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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**<sup>+</sup>;  $L^{(R,Me)}$  = 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**<sup>4+</sup>), which can be explained by the tetramerization of the intermediately formed cationic phosphorus monosulfide  $[L^{(R,Me)}PS]^+$  (**8a,b**<sup>+</sup>). 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**<sup>4+</sup> to give  $P^{(II)}$  centered cation  $[L^{(R,Me)}_2P]^+$  (**12a,b**<sup>+</sup>) and phosphorus disulfide  $[(DMAP)_2PS_2]^+$  (**14**<sup>+</sup>).

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  $(Me_3Si)_2S$ ).<sup>1</sup> 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).<sup>1</sup> **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).<sup>2</sup> 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**<sup>+</sup> ( $L^{(R,Me)}$  = imidazolium-2-yl, R = Aryl, Alkyl; R' = H, Me, Cl)<sup>3</sup> towards substitution<sup>3,4</sup> (e.g. **4**<sup>+</sup>, **5**<sup>+</sup>), coordination,<sup>5</sup> oxidation<sup>6</sup> or reduction<sup>7</sup>

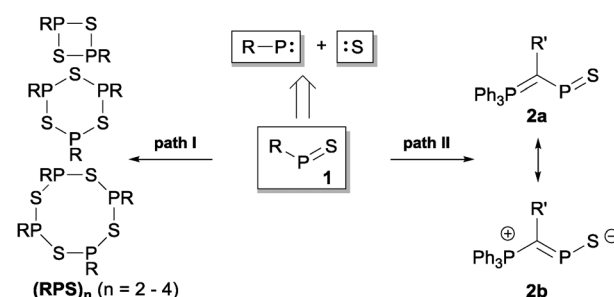


Fig. 1 Formation of oligomeric phosphorus sulfides  $(RPS)_n$  ( $n = 2-4$ ; R = Aryl, R' = Alkyl; path I) and phosphorus monosulfide **2a,b** (path II).

(e.g. **6**<sup>+</sup>, **7**<sup>+</sup>) 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**<sup>+</sup> (a: R = Me; b: R = iPr) from the reaction of **3a,b**<sup>+</sup> with  $(Me_3Si)_2S$  and the respective oligomerization to tetra-cations **9a,b**<sup>4+</sup> 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]<sub>4</sub> 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

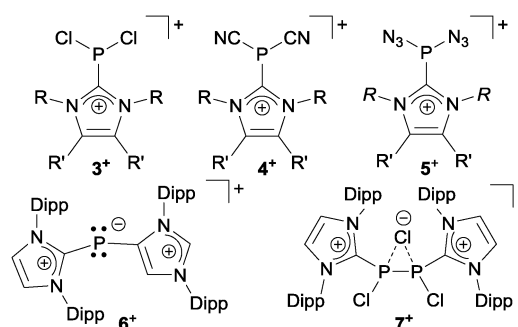


Fig. 2 Selected P-centered cations **3–7**<sup>+</sup> featuring imidazoliumyl-substituents (Dipp = 2,6-diisopropylphenyl).

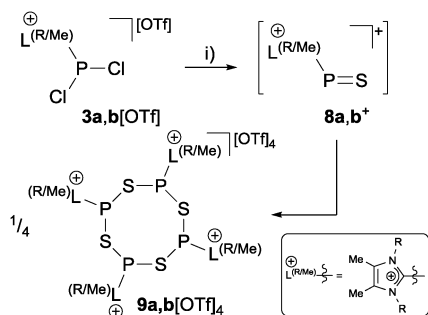
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**Scheme 1** Preparation of tetrameric imidazoliumyl-substituted phosphorus-sulfur heterocycles **9a,b**[OTf]<sub>4</sub> from the intermediately formed cation **8a,b**<sup>+</sup> (a: R = Me; b: R = iPr); (i) +(Me<sub>3</sub>Si)<sub>2</sub>S, C<sub>6</sub>H<sub>5</sub>F, rt, −2Me<sub>3</sub>SiCl.

