

This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.

Author(s): Queen, Joshua D.; Irvankoski, Sini; Fettinger, James C.; Tuononen, Heikki M.; Power, Philip P.

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

Year: 2021

Version: Published version

Copyright: © 2021 American Chemical Society

Rights: CC BY-NC-ND 4.0

Rights url: <https://creativecommons.org/licenses/by-nc-nd/4.0/>

Please cite the original version:

Queen, J. D., Irvankoski, S., Fettinger, J. C., Tuononen, H. M., & Power, P. P. (2021). A Monomeric Aluminum Imide (Iminoalane) with Al–N Triple-Bonding : Bonding Analysis and Dispersion Energy Stabilization. *Journal of the American Chemical Society*, 143(17), 6351-6356. <https://doi.org/10.1021/jacs.1c02463>

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

Joshua D. Queen, Sini Irvankoski, James C. Fettinger, Heikki M. Tuononen,* and Philip P. Power*



Cite This: *J. Am. Chem. Soc.* 2021, 143, 6351–6356



Read Online

ACCESS |



Metrics & More



Article Recommendations

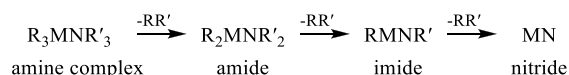


Supporting Information

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 $\text{Ar}^{\text{iPr8}}\text{AlNR}^{\text{Me6}}$ (**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

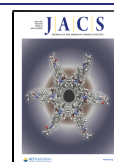
range 1.796–1.842 Å, which is slightly longer than that seen in the alumazine derivative, have also been reported.^{24–29}

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 $:\text{AlCp}^*$ (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 -diketiminato $:\text{Al}^{\text{Dipp}}\text{NacNac}$ ($\text{DippNacNac} = \text{HC}\{\text{CMe}(\text{NDipp})\}_2$) 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

Received: March 4, 2021

Published: April 21, 2021



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

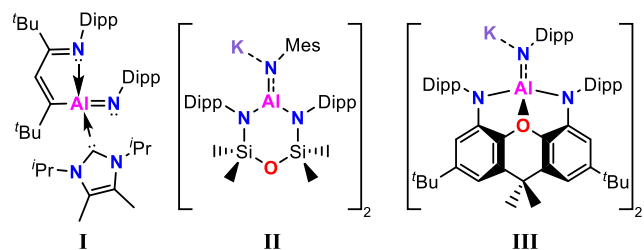


Figure 1. Structurally characterized terminal aluminum imides. Mes = 2,4,6-Me₃C₆H₂; Dipp = 2,6-ⁱPr₂C₆H₃.^{36–38}

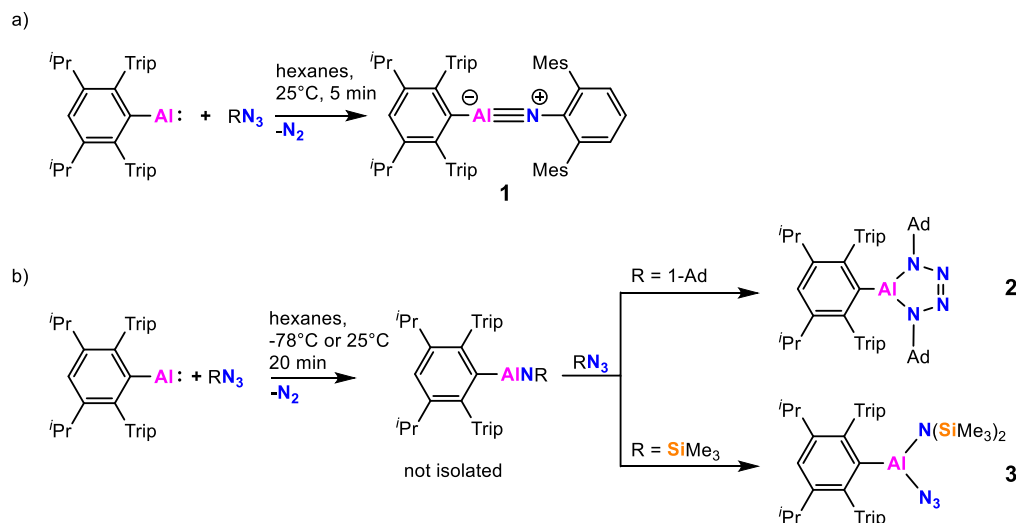
short (1.705(2) Å) Al–N bond. Recently, the groups of Coles and Aldridge separately reported that the reaction of anionic Al(I) aluminyls with organoazides gave terminal aluminum imides **II** and **III** (Figure 1) with Al–N distances of 1.7251(11) and 1.723(2) Å, supported by multidentate NON ligands 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-(C₆H₂-2,6-^{*i*}Pr₂)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 alanediyli :AlAr^{*i*Pr⁸} (Ar^{*i*Pr⁸} = C₆H-2,6-(C₆H₂-2,4,6-^{*i*}Pr₃)₂-3,5-^{*i*}Pr₂) with a one-coordinate Al atom.⁴⁴ We show here that its reaction with Ar^{*i*Pr⁴}Me₆N₃ (Ar^{*i*Pr⁴} = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂) gives the aluminum imide Ar^{*i*Pr⁸}AlNAr^{*i*Pr⁴} (**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*Pr⁴}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-^{*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*}Pr₃C₆H₂; Mes = 2,4,6-Me₃C₆H₂; 1-Ad = 1-adamantyl.

