

## RESEARCH ARTICLE

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## Superacidic aluminum azido species: precursors to triazolyl dimers, trimers and tetramers†

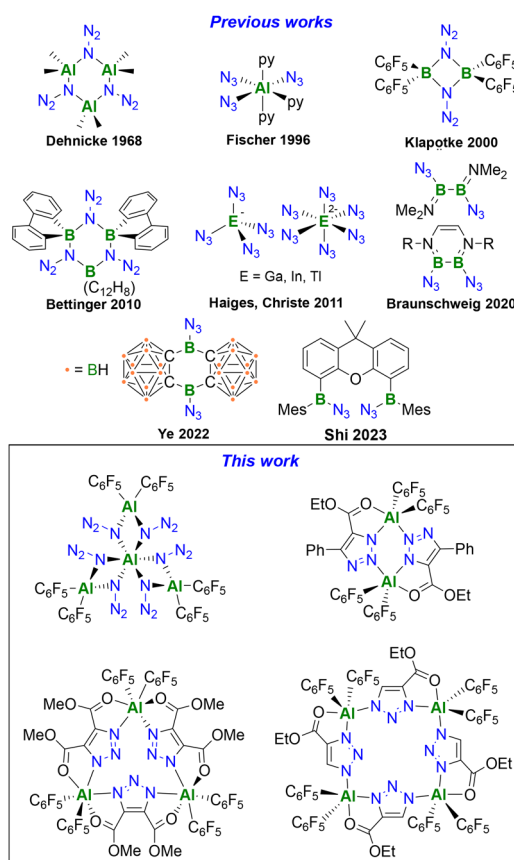
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The aluminum-azido species  $(\text{Me}_3\text{SiN}_3)\text{Al}(\text{C}_6\text{F}_5)_3$  thermally converts to  $[(\text{C}_6\text{F}_5)_2\text{Al}(\mu\text{-N}_3)]_2$  **2**. Further reactions with  $\text{Me}_3\text{SiN}_3$  afford  $[(\text{C}_6\text{F}_5)_2\text{Al}(\mu\text{-N}_3)_2]_3\text{Al}$  which contains unique four Al centers bound to six bridging azides. Compound **2** is shown to be a Lewis superacid both experimentally and theoretically, forming dimeric products in reactions with diphenylphosphine oxide or tetrahydrofuran and a monomeric adduct with an NHC donor. Compound **2** also undergoes “click” reactions with alkynes to give dimeric, trimeric and tetrameric products depending on the nature of the substitution on the alkyne, which demonstrates the ability of the reagent to control the nature of aggregation.

## Introduction

Since the first synthesis of azido benzene by Griess in 1864,<sup>1,2</sup> organic azides have been extensively studied for applications in organic synthesis, bioorthogonal chemistry and materials science.<sup>3–13</sup> Polyazido compounds are high-energy materials thanks to the high nitrogen content and the energetically favorable release of  $\text{N}_2$ .<sup>14</sup> As a result they often exhibit poor thermal stability and are sensitive to mechanical stimuli.<sup>15–20</sup> Thus, a major theme in the study of azido compounds has been to probe their reactivity and stability.<sup>11,19,21–23</sup> The incorporation of strongly Lewis acidic or steric bulky moieties has been shown to significantly increase the stability of azido compounds, leading to the formation of isolable molecular species.<sup>24–26</sup> While monoazido boranes such as  $\text{R}_{(3-n)}\text{B}(\text{N}_3)_n$ <sup>19,27</sup> 1-azido-2,3,4,5-tetraphenylborole<sup>28</sup> and carbene-stabilized azidoborane,<sup>29–31</sup> have been reported, more electrophilic boranes generally form more diverse molecular structures. For example, the trimers  $(\text{Cl}_2\text{B}(\mu\text{-N}_3))_3$  and  $(\text{Br}_2\text{B}(\mu\text{-N}_3))_3$ <sup>32,33</sup> were reported in the 1960s, while Klapotke reported the dimer  $[(\text{C}_6\text{F}_5)_2\text{B}(\mu\text{-N}_3)]_2$ <sup>24,25</sup> in 2000. Subsequently

Bettinger *et al.* described the trimeric 9-azido-9-borabluorene (Scheme 1)<sup>34,35</sup> while Braunschweig *et al.* synthesized the diborane(4) diazides (Scheme 1).<sup>36,37</sup> The reactivity of borane–



Scheme 1 Selected examples of group 13 azides.

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azides has drawn limited attention. We previously reported the use of  $((\text{C}_6\text{F}_5)_2\text{B}(\mu\text{-N}_3))_2$  in uncatalyzed “click” reactions with various alkynes.<sup>38–40</sup> Ye *et al.* reported the reactivity of the super Lewis acid carborane-derived 9,10-diazo-9,10-dibora-anthracene (Scheme 1)<sup>21</sup> with B–H, Si–H and Ge–H bonds. Most recently, Guan, Lin, Shi and co-workers published the use of bis-azidoboranes fused by biphenylene/xanthrene (Scheme 1)<sup>41</sup> to generate transient nitrene species for further reactions.

