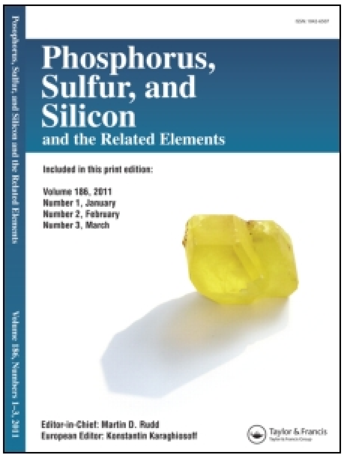


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Rings and Cages from Ph_3PC and PCl or AsCl Units

Hans-Peter Schrödel; Florian Breitsameter; Konstantin Karaghiosoff; Heinrich Nöth; Alfred Schmidpeter

To cite this Article Schrödel, Hans-Peter , Breitsameter, Florian , Karaghiosoff, Konstantin , Nöth, Heinrich and Schmidpeter, Alfred(2001) 'Rings and Cages from Ph_3PC and PCl or AsCl Units', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 59 — 63

To link to this Article: DOI: 10.1080/10426500108546590
URL: http://dx.doi.org/10.1080/10426500108546590

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 59-63
Reprints available directly from the publisher
Photocopying permitted by license only

Rings and Cages from Ph_3PC and PCl or AsCl Units

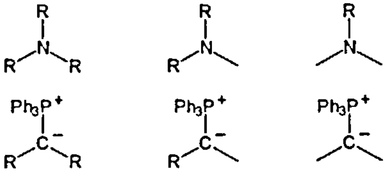
HANS-PETER SCHRÖDEL, FLORIAN BREITSAMETER, KONSTANTIN KARAGHIOSOFF, HEINRICH NÖTH and ALFRED SCHMIDPETER

Department Chemie, Ludwig-Maximilians Universität München, Butenandtstr. 9, D-81377 München, Germany

Like the combination of PCl and AsCl with imino units leads to chlorophosphazanes and chloroarsazanes $(RNECl)_{2,3,4}$, their combination with ylidediyl units results in the oligomeric compounds $(PhP_3CECl)_{2,3,4,}$ which tend, however, more to ionic structures.

Keywords: 1,3-diphosphetanes; 1,3-diarsetanes; 1,3,5-triphosphinanes; 1,3,5-triarsinanes; 1,3,5,7-tetraphosphabarrelanes; 1,3,5,7-tetraarsabarrelanes

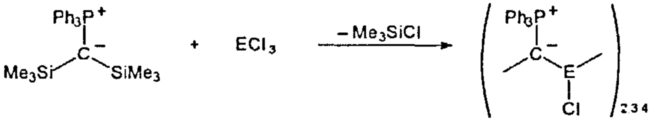
Amines and ylides are isoelectronic molecules. For their mutual conversion a carbon atom and a group 15 atom (N, P) have to interchange their positions. In the ylides this way one positive (nuclear) charge is moved from the center to the substituent and away from the electron lone pair. Ylides are consequently stronger bases than amines. In the same sense ylides provide substituents (ylidyl substituents) analogous to amino groups, however more effective as donors than those. This has been proved for an number of examples [1-8].



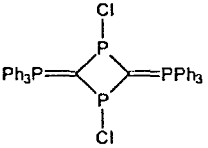
Finally an ylidediyl unit is isolobal to an imino group and may in combination with other divalent units likewise serve as a versatile building block of rings.

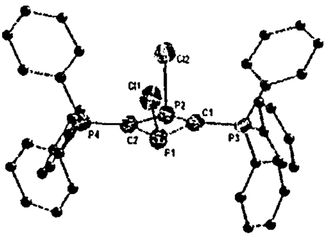
The reaction of primary amines with phosphorus or arsenic trichloride has been studied for more than hundred years and yields chlorophosphazanes and chloroarsazanes $(RNECl)_n$, n = 2, 3, 4, that (as far as their structures are known) are monocyclic non-ionic compounds with alternating RN and PCl or AsCl units [9].

