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Phosphorus Clusters

Isolation of a Neutral P_8 Cluster by [2+2] Cycloaddition of a Diphosphene Facilitated by Carbene Activation of White Phosphorus**

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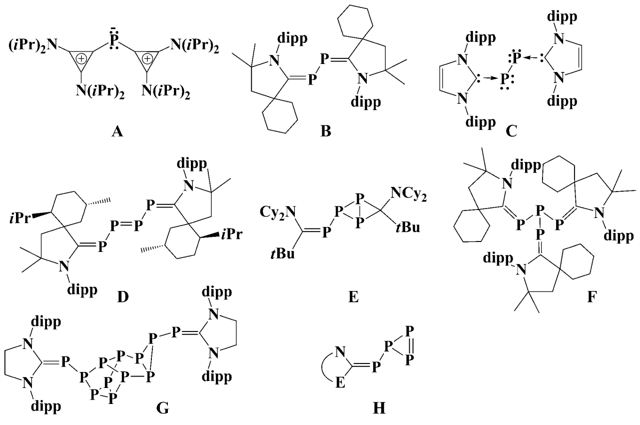
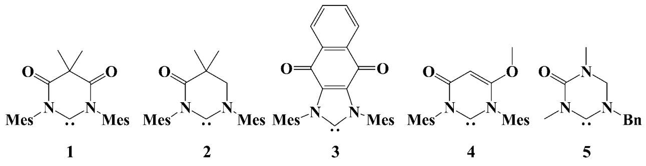
The industrial preparations of organophosphorus compounds typically utilize chlorinated phosphorus starting materials, which are derived from readily available white phosphorus (P_4).[1,2] Ideally, more sustainable and environmentally benign processes would directly convert P_4 into useful organophosphorus products.[1,2] For this reason, the activation of P_4 as opposed its chlorination and subsequent functionalization has become a topical objective.

Two primary areas of research include the activation of P_4 with transition metals,[3,4] and more recently main-group species,[5] as a means to eliminate the use of chlorinated phosphorus compounds. The former area has been spearheaded by Cummins,[3a–c,6] who has demonstrated the ability to functionalize P_4, affording remarkable molecules such as AsP_3.[6a] For the latter, stable singlet carbenes have been utilized to activate P_4 as well as to stabilize P_1, P_2, P_4, and even P_{12} fragments (Scheme 1).[7,8] When the steric demands of the chosen carbene ligand are low, small P_1 and P_2 species such as **A**, **B**, and **C** can be isolated.[7a,8] For the larger P_4 and P_{12} clusters (**D**–**G**), a common unstable monocarbene adduct (**H**) has been proposed through mechanistic studies.[7a,b]



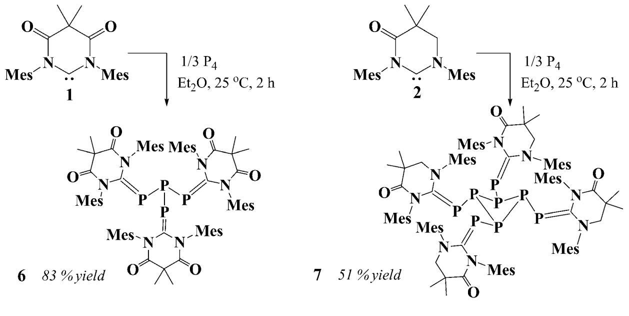
Scheme 1. Phosphorus fragments supported by stable carbenes. Dipp = 2,6-$(iPr)_2C_6H_3$; E = NR or CR_2.

Herein we report that carbenes decorated with carbonyl moieties can activate white phosphorus in a manner analogous to the more nucleophilic *N*-heterocyclic carbenes (NHCs) and cyclic alkyl amino carbenes (CAACs). Carbonyl-decorated carbenes (CDCs) have already been shown to exhibit a rich and versatile reactivity, motivating our investigation.[9–13] For this study, we investigated carbenes **1**–**5** (Scheme 2), which differ in the number and location of carbonyl groups along with additional functionality in the backbone; however, only clean reactions with **1** and **2** were observed.



Scheme 2. CDCs investigated in this study. Mes = 2,4,6-$(CH_3)_3C_6H_2$.

