(Phosphanyl)phosphaketenes as building blocks for novel phosphorus heterocycles.
(Phosphanyl)phosphaketenes as building blocks for novel phosphorus heterocycles†

Max M. Hansmann, David A. Ruiz, Liu (Leo) Liu, Rodolphe Jazzar and Guy Bertrand*

Although BH₃ simply coordinates the endocyclic P of (phospholino)phosphaketene 1Dipp, the bulkier B(C₆F₅)₃ gives rise to a zwitterionic diposphirenium, which is a novel type of 2n-electron aromatic system as shown by the calculated NICS values. While the reaction of 1Dipp with Na₄(PCO(dioxane))₄ is unselective, the same reaction with the sterically bulky (phospholino)phosphaketene 1Ar⁺⁺ [Ar⁺⁺ = 2,6-bis(di(4-tert-butylphenyl)methyl)-4-methylphenyl] selectively affords a sodium bridged dimer containing a hitherto unknown \( \lambda^3,\lambda^3,\lambda^3 \)-tri phosphete core. The latter formally results from \(^1P^-\) addition to a 1,3-P/C-dipole. Similarly, adamantyl isonitrile adds to 1Dipp giving a 4-membered phosphacycle. In contrast to 1, the phosphaketene derived from the electrophilic diazaphospholidine-4,5-dione is unstable and reacts with a second molecule of Na [PCO(dioxane)]₄ to afford a 1,3,4-oxadiphospholonide derivative.

Introduction

Compared to the well-known isocyanates [R–N==C==O], the chemistry of their heavier homologues, namely phosphaketenes [R–P==C==O], has been largely unexplored. This is presumably the result of limited synthetic access and poor stability of their alkyl and aryl substituted derivatives.† Indeed, pioneering work by Appel et al. showed that although the very bulky [C₆H₅(CH₂)₃]–P==C=O can be isolated at room temperature, 1Bu-PCO dimerizes above ~60 °C.‡ However, the recent discovery of efficient preparation of phosphaethynolate salts (PCO–M)³ without loss of CO to give access to these reactions, the phosphaketene group acts as a phosphine-carbonyl adduct. This behavior is reminiscent of the chemistry of transition metal carbonyl complexes, and it is noteworthy that before our work the chemistry of main group polyboranes was essentially limited to boranes,¹⁴ polyboranes¹⁵ and carbenes.¹⁶ Herein we report that the P–PCO scaffold can also react without loss of CO to give access to a variety of hitherto unknown phosphorus heterocycles.

Results and discussion

We started our investigation by studying the electrophilic activation of the [P–PCO] moiety of 1Dipp, with the aim of triggering the loss of carbon monoxide. We chose two different boron-derived Lewis acids. Upon addition of excess BH₃, simple coordination to the endocyclic P center occurs giving 4, as

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shown by the $^{31}$P NMR spectrum [-226 ppm (d), +131 ppm (br. d), $J_{PP} = 295$ Hz] and by a single crystal X-ray diffraction study (Scheme 2; Fig. 1, top). To understand the regioselectivity of the reaction, three BH$_3$ adduct isomers were optimized at the B3LYP-D3BJ/def2-TZVP level of theory (Fig. 2). The results show that the observed product 4 is more thermodynamically stable than 4b and 4c by +13.2 and +24.7 kcal mol$^{-1}$ (gas-phase electronic energies), respectively. Moreover, since the absolute coefficient of the HOMO of 1Dipp at the endocyclic P (0.42) is much larger than those at the phosphorus of PCO (0.32) and at O (0.11), 4 is also the kinetic product of the reaction.

Due to the steric environment around the endocyclic P atom, we wondered whether a larger borane would react at a different site (Scheme 2). Mixing 1Dipp and B(C$_6$F$_5$)$_3$ resulted in a new product as observed by $^{31}$P NMR spectroscopy with two sharp doublets at $\delta = +206$ and $-11$ ppm ($J_{PP} = 215$ Hz). An X-ray diffraction study revealed the formation of the unusual zwit-terioric diphosphirenium 5 (Fig. 1, bottom). The PP bond distance (2.0804(14) Å) becomes significantly shorter than in 1Dipp (2.3782(8) Å)$^{20}$ and is in the outer range for PP double bonds (1.985–2.050 Å).$^{24}$ Concomitantly, the CO bond elongates from 1.170(3) Å in 1Dipp to 1.289(4) Å in 5. It is important to note that the computed nucleus independent chemical shift (NICS)$^{19}$ values for the central three-membered ring are negative [NICS(0) = −17.33 and NICS(1) = −11.71 ppm], which suggests that the three-membered ring of 5 is a 2π-electron aromatic system. Mechanistically, the interaction of the borane with the oxygen atom induced a ring closure between the carbon ketene center. Alternatively, a reviewer suggested that the borane abstracts the PCO moiety to form a close ion contact-pair [P$^+$/PCO·BR$_3$] followed by coordination of the phosphaalkyne to the electrophilic phosphorus center.$^{29}$ However, DFT calculations indicate that the heterolytic cleavage of the P–P bond is energetically very costly. Moreover, a transition state in agreement with a concerted Lewis acid activation of 1 has been located using the small BF$_3$ Lewis acid as a model (Fig. S1†). Interestingly, 5 can be regarded as 1*, the cyclic isomer of 1 trapped by a Lewis acid. DFT calculations predict an energy barrier of 22.4 kcal mol$^{-1}$ for the endergonic interconversion of 1 into its cyclic isomer 1* ($\Delta E = 22.1$ kcal mol$^{-1}$) (Scheme 3). Note that the [P]−OCP (1**) and [P=O]−CP (1***) isomers are predicted to be 15.2 and 11.5 kcal mol$^{-1}$, respectively, higher in energy than 1.$^{21}$
While the reaction of 1\textsuperscript{dipp} with Na[PCO(dioxane)]\textsubscript{2} is unselective, giving rise to several compounds, we observed that the same reaction with the sterically bulky (phosphino)phosphaketene 1\textsuperscript{Ar**}, featuring 2,6-bis[di(4-tert-butylphenyl)methyl]-4-methylphenyl substituents\textsuperscript{22} was highly selective. Independent of the excess Na[PCO(dioxane)]\textsubscript{2} used (or one equivalent), the \textsuperscript{31}P NMR spectrum showed the formation of a single product [+126.1 (d), +69.6 ppm (t), \(J_{PP} = 302\) Hz]. An X-ray diffraction study revealed that it was the sodium bridged dimer 6 containing the hitherto unknown \(\lambda^2,\lambda^2,\lambda^3\)-triphosphete core (Scheme 4, Fig. 3). Upon addition of 15-crown-5 to the \(1\text{Dipp}\) used (or one equivalent), the \textsuperscript{31}P NMR signals [+119.7 (d) and +78.8 ppm (t), \(J_{PP} = 310\) Hz] was observed and the corresponding monomer 7 could be characterized by X-ray diffraction (Fig. 4).