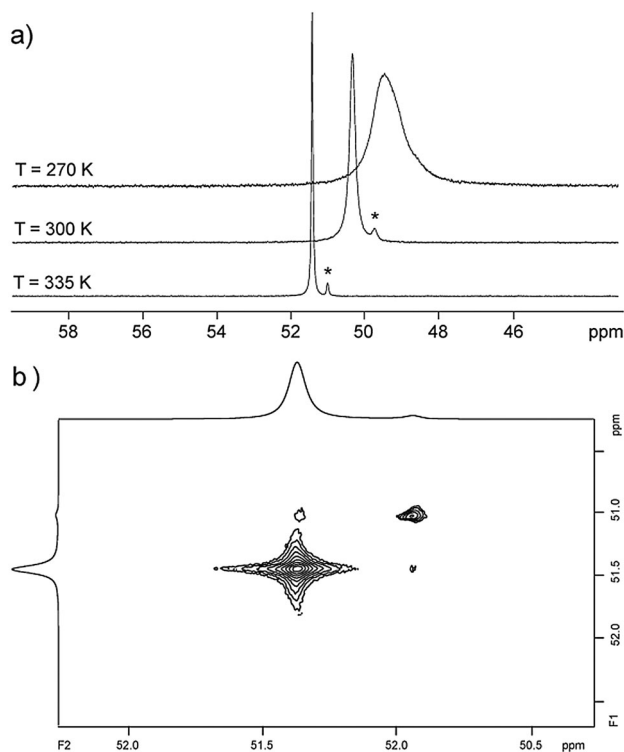
minor singlet in the typical region of tri-coordinate phosphorus derivatives (**9a**<sup>4+</sup>:  $\delta(\text{P})_{\text{major/minor}} = 48.2 \text{ ppm}/48.0 \text{ ppm}$ ; **9b**<sup>4+</sup>:  $\delta(\text{P})_{\text{major/minor}} = 50.5 \text{ ppm}/50.3$ ) indicating the oligomerization of the intermediately formed cationic phosphorus monosulfide **8a,b**<sup>+</sup>. 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<sub>4</sub>S<sub>4</sub> ring is thermodynamically (considering ring strain and steric effects) favored. The variable-temperature (VT) <sup>31</sup>P NMR spectra for **9b**[OTf]<sub>4</sub> are depicted in Fig. 3a, evidencing a dynamic behavior and the presence of two highly symmetric conformational isomers (crown (C<sub>4v</sub>) vs. boat-chair (C<sub>s</sub>) conformer) of the P<sub>4</sub>S<sub>4</sub> ring in solution (Scheme 2). A significant broadening of the two resonances upon



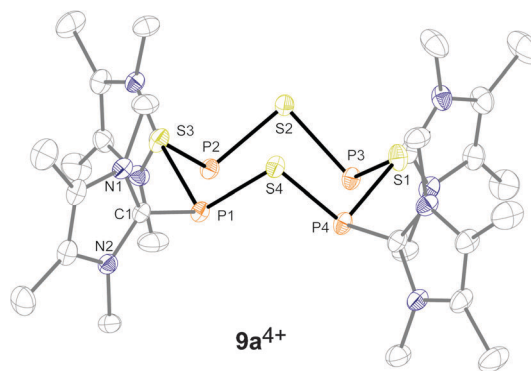
**Scheme 2** Interconversion process of cations **9a,b**<sup>4+</sup> from the conformational isomer with crown shape (*C*<sub>4v</sub>) to the boat-chair (*C*<sub>s</sub>) conformer without considering the imidazoliumyl substituents.

cooling is observed. The VT  $^1\text{H}$  NMR spectra also show additional dynamic behavior of the iPr-groups. We thus confirmed the existence of two conformational isomers independently by  $^{31}\text{P}$  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  $^{31}\text{P}$  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.

