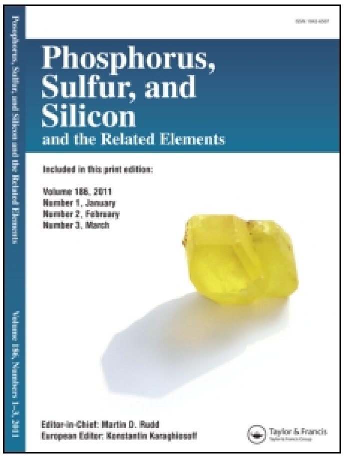

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Azaphosphatranes and Pro-Azaphosphatranes

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AZAPHOSPHATRANES AND PRO-AZAPHOSPHATRANES

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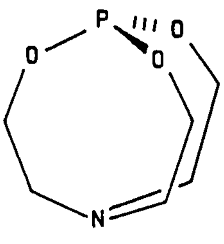
Abstract. Reactions of $P(MeNCH_2CH_2)_3N$, a new powerfully basic pro-azaphosphatrane, are discussed. Some of these reactions, such as oxidation with chalcogens and adduct formation with BH_3 and CS_2, lead to pro-azaphosphatranes in which the phosphorus has become formally tetracoordinate. Other reactions, such as protonation or oxidation followed by BF_3 adduct formation leads to $HP(MeNCH_2CH_2)_3N^+$ and $F_3BOP(MeNCH_2CH_2)_3N$, respectively, which possess phosphatrane structures featuring five-coordinate phosphorus.

Earlier it was shown from our laboratories that the prophosphatrane 1 is formed in low yield 1 (ca. 10%) and is quite unstable with respect to polymerization.[1] It was thus necessary to oxidize this compound in solution to obtain stable pro-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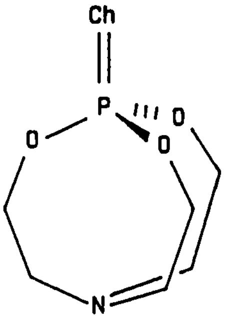
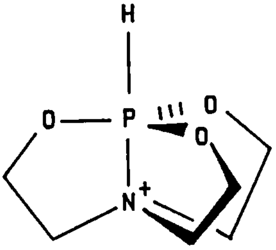


	Ch
2a	O
2b	S
2c	Se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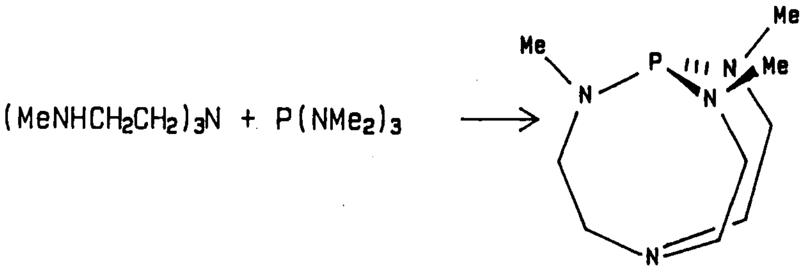
phosphatrane compounds such as 2a-c or to protonate 1 to form the novel hypercoordinate phosphatrane 3, which was structured by X-ray means.

We have recently synthesized by reaction 1 the pro-azaphosphatrane 4 in 50% yield.[2] In contrast to 1, compound 4 is a stable sublimable solid which can be stored indefinitely in the absence of moisture.

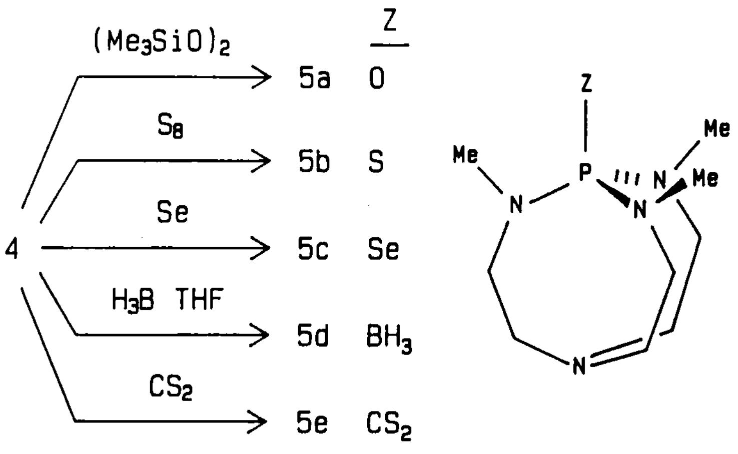


4

(1)

Compound 4 is readily converted to the tetracoordinated phosphatranes 5a-e as shown below.[2] The structures of 5b and 5e, determined by X-ray means,[3] confirm the open structure indicated by ^{1}H, ^{31}P and ^{13}C nmr spectroscopy.

In the presence of BF_3, 5a provides isolable 6, in which the five-coordination of phosphorus is suggested by the upfield ^{31}P chemical shift (-2.2 ppm), its characteristic ^{1}H nmr spectrum and the loss of the P=O stretching band of 5a in the ir spectrum. Apparently the BF_3 moiety is capable of polarizing the phosphoryl oxygen sufficiently to stabilize the chelated pentacoordinate structure in which the multiplicity of the thermodynamically stable P=O bond is broken.



