

Construction of σ -aromatic AlB_2 ring via A Borane Coupling with A Dicoordinate Cyclic (Alkyl)(Amino)Aluminyll Anion

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ABSTRACT: Since the ground-breaking discovery in 2018 that the synthesis of bottleable nucleophilic aluminyll anion is feasible, a handful of derivatives have been developed to date, which are, however, limited to diamino- and dialkyl-substituted species. Herein, we report the synthesis of a cyclic (alkyl)(amino)aluminyll anion based on a five-membered framework. The dicoordinate aluminum center features both a lone pair of electrons and unoccupied $3p$ -orbital, thus, being genuinely isoelectronic with carbenes. We show the bond formation and bond activation at the Al sphere: thus, not only does it undergo electron redistribution with borane to furnish a heteroatomic Group 13 ring exhibiting σ -aromatic nature concomitant with a three-center two electron AlB_2 bond, but also the ambiphilic nature allow for oxidative addition of Si—H, N—H, and even C—C bonds at the aluminum center.

INTRODUCTION

On account of the high electrophilicity of aluminum concomitant with the small electronegativity ($\chi = 1.61$), archetypal aluminum compounds in the most stable +III oxidation state are considered to be electron-pair acceptors. Intrinsic electron deficiency of Al(III) compounds allows them to be used for applications such as Lewis acid catalysts for various chemical reactions.^{1,2} Contrary, the chemistry of aluminum compounds in the low oxidation state has relatively slowly developed, albeit their potential application.^{3–5} Among them, it is only recently that the isolation of anionic nucleophilic Al(+I) species has been experimentally demonstrated (Figure 1). In 2018, Aldridge, Goicoechea and co-workers reported the first example of the anionic Al(I) nucleophile **I**, the Al center of which is substituted by two nitrogen atoms and thermodynamically stabilized by an intramolecular coordination of one oxygen atom.⁶ It has also been described that adding [2.2.2]cryptand to **I** leads to a monomeric derivative **II**.⁷ Afterwards, the groups of Coles, and Hill and McMullin, reported the dimeric forms of base-free diamino aluminyll anions **III** and **IV** based on six- and seven-membered rings, respectively.^{8,9} Very recently, Yamashita et al. reported a dialkyl-substituted potassium aluminyll complex **V** bearing a two-center two-electron Al—K bond.¹⁰

While the exploration of nucleophile Al(I) species is in its infancy, they appear to underpin a unique chemical utility. For instance, it has been proven that the nucleophilic nature of **I**, **IV** and **V** allows access to relevant metal derivatives such as Al—Mg,^{6,9} Al—Ca,⁹ Al—Au,¹¹ and Al—Y¹² complexes. By employing **I–V**, activation of small molecules such as dihydrogen (H_2), arenes, alkenes, alkynes, carbon monoxide (CO), carbon dioxide (CO_2), dinitrogen monoxide (N_2O), tetrahydrofuran (THF), selenium (Se),

has also been documented to date.^{13–18} Despite the considerable progress over the years in this field, the extant structural motif of nucleophilic Al(+I) species is limited to diamino- **I–IV** and dialkyl- **V** derivatives, among which only **III** and **IV** bear the dicoordinate Al center, as well as, only **V** features five-membered framework. The deficiency of variation mainly stems from the paucity of available synthetic routes.