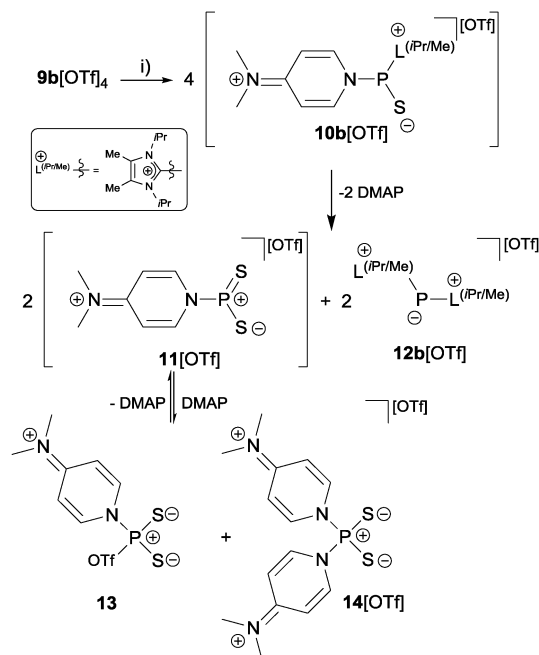
Satisfactory crystal structure analyses could be performed confirming the formation of the suggested eight-membered organophosphorus–sulfur heterocycles (Fig. 4). In the case of compound **9b**[OTf]<sub>4</sub> the refinement of the X-ray data confirmed the crown-shaped P<sub>4</sub>S<sub>4</sub> moiety, similarly to cation **9a**<sup>4+</sup>, however, due to severe disorder caused by alternating ring orientation full refinement was only possible after treatment by an appropriate disordered model.<sup>8</sup> The P<sup>III</sup>–S bond lengths (av. 2.129 Å) in **9a**<sup>4+</sup> are in the typical range for P<sup>III</sup>–S single bonds and compare well with those reported by Sheldrick *et al.* for the neutral derivative (MesPS)<sub>4</sub> (av. 2.117 Å; Mes = 2,4,6-trimethylphenyl).<sup>1b</sup> 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**<sup>4+</sup>: av. 106.9° vs. ~101° in NHCs)<sup>9</sup> 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.<sup>5,10,11</sup>



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



**Fig. 4** Molecular structure of tetracation **9a<sup>4+</sup>** in **9a**[OTf]<sub>4</sub>. 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]<sub>4</sub> with DMAP and proposed intermediates; (i) +4 DMAP, MeCN, rt.

To confirm that the formation of tetracations **9a,b**<sup>4+</sup> proceeds *via* monomeric phosphorus mono-sulfides **8a,b**<sup>+</sup>, we reacted **9a,b**[OTf]<sub>4</sub> with DMAP in MeCN, since this Lewis base has been widely used to stabilize low-coordinate phosphorus species.<sup>12</sup> The  $\sigma$ -donor strength of DMAP should be high enough to deoligomerize tetracations **9a,b**<sup>4+</sup> to cations **10a,b**<sup>+</sup> which represent DMAP adducts of the elusive cations **8a,b**<sup>+</sup> (Scheme 3). The reaction of 4 equivalents DMAP in MeCN proceeds comparably clean with **9b**[OTf]<sub>4</sub> at ambient temperature giving pale-yellow solutions. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the reaction mixture of **9b**[OTf]<sub>4</sub> 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.<sup>8,13</sup> From the distinctive chemical shift a dimeric derivative with tetra-coordinate phosphorus atoms