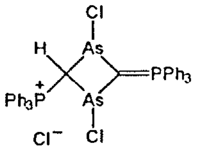
The corresponding reactions of triphenylphosphonium bis(trimethylsilyl)ylide with PCl_3 [10] and $AsCl_3$ [11] yield the compounds $(Ph_3PCECl)_n$ in which ylidediyl units take the place of imino groups. They are analogous in composition and molecular size to the cyclophosphazanes/arsazanes. They show, however, a stronger and with n increasing tendency to ionize; as a consequence they also partly deviate in structure.

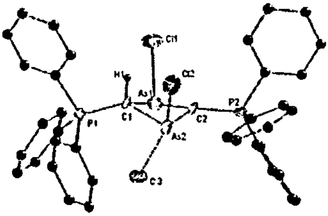


For n = 2 four-membered rings (1,3-diphosphetanes [12] and -diarsetanes) are found with the two chlorine subsituents at the same side of the ring. In case of E = P long distances *d*PCl = 220 and 225 pm are observed [10], and if one chlorine atom is replaced by an electron donating substituent, the other PCl bond dissociates [13].

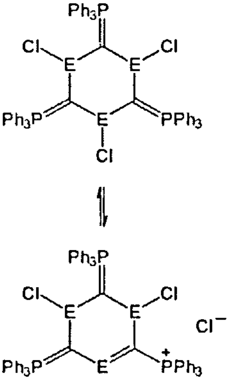


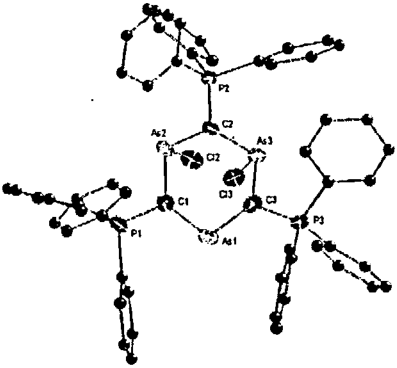






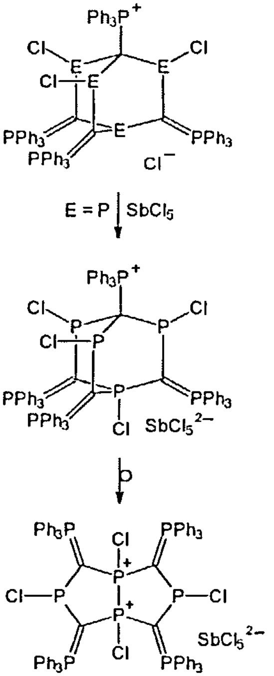
The compounds readily take up HCl. In the arsenic compound the HCl in fact adds to one of the AsC bonds: While the AsCl bond at the not directly involved arsenic ring member is already long, *d*AsCl = 234 pm, the concerned As atom approaches ψ-tbp coordination with even longer and rather different axial AsCl bonds, *d*AsCl = 241 and 278 pm [11].

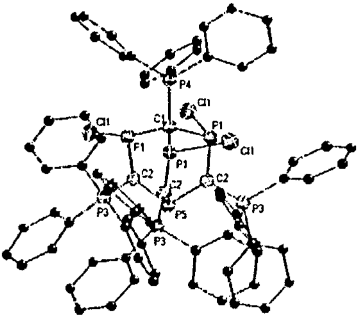


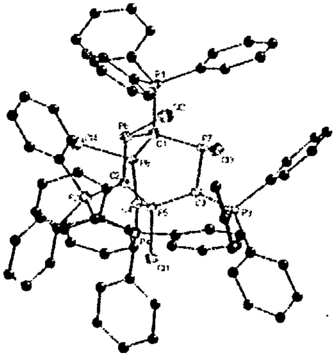


With n = 3 the compounds form six-membered rings (1,3,5-triphosphinane [13] and -triarsinane rings). In solution the covalent molecules are in equilibrium with the ionic form. For the arsenic compound in the crystal the ionic form is found with $AsCl_4^-$ as the anion. The AsCl bonds left in the cation point to opposite sides of the ring and are once more rather long , *d*AsCl = 235 pm. The arsenic atom that has lost the chloride, compensates this loss of electrons by increasing the bond order to the neighboring carbon ring members. These bonds are short, *d*AsC = 184 pm, as compared to 192 pm of the adjacent AsC bonds in the ring and to 196 pm for single bonds in general, and they are similar to those in arsabenzene, *d*AsC = 185 pm.