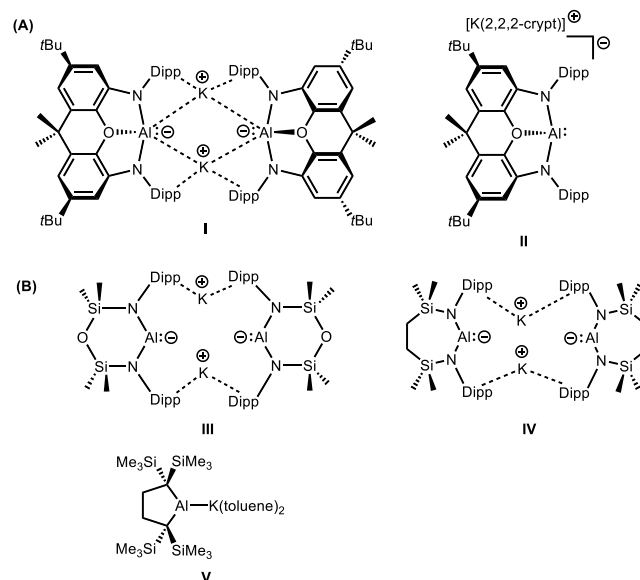


Figure 1. Reported Examples of Potassium Aluminyll Species. (A) Lewis based-stabilized diamino aluminyll anions (**I** and **II**). (B) Lewis base-free diamino (**III** and **IV**) and dialkyl (**V**) aluminyll anions. Dipp = 2,6-diisopropylphenyl, 2,2,2-crypt = [2.2.2]cryptand.

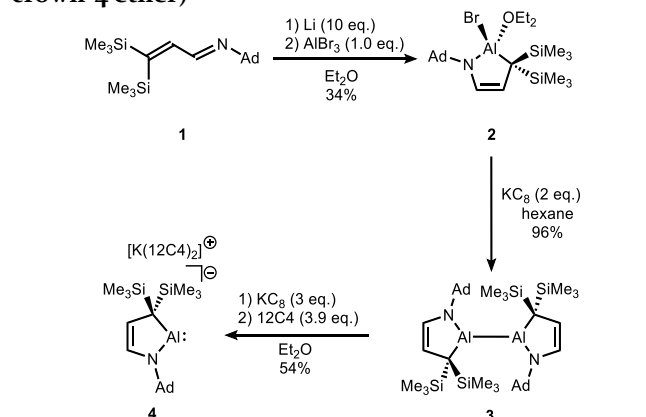
In order for the unique chemistry of nucleophilic Al(+I) species to be further developed, readily accessible examples with diverse steric and electronic characteristics need to come forward. In this contribution, we report the synthesis, single-crystal X-ray diffraction, and computational studies of a cyclic (alkyl)(amino)aluminum anion (CAAAL). This compound undergoes a coupling reaction with borane rendering a heteroatomic AlB_2 ring. We also describe the reactivity towards silane, ammonia and biphenylene.

RESULTS AND DISCUSSION

In the carbene chemistry, the geometric and electronic diversities of carbenes have brought a variety of applications in many areas and enriched the research field. Among them, cyclic (alkyl)(amino)carbenes (CAACs),^{19–23} which have the higher nucleophilicity (more σ -donating) and electrophilicity (more π -accepting) with respect to those of N-heterocyclic carbenes (NHCs),^{24–29} have proved to be superior to NHCs for stabilizing a variety of paramagnetic species, as well as for activating small molecules, implying the great potentials of CAAC analogues involving other low-valent p-block elements.^{30,31} Notwithstanding, Group 13 analogues of CAACs have never to our knowledge been reported thus far, which prompted us to set out to pursue the Al analogue of CAACs.

Starting from α,β -unsaturated imine **1**, the three-step reaction furnishes compound **4** in a gram scale (Scheme 1). Treatment of **1** with 10 equivalents of lithium in diethyl ether (Et_2O), followed by the addition of $AlBr_3$ afforded an ether-coordinated Al(III) complex **2** in 34% isolated yield. Reduction of **2** with 2.0 equivalents of potassium graphite (KC_8) in hexane at 60 °C gave a dialane derivative **3** as a yellow solid in 96% isolated yield. When Et_2O was added to the mixture of **3** and 3.0 equivalents of KC_8 at room temperature, an intense yellow solution was obtained within 1 h. After workup with 12-crown-4 ether (12C4), **4** was gained as intense yellow crystals in 54% isolated yield. All products **2**, **3** and **4** were fully characterized by standard spectroscopic, analytical and crystallographic methods.

