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A Monomeric Aluminum Imide (Iminoalane) with Al–N Triple-Bonding: Bonding Analysis and Dispersion Energy Stabilization

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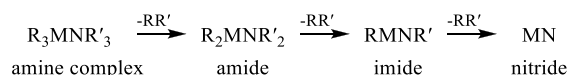


Supporting Information

ABSTRACT: The reaction of $\text{:AlAr}^{\text{iPr8}}$ ($\text{Ar}^{\text{iPr8}} = \text{C}_6\text{H}_2-2,6-(\text{C}_6\text{H}_2-2,4,6-\text{iPr}_3)_2-3,5-\text{iPr}_2$) with $\text{Ar}^{\text{Me6}}\text{N}_3$ ($\text{Ar}^{\text{Me6}} = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_2-2,4,6-\text{Me}_3)_2$) in hexanes at ambient temperature gave the aluminum imide $\text{Ar}^{\text{iPr8}}\text{AlNAr}^{\text{Me6}}$ (**1**). Its crystal structure displayed short Al–N distances of 1.625(4) and 1.628(3) Å with linear (C–Al–N–C = 180°) or almost linear (C–Al–N = 172.4(2)°; Al–N–C = 172.5(3)°) geometries. DFT calculations confirm linear geometry with an Al–N distance of 1.635 Å. According to energy decomposition analysis, the Al–N bond has three orbital components totaling $-1350 \text{ kJ mol}^{-1}$ and instantaneous interaction energy of -551 kJ mol^{-1} with respect to $\text{:AlAr}^{\text{iPr8}}$ and $\text{Ar}^{\text{Me6}}\text{N}_3$. Dispersion accounts for -89 kJ mol^{-1} , which is similar in strength to one Al–N π -interaction. The electronic spectrum has an intense transition at 290 nm which tails into the visible region. In the IR spectrum, the Al–N stretching band is calculated to appear at ca. 1100 cm^{-1} . In contrast, reaction of $\text{:AlAr}^{\text{iPr8}}$ with 1-AdN₃ or Me₃SiN₃ gave transient imides that immediately reacted with a second equivalent of the azide to give $\text{Ar}^{\text{iPr8}}\text{Al}[(\text{NAd})_2\text{N}_2]$ (**2**) or $\text{Ar}^{\text{iPr8}}\text{Al}(\text{N}_3)\{\text{N}(\text{SiMe}_3)_2\}$ (**3**).

The chemistry of compounds with group 13 element–nitrogen bonding has been extensively studied.^{1–9} Current interest is driven by their applications as precursors for group III–V materials,¹⁰ H₂ storage media,^{11–13} and an interest in M–N (M = Al–Tl) multiple bonding. Early work on the group 13 amine complexes showed they could be condensed at elevated temperature with release of RR' (R,R' = organic group or hydrogen): a common route to amide, imide, and nitride compounds¹⁴ (Scheme 1).

Scheme 1. Stepwise Condensation of Group 13 Amine Complexes to Nitrides



The group 13 metal imides (also called N-iminometallanes) of formula $[\text{RMNR}']_n$ (R = alkyl, aryl, hydrogen, halide; R' = alkyl, aryl, silyl, hydrogen; M = Al–In; n = 4–8) were first studied in detail by Cesari and co-workers in the 1960s and '70s, and several examples featuring cage structures with alternating metal and nitrogen vertices were structurally characterized.^{15–19} Roesky and co-workers characterized the quasi-isomeric tetrameric amido–Al(I) compound $[\text{AlN}(\text{Dipp})(\text{SiMe}_3)]_4$ (Dipp = 2,6-*i*Pr₂–C₆H₃) with a tetrahedral Al₄ core and terminal amide groups.²⁰ The lower imido aggregates (n = 1–3) remain scarce but are especially interesting since M–N multiple bonding becomes possible. Thus, the unique trimer $[\text{Al}(\text{Me})\text{N}(\text{Dipp})]_3$,²¹ which is an Al analogue of borazine (i.e., an “alumazine”), features relatively short (ca. 1.78 Å) Al–N bonds. The planar Al₃N₃ ring has 6- π electrons but has little aromatic character as shown by its reaction chemistry.^{22,23} Several dimeric, $[\text{RAINR}']_2$ compounds with Al₂N₂ cores and short Al–N distances in the