The compounds with n = 4 are ionic in solution and in solid state. They do not form the expected eight-membered ring, but a cage of alternating units (1,3,5,7-tetraphosphabarrelane [14] and -tetraarsabarrelane). While in case of n = 3 the dissociation of an PCl/AsCl bond is accompanied by the formation of PC/AsC π-bonds, in case of n = 4 an additional PC/AsC σ-bond is formed, giving rise to a bicyclic structure. The PCl and AsCl bonds left in the cations, *d*PCl = 235 pm and *d*AsCl = 249 pm, are by far the longest ones observed so far for a three-coordinate, pyramidal phosphorus or arsenic atom.







The tetraphosphabarrelane cation is readily chlorinated at its bridgehead phosphorus atom. The resulting dication is not stable in solution, however. It rearranges by converting the bicyclo[2.2.2]octane to the bicyclo[3.3.0]octane structure, in which a PC bond has been lost and a PP bond has been formed. This structure presents the initially expected tetrachloro-1,3,5,7-tetraphosphocane ring with - as consequence of the 2e-oxidation - an additional transanular PP bond.

The discussed ECl bond lengths may be compared to those in the trichlorides, PCl_3: 204 pm, $AsCl_3$: 216 pm. Their elongation observed in all the compounds $(Ph_3PCECl)_n$ is explained by negative hyperconjugation, i.e. by *charge transfer from the ylide* p_z *orbital to the* σ^* orbital of the ECl bond. In particular the bonds are always longer than those found in chlorocyclophosphazanes/arsazanes, e.g. $(t\text{BuNECl})_2$, *d*PCl = 211 pm and *d*AsCl = 225 pm.

References

[1] A. Schmidpeter, M. Thiele, Angew. Chem. **103**, 333–335 (1991); Angew. Chem. Int. Ed. Engl. **30**, 308–310 (1991).

[2] A. Schmidpeter, G. Jochem, Tetrahedron Lett. **33**, 471–474 (1992).

[3] A. Schmidpeter, G. Jochem, K. Karaghiosoff, C. Robl, Angew. Chem. **104**, 1420–1421 (1992); Angew. Chem. Int. Ed. Engl. **31**, 1350–1352 (1992).

[4] G. Jochem, H. Nöth, A. Schmidpeter, Angew. Chem. **105**, 1117–1119 (1993); Angew. Chem. Int Ed. Engl. **32**, 1089–1091 (1993).

[5] A. Schmidpeter, H. Nöth, G. Jochem, H.-P. Schrödel, K. Karaghiosoff, Chem. Ber. **128**, 379–393 (1995).

[6] G. Jochem, K. Karaghiosoff. S. Plank, S. Dick, A. Schmidpeter, Chem. Ber. **128**, 1207–1219 (1995).

[7] G. Jochem, F. Breitsameter, A. Schier, A. Schmidpeter, Heteroatom Chem. **7**, 239–247 (1996).

[8] A. Schmidpeter, G. Jochem, C. Klinger. C. Robl, H. Nöth, J. Organomet. Chem. **529**, 87–102 (1997).

[9] R. Keat, D.B. Sowerby, in The Chemistry of Inorganic Homo- and Heterocycles, Vol 2, Academic Press, London 1987.

[10] H.-P. Schrödel, G. Jochem, A. Schmidpeter, H. Nöth, Angew. Chem., 107, 2006–2010 (1995); Angew. Chem. Int. Ed. Engl. **34**, 1853–1856 (1995).

[11] F. Breitsameter, A. Schmidpeter, H. Nöth, Chem.Eur. J. **6**, ###-### (2000).

[12] H.-P. Schrödel. A. Schmidpeter, Chem. Ber. **130**, 1519–1527 (1997).

[13] A. Schmidpeter, G. Jochem, M. Thiele, Phosphorus Sulfur Silicon **76**, 13–16 (1993).

[14] H.-P. Schrödel, A. Schmidpeter, H. Nöth, Z. Naturforsch. B **53**, 1285–1293 (1998).