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Diphosphiranium (P_2C) or Diphosphetanium (P_2C_2) Cyclic Cations: Different Fates for the Electrophile-Initiated Cyclodimerization of a Phosphaalkene

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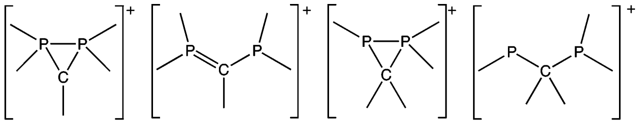
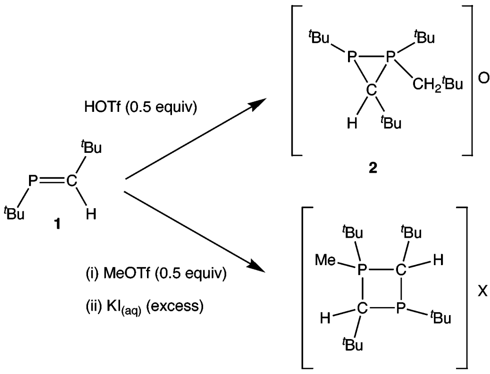
Highly strained phosphorus heterocycles are attractive synthetic targets due to their novel structures, bonding, and their utility as building blocks in organophosphorus chemistry.[1] Moreover, phosphorus heterocycles often have no isolable counterparts in nitrogen chemistry, and consequently, they provide unique insight into the striking differences between the chemistry of the first and second periods. A dramatic illustration of this difference is provided by the pioneering investigations of the $(P_2CR_5)^+$ cation which was isolated as the symmetric diphosphiranium (**A**) rather than the open form (**B**); in contrast, $(N_2CR_5)^+$ adopts form **B**.[2,3] The isolation of an asymmetric diphosphiranium (**C**) remains an elusive goal due, in part, to the challenge of finding suitable synthetic routes to this unusual species. The asymmetric diaziridinium cation, the nitrogen analogue of **C**, has not been isolated but has been proposed as a reaction intermediate.[4,5] Interestingly, calculations on $(P_2CH_5)^+$ suggest that **C** is lower in energy than **A** by ca. 47 kcal/mol.[6,7] Significantly, the first spectroscopic evidence for structure-type **C** was obtained in the P-methylation of diphosphirane $(Mes^*P)_2CH_2$; however, this species could not be isolated.[7] Analogous to the aforementioned chemistry of **A** and **B**, we envisage diphosphiranium **C** as a intramolecular phosphine−phosphenium alternative to the acyclic 3-phosphino-1-phosphenium ion (**D**). The intra- or intermolecular coordination chemistry of phosphines with phosphenium ions has recently been exploited to systematically develop a series of novel cyclic and acyclic *catena*-phosphorus cations.[8]



A **B** **C** **D**

We recently reported the spectroscopic detection of diphosphiranium ions (**C**) formed from the reaction of phosphaalkenes ($Mes^*P{=}CH_2$ or $MesP{=}CPh_2$) with in situ generated phosphenium ions.[9] We propose that **D** is an intermediate in this transformation. Unfortunately, attempts to isolate pure materials from these reaction mixtures were unsuccessful due to side reactions and the low stability of the product. With the goal of obtaining isolable species, we hypothesized that phosphaalkene **1**,[10] bearing bulky ^{t}Bu substituents, might effectively stabilize highly reactive species such as **C**. Herein, we report the first crystallographically characterized diphosphiranium salt of type **C** and the unexpected synthesis of an unprecedented diphosphetanium salt. Importantly, we have discovered that the reaction of phosphaalkenes with electrophiles provides an effective route to novel phosphorus heterocycles.



3a: X=OTf
3b: X=I

A colorless solution of **1** in CH_2Cl_2 was treated with of HOTf (0.5 equiv), and subsequently, the reaction mixture was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. Remarkably, the spectrum revealed that **1** ($\delta = 274$) was entirely consumed and was replaced by signals assigned to two products (or isomers) containing direct P−P bonds ($\delta = -36.8, -120.4$; $J_{PP} = 247$ Hz; 40%; $-44.9, -49.1$; $J_{PP} = 261$ Hz; 60%). In contrast to our previous investigations,[9] no additional products were observed in the reaction of **1** with HOTf. Moreover, the products were stable in solution and, consequently, single crystals of the major species could be obtained from a concentrated toluene/hexanes solution. The molecular structure confirms the identity of the major product as the unsymmetrical diphosphiranium **2** (Figure 1a). The minor product has not yet been isolated.