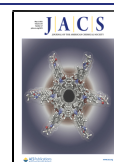
range 1.796–1.842 Å, which is slightly longer than that seen in the alumazine derivative, have also been reported.^{24–29}

Monomeric RAINR' compounds remain unknown, which is probably a result of high association energies (cf. dimerization of HAlNH is exothermic by ca. 580 kJ mol^{–1}).³⁰ Their synthesis via hydrocarbon or dihydrogen elimination usually proceeds at elevated temperatures that often results in C–H activation of the ligands.³¹ However, an alternative synthesis by the reaction of organoazides with M(I) species at low temperatures avoids C–H activation. For example, Roesky and co-workers reported that the reaction of :AlCp^* (Cp* = $\eta^5\text{-C}_5\text{Me}_5$), formed by dissociation of $(\text{AlCp}^*)_4$ at elevated temperature, with R₃SiN₃ (R = *i*Pr, Ph, *t*Bu), gave the imido dimers $\{\text{Cp}^*\text{Al}(\mu\text{-NSiR}_3)\}_2$.²⁶ Using the larger, chelated Al(I) β -diketiminate $\text{:Al}^{\text{Dipp}}\text{NacNac}$ ($\text{DippNacNac} = \text{HC}\{(\text{CMe})(\text{NDipp})\}_2$) gave the transient imides $^{\text{Dipp}}\text{NacNacAl} = \text{NR}$ which reacted with a second equivalent of the azide to give cyclic AlN₄ products $^{\text{Dipp}}\text{NacNacAl}[(\text{NR})_2\text{N}_2]$.^{32,33} Attempts to stabilize the imide using more sterically demanding *m*-terphenyl azides failed to give an isolable aluminum imide, although this route did yield a corresponding Ga imide.³⁴ The Al imide underwent C–H activation of a methyl group on a flanking ring of the $^{\text{Dipp}}\text{NacNac}$ ligand or C–C activation of the aryl ring of the nitrogen terphenyl ligand.³⁵

Nonetheless, monomeric aluminum imides were obtained by coordinative blocking of the Al atoms. Cui and co-workers

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showed that addition of an NHC (N-heterocyclic carbene) to $:\text{Al}[\text{HC}\{(\text{C}^t\text{Bu})(\text{NDipp})\}_2]$ resulted in insertion of the Al atom into the N–C bond of the β -diketiminate ligand.³⁶ This gave the four-coordinate terminal Al imide **I** (Figure 1) with a

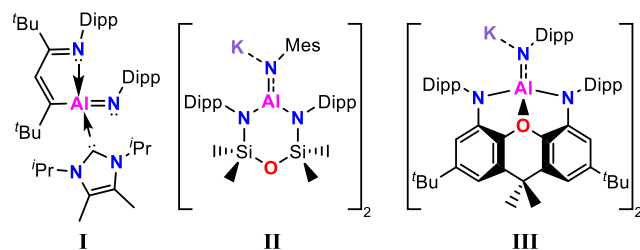


Figure 1. Structurally characterized terminal aluminum imides. Mes = 2,4,6-Me₃C₆H₂; Dipp = 2,6-ⁱPr₂C₆H₃.^{36–38}

