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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### 1,3-Bisylidylsubstituted Cyclotetraphosphines

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## 1,3-Bisylidylsubstituted Cyclotetraphosphines

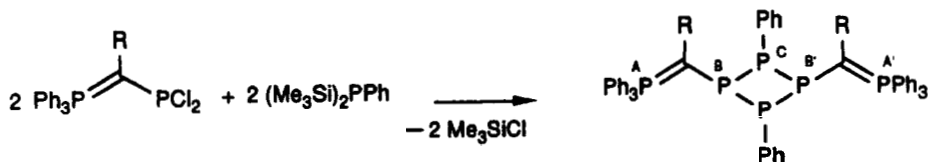
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Ylide substituents effectively stabilize low coordination of phosphorus as long as it is bonded to electronegative partners<sup>1,2</sup>. Thus ylidyl-thioxophosphines and -selenoxophosphines are monomeric in solution and crystal<sup>3</sup>. In contrast ylidsubstituted diphosphines are unstable towards dimerization in accord with the anticipated polarity of the PP-bond:



Consequently, the reaction of ylidylchlorophosphines and bis(trimethylsilyl)phenylphosphine yields cyclotetraphosphines:

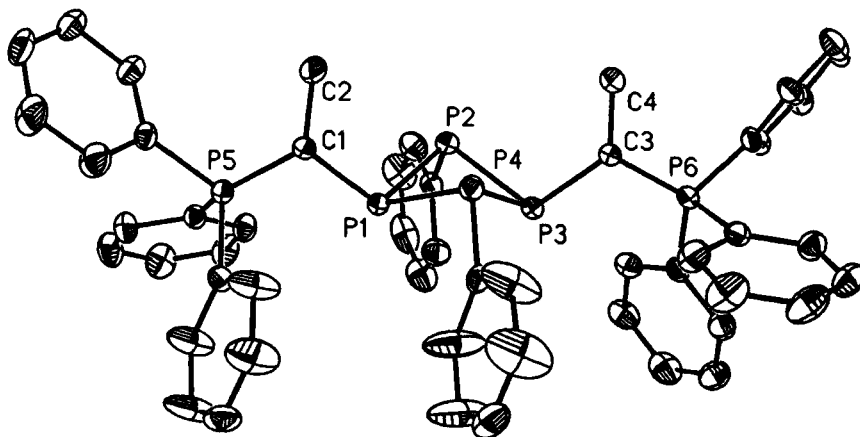


### <sup>31</sup>P-NMR Data of the cyclotetraphosphines

R	$\delta_A$	$\delta_B$	$\delta_C$	${}^6J_{AA'}$	${}^2J_{AB}$	${}^4J_{AB'}$	${}^3J_{AC}$	${}^2J_{BB'}$	${}^1J_{BC}$
Me	23.8	-13.6	-44.0	2.0	163.2	2.9	6.2	150.0	-129.9
3-MeC <sub>6</sub> H <sub>4</sub>	19.4	-22.0	-29.1	2.9	183.2	3.0	5.6	179.7	-131.8

Their <sup>31</sup>P-NMR spectra represent AA'BB'C<sub>2</sub>-spinsystems indicating the expected head/tail-dimer in an all-trans configuration. The two-bond PP-coupling constants  $J_{BB'}$  are exceptionally high and point to a transannular approach of the lone pairs at the two concerned phosphorus ring members. A similarly strong coupling was observed before only for a head/head-dimer<sup>4</sup>.

These conclusions are confirmed by the X-ray structure analysis of the methyl-substituted derivative:



Molecular structure of the methyl derivative (without hydrogen atoms, thermal ellipsoids at the 25% probability level)

The tetraphosphine ring is folded, with all substituents in equatorial positions. The ylide carbon atoms are (almost) planar coordinated (sum of angles  $360^\circ$  and  $356^\circ$ ). As it is generally the case in *C*-phosphino-substituted phosphonium ylides the phosphonio-groups are orientated synperiplanar to the electron lone pairs<sup>5,6</sup> at P1 and P3. The structure seems to strive for a relatively long distance between the phosphonium centers P5 and P6: The tetraphosphetane ring is less strongly folded along P2...P4 than along P1...P3 (interplanar angles  $139.8^\circ$  and  $122.5^\circ$ , respectively) and the pyramids at P1 and P3 are less steep than those at the phenyl-substituted atoms P2 and P4 (averaged sum of angles  $299^\circ$  and  $289^\circ$ , respectively).

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