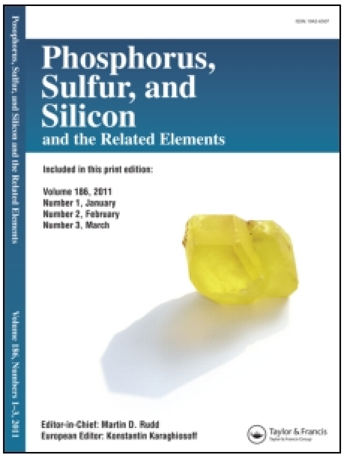

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COORDINATION-STABILIZED MONOMERIC METAPHOSPHATES

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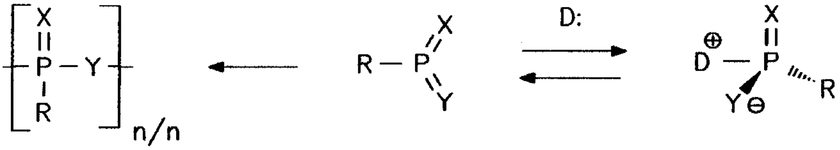
Abstract Monomeric meta(thio)phosphates and phosphonates are thermodynamically stabilized by coordinative saturation when generated in presence of neutral donors. Solvents can act as such donors, like HMPA in thiation reactions with Lawesson' reagent where the $ArPS_2$ adduct is isolated in crystalline state. Chemistry of the adducts includes release of the monomers. In chloro meta(thio)phosphate adducts the halogen is substituted by a second donor molecule to form high yields of crystalline dichalcogenophosphenium cations stabilized by twofold donor coordination.

A number of kinetically stabilized tricoordinated P(V) compounds has become accessible by the method of steric protection.[1] This approach, however, does not work when applied to oxo derivatives like monomeric metaphosphates and phosphonates which unexceptionally undergo oligomerization unless trapped by addition[2] or cycloaddition[3] reactions.

This strong tendency to valence shell expansion can, however, also be exploited for preserving the monomer units **1**, thus thermodynamically stabilizing them by coordinative saturation[4,5]. When generated in presence of donors D:, meta(thio)phosphate esters, thioesters, amides and halides, as well as meta(thio) phosphonates, form crystalline betaines **3** which were fully characterized by elemental analyses and NMR spectra. Educts may be P(V) (ester chlorides,[6,7] oligomers **2**, chloroacid anions[8]) or P(III) compounds (neutral or partial esters).



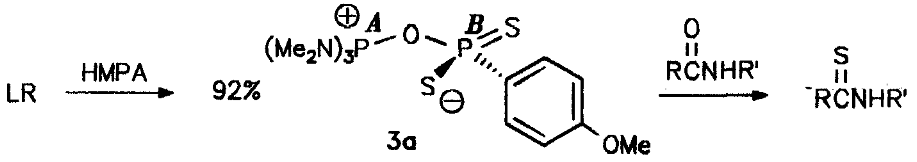
2 1 3

X, Y = O, S; R = C, N, O, S, Hal function;

D : = pyridines, quinuclidine, NMI, DABCO, HMPA

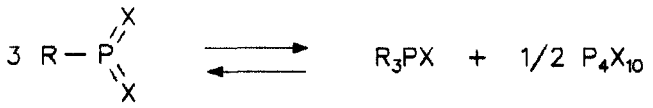
Unlike products obtained from 1 with other trapping agents compounds 3 represent genuine meta(thio)phosph(on)ate adducts. In solution they are capable of transferring the monomer unit 1 to stronger donors at room temperature in high yields. Exchange reactions also take place between 3 and SO_3 betaines. Dissociation of monothio compounds 3 may result in symmetrization to dithio and dioxo compounds, the ease and preparative utilization of it depending on the donor qualities of D: and R. Monothionoester compounds 3 can be subject to isomerization.

Dithiophosphonate betaines, formed from $(ArPS_2)_2$ in high yields, act as potent thiation reagents towards oxo compounds. Contrary to literature reports[9], HMPA is not an inert solvent for Lawesson's reagent, but yields **3a** already at room temperature. Whilst Ph_3PO had been shown to undergo O/S exchange with LR like carbonyl compounds[10], the HMPA betaine **3a** is perfectly stable above 100° C.



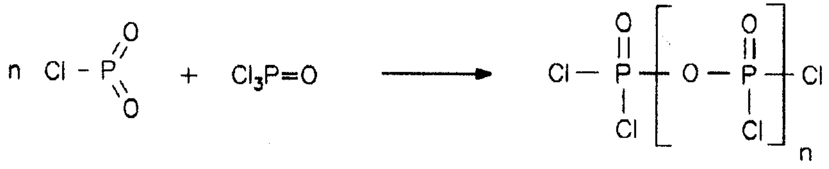
δP^A 27,4ppm; δP^B 116,4 ppm; J_{PP} 43,9 Hz

During vaporization in a mass spectrometer the betaines 3 release monomers 1 which are subject to chemical transformations prior to the electron beam impact.[11] The thermal chemistry of 1 thus revealed includes, in addition to association-dissociation equilibria and symmetrizations, reorganization reactions (R = Cl, MeS; X = O, S)



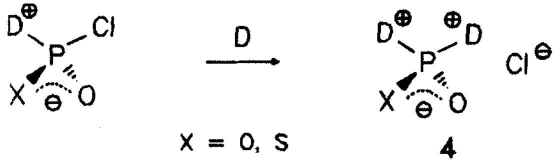
$$3\ R-P(=X)_2 \rightleftharpoons R_3PX + 1/2\ P_4X_{10}$$

and P-Cl bond insertions (oligophosphoryl chloride formation, n = 1, 2).



