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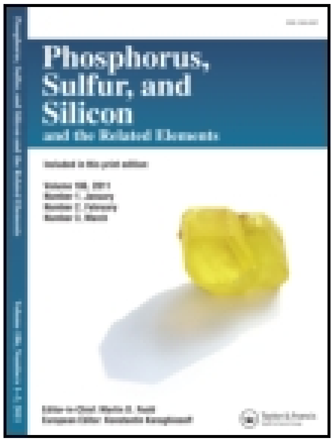

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NEW NONGEMINAL CYCLOPHOSPHAZENES

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NEW NONGEMINAL CYCLOPHOSPHAZENES

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A series of new nongeminally-substituted cyclic phosphazenes with various substituents has been prepared via deprotonation-substitution reactions at the Me groups of both the cis *and* trans *isomers of* $[(Me)(Ph)PN]_3$. *Treatment of* $[(Me)(Ph)PN]_3$ *with* n-*BuLi followed by reaction with organic electrophilic reagents affords a variety of cyclic derivatives,* $[(RCH_2)(Ph)PN]_3$, $[R = Me, Cl, Br, I, (CH_2)_2Br, CH_2CH{=}CH_2, SR, C({=}O)OLi, C({=}O)OMe, C({=}O)OEt]$. *The structures of theses* cis *cyclic phosphazenes, which were obtained by x-ray diffraction, illustrate the basket-like shape of the molecules. Heating the* cis *and* trans *isomers of the parent* $[(Me)(Ph)PN]_3$ *produced mixtures of cyclic trimers and tetramers. The latter were isolated and characterized by x-ray crystallography. Nanoparticles of gold and silver were prepared by reduction of metal salts with a reducing agent in the presence of selected trimers.*

Keywords: Nanoparticles; nongeminal; P—C substituents; phosphazene; tetramer; trimer

Although a number of cyclic phosphazenes with alkyl and aryl groups have been prepared and studied,[1] nongeminal substitution of alky and aryl groups at phosphorus is relatively new. By contrast, the preparation of phosphazene polymers with nongeminal alkyl and aryl substituents, e.g., $[(Me)(Ph)PN]_n$, via condensation polymerization of N-silylphosphoranimines is well-established.[2] Cyclic phosphazenes with nongeminal substituents present interesting stereochemical variety since two isomers are possible for nongeminal trimers, $[RR'PN]_3$ and four isomers may exist for the corresponding tetramers. In this

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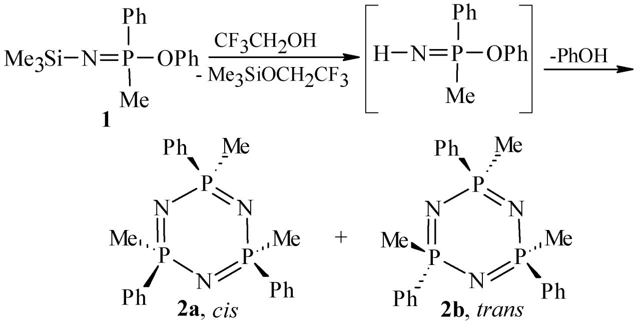
article we discuss the preparation, characterization, and selected reactions of cyclic phosphazenes with nongeminally substituted methyl and phenyl groups.

RESULTS AND DISCUSSION

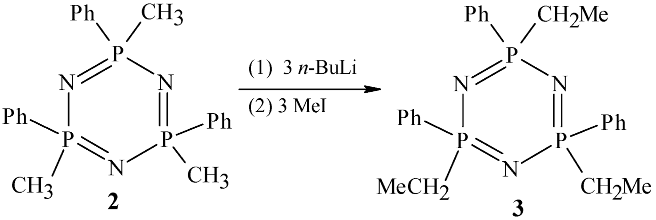
The diverse reactivity of a class of silicon-nitrogen-phosphorus compounds known as N-silylphosphoranimines, $Me_3SiN{=}P(X)R'R''$, has been exploited to make a number of new compounds, including the polyphosphazenes with P—C bonded alkyl and aryl substituents.[2] In the course of these studies, it was found that treatment of $Me_3SiN{=}P(X)(Me)(Ph)$, where X = OPh or OCH_2CF_3, with simple alcohols facilitates cleavage of the silicon-nitrogen bonds as well as the phosphorus-oxygen bonds. While mixtures of products were obtained with most alcohols, treatment of $Me_3SiN{=}P(OPh)(Me)(Ph)$, **1**, with CF_3CH_2OH in a 6:1 mole ratio in the absence of solvent gives ca. 90% yields of a mixture of the *cis* and *trans* isomers of $[(Me)(Ph)PN]_3$, **2**.[3] A large amount of phenol was also formed suggesting that the initial reaction might have produced the intermediate N—H phosphoranimine which then lost PhOH (Eq. 1). It was necessary to remove the PhOH by washing with aqueous base before these isomers were separated by column chromatography. The ratio of *trans* to *cis* isomers was ca. 2.8 to 1. Both isomers were fully characterized by NMR spectroscopy, x-ray crystallography, and elemental analysis. The *cis* isomer is particularly interesting since the phenyl groups on the same side of the nearly planar PN ring resemble a basket.



