Tetra-cationic Imidazoliumyl-Substituted Phosphorus-Sulfur Heterocycles from a Cationic Organophosphorus Sulfide

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Tetra-cationic Imidazoliumyl-Substituted Phosphorus-Sulfur Heterocycles from a Cationic Organophosphorus Sulfide

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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= *i*Pr) 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 $P^{(I)}$ 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 (figure 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] oxidation[6] or reduction[7] (e.g. **6**$^+$,**7**$^+$) and successfully isolated a series of novel cationic derivatives with intriguing bonding motives (figure 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 = *i*Pr) 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][3] were reacted with 1 eq. $(Me_3Si)_2S$ in fluorobenzene for 5 h at ambient temperature, accompanied by the formation of colorless

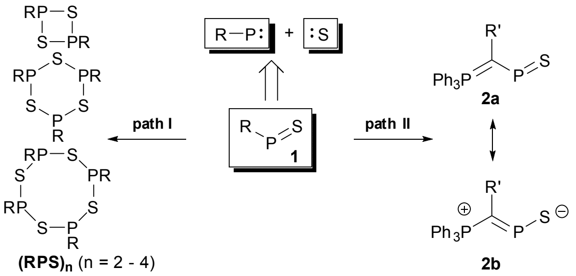


Figure 1. Formation of oligomeric phosphorus sulfides **(RPS)$_n$** (n = 2-4; R = Aryl, R' = Alkyl; path I) and phosphorus monosulfide **2a,b** (path II).

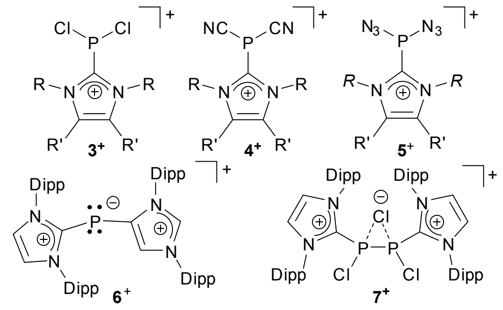
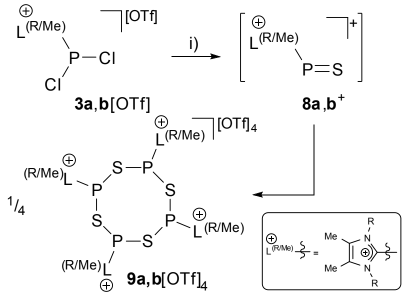


Figure 2. Selected P-centered cations **3-7**$^+$ featuring imidazoliumyl-substituents (Dipp = 2,6-diisopropylphenyl).



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 = *i*Pr); i) + $(Me_3Si)_2S$, C_6H_5F, rt, $-2Me_3SiCl$.

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† Electronic Supplementary Information (ESI) available: For detailed experimental procedures and characterization details of new compounds, NMR spectra, crystallographic details and computational data see DOI: 10.1039/x0xx00000x

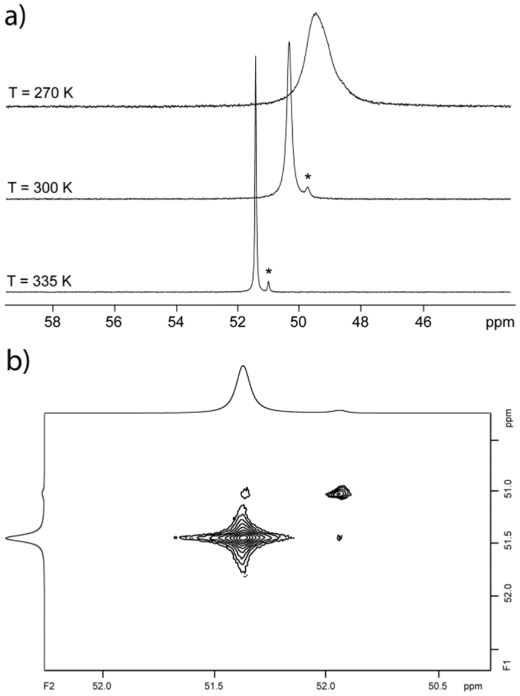
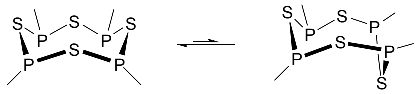


