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# Phosphorus, Sulfur, and Silicon and the Related Elements

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## N-Phosphoryl-2-oxo-1,2azaphospholanes: First Example of Cyclic O,O-Bidentate Ligands with the P-N-P Backbone

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### *N*-PHOSPHORYL-2-OXO-1,2-AZAPHOSPHOLANES: FIRST EXAMPLE OF CYCLIC O,O-BIDENTATE LIGANDS WITH THE P-N-P BACKBONE

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**Abstract** A convenient one-pot synthesis of N-phosphoryl-2-oxo-1,2-azaphospholanes was developed starting from commercially available or simple-to-prepare phosphorus (III) acid chlorides and 3-bromopropylamine. The compounds readily form complexes with f-elements of ML,  $ML_2$ , and  $M_2L_3$  composition including ( $\mu_2$ -peroxo)-bridged uranium complexes, depending on both the ligand and metal nature.

Keywords 1,2-Azaphospholanes; complexes; ligands

Bidentate chelate ligands with the P-N-P backbone in which oxygen or sulfur atoms of the phosphoryl groups serve as coordination sites are known to coordinate to a number of metals.<sup>1</sup> Some ligands of this type are useful as selective metal extractants<sup>2</sup> or find application as NMR shift reagents,<sup>3</sup> and their lanthanide complexes possess high luminescent properties,<sup>4</sup> whereas silver and palladium ones are promising for homogeneous catalysis.<sup>5</sup> Note that all such ligands known until now present linear compounds, whereas cyclic ligands are known to be advantageous for selectivity over the complex formation. Therefore, we have developed facile cascade synthesis of cyclic ligand systems with a P-N-P backbone **3a–c** based on an intramolecular Arbuzov reaction of N,N-bis-P(III)-substituted 3-bromopropylamines **1a**,**b**, generated in situ from phosphorus (III) acid chlorides, followed by either oxidation or the second intermolecular Arbuzov reaction of the intermediate 2-oxo-1,2-azaphospholanes **2a,b** (Scheme 1).<sup>6</sup> In the case of compounds **3b,c** having two chiral P-atoms, the diastereomers were separated by column chromatography. A comparison of X-ray and NMR data allowed us to conclude that the opposite configuration of asymmetric centers  $(R^*, S^*)$  is typical for the isomer having downfield chemical shift of the endocyclic P-atom in the <sup>31</sup>P-NMR spectra and smaller J<sub>P-P</sub> coupling constant.

2-Oxo-1,2-azaphospholanes **3a–c** readily form complexes with *f*-elements in neutral media. Depending on the nature of both the ligand and metal, the isolated complexes differ in composition (ML, ML<sub>2</sub>, and M<sub>2</sub>L<sub>3</sub>). Thus, reacting with Eu(III) nitrate,  $R^*, S^*$ -**3b** afforded the [Eu(L<sub>2</sub>)(NO<sub>3</sub>)<sub>3</sub>] complex, that is, ML<sub>2</sub>, whereas both diastereomers of **3c** form with Eu(III), Nd(III), and Pr(III) nitrates complexes [Ln<sub>2</sub>L<sub>3</sub>(NO<sub>3</sub>)<sub>6</sub>], regardless

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Scheme 1 One-pot synthesis of N-phosphoryl-2-oxo-1,2-azaphospholanes 3a-c.

of the metal-to-ligand molar ratio. In all of the above complexes the ligands possess an O,O-bidentate bridging or chelate coordination mode. Reaction of both isomers of ligands **3b,c** with uranyl nitrate in EtOH resulted in complexes  $[UO_2(L)(NO_3)_2]$  of ML composition, also with chelate coordination of a ligand. At the same time, in the case of **3a** a similar reaction afforded, depending on the reaction time, either the complex **4** with monodentate coordination via the endocyclic P=O moiety or ( $\mu_2$ -peroxo)-bridged uranium complex **5** with two fused 8-membered cycles (Scheme 2). Furthermore, the complex [ $\{UO_2(3c)NO_3\}_2(\mu_2-O_2)$ ] **6** (Figure 1) of similar structure was isolated in trace quantities from the reaction of  $R^*, S^*-3c$  with uranyl nitrate in CH<sub>3</sub>CN solution.



Figure 1 General view of the [ $\{UO_2(R^*, S^*-3c)NO_3\}_2(\mu_2-O_2)$ ] complex 6.



Scheme 2 Formation of uranium complexes 4 and 5.

Such peroxo-species are believed to form under the direct action of atmospheric molecular oxygen on soluble intermediate complexes reflecting the oxophility of the  $(UO_2)^{2+}$  group, similar to examples known from the literature.<sup>7</sup> However, the detailed mechanism of dioxygen insertion is still unclear.

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