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Aminophosphinidene derivatives

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AMINOPHOSPHINIDENE DERIVATIVES

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Abstract Elimination and fragmentation reactions lead to carbene analogous iminophosphanes which undergo 2+1 addition as well as insertion reactions. Secondary aminophosphanes and amino substituted three-membered phosphorus rings are phosphinidene transfer reagents and therefore valuable building units for cyclic and acyclic compounds. Synthetic routes to amino substituted diphosphenes and their reaction behaviour are reported.

CARBENE ANALOGOUS IMINOPHOSPHANES

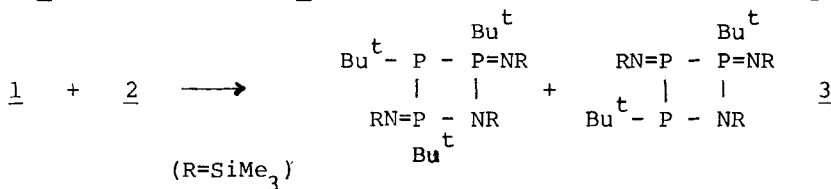
Frontier orbital theory predicts¹ for methylenephosphane two almost degenerate orbitals π and σ , with the π slightly above the σ . In contrast to in iminophosphane the σ orbital is distinctively over the π orbital.

In accord with these theoretical predictions is the reaction route of P-alkylated iminophosphanes 1 which easily undergoes (2+1)-cycloaddition to give the azadiphosphiranes 2^{2,3}.



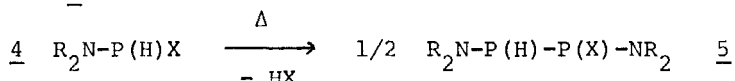
On the contrary the isoelectronic phosphalkenes $\text{Bu}^t - \text{P} = \text{CHR}$ ^{3,4} show the expected olefinic behaviour.

Another example of the carbene analogy is the ring expansion reaction of 2 by insertion of 1 to give the azatriphosphetidines 3⁵.



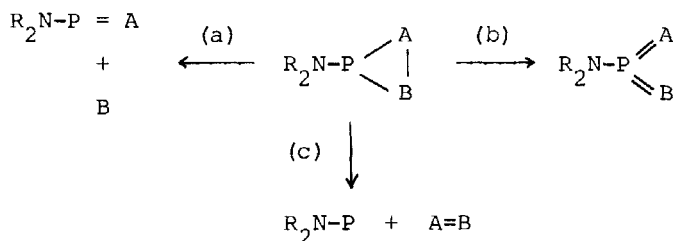
AMINOPHOSPHINIDENES TRANSFER REAGENTS

Various secondary aminophosphanes 4 ($X=NR_2'$, F) ⁶ has been synthesized and studied with respect to their behaviour as aminophosphinidene transfer reagents, according to their formation of diphosphanes 5

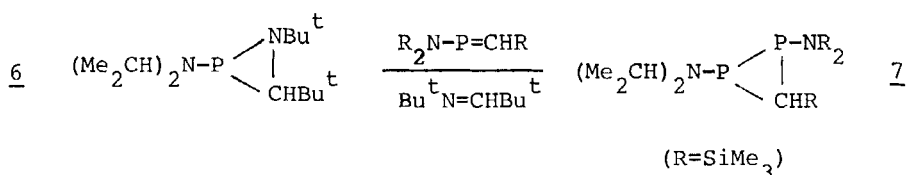


Good sources for this reaction are the cases $X=F$, $R=SiMe_3$ and $X=NR_2'$, $R=R'=CHMe_2$.

Three membered λ^3 -phosphorus heterocycles decompose into three reaction channels - route (a), (b) and (c) - depending on the fragments A and B, as it is shown for the isovalent systems azadiphosphirane ($A=NBu^t$, $B=PBu^t$) ⁷ (a), diazaphosphirane ($A=NBu^t$, $B=NBu^t$) ⁸ (b) and azaphosphirane ($A=NBu^t$, $B=CHBu^t$) or phosphirane ($A=B=CHBu^t$) ³ (c).

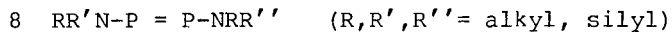


The synthetic utility of the azaphosphirane 6 as a source for aminophosphinidene is proven by its thermally induced decomposition; e.g. from aminomethylenephosphene the corresponding diphosphirane 7 is obtained ⁹.



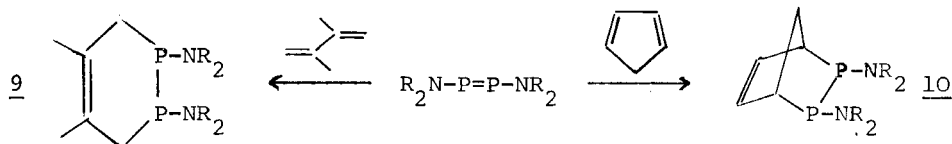
DIAMINODIPHOSPHENES

Various symmetrically ($R'=R''$) and unsymmetrically substituted ($R'\neq R''$) diaminodiphosphenes 8 of different kinetic stabilities were synthesized¹⁰.

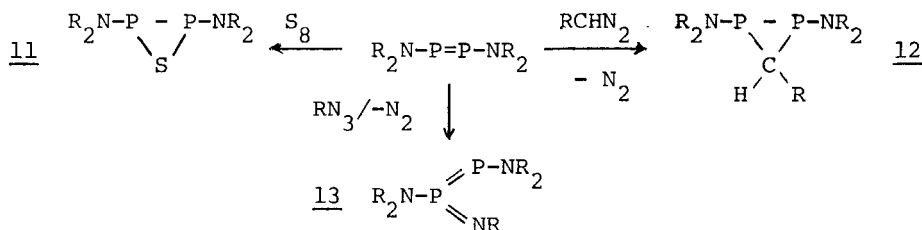


In diaminodiphosphenes 8 the $\delta^{31}P$ n.m.r. shift strongly depends on substituents (at N): Increased replacement of silyl by alkyl groups causes $\delta^{31}P$ high field shifting, as well as strong temperature dependance of the resonances. According to theory¹¹ the coplanar versus bisorthogonal conformations are depending on substituents; e.g. silyl groups promote bisorthogonality. This agrees with a structure elucidation¹⁰.

Diaminodiphosphenes like $R_2N-P=P-NR_2$ ($R=SiMe_3$) react with dienes (2,3-dimethylbutadiene or cyclopentadiene) to the corresponding (2+4)-cycloadducts 9³ and 10¹² (Diels Alder reaction).



Oxidation with sulfur or silyldiazoalkane leads to thiadiphosphirane 11 (diphosphirane 12 resp.)^{3,12}. In the presence of silylazide the corresponding open form, the iminodiphosphene 13 is formed³.



These reactions are compared with the corresponding reactions of amino substituted iminophosphanes and methylenephosphenes.

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