VIP P_4 Activation

DOI: 10.1002/anie.200703055

Carbene Activation of P_4 and Subsequent Derivatization**

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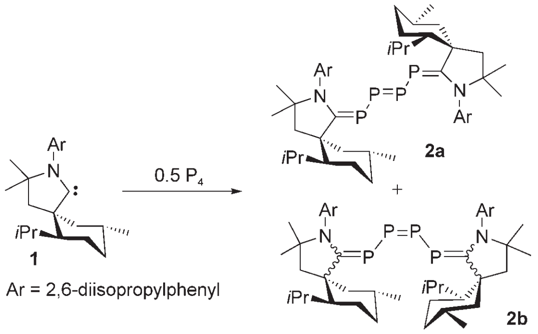
White phosphorus (P_4) is readily available, and is the most reactive allotrope of the element. It is the classical starting material for the industrial preparation of organophosphorus derivatives.[1] Typically P_4 is treated with Cl_2 gas to make PCl_3 or PCl_5, which is subsequently substituted with organic substrates. To meet the growing demand in phosphorus derivatives and the increasingly stringent environmental regulations, new processes using white phosphorus but avoiding chlorine are highly desirable. Recently Peruzzini et al.[2] wrote that "the ideal replacement would be a metal-mediated catalytic process that directly combines white phosphorus and organic molecules". This aim has not yet been reached, but coordination and functionalization of P_4 by transition-metal complexes, leading to a variety of P_x^{n-} ligands, have been investigated extensively.[3,4] Noteworthy is the elegant work of the Cummins group using P_4 to produce P_1 and P_2 niobium complexes that can be used as phosphorus-transfer agents.[3c–f]

We have already shown that stable cyclic (alkyl)(amino)carbenes (CAACs)[5] can mimic the behavior of transition metals, and in some cases even surpass their efficiency.[6] Indeed, CAACs can activate H_2, a reaction that has long been known for transition metals, but also NH_3, a much more difficult task for metals. Herein we report that CAACs can activate P_4 and importantly give rise to highly reactive products that can be further used for the construction of P_4-containing molecules that feature phosphorus–carbon bonds. Since an optically pure CAAC is used, the stereoselectivity of the reactions is also discussed.



Scheme 1. Reaction of CAAC **1** with a half equivalent of P_4.

Reaction of CAAC **1**[5a] with P_4 in hexanes (Scheme 1) instantly gives rise to a dark blue solution. The ^{31}P NMR spectrum reveals two AA′XX′ systems in a 9:1 ratio (major component, $\delta = 566$ and 121 ppm, $J_{AA'} = -679.4$, $J_{AX} = -248.7$, $J_{AX'} = -70.7$, $J_{XX'} = -13.7$ Hz; minor component, $\delta = 451$ and 115 ppm, $J_{AA'} = -511.2$, $J_{AX} = -424.7$, $J_{AX'} = -10.8$, $J_{XX'} = -319.1$ Hz). These data suggest the presence of (*E*)-[7a] and (*Z*)-diphosphene isomers[7b,c] with pendant *C*-amino phosphaalkene substitutents,[8] **2a** and **2b**, respectively. This hypothesis has been confirmed by a single-crystal X-ray diffraction study of the major isomer **2a** (m.p. 184–185 °C; Figure 1).[9] The P-P-P-P chain is nearly planar (dihedral angle 177.4°) and is coplanar with both CAAC rings (P-P-C-C dihedral angles of 174.5 and 177.8°). The central P2–P3 bond length (2.08 Å) is in the typical range for a P=P double bond,[10] while the P1–P2 and P3–P4 bond lengths (2.19–2.20 Å) are typical of P–P single bonds;[11] the P–C bond lengths (1.75–1.76 Å) are in the range for *C*-amino phosphaalkenes.[8] Probably because the menthyl substituent is more rigid than the 2,6-diisopropylphenyl group, the two phosphaalkene fragments of **2a** have a *Z* configuration.

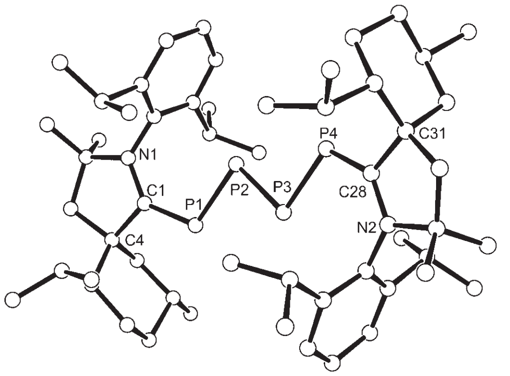


Figure 1. Solid-state structure of **2a** (hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P2 2.191(5), P2-P3 2.083(4), P3-P4 2.197(5), P1-C1 1.761(11), P4-C28 1.750(11), N1-C1 1.400(14), N2-C28 1.396(13); C1-P1-P2 110.9(4), P3-P2-P1 92.62(18), P2-P3-P4 93.22(17), C28-P4-P3 109.8(4), N1-C1-C4 109.0(9), N2-C28-C31 108.0(9).