Figure 3. a) VT ^{31}P NMR spectra of **9b**[OTf]$_4$ recorded in CD$_3$CN;^{8} * indicates minor amounts of the conformational isomer of **9b**$^+$; b) ^{31}P EXSY NMR spectrum of **9b**[OTf]$_4$ recorded at 335 K with a mixing time of t_m = 0.55 sec.

precipitates. After workup, compounds **9a,b**[OTf]$_4$ were isolated in excellent yields (>90%; scheme 1). The ^{31}P{^{1}H} NMR spectra of the dissolved compounds in d$_3$-MeCN display one major resonance next to a minor singlet in the typical region of tri-coordinate phosphorus derivatives (**9a**$^{4+}$: δ(P)$_{\text{major/minor}}$ = 48.2 ppm/48.0 ppm; **9b**$^{4+}$: δ(P)$_{\text{major/minor}}$ = 50.5 ppm/50.3 ppm) 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 P$_4$S$_4$ ring is thermodynamically (considering ring strain and steric effects) favored. The variable-temperature (VT) ^{31}P NMR spectra for **9b**[OTf]$_4$ are depicted in figure 3 a), evidencing a dynamic behavior and the presence of two highly symmetric conformational isomers (crown (C_{4v}) *vs.* boat-chair (C_s) conformer) of the P$_4$S$_4$ ring in solution (scheme 2). A significant broadening of the two resonances upon cooling is observed. The VT ^{1}H NMR spectra also show additional dynamic behavior of the *i*Pr-groups. We thus confirmed the existence of two conformational isomers independently by ^{31}P EXSY NMR experiments (figure 3 b), 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 ^{31}P 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 A$_4$ spin-system for both isomers.

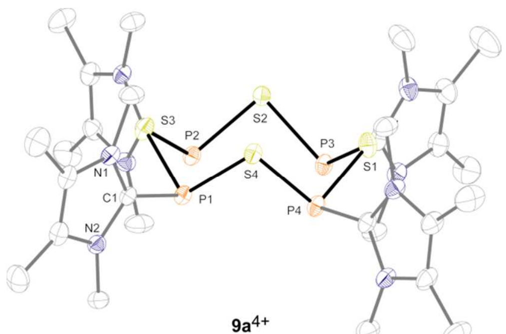


9^+ (C_{4v}) 9^+ (C_s)

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.

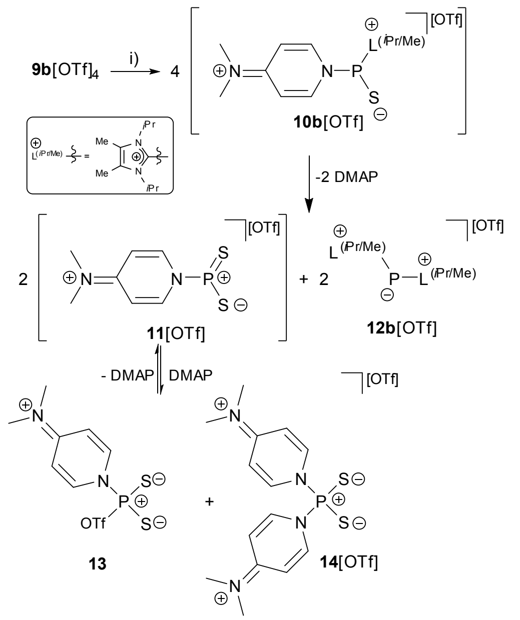
Satisfactory crystal structure analyses could be performed confirming the formation of the suggested eight-membered organophosphorus-sulfur heterocycles. In the case of compound **9b**[OTf]$_4$ the refinement of the x-ray data confirmed the crown-shaped P$_4$S$_4$ moiety, similarly to cation **9a**$^{4+}$, however, due to severe disorder caused by alternating ring orientation full refinement was only possible after treatment by an appropriate disordered model.[9] The P$^{\text{III}}$-S bond lengths (av. 2.129 Å) in **9a**$^{4+}$ are in the typical range for P$^{\text{III}}$–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. 1.817Å), together with the internal angle N1–C1–N2 of the imidazoliumyl moieties (**9a**$^{4+}$: av. 106.9° *vs.* ~ 101° in NHCs)[10] 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.[5,11,12]

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.[13] 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



$9a^{4+}$

Figure 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.