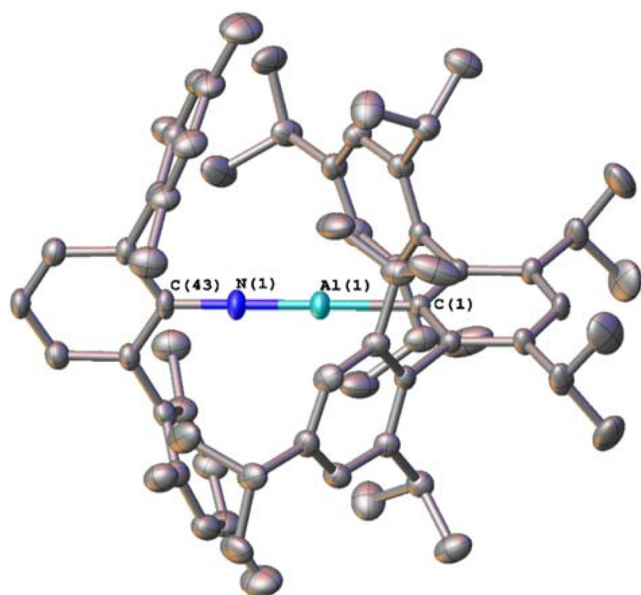


Figure 2. Thermal ellipsoid plot (50%) of one of the crystallographically independent molecules of $\text{Ar}^{\text{iPr}^8}\text{AlNAr}^{\text{Me}^6}$ (**1**). H atoms and *n*-hexane solvent not shown. Selected bond lengths (Å) and angles (deg) {values in braces correspond to the other crystallographically 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 $\text{D}^{\text{iPr}^8}\text{NacAl=NAr}^{\text{iPr}^4}$.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

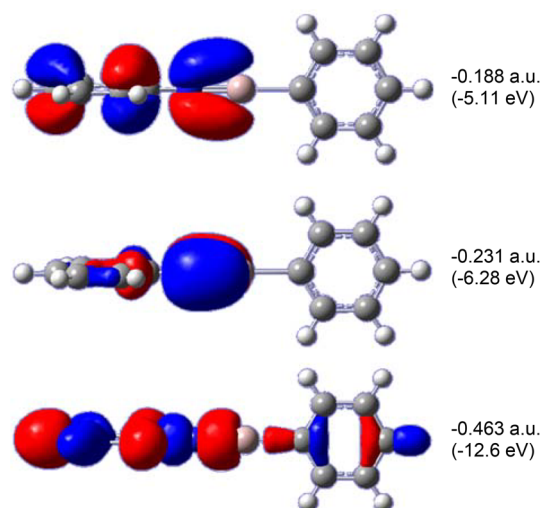


Figure 3. Occupied PBE1PBE-GD3BJ/def2-TZVP orbitals of Ph–NAl–Ph localized on the AlN bond (NPh moiety on the left, AlPh moiety on the right; isosurface value ± 0.05 au).

