P–P Activation

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Nonmetal-Mediated Fragmentation of P_4: Isolation of P_1 and P_2 Bis(carbene) Adducts**

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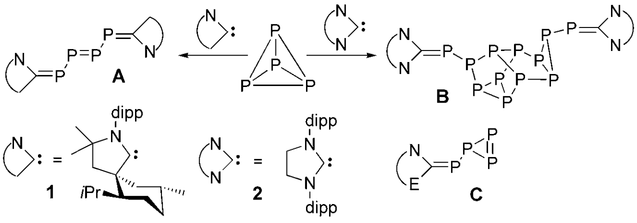
Transition metals are well-known for activating small molecules and for stabilizing highly reactive species. A recent trend in the accomplishment of either of these goals is the use of nonmetals,[1] especially stable singlet carbenes. Robinson and co-workers have reported that N-heterocyclic carbenes (NHCs) give rise to stable adducts with HBBH[2] and Si_2,[3] which are otherwise not isolable.[4] We have shown that cyclic (alkyl)(amino)carbenes (CAACs) can activate CO,[5] H_2,[6] and even NH_3,[7] which is difficult when attempted with transition-metal centers.[7,8]

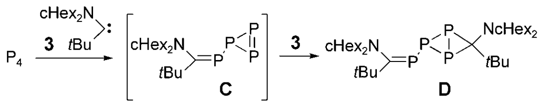
White phosphorus (P_4) is a small molecule that is of industrial interest as it is the classical starting material for the large-scale preparation of organophosphorus derivatives.[9] The reactivity of P_4 with transition metals has been widely studied,[10–12] and is therefore an excellent model to further test if carbenes can undergo reactions in the same manner as transition metals. Our research group has already shown that the bulky rigid CAAC **1** opens P_4 and simultaneously stabilizes the resulting acyclic P_4 species (**A**,[13a] Scheme 1), which is otherwise highly reactive. Moreover, when a bulky NHC **2** was used, the NHC-stabilized P_{12} cluster **B** was isolated in high yield.[13b] Therefore, singlet carbenes can activate and induce the aggregation of white phosphorus and stabilize the resulting species, in a similar manner to transition metals. However, the most synthetically useful organophosphorus derivatives contain only one or two phosphorus atoms, and therefore it is of primary importance to induce the fragmentation of P_4, which can be accomplished by using transition metals.[10] Cummins et al. have even shown that the resulting P_1– and P_2–niobium complexes can be used as phosphorus transfer agents.[14]



Scheme 1. Activation and aggregation of white phosphorus by singlet carbenes. Dipp = 2,6-diisopropylphenyl.

Herein we report that carbenes can induce the fragmentation of white phosphorus in the same manner as transition metals. Depending on the nature of the activator, carbene-stabilized P_2 and P_1 species can be isolated. Preliminary mechanistic studies of the reaction that leads to **A** and **B**, in particular trapping experiments, showed that both carbenes **1** and **2** first formed an unstable monocarbene adduct of type **C**. A second carbene molecule subsequently induces a ring-opening reaction and the formation of bis(carbene) adducts of type **A**.[13] The different outcomes of the reactions shown in Scheme 1 can be rationalized by the different electronic properties of CAACs and NHCs. CAACs are more electrophilic (π acceptor) and strengthen the PC bonds of **A**,[5,6] while NHCs are less basic and are therefore better leaving groups, and favor the formation of clusters such as **B**. This analysis indicates that strongly basic but electrophilic carbenes should be the best candidates to induce the fragmentation of white phosphorus, provided that they are small enough to further attack the P_4 fragments of adducts of type **A** or **C**.

According to our previous investigations, the acyclic (alkyl)(amino)carbene **3**[15] (Scheme 2) is one of the most electrophilic stable carbenes known. An excess of carbene **3** (3.5 equivalents) was added to a suspension of white phosphorus in ether. After two hours at room temperature and subsequent workup, the bis(carbene) P_4 adduct **D** was isolated as light-yellow crystals in 66% yield (based on P_4), and its bis(carbene) P_4 adduct structure was unambiguously assigned by a single crystal X-ray diffraction study[16] (Figure 1). This bicyclic compound clearly results from the cycloaddition of carbene **3** onto the adduct of type **C**.



Scheme 2. Reaction of white phosphorus with acyclic (alkyl)(amino)carbene **3**.