(1)

Detailed studies of the thermolysis of cyclic phosphazenes fully substituted with phenyl or methyl groups have shown that while ring opening allows for the interconversion of trimers and tetramers, no polymer formation can be observed.[4] The same type of equilibrium between trimers and tetramers occurs when either the *cis* or the *trans* isomers of **2** are heated. At 220°C the trimers predominate with the *trans* isomer favored over the *cis* by at least 3:1. Less than 15% of the trimers were converted to tetramers at this temperature as determined by ^{31}P NMR spectroscopy. However, at 250°C, up to 70% of the trimers were converted to tetramers after almost two weeks. Thus it was possible to isolate significant quantities of the tetramers. Indeed, each of the four possible isomers were separated using a sequence based on solubility differences, column chromatography, and formation of HCl adducts. Crystallographic analysis of each isomer shows that these have geometries that may be identified as cone, partial cone, 1,2-alternate, and 1,3-alternate by analogy to calix[4]arene or as *cis*, *α-trans, β-trans,* and *γ-trans* respectively.[5]

Like the well-studied polymer, poly(methylphenylphosphazene), $[Me(Ph)PN]_n$, there are three reactive sites in the simple *cis* and *trans* isomers of the trimer $[(Me)(Ph)PN]_3$, **2**. Although the aryl groups are susceptible to electrophilic aromatic substitution[6] and the lone pairs of electrons on the backbone nitrogen atom coordinate readily to many Lewis acids,[7] the methyl group provides the richest source of new polymers via deprotonation-substitution reactions.[8] Hence, we have focused on the derivatization of methyl groups[1] to form new nongeminal substituted cyclic phosphazenes.[9] Simple deprotonation with *n*-BuLi followed by treatment with the simple electrophile MeI was used to demonstrate the feasibility of the process (Eq. 2). The *trans* isomer cleanly goes to the tri-substituted derivative with three equivalents of the reagents, but the *cis* isomer yields both di- and tri-substituted products under similar conditions. This is likely due to the fact that the deprotonated ion formed from the *cis* isomer is less soluble. A variety of other electrophiles have been used since the initial report[9] and afford variations of mono-, di-, and tri-substituted nongeminal cyclics, $[(RCH_2)(Ph)PN]_3$, where R = Cl, Br, I, $(CH_2)_2Br$, $CH_2CH{=}CH_2$, SR, C(=O)OLi, C(=O)OMe, and C(=O)OEt.



(2)

Several of these new cyclic phosphazenes have been used to stabilize metal nanoparticles as has been observed for the analogous polymer, $[(Me)(Ph)PN]_n$.[10] Nanoparticles of gold and silver were prepared by reduction of metal salts such as $NaAuCl_4$ or $AgNO_3$ with a reducing agent (e.g., $NaBH_4$) in the presence of the trimer $[(LiOOCCH_2)(Ph)PN]_3$ in water. The metal nanoparticle composites were characterized by UV-vis spectroscopy and transmission electron microscopy (TEM).

REFERENCES

[1] a) K. D. Gallicano, R. T. Oakley, and N. L. Paddock, *J. Inorg. Nucl. Chem.*, **42,** 923 (1980); b) K. D. Gallicano, R. T. Oakley, N. L. Paddock, and R. D. Sharma, *Can. J. Chem.*, **59,** 2654 (1981); c) R. T. Oakley and N. L Paddock, *Can. J. Chem.*, **53,** 3038 (1975); d) T. N. Ranganathan, S. M. Todd, and N. L. Paddock, *Inorg. Chem.*, **12,** 316 (1973); e) P. J. Harris and L. A. Jackson, *Organometallics*, **2,** 1477 (1983).

[2] R. H. Neilson and P. Wisian-Neilson, *Chem. Rev.*, **88,** 541 (1988).

[3] P. Wisian-Neilson, R. S. Johnson, H. Zhang, et al., *Inorg. Chem.*, **41,** 4775 (2002).

[4] a) H. R. Allcock and D. B. Patterson, *Inorg. Chem.*, **16,** 197 (1977); b) H. R. Allcock and G. Y. Moore, *Macromolecules*, **8,** 377 (1975).

[5] a) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62,** 247 (1962); b) A. J. Berlin, B. Grushkin, and L. R. Moffet, Jr., *Inorg. Chem.*, **7,** 589 (1968).

[6] P. Wisian-Neilson, M. Bahadur, J. M. Iriarte, and C. E. Wood, *Macromolecules*, **27,** 4471 (1994).

[7] P. Wisian-Neilson and F. J. Garcia-Alonso, *Macromolecules*, **26,** 7156 (1993).

[8] a) P. Wisian-Neilson, M. S. Islam, S. Ganapathiappan, et al., *Macromolecules*, **22,** 4382 (1989); b) A. L. Crumbliss, D. Cooke, J. Castillo, and P. Wisian-Neilson, *Inorg. Chem.*, **32,** 6088 (1993); c) P. Wisian-Neilson, L. Bailey, and M. Bahadur, *Macromolecules*, **27,** 7713 (1994); d) P. Wisian-Neilson and G.-F. Xu, *Macromolecules*, **29,** 3457 (1996); e) P. Wisian-Neilson and M. A. Schaefer, *Macromolecules*, **22,** 2003 (1989); f) P. Wisian-Neilson and C. Zhang, *Macromolecules*, **31,** 908 (1998).

[9] J.-H. Jung, H. Zhang, and P. Wisian-Neilson, *Inorg. Chem.*, **41,** 6720 (2002).

[10] C. H. Walker, J. V. St. John, and P. Wisian-Neilson, *J. Am. Chem. Soc.*, **123,** 3846 (2001).