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

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Although BH₃ simply coordinates the endocyclic P of (phospholidino)phosphaketene 1Dipp, the bulkier B(C₆F₅)₃ gives rise to a zwitterionic diphosphirenium, which is a novel type of 2e⁻ electron aromatic system as shown by the calculated NICS values. While the reaction of 1Dipp with Na₄(PCO(dioxane))₉ is unselective, the same reaction with the sterically bulky (phospholidino)phosphaketene 1Ar₃ [Ar= 2,6-bis(di(4-tert-butylphenyl) methyl)-4-methylphenyl] selectively affords a sodium bridged dimer containing a hitherto unknown N₃⁺,C₃⁺,C₃⁻ triphosphete core. The latter formally results from a P⁻ 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)] 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 [CsH₄(tBu)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)₄ has allowed access to group 14 (Si, Sn, Ge, Pb) and transition metal (Re, Au, Co, W) substituted phosphaketenes. In addition, the reaction of chlorodiaphospholidines and phospholines with Na[PCO(dioxane)] has allowed for the isolation of (phosphino)phosphaketenes 1 and 11, respectively (Scheme 1). Although the phosphaketene moiety of 1 reacts with the unsaturated backbone to give various rearrangement products, ¹(phospholidino)-phosphaketene 1Dipp is thermally very stable (heating a toluene solution of 1Dipp overnight at 80 °C does not lead to decomposition or any rearrangement products), which allows for studying the reactivity of the [P]–PCO moiety. We have already reported that elimination of CO occurred under irradiation of ¹Ar⁺, affording the corresponding room temperature stable phosphinidene 2Ar⁺, while addition of phosphines to ¹Ar⁺ and 1Dipp leads to adducts 3.¹² In both of these reactions, the phosphaketene group acts as a phosphinidene-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 carbonyl compounds 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-terionic diphosphirenium 5 (Fig. 1, bottom). The PP bond distance (2.0804(14) Å) becomes significantly shorter than in

$1^{\text{Dipp}}$ (2.3782(8) Å)$^{20}$ and is in the outer range for PP double bonds (1.985–2.050 Å).$^{21}$ Concomitantly, the CO bond elongates from 1.170(3) Å in $1^{\text{Dipp}}$ 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 $2\pi$-electron aromatic system. Mechanistically, the interaction of the borane with the oxygen atom induced a ring closure between the carbon ketene system. Alternatively, a reviewer suggested that the borane abstracts the PCO atom and the endocyclic P center. 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.$^{22}$
While the reaction of 1 with Na[PCO(dioxane)] is unselective, giving rise to several compounds, we observed that the same reaction with the sterically bulky (phosphino)phosphaketene 1′′′′, featuring 2,6-bis[di(4-tert-butylphenyl)methyl]-4-methylphenyl substituents, was highly selective. Independent of the excess Na[PCO(dioxane)] used (or one equivalent), the 31P NMR spectrum showed the formation of a single product [+ 126.1 (d), + 69.6 ppm (t), JPP = 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 P- leading to the PPC unit. Indeed, when the 13C labeled phosphaketene 1′′′′′ was reacted with non-13C-labeled Na[PCO(dioxane)], we observed an intense broad resonance at δ13C = 250.2 ppm demonstrating that the PPC unit remains, at least to a large extent, in the final product. Mechanistically, DFT calculations indicate that the reaction involves an initial attack onto the carbon atom of the CO moiety followed by cyclization with simultaneous loss of CO (ΔG‡ = 16.1 kcal mol⁻¹) (see Fig. S2 in ESI†). Aside from the formation of a novel type of phosphorus heterocycle, these results are interesting because they give important information on the synthesis of (phosphino)phosphaketenes 1. Indeed, to prepare the latter, it is crucial to use only one equivalent of Na[PCO(dioxane)] and toluene as the solvent in which Na[PCO(dioxane)] 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. As isonitriles and carbon monoxide are isoelectronic, we were interested in the thermal substitution of the CO in phosphaketene 1′′′′′ by an isonitrile, using our recently reported ligand exchange strategy. Surprisingly, the isonitrile does not add at the phosphorus center of PCO to displace CO, as previously observed with phosphines, but attacks at the carbon. This is followed by a cyclization involving the endocyclic P and the resulting heterocycle 8 was isolated in 85% yield (δ31P = 148.0 and 88.3 ppm, J = 370 Hz) (Scheme 5, Fig. 5).

The formal insertion of an isonitrile giving 8 can be rationalized by a mechanism similar to that postulated for the insertion of 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
substitution of CO by the isonitrile is also exergonic by 5.5 kcal mol\(^{-1}\) but with a higher activation energy barrier (27.1 kcal mol\(^{-1}\)).

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 \(\delta = +323 \text{ (dd, } J = 466 \text{ Hz, } 282 \text{ Hz)}; +48 \text{ (d, } J = 282 \text{ Hz)}; +45 \text{ (d, } J = 466 \text{ Hz) ppm}.\) 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.\(^{26}\) 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 diphosphenium 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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Notes and references

21 The [P]-PCO to [P]-OCP energy difference is in good agreement with the recently calculated value, see ref. 11.


24 The $^{13}$C NMR signal is broad as a result of the coupling with several different phosphorus nuclei (see ESI†).