Gratifyingly, treatment of P_4 with three equivalents of carbenes **1** or **2** resulted in rapid activation at room temperature (Scheme 3). For **1**, addition of the carbene to a suspension of P_4 in diethyl ether resulted in a dark red-orange solution followed by the precipitation of a red-orange solid after five minutes. Isolation of the resulting solid afforded the triscarbene-P_4 complex **6** as determined by NMR spectroscopy and single-crystal X-ray diffraction (Figure 1).



Scheme 3. Reaction of white phosphorus with carbonyl-decorated carbenes **1** and **2**.

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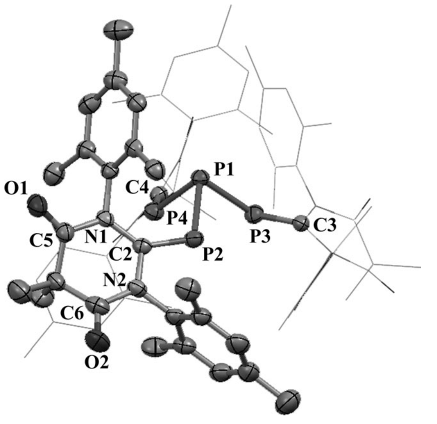


Figure 1. ORTEP drawing (ellipsoids set at 50% probability) for **6**. H atoms are omitted and two carbene moieties are represented by thin lines for clarity.[16]

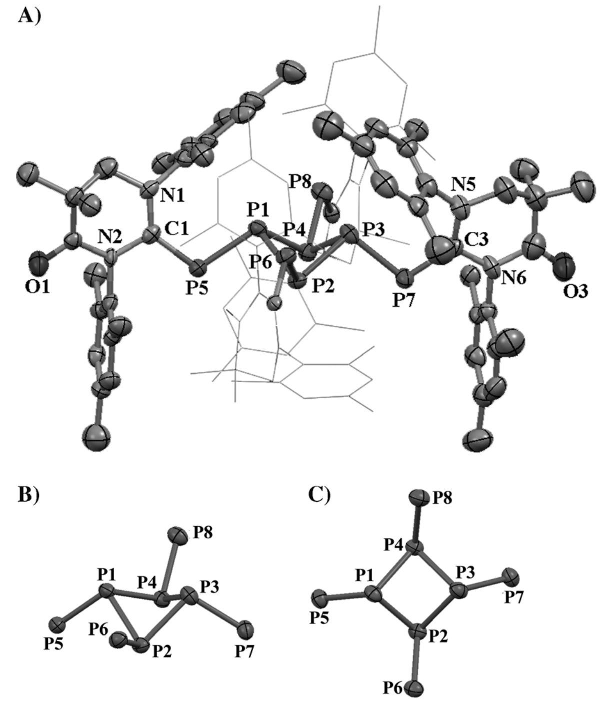


Figure 2. A) ORTEP drawing (ellipsoids set at 50% probability) for **7**. H atoms are omitted and two carbene moieties are represented by thin lines for clarity. B) Side view of the P_8 cluster in **7**. C) Top view of the P_8 cluster in **7**.[16]

The ^{31}P NMR spectrum of **6** exhibits a doublet centered at $\delta = +103.6$ ppm (C_6D_6) and a quartet at $\delta = -20.0$ ppm ($^1J_{P-P} = 283$ Hz), which integrate to 3 and 1, respectively. These chemical shifts are similar to what Bertrand observed for **F**, albeit the three equivalent phosphorus atoms are shifted downfield considerably (+103.6 ppm for **6** versus +68.1 ppm for **F**),[7a] indicating that carbene **1** is more electrophilic than the CAAC.[12]

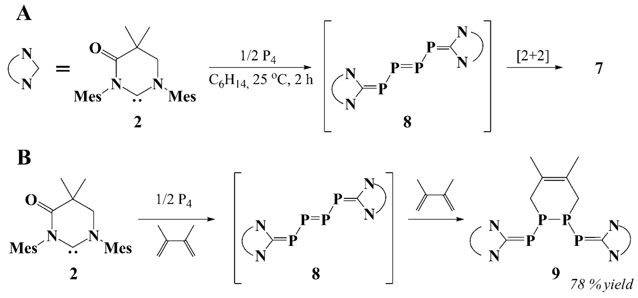
Surprisingly, the ^{1}H NMR of **6** displayed inequivalent mesityl substitutents as well as inequivalent α-methyl groups in the carbene backbone. This indicated a lack of free rotation about the C–P bond. A single-crystal X-ray diffraction study (Figure 1) not only confirmed the structure of **6** shown in Scheme 3, but corroborated our assessment from ^{1}H NMR that there is significant multiple C–P bond character in **6**. Indeed, the C2–P2 distance was found to be 1.728(6) Å which is similar to **F** (1.733 Å) and known phosphaalkenes derived from carbenes (ca. 1.73–1.76 Å).[14]