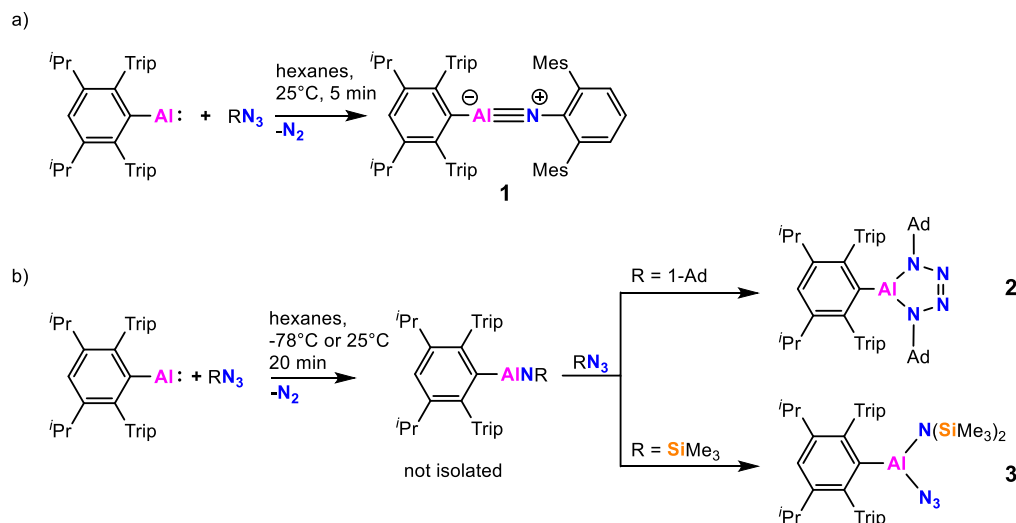
short (1.705(2) Å) Al–N bond. Recently, the groups of Coles and Aldridge separately reported that the reaction of anionic Al(I) aluminyls with organoazides gave terminal aluminum imides **II** and **III** (Figure 1) with Al–N distances of 1.7251(11) and 1.723(2) Å, supported by multidentate NON ligands that exist as dimers with bridging K⁺ cations.^{37,38} It was shown that the Al=N bonds reacted readily with small molecules such as CO and CO₂.^{36–38}

No compounds of formula RAINR' in which Al and N are two-coordinate have been isolated and characterized. The reaction of laser-ablated Al atoms with NH₃ gas gave the planar trans-bent parent compound HAlNH as a minor product, identified by IR spectroscopy in a solid argon matrix.³⁹ *Ab initio* computations by Davy and Jaffrey found HAlNH to be “quasi-linear” with only a 0.2 kcal mol^{−1} barrier between the linear and bent geometries and a short Al–N bond distance of 1.63 Å, which may be interpreted on the basis of Al–N triple bonding. Computations for HAlNH and MeAlNMe showed linear geometries with short (ca. 1.63–1.65 Å) Al–N distances,^{11,30,40,41} and NBO analysis of MeAlNMe by Gilbert indicated that it had an Al–N triple bond composed of one σ - and 2 π -bonds.⁴²

Previously, our group described the synthesis of gallium and indium imides with two-coordination at both the group 13 metal and N atoms by reaction of an *m*-terphenyl azide with the dimetallenes Ar^{*i*Pr₄}MMAr^{*i*Pr₄} (M = Ga, In; Ar^{*i*Pr₄} = C₆H₃-2,6-(C₆H₃-2,6-ⁱPr₂)₂), which exist in equilibrium with :MAr^{*i*Pr₄} monomers in solution.⁴³ This suggested that a similar Al species could be isolable, but the lack of an analogous Al(I) precursor (i.e., ArAlAlAr or :AlAr) precluded its synthesis. Recently, we reported the monomeric alanedyl :AlAr^{*i*Pr₈} (Ar^{*i*Pr₈} = C₆H-2,6-(C₆H₂-2,4,6-ⁱPr₃)₂-3,5-ⁱPr₂) with a one-coordinate Al atom.⁴⁴ We show here that its reaction with Ar^{*i*Pr₈}Me₆N₃ (Ar^{*i*Pr₈}Me₆ = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂) gives the aluminum imide Ar^{*i*Pr₈}AlNAr^{*i*Pr₈}Me₆ (**1**) having two-coordinate Al and N atoms with a notably short Al–N bond length of 1.625(4) or 1.628(3) Å consistent with Al–N triple bonding. Additionally, the reaction of :AlAr^{*i*Pr₈} with the less sterically demanding azides 1-AdN₃ (1-Ad = 1-adamantyl) or Me₃SiN₃ gives transient imides which react immediately with a second equivalent of azide to give products featuring ring closure or silyl migration.

