https://doi.org/10.1021/jacs.7b11791

Peer reviewed version

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10.1021/jacs.7b11791

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A Transient Vinylphosphinidene via a Phosphirene-Phosphinidene Rearrangement

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Supporting Information Placeholder

\textbf{ABSTRACT:} A room-temperature-stable crystalline 2\textit{H}-phosphirene (1), was prepared by treatment of an electrophilic di-amidocarbene with tert-butylphosphaalkyne. Compound 1 is shown to react as a vinylphosphinidene generated via phosphirene-phosphinidene rearrangement. Thermalysis is shown to effect C-N bond scission while reactions with CaCl\textsubscript{2} or (th)AuCl affords formal oxidation of the phosphinidene center and the phosphinidene-insertion into an aromatic C-C bond of a mesityl group respectively. The latter reaction is the first example of a phosphorus analog of the B"{u}chner ring expansion reaction.

It is also interesting to note that the literature describing the reactivity of cyclopropene derivatives is known to involve cyclopropene-carbene rearrangements (Figure 1a).\textsuperscript{3b,3c} skeletal rearrangements leading to vinylidenes and vinylcarbenes, or 1,2-

\begin{figure}[h]
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\caption{(a) Cyclopropene-carbene rearrangements. (b) 1\textit{H}-Phosphirene-2\textit{H}-phosphirene rearrangements. (c) Isolable 2\textit{H}-phosphirenes A and B. (d) Pyrolysis of a vinylphosphirane C. (e) B"{u}chner ring expansion. (f) 2\textit{H}-Phosphirene-vinylphosphinidene rearrangements.}
\end{figure}
migrations leading to cyclopropyldienes. Mathey et al. reported the pyrolysis of a vinylphosphirane C, leading to a vinylphosphinidene intermediate, which subsequently convert to phosphapropyne (Figure 1d). These observations prompt the question: does the strained C-P ring in phosphirenes undergo analogous reactions of cyclopentene-carbene rearrangements, affording a phosphirene-phosphinidene rearrangement (Figure 1b) offering access to a reactive phosphinidene? It is noteworthy that aside from the phosphinidene transffer reagents, \(^{4b,15}\) the most commonly used strategies for generation of extremely reactive phosphinidenes involve the thermolysis or photolysis of suitable precurers, including cyclic oligophosphines, \(^{11}\) P-substituted phosphiranes, \(^{12}\) phospha-Wittig reagents, \(^{13}\) dibenzo-7-phosphanorbornadiene, \(^{14}\) and (phosphino)phosphaketone. \(^{15}\) In the present work, we report the preparation of a 2H-phosphirene 1, and its thermally or chemically induced rearrangements (Figure 1f). Of particular interest is that 1 reacts via an elusive vinylphosphinidene intermediate inserting into a C-N bond or an aromatic C-C bond of a mesityl group. The latter reaction represents the first phosphorus analog of the Büchner ring expansion (Figure 1e). \(^{16}\)

Reaction of the highly electrophilic cyclic diamidocarbene (mes-DAC)\(^{17}\) with an equimolar portion of \(\text{BuC}=\text{P}\) at room temperature in benzene resulted in consumption of the starting material within 10 min (Figure 2a). Compound 1 was isolated as a white powder in 88% yield. The \(^{31}\)P NMR spectrum of 1 displays a sharp signal at 133.6 ppm, which is more downfield than A (71.7 ppm)\(^{6a}\) or B (48.1 ppm). \(^{50}\) Single crystals of 1 (Figure 2b) suitable for an X-ray diffraction study were grown by slow vapor diffusion of pentane into a saturated CH\(_2\)Cl\(_2\) solution. These data confirmed the formulation as (mes-DAC)(BuC=P) in which the C-P three-membered ring appears to be a scannle triangle with the C(1)-P, C(2)-P, and C(1)-C(2) bond lengths of 1.913(4) Å, 1.656(4) Å, and 1.461(5) Å, respectively. The C(1)-P-C(2) angle (47.7(1)°) is more acute than those of C(2)-C(1)-P (56.9(2)°) and C(1)-C(2)-P (75.4(2)°). The bond lengths of C(1)-P (1.882(9) Å) and C(2)-P (1.635(9) Å) in Regitz’s 2H-phosphirene tungsten pentacarbonyl complex are shorter compared to those of 1, while the C(1)-C(2) bond length (1.48(1) Å) is longer. \(^{6a}\) It is interesting to note that 2H-phosphasilirenes \(^{18}\) and 2H-phosphagermirenes \(^{19}\) have been prepared by an analogous reaction of silylene or germylene with phosphalkynes. Nonetheless, 1 is the first crystallographically characterized free 2H-phosphirene.

![Figure 2](image)

**Figure 2.** (a) Synthesis of 1. (b) POV-ray depiction of the molecular structure of 1 with H atoms omitted for clarity. C, black; N, blue; O, red; P, orange. (c) IsoSurface of the HOMO and LUMO of 1 (isovalue = 0.05).