As described previously by Bertrand,[7a] the formation of **6** most likely results from the addition of two CDCs **1** to an initially formed species of type **H**. Curiously, when the carbene is changed to the less electrophilic carbene **2**,[10,11b] the product obtained is quite different (Scheme 3). Indeed, when three equivalents of **2** (featuring single carbonyl) are added to P_4 in Et_2O, an instantaneous dark green suspension is observed. The dark green color rapidly changes to a bright orange within one minute. Isolation and characterization of the resulting orange precipitate revealed the formation of the tetrakiscarbene-P_8 complex **7**.

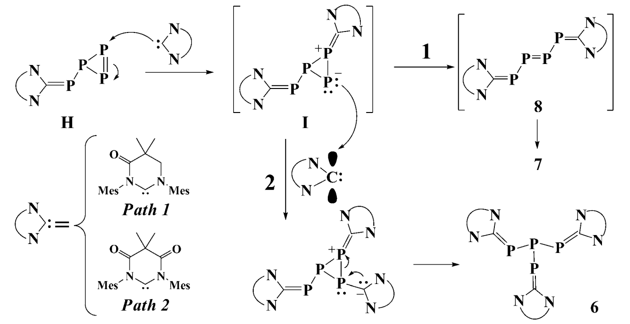
The ^{31}P NMR of **7** is reminiscent of an AA′XX′ spin system with signals centered $\delta = +41.6$ ppm and -45.2 ppm. In the ^{1}H NMR the carbene peaks were all shifted downfield by about 0.2 ppm when compared to the free ligand **2**.[10] Based on these data alone, we were unable to conclusively assign the structure of **7**. To fully elucidate the structure, single crystals of **7** were subjected to an X-ray diffraction analysis. **7** is comprised of a central P_8 cluster that is surrounded by four carbene ligands (Figure 2A). Close inspection of the P_8 cluster reveals a central P_4 butterfly (Figure 2B,C) that is capped at each phosphorus atom with a phosphaalkene moiety. The structure of **7** is to our knowledge the first example of a neutral P_8 cluster that is supported by a carbene.[6b] Compound **7** is quite similar to that of the tetraanionic P_8 cluster $[Na(DME)]_4[(tBu_3Si)_4P_8]$ first prepared by Wiberg and co-workers[15] with the central P_4 atoms adopting distorted-tetrahedral geometries (average Σ_{P-P-P} angles 276°). However, close inspection of the central P_4 ring reveals a more puckered ring in **7** as evidenced by the shorter intraannular P–P distances (average diagonal P–P distance 2.78 Å for **7** versus 3.19 Å for Wiberg's compound) and the larger displacement of P1 from a plane defined by P2-P3-P4 (displacement distance 1.754 Å for **7** versus 0.270 Å for Wiberg's compound).[15]

Wiberg delineated the mechanism for the formation of the tetraanionic P_8 cluster, which occurs by a [2+2] cycloaddition dimerization of a linear P_4-diphosphene similar to compound **D** reported by Bertrand.[7b,15] We therefore hypothesized that **7** also formed by an in situ [2+2] cycloaddition reaction of a transient diphosphene (**8**, Scheme 4A). Apart from Wiberg's studies, the appearance of the dark green color upon addition of carbene **2** to P_4 also serves as evidence for the formation of the transient diphosphene **8**. As the P_4-diphosphene **D** from Bertrand was isolated as a dark blue solid,[7b] we believe that the dark green color observed corresponds to the formation of **8**. To verify this proposed mechanism, we performed a Diels–Alder experiment to trap the putative diphosphene **8** (Scheme 4B).[7b]

Addition of **2** to a suspension of P_4 in hexanes saturated with 2,3-dimethyl-1,3-butadiene (**2**/P_4 ratio 2:1; 1 mL butadiene dissolved in hexanes) resulted in an instantly observed



Scheme 4. A) Proposed mechanism for the formation of **7**. B) Diels–Alder experiment to trap the putative diphosphene **8**.