Compound **1** was prepared by reaction of :AlAr^{*i*Pr₈} with Ar^{*i*Pr₈}Me₆N₃ (Scheme 2a) in hexanes at ambient temperature, giving immediate vigorous evolution of N₂ and formation of a red solution. After ca. 5 min, the solids had dissolved and gas evolution had ceased. Storage at ca. −30 °C for 3 days gave orange plates of **1** in ca. 91% yield. The crystal structure of **1** (Figure 2) contains two crystallographically independent molecules. One of these lies along the 2-fold proper rotation axis of the I2/a space group and contains a strictly linear C–Al–N–C core. The second molecule maintains a planar C–Al–N–C array but deviates slightly from linearity at the Al (C–Al–N = 172.5(3)°) and N (Al–N–C = 171.4(2)°) atoms. The Al–N bond lengths of 1.625(4) and 1.628(3) Å are the shortest reported to date and agree with those calculated for HAlNH and MeAlNMe.^{11,30,40,41} The linear structure of **1** is in marked contrast to the heavier congeners Ar^{*i*Pr₄}M=NAr' (M = Ga, In; Ar' = C₆H₃-2,6-(C₆H₂-2,6-Me₂-4-ⁱBu)₂) which are strongly bent at the M and N atoms (Ga–N = 1.701(2) Å; C–Ga–N = 148.2(2)°; Ga–N–C =

Scheme 2. Synthesis of Compounds **1**, **2**, and **3**^a



^a(a) Synthesis of compound **1**; (b) synthesis of compounds **2** and **3**; Trip = 2,4,6-ⁱPr₃C₆H₂; Mes = 2,4,6-Me₃C₆H₂; 1-Ad = 1-adamantyl.

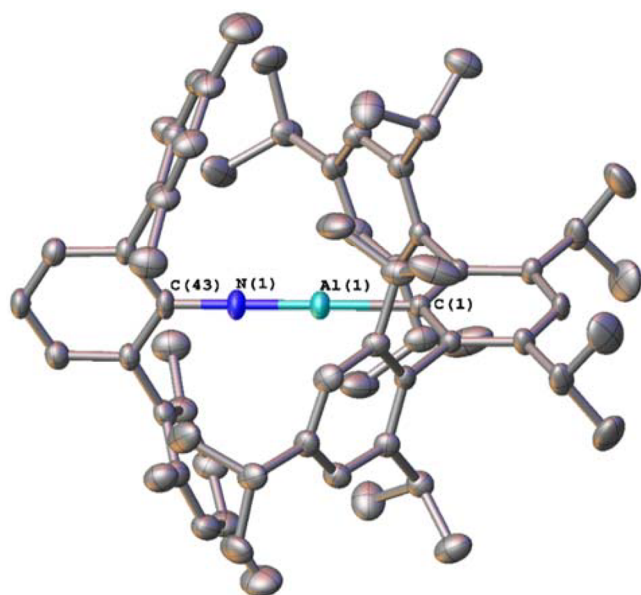


Figure 2. Thermal ellipsoid plot (50%) of one of the crystallographically independent molecules of $\text{Ar}^{\text{iPr}_8}\text{AlNAr}^{\text{Me}_6}$ (**1**). H atoms and *n*-hexane solvent not shown. Selected bond lengths (Å) and angles (deg) {values in braces correspond to the other crystallographically independent molecule of **1**}: Al(1)–N(1): 1.625(4) {1.628(3)}, Al(1)–C(1): 1.935(4) {1.931(3)}, N(1)–C(43): 1.378(5) {1.366(4)}, C(1)–Al(1)–N(1): 180 {172.4 (2)}, Al(1)–N(1)–C(43): 180 {172.5(3)}, C(1)–Al(1)–N(1)–C(43): 0 {167.0(2)}.

141.7(3)°; In–N = 1.928(2) Å; C–In–N = 142.2(1)°; In–N–C = 134.9(2)°.⁴³

The UV–vis electronic spectrum of **1** has a single absorbance at 290 nm which tails into the visible region, producing an orange color. Time-dependent DFT calculations on **1** suggest that the low-intensity absorption tail is mostly due to the HOMO → LUMO+1 transition at 387 nm, whereas the main feature is due to two high-intensity transitions at 287 and 316 nm. The Al–N stretching band of **1** was calculated to be ca. 1100 cm^{-1} ; however, no distinct spectral features are apparent for assignment of the band.

