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migrations leading to cyclopropylidenes.⁸ Mathey *et al.* reported the pyrolysis of a vinylphosphirane **C**, leading to a vinylphosphinidene intermediate, which subsequently convert to phosphapropyne (Figure 1d).⁹ These observations prompt the question: does the strained C₂P ring in phosphirenes undergo analogous reactions of cyclopropene-carbene rearrangements, affording a phosphirene-phosphinidene rearrangement (Figure 1b) offering access to a reactive phosphinidene? It is noteworthy that aside from the phosphinidene transfer reagents,^{4b, 10} the most commonly used strategies for generation of extremely reactive phosphinidenes involve the thermolysis or photolysis of suitable precursors, including cyclic oligophosphines,¹¹ P-substituted phosphiranes,¹² phospho-Wittig reagents,¹³ dibenzo-7-phosphanorbornadiene,¹⁴ and (phosphino)phosphaketene.¹⁵ In the present work, we report the preparation of a 2*H*-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 *t*BuC≡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 ³¹P 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).^{6b} Single crystals of **1** (Figure 2b) suitable for an X-ray diffraction study were grown by slow vapor diffusion of pentane into a saturated CH₂Cl₂ solution. These data confirmed the formulation as (^{Mes}DAC)(*t*BuC=P) in which the C₂P three-membered ring appears to be a scalene 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 2*H*-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 2*H*-phosphasilirenes¹⁸ and 2*H*-phosphagermirenes¹⁹ have been prepared by an analogous reaction of silylene or germylene with phosphalkynes. Nonetheless, **1** is the first crystallographically characterized free 2*H*-phosphirene.

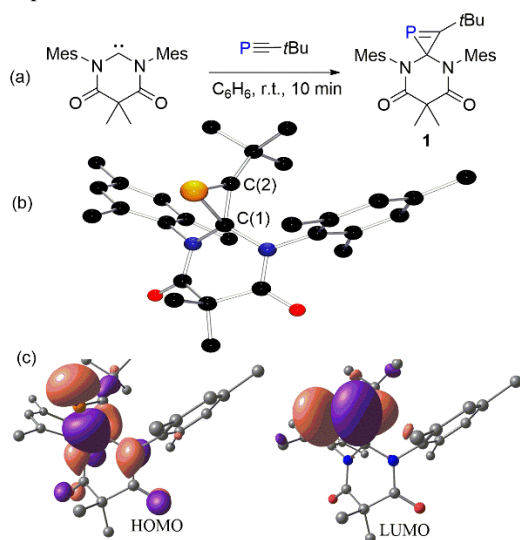


Figure 2. (a) Synthesis of **1**. (b) POV-ray depiction of the molecular structure of **1** with H atoms omitted for clarity. C, black; N, blue;

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 C₂P ring, whereas the LUMO is principally the C(2)-P π* antibonding orbitals (Figure 2c). This stands in contrast to the observation for acyclic phosphalkenes where the HOMO is the C-P π orbital.²⁰

A toluene solution of **1** was heated at 110 °C for 12 h. The ³¹P NMR spectrum showed that **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 2*H*-phosphirene moiety underwent 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 for 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**.

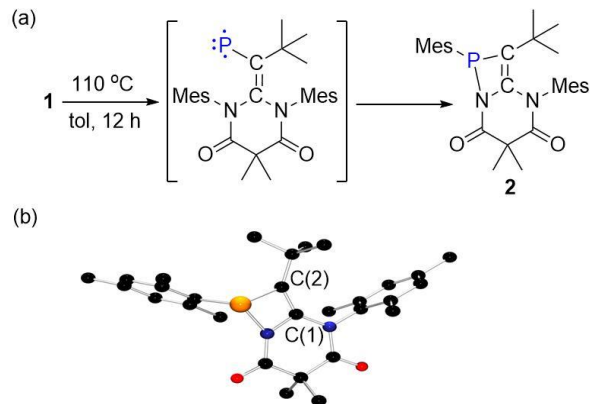


Figure 3. (a) Proposed reaction pathway for thermolysis of **1**. (b) POV-ray depiction of the molecular structure of **2** with H atoms omitted for clarity. C, black; N, blue; O, red; P, orange.

