Communication

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

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ABSTRACT: The reaction of :AlAr^{iPr8} (Ar^{iPr8} = C$_6$H-2,6-(C$_6$H$_2$-2,4,6-^{i}Pr$_3$)$_2$-3,5-^{i}Pr$_2$) with Ar^{Me6}N$_3$ (Ar^{Me6} = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-Me$_3$)$_2$) in hexanes at ambient temperature gave the aluminum imide Ar^{iPr8}AlNAr^{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 kJ mol^{-1} and instantaneous interaction energy of −551 kJ mol^{-1} with respect to :AlAr^{iPr8} and Ar^{Me6}N̈:. 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 :AlAr^{iPr8} with 1-AdN$_3$ or Me$_3$SiN$_3$ gave transient imides that immediately reacted with a second equivalent of the azide to give Ar^{iPr8}Al[(NAd)$_2$N$_2$] (**2**) or Ar^{iPr8}Al(N$_3$){N(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] H$_2$ 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 compounds[14] (Scheme 1).

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

$$R_3MNR'_3 \xrightarrow{-RR'} R_2MNR'_2 \xrightarrow{-RR'} RMNR' \xrightarrow{-RR'} MN$$

amine complex   amide   imide   nitride
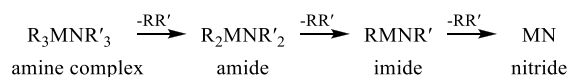
The group 13 metal imides (also called N-iminometallanes) of formula [RMNR′]$_n$ (R = alkyl, aryl, hydrogen, halide; R′ = alkyl, aryl, silyl, hydrogen; M = Al−In; n = 4−8) were first studied in detail by Cesari and co-workers in the 1960s and '70s, and several examples featuring cage structures with alternating metal and nitrogen vertices were structurally characterized.[15−19] Roesky and co-workers characterized the quasi-isomeric tetrameric amido-Al(I) compound [AlN-(Dipp)(SiMe$_3$)]$_4$ (Dipp = 2,6-^{i}Pr$_2$−C$_6$H$_3$) with a tetrahedral Al$_4$ 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 [Al(Me)N(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 Al$_3$N$_3$ ring has 6-π electrons but has little aromatic character as shown by its reaction chemistry.[22,23] Several dimeric, [RAlNR′]$_2$ compounds with Al$_2$N$_2$ 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 RAlNR′ 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* = η^5-C$_5$Me$_5$), formed by dissociation of (AlCp*)$_4$ at elevated temperature, with R$_3$SiN$_3$ (R = ^{i}Pr, Ph, ^{t}Bu), gave the imido dimers {Cp*Al(μ-NSiR$_3$)}$_2$.[26] Using the larger, chelated Al(I) β-diketiminate :Al^{Dipp}NacNac (^{Dipp}NacNac = HC{(CMe)-(NDipp)}$_2$) gave the transient imides ^{Dipp}NacNacAl = NR which reacted with a second equivalent of the azide to give cyclic AlN$_4$ products ^{Dipp}NacNacAl[(NR)$_2$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 ^{Dipp}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
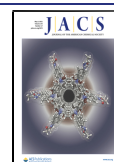
showed that addition of an NHC (N-heterocyclic carbene) to :Al[HC{(C^{t}Bu)(NDipp)}$_2$] resulted in insertion of the Al atom into the N−C bond of the β-diketiminate ligand.[36] This gave the four-coordinate terminal Al imide **I** (Figure 1) with a
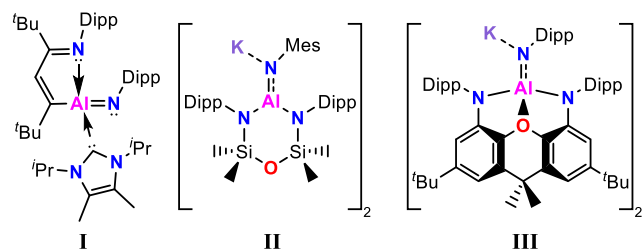