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 $:\text{Al}^{\text{D}^{\text{iPr}^8}}\text{NacNac}$ or an alumanyl 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 $:\text{AlAr}^{\text{iPr}^8}$ 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

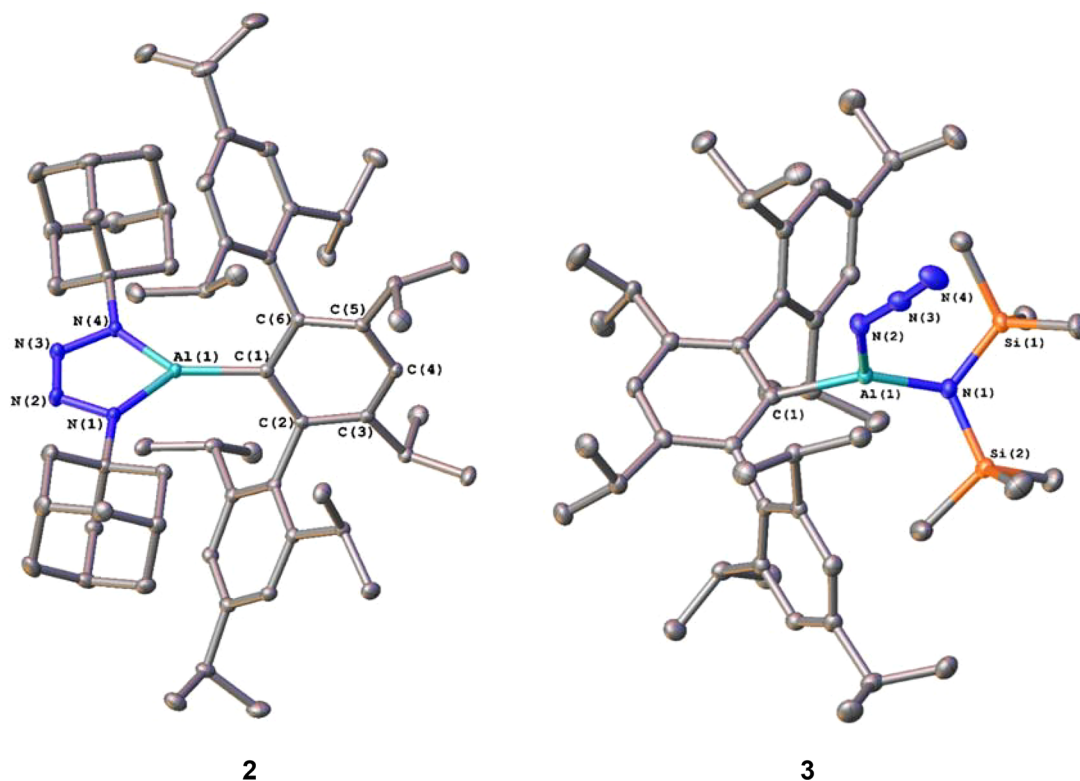


Figure 4. Thermal ellipsoid plots (50%) of $\text{Ar}^{i\text{Pr}8}\text{Al}[(\text{NAd})_2\text{N}_2]$ (**2**, left) and $\text{Ar}^{i\text{Pr}8}\text{Al}(\text{N}_3)\{\text{N}(\text{SiMe}_3)_2\}$ (**3**, right). Hydrogen atoms and toluene are not shown. Selected bond lengths (Å) and angles (deg): **2**: 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.