temperature giving pale-yellow solutions. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of **9b**[OTf]$_4$ and DMAP after reaction times of 10 min to 7d are depicted in figure 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.[9,14] From the distinctive chemical shift a dimeric derivative with tetra-coordinate phosphorus atoms (cf. $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$: $\delta(P) = 21.0$ ppm)[15] can be excluded and we thus propose the formation of DMAP adduct $\mathbf{10b}^+$ which is also supported by our NMR investigation.[9] We were not able to isolate **10b**[OTf], however, we assume that cation $\mathbf{10b}^+$ readily dismutates to cations $\mathbf{11}^+$ ($\delta(P) = 215.8$ ppm) and $\mathbf{12b}^+$ ($\delta(P) = -126.1$ 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 $POCl_3$[16] and scrambling reactions of imidazoliumyl-substituted $[L^{(Me,Me)}PCl_2]^+$ cations.[4] P^I centered cation $\mathbf{13b}^+$ ($\delta(P) = -126.1$ ppm) was recently reported by Macdonald *et al.* and unambiguously confirmed by its characteristic chemical shift (cf. lit: $\delta(P) = -124.2$ ppm, CD_2Cl_2).[17] Cations of type $\mathbf{12a}^+$ are also known and reported by Schmidpeter *et al.* as ylidylphosphorusdisulfide containing a tri-coordinate $R–PS_2$ 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. $Ph_3PCMe–PS_2$: $\delta(P)_{PS2} = 243.4$ ppm, d_8-THF).[2] In an equilibrium reaction of cation $\mathbf{11}^+$ 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 (**Eq. 1**; $\delta(P) = 72.5$ ppm, triplet, $^3J_{PH} = 9.0$ Hz; cf. $PyPS_2Br$: $\delta(P) = 65.5$ ppm, Py = pyridine; d_3-MeCN).[18] The formation of cation $\mathbf{14}^+$ results either from the equilibrium reaction of $\mathbf{11}^+$ (**Eq. 2**) or **13** (**Eq. 3**) with DMAP which is liberated during the dismutation of cation $\mathbf{10b}^+$ (scheme 3). The ^{31}P NMR spectrum displays a quintet resonance which is indicative for the presence of two DMAP substituents consistent with the C_{2v} symmetry of cation $\mathbf{14}^+$ ($\delta(P) = 96.9$ ppm; cf. $[Py_2PS_2]^+$: $\delta(P) = 104.7$ ppm, quintet, $^3J_{PH} = 9.6$ Hz; Py = pyridine; d_3-MeCN). Similar equilibria and cations have been observed by Meisel *et al.* who reported on the pyridine (Py) stabilized phosphorus disulfide $[Py_2PS_2]^+$ cation.[19] Two crystalline polymorphs of **14**[OTf] were obtained after layering the reaction mixtures with Et_2O (figure 6).[20] The obtained structural parameters compare well with those reported for the related pyridine cation $[Py_2PS_2]^+$ by Meisel *et al.*[19]

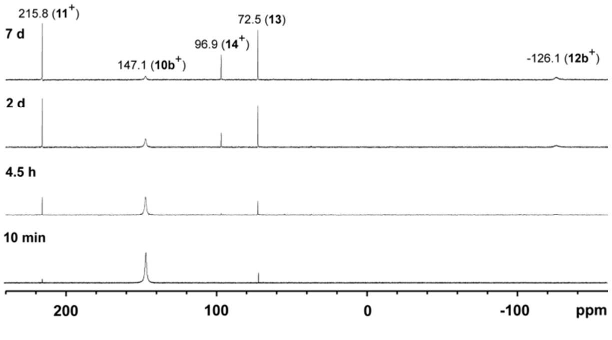


Figure 5. $^{31}P\{^1H\}$ NMR spectra of the 1:4 reaction of **9b**[OTf]$_4$ and DMAP in CD_3CN showing the scrambling reaction to cations $\mathbf{11}^+$, $\mathbf{12b}^+$, $\mathbf{14}^+$ and adduct **13**.

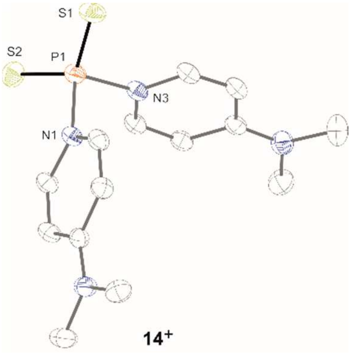


Figure 6. Molecular structure of $\mathbf{14}^+$ in **14**[OTf]. All hydrogen atoms and the triflate anion are omitted for clarity. Selected bond lengths in Å and angles in °: P1–S1 1.9309(8), P1–S2 1.9321(8), P1–N1 1.782(2), P1–N2 1.798(2), S1–P1–S2 124.09(4), N1–P1–N2 96.77(8), S–P1–N av. 108.14.