In an attempt to explore the generality of this new reaction, phosphaalkene **1** was treated with MeOTf (0.5 equiv) in CH_2Cl_2 solution. Surprisingly, a single, yet entirely different, product was detected in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture ($\delta = 61.6, 18.1$; $^2J_{PP} = 15$ Hz). Moreover, this product is air- and moisture-stable, and its ^1H NMR spectrum shows a doublet resonance consistent with a $P{-}CH_3$ group ($\delta = 2.30$; $^2J_{PH} = 11$ Hz). These observations are in stark contrast to those observed for air-sensitive diphosphiranium **2** and, while consistent with a dimer, suggest that Me^+ interacts with the P rather than the C in **1**. After exchange of the triflate in **3a** with iodide, X-ray crystallography revealed that the product was a 1,3-diphosphetanium salt (**3b**) containing a P_2C_2 ring (Figure 1b).[11]

To our knowledge, compounds **2** and **3b** represent the first structurally characterized diphosphiranium (type **C**) and 1,3-diphosphetanium cations, respectively.[12−14] Each was isolated as a single diastereomer. The P−P bond length in **2** (2.1637(5) Å) is slightly shorter than a typical P−P single bond (2.25 Å)[15] and is longer than that in the diphosphiranium (type **A**) (2.1195(11) Å).[2] The P−C bond lengths are largely typical for P−C single bonds (ca. 1.85 Å)[15] with slightly shorter bond lengths observed at the phosphonium center (P1−C1 = 1.8359(14) Å; P1−C2 = 1.8148(14) Å). The small internal ring bond angles at P1 (55.82(5)°), P2 (52.69(4)°), and C2 (71.49(5)°) reflect the strain in the P_2C ring. The P_2C_2 heterocycle **3b** crystallizes with two separate molecules in the asymmetric unit. Most of the P−C bond lengths in **3b** are

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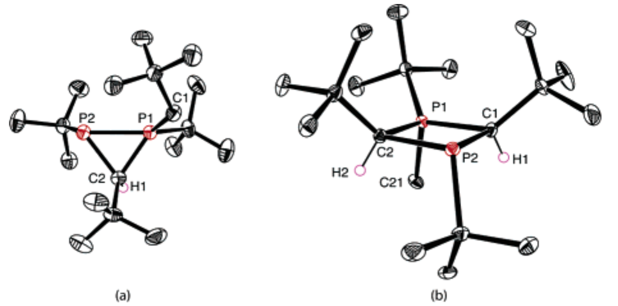
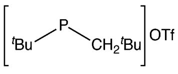


Figure 1. Molecular structures of (a) the diphosphiranium cation in **2** and (b) the 1,3-diphosphetanium cation in **3b** (two virtually identical molecules appear in the asymmetric unit). For clarity, only ring hydrogen atoms are shown.

typical of P−C bonds, with the exception of a short bond of the P−Me (av 1.807(3) Å). Interestingly, the P_2C_2 ring in diphosphetanium **3b** is nearly planar (av dihedral angle ∼3°), and the ring itself is a slightly distorted square (sum of internal angles is 359.82(29)°), with individual angles being ∼90°. The observed planarity of the P_2C_2 ring in **3b** is in contrast to the puckered structures often observed for neutral diphosphetanes.[1]

Once the nature of the products of the reaction had been established, we undertook preliminary investigations to identify intermediates in these unexpected reactions. ^{31}P NMR spectra of reaction mixtures containing **1** and HOTf (1:1) showed quantitative formation of a new signal ($\delta = 210$) which was assigned to phosphenium triflate **4** (there is likely some coordination of the phosphenium by triflate).[16] Further evidence that **4** is an intermediate in the formation of **2** from **1** and HOTf was obtained by treating in situ generated **4** with **1** (1:1) to obtain **2** quantitatively. The mechanism of formation of **3a** from **1** and MeOTf is perhaps even more intriguing. We speculated that the phosphaalkene must initially be methylated at P to afford a rare methylenephosphonium ion **5**.[17] To test this hypothesis, **1** was treated with MeOTf (1:5), and NMR studies suggest that **5** is the major product along with **3a**. The signals observed in the ^{31}P and ^{13}C NMR spectra of the reaction mixture are consistent with this assignment (^{31}P $\delta = 176$; ^{13}C $\delta_{P=C} = 153$; ${}^{1}J_{PC} = 98$ Hz). On the basis of the arrangement of the ^{t}Bu substituents in **3b**, we postulate that the reaction must follow a stepwise rather than a concerted reaction mechanism. A concerted [2 + 2] cycloaddition of **1** to **5** would necessitate a *trans* configuration of the ^{t}Bu substituents in **3**. In contrast, the stepwise addition of **5** to **1** could afford intermediate [^{t}Bu(Me)P−CH(^{t}Bu)−P(^{t}Bu)═CH(^{t}Bu)]OTf, which, after a necessary rotation of CH(^{t}Bu) to enable ring closure, gives the observed arrangement of ^{t}Bu groups in **3** (3 above, 1 below the P_2C_2 plane). The reason for the umpolung-like reactivity of the P═C bond when Me^+ is used as the electrophile in place of H^+ is perplexing and requires further investigation.[18]



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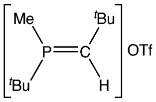

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In conclusion, we have demonstrated that phosphaalkenes are convenient precursors to highly strained phosphorus heterocycles which have no isolable counterparts in nitrogen chemistry. Future work will focus on investigating the scope and mechanism of these unprecedented reactions. In addition, the possibility to use **2** and **3** as dormant ring-closed forms of the propagating species in the cationic polymerization of phosphaalkenes is of considerable interest to us.

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Supporting Information Available: Experimental procedures, spectroscopic data, additional figures, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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