■ AUTHOR INFORMATION

Corresponding Authors

Philip P. Power – Department of Chemistry, University of California, Davis, Davis, California 95616, United States; orcid.org/0000-0002-6262-3209; Email: pppower@ucdavis.edu

Heikki M. Tuononen – Department of Chemistry, NanoScience Centre, University of Jyväskylä, FI-40014

Jyväskylä, Finland; orcid.org/0000-0002-4820-979X;
Email: heikki.m.tuononen@jyu.fi

Authors

Joshua D. Queen – Department of Chemistry, University of California, Davis, Davis, California 95616, United States;
orcid.org/0000-0002-6726-417X

Sini Irvankoski – Department of Chemistry, NanoScience Centre, University of Jyväskylä, FI-40014 Jyväskylä, Finland;
orcid.org/0000-0002-0844-5448

James C. Fettinger – Department of Chemistry, University of California, Davis, Davis, California 95616, United States;
orcid.org/0000-0002-6428-4909

Complete contact information is available at:
<https://pubs.acs.org/10.1021/jacs.1c02463>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the US National Science Foundation (CHE-156551) for supporting this work and for the purchase of a dual source X-ray diffractometer (CHE-0840444). This project received funding from the European Research Council under the European Union's Horizon 2020 research and innovation programme (grant agreement #772510 to H.M.T.).