(*cf.* [(Et<sub>2</sub>N)<sub>2</sub>PS<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub>;  $\delta(P) = 21.0$  ppm)<sup>14</sup> can be excluded and we thus propose the formation of DMAP adduct **10b**<sup>+</sup> which is also supported by our NMR investigation.<sup>8</sup> We were not able to isolate **10b**[OTf], however, we assume that cation **10b**<sup>+</sup> readily dismutates to cations **11**<sup>+</sup> ( $\delta(P) = 215.8$  ppm) and **12b**<sup>+</sup> ( $\delta(P) = -126.1$  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<sub>3</sub><sup>15</sup> and scrambling reactions of imidazoliumyl-substituted [L<sup>(Me,Me)</sup>PCl<sub>2</sub>]<sup>+</sup> cations.<sup>4</sup> P<sup>i</sup> centered cation **13b**<sup>+</sup> ( $\delta(P) = -126.1$  ppm) was recently reported by Macdonald *et al.* and unambiguously confirmed by its characteristic chemical shift (*cf.* lit:  $\delta(P) = -124.2$  ppm, CD<sub>2</sub>Cl<sub>2</sub>).<sup>16</sup> Cations of type **12a**<sup>+</sup> are also known and reported by Schmidpeter *et al.* as ylidylphosphorus-disulfide containing a tri-coordinate R-PS<sub>2</sub> 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<sub>3</sub>PCMe-PS<sub>2</sub>:  $\delta(P)_{PS_2} = 243.4$  ppm, d<sub>8</sub>-THF).<sup>2</sup> In an equilibrium reaction of cation **11**<sup>+</sup> 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, <sup>3</sup>J<sub>PH</sub> = 9.0 Hz; *cf.* PyPS<sub>2</sub>Br:  $\delta(P) = 65.5$  ppm, Py = pyridine; d<sub>3</sub>-MeCN).<sup>17</sup> The formation of cation **14**<sup>+</sup> results either from the equilibrium reaction of **11**<sup>+</sup> (eqn (2)) or **13** (eqn (3)) with DMAP which is liberated during the dismutation of cation **10b**<sup>+</sup> (Scheme 3). The <sup>31</sup>P NMR spectrum displays a quintet resonance which is indicative for the presence of two DMAP substituents consistent with the C<sub>2v</sub> symmetry of cation **14**<sup>+</sup> ( $\delta(P) = 96.9$  ppm; *cf.* [Py<sub>2</sub>PS<sub>2</sub>]<sup>+</sup>:  $\delta(P) = 104.7$  ppm, quintet, <sup>3</sup>J<sub>PH</sub> = 9.6 Hz; Py = pyridine; d<sub>3</sub>-MeCN). Similar equilibria and cations have been observed by Meisel *et al.* who reported on the pyridine (Py) stabilized phosphorus disulfide [Py<sub>2</sub>PS<sub>2</sub>]<sup>+</sup> cation.<sup>18</sup> Two crystalline polymorphs of **14**[OTf] were obtained after layering the reaction mixtures with Et<sub>2</sub>O (Fig. 6).<sup>19</sup> The obtained structural parameters compare well with those reported for the related pyridine cation [Py<sub>2</sub>PS<sub>2</sub>]<sup>+</sup> by Meisel *et al.*<sup>18</sup>

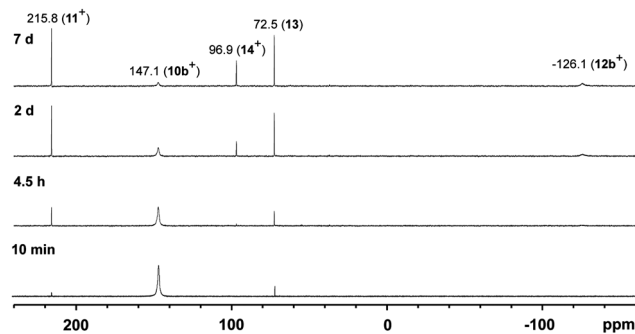
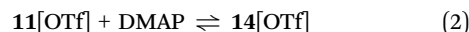


Fig. 5 <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the 1:4 reaction of **9b**[OTf]<sub>4</sub> and DMAP in CD<sub>3</sub>CN showing the scrambling reaction to cations **11**<sup>+</sup>, **12b**<sup>+</sup>, **14**<sup>+</sup> and adduct **13**.

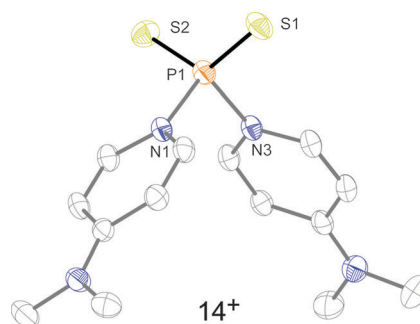


Fig. 6 Molecular structure of **14**<sup>+</sup> in **14**[OTf]. All hydrogen atoms and the triflate anion are omitted for clarity. Selected bond lengths in Å and angles in °: P1–S1 1.9309(8), P1–S2 1.9321(8), P1–N1 1.782(2), P1–N2 1.798(2), S1–P1–S2 124.09(4), N1–P1–N2 96.77(8), S–P1–N av. 108.14.

