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Tetra-cationic imidazoliumyl-substituted phosphorus–sulfur heterocycles from a cationic organophosphorus sulfide†

Florian D. Henne,^a Fabian A. Watt,^a Kai Schwedtmann,^a Felix Hennersdorf,^a Malte Kokoschka^{b,c} and Jan J. Weigand^{*a}

The reaction of imidazoliumyl-substituted $P^{(III)}$ cations of type $[L^{(R,Me)}PCl_2]^+$ (**3a,b**⁺; $L^{(R,Me)}$ = imidazolium-2-yl a: R = Me; b: R = iPr) with $(Me_3Si)_2S$ leads to the formation of tetra-cationic, eight-membered phosphorus sulfur heterocycles $[L^{(R,Me)}PS]_4^{4+}$ (**9a,b**⁴⁺), which can be explained by the tetramerization of the intermediately formed cationic phosphorus monosulfide $[L^{(R,Me)}PS]^+$ (**8a,b**⁺). The P_4S_4 ring adopts a crown conformation as observed for cyclo- S_8 . The Lewis base DMAP (4-dimethylaminopyridine) initiates a deoligomerization- and dismutation reaction of **9a,b**⁴⁺ to give $P^{(II)}$ centered cation $[L^{(R,Me)}_2P]^+$ (**12a,b**⁺) and phosphorus disulfide $[(DMAP)_2PS_2]^+$ (**14**⁺).

Organophosphorus–sulfur heterocycles with the general constitution $(RPS)_n$ ($n = 2–4$) and phosphorus in the oxidation state +III remain scarce, since their main access is from the reaction of a dichlorophosphane $RPCL_2$ (R = Aryl) and a source of sulfide (S^{2-} ; e.g. M_2S (M = Li, Na) or $(Me_3Si)_2S$).¹ The formation of these compounds can formally be viewed as a combination of divalent $RP:$ and $S:$ units to give monomeric phosphorus mono-sulfides such as **1**, which then can either yield oligomerization products (Fig. 1; path I) or ylidylphosphorus sulfide **2a** (path II).¹ **2a** represents a rare example of a stable and structurally confirmed monomeric ylidylphosphorus monosulfide. Its stability is rationalized by a high contribution of the zwitterionic resonance formula **2b** (path II).² Aiming at the synthesis of new cationic phosphorus species, we are investigating reactions of imidazoliumyl-substituted P-centered cations such as $[L^{(R,R')}PCl_2]^+$ **3**⁺ ($L^{(R,Me)}$ = imidazolium-2-yl, R = Aryl, Alkyl; R' = H, Me, Cl)³ towards substitution^{3,4} (e.g. **4**⁺, **5**⁺), coordination,⁵ oxidation⁶ or reduction⁷

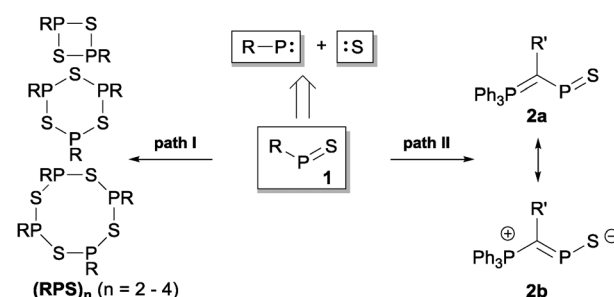


Fig. 1 Formation of oligomeric phosphorus sulfides $(RPS)_n$ ($n = 2–4$; R = Aryl, R' = Alkyl; path I) and phosphorus monosulfide **2a,b** (path II).