REFERENCES

- (1) Downs, A. J.; Aldridge, S. *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*. Wiley: Chichester, 2011 pp 122–131, 257–264.
- (2) Timoshkin, A. Y. Group 13 Imido Metallanes and their Heavier Analogs [RMYR]_n (M = Al, Ga, In; Y = P, N, As, Sb). *Coord. Chem. Rev.* **2005**, *249*, 2094–2131.
- (3) Gardiner, M. G.; Raston, C. L. Advances in the chemistry of Lewis base adducts of alane and gallane. *Coord. Chem. Rev.* **1997**, *166*, 1–34.
- (4) Carmalt, C. J. Amido compounds of gallium and indium. *Coord. Chem. Rev.* **2001**, *223*, 217–264.
- (5) Brothers, P. J.; Power, P. P. Multiple Bonding Involving the Heavier Main Group 3 Elements Al, Ga, In, and Tl. *Adv. Organomet. Chem.* **1996**, *39*, 1–69.
- (6) Schauer, S. J.; Robinson, G. H. Aminoalane Dimers and Trimers. An Examination of Structural and Steric Trends. *J. Coord. Chem.* **1993**, *30*, 197–214.
- (7) Uhl, W. Aluminum and Gallium Hydrazides. *Struct. Bonding (Berlin, Ger.)* **2003**, *105*, 41–66.
- (8) Veith, M. Cage Compounds with Main-Group Metals. *Chem. Rev.* **1990**, *90*, 3–16.
- (9) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood-Wiley: Chichester, 1979, Chapter 4.
- (10) Jegier, J. A.; Gladfelter, W. L. The Use of Aluminum and Gallium Hydrides in Materials Science. *Coord. Chem. Rev.* **2000**, *206–207*, 631–650.
- (11) Grant, D. J.; Dixon, D. A. Thermodynamic Properties of Molecular Borane Phosphines, Alane Amines, and Phosphine Alanes and the [BH₄⁻][PH₄⁺], [AlH₄⁻][NH₄⁺], and [AlH₄⁻][PH₄⁺] Salts for Chemical Hydrogen Storage Systems from ab Initio Electronic Structure Theory. *J. Phys. Chem. A* **2005**, *109*, 10138–10147.
- (12) Marder, T. B. Will We Soon Be Fueling our Automobiles with Ammonia–Borane? *Angew. Chem., Int. Ed.* **2007**, *46*, 8116–8118.
- (13) Langmi, H. W.; McGrady, G. S. Non-hydride systems of the main group elements as hydrogen storage materials. *Coord. Chem. Rev.* **2007**, *251*, 925–935.
- (14) Laubengayer, A. W.; Smith, J. D.; Ehrlich, G. G. Aluminum-Nitrogen Polymers by Condensation Reactions. *J. Am. Chem. Soc.* **1961**, *83*, 542–546.
- (15) Cesari, M.; Perego, G.; Del Piero, G.; Cucinella, S.; Cernia, E. The chemistry and the stereochemistry of poly(*N*-alkyliminoalanes): II. The crystal and molecular structure of the hexamer, (HAIN-*i*-Pr)₆. *J. Organomet. Chem.* **1974**, *78*, 203–213.
- (16) Del Piero, G.; Cesari, M. C.; Perego, G.; Cucinella, S.; Cernia, E. The chemistry and the stereochemistry of poly(*N*-alkyliminoalanes): XI. The crystal and molecular structure of the hexamer (HAIN-*n*-Pr)₆ and the octamer (HAIN-*n*-Pr)₈. *J. Organomet. Chem.* **1977**, *129*, 289–298.
- (17) Del Piero, G.; Cesari, M.; Dozzi, G.; Mazzei, A. The chemistry and the stereochemistry of poly(*n*-alkyliminoalanes): X. The crystal and molecular structure of the tetramers (HAIN-*i*-Pr)₄ and (MeAlN-*i*-Pr)₄. *J. Organomet. Chem.* **1977**, *129*, 281–288.
- (18) Belgardt, T.; Waezsada, S. D.; Roesky, H. W.; Gornitzka, H.; Häming, L.; Stalke, D. Synthesis and Characterization of (Pentafluorophenyl)amino-based Amino- and Iminometallanes. Crystal Structures of (MeAlNC₆F₅)₄ and NHC₆F₅Ga(MesGa)₃(μ₃-NC₆F₅)₄ (Mes = 2,4,6-Me₃C₆H₂). *Inorg. Chem.* **1994**, *33*, 6247–6251.
- (19) Reddy, N. D.; Roesky, H. W.; Noltemeyer, N.; Schmidt, H.-G. Reactions of AlH₃·NMe₃ with Nitriles: Structural Characterization and Substitution Reactions of Hexameric Aluminum Imides. *Inorg. Chem.* **2002**, *41*, 2374–2378.
- (20) Schiefer, M.; Reddy, N. D.; Roesky, H. W.; Vidovic, D. Synthesis and Structural Characterization of an Exclusively N-Based Tetrameric Aluminum(I) Compound. *Organometallics* **2003**, *22*, 3637–3638.
- (21) Waggoner, K. M.; Hope, H.; Power, P. P. Synthesis and Structure of [MeAlN(2,6-*i*-Pr₂C₆H₃)₃]: An Aluminum-Nitrogen Analogue of Borazine. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699–1700.
- (22) Pinkas, J.; Löbl, J.; Roesky, H. W. Chemical Reactivity of Alumazene. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 759–763.
- (23) Löbl, J.; Necas, M.; Pinkas, J. Alumazene adducts with triphenylphosphine oxide. *Main Group Chem.* **2006**, *5*, 79–88.
- (24) Wehmschulte, R. J.; Power, P. P. Reactions of (H₂AlMes*)₂ (Mes* = 2,4,6-*t*-Bu₃C₆H₂) with H₂EAR (E = N, P, or As; Ar = aryl): Characterization of the Ring Compounds (Mes*AlNPh)₂ and (Mes*AlEPh)₃ (E = P or As). *J. Am. Chem. Soc.* **1996**, *118*, 791–797.
- (25) Wehmschulte, R. J.; Power, P. P. Reaction of the Primary Alane (2,4,6-*t*-Bu₃H₂C₆AlH₂)₂ with Nitriles, Isonitriles, and Primary Amines. *Inorg. Chem.* **1998**, *37*, 6906–6911.
- (26) Schulz, S.; Voigt, A.; Roesky, H. W.; Häming, L.; Herbst-Irmer, R. Synthesis of Dimeric Iminoalanes by Oxidative Addition of Azides to (Cp*Al)₄: Structural Characterization of (Cp*AlNSi^tBu)₂ (Cp* = C₅Me₅). *Organometallics* **1996**, *15*, 5252–5253.
- (27) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. Synthesis and Structure of the First Dimeric Iminoalane Containing an Al₂N₂ Heterocycle. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969–970.
- (28) Fischer, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. [CpAlN(2,6-*i*-Pr₂C₆H₃)₂]₂: A Dimeric Iminoalane Obtained by Alkane Elimination. *Inorg. Chem.* **1996**, *35*, 271–272.
- (29) Schulz, S.; Thomas, F.; Priesmann, W. F.; Nieger, M. Synthesis and X-Ray Structure of Base-Stabilized Iminoalanes. *Organometallics* **2006**, *25*, 1392–1398.
- (30) Hamilton, T. P.; Shaikh, A. D. Theoretical Study of the Dimerization of Multiply-Bonded Aluminum-Nitrogen Compounds. *Inorg. Chem.* **1997**, *36*, 754–755.
- (31) Waggoner, K. M.; Power, P. P. Reactions of trimethylaluminum or trimethylgallium with bulky primary amines: structural characterization of the thermolysis products. *J. Am. Chem. Soc.* **1991**, *113*, 3385–3393.
- (32) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. [HC{(CMe)(NAr)}₂Al{(NSiMe₃)₂N₂}] (Ar = 2,6-*i*-Pr₂C₆H₃): The

