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Research paper

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Jingjing Cui, Yongxin Li, Rakesh Ganguly, Rei Kinjo

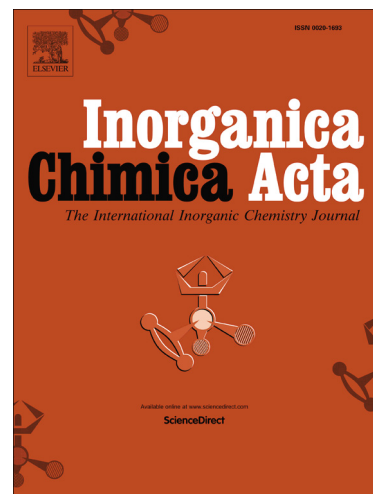
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Synthesis and Thermal Reactivity of a Me₃N-stabilized Cyclic (Alkyl)(Amino)Oxophosphonium Ion

Jingjing Cui,^[a] Yongxin Li,^[b] Rakesh Ganguly^[b] and Rei Kinjo*^[a]

^[a]*Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371*

^[b]*NTU-CBC Crystallography Facility*

Abstract

Reaction of cyclic (alkyl)(amino)phosphorous chloride **3** with GaCl₃ followed by the treatment with Me₃NO afforded trimethylamine-stabilized oxophosphonium ion **5**, which was fully characterized by NMR spectroscopy and X-ray diffraction analysis. Computational study using DFT calculations indicates that the incorporation of a carbon atom next to the P center accumulate electron density on the P center. Oxophosphonium ion **5** is air and moisture stable but undergoes thermal decomposition to afford a phosphorus oxychloride **7** as well as a few single crystals of the by-product **8**. Reaction mechanisms for the formation of **7** and **8** may involve a Lewis base free oxophosphonium ion **6**.

Introduction

Trigonal planar phosphorus cations and its nitrogen analogues¹⁻⁵ have attracted considerable attention in material science and synthetic chemistry as some of the former indeed play a key role in polymer chemistry^{3,6} whereas the latter are postulated as reactive intermediates in organic synthesis.⁷ Among them, chalcogenophosphoniums have been studied over several decades. In 1989, Burford and co-workers first structurally characterized dithia- and diselena-diphosphetane dications **A** which can be deemed the dimeric forms of the terminal thioxo- and selenoxophosphonium ions, respectively (Figure 1a).⁸ The same group also reported the isolation of the neutral zwitterionic 1,3,2,4-diazaphosphoniaaluminatacyclobutane **B**⁹ as well as Lewis base-stabilized thioxophosphonium ions **C**.¹⁰ It has been proposed by Schmidpeter et al. that selenoxophosphonium ion **D** can be isolated as the monomeric form¹¹ but to the best of our knowledge its structural authentication has not been done thus far. A recent seminal work by Masuda and co-workers demonstrated that starting from N-heterocyclic phosphane chloride **E**, a Lewis base-stabilized terminal oxophosphonium ions **F** can be prepared in two steps (Figure 1b).¹² According to their report, the base-free oxophosphonium ions **G** were not detected during the formation of **E**. Likewise, carbene-stabilized oxo- and thioxophosphonium ions **H** have been developed by Chauvin and Canac et al. in 2012.¹³

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