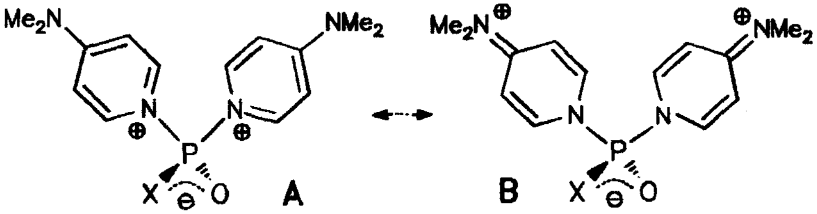
$$n\ Cl-PO_2 + Cl_3P{=}O \longrightarrow Cl-P(O)(Cl)-[O-P(O)(Cl)]_n-Cl$$

Chloro meta(thio)phosphate betaines still exert strong acid chloride properties. The chlorine is readily substituted by a second donor molecule to form high yields of crystalline bis(onio)(thio)phosphate salts **4** which were isolated as chlorides, tetraphenyloborates, triflates, and hexachloroantimonates.[12] Compounds **4** constitute donor-stabilized dichalcogenophosphenium cations $[O{=}P{=}X]^+$ (X = O, S); dithio derivatives were not yet obtained in a pure state.



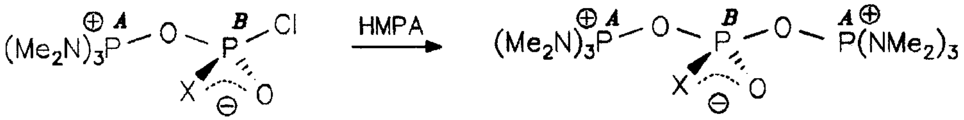
Chlorides of **4**, in marked contrast to BPh_4 or other salts, display much the same patterns in their mass spectra as do the chloro betaines, thus showing the formation of **4** to be thermally reversible.

X-ray studies of the bis(4-dimethylaminopyridinio)thiophosphate cation (as BPh_4 salt) disclose an unusually large O-P-S angle of 124,1°, resembling the parent betaines, and a small N-P-N angle of 97,8°. The latter, along with other parameters and again in line with the betaines, indicates the exocyclic imonium resonance structure **B** to predominate.



	X = O		X = S	
	F.°C	$\delta^{31}P$	F.°C	$\delta^{31}P$
TfO^-	225-28	-13,7	188-90	44,0
BPh_4^-	211-15	-14,2	193-96	44,3
$SbCl_6^-$	175-78	-13,6	209-12	44,1

Dications **4** with HMPA as donor may deserve particular interest because of the P-O-P-O-P sequence involved.



	$\delta^{31}P^{A}$ ($^{2}J_{PP}$)	$\delta^{31}P^{B}$ ($^{2}J_{PP}$)
X = O	30,1(d)(16,7)	-24,0(t)(16,9)
X = S	28,5(d)(23,1)	31,3(t)(23,1)

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REFERENCES

1. M. Regitz and O. J. Scherer, Multiple Bond and Low Coordination in Phosphorus Chemistry (Thieme, Stuttgart/New York 1990).
2. L. D. Quin et al., Phosphorus, Sulfur and Silicon **49/40**, 313 (1990).
3. M. Regitz and H. Eckes, Tetrahedron **45**, 1039 (1981).
4. H. Teichmann, D. Wilbrandt and J. Schulz, Phosphorus, Sulfur and Silicon **49/40**, 251 (1990).
5. H. Teichmann and H. Schulz, Z. Anorg. Allg. Chem. **601**, 163 (1991).
6. H. Teichmann, J. Schulz and D. Wilbrandt, Z. Chem. **30**, 18 (1990).
7. R. J. P. Corriu, G. F. Lanneau and D. Leclercq, Tetrahedron **45**, 1959 (1989).
8. H. Teichmann and J. Schulz, Phosphorus, Sulfur and Silicon **54**, 31 (1990).
9. S. Scheibye, B. S. Pedersen and S.-O. Lawesson, Bull. Soc. Chim. Belg. **87**, 229 (1978).
10. H. Hoffmann and G. Schumacher, Tetrahedron Letters **1967**, 2963.
11. H. Teichmann, J. Schulz, B. Costisella and D. Habisch, Z. Anorg. Allg. Chem. **606**, 233 (1991).
12. Formation of the dioxo triflate from MeOP(O)Cl_2 and dimethylaminopyridine has recently been reported: R. Weiss and S. Engel, Angew. Chem. **104**, 239 (1992).