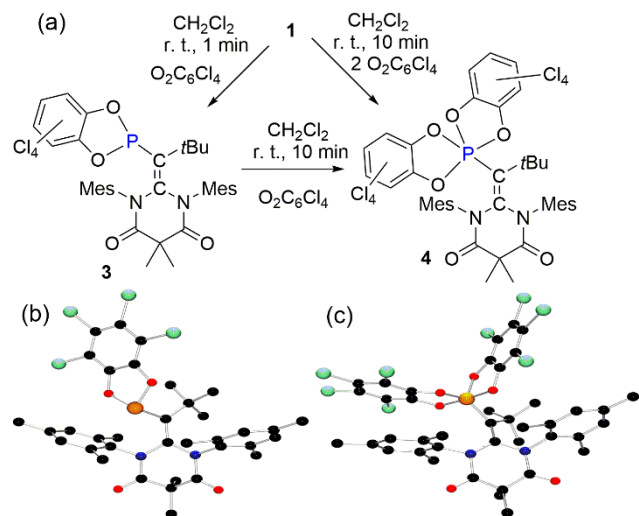


Figure 4. (a) Reactions of **1** with 3,4,5,6-Tetrachloro-1,2-benzoquinone leading to **3** and **4**. POV-ray depiction of the molecular structures of (b) **3** and (c) **4** with H atoms omitted for clarity. C, black; N, blue; O, red; P, orange; Cl, green.

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 arylphosphinidenes.¹² This has been attributed to the absence of π -donor substituents.^{15a, 23} 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**.

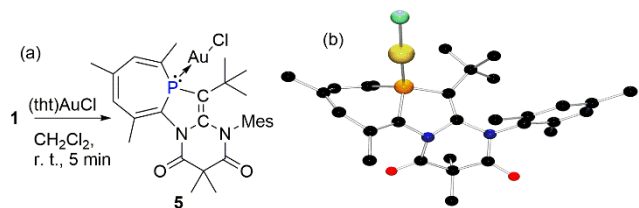


Figure 5. (a) Reaction of **1** with (tht)AuCl affording **5**. (b) POV-ray depiction of the molecular structure of **5** with H atoms omitted for clarity. C, black; N, blue; O, red; P, orange; Au, yellow; Cl, green.

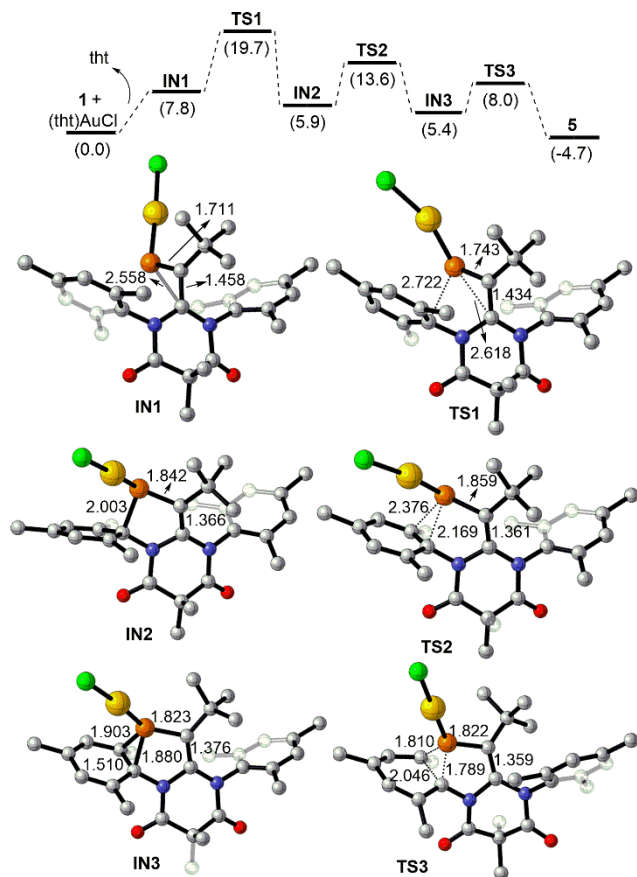


Figure 6. Free energy reaction profile (kcal/mol) for the formation of **5**. In the 3D structures, selected bond lengths are given in angstroms.