Figure 1. Structurally characterized terminal aluminum imides. Mes = 2,4,6-Me$_3$C$_6$H$_2$; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$.[36−38]

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 CO$_2$.[36−38]

No compounds of formula RAlNR′ in which Al and N are two-coordinate have been isolated and characterized. The reaction of laser-ablated Al atoms with NH$_3$ 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^{iPr4}MMAr^{iPr4} (M = Ga, In; Ar^{iPr4} = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$), which exist in equilibrium with :MAr^{iPr4} 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 alanediyl :AlAr^{iPr8} (Ar^{iPr8} = C$_6$H-2,6-(C$_6$H$_2$-2,4,6-^{i}Pr$_3$)$_2$-3,5-^{i}Pr$_2$) with a one-coordinate Al atom.[44] We show here that its reaction with Ar^{Me6}N$_3$ (Ar^{Me6} = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-Me$_3$)$_2$) gives the aluminum imide Ar^{iPr8}AlNAr^{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^{iPr8} with the less sterically demanding azides 1-AdN$_3$ (1-Ad = 1-adamantyl) or Me$_3$SiN$_3$ 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^{iPr8} with Ar^{Me6}N$_3$ (Scheme 2a) in hexanes at ambient temperature, giving immediate vigorous evolution of N$_2$ 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^{iPr4}M=NAr′ (M = Ga, In; Ar′ = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,6-Me$_2$-4-^{t}Bu)$_2$) 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
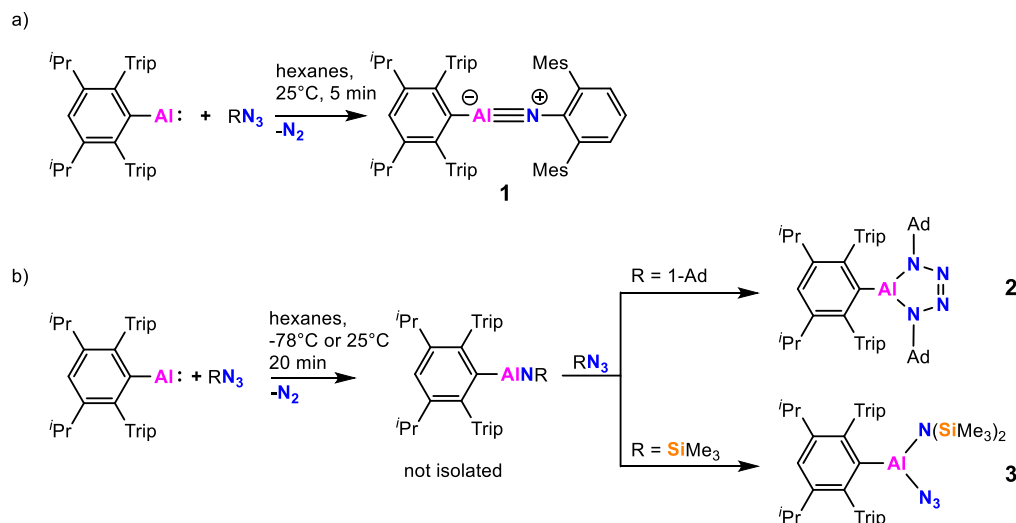
^{a}(a) Synthesis of compound **1**; (b) synthesis of compounds **2** and **3**; Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$; Mes = 2,4,6-Me$_3$C$_6$H$_2$; 1-Ad = 1-adamantyl.

