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

Kota Koshino, Rei Kinjo\*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore

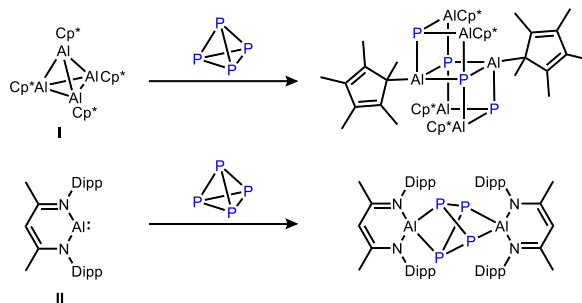
**ABSTRACT:** A stable cyclic (alkyl)(amino)alumanyl anion (CAAAI) **1** reacts with white phosphorus ( $P_4$ ) under ambient conditions, in which  $P_4$  is fragmented into a  $P_1$  unit to afford a bis(alumanyl)phosphide **2**, demonstrating the direct formation of a P anion from an Al anion. Structural 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:  $\delta^+$ , P:  $\delta^-$ ) and relatively short Al—P bonds, indicative of the  $\sigma$ -donating and  $\pi$ -accepting nature of CAAAI groups.

The functionalization of white phosphorus ( $P_4$ ) through a chlorine-free process has been of paramount significance in phosphorous chemistry.<sup>1,2</sup> 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 ( $PCl_3$ ,  $PCl_5$ ).<sup>3</sup> 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.<sup>4</sup> 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.<sup>5</sup> In 2004, Roesky et al. demonstrated that NacNacAl(I) **II** (NacNac = [DippNC(Me)CHC(Me)NDipp]<sup>-</sup>, Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) undergoes the P—P bond insertion with  $P_4$  to furnish an  $Al_2P_4$  molecule.<sup>6</sup>

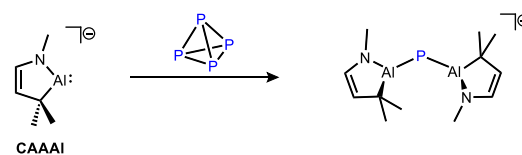
Since the seminal work by Aldridge, Goicoechea and co-workers,<sup>7</sup> several anionic Al species have been isolated to date and the field is rapidly growing over the last few years.<sup>8</sup> Significantly, it has been demonstrated that the diamino-<sup>7, 9–12</sup> and dialkyl-<sup>13</sup> substituted alumanyl anions are able to activate various small molecules<sup>7–20</sup> and can serve as useful reagents for introducing an alumanyl ligand on to metals<sup>21,22</sup>. Recently, we have reported the first synthesis of a cyclic (alkyl)(amino)alumanyl anion (CAAAI), in which the dicoordinate Al(I) center is supported by alkyl- and amino-substituents.<sup>23</sup> Our preliminary studies have shown that not only does CAAAI un-

dergo 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 CAAAI 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).

## (a) Insertion of Al(I) into P—P bonds of $P_4$



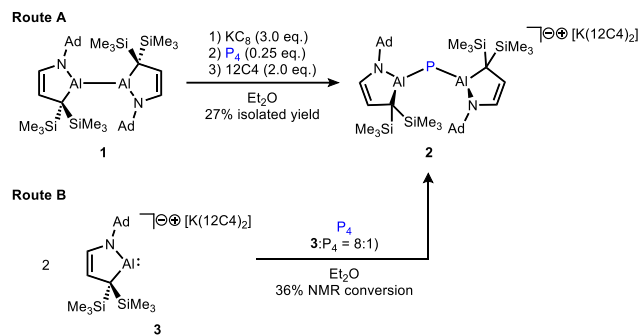
## (b) This work: Fragmentation of $P_4$



**Figure 1.** (a) Reported examples of  $P_4$  activation by Al(I) species ( $Cp^* = Me_5C_5$ , Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). (b) Present work.

