Fragmentation of White Phosphorus by a Cyclic (Alkyl)(Amino)Alumanyl Anion

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ABSTRACT: A stable cyclic (alkyl)(amino)alumanyl anion (CAAAl) **1** reacts with white phosphorus (P_4) under ambient conditions, in which P_4 is fragmented into a P_1 unit to afford a bis(alumanyl)phosphide **2**, demonstrating the direct formation of a P anion from an Al anion. Structural and electronic features of the latter were fully characterized by the standard spectroscopic means, X-ray diffraction analysis, and computational studies, which revealed that **2** bears the highly polarized (Al: δ+, P: δ–) and relatively short Al—P bonds, indicative of the σ-donating and π-accepting nature of CAAAl groups.

The functionalization of white phosphorus (P_4) through a chlorine-free process has been of paramount significance in phosphorous chemistry.[1,2] Over the past decades, a number of transition-metals have been reported for P_4 activation, which allows access to a variety of phosphorus-containing metal complexes without using phosphorous chloride precursors (PCl_3, PCl_5).[3] Analogously, various main-group molecules are also known to react with P_4, representing a useful protocol for the direct bond formation between the phosphorus and the p-block elements.[4] Among them, the reaction between P_4 and monovalent aluminum species Al(I) has still remained unexplored and only two examples of the Al(I) insertion into P—P bonds of P_4 have been reported thus far (Figure 1a). In 1994, Schnöckel et al. reported that (pentamethylcyclopentadienyl)Al(I) tetramer **I** completely cleaves all P—P bonds in P_4 at the Al(I) centers to afford an Al_6P_4 cluster.[5] In 2004, Roesky et al. demonstrated that NacNacAl(I) **II** (NacNac = [DippNC(Me)CHC(Me)NDipp]$^-$, Dipp = 2,6-*i*$Pr_3C_6H_3$) undergoes the P—P bond insertion with P_4 to furnish an Al_2P_4 molecule.[6]

Since the seminal work by Aldridge, Goicoechea and co-workers,[7] several anionic Al species have been isolated to date and the field is rapidly growing over the last few years.[8] Significantly, it has been demonstrated that the diamino-[7, 9–12] and dialkyl-[13] substituted alumanyl anions are able to activate various small molecules[7–20] and can serve as useful reagents for introducing an alumanyl ligand on to metals[21,22] Recently, we have reported the first synthesis of a cyclic (alkyl)(amino)alumanyl anion (CAAAl), in which the dicoordinate Al(I) center is supported by alkyl- and amino-substituents.[23] Our preliminary studies have shown that not only does CAAAl undergo electron redistribution with borane to furnish an AlB_2 ring but also activate Si–H, N–H, and even C–C bonds at the aluminum center, which prompted us to investigate the reaction of CAAAl with P_4. In this contribution, we present the fragmentation of P_4 by an alumanyl anion, as well as, the isolation, single-crystal X-ray diffraction, and computational studies of the corresponding product, bis(alumanyl)phosphide (Figure 1b).

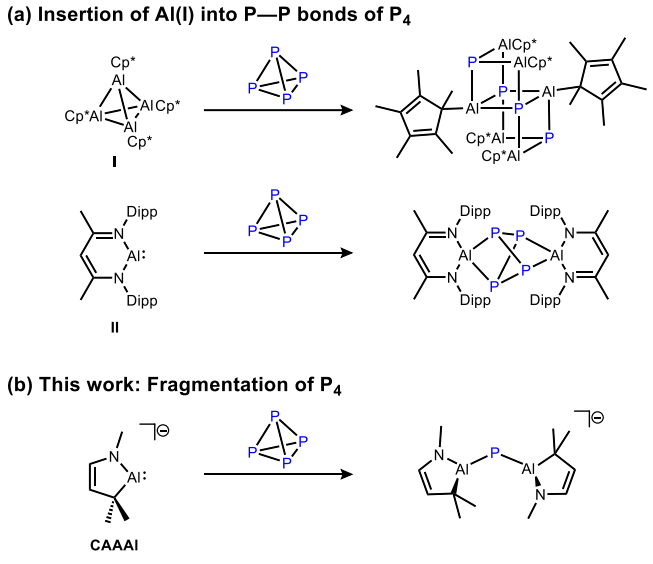
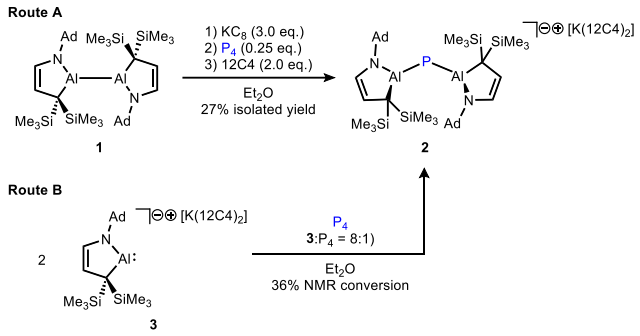


