Communication

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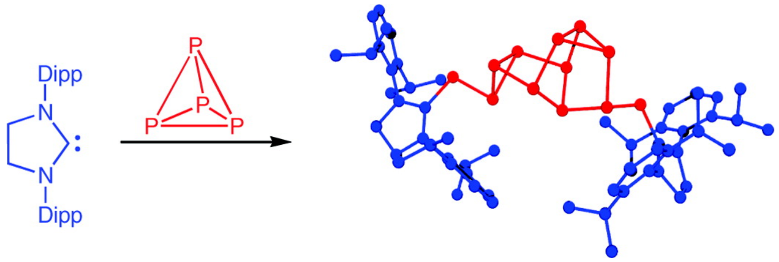

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NHC-Mediated Aggregation of P_4: Isolation of a P_{12} Cluster

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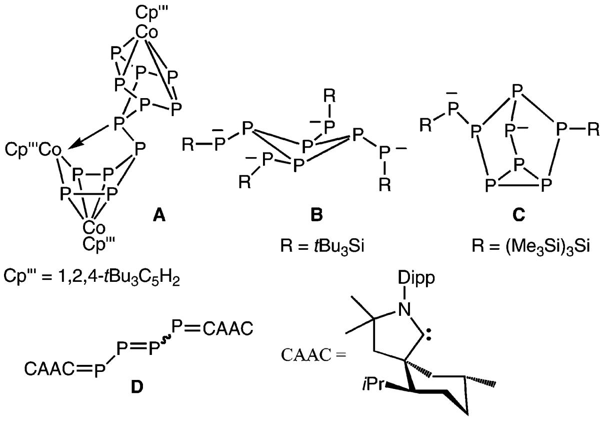
Since the discovery by Ginsberg and Lindsell of the first P_4 transition metal complex,[1] metal-mediated degradation of white phosphorus (P_4) has been widely studied, and a variety of complexes featuring P_1-P_4 fragments have been isolated.[2] Not only do transition metals induce the cleavage of P_4 but they also promote the reaggregation of the small fragments, although complexes with nuclearity higher than six are usually obtained as byproducts in low yields.[2b] Complex **A** is the only example of P_{12}-containing complex[3] and is the largest cluster obtained from P_4;[4] its structure has been established by ^{31}P NMR spectroscopy (Scheme 1). There are also a few studies concerning the reaction of P_4 with main group element derivatives;[5,6] however, the reactions usually proceed without inducing the fragmentation or aggregation of P_4. The only notable exceptions are the reactions of white phosphorus with tBu$_3$SiNa[7] and $(Me_3Si)_3SiK$,[8] which lead to P_8-containing molecules **B** and **C**, respectively.

We have recently shown that stable cyclic (alkyl)(amino)carbenes (CAACs)[9] also react with white phosphorus without inducing fragmentation or aggregation of P_4; indeed, 2,3,4,5-tetraphosphatrienes **D** were obtained in good yields.[10] Since the chemical reactivity of CAACs is often different[11] than that of N-heterocyclic carbenes (NHCs),[12] these results prompted us to investigate the reactivity of the latter with P_4. Here we report that NHC **1**[13] not only reacts with white phosphorus but also allows for the high yield synthesis of a P_{12}-containing compound. The mechanism of the formation of this cluster has been studied theoretically, and some of the fragments involved have either been characterized by spectroscopy or trapped chemically.

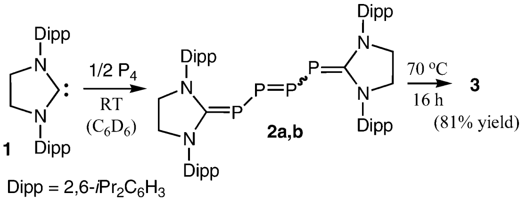
Upon mixing P_4 with 2 equiv of NHC **1** in C_6D_6, a blue solution immediately formed. The ^{31}P NMR spectrum of the crude reaction mixture revealed two sets of signals similar to those observed for **D**,[10] suggesting the formation of (Z)- and (E)-tetraphosphatriene isomers **2a** and **2b** (**2a**: major,[14] 396.7 and 69.4 ppm, $J_{AA'} = -523.2$, $J_{AX} = -420.8$, $J_{AX'} = -9.3$, $J_{XX'} = -331.5$ Hz; **2b**: minor, 506.5 and 63.0 ppm, $J_{AA'} = -647.5$, $J_{AX} = -302.3$, $J_{AX'} = -9.2$, $J_{XX'} = -25.8$ Hz) (Scheme 2). However, over time, the signals attributed to **2** decreased and a series of 10 very broad peaks appeared from +120 to −160 ppm, precluding the isolation of **2**. A mixture of **1** and P_4 was then heated to 70 °C overnight, yielding an air-sensitive, thermally stable yellow precipitate (81% isolated yield), in addition to NHC **1**. Analysis of the precipitate by ^{31}P-{^{1}H} NMR spectroscopy revealed exclusively the same series of 10 peaks as noted previously, in an approximately 1:1:1:1:1:1:1:3:1:1 ratio, suggesting the presence of a species **3** containing 12 phosphorus atoms. The ^{13}C{^{1}H} NMR spectrum indicated the presence of two different P═C fragments, as shown by two doublets at 191 ($^1J_{PC} = 128$ Hz) and 189 ppm ($^1J_{PC} = 131$ Hz).