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



In the solid-state (Figure 2A), **4** exists as a separate ion pair, and the shortest distance between the central aluminum atom and the crown ether-coordinated potassium cation is 6.660 Å, which is larger than a sum of the van der Waals' radii of Al and K (4.59 Å),^{32,33} indicating no interaction between them. All five atoms of the central $AlNC_3$ ring are nearly coplanar (the sum of internal pentagon angles = 540.0°). The Al center is two-coordinate with the sp^3 carbon atom and the nitrogen atom, with the N—Al—C bond angle of 86.8(1)°, which is smaller than those of **2** and **3** [**2**: 95.8(2)°, **3**: 94.1(1) and 94.1(1)°], suggesting the high p -character of the Al—C and the Al—N bonds. Indeed, the Al—C and the Al—N bonds of **4** [Al—C: 2.095(3) Å, Al—N: 1.895(2) Å] are longer than those of **2** [Al—C: 1.984(5) Å, Al—N: 1.826(3) Å] and **3** [Al—C: 1.981(3) Å and 1.981(3) Å, Al—N: 1.814(2) Å and 1.817(2) Å]. The Al—C and the Al—N bond distances of **4** are comparable to those of **V** [Al—C: 2.0846(9) Å], **III** and **IV** [Al—N: **III**: 1.879(2)–1.896(2) Å, **IV**: 1.887(2)–1.892(2) Å], respectively.

We carried out density functional theory (DFT) calculations at the PBE1PBE-D3/def-TZVP level of theory in order to better understand the bonding situation and electronic structure of the anionic part of **4**. The highest occupied molecular orbital (HOMO) of the anionic part of **4** corresponds to the Al-centered in-plan lone pair (Figure 2B), whereas the lowest unoccupied molecular orbital+1 (LUMO+1) is mainly represented by the vacant p-orbital on the Al center (Figure 2C), confirming the isoelectronic structure with CAACs. The energy level of the HOMO of the anionic part of **4** (−0.46 eV) is higher than those of the anionic part of **II** (−1.05 eV)⁶ and **V** (−3.76 eV).¹⁰ The former is attributed to the replacement of one of the amino groups with the less-electronegative alkyl group in **4**, whereas the latter reflects the anionic and dicoordinate nature of **4**. A natural population analysis (NPA) shows that the charge (+0.561) of the Al center in **4** is more electronegative than that (+1.278) in **3**. The UV-vis spectrum of **4** exhibits a strong absorption band with $\lambda_{max} = 422$ nm (Figure S35A), which is assigned to the transition from the HOMO to the LUMO+1 on the basis of Time-dependent DFT calculations (Figure S43).

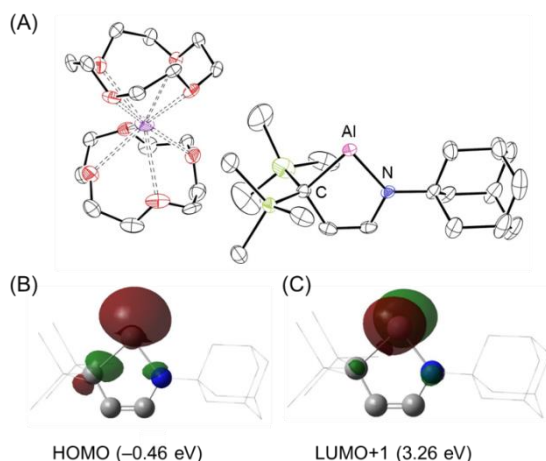


Figure 2. The solid-state structure of **4** and key frontier molecular orbitals of the anionic part of **4**. (A) Solid-state molecular structure of **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. (B and C) Molecular orbitals of the anionic part of **4**. Plots of the HOMO (B) and LUMO+1 (C) calculated at the PBE1PBE-D3/def-TZVP level. Isovalue = 0.05. Hydrogen atoms are omitted for clarity.

