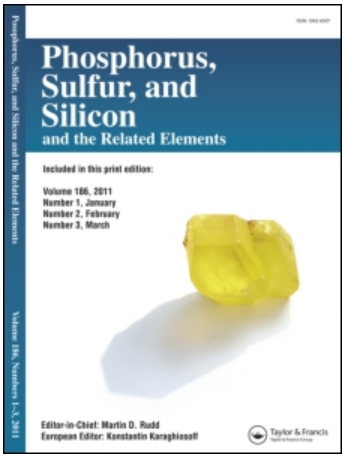

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ELECTRONIC AND STRUCTURAL ASPECTS OF RECTANGULAR PYRAMIDAL HYPERVALENT 10-P-5 COMPOUNDS

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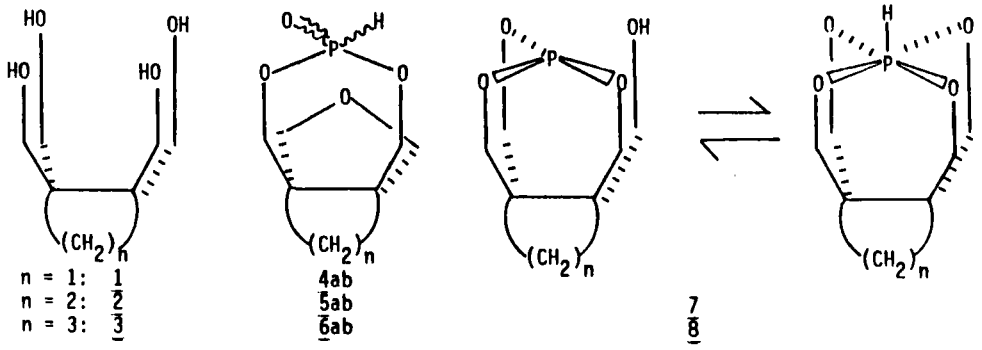
Abstract New examples of cationic and neutral trigonal bipyramidal and rectangular pyramidal 10-P-5 species are presented. Their spectral properties (especially their NMR characteristics) and the factors stabilizing them are discussed.

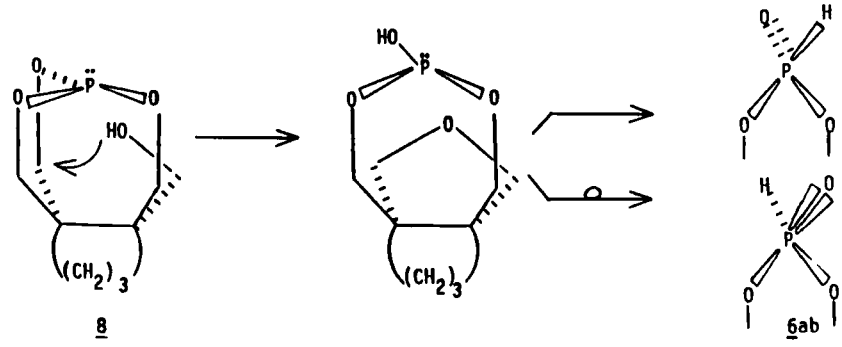
The square pyramidal (SP) and rectangular pyramidal (RP) geometries for hypervalent phosphorus lie higher than the TBP conformation. Where substantial deviations from TBP toward SP or RP geometries have been found, it is generally the case that two bidentate five-membered ring chelates containing an unsaturated C-C bond are present in the spirocyclic structures[1]. In the two cases wherein both chelates are saturated, one of the rings is a four-membered one that appears to strain the structure from 84 to 87% along the Berry coordinates toward SP[1]. Because the steric and electronic factors influencing distortions from the TBP conformation are not well understood, we have begun a program of synthesizing compounds in which the hypervalent non metal is locked into an RP configuration by molecular constraints.

To this end we have synthesized the tetraols 1-3[2] and allowed them to react with P(III) and P(V) phosphorus reagents. Heating 1, 2 or 3 with $P(NMe_2)_3$ appparently gives (in addition to polymer) the interesting isomers 4ab, 5ab and 6ab, respectively, as sublimable solids. In the cases of 2 and 3, an