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*-O₂C₆Cl₄),^{10c, 24} in CH₂Cl₂ showed the formation of a single product. The new product **3**, isolated in 85% yield, showed a ³¹P NMR signal at 214.7 ppm, which is consistent with values determined for trivalent dioxaphospholes.²⁴⁻²⁵ An X-ray diffraction study confirmed the formulation of **3** as (Mes₂DAC)(*t*BuCP(O₂C₆Cl₄)) (Figure 4b). Altering the stoichiometry to a 1:2 ratio of **1**:*o*-O₂C₆Cl₄ or treatment of **3** with another equivalence of *o*-O₂C₆Cl₄ gave product **4** in 88 and 90% yields respectively. Compound **4** exhibits a ³¹P 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 (Mes₂DAC)(*t*BuCP(O₂C₆Cl₄)₂) (Figure 4c), the penta-coordinated phosphorus center was produced by the Ramirez reaction.²⁶ The products **3** and **4** can be formally viewed as the sequential oxidation products of the vinylphosphinidene center induced by *o*-O₂C₆Cl₄. Indeed, the approach of *o*-O₂C₆Cl₄ toward the C₂P 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 cyclopropene derivatives.²⁷ Moreover, the group of Mathey investigated the cycloaddition reactivity of transient vinylphosphinidene tungsten complexes.²⁸ Thus we probed the stoichiometric reaction of **1** with (tht)AuCl (Figure 5a). Stirring the reagents in CH₂Cl₂, rapidly led to the formation of a single product **5**

(11.1 ppm) which was isolated as a white powder in 89% yield, as observed by ^{31}P NMR. The ^1H NMR spectrum of the isolated product, **5** (CDCl_3), showed a diagnostic doublet integrating for one proton ($J_{\text{P-H}} = 39.6$ Hz) in the alkene region ($\delta = 6.26$ ppm). Layering pentane onto a concentrated fluorobenzene solution of **5** allowed for the formation of single crystals suitable for an X-ray diffraction study. Surprisingly, **5** was shown to contain a newly formed phosphorus-containing seven-membered ring arising from the insertion of a phosphinidene into one of the mesityl groups (Figure 5b). At the same time, the phosphorus atom is coordinated to a AuCl fragment. The C_6P seven-membered ring adopts a boat configuration with the presence of alternating C-C and C=C bonds and a pyramidalized phosphorus center. Compound **5** is a tricyclic system with a 2,3-dihydro-1*H*-1,3-azaphosphole ring fused to both the C_6P ring and the DAC ring.

The formation of **5** was further investigated via DFT calculations (SMD-M06-2X/Def2-TZVP//M06-2X/Def2-SVP). Interestingly, simple coordination of **1** with AuCl affords an intermediate **IN1** (7.8 kcal/mol) with a singlet ground state (the triplet of **IN1** is 25.6 kcal/mol higher in energy), in which the C1-P separation has been significantly elongated to 2.558 Å in comparison with **1** (1.919 Å). This phenomenon is mainly attributed to the donation of electron density from the HOMO of **1** to the strongly Lewis acidic Au center. Subsequently, a transition state **TS1** involving a phosphirene-phosphinidene rearrangement and an electrophilic attack of a mesityl ring by the phosphorus center is identified with an activation barrier of 19.7 kcal/mol, leading to the dearomatization of the mesityl group and the formation of a zwitterionic intermediate **IN2** (5.9 kcal/mol). The following addition of phosphinidene to one of the aromatic C-C bond via **TS2** (13.6 kcal/mol) gives phosphirane AuCl **IN3** (5.4 kcal/mol). Finally, the cleavage of the C-C bond is achieved in **TS3** (8.0 kcal/mol) to form **5** (-4.7 kcal/mol). Notably, this observed ring expansion pathway is similar to the pathway observed for the Büchner ring expansion in which carbene intermediates stepwise split aromatic C-C bonds.^{16a}

In summary, we have reported the full characterization of an isolable free 2*H*-phosphirene. This species (**1**) is shown to react via a phosphirene-phosphinidene rearrangement, via an unprecedented vinylphosphinidene intermediate. Both the thermolysis of **1** and the reaction of **1** with (tht)AuCl proceed through a transient vinylphosphinidene intermediate that undergoes C-N and aromatic C-C bond activations to give compounds **2** and **5**, respectively. The latter reaction is, to our knowledge, the first example of a phosphorus analog of the Büchner ring expansion. These results provide access to an elusive and reactive vinylphosphinidene. The reactivity of **1** with other electrophiles and more detailed mechanistic studies are the subjects of ongoing research.

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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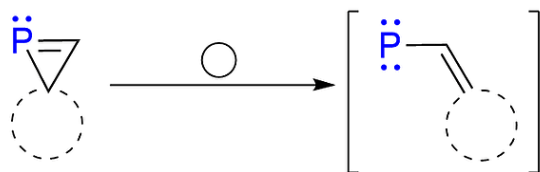
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Phosphirene-Phosphinidene Rearrangement

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