4 is insoluble in nonpolar solvents (hexane, benzene and toluene), slightly soluble in Et₂O, and well dissolved in THF, but it easily decomposes to an unidentified mixture at room temperature. In the solid-state **4** is stable up to 145.5 °C but appears to be highly sensitive toward oxygen and moisture. To gain further insight into the chemical property of **4**, we investigated the reactivity of **4** toward borane dimethyl sulfide complex (BH₃·SMe₂) (Scheme 2) and substrates featuring robust σ-bonds (Figure 5A).

The reaction of **4** with 3.0 equivalents of BH₃·SMe₂ proceeded quickly as indicated by the fast decoloration of the reaction mixture. Colorless crystals of **5** were obtained by recrystallization in 75% isolated yield, and an X-ray diffraction study revealed the formation of the trigonal AlB₂ ring (Figure 3). It has been reported that reactions of BH₃ with carbenes (NHC, CAAC) or boryllithium afford the corresponding adducts such as NHC-BH₃, CAAC-BH₃ and [boryl-BH₃Li(thf)]₂.^{34–36} Meanwhile, the formation of **5** via the three-molecule complexation reaction represents a new class of reactivity of a low-valent main group molecule toward BH₃. Note that compound **5** is the first structurally authenticated example of an aluminum complex of diboran(6).³⁷ The Al—B distances [2.139(5) Å and 2.169(5) Å] of **5** are in good agreement with precedent ranges for Al(sp³)—B(sp²) σ-bonds [2.119(3) Å—2.155(2) Å], whereas the B—B distance [1.854(7) Å] is in the range for a reported B(sp³)—B(sp³) single bond (1.675(16)—1.924(3) Å). The ¹H NMR spectrum of **5** shows two broad peaks at 0.10 ppm and 0.37 ppm, which are assigned to Al—H—B protons and B—H protons, respectively, according to theory. The presence of those Al—H—B and B—H bonds were detected by the solid-state IR spectroscopy at 2016 cm⁻¹ (Al—H—B), and 2390 cm⁻¹ (B—H) (Figure S38), in good agreement with the values (Al—H—B 2089 cm⁻¹, B—H 2521 cm⁻¹, 2437 cm⁻¹) expected by calculation.

Scheme 2. Reaction of **4** with BH₃·SMe₂.

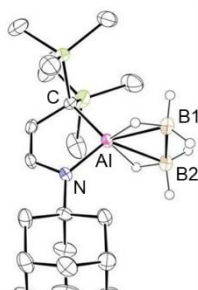
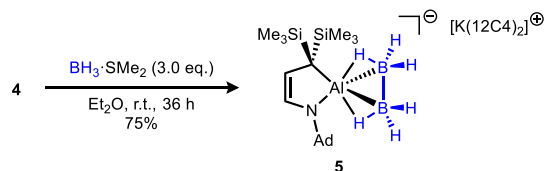


Figure 3. The solid-state structure of **5**. All hydrogen atoms except for those on the B and Al atoms and the cationic part [K(12C4)₂]⁺ are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