CAAC adducts **2** are very different from those resulting from the reaction of heavier carbene analogues with P_4. The silylene [(*t*BuNCHCHN*t*Bu)Si], reported by Denk, West, and co-workers, catalyzes the formation of red phosphorus,[12]

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[**] We are grateful to the NSF (CHE 0518675) for financial support, the University of Bielefeld for computer facilities, and the Natural Sciences and Engineering Research Council of Canada for a postdoctoral fellowship (J.D.M.).

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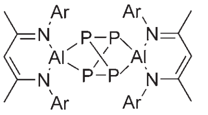
whereas the silylene [HC(CMeNAr)($H_2C{=}CNAr$)Si] from Driess and co-workers[13] and the carbene-like aluminum derivative [HC(CMeNAr)$_2$Al] from Roesky and co-workers[14] insert into one or two P−P bonds, affording polycyclic materials **A**–**C**. In contrast, derivatives **2** have to be regarded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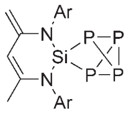
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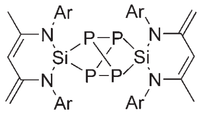
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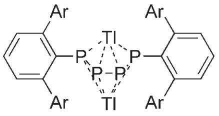
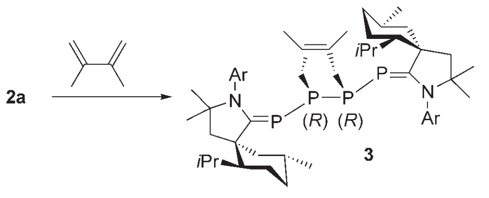

D

as the first examples of a 2,3,4,5-tetraphosphatriene, and in fact a neutral P_4 chain, as seen in **2**, is unprecedented. The closest analogues are the doubly anionic dithallium-stabilized diaryltetraphosphabutadienediide **D**[15] and (*Z*)-(*t*Bu$_3$SiP(Na)P=PP(Na)Si*t*Bu$_3$).[16]

Since adducts **2** feature a diphosphene and two phosphalkene fragments, which are highly reactive functional groups, they can be used further for the construction of more complex molecules. As an example, reaction of the (*E*)-diphosphene **2a** with 2,3-dimethylbutadiene proceeded cleanly overnight to give a yellow-colored solution (Scheme 2). A single-crystal



Scheme 2. Diastereoselective [4+2] cycloaddition of CAAC–P_4 adduct **2a** and 2,3-dimethylbutadiene.

X-ray diffraction study (Figure 2) demonstrated that compound **3** results from a [4+2] cycloaddition between the diphosphene moiety of **2a** and the diene. The phosphaalkenes are situated in an *E* configuration (P-P-P-P dihedral 166.7°), which is reminiscent of the stereochemistry of **2a**. More surprisingly, a close examination of the ^{31}P NMR spectrum of the crude reaction mixture (Figure 3) shows that the Diels–Alder reaction, and therefore the construction of two phosphorus–carbon bonds, occurs with more than 95% diastereoselectivity.

To gain insight into the mechanism of the reaction leading to adducts **2**, calculations at the B3LYP/6-311g(d,p) level were performed on the parent CAAC **1′** (Scheme 3).[17] It was found that **1′** reacts with P_4 in a nucleophilic manner at one of the apical phosphorus atoms. This first step is exothermic by 18.3 kcal mol^{-1} and proceeds with a very small energy barrier (3.6 kcal mol^{-1}) to give triphosphirene **4′**. Interestingly such a process has already been observed in the reaction of transition-metal complexes with P_4, and several complexes containing metal-stabilized monosubstituted triphosphirene fragments have been reported.[18] A second carbene unit then reacts, without energy barrier, at one of the unsaturated phosphorus centers of the triphosphirene moiety, giving adduct **5′**. The latter undergoes a facile ring opening (E_a = 3.8 kcal mol^{-1}) to afford the 2,3,4,5-tetraphosphatriene **2′**, which is located 11 kcal mol^{-1} in energy below **5′**.