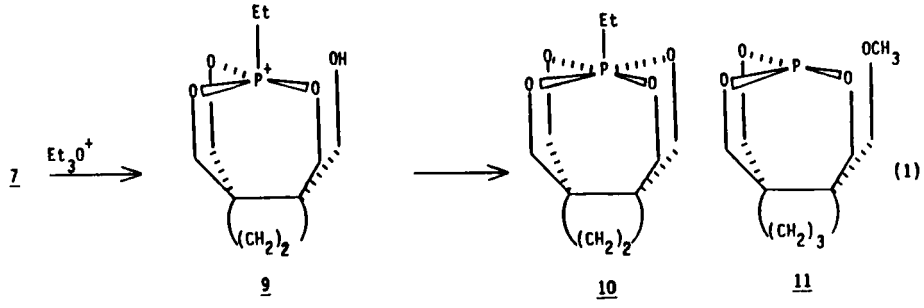
additional product 7 and 8, respectively, cosublimes and can be purified by recrystallization. Apparently the analogous product with 1 is forbidden by the cyclopropane ring which too greatly separates the alkoxy groups. Although both 7 and 8 display solution $\delta^{31}P$ values (116 and 111 ppm, respectively) typical of phosphite esters, their CH_2O protons appear as AB quartets consistent with rapid equilibration between the three and five-coordinate structures. The absence of POCH and PH coupling also suggests fluxionality of the PH proton in the above equilibrium. In the infrared, a peak for both compounds is observed in the 2300 cm^{-1} region which can be assigned to the PH stretching frequency. The interesting rearrangement of 8 upon standing in



solution to 6ab may occur as follows:

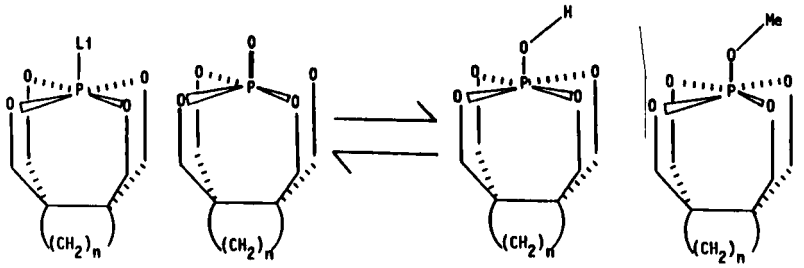


An attempt to make 10 by reaction (1) gave a sublimable solid whose major constituent appears to be 11 as shown by ^{31}P nmr (112 ppm) and an appropriately complex ^{1}H nmr spectrum. A minor peak in the ^{31}P nmr at -12 ppm may indicate the presence of a small amount of 10, which to date has not been separated. The anion 9 exhibits a ^{31}P peak in the phosphonium region. Treatment of 9 with base yields 10. In the presence of n-BuLi, both 7 and 8 give a single ^{31}P peak at -32 ppm suggestive of the formation of 12 and 13, respectively, which can be isolated as white solids. A variety of methylating agents appeared to cause decomposition of 12 and 13 and neither the methyl analogue of 10 nor 11 (nor the analogues where n = 3) could be isolated. Transition metal complexes of phosphite esters such as 7 and 8 can also apparently contain four or five-coordinate phosphorus.



(1)

Reaction of 2 and 3 with O=P(triazole)$_3$ affords 14 and 15, respectively, which are also accessible from the parent phosphites 7 and 8 by ozonolysis. In CH_3CN solution 14 is mainly in the form of the 10-P-5 tautomer ($\delta^{31}P$ = -12.2) while 15 exists predominantly in the 10-P-4 configuration ($\delta^{31}P$ = -6). In the presence of pyridine or n-BuLi, the corresponding 10-P-5 anions are formed which can be alkylated to 16 and 17 ($\delta^{31}P$ = -12). Reaction of 1 with O=P(triazole)$_3$ has thus far afforded no tractable product.

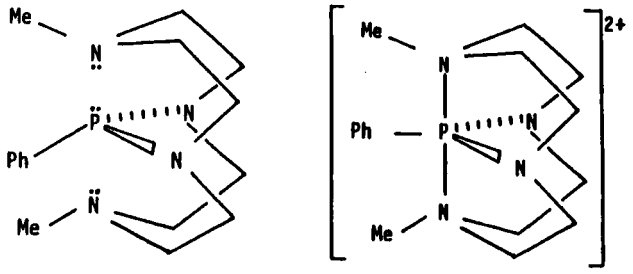


n = 2: 12 14 16

n = 3: 13 15 17

All five-coordinate species characterized thus far are formed in very low yield (<5%). From these preliminary experiments, it is clear that rigid SP nonmetal compounds can be formed involving a combination of six- and seven-membered saturated rings in a cage system. However, the stability of these compounds seems to be strongly influenced by the size of the carbon ring below the cage. It also appears that hypervalency in these systems is favored when there are five electronegative oxygens rather than four around the RP phosphorus atom.

From a new cyclic tetramine we were able to synthesize 18 which in the mass spectrometer and on reaction with bromine yields the new hypervalent dication 19.



18 19

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