(e.g. **6**⁺, **7**⁺) and successfully isolated a series of novel cationic derivatives with intriguing bonding motives (Fig. 2). In this contribution we present the results of the attempted preparation of the imidazoliumyl-substituted $[L^{(R,Me)}PS]^+$ cations **8a,b**⁺ (a: R = Me; b: R = iPr) from the reaction of **3a,b**⁺ with $(Me_3Si)_2S$ and the respective oligomerization to tetra-cations **9a,b**⁴⁺ which can be isolated as triflate salts (Scheme 1). Compounds **3a,b**[OTf] (ref. 3) were reacted with 1 eq. $(Me_3Si)_2S$ in fluorobenzene for 5 h at ambient temperature, accompanied by the formation of colorless precipitates. After workup, compounds **9a,b**[OTf]₄ were isolated in excellent yields (>90%; Scheme 1). The $^{31}P\{^1H\}$ NMR spectra of the dissolved compounds in d_3 -MeCN display one major resonance next to a

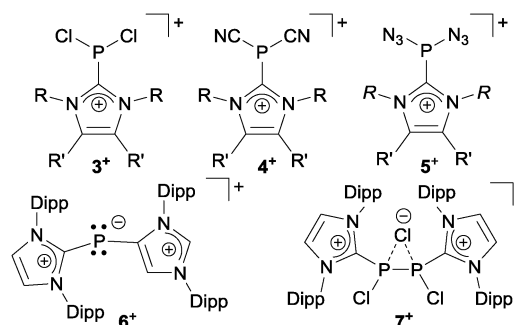


Fig. 2 Selected P-centered cations **3–7**⁺ featuring imidazoliumyl-substituents (Dipp = 2,6-diisopropylphenyl).

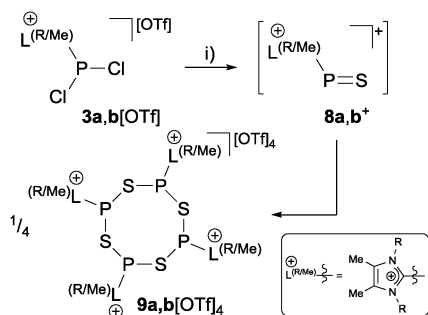
^a Department of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany. E-mail: jan.weigand@tu-dresden.de

^b Department of Computational Chemistry, Academy of Sciences of the Czech Republic, 16610 Praha 6, Czech Republic

^c Department of Physical Chemistry, Palacký University, 771 46 Olomouc, Czech Republic

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Scheme 1 Preparation of tetrameric imidazoliumyl-substituted phosphorus-sulfur heterocycles **9a,b**[OTf]₄ from the intermediately formed cation **8a,b**⁺ (a: R = Me; b: R = iPr); (i) + (Me₃Si)₂S, C₆H₅F, rt, −2Me₃SiCl.

minor singlet in the typical region of tri-coordinate phosphorus derivatives (**9a**⁴⁺: δ(P)_{major/minor} = 48.2 ppm/48.0 ppm; **9b**⁴⁺: δ(P)_{major/minor} = 50.5 ppm/50.3) indicating the oligomerization of the intermediately formed cationic phosphorus monosulfide **8a,b**⁺. However, no evidence for the formation of other ring sizes was found, showing a high selectivity of the oligomerization process. It can be assumed that, under these conditions, the formation of the P₄S₄ ring is thermodynamically (considering ring strain and steric effects) favored. The variable-temperature (VT) ³¹P NMR spectra for **9b**[OTf]₄ are depicted in Fig. 3a, evidencing a dynamic behavior and the presence of two highly symmetric conformational isomers (crown (C_{4v}) vs. boat-chair (C_s) conformer) of the P₄S₄ ring in solution (Scheme 2). A significant broadening of the two resonances upon