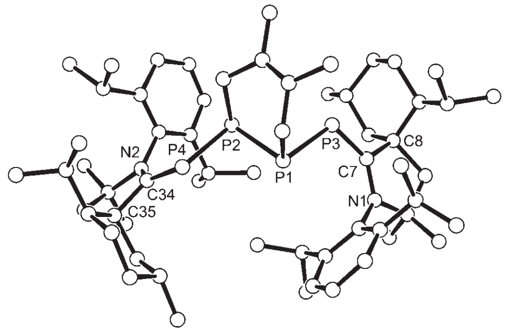


Figure 2. Solid-state structure of **3** (hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P2 2.227(3), P1-P3 2.236(3), P2-P4 2.226(3), P4-C7 1.744(7), P3-C34 1.730(8), N1-C34 1.379(10), N2-C7 1.363(9); C7-P4-P2 114.3(3), C34-P3-P1 110.1(3), P2-P1-P3 94.21(10), P4-P2-P1 92.55(10), N1-C34-C35 108.3(6), N2-C7-C8 109.4(6).

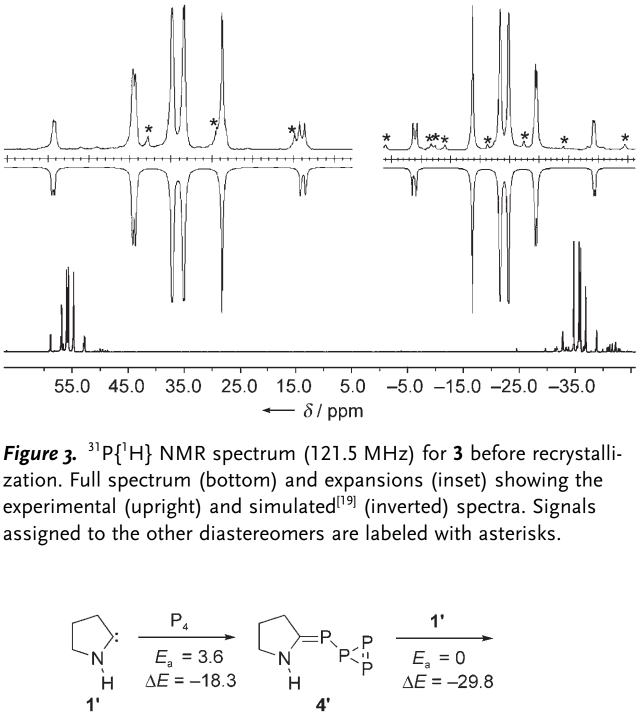
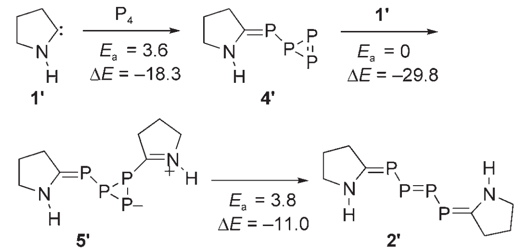
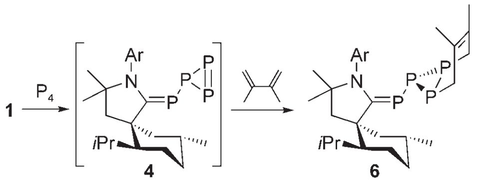


Figure 3. ^{31}P{^{1}H} NMR spectrum (121.5 MHz) for **3** before recrystallization. Full spectrum (bottom) and expansions (inset) showing the experimental (upright) and simulated[19] (inverted) spectra. Signals assigned to the other diastereomers are labeled with asterisks.



Scheme 3. Calculated reaction pathway for the reaction of the parent CAAC **1′** with P_4. The energie values are in kcal mol^{-1}.[17]

Because of the predicted analogy between the first step of the reaction of P_4 with CAAC and transition metals, it was of interest to demonstrate the existence of a triphosphirene intermediate of type **4**. Thus, CAAC **1** was treated with P_4 in the presence of a large excess of 2,3-dimethylbutadiene. The desired [4+2] cycloaddition product **6** (Scheme 4) was obtained in 52 % yield as a single diastereomer, and its solid-state structure was determined by a single-crystal X-ray diffraction study (Figure 4).



Scheme 4. Trapping of transient triphosphirene **4** by 2,3-dimethylbutadiene leads to adduct **6** as a single diastereomer.