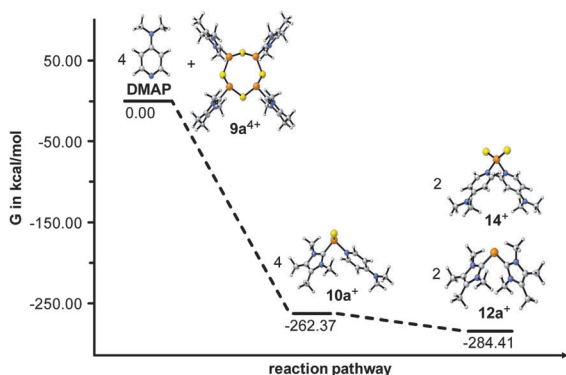


Fig. 7 Gibbs free energy in kcal mol<sup>-1</sup> of the observed and proposed phosphorus species.

In order to confirm our findings and support the suggested dismutation, quantum chemical calculations have been performed from the reaction of **9a**<sup>4+</sup> with 4 eq. DMAP to derive geometry and Gibbs free energy of the involved species as well as the suggested reaction intermediate **10a**<sup>+</sup>.<sup>20</sup> The density functional theory (DFT) hybrid model B3LYP<sup>21</sup> was used in combination with Grimme's atom-pairwise dispersion correction (D3).<sup>22</sup> Fig. 7 illustrates the Gibbs free energy  $\Delta G$  of educts (**9a**<sup>4+</sup>, DMAP), products (**12b**<sup>+</sup>, **14**<sup>+</sup>) and the proposed intermediate (**10a**<sup>+</sup>) calculated at the B3LYP-D3/def-SVP level of theory. The whole reaction pathway is thermodynamically favored ( $\Delta G = -284.4$  kcal mol<sup>-1</sup>). The proposed reaction intermediate **10a**<sup>+</sup> is energetically less favorable by 22 kcal mol<sup>-1</sup> compared to the final products, but 262 kcal mol<sup>-1</sup> lower in energy than the educt molecules ( $\Delta G = -262.4$  kcal mol<sup>-1</sup>). This observation is perfectly in line with the assumption of **10a**<sup>+</sup> being the main reaction intermediate.

In summary, we reported on the oligomerization reaction of cationic phosphorus monosulfides **8a,b**<sup>+</sup> which were formed *in situ* from the reaction of  $[L^{(R,Me)}PCl_2]^+$  cations **3a,b**<sup>+</sup> ( $L^{(R,Me)}$  = 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**<sup>4+</sup> primarily exist as crown conformers similar to cyclo-S<sub>8</sub>, however, the boat-chair (*C<sub>s</sub>*) conformers of the P<sub>4</sub>S<sub>4</sub> rings also exist in solution according to 2D-EXSY <sup>31</sup>P NMR experiments. Cations **9a,b**<sup>4+</sup> can be deoligomerized by DMAP to yield adducts **10a,b**<sup>+</sup> of the elusive cations **8a,b**<sup>+</sup>. Subsequent dismutation of **10a,b**<sup>+</sup> gives cations  $[L^{(R,Me)}_2P]^+$  (**12a,b**<sup>+</sup>) and  $[(DMAP)_2PS_2]^+$  (**14**<sup>+</sup>) as final products. The suggested reaction pathway was supported by DFT calculations.

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for Information Services and High Performance Computing (ZIH) for the generous allocation of computation time.

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- The low symmetry of **13** and the presence of the triflate anion encourage an effective quadrupole relaxation and prevents the observation of the  $^1J(^{31}P, ^{14}N)$  coupling. The same accounts for the more symmetric cation **14**<sup>+</sup>.
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- Similarly to the highly reactive intermediate **10b**<sup>+</sup>, the tetramethyl substituted derivative **10a**<sup>+</sup> was also observed in the reaction of **9a**[OTf]<sub>4</sub> and 4 eq. DMAP at  $\delta(P) = 144.7$  ppm. From the reaction spectra, chemical shifts as  $\delta(P) = 216.6$  ppm, 97.3 ppm, 70.9 ppm and –113.2 ppm can be assigned to **11**<sup>+</sup>, **14**<sup>+</sup>, **13** and **12a**<sup>+</sup>, respectively. The reaction NMR is depicted in the supporting information; Details of the two polymorphs are given in the ESI†.
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