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

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ABSTRACT: The reaction of :AlArPr (ArPr = C6H-2,6-(C5H5-2,4,6-Pr3)3,5-Pr2) with A2Me6N3 (A2Me6 = C6H-2,6-(C5H5-2,4,6-Me5)) in hexanes at ambient temperature gave the aluminum imide ArPrAlNMeAlPr2 (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 :AlArPr and A2Me6N3. Dispersion accounts for −89 kJ mol⁻¹, which is similar in strength to one Al–N z-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 :AlArPr with 1-AdN3 or Me6SiN3 gave transient imides that immediately reacted with a second equivalent of the azide to give ArPrAl[(NAd)2N2]2 (2) or ArPrAl(NMe)3[N(SiMe3)2] (3).

The chemistry of compounds with group 13 element-nitrogen bonding has been extensively studied. Current interest is driven by their applications as precursors for group III–V materials, H₂ storage media, and an interest in M–N (M = Al–Ti) 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 compounds1–3 (Scheme 1).

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

The group 13 metal imides (also called N-iminometallanes) of formula [RMNR₃]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 A. Roessky and co-workers characterized the quasi-isometric tetrameric amido-Al(I) compound [AlN(Dipp)(SiMe₃)₄]₄ (Dipp = 2,6-Pr₃-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 [AlMe₃N(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, [RAINR']₂ compounds with Al₃N₃ cores and short Al–N distances in the range 1.796–1.842 Å, which is slightly longer than that seen in the aluminazine derivative, have also been reported. 24–29

Monomeric RAINR’ compounds remain unknown, which is probably a result of high association energies (cf. dimerization of HAiNH 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, Roessky and co-workers reported that the reaction of AlCP₈ (CP₈ = η¹-C₅Me₅) formed by dissociation of AlCP₈⁺, at elevated temperature, with R₃SiN (R = Pr, Ph, Bu), gave the imido dimers {CP₈Al(μ-NSiR₃)₂}₂. 32 Using the larger, chelated Al(1) β-diketiminate :AlPr₂NacNac (Pr₂NacNac = HC{(CMe)₃CH}₂) gave the transient imides Pr₂NacNacAl = NR which reacted with a second equivalent of the azide to give cyclic AlₙNₙ products Pr₉NacNacAl[μ(1,N₉)₉]₃. 33 Attempts to stabilize the imide using more sterically demanding tert-phenyl 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 Pr₂NacNac 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 a \( \text{Al}[\text{HC}(\text{C'Bu})(\text{NDipp})]_{2} \) resulted in insertion of the Al atom into the N–C bond of the \( \beta \)-diketiminate ligand. This gave the four-coordinate terminal Al imide 1 (Figure 1) with a 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) supported by multidentate imides. Aldridge showed that a reaction of \( \text{Al}(\text{NDipp})_{2} \) with organoazides gave terminal aluminum imides which react immediately with a second \( \text{Al} \) atom. We show here that its reaction with \( \text{ArMe}_{6}\text{N}_{3} \) (Scheme 2a) in hexanes at ambient temperature, giving immediate vigorous evolution of \( \text{N}_{2} \) and formation of a bright 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. 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 \( \text{Ar}^{\text{Pr}}\text{MMAr}^{\text{Pr}} \) (\( \text{M} = \text{Ga, In}; \text{Ar}^{\text{Pr}}\text{H}_{2}-2,6-(\text{C}_{6}\text{H}_{3}-2,6-\text{Me}_{3})_{2} \)) which exist in equilibrium with \( \text{MMAr}^{\text{Pr}} \) monomers in solution. This suggested that a similar \( \text{Al} \) species could be isolable, but the lack of an analogous \( \text{Al}(1) \) precursor (i.e., \( \text{ArAlAlAr} \) or \( \text{AlAr} \)) precluded its synthesis. Recently, we reported the monomeric alane\-\( \text{AlAr}^{\text{Pr}}\text{H}_{2} (\text{Ar}^{\text{Pr}}\text{H}_{2} \equiv \text{C}_{6}\text{H}_{3}-2,6-(\text{C}_{6}\text{H}_{3}-2,6-\text{Me}_{3})_{2} \)) with a one-coordinate \( \text{Al} \) atom. We show here that its reaction with \( \text{ArMe}_{6}\text{N}_{3} \) (\( \text{Ar}^{\text{Pr}}\text{H}_{2} \equiv \text{C}_{6}\text{H}_{3}-2,6-(\text{C}_{6}\text{H}_{3}-2,6-\text{Me}_{3})_{2} \)) gives the aluminum imide \( \text{Ar}^{\text{Pr}}\text{AlArMe}_{6} \) (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 \( \text{AlAr}^{\text{Pr}}\text{H}_{2} \) with the less sterically demanding azides 1-\( \text{AdN}_{3} \) (1-\( \text{Ad} = 1\)-adamantyl) or \( \text{MeSiN}_{3} \) gives transient imides which react immediately with a second equivalent of azide to give products featuring ring closure or silyl migration.