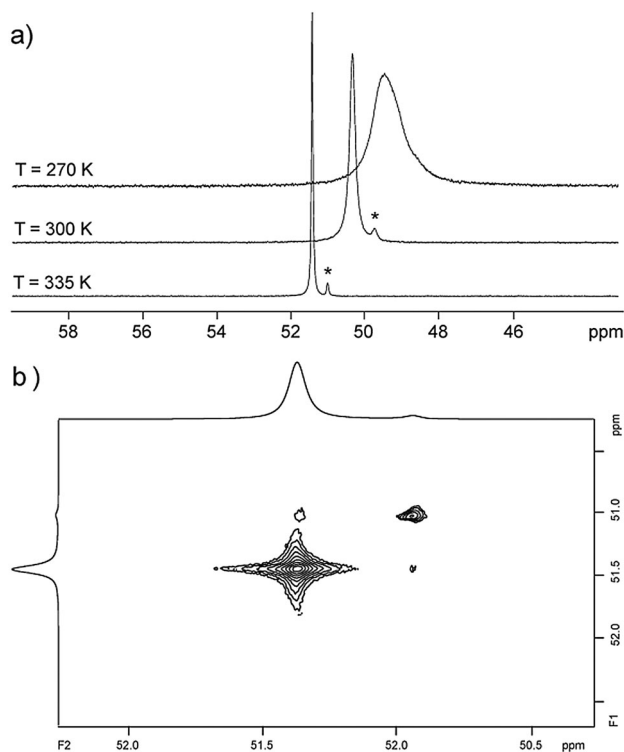


Fig. 3 (a) VT ³¹P NMR spectra of **9b**[OTf]₄ recorded in CD₃CN (see ESI†) * indicates minor amounts of the conformational isomer of **9b**⁴⁺; (b) ³¹P EXSY NMR spectrum of **9b**[OTf]₄ recorded at 335 K with a mixing time of *t*_m = 0.55 s.



Scheme 2 Interconversion process of cations **9a,b**⁴⁺ from the conformational isomer with crown shape (C_{4v}) to the boat-chair (C_s) conformer without considering the imidazoliumyl substituents.

cooling is observed. The VT ¹H NMR spectra also show additional dynamic behavior of the iPr-groups. We thus confirmed the existence of two conformational isomers independently by ³¹P EXSY NMR experiments (Fig. 3b), although quantitative accuracy (to determine kinetic processes or exchange rates) was limited by the narrow temperature range in which useful spectra could be measured. The ³¹P EXSY NMR experiments suggest exchange of two conformers in which one of the sulfur-bridges reversibly changes its relative position, giving either the approximate C_{4v} or C_s symmetric cations **9a,b**⁴⁺ (Scheme 2). The cross peaks in the 2D spectrum demonstrate the exchange between the two symmetric conformers in solution, consistent with the observation of singlet resonances as expected for an A₄ spin-system for both isomers.

Satisfactory crystal structure analyses could be performed confirming the formation of the suggested eight-membered organophosphorus-sulfur heterocycles (Fig. 4). In the case of compound **9b**[OTf]₄ the refinement of the X-ray data confirmed the crown-shaped P₄S₄ moiety, similarly to cation **9a**⁴⁺, however, due to severe disorder caused by alternating ring orientation full refinement was only possible after treatment by an appropriate disordered model.⁸ The P^{III}–S bond lengths (av. 2.129 Å) in **9a**⁴⁺ are in the typical range for P^{III}–S single bonds and compare well with those reported by Sheldrick *et al.* for the neutral derivative (MesPS)₄ (av. 2.117 Å; Mes = 2,4,6-trimethylphenyl).^{1b} The pyramidalization of the P atoms, as well as the lengths of the C–P bonds (av. 1.817 Å), together with the internal angle N1–C1–N2 of the imidazoliumyl moieties (**9a**⁴⁺: av. 106.9° vs. ~101° in NHCs)⁹ are in agreement with the ability of the imidazoliumyl fragment to (a) delocalize the positive charge, (b) reduce the nucleophilicity of a directly bonded P atom and thus may account for the stability of these cations.^{5,10,11}