First Five-Membered AlN₄ Ring System. *Angew. Chem., Int. Ed.* **2000**, *39*, 4531–4533.

(33) Zhu, H.; Yang, Z.; Magull, J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. Synthesis and Structural Characterization of a LAl(N₃)N[μ-Si(N₃)(tBu)₂]NAl(N₃)L and a Monomeric Aluminum Hydride Amide LAlH(NHAr) (L = HC[(CMe)(NAr)]₂, Ar = 2,6-*i*-Pr₂C₆H₃). *Organometallics* **2005**, *24*, 6420–6425.

(34) Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. Stable, Monomeric Imides of Aluminum and Gallium: Synthesis and Characterization of [{HC(CMeDippN)₂}MN-2,6-Trip₂C₆H₃] (M = Al or Ga; Dipp = 2,6-*i*-Pr₂C₆H₃; Trip = 2,4,6-*i*-Pr₃C₆H₂). *Angew. Chem., Int. Ed.* **2001**, *40*, 2172–2174.

(35) Zhu, H.; Chai, J.; Chandrasekhar, V.; Roesky, H. W.; Magull, J.; Vidovic, D.; Schmidt, H.-G.; Noltemeyer, M.; Power, P. P.; Merrill, W. A. Two Types of Intramolecular Addition of an Al–N Multiple-Bonded Monomer LAlNAr' Arising from the Reaction of LAl with N₃Ar' (L = HC[(CMe)(NAr)]₂, Ar' = 2,6-Ar₂C₆H₃, Ar = 2,6-*i*-Pr₂C₆H₃). *J. Am. Chem. Soc.* **2004**, *126*, 9472–9473.

(36) Li, J.; Li, X.; Huang, W.; Hu, H.; Zhang, J.; Cui, C. Synthesis, Structure, and Reactivity of a Monomeric Iminoalane. *Chem. - Eur. J.* **2012**, *18*, 15263–15266.

(37) Anker, M. D.; Schwamm, R. J.; Coles, M. P. Synthesis and Reactivity of a Terminal Aluminum-Imide Bond. *Chem. Commun.* **2020**, *56*, 2288–2291.

(38) Heilmann, A.; Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. Carbon Monoxide Activation by a Molecular Aluminium Imide: C–O Bond Cleavage and C–C Bond Formation. *Angew. Chem., Int. Ed.* **2020**, *59*, 4897–4901.

(39) Lanzisera, D. V.; Andrews, L. Reactions of Laser-Ablated Aluminum Atoms with Ammonia. Infrared Spectra of HAlNH₂, AlNH₂, and HAlNH in Solid Argon. *J. Phys. Chem. A* **1997**, *101*, 5082–5089.

(40) Timoshkin, A. Y.; Schaefer, H. F. Theoretical Studies of [MYR₂]_n Isomers (M = B, Al, Ga; Y = N, P, As; R = H, CH₃): Structures and Energetics of Monomeric and Dimeric Compounds (n = 1, 2). *J. Phys. Chem. A* **2008**, *112*, 13180–13196.

(41) Zhang, S.-L.; Yang, M.-C.; Su, M.-D. A computational study to determine whether substituents make E₁₃=nitrogen (E₁₃ = B, Al, Ga, In, and Tl) triple bonds synthetically accessible. *RSC Adv.* **2019**, *9*, 12195–12208.