Reduction of dialane **1** with three equivalents of potassium graphite (KC<sub>8</sub>), followed by treatment of the resulting solution with P<sub>4</sub> 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 <sup>31</sup>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<sub>4</sub> (-516.5 ppm), and in the close range reported for phosphides featuring σ-donating substituents such as boryl(phosphino)phosphide (-226.3 ppm)<sup>24</sup> and boryl(silyl)phosphide (-257.3 ppm).<sup>25</sup> Meanwhile, treatment of CAAAl **3** with P<sub>4</sub> in a 8:1 ratio in diethyl ether (Et<sub>2</sub>O) at room temperature for 30 minutes afforded **2** in 36% NMR conversion (Scheme 1, Route B). While polyphosphides such as K<sub>3</sub>P<sub>7</sub> can be considered as potential byproducts, in the <sup>31</sup>P{<sup>1</sup>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<sub>4</sub> 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.

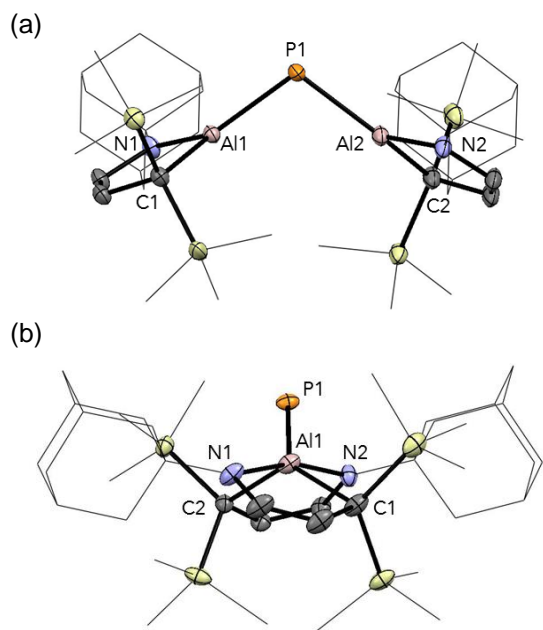
**Scheme 1. Synthesis of 2 (Ad = 1-adamantyl, 12C4 = 12-crown-4 ether)**



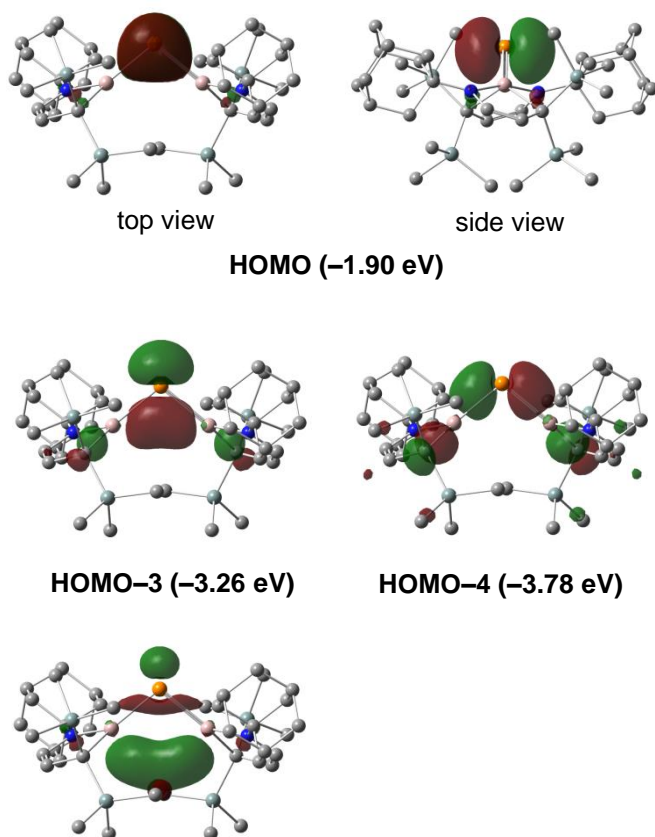
In the solid-state (Figure 2), **2** consists of the separate ionic pairs involving the anionic part [(CAAAl)<sub>2</sub>P]<sup>-</sup> and the cationic part [K(12C<sub>4</sub>)<sub>2</sub>]<sup>+</sup>. The shortest distance between the P and the K is 6.451 Å, which is larger than a sum of the van der Waals' radii of P and K (4.55 Å), confirming no interaction between them.<sup>26</sup> The anionic part involves one P atom and two CAAAl groups, confirming that P<sub>4</sub> serves as a P<sub>1</sub> source.<sup>27</sup> Each AlNC<sub>3</sub> five-membered ring is nearly coplanar (the sum of internal pentagon angles = 539.99° and 539.96°, respectively), whereas they are twisted (the C<sub>1</sub>-Al<sub>1</sub>-Al<sub>2</sub>-N<sub>2</sub> dihedral angle is 18.23°). The