Imide **1** slowly decomposes in solution over ca. 12 h at ambient temperature as indicated by fading of the orange color to colorless. ¹H NMR spectroscopy (Figure S3, Supporting Information) is consistent with decomposition via C–H activation of one of the methyl groups on the flanking rings that is analogous to that in $\text{Dipp}^{\text{Nac}}\text{AlNAr}^{\text{iPr}_4}$.³⁵ A singlet at δ 3.50 ppm is assigned to the resulting amine proton, while the Al–CH₂ group gives a multiplet at δ 0.05–0.13 ppm. Solid **1** is thermally stable at ambient temperature for at least several days but rapidly decomposes to a white solid above 83 °C.

Dispersion corrected DFT calculations for **1** at the PBE1PBE–GD3BJ/def2-TZVP level yield an optimized structure with a linear C–Al–N–C core and an Al–N bond length of 1.635 Å in excellent agreement with the crystal structure. The Kohn–Sham orbitals (Figure S15, Supporting Information) and those of the model system Ph–NAl–Ph (Figure 3) show three major components to the Al–N bond, one of σ -type and two nondegenerate of π -type. NBO analysis yielded three two-center Al–N bonding orbitals with occupations close to 2 electrons and ca. 90% localization on the N atom.⁴⁵ Consequently, the calculated Wiberg bond index for the Al–N bond is only 0.89. More detailed bonding

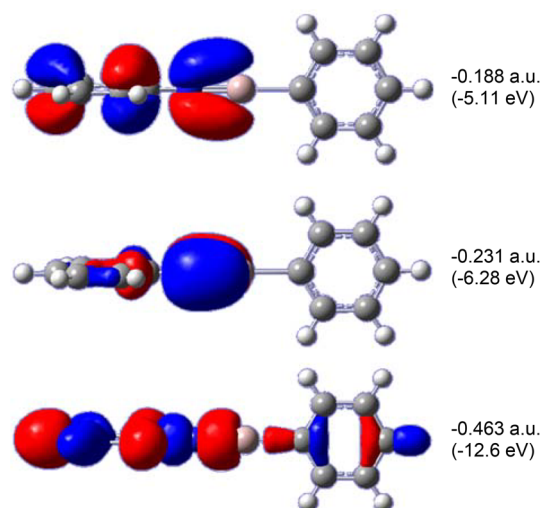


Figure 3. Occupied PBE1PBE-GD3BJ/def2-TZVP orbitals of Ph–NAl–Ph localized on the AlN bond (NPh moiety on the left, AlPh moiety on the right; isosurface value ± 0.05 au).

analyses using the ETS–NOCV method and fragments $:\text{AlAr}^{\text{iPr}_8}$ and $\text{Ar}^{\text{Me}_6}\text{N}:$ at the geometries they adopt in **1** also revealed three primary contributions to the Al–N bond. The major component (-1120 kJ mol^{-1} , ca. 83% of the total orbital interaction of -1350 kJ mol^{-1}) involves charge flow from Al to N, whereas the two minor components (-100 and -102 kJ mol^{-1} , each ca. 8% of the total orbital interaction) describe backdonation from N to Al. Taken as a whole, the Al–N bond in **1** has the formal characteristics of a triple bond with donation from Al to N greatly exceeding backdonation from N to Al. The calculated instantaneous interaction energy between $:\text{AlAr}^{\text{iPr}_8}$ and $\text{Ar}^{\text{Me}_6}\text{N}:$ is -551 kJ mol^{-1} (cf. Gibbs interaction energy of -429 kJ mol^{-1} taking into account fragment relaxation) with significant stabilization, -89 kJ mol^{-1} , from dispersion interactions. The possibility of charge-shift character in the Al–N bond has not yet been supported by computational data.^{46–48}