Figure 1. Structurally characterized terminal aluminum imides. \( \text{Mes} = 2,4,6\)-\( \text{Me}_{3}\text{C}_{6}\text{H}_{2}; \text{Dipp} = 2,6\)-\( \text{Pr}_{2}\text{C}_{6}\text{H}_{3} \).

Scheme 2. Synthesis of Compounds 1, 2, and 3

(a) Synthesis of compound 1; (b) synthesis of compounds 2 and 3; Trip = 2,4,6-\( \text{Pr}_{3}\text{C}_{6}\text{H}_{2} \); \( \text{Mes} = 2,4,6\)-\( \text{Me}_{3}\text{C}_{6}\text{H}_{2} \); 1-\( \text{Ad} = 1\)-adamantyl.
analyses using the ETS-NOCV method and fragments :AlAr$_{3}$ and Ar$_{3}$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 :AlAr$_{3}$ and Ar$_{3}$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 Ad$_{3}$N$_{3}$ or Me$_{3}$SiN$_{3}$ to :AlAr$_{3}$ gives the transient imides Ar$_{3}$N: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$_{3}$ -SiH$_{3}$, and 1-Ad react in a 2:1 ratio with :Al[($^{13}$NacNac)N] 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=N NR moiety, which undergoes ring closure with a second equivalent of the azide. The reaction of :AlAr$_{3}$ with 2 equiv of 1-Ad$_{3}$N$_{3}$ 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)$^{\circ}$ and C(1)−C(6)−C(5)−C(4) = 20.06(14)$^{\circ}$. 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$_{3}$ 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 nitrogen atom of the...
transient imide has occurred. Such migrations have been observed in a number of reactions of Me₃SiN₃ with low valent main group compounds.⁴⁹−⁵⁴

Computationally, the reaction of :AlAr⁺Pr₈ with Me₃SiN₃ yielded Ar⁺Pr₈AlN(N₂)SiMe₃ which readily releases N₂ with a free energy barrier of 46 kJ mol⁻¹ to afford Ar⁺Pr₈AlNSiMe₃ at −306 kJ mol⁻¹ (Figure S17, Supporting Information). Addition of a second equivalent of Me₃SiN₃ gave two products, cis- and trans-Ar⁺Pr₈Al[N(SiMe₃)N₂]NSiMe₃, depending on the relative orientation of Ar⁺Pr₈AlNSiMe₃ and Me₃SiN₃. The cis-isomer has the two SiMe₃ 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 SiMe₃ 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⁺Pr₈ 1-AdN₃ pair with the exception that substituent migration is energetically unfeasible and 2 is formed rapidly via ring closure.

In summary, the alaneyl :AlAr⁺Pr₈ reacts with the m-terphenyl azide Ar⁺Me₆N₃ to yield the monomer Ar⁺Pr₈AlNAr⁺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⁺Pr₈ moiety to the :NAr⁺Me₆ nitrene and weak π-donation from the latter to :AlAr⁺Pr₈. 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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REFERENCES