Al<sub>1</sub>-P<sub>1</sub>-Al<sub>2</sub> moiety shows a pronounced bent structure with the Al<sub>1</sub>-P<sub>1</sub>-Al<sub>2</sub> 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<sub>2</sub>P]<sup>-</sup>.<sup>28</sup> The bond angles of the C<sub>1</sub>-Al<sub>1</sub>-N<sub>1</sub> and the C<sub>2</sub>-Al<sub>2</sub>-N<sub>2</sub> [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<sup>3</sup>,λ<sup>3</sup>-phosphanylalumanes R<sub>2</sub>AlPR'<sub>2</sub> [2.334(2)-2.379(3) Å],<sup>29</sup> as well as, the six-membered [RAlPR']<sub>3</sub> molecules [2.323(3)-2.336(3) Å].<sup>30</sup> 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)<sub>2</sub>P]<sup>-</sup> agree well with the crystal structure of **2**, and the estimated <sup>31</sup>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<sub>2</sub>P plane. The HOMO-3 is the in-plane lone pair of electrons on the P atom, which is slightly delocalized to the vacant 3p-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)<sub>2</sub>P]<sup>-</sup> resemble the frontier orbitals of divalent carbon(o) compounds L→C(o)←L,<sup>31</sup> which is in line with the fact that [(CAAAl)<sub>2</sub>P]<sup>-</sup> and L→C(o)←L are formally in isolobal relationship. Interestingly, the interaction between two unoccupied 3p-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<sup>3</sup>,λ<sup>3</sup>-phosphanylalumanes [tBu<sub>2</sub>Al-PMes<sub>2</sub> (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>),<sup>29b</sup> 0.65; tmp<sub>2</sub>Al-PPh<sub>2</sub> (tmp = 2,2,6,6-tetramethylpiperidino),<sup>29d</sup> 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 3p-orbitals is manifested by the second-order perturbation analysis with the stabilization energy of 13.88 kcal·mol<sup>-1</sup> (Table S3 and S4). Natural Population Analysis (NPA) reveals that the Al-P bonds are highly polarized (Al<sub>1</sub>; +1.58, P<sub>1</sub>; -1.37, Al<sub>2</sub>; +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.<sup>32</sup>



**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  $[K(12C_4)_2]^+$  are omitted for clarity. Thermal ellipsoids are shown at the 50% probability.



### LUMO (2.15 eV)

**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<sub>1</sub> unit by activating with a cyclic (alkyl)(amino)aluminum 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)

### ■ AUTHOR INFORMATION

#### Corresponding Author

**Rei Kinjo** – Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore; [orcid.org/0000-0002-4425-3937](https://orcid.org/0000-0002-4425-3937); Email: [rkinjo@ntu.edu.sg](mailto:rkinjo@ntu.edu.sg)

#### Author

**Kota Koshino** – Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore; [orcid.org/0000-0003-1336-405X](https://orcid.org/0000-0003-1336-405X)

#### Notes

The authors declare no competing financial interest.

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## SYNOPSIS TOC

