d	CDCl_3
7	75.9	CDCl_3	12	-2.6	CD_3CN
8	72.2 ^b	CDCl_3	13	-20.6	CD_3CN
9	104.5 ^c	C_6D_6			

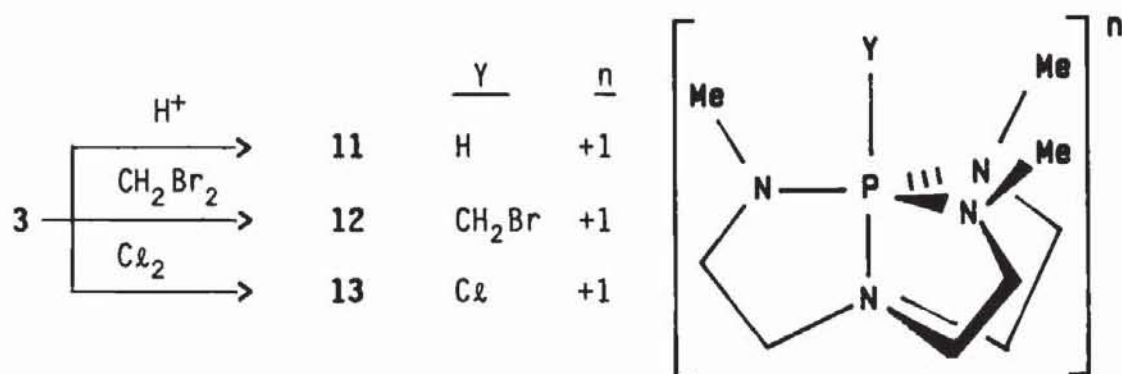
^a Relative to external 85% H_3PO_4

^b $^1\text{JPSe} = 928$ Hz

^c $^1\text{JPB} = 109$ Hz

^d $^1\text{JPH} = 491$ Hz

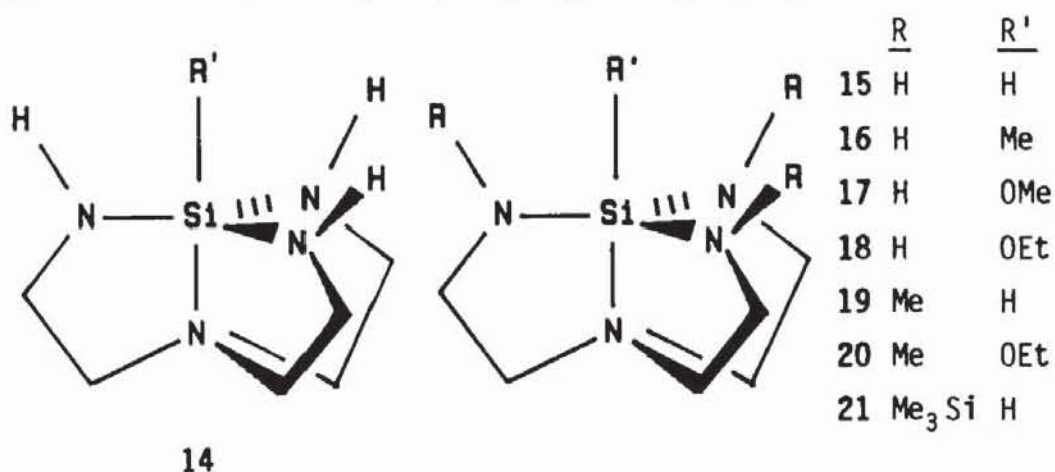
In **10**, the Me group on phosphorus apparently is incapable of inducing transannulation to form the corresponding five-coordinate azaphosphatrane structure. By increasing the electronegativity of the electrophilic substituent, however, the cationic azaphosphatranes in Scheme 2 can be synthesized. The evidence for the five-coordinate structure of these compounds consists of their upfield ^{31}P chemical shifts in the region normally associated with the *tbp* phosphorus stereochemistry. An X-ray crystallographic study of **11** is currently in progress.



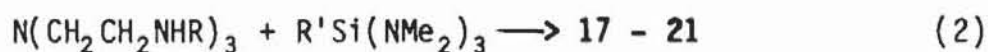
Scheme 2

AZASILATRANES

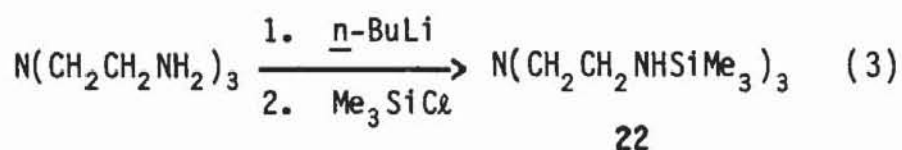
The only azasilatranes reported in the literature are those of type **14** where R' is hydrogen (**15**), methyl (**16**) or a



variety of other hydrocarbon groups.³ Using a route similar to that reported earlier³ (reaction 2) we have synthesized the new azasilatranes **17 - 21**. For the synthesis of **21**, the new



tren derivative **22** made by reaction (3) was utilized.