Scheme 5. Proposed reaction pathways for the formation of **6** and **7**.

yellow solution followed by the precipitation of a yellow solid. After 12 h, the solid was isolated and confirmed to be compound **9** by ^{1}H and ^{31}P NMR spectroscopy as well as X-ray diffraction, thus confirming our hypothesized mechanism. Interestingly, by using hexanes as the solvent, only a single diastereomer of **9** precipitates, facilitating characterization by NMR spectroscopy. The ^{31}P NMR spectrum exhibits two signals centered at -42.44 and $+23.33$ ppm ([D$_8$]THF). These signals are characteristic of the expected AA′MM′ spin system for **9**. The crystal structure of **9** (Figure 3) reveals a central linear P$_4$ chain in which the phosphaalkenes (average P–C distances 1.73 Å)[14] are oriented in an *E* configuration (P-P-P-P dihedral angle 132.5°).

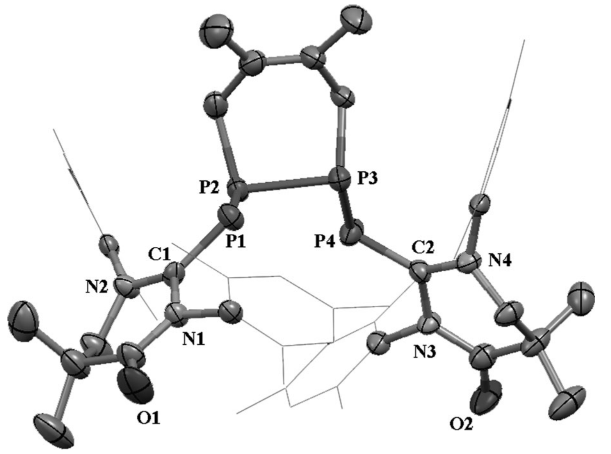


Figure 3. ORTEP drawing (ellipsoids set at 50% probability) for **9**. H atoms are omitted and mesityl substituents on carbene ligands are represented by thin lines for clarity.[16]

We thought it curious that the reaction of carbenes **1** and **2** with P$_4$ provided drastically different products given that: 1) the carbenes differ only in their electrophilicities;[10,11b] 2) there are negligible steric differences between **1** and **2** (%$V_{\mathrm{bur}} = 37.8\,\%$ and 37.8%; respectively);[10] 3) the reactions were carried out under identical conditions (that is, carbene/P$_4$ 3:1); and 4) it has been proposed that compound **6** and transient diphosphene **8** both originate from an intermediate that would be similar to **H**.[7a,b] However, when considering the mechanisms proposed by Bertrand for the formation of **D** and **F**,[7b] it became apparent how the electrophilicity of the chosen carbene can dictate the identity of the final product.

The reaction mechanisms in Scheme 5 describe how both **6** and diphosphene **8** can be obtained from a monocarbene-P$_4$ intermediate similar to **H**. Initial attack on **H** by a carbene would result in the zwitterionic intermediate **I**, which has a formal negative charge on a β-phosphorus atom. For a weakly electrophilic carbene such as **2**, the reaction proceeds by a ring-opening mechanism to afford the linear P$_4$-diphosphene as described by Path 1.[7b] However, when the strongly electrophilic carbene **1** is used, the reaction follows Path 2, and the phosphorus anion in **I** attacks the carbene empty p-orbital, eventually leading to the P$_4$ cluster observed in **6**.

In conclusion, we have shown that CDCs are capable of P$_4$ activation and aggregation. Unique to the second reaction type is the ability to rapidly prepare and isolate a neutral P$_8$ cluster, which, to our knowledge, is the first neutral P$_8$ cluster of its kind. We have also shown that the electrophilicity of the chosen CDC greatly impacts the resultant product. Future efforts will be geared toward investigating compounds **6** and **7** as potential phosphorus transfer reagents for the preparation of useful organophosphorus compounds. Such advances will help aid in the development of more sustainable and environmentally benign methods for the preparation of phosphorus derivatives.

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[16] CCDC 923564 (**6**), CCDC 923565 (**7**), and CCDC 923566 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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