The bonding in 1 was probed with density functional theory (DFT) calculations, coupled with natural bond orbital (NBO) analysis (M06-2X/TZVP/M06-2X/Def2-SVP). The C(1) (0.18 a.u.) and P (0.61 a.u.) atoms are positively charged, while the C(2) atom is negatively charged (-0.38 a.u.). The Wiberg bond indices (WBIs) of C(1)-C(2), C(1)-P and C(2)-P are 1.09, 0.83, and 1.69, respectively, demonstrating the multiple bond nature of C(2)-P. Moreover, the HOMO primarily involves the degenerate bonding orbitals of the C(2)-P ring, whereas the LUMO is principally the C(2)-P π*-antibonding orbitals (Figure 2c). This stands in contrast to the observation for acyclic phosphalkynes where the HOMO is the C-P π orbital. \(^{20}\)

A toluene solution of 1 was heated at 110 °C for 12 h. The \(^{31}\)P NMR spectrum showed 1 quantitatively converted into a new species 2 (72.5 ppm) (Figure 3a). Slow evaporation of a saturated toluene solution of 2 allowed for the formation of single crystals suitable for an X-ray diffraction study. 2 was determined to be a rearrangement product, in which the 2H-phosphirene moiety undertook a ring-expansion reaction to form a rare example of a stable 1,2-dihydro-1,2,3-azaphosphete (Figure 3b). \(^{21}\) The C(2)-P bond distance (1.835(7) Å) becomes significantly longer than in 1 (1.656(4) Å) and is in the range of C-P single bonds. \(^{22}\) Concomitantly, the C(1)-C(2) bond shortens from 1.461(5) Å in 1 to 1.360(9) Å in 2.

![Figure 3](image)

**Figure 3.** (a) Proposed reaction pathway for thermolysis of 1. (b) POV-ray depiction of the molecular structure of 2 with H atoms omitted for clarity. C, black; N, blue; O, red; P, orange.
Figure 4. (a) Reactions of 1 with 3,4,5,6-Tetrachloro-1,2-benzoquinone leading to 3 and 4. POV-ray depiction of the molecular structures of (b) 3 and (c) 4 with H atoms omitted for clarity. C, black; N, blue; O, red; P, orange; Cl, green.

Figure 5. (a) Reaction of 1 with (tht)AuCl affording 5. (b) POV-ray depiction of the molecular structure of 5 with H atoms omitted for clarity. C, black; N, blue; O, red; P, orange; Au, yellow; Cl, green.

The formation of 2 can be formally viewed as an insertion of a transient phosphinidene center into a C-N bond (Figure 3a), although the precise mechanistic picture may be more complicated. The electronic ground state of the vinylphosphinidene is a triplet similar to that previously reported for arylyphosphinidenes. This has been attributed to the absence of π-donor substituents. The P-C(2) and C(1)-C(2) distances are computed to be 1.782 Å and 1.396 Å, respectively while the Mulliken spin density of the vinylphosphinidene is computed to be primarily localized at P center (1.72), consistent with the diradical nature of P. Subsequent reaction of this transient phosphinidene with the proximal C-N bond affords 2.

Figure 6. Free energy reaction profile (kcal/mol) for the formation of 5. In the 3D structures, selected bond lengths are given in angstroms.

Efforts to chemically induce phosphirene-phosphinidene rearrangement were undertaken (Figure 4a). The reaction of 1 with a stoichiometric amount of 3,4,5,6-tetrachloro-1,2-benzoquinone (o-O$_2$C$_6$H$_4$Cl)$_2$ in CH$_2$Cl$_2$ showed the formation of a single product. The new product 3, isolated in 85% yield, showed a $^{31}$P NMR signal at 214.7 ppm, which is consistent with values determined for trivalent dioxaphospholes. An X-ray diffraction study confirmed the formulation of 3 as (MeD)$(\text{BuCP}(O_2C_6H_4Cl))$ (Figure 4b). Altering the stoichiometry to a 1:2 ratio of o-O$_2$C$_6$H$_4$Cl$_2$ or treatment of 3 with another equivalence of o-O$_2$C$_6$H$_4$Cl$_2$ gave product 4 in 88 and 90% yields respectively. Compound 4 exhibits a $^{31}$P NMR signal at -1.2 ppm. This shift is significantly down-field compared to those of 1 (133.6 ppm) and 3 (214.7 ppm). A single crystal X-ray diffraction study of 4 unambiguously revealed it to be (MesD)$(\text{BuCP}(O_2C_6H_4Cl))$ (Figure 4c), the penta-coordinated phosphorus center was produced by the Ramirez reaction. The products 3 and 4 can be formally viewed as the sequential oxidation products of the vinylphosphinidene center induced by o-O$_2$C$_6$H$_4$Cl$_2$. Indeed, the approach of o-O$_2$C$_6$H$_4$Cl$_2$ toward the C$_2$P ring in 1 results in the transition state of phosphirene-phosphinidene rearrangement with the activation barrier of 22.5 kcal/mol (See SI), leading to the formation of 3 (-43.5 kcal/mol)

Transition-metal complexes are capable of inducing ring opening of cyclopropane derivatives. Moreover, the group of Mathey investigated the cycloaddition reactivity of transient vinylphosphinidene tungsten complexes. Thus we probed the stoichiometric reaction of 1 with (tht)AuCl (Figure 5a). Stirring the reagents in CH$_2$Cl$_2$, rapidly led to the formation of a single product 5.
is also grateful for the award of an Einstein Fellowship at TU Berlin. L.L.C. is grateful for the award of an Ontario Graduate Scholarship.

REFERENCES


ASSOCIATED CONTENT
Supporting Information
Synthetic, spectroscopic, crystallographic and computational data have been deposited in the SI. The Supporting Information is available free of charge on the ACS Publications website.

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ACKNOWLEDGMENT
D.W.S. gratefully acknowledges the financial support from NSERC Canada and the award of Canada Research Chair. D.W.S.
Phosphirene-Phosphinidene Rearrangement

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