Evidence for the *tbp* stereochemistry around silicon in the azasilatranes stems from our X-ray crystallographically determined structure of **20**⁶ and the upfield ²⁹Si nmr shifts of such compounds (Table II) which fall in the range typically observed for silatranes.⁷

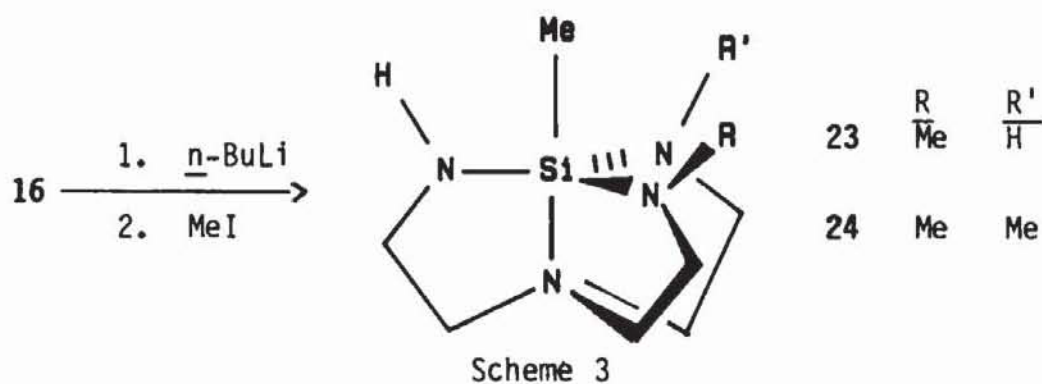
TABLE II ²⁹Si nmr chemical shifts of azasilatranes.^a

Compound	$\delta^{29}\text{Si}$	Solvent	Compound	$\delta^{29}\text{Si}$	Solvent
15	-82.3	CDCl_3	20	-87.7	CDCl_3
16	-68.0 ^{7b}	CDCl_3	21	-70.1 ^b	CDCl_3
17	-82.5	CDCl_3	25	-64.7	CD_2Cl_2
18	-82.9	CDCl_3	27	-83.0	CD_2Cl_2
19	-62.2	CDCl_3			

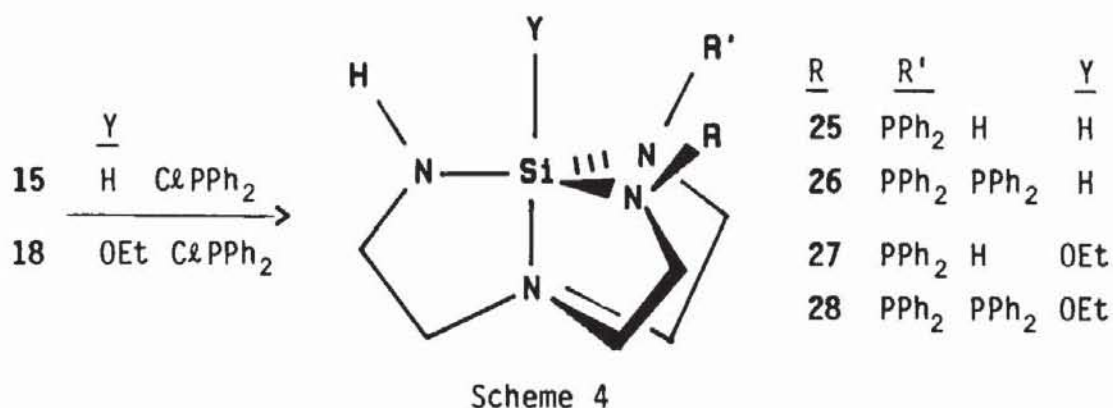
^a Relative to external TMS

^b $\delta^{29}\text{Si}$ for the Me_3Si group is 3.2 ppm.

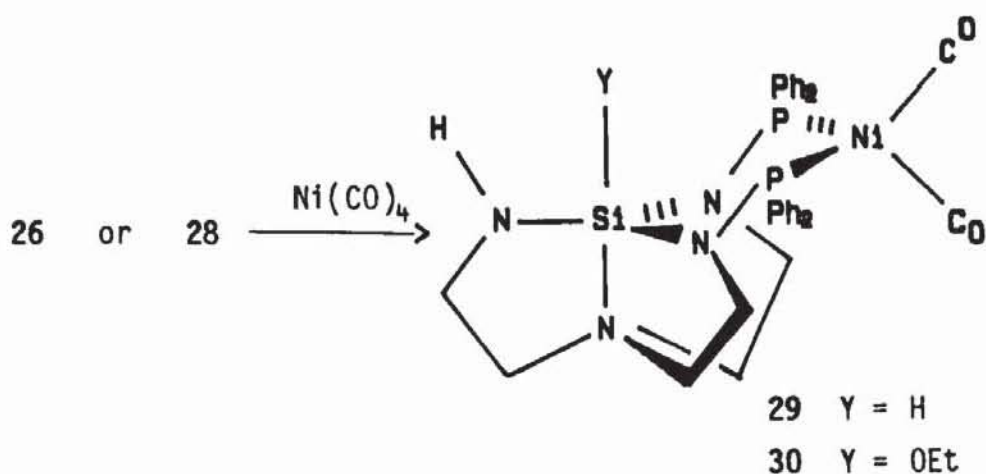
Since azasilatranes such as **15** - **18** possess three N-H groups, it was of interest to initiate an investigation of the possibility for nucleophilic substitution of the labile hydrogen on this functionality, despite the presence of steric crowding around the silicon. Treatment of **16** with one equivalent each of *n*-BuLi and MeI gives rise to a mixture of **23** and **24** (plus unreacted **16**) in Scheme 3. Treatment of **15** or **18**



with one equivalent each of ClPPh_2 and NEt_3 provided a mixture of the phosphino-substituted azasilatranes **25** - **28**. With excess reagents the disubstituted compounds **26** and **28** shown in Scheme 4 were obtained. Formation of trisubstituted phosphino derivatives was not observed under the conditions employed.



Compounds **25** - **28** are potentially interesting metal ligands. We have demonstrated the bidentate nature of **26** and **28** by their reaction with $\text{Ni}(\text{CO})_4$ to form **29** and **30** in Scheme 5.



Scheme 5

ACKNOWLEDGMENTS

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