Figure 1. (a) Reported examples of P_4 activation by Al(I) species (Cp* = Me_5C_5. Dipp = 2,6-*i*$Pr_2C_6H_3$). (b) Present work.

Reduction of dialane **1** with three equivalents of potassium graphite (KC_8), followed by treatment of the resulting solution with P_4 and 12-crown-4 ether afforded an orange solution, from which yellow crystals of the bis(alumanyl)phosphide **2** suitable for X-ray diffraction analysis, after workup, were gained in 27% isolated yield (Scheme 1, Route A). The ^{31}P NMR spectrum of **2** shows a relatively sharp singlet with the half-width of 8.3 Hz at –295.4 ppm, which is shifted downfield from that of P_4 (–516.5 ppm), and in the close range reported for phosphides featuring σ-donating substituents such as boryl(phosphino)phosphide (–226.3 ppm)[24] and boryl(silyl)phosphide (–257.3 ppm).[25] Meanwhile, treatment of CAAAl **3** with P_4 in a 8:1 ratio in diethyl ether (Et_2O) at room temperature for 30 minutes afforded **2** in 36% NMR conversion (Scheme 1, Route B). While polyphosphides such as K_3P_7 can be considered as potential byproducts, in the ^{31}P{^{1}H} NMR spectrum after the workup, no peaks corresponding to the polyphosphides were detected (Figure S8). It is important to note that the reaction of **1** with P_4 in a 4:1 ratio yielded the greater amount of unidentifiable byproducts than that in the 8:1 ratio. Many attempts to isolate **2** generated via this synthetic route were unsuccessful due to the presence of the byproducts.

Scheme 1. Synthesis of 2 (Ad = 1-adamantyl, 12C4 = 12-crown-4 ether)



In the solid-state (Figure 2), **2** consists of the separate ionic pairs involving the anionic part $[(CAAAl)_2P]^-$ and the cationic part $[K(12C4)_2]^+$. The shortest distance between the P and the K is 6.451 Å, which is larger than a sum of the van der Waals' radii of P and K (4.55 Å), confirming no interaction between them.[26] The anionic part involves one P atom and two CAAAl groups, confirming that P_4 serves as a P_1 source.[27] Each $AlNC_3$ five-membered ring is nearly coplanar (the sum of internal pentagon angles = 539.99° and 539.96°, respectively), whereas they are twisted (the C1–Al1–Al2–N2 dihedral angle is 18.23°). The Al1—P1—Al2 moiety shows a pronounced bent structure with the Al1—P1—Al2 bond angle of 106.89(2)°, which is comparable to the C—P—C bond angles [102.74(6)–104.25(12)°] reported for diarylphosphides $[Ar_2P]^-$.[28] The bond angles of the C1—Al1—N1 and the C2—Al2—N2 [92.54(7)° and 92.48(7)°, respectively] are larger than that of **3** [86.8(1)°] and slightly smaller than that of **1** [94.1(1)°]. It is noteworthy that the Al—P bonds [2.246(1) Å] in **2** are shorter than those of λ^3,λ^3-phosphanylalumanes $R_2AlPR'_2$ [2.334(2)–2.379(3) Å],[29] as well as, the six-membered $[RAlPR']_3$ molecules [2.323(3)– 2.336(3) Å].[30] The Al—C and the Al—N bond lengths of **2** [Al—C: 2.009(2) Å and 2.030(2) Å, Al—N: 1.860(2) Å and 1.861(2) Å] are shorter than those of **3** [Al—C: 2.095(3) Å, Al—N: 1.895(2) Å] and longer than those of **1** [Al—C: 1.981(3) Å and 1.981(3) Å, Al—N: 1.814(2) Å and 1.817(2) Å].