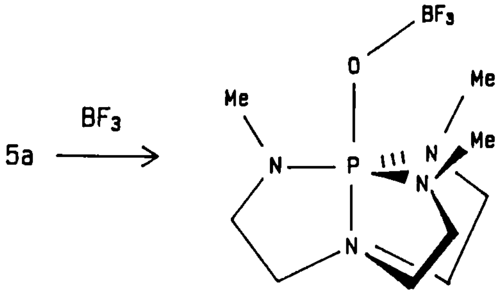
(2)

(3)

(4)

(5)

(6)



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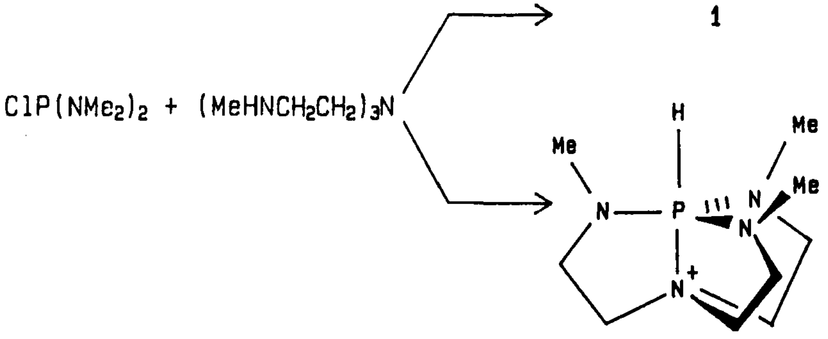
(7)

In an effort to improve the yield of 1, we attempted reaction (8). Instead of observing the formation of 1, an 82% yield of 7 was realized as the chloride salt, in spite of the presence of excess Et_3N.[4] That pro-azaphosphatrane 1 is the strongest phosphorus base thus far reported, is demonstrated by its ability to deprotonate a variety of weak acids including water and protonated "proton sponge" (1,8-bis-dimethylamino-naphthalene). The salt $7(Cl^-)$ does deprotonate in contact with dry NaOH, but only after a temperature of 200° is reached,



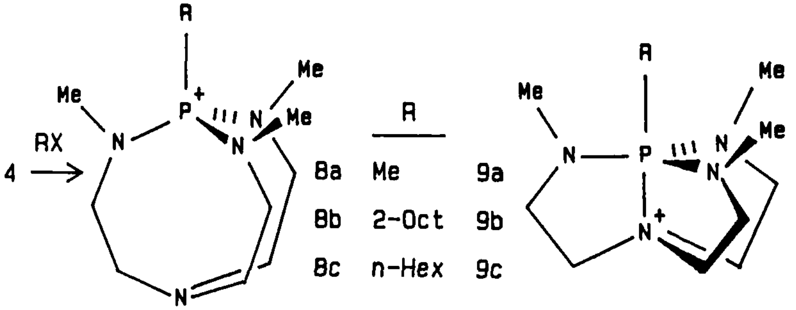
(8)

(9)

7

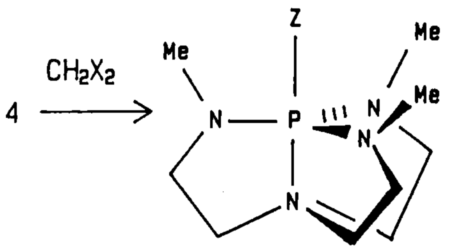
producing a 53% yield of 1. The structure of 7(Cl$^-$), which has been verified by X-ray crystallography, features a trigonal bipyramidal five-coordinate phosphorus atom in which the non-apicophilic hydrogen substituent is in an axial position. The ^{31}P chemical shift of this compound (-11 ppm) is in the expected region for compounds of this type.

Interestingly, alkyl halides are attacked by the "soft" phosphorus of 4 instead of its "hard" nitrogen, giving 8a-c. However, this does not occur in order to facilitate transannulation to 9a-c. Apparently, the R groups are not



(10)

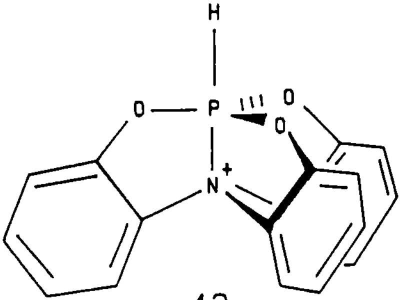
sufficiently electronegative to encourage an axial P-N bond to form. On the other hand, methylene halides (reaction 11) do facilitate transannulation:



	Z
10	CH_2Br
11	CH_2I

(11)

On the basis of solution nmr data, it was recently reported[5] that 12 is formed upon protonation of the corresponding pro-phosphatrane. The instability of this cation precluded its isolation, however. Comparing these results with those described here, it appears that the fused benzo rings in atranes such as 12 permit less flexibility in the polycyclic cage compared with our systems.



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