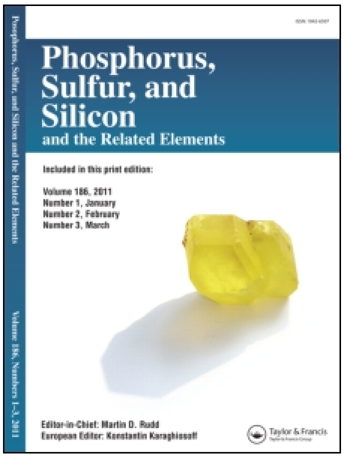

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1,3-Bisylidylsubstituted Cyclotetraphosphines

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1,3-Bisylidylsubstituted Cyclotetraphosphines

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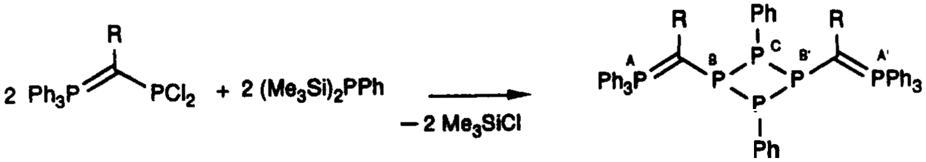
Ylide substituents effectively stabilize low coordination of phosphorus as long as it is bonded to electronegative partners[1,2]. Thus ylidyl-thioxophosphines and -selenoxophosphines are monomeric in solution and crystal[3]. In contrast ylidsubstituted disphosphines are unstable towards dimerization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

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

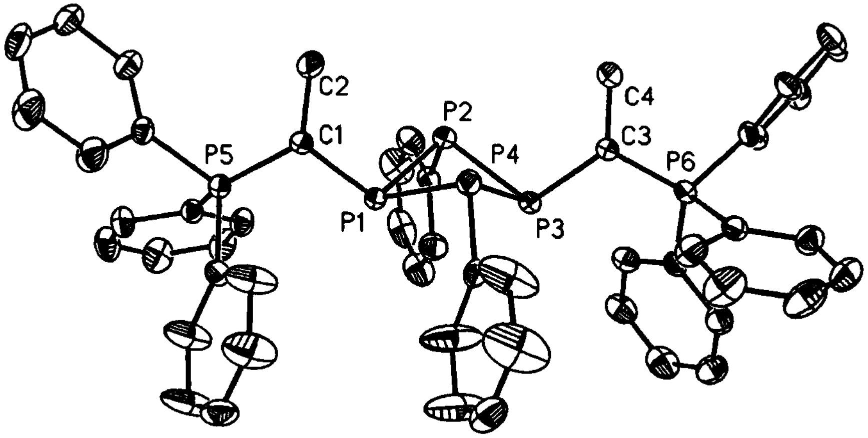


^{31}P-NMR Data of the cyclotetraphosphines

R	δ_A	δ_B	δ_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$_6$H$_4$	19.4	-22.0	-29.1	2.9	183.2	3.0	5.6	179.7	-131.8

Their ^{31}P-NMR spectra represent AA'BB'C$_2$-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 transanular 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[4].

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° and 356°). As it is generally the case in *C*-phosphino-substituted phosphonium ylides the phosphonio-groups are orientated synperiplanar to the electron lone pairs[5,6] 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° and 122.5°, 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° and 289°, respectively).

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