This result indicates that the acyclic (alkyl)(amino)carbene **3** is sufficiently nucleophilic to open the P_4 tetrahedron, but so electrophilic that it undergoes a cyclopropanation reaction, rather than inducing the ring-opening of the initally formed adduct **C**. Therefore, we chose the cyclohexyl CAAC **4**,[17] in the hope that such a small CAAC would be able to induce the formation of an adduct of type **A**, but then react again and induce the fragmentation of the P_4 chain. Upon addition of three equivalents of CAAC **4** to an

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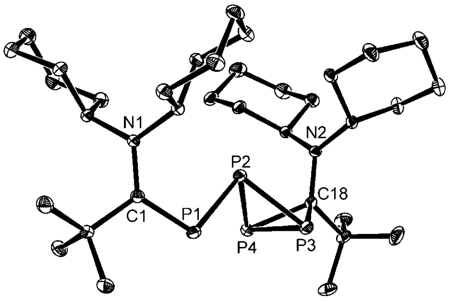
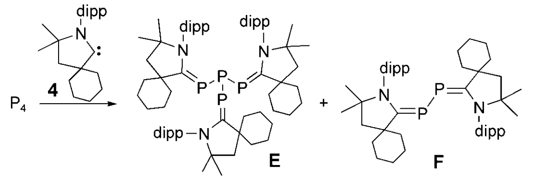


Figure 1. Thermal ellipsoids plot (40% probability surface) for **D** (hydrogen atoms omitted for clarity). Selected bond distances [Å] and angles [°]: P(1)–P(2) 2.2320(19), P(2)–P(3) 2.220(2), P(2)–P(4) 2.2342(17), P(3)–P(4) 2.1700(19), C(1)–P(1) 1.747(2), C(18)–P(3) 1.912(2), C(18)–P(4) 1.925(2), N(1)–C(1) 1.3893(19), N(2)–C(18) 1.4472(18); P(1)-P(2)-P(3) 93.29(3), P(1)-P(2)-P(4) 91.99(6), P(3)-P(2)-P(4) 58.31(7), P(2)-P(4)-P(3) 60.51(5), P(3)-P(4)-P(2) 60.51(5).

suspension of P_4 in ether, two new products **E** and **F** were isolated in moderate yields (67% and 12%, respectively, based on P_4; Scheme 3).



Scheme 3. Reaction of white phosphorus with the nonhindered CAAC **4**.

The ^{31}P NMR spectrum of the major product **E** shows a doublet signal at $\delta = +68.1$ ppm and a quartet signal at $\delta = -66.2$ ppm, with a large P–P coupling constant (227 Hz). These data indicated the presence of three magnetically equivalent P nuclei that were directly connected to another P center. This hypothesis was confirmed by a single crystal X-ray diffraction study (Figure 2). Very surprisingly, the formation of tris(carbene) P_4 adduct **E** implies that two CAACs **4** react on the initially formed adduct of type **C**.

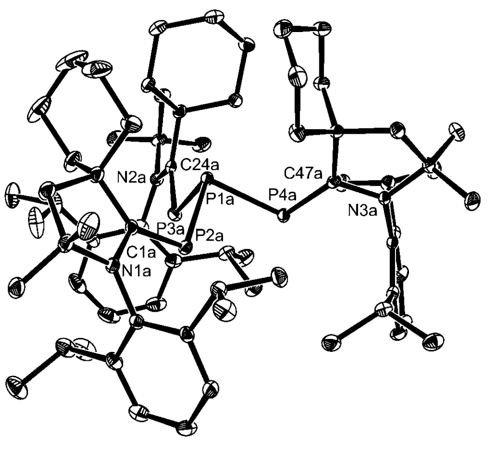
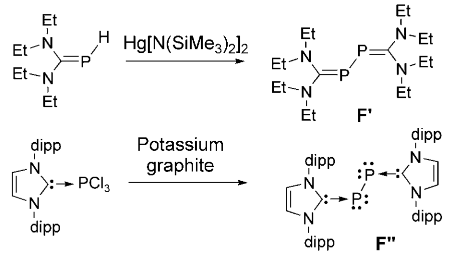


Figure 2. Thermal ellipsoids plot (40% probability surface) for E (hydrogen atoms omitted for clarity). Selected bond distances [Å] and angles [°]: P(1a)–P(2a) 2.2168(6), P(1a)–P(3a) 2.2270(6), P(1a)–P(4a) 2.2192(7), C(1a)–P(2a) 1.7328(19), C(24a)–P(3a) 1.7343(18), C(47a)–P(4a) 1.7324(18), N(1a)–C(1a) 1.374(2), N(2a)–C(24a) 1.370(2), N(3a)–C(47a) 1.368(2); P(2a)-P(1a)-P(4a) 90.15(2), P(3a)-P(1a)-P(4a) 90.15(2), P(2a)-P(1a)-P(4a) 90.15(2), C(1a)-P(2a)-P(1a) 108.22(6), C-(24a)-P(3a)-P(1a) 106.62(6), C(47a)-P(4a)-P(1a) 108.45(7).