(1) Downs, A. J.; Aldridge, S. The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Pecularities. Wiley: Chichester, 2011 pp 122−131, 257−264.
(2) Timoshkin, A. Y. Group 13 Imido Metallenes and their Heavier Analogs [RMYR], (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.; Gładfelter, W. L. The Use of Aluminium 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-hydrate 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.; Pereggi, G.; Del Piero, G.; Cunicella, S.; Cernia, E. The chemistry and the stereochemistry of poly(N-alkylaminoalanes): 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.; Pergeggi, G.; Cunicella, S.; Cernia, E. The chemistry and the stereochemistry of poly(N-alkylaminoalanes): 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-alkylaminoalanes): X. The crystal and molecular structure of the tetramers (HAIN+i-Pr)4 and (MeAIN+i-Pr)4. J. Organomet. Chem. 1977, 129, 281−288.
(18) Belgardt, T.; Waesesa, S. D.; Roeky, H. W.; Gorntitzka, H.; Häming, L.; Stalke, D. Synthesis and Characterization of (Pentafluorophenyl)amino-based Amino- and Iminomettalanes. Crystal Structures of (MeAlNC6F5)4 and NH2C6F5GA(MesGa)3(μ3-NC6F5)2. Inorg. Chem. 1994, 33, 6247−6251. (19) Reddy, N. D.; Noltemeyer, N.; Schmidt, H. G. Reactions of AlH2-NMe2 with Nitriles: Structural Characterization and Substitution Reactions of Hexameric Aluminum Imides. Inorg. Chem. 2002, 41, 2374−2378.
(20) Schiefer, M.; Reddy, N. D.; Roeky, 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 [MeAIN(2,6-i-PrC6H4)]3; An Aluminum-Nitrogen Analogue of Borazane. Angew. Chem., Int. Ed. Engl. 1988, 27, 1699−1700.
(22) Pinkas, J.; Löbl, J.; Roeky, 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 triphenyolphosphine oxide. Main Group Chem. 2006, 5, 79−88.
(24) Wehmschulte, R. J.; Power, P. P. Reactions of (H2AlMes)2: A Dimeric Iminoalane Obtained by Alkane Elimination. Inorg. Chem. 2007, 46, 271−272.
(25) Wehmschulte, R. J.; Power, P. P. Reaction of the Primary Alane (HAlN-i-Pr2C6H3): The chemistry and the stereochemistry of poly(N-alkyliminoalanes): An Aluminum-Nitrogen Analogue of Borazine. Angew. Chem., Int. Ed. Engl. 1996, 35, 6252−6253.
(26) Schulz, S.; Voigt, A.; Roeky, H. W.; Häming, L.; Herbster-Irmer, R. Synthesis of Dimeric Iminoalanes by Oxidative Addition of Azides to [Cp*AlMe2]2: Structural Characterization of [Cp*[AlMe2(Ni)]2. Organometallics 1996, 15, 5252−5253.
(27) Schulz, S.; Häming, L.; Herbster-Irmer, R.; Roeky, H. W.; Sheldrick, G. M. Synthesis and Structure of the First Dimeric Iminoalane Containing an Al2N2 Heterocyclic. 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-PrC6H4)]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.; Roeky, H. W.; Schmidt, H-G.; Noltemeyer, M. [HC(CMe3)(NAr)]2Al[N(SiMe3)2]2Ar (3 = 2,6-Pr2C6H4): The
(33) Zhu, H.; Yang, Z.; Magull, J.; Roessky, H. W.; Schmidt, H.-G.; Noltemeyer, M. Synthesis and Structural Characterization of a LAl(N)2[N(μ-Si(N)(tBu)3)]2NAl(N)L and a Monomeric Aluminum Hydride Amide LAlH[N(NAr)] (L = HC(=CMe)(=NAr))2, Ar = 2,6-Pr2C6H4. Organometallics 2005, 24, 6420–6425.

(34) Hardman, N. J.; Cui, C.; Roessky, 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-Pr2C6H4; Trip = 2,4,6-iPr3C6H2). Angew. Chem., Int. Ed. 2001, 40, 2172–2174.

(35) Zhu, H.; Chai, J.; Chandrasekhar, V.; Roessky, 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 N2Ar (L = HC(=CMe)(=NAr))2, Ar′ = 2,6-Ar2C6H4, Ar = 2,6-iPr3C6H2. 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, 15263–15268.

(37) Anker, M. D.; Schwamm, R. J.; Coles, M. P. Synthesis and Reactivity of a Terminal Aluminum-Iclide 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 Aluminum Iride: 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, and HAlNH in Solid Argon. J. Phys. Chem. A 2000, 104, 12195–12208.

(40) Timoshkin, A. Y.; Schaefer, H. F. Theoretical Studies of [MYR]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 Stain Energies, and Isomerizations of Cyclic Iminoboranes and Iminolanes. 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.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. The Monomeric AlanediyliAlAAsI2 (Ar′As = C6H2-2,6-(CMe2)2-4,6-Pr′3): An Organoaluminium(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 (|ΔχIPb(Al-N)| = 1.43; |ΔχIPb(Li-I)| = 1.68). Source of |ΔχIPb|: Huheey, J. E. Inorganic Chemistry, 2nd Ed. pp 162. New York, 1978.

(46) Plosnik, 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 Van der Waals 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 alkylene analogues ArEEAr (Ar = C6H2-2,6(CMe2)2-4,6-Pr′3): 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-