The peripheral bonding situation of the AlB₂ unit in **5** was further investigated computationally using the adaptive natural density partitioning (AdNDP) method.³⁸ The two-center two-electron (2c-2e) σ-bonding is confirmed at the four exocyclic B—H bonds (Figure S45). Besides, the delocalized three-center two-electron (3c-2e) bonding character is seen at the AlB₂ unit and two Al—H—B moieties (Figure 4), which was further confirmed by Natural Bond Orbital (NBO) analysis (Table S2). Wiberg bond index (WBI) values smaller than 1 for Al—B₁ (0.29), Al—B₂ (0.27) and B₁—B₂ (0.87) (Table S4) are in line with the 3c-2e σ-bonding within the AlB₂ unit, in which 1.92 electrons are shared amongst the Al, B₁ and B₂ atoms with occupancies of 4.7% (Al), 48.0% (B₁) and 47.3% (B₂). Natural population analysis (NPA) indicates a highly polarized nature at the Al(δ⁺)—B(δ⁻) moiety (Al; +1.88, B₁; -0.80, B₂; -0.77) (Table S3). The calculated nucleus-independent chemical shifts (NICS) values [NICS(0) = -27.21 ppm, NICS(1) = -7.76 ppm and -7.67 ppm] of the AlB₂ ring of **5** indicates the aromatic nature. In particular, relatively the more negative NICS(0) values, with respect to the NICS(1) values, suggests the pronounced σ-aromatic character, in line with the 3c-2e bonding of the AlB₂ unit. Significantly, it has been computationally revealed that [B₃H₈]⁻, a highly relevant molecule of **5**, is σ-aromatic species.³⁹ While almost all of the reported synthetic strategies for [B₃H₈]⁻ from BH₃ requires external alkaline metals,^{40,41} it can be deemed that **5** is formally formed by the donation of a pair of electrons on the Al center of **4** to the vacant orbital of boranes, concomitant with the back donation of the B—H bonding electrons from each borane to the Al center. Noteworthy to highlight that little formation of the triangle AlB₂ unit with 3c-2e bonding has been described in the literature.^{42,43}

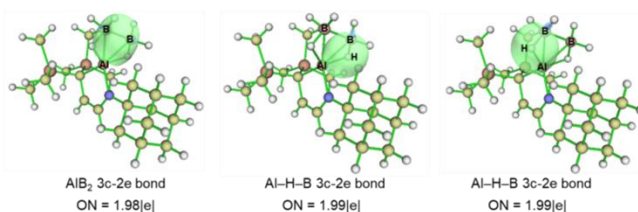


Figure 4. Bonding analysis of the anionic part of **5** using AdNDP method (isosurface values = 0.05).

Next, we investigated the reactivity of **4** towards silane, ammonia, and biphenylene (Figure 5A). Adding phenylsilane to a suspension of **4** in Et₂O at room temperature led to a rapid fading of the yellow color. After workup, **6** was obtained as a white solid in 66% isolated yield. The ¹H NMR spectrum of **6** shows two broad singlets at 3.745 ppm and 3.771 ppm, which correspond to the protons on the Si and Al atoms, respectively, confirming that the Si—H bond underwent the oxidative addition at the Al center of **4**. An X-ray diffraction analysis of **6** (Figure 5B) shows that the Al—Si distance [2.546(3) Å] is in line with the known Al(sp³)—Si(sp³) single bonds [2.446(1)—2.5400(8) Å], which is longer than that [2.487(1) Å] of NacNacAl(H)SiH₂Ph (NacNac = [DippNC(Me)CHC(Me)NDipp]).⁴⁴ This result to our knowledge shows the first example of the hydridic Si—H bond activation by the anionic aluminum species.