Recrystallization from hot CD_3CN gave yellow single crystals that upon analysis by X-ray diffraction revealed a system containing 12 phosphorus atoms capped by two NHC ligands (Figure 1). The polycyclic structure consists of three five-membered rings, two three-membered rings, and one six-membered ring with P−P bond lengths between 2.176 and 2.233 Å, typical of P−P single bonds. The architecture of the P_{12} core of **3** is very different from that found in the P_{12} transition metal complex **A**[3] and is obviously unprecedented, although the nonaphosphane core (P3−P7 and P9−P12) is reminiscent of the organosubstituted polyphosphines and polyphosphorus anions investigated by Baudler.[15]

Scheme 1



Scheme 2



In order to gain insight into the mechanism of the reaction leading to cluster **3**, trapping experiments of possible intermediates were attempted. Thus, NHC **1** was reacted with 0.5 equiv of P_4 in the presence of 2,3-dimethylbutadiene. Analysis of the reaction mixture by ^{31}P NMR revealed the presence of two products in a 1/5 ratio. Both compounds were isolated and fully characterized including by single-crystal X-ray diffraction studies. The isolated minor and major products, **4** (9% yield) and **5** (79% yield), were identified as the [4 + 2] cycloadducts of dimethylbutadiene with the PP double bond of triphosphirene **6**[16] and (E)-tetraphosphatriene **2b**, respectively (Figure 2).

Calculations (B3LYP/6-311G**, ZPE corrected)[17a] using the parent NHC (H instead of Dipp) show that **6** and **2** are able to undergo, without energy barrier, an exothermic [3 + 2] cycloaddition ($\Delta E = -13.3$ kcal/mol) to give an intermediate **7** (Figure 2). The latter rearranges, with loss of two NHCs, into heptaphosphanorbornadiene **8**,[17b] which is known in the coordination sphere of transition metals.[3,18] Last, derivative **8** can undergo, without energy barrier, a $[\pi^2 + \pi^2 + \pi^2]$ reaction[19] with another triphos-

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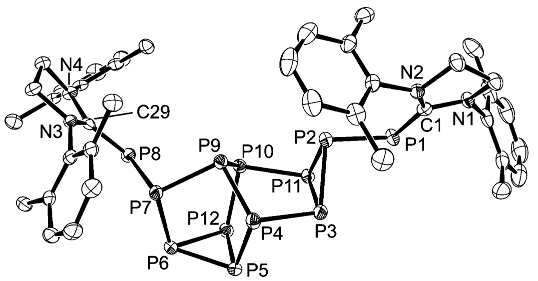

Figure 1. Structure of **3** (50% thermal ellipsoids are shown). Hydrogen atoms and CH_3 fragments of the aryl-*i*Pr groups have been omitted for clarity. Selected bond lengths (Å): P1−C1 1.756(3), P8−C29 1.777(4), N1−C1 1.374(4), N2−C1 1.357(4), N3−C29 1.358(4) N4−C29 1.369(4); P−P bond length range = 2.176−2.233.

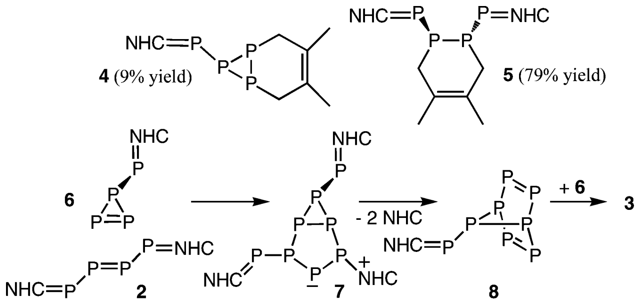

Figure 2. Products **4** and **5**, resulting from the trapping of (*E*)-tetraphosphatriene **2b** and triphosphirene **6**, respectively (top). Postulated mechanism for the formation of P_{12} cluster **3** (bottom).

phirene **6** to afford the observed P_{12}-containing species **3** ($\Delta E = -54.9$ kcal/mol).

This work demonstrates that N-heterocyclic carbenes are at least as powerful as transition metal complexes for promoting the aggregation of P_4. The understanding of the reaction pathway leading to the P_{12} cluster **3** paves the way for the rational design of even larger carbene-stabilized phosphorus allotropes, with the aim of preparing phosphorus-based nanoparticles.

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Supporting Information Available: Full experimental and spectroscopic data for compounds **2**−**5**, complete ref 17a, and X-ray crystallographic data for **3**−**5** (CCDC numbers 655890−655892). This material is available free of charge via the Internet at http://pubs.acs.org.

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