The minor product **F** was determined to be the desired bis(carbene) P_2 adduct, and therefore the reaction that leads to **F** represents the first example of fragmentation of P_4 with a neutral organic species. Interestingly, compound **F** is reminiscent of compounds **F′**[18] and **F″**,[19] which were prepared as shown in Scheme 4, and characterized as 2,3-diphosphabutadiene and NHC-stabilized bis(phosphinidene), respectively.



Scheme 4. Reported syntheses[18,19] and electronic structure of compounds related to **F**.

The ^{31}P NMR chemical shift for **F** ($\delta = +59.4$ ppm) is comparable to that of **F′** ($\delta = 54.2$ ppm), and is at a lower field than **F″** ($\delta = -52.4$ ppm); similarly, the P–C bond length (Figure 3) in **F** (1.719(7) Å) is shorter than in **F″** (1.750(2) Å). Both of these data indicate that **F** has a 2,3-diphosphabutadiene structure, which is expected because of the higher electrophilicity of CAACs than NHCs.

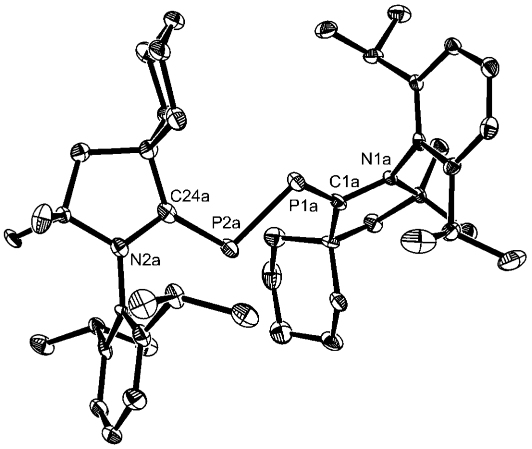
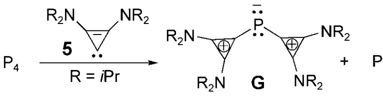


Figure 3. Thermal ellipsoids plot (40% probability surface) for F (hydrogen atoms omitted for clarity). Selected bond distances [Å] and angles [°]: Selected bond distances [Å] and angles [°]: P(1a)–P(2a) 2.184(3), C(1a)–P(1a) 1.719(7), N(1a)–C(1a) 1.387(9); C(1a)-P(1a)-P(2a) 105.1(2); C(1a)-P(1a)-P(2a)-C(24a) 149.22.

Compound **F** most probably results from the attack of the carbene to the β-phosphorus centers of a bis(carbene) adduct of type **A**. In order to obtain a P_1 adduct by attack at a phosphorus center in a position that is α to the carbene(s) of adducts **A** or **C**, we have used the least sterically demanding stable carbene known to date, namely bis(diisopropylamino)cyclopropenylidene (**5**).[20] The ^{31}P NMR spectrum of the reaction mixture of P_4 and three equivalents of carbene **5** after 12 hours at room temperature revealed an ABX system ($\delta_A = 242.8$, $\delta_B = 237.0$, $\delta_X = 157.0$ ppm, $J_{AX} = -484.7$ Hz, $J_{AB} =$

$+38.8$ Hz, $J_{BX} = -481.1$ Hz) and a singlet signal at $\delta = -93.2$ ppm. All attempts to purify the mixture led to the disappearance of the second-order system, but, in the presence of chloroform or any salts, the high-field singlet remained unchanged. When chloroform was used, single crystals suitable for X-ray diffraction readily formed upon standing at room temperature. The isolated product was the bis(carbene) P_1 cation **G** with Cl^- as counterion (obtained in 74% yield based on P_4; Scheme 5, Figure 4). Analogous $(NHC)_2P^+$ systems that used $(R_3P)_2P^+$, $(RNPCl)_2$, or PCl_3 as P^I source have previously been reported by Schmidpeter et al.[21] and MacDonald et al.[22] On the other hand, although we have not yet been able to identify the P_3 fragment, its anionic nature is clear, and therefore it is likely to be an allylic triphosphorus anion that is unsymmetrically substituted by cyclopropenylidenes.



Scheme 5. Reaction of P_4 with cyclopropenylidene **5**.