Addition of AdN_3 or Me_3SiN_3 to $:\text{AlAr}^{\text{iPr}_8}$ gives the transient imides $\text{Ar}^{\text{iPr}_8}\text{AlNR}$ ($\text{R} = 1\text{-Ad}, \text{SiMe}_3$), which immediately react with a second equivalent of the azide (Scheme 2b). Roesky, Aldridge, and co-workers have shown that organic azides with small substituents such as $-\text{SiMe}_3$, $-\text{SiPh}_3$, and 1-Ad react in a 2:1 ratio with $:\text{Al}[\text{Dipp}^{\text{Nac}}\text{Nac}]\text{Al}$ or an aluminyll anion to give planar AlN_4 heterocycles.^{32,33,38} Reaction with the first equivalent of azide results in N_2 loss and a highly reactive species with a terminal $\text{Al}=\text{NR}$ moiety, which undergoes ring closure with a second equivalent of the azide. The reaction of $:\text{AlAr}^{\text{iPr}_8}$ with 2 equiv of 1-AdN_3 gave **2** (Figure 4, left) as colorless crystals. The Al–N bonds are 1.8126(9) and 1.8220(11) Å which are in the typical range for these AlN_4 compounds.^{32,33,38} However, steric congestion between the terphenyl flanking rings and the adamantyl groups result in a deformation of the central ring of the terphenyl ligand, illustrated by torsion angles of $\text{C}(1)\text{--}\text{C}(2)\text{--}\text{C}(3)\text{--}\text{C}(4) = 20.43(14)^\circ$ and $\text{C}(1)\text{--}\text{C}(6)\text{--}\text{C}(5)\text{--}\text{C}(4) = 20.06(14)^\circ$. The ¹H and ¹³C{¹H} NMR spectra of **2** also display broad signals indicating restricted movement of the 1-adamantyl and terphenyl flanking groups. The reaction of $:\text{AlAr}^{\text{iPr}_8}$ with 2 equiv of Me_3SiN_3 gives the amido- azido-alane **3** (Figure 4, right) as colorless crystals in which silyl migration from the second equivalent of azide to the nitrogen atom of the