(Eq. 1) **11**[OTf] ⇌ **13**
(Eq. 2) **11**[OTf] + DMAP ⇌ **14**[OTf]
(Eq. 3) **13** + DMAP ⇌ **14**[OTf]

In order to confirm our findings and support the suggested dismutation, quantum chemical calculations have been performed from the reaction of $\mathbf{9a}^{4+}$ with 4 eq. DMAP to derive geometry and Gibbs free energy of the involved species as well as the suggested reaction intermediate $\mathbf{10a}^+$.[21] The density functional theory (DFT) hybrid model B3LYP[22] was used in combination with Grimme'satom-pair wise dispersion

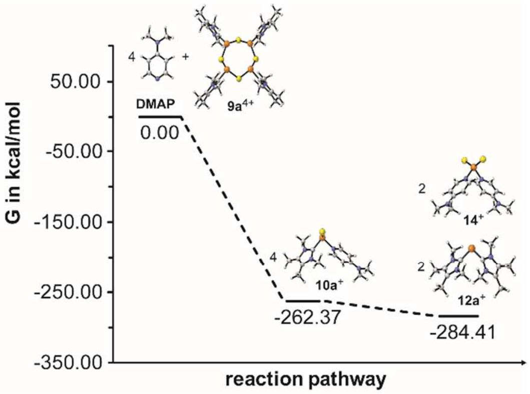


Figure 7. Gibbs free energy in kcal/mol of the observed and proposed phosphorus species.

correction (D3).[23] Figure 7 illustrates the Gibbs free energy Δ*G* 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 (Δ*G* = -284.4 kcal/mol). The proposed reaction intermediate **10a**$^{+}$ is energetically less favorable by 22 kcal/mol compared to the final products, but 262 kcal/mol lower in energy than the educt molecules (Δ*G* = -262.4 kcal/mol). This observation is perfectly in line with the assumption of **10a**$^{+}$ being the main reaction intermediate.

Conclusions

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 = *i*Pr) 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-S_8, however, the boat-chair (C_s) conformers of the P_4S_4 rings also exist in solution according to 2D-EXSY ^{31}P 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 $[L^{(R,Me)}{}_2P]^{+}$ (**12**a,b^{+}) and $[(DMAP)_2PS_2]^{+}$ (**14**$^{+}$) as final products. The suggested reaction pathway was supported by DFT calculations.

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20 Similarly to the highly reactive intermediate **10b**$^{+}$, the tetramethyl substituted derivative **10a**$^{+}$ was also observed in the reaction of **9a**$[OTf]^{4}$ and 4 eq. DMAP at δ(P) = 144.7 ppm. From the reaction spectra, chemical shifts as δ(P) = 216.6 ppm, 97.3 ppm, 70.9 ppm and -113.2 ppm can be assigned to **11**$^{+}$, **14**$^{+}$, **13** and **12a**$^{+}$, respectively. The reaction NMR is depicted in the supporting information; Details of the two polymorphs are given in the Supporting Information.

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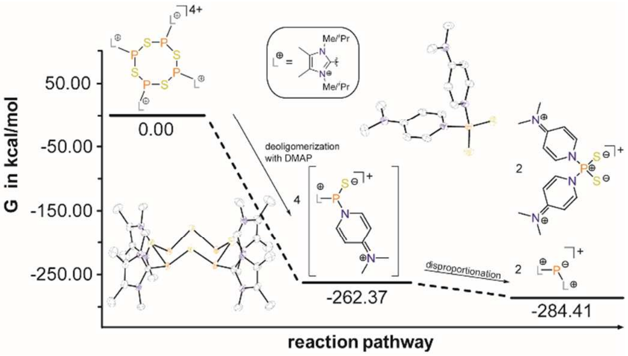

The formation of novel tetracationic cyclo-P_4S_4 derivatives $[LPS]_4^{4+}$ *via* oligomerization of $[LPS]^+$ is presented. Subsequent deoligomerization- and dismutation reactions induced by 4-dimethylaminopyridine are discussed herein.