(42) Gilbert, T. M. Ab Initio Computational Studies of Heterocycloalkynes: Structures, Natural Bond Orders, Ring Strain Energies, and Isomerizations of Cyclic Iminoboranes and Iminoalanes. *Organometallics* **2000**, *19*, 1160–1165.

(43) Wright, R. J.; Phillips, A. D.; Allen, T. L.; Fink, W. H.; Power, P. P. Synthesis and Characterization of the Monomeric Imides Ar'MNAr'' (M = Ga or In; Ar' or Ar'' = Terphenyl Ligands) with Two-Coordinate Gallium and Indium. *J. Am. Chem. Soc.* **2003**, *125*, 1694–1695.

(44) Queen, J. D.; Lehmann, A.; Fettingner, J. C.; Tuononen, H. M.; Power, P. P. The Monomeric Alane-diyl:AlAr^{iPr8} (Ar^{iPr8} = C₆H-2,6-(C₆H₂-2,4,6-Pr^t₃)₂-3,5-Pr^t₂): An Organoaluminum(I) Compound with a One-Coordinate Aluminum Atom. *J. Am. Chem. Soc.* **2020**, *142*, 20554–20559.

(45) This is consistent with the Al–N bond having similar polarity to the Li–I bond ($\Delta\chi_p(\text{Al–N}) = 1.43$; $\Delta\chi_p(\text{Li–I}) = 1.68$). Source of χ_p values: Huheey, J. E. *Inorganic Chemistry*, 2nd Ed. pp 162. New York, 1978.

(46) Ploshnik, E.; Danovich, D.; Hiberty, P. C.; Shaik, S. The Nature of the Idealized Triple Bonds Between Principal Elements and the σ Origins of Trans-Bent Geometries—A Valence Bond Study. *J. Chem. Theory Comput.* **2011**, *7*, 955–968.

(47) Huo, S.; Li, X.; Zeng, Y.; Sun, Z.; Zheng, S.; Meng, L. Nature of E–E bonds in heavier ditetrel alkyne analogues ArEEAr (Ar = C₆H₃-2,6-(C₆H₃-2,6-Pr^t₂)₂; E = Si, Ge, Sn, and Pb). *New J. Chem.* **2013**, *37*, 3145–3151.

(48) Power, P. P. An Update on Multiple Bonding between Heavier Main Group Elements: The Importance of Pauli Repulsion, Charge-

Shift Character, and London Dispersion Force Effects. *Organometallics* **2020**, *39*, 4127–4138.

(49) Jutzi, P.; Neumann, B.; Reumann, G.; Stämmler, H.-G. Novel Ga₂N₂ Ring Systems by Reaction of Pentamethylcyclopentadienylgallium with Organic Azides. *Organometallics* **1999**, *18*, 2037–2039.

(50) Schulz, A.; Thomas, M.; Villingner, A. Tetrazastannoles versus distannadiazanes – a question of the tin(II) source. *Dalton. Trans.* **2019**, *48*, 125–132.

(51) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. Reaktionen von Germylenen mit Aziden: Iminogermane, Azidogermane, Tetrazagermole und Hexaazadigermadispirododecane. *Chem. Ber.* **1989**, *122*, 245–252.

(52) Hitchcock, P. B.; Lappert, M. F.; Protchenko, A. V.; Uiterweerd, P. G. H. Synthesis and structures of halides and pseudohalides of bis[2,6-bis(dimethylamino)phenyl]tin(IV). *Dalton Trans.* **2009**, 353–361.

(53) Hardman, N. J.; Power, P. P. Unique structural isomerism involving tetrazole and amide/azide derivatives of gallium. *Chem. Commun.* **2001**, 1184–1185.

(54) Krahfuss, M. J.; Radius, U. N-Heterocyclic Silylene Main Group Element Chemistry: Adduct Formation, Insertion into E–X Bonds and Cyclization of Organoazides. *Eur. Eur. J. Inorg. Chem.* **2021**, 548–561.