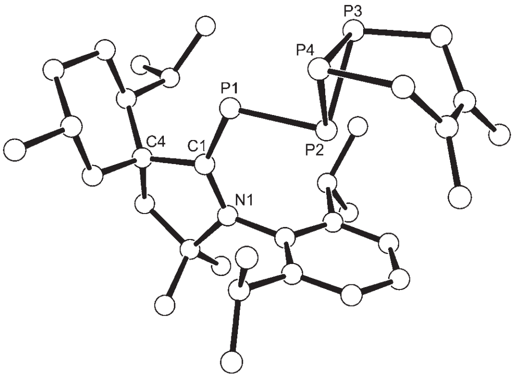


Figure 4. Solid-state structure of **6** (hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-C1 1.737(3), P1-P2 2.2288(13), P2-P4 2.2136(16), P2-P3 2.2174(16), P3-P4 2.1883(16), N1-C1 1.351(4); C1-P1-P2 109.70(11), P4-P2-P3 59.19(5), P4-P2-P1 91.10(5), P3-P2-P1 92.22(5), P4-P3-P2 60.32(6), P3-P4-P2 60.49(6), N1-C1-C4 108.7(3).

These preliminary results demonstrate that an enantiomerically pure CAAC can cleanly activate P_4 to afford highly reactive products. This type of activation allows for the construction of two phosphorus–carbon bonds with high diastereoselectivity. Taking into account the reactivity of the pendant phosphaalkene units, the possibility of finding synthetic and catalytic cycles allowing the preparation of chiral organophosphorus derivatives directly from P_4 are under investigation; the use of other stable carbenes as activators is also being studied.

Experimental Section

All manipulations were performed in an inert atmosphere of dry argon by using standard Schlenk techniques or in an mBraun glove box. Dry, oxygen-free solvents were employed. ^{31}P NMR spectra were recorded on a Bruker Avance 300 or Varian Inova 400 and 500 spectrometers. ^{31}P NMR chemical shifts are reported relative to 85 % H_3PO_4.

2: CAAC **1** (200 mg, 0.524 mmol) was added to a rapidly stirred suspension of P_4 (32.5 mg, 0.262 mmol) in hexanes (10 mL). Immediately upon addition, a blue-colored solution formed. The mixture was stirred for two hours at room temperature, and the solution was filtered through a glass microfiber filter. Upon concentration of the solution under vacuum, a dark blue crystalline material precipitated and was isolated by filtration. Slow evaporation of a hexanes solution of this material gave **2a** as single crystals suitable for an X-ray diffraction study; 65 % yield; m.p. 184–185 °C.

3: CAAC **1** (500 mg, 1.31 mmol) and P_4 (81.1 mg, 0.66 mmol) were combined in hexanes (20 mL) and stirred overnight. To the resulting blue solution was added 2,3-dimethylbutadiene (200 μL), and, after the solution had been stirred overnight, a yellow solution remained. Analysis by ^{31}P NMR showed nearly quantitative formation of **3**. The solution was then filtered through a glass fiber plug, and all volatiles were removed under vacuum. Adduct **3** was recrystallized by diffusion of a diethyl ether solution (15 mL) into acetonitrile (20 mL); 35 % yield; m.p. 130 °C (decomp); $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_6]benzene, 25 °C): $\delta = 55.8$ and -35.8 ppm ($J_{AA'} = -240.8$, $J_{AB} = -203.1$, $J_{AB'} = 237.4$, $J_{BB'} = -7.6$).[19]

6: CAAC **1** (150 mg, 0.393 mmol) was added to a rapidly stirred mixture of P_4 (45.8 mg, 0.393 mmol) and 2,3-dimethylbutadiene (2 mL) in hexanes (3 mL). Immediately upon addition, a faint blue-colored solution formed, which then turned yellow over 1 h. The solution was stirred overnight and the solvents removed under vacuum. Analysis of the crude material by ^{31}P NMR spectroscopy showed exclusive formation of **6**. The yellow residue was then dissolved in hexanes and filtered through a glass wool plug. Concentration of the solution by evaporation under vacuum gave **6** as yellow crystals; 52 % yield; m.p. 206–210 °C; $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_6]benzene, 25 °C): $\delta = 17.6$, -171.6, and -200.8 ppm ($J_{AM} = -212.1$, $J_{AX} = 154.9$, $J_{MX} = -202.6$, $J_{AX'} = 143.6$, $J_{MX'} = -133.6$, $J_{XX'} = -149.8$).[19]

Received: July 9, 2007

Keywords: carbenes · cycloaddition · diastereoselectivity · diphosphenes · phosphorus

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