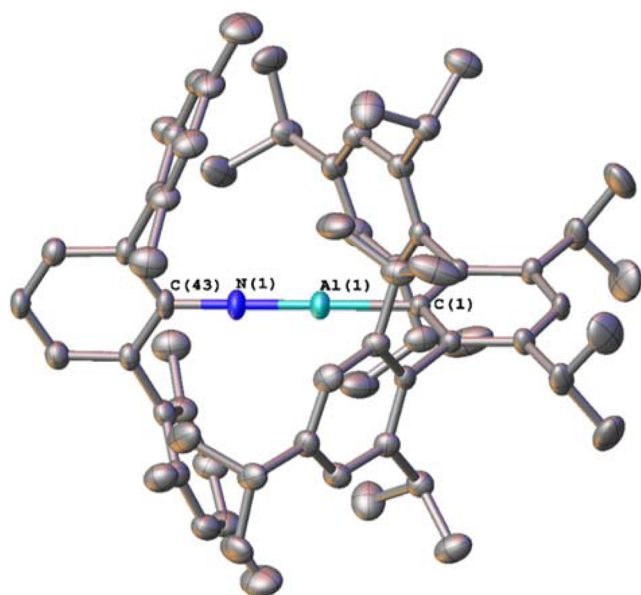**Figure 2.** Thermal ellipsoid plot (50%) of one of the crystallographically independent molecules of Ar^{iPr8}AlNAr^{Me6} (**1**). H atoms and *n*-hexane solvent not shown. Selected bond lengths (Å) and angles (deg) {values in braces correspond to the other crystallographically independent molecule 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. ^{1}H 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 ^{Dipp}NacNacAl=NAr^{iPr4}.[35] A singlet at δ 3.50 ppm is assigned to the resulting amine proton, while the Al-CH$_2$ 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
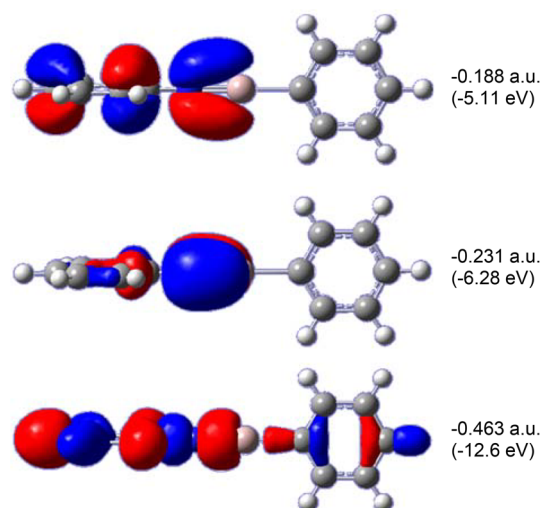

Figure 3. Occupied PBE1PBE-GD3BJ/def2-TZVP orbitals of Ph-NAl-Ph localized on the AlN bond (NPh moiety on the left, AlPh moiety on the right; isosurface value ±0.05 au).