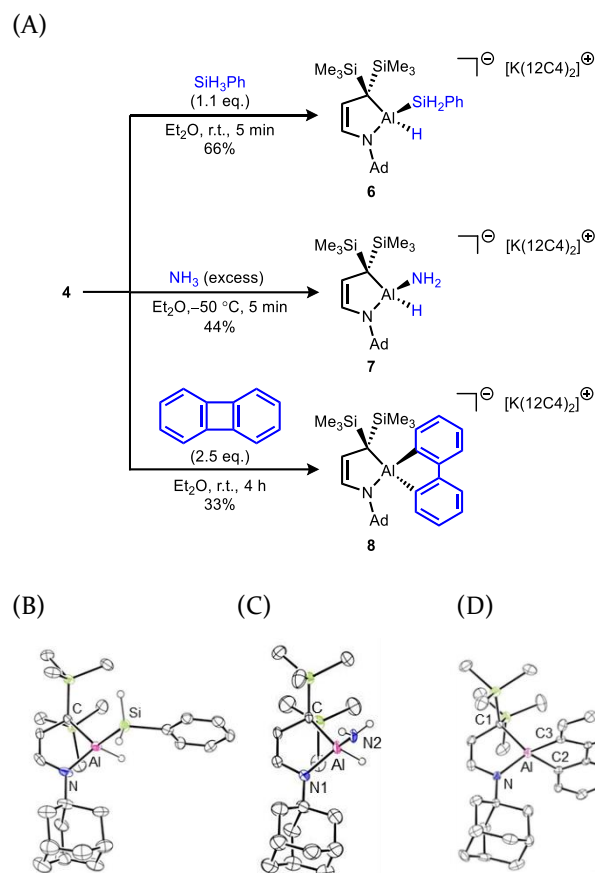


Figure 5. Reactions of **4** with phenylsilane, ammonia and biphenylene and crystallographic characterization of products. (A) Reactions of **4** with phenylsilane, ammonia and biphenylene. (B–D) The solid-state molecular structures of **6** (B), **7** (C) and **8** (D). All hydrogen atoms (except for those on Al and Si in **6**, and Al and N₂ in **7**) and the cationic part

[K(12C₄)₂]⁺ are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

When an Et₂O suspension of **4** was exposed to an excess of dry NH₃ and stirred at -50 °C for 5 minutes, the solution became colorless. After the removal of all volatiles, recrystallization from toluene afforded **7** as colorless crystals in 44% isolated yield. The solid-state structure of **7** (Figure 5C) confirms the formation of tetracoordinate Al center, indicative of the oxidative addition of NH₃ at the Al center of **4** during the reaction. The Al—N₂ contact [1.759(6) Å] of **7** is similar to the corresponding Al—N distance [1.7859(19) Å] found in NacNacAl(H)NHtBu.⁴⁴ In the ¹H NMR spectrum of **7**, no peaks corresponding to the protons on the Al and N atoms were detected, probably due to the quadrupolar coupling with ²⁷Al nuclei. Yet, the presence of the Al—H and the N—H bonds are decisively confirmed by the solid-state IR spectroscopy at 1727 cm⁻¹ (Al—H), and 1558 cm⁻¹ (N—H) (Figure S40), in line with the computationally estimated values (Al—H 1741 cm⁻¹, N—H 1556 cm⁻¹). It is salient to mention that the oxidative addition of ammonia with Group 13 molecules is limited to a digallene,⁴⁵ and our result represents the first oxidative addition at the low-valent Al center.

The oxidative addition with **4** is not limited to the polarized heteroatomic σ-bonds. Treatment of **4** with 2.5 equivalents of biphenylene in Et₂O at ambient condition resulted in an instant color change from yellow to dark brown. After filtration followed by recrystallization, product **8** was obtained as brown crystals in 33% isolated yield. An X-ray diffraction analysis of **8** (Figure 5D) confirms that a bridged C—C bond in biphenylene was cleaved during the reaction concomitant with the formation of two new Al—C bonds to yield the tetracoordinate Al center, manifesting the oxidative addition of a non-polar C—C bond.⁷

CONCLUSION

Fifteen years after the first isolation of cyclic (alkyl)(amino)carbenes (CAACs), a cyclic (alkyl)(amino)aluminum species **4**, an Al analogue of CAAC, has joined the class of bottleable anionic aluminum species. DFT calculations revealed that the dicoordinate Al center in **4** possesses both a lone pair of electrons and unoccupied p-orbital, being ambiphilic. We have shown that over the Al(I) center of **4**, borane undergoes a B—B coupling reaction rendering a heteroatomic AlB₂ ring **5**. Furthermore, likewise to CAACs, the Al(I) center of **4** readily cleaves not only polar Si—H, N—H bonds but also non-polar C—C bond under the very mild condition. This novel family of anionic aluminum species should be useful as a building block for developing various aluminum molecules which are inaccessible by the conventional means.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.XXXXXXX>.

Crystallographic data for compounds **2**, **3**, **4**, **5**, **6**, **7**, **8** (CIF) Synthesis procedures, spectral data, selected crystal parameters, and theoretical calculations (PDF)

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Notes

The authors declare no competing financial interest.

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SYNOPSIS TOC