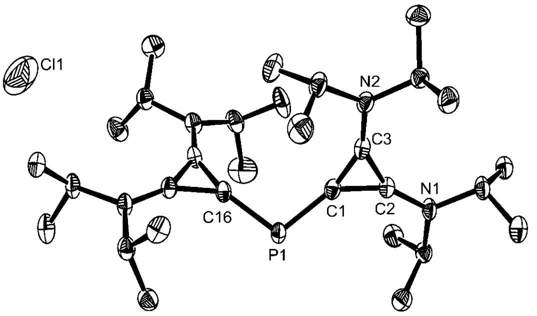


Figure 4. Thermal ellipsoids plot (40% probability surface) for **G**Cl. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:P(1)–C(1) 1.787(2), P(1)–C(16) 1.788(2), N(1)–C(2) 1.323(3), N(2)–C(3) 1.328(3), C(1)–C(3) 1.397(3), C(1)–C(2) 1.404(3), C(2)–C(3) 1.388(3); C(1)-P(1)-C(16) 104.68(9).

The results reported herein demonstrate that reactions of P_4, namely, activation, aggregation, and importantly, fragmentation, which have previously been carried out by using transition metals, can also be achieved by using stable singlet carbenes. The next challenge is to use the resulting adducts, especially **F** and **G**, to prepare useful organophosphorus derivatives. This procedure would avoid the use of Cl_2 gas, which is important to meet the growing demand for phosphorus derivatives that are produced by using environmentally friendly processes.

Experimental Section

All manipulations were performed under an atmosphere of dry argon by using standard Schlenk techniques.

Synthesis of **D**: Ether (40 mL) was added to a mixture of carbene **3** (4.07 mmol) and P_4 (1.16 mmol) at room temperature and the resulting suspension stirred for 2 h. The solvent was removed under vacuum, and the solid residue washed with hexane (6 mL) at –35 °C to afford **D** (480 mg, 66.4% based on P_4). Single crystals of **D** were grown by layering acetonitrile over a THF solution. m.p. 150 °C; $^{31}P\{^1H\}$ NMR (202.5 MHz, $[D_8]$THF, 25 °C): $\delta = 238.8$ (dt, $^1J_{PP} = 220$ Hz and $^2J_{PP} = 87$ Hz), -105.8 (dt, $^1J_{PP} = 220$ Hz and $^2J_{PP} = 167$ Hz), -168.2 ppm (dd, $^1J_{PP} = 167$ Hz and $^2J_{PP} = 87$ Hz); ^{13}C NMR (125.75 MHz, $[D_8]$THF, 25 °C): $\delta = 227.6$ (d, $^1J_{PC} = 89$ Hz, C_{carb}), 101.5 ppm (br s, C_{cyclo}).

Synthesis of **E** and **F**: A solution of carbene **4** (3.25 g, 10.01 mmol) in ether (20 mL) was added at room temperature to a suspension of P_4 (0.41 g, 3.34 mmol) in ether (20 mL). The mixture was stirred at room temperature for 2 h and then half of the solvent was removed under vacuum. The remaining solution was cooled to –30 °C and the resulting precipitate filtered to give **F** as a bright yellow powder (580 mg, 12.1% yield based on P_4). Evaporation of the filtrate gave a dark red powder, which was washed three times with acetonitrile (3 × 30 mL), and dried under vacuum to give **E** as a bright-yellow powder (2.5 g, 67.4% yield based on P_4). Single crystals were grown from a saturated solution of **F** in diethyl ether at room temperature, and single crystals of **E** were obtained by slow evaporation of a solution of **E** in hexane at room temperature. **E**: m.p. 142 °C; ^{13}C NMR (125.75 MHz, $[D_6]$benzene, 25 °C): $\delta = 207.4$ ppm (m, C_{carb}). **F**: m.p. 216 °C; $^{13}C\{^1H\}$ NMR (125.75 MHz, $[D_6]$benzene, 25 °C): $\delta = 202.2$ ppm (dd, $^1J_{PC} = 32$ Hz, $^2J_{PC} = 26$ Hz, C_{carb}).

Synthesis of **G**Cl^-: White phosphorus (P_4; 0.17 g, 1.40 mmol) was added to a solution of carbene **5** (1.00 g, 4.24 mmol) in THF (5 mL). After stirring for 12 h at room temperature, chloroform (5 mL) was added to the crude reaction mixture. After stirring at room temperature for 30 min, the volatile components were removed under vacuum, and the resulting red solid washed with Et_2O (3 × 20 mL) to afford a dark-orange powder. Yield: 564 mg (74% based on P_4). Single crystals of **G**Cl were readily obtained by slow evaporation of a solution of **G**Cl in chloroform at room temperature. m.p. 174 °C (dec.); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 3.79$ (sept, $J = 6.5$ Hz, 4 H), 1.25 ppm (d, $J = 6.5$ Hz, 24 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 136.5$ (C_{ring}), 123.7 (d, $^1J_{C-P} = 104.6$ Hz, C_{carb}), 51.3, 21.5 ppm. For compounds **D**–**G**, only selected NMR data are given. For full details, see the Supporting Information.

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