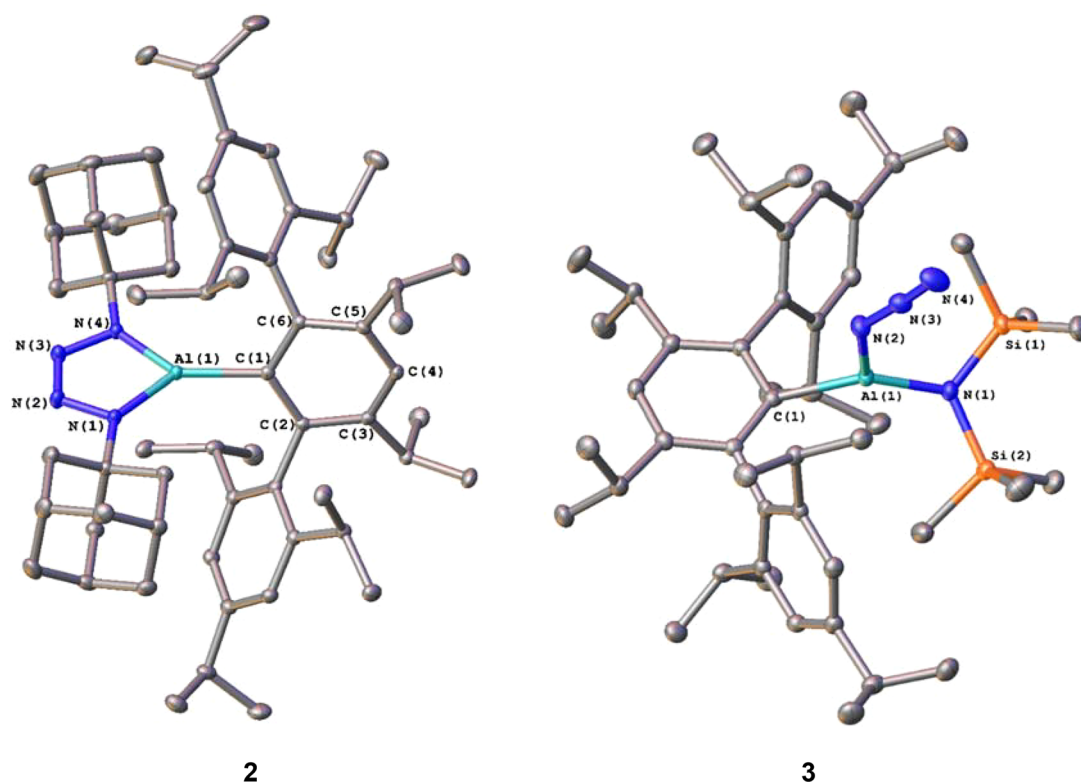


Figure 4. Thermal ellipsoid plots (50%) of $\text{Ar}^{i\text{Pr}8}\text{Al}[(\text{NAd})_2\text{N}_2]$ (**2**, left) and $\text{Ar}^{i\text{Pr}8}\text{Al}(\text{N}_3)\{\text{N}(\text{SiMe}_3)_2\}$ (**3**, right). Hydrogen atoms and toluene are not shown. Selected bond lengths (Å) and angles (deg): **2**: Al(1)–C(1): 1.9710(12), Al(1)–N(1): 1.8126(9), Al(1)–N(4): 1.8220(11), N(1)–N(2): 1.3899(15), N(2)–N(3): 1.2643(16), N(3)–N(4): 1.3853(12), C(1)–Al(1)–N(1): 135.49(4), C(1)–Al(1)–N(4): 138.11(4), N(1)–Al(1)–N(4): 86.39(4). **3**: Al(1)–C(1): 1.9775(14), Al(1)–N(1): 1.8088(12), N(1)–Si(1): 1.7518(12), N(1)–Si(2): 1.7546(12), Al(1)–N(2): 1.8210(13), N(2)–N(3): 1.2132(18), N(3)–N(4): 1.1407(19), C(1)–Al(1)–N(1): 143.91(6), C(1)–Al(1)–N(2): 102.62(6), N(1)–Al(1)–N(2): 113.44(6), N(2)–N(3)–N(4): 175.71(16).

transient imide has occurred. Such migrations have been observed in a number of reactions of Me_3SiN_3 with low valent main group compounds.^{49–54}

Computationally, the reaction of $:\text{AlAr}^{i\text{Pr}8}$ with Me_3SiN_3 yielded $\text{Ar}^{i\text{Pr}8}\text{AlN}(\text{N}_2)\text{SiMe}_3$ which readily releases N_2 with a free energy barrier of 46 kJ mol^{-1} to afford $\text{Ar}^{i\text{Pr}8}\text{AlNSiMe}_3$ at -306 kJ mol^{-1} (Figure S17, Supporting Information). Addition of a second equivalent of Me_3SiN_3 gave two products, *cis*- and *trans*- $\text{Ar}^{i\text{Pr}8}\text{Al}[\text{N}(\text{SiMe}_3)\text{N}_2]\text{NSiMe}_3$, depending on the relative orientation of $\text{Ar}^{i\text{Pr}8}\text{AlNSiMe}_3$ and Me_3SiN_3 . The *cis*-isomer has the two SiMe_3 groups on the same side of the dative Al–N bond and readily forms **3** via silyl migration, whereas the *trans*-isomer can form the SiMe_3 analogue of **2** via ring closure. Of the two possible products, **3** is kinetically preferred and thermodynamically favored by 113 kJ mol^{-1} . The potential energy surface is expected to be largely similar for the $:\text{AlAr}^{i\text{Pr}8}$ – 1-AdN_3 pair with the exception that substituent migration is energetically unfeasible and **2** is formed rapidly via ring closure.

In summary, the alanediyli $:\text{AlAr}^{i\text{Pr}8}$ reacts with the *m*-terphenyl azide $\text{Ar}^{\text{Me}6}\text{N}_3$ to yield the monomer $\text{Ar}^{i\text{Pr}8}\text{AlNAr}^{\text{Me}6}$ in which the Al and N atoms have linear, or almost linear, coordination and short Al–N distances of 1.625(4) or 1.628(3) Å, consistent with Al–N triple bonding. Calculations show that the Al–N bond is composed of strong σ -donation from the $:\text{AlAr}^{i\text{Pr}8}$ moiety to the $:\text{NAr}^{\text{Me}6}$ nitrene and weak π -donation from the latter to $:\text{AlAr}^{i\text{Pr}8}$. The calculations also indicate a key contribution from dispersion energies that, together with steric effects from the terphenyl substituents,

provide sufficient stabilization for the room-temperature characterization of **1**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c02463>.

Experimental details for compounds 1–3, NMR, electronic, and IR spectral data, and computational details (PDF)

(XYZ)

Accession Codes

CCDC 2065246–2065248 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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