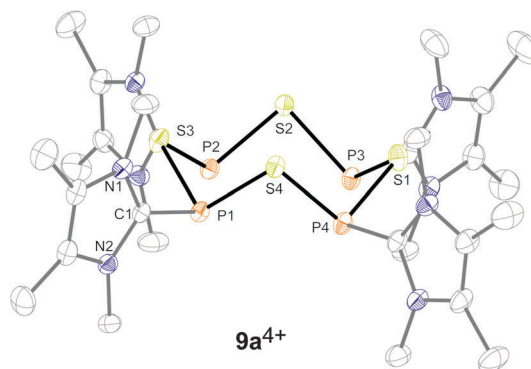
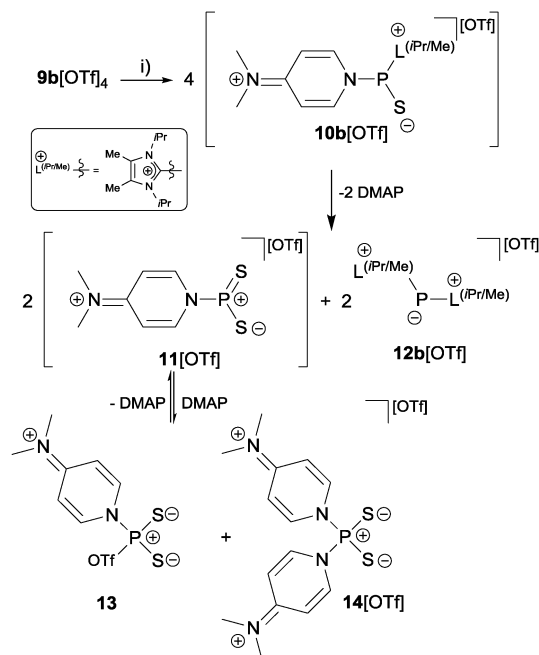


Fig. 4 Molecular structure of tetracation **9a**⁴⁺ in **9a**[OTf]₄. All hydrogen atoms and triflate anions are omitted for clarity. Selected bond lengths in Å and angles in °: P1–S1 2.1306(9), P1–S4 2.1364(9), P2–S1 2.1234(9), P1–C1 1.820(3), S1–P1–S4 101.99(4), S1–P1–C1 99.31(8), S4–P1–C1 101.26(9), N1–C1–N2 101.26(9).





Scheme 3 Deoligomerization of **9b**[OTf]₄ with DMAP and proposed intermediates; (i) +4 DMAP, MeCN, rt.

To confirm that the formation of tetracations **9a,b**⁴⁺ proceeds *via* monomeric phosphorus mono-sulfides **8a,b**⁺, we reacted **9a,b**[OTf]₄ with DMAP in MeCN, since this Lewis base has been widely used to stabilize low-coordinate phosphorus species.¹² The σ -donor strength of DMAP should be high enough to deoligomerize tetracations **9a,b**⁴⁺ to cations **10a,b**⁺ which represent DMAP adducts of the elusive cations **8a,b**⁺ (Scheme 3). The reaction of 4 equivalents DMAP in MeCN proceeds comparably clean with **9b**[OTf]₄ at ambient temperature giving pale-yellow solutions. The ³¹P{¹H} NMR spectra of the reaction mixture of **9b**[OTf]₄ and DMAP after reaction times of 10 min to 7d are depicted in Fig. 5. After 10 min a broad resonance at $\delta(P) = 147.1$ ppm is observed which splits into 2 singlets at low temperature ($\delta(P) = 140.3$ ppm and $\delta(P) = 144.4$ ppm; 253 K). We believe that the splitting of the resonances results from two rotational isomers caused by a restricted rotation of the *i*Pr groups at low temperature.^{8,13} From the distinctive chemical shift a dimeric derivative with tetra-coordinate phosphorus atoms