To understand the detail of the electronic structure of **2** Density functional theory (DFT) calculations were carried out at the PBE1PBE-D3/def-TZVP level of theory (Figure 3). The optimized geometry of the anionic part $[(CAAAl)_2P]^-$ agree well with the crystal structure of **2**, and the estimated ^{31}P chemical shift by GIAO calculation (–271.8 ppm) is consistent with the experimental value (–295.4 ppm). The highest occupied molecular orbital (HOMO) corresponds to the lone pair of electrons on the P atom projected out of the Al_2P plane. The HOMO–3 is the in-plane lone pair of electrons on the P atom, which is slightly delocalized to the vacant 3*p*-orbitals on the Al center via the donor-acceptor interaction, whereas the HOMO–4 involves the Al—P σ-bonds. It is worth noting that the HOMO and the HOMO–3 of $[(CAAAl)_2P]^-$ resemble the frontier orbitals of divalent carbon(0) compounds L→C(0)←L,[31] which is in line with the fact that $[(CAAAl)_2P]^-$ and L→C(0)←L are formally in isolobal relationship. Interestingly, the interaction between two unoccupied 3*p*-orbitals on the Al atoms is seen in the lowest unoccupied molecular orbital (LUMO). The UV-vis spectrum of **2** shows a broad absorption band from 375 nm to 600 nm (Figure S9), which is assigned to the transition from the HOMO to the LUMO by means of Time-dependent DFT calculation (Figure S10). Natural Bond Orbital (NBO) analysis shows that Wiberg bond index (WBI) of 1.11 for the Al—P bonds (Table S2). The relatively larger WBI value of **2**, with respect to WBI values for Al—P bonds of reported λ^3,λ^3-phosphanylalumanes [*t*Bu_2Al–$PMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$),[29b] 0.65; tmp_2Al–PPh_2 (tmp = 2,2,6,6-tetramethylpiperidino), [29d] 0.69], indicates the strong interaction between the P and Al atoms in **2** (Figure S11). Indeed, the donor-acceptor interaction from the in-plane P lone pair to the vacant Al 3*p*-orbitals is manifested by the second-order perturbation analysis with the stabilization energy of 13.88 kcal·mol^{-1} (Table S3 and S4). Natural Population Analysis (NPA) reveals that the Al—P bonds are highly polarized (Al1; +1.58, P1; –1.37, Al2; +1.58) (Table S5). These data propose that the CAAAl groups feature σ-donating and π-accepting nature, analogous to cyclic (alkyl)(amino)carbenes CAACs.[32]

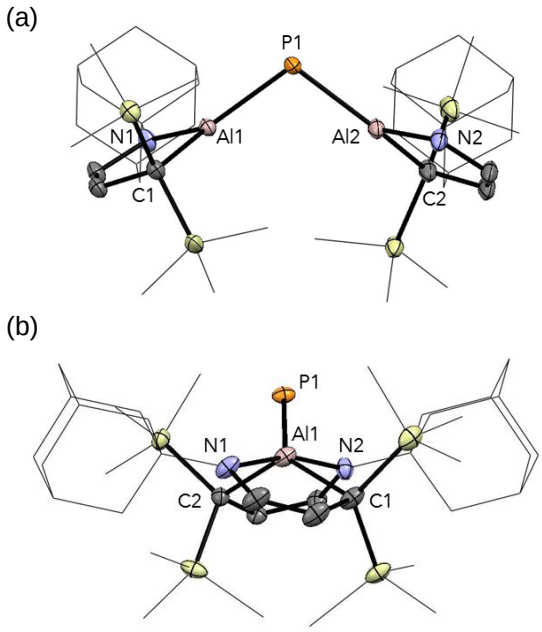


Figure 2. Solid-state structure of the anionic part of **2**. (a) A top view. (b) A side view. All hydrogen atoms and the cationic part $[K(12C4)_2]^+$ are omitted for clarity. Thermal ellipsoids are shown at the 50% probability.