analyses using the ETS-NOCV method and fragments :AlAr^{iPr8} and Ar^{Me6}N̈: 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 :AlAr^{iPr8} and Ar^{Me6}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$_3$SiN$_3$ to :AlAr^{iPr8} gives the transient imides Ar^{iPr8}AlNR (R = 1-Ad, 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 -SiMe$_3$, -SiPh$_3$, and 1-Ad react in a 2:1 ratio with :Al[^{Dipp}NacNac] or an aluminyl 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 Al=NR moiety, which undergoes ring closure with a second equivalent of the azide. The reaction of :AlAr^{iPr8} 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 C(1)−C(2)−C(3)−C(4) = 20.43(14)° and C(1)−C(6)−C(5)−C(4) = 20.06(14)°. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** also display broad signals indicating restricted movement of the 1-adamantyl and terphenyl flanking groups. The reaction of :AlAr^{iPr8} with 2 equiv of Me$_3$SiN$_3$ 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
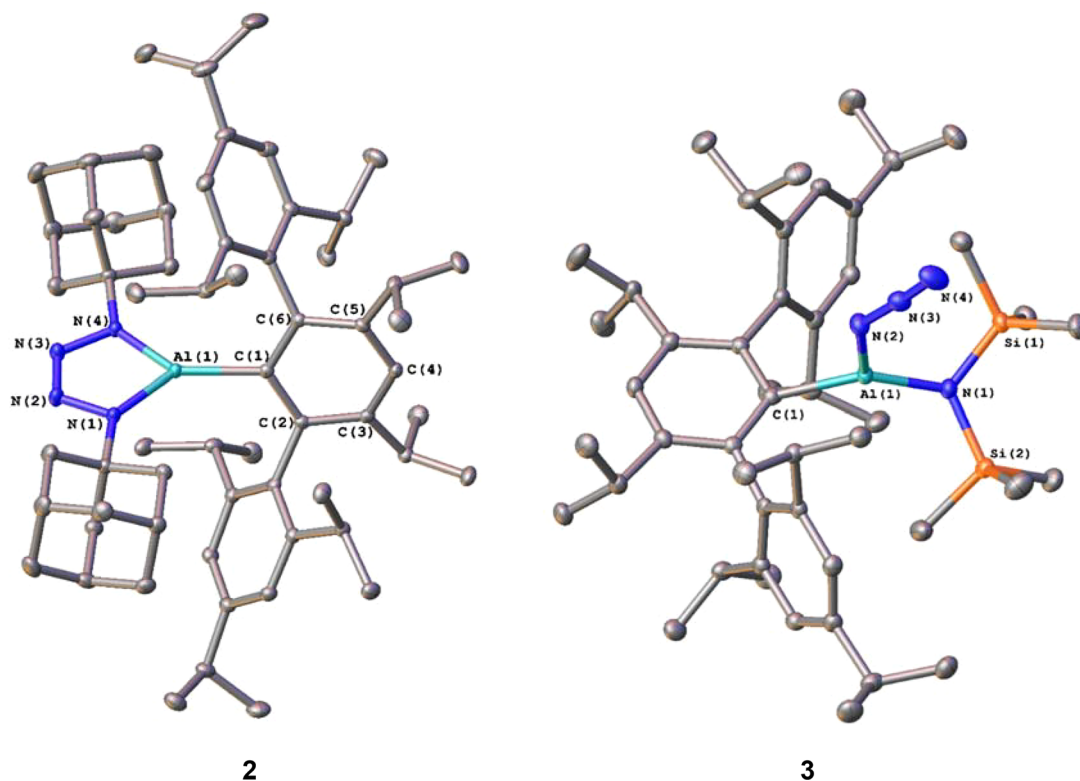
Figure 4. Thermal ellipsoid plots (50%) of $Ar^{iPr8}Al[(NAd)_2N_2]$ (**2**, left) and $Ar^{iPr8}Al(N_3)\{N(SiMe_3)_2\}$ (**3**, right). Hydrogen atoms and toluene are not shown. Selected bond lengths (Å) and angles (deg): **2**: Al(1)−C(1): 1.9710(12), Al(1)−N(1): 1.8126(9), Al(1)−N(4): 1.8220(11), 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 $:AlAr^{iPr8}$ with Me_3SiN_3 yielded $Ar^{iPr8}AlN(N_2)SiMe_3$ which readily releases N_2 with a free energy barrier of 46 kJ mol^{-1} to afford $Ar^{iPr8}AlNSiMe_3$ at −306 kJ mol^{-1} (Figure S17, Supporting Information). Addition of a second equivalent of Me_3SiN_3 gave two products, *cis*- and *trans*-$Ar^{iPr8}Al[N(SiMe_3)N_2]NSiMe_3$, depending on the relative orientation of $Ar^{iPr8}AlNSiMe_3$ 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 $:AlAr^{iPr8}$ 1-AdN$_3$ pair with the exception that substituent migration is energetically unfeasible and **2** is formed rapidly via ring closure.

In summary, the alanediyl $:AlAr^{iPr8}$ reacts with the *m*-terphenyl azide $Ar^{Me6}N_3$ to yield the monomer $Ar^{iPr8}AlNAr^{Me6}$ 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 $:AlAr^{iPr8}$ moiety to the $:NAr^{Me6}$ nitrene and weak π-donation from the latter to $:AlAr^{iPr8}$. 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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