(*cf.* [(Et₂N)₂PS₂][AlCl₄]₂; $\delta(P) = 21.0$ ppm)¹⁴ can be excluded and we thus propose the formation of DMAP adduct **10b**⁺ which is also supported by our NMR investigation.⁸ We were not able to isolate **10b**[OTf], however, we assume that cation **10b**⁺ readily dismutates to cations **11**⁺ ($\delta(P) = 215.8$ ppm) and **12b**⁺ ($\delta(P) = -126.1$ ppm) *via* an intermolecular scrambling reaction, *i.e.* an intermolecular exchange of imidazolium-2-yl and sulfur substituents. Related exchange reactions were discussed for the DMAP induced disproportionation of POCl₃¹⁵ and scrambling reactions of imidazoliumyl-substituted [L^(Me,Me)PCl₂]⁺ cations.⁴ Pⁱ centered cation **13b**⁺ ($\delta(P) = -126.1$ ppm) was recently reported by Macdonald *et al.* and unambiguously confirmed by its characteristic chemical shift (*cf.* lit: $\delta(P) = -124.2$ ppm, CD₂Cl₂).¹⁶ Cations of type **12a**⁺ are also known and reported by Schmidpeter *et al.* as ylidylphosphorus-disulfide containing a tri-coordinate R-PS₂ moiety. For these types of compounds the chemical shift strongly depends on the nature of the supporting substituent R and is typically observed in the range of $\delta(P) = 170$ –240 ppm (*cf.* Ph₃PCMe-PS₂: $\delta(P)_{PS_2} = 243.4$ ppm, d₈-THF).² In an equilibrium reaction of cation **11**⁺ with the triflate anion the formation of **13** is explained and supported by the pronounced upfield shifted triplet resonance due to the coupling to the *ortho*-protons of the DMAP ligand (eqn (1); $\delta(P) = 72.5$ ppm, triplet, ³J_{PH} = 9.0 Hz; *cf.* PyPS₂Br: $\delta(P) = 65.5$ ppm, Py = pyridine; d₃-MeCN).¹⁷ The formation of cation **14**⁺ results either from the equilibrium reaction of **11**⁺ (eqn (2)) or **13** (eqn (3)) with DMAP which is liberated during the dismutation of cation **10b**⁺ (Scheme 3). The ³¹P NMR spectrum displays a quintet resonance which is indicative for the presence of two DMAP substituents consistent with the C_{2v} symmetry of cation **14**⁺ ($\delta(P) = 96.9$ ppm; *cf.* [Py₂PS₂]⁺: $\delta(P) = 104.7$ ppm, quintet, ³J_{PH} = 9.6 Hz; Py = pyridine; d₃-MeCN). Similar equilibria and cations have been observed by Meisel *et al.* who reported on the pyridine (Py) stabilized phosphorus disulfide [Py₂PS₂]⁺ cation.¹⁸ Two crystalline polymorphs of **14**[OTf] were obtained after layering the reaction mixtures with Et₂O (Fig. 6).¹⁹ The obtained structural parameters compare well with those reported for the related pyridine cation [Py₂PS₂]⁺ by Meisel *et al.*¹⁸

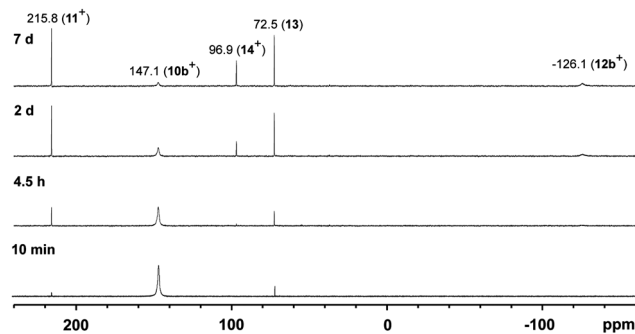
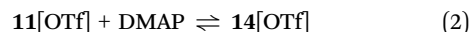


Fig. 5 ³¹P{¹H} NMR spectra of the 1:4 reaction of **9b**[OTf]₄ and DMAP in CD₃CN showing the scrambling reaction to cations **11**⁺, **12b**⁺, **14**⁺ and adduct **13**.