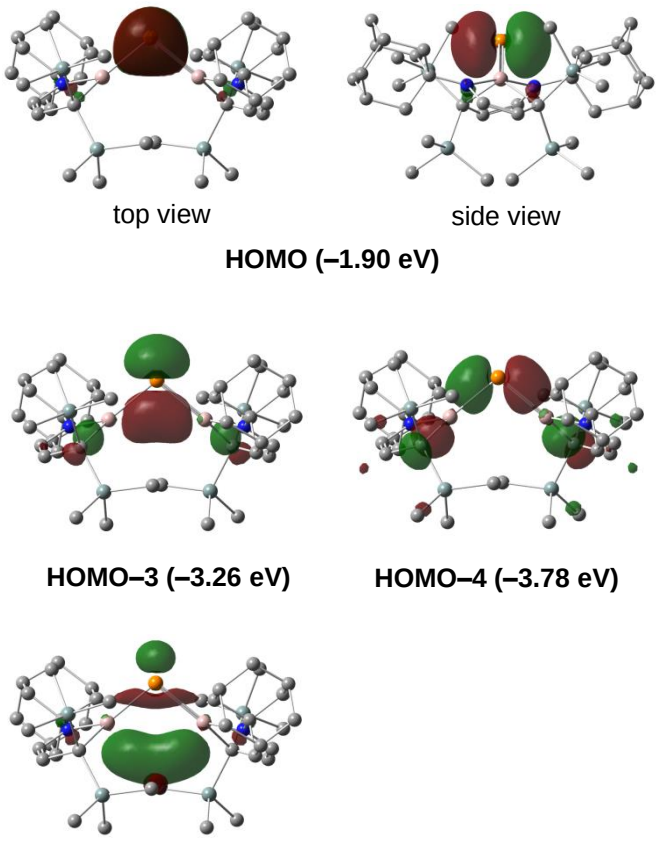


Figure 3. Selected key molecular orbitals of the anionic part of **2**, calculated at the PBE1PBE-D3/def-TZVP level of theory (isovalue = 0.05). All hydrogen atoms are omitted for clarity.

In summary, we have demonstrated that white phosphorus can be fragmented into a P_1 unit by activating with a cyclic (alkyl)(amino)alumanyl anion **1**. This protocol gives rise to bis(alumanyl)phosphide **2**, which is not readily accessible by the conventional method, demonstrating the direct conversion of an anionic Al species to an anionic P species. **2** features the polarized and relatively short Al—P bonds. Investigation on the reactivity of **2** is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.XXXXXXXX.
Crystallographic data for compounds **2** (CIF)
Synthesis procedures, spectral data, selected crystal parameters, and theoretical calculations (PDF)
Cartesian coordinates of the calculated structures (XYZ)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We are grateful to Nanyang Technological University (NTU) and the Singapore Ministry of Education (MOE2018-T2-2-048(S)) for financial supports. We also thank Dr. Yongxin Li (NTU) for assistance in X-ray diffraction analysis.

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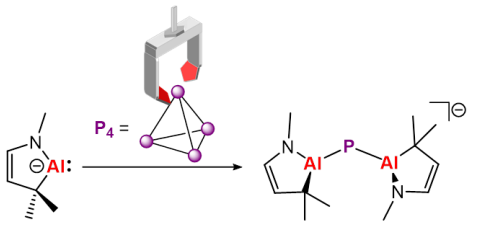
SYNOPSIS TOC



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