The formation of the triphosphate scaffold formally results from a \([1 + 3]\)-cycloaddition of \(\text{P}^-\) to the PPC unit. Indeed, when the \(^1\text{C}\) labeled phosphaketene 1\textsuperscript{Ar**} was reacted with non-\(^1\text{C}\)-labeled Na[PCO(dioxane)]\textsubscript{2}, we observed an intense broad resonance at \(\delta^{1\text{C}} = 250.2\) ppm demonstrating that the PPC unit of Na[PCO(dioxane)]\textsubscript{2} is only poorly soluble. Otherwise, instead of 1, heterocycles of type 6 are formed as the major product.

Serendipitously, we also prepared another novel type of phosphorus heterocycle formally resulting from a \([1 + 3]\)-cycloaddition of "P\textsuperscript{**}\" from NaPCO to the PPC unit. When the \(^{13}\text{C}\) labeled phosphaketene 1\textsuperscript{Ar**} was reacted with non-\(^{13}\text{C}\)-labeled Na[PCO(dioxane)]\textsubscript{2}, we observed an intense broad resonance at \(\delta^{1\text{C}} = 250.2\) ppm demonstrating that the PPC unit of Na[PCO(dioxane)]\textsubscript{2} is only poorly soluble. Otherwise, instead of 1, heterocycles of type 6 are formed as the major product.

The formal insertion of an isonitrile giving 8 can be rationalized by a mechanism similar to that postulated for the insertion of \(\text{P}^-\) leading to 6. According to DFT calculations, this process is exergonic by 6.1 kcal mol\(^{-1}\) with an energy barrier of 23.3 kcal mol\(^{-1}\) (Fig. 6, right). Note that direct
The substitution of CO by the isonitrile is also exergonic by 5.5 kcal mol\(^{-1}\)/C\(_{1}\) but with a higher activation energy barrier (27.1 kcal mol\(^{-1}\)/C\(_{1}\)) (Fig. 6, left).

The difficulty in synthesizing (phosphino)phosphaketenes is illustrated by our attempt to prepare 11 derived from the electrophilic diazaphospholidine-4,5-dione (Scheme 6). A single product was formed upon mixing 9 with NaPCO, but the \(^{31}\)P NMR spectrum revealed the presence of three different phosphorus nuclei \(^{31}\)P NMR \(\delta = +323\) (dd, \(J = 466\) Hz, 282 Hz); +48 (d, \(J = 282\) Hz); +45 (d, \(J = 466\) ppm). An X-ray diffraction study revealed the 1,3,4-oxadiphospholonide core 10 (Fig. 7), a type of heterocycle previously only observed by Grützmacher et al. in the reaction of NaPCO with tetraphenyl-cyclopentadienone. Interestingly, in the solid-state this compound features a linear polymeric network structure in which the sodium cation is bridging between the diketone moiety and the phosphorus heterocycle (Fig. 8).

Mechanistically, it seems reasonable to postulate the initially formed (phosphino)phosphaketene 11 spontaneously rearranges into the spirocyclic zwitterionic derivative 12 which resembles the borane adduct 5. Then, a second equivalent of NaPCO induces a ring opening giving 13, which undergoes a ring closure leading to the observed product 10.

Conclusions

This work has shown that (phosphino)phosphaketenes are powerful building blocks in heterocyclic chemistry. In contrast to our recent reported CO substitution approach,\(^{12}\) this work...
demonstrates the feasibility of nucleophiles to add to carbon on the phosphaketene moiety. The endocyclic P center can either activate the phosphaketene by forming highly reactive diphosphirenium species or engage in ring closing reactions. Importantly the stability and chemical behaviour of these novel heterocycles is strongly dependent on the nature of the phosphino substituents.

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