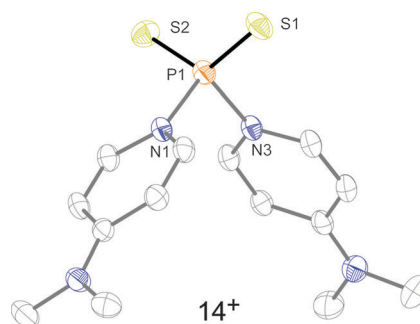


Fig. 6 Molecular structure of **14**⁺ in **14**[OTf]. All hydrogen atoms and the triflate anion are omitted for clarity. Selected bond lengths in Å and angles in °: P1–S1 1.9309(8), P1–S2 1.9321(8), P1–N1 1.782(2), P1–N2 1.798(2), S1–P1–S2 124.09(4), N1–P1–N2 96.77(8), S–P1–N av. 108.14.

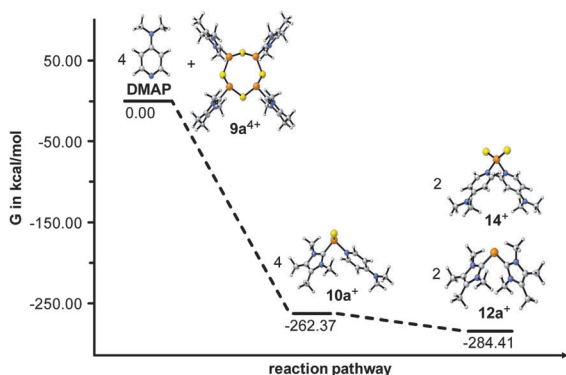


Fig. 7 Gibbs free energy in kcal mol⁻¹ of the observed and proposed phosphorus species.

In order to confirm our findings and support the suggested dismutation, quantum chemical calculations have been performed from the reaction of **9a**⁴⁺ with 4 eq. DMAP to derive geometry and Gibbs free energy of the involved species as well as the suggested reaction intermediate **10a**⁺.²⁰ The density functional theory (DFT) hybrid model B3LYP²¹ was used in combination with Grimme's atom-pairwise dispersion correction (D3).²² Fig. 7 illustrates the Gibbs free energy ΔG of educts (**9a**⁴⁺, DMAP), products (**12b**⁺, **14**⁺) and the proposed intermediate (**10a**⁺) calculated at the B3LYP-D3/def-SVP level of theory. The whole reaction pathway is thermodynamically favored ($\Delta G = -284.4$ kcal mol⁻¹). The proposed reaction intermediate **10a**⁺ is energetically less favorable by 22 kcal mol⁻¹ compared to the final products, but 262 kcal mol⁻¹ lower in energy than the educt molecules ($\Delta G = -262.4$ kcal mol⁻¹). This observation is perfectly in line with the assumption of **10a**⁺ being the main reaction intermediate.

In summary, we reported on the oligomerization reaction of cationic phosphorus monosulfides **8a,b**⁺ which were formed *in situ* from the reaction of $[L^{(R,Me)}PCl_2]^+$ cations **3a,b**⁺ ($L^{R,Me}$ = imidazolium-2-yl a: R = Me; b: R = iPr) and $(Me_3Si)_2S$. The obtained tetra-cationic, eight-membered phosphorus-sulfur heterocycles $[L^{(R,Me)}PS]_4^{4+}$ **9a,b**⁴⁺ primarily exist as crown conformers similar to cyclo-S₈, however, the boat-chair (*C_s*) conformers of the P₄S₄ rings also exist in solution according to 2D-EXSY ³¹P NMR experiments. Cations **9a,b**⁴⁺ can be deoligomerized by DMAP to yield adducts **10a,b**⁺ of the elusive cations **8a,b**⁺. Subsequent dismutation of **10a,b**⁺ gives cations $[L^{(R,Me)}_2P]^+$ (**12a,b**⁺) and $[(DMAP)_2PS_2]^+$ (**14**⁺) as final products. The suggested reaction pathway was supported by DFT calculations.

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