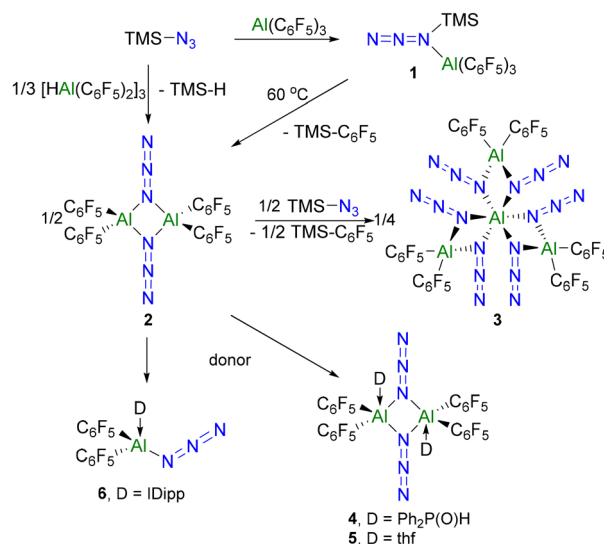
Heavier analogues of group 13 polyazides are generally less studied. For gallium, indium and thallium, the polyazido species  $\text{M}(\text{N}_3)_3$ ,  $(\text{CH}_3\text{CN})\text{M}(\text{N}_3)_3$  ( $\text{M} = \text{Ga}, \text{In}, \text{Tl}$ ),  $[\text{Ga}(\text{N}_3)_5]^{2-}$ , and  $[\text{M}(\text{N}_3)_6]^{3-}$  ( $\text{M} = \text{In}, \text{Tl}$ ) (Scheme 1) have been fully characterized by Haiges, Christie and co-workers (Scheme 1).<sup>42</sup> In the case of aluminum, while the first Al-azide  $(\text{Me}_2\text{Al}(\mu\text{-N}_3))_3$  (Scheme 1) was reported by Dehnicke in 1968, only a few other Al-azides have been described since. The Al-monoazides  $\text{LAlN}_3$  ( $\text{L} = [(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{NR}]^{2-}$ ) and  $\text{Ar}^{\text{IPr8}}\text{Al}(\text{N}_3)[\text{N}(\text{SiMe}_3)_2]$  have been described by Bertrand *et al.*<sup>43</sup> and Power *et al.*,<sup>44</sup> respectively, while Uhl *et al.* and Fischer and coworkers reported the trimeric  $[(\text{CH}_3\text{Si})_2\text{CH}_2\text{Al}(\mu\text{-N}_3)]_3$ <sup>45</sup> and the monomeric triazide  $\text{py}_3\text{Al}(\text{N}_3)_3$ <sup>46</sup> (Scheme 1), respectively. Apart from the use of azido-alane  $\text{Et}_2\text{AlN}_3$ <sup>47</sup> as an  $\text{N}_3$  source in the preparation of N-rich compounds and materials,<sup>48–52</sup> little is known about the reactivity of Al-polyazides.

We reasoned that the incorporation of strong electron withdrawing groups on aluminum would enhance the stability and Lewis acidity of polyazido species and thus favor expanded coordination geometries for aggregation. Herein, we report the preparation of aluminum-azido derivatives incorporating  $\text{C}_6\text{F}_5$  substituents and demonstrated that such species provide access to polytriazolyl derivatives *via* “click” reactions resulting in dimeric, trimeric and tetrameric aluminum species, where the reagent determines the nature of the aggregation.

## Results and discussion

We initiated our investigation with the reaction of trimethylsilylazide ( $\text{Me}_3\text{SiN}_3$ ) and  $\text{Al}(\text{C}_6\text{F}_5)_3$  in a ratio of 1 : 1 at room temperature. A white solid **1** was obtained and isolated in 90% yield (Scheme 2). This species exhibited  $^{19}\text{F}$  NMR signals at  $-123.0$ ,  $-150.0$  and  $-160.1$  ppm, inferring a tetracoordinated Al center based on the gap between the signal for the *meta*- and *para*-fluorines.<sup>53–55</sup> The IR absorption peaks of **1** at  $2170$  and  $1358\text{ cm}^{-1}$  confirm the presence of the azido moiety.<sup>56</sup> Single crystal X-ray diffraction (XRD) analysis of the colorless crystals of **1** revealed the presence of the azide-alane adduct  $(\text{Me}_3\text{SiN}_3)\text{Al}(\text{C}_6\text{F}_5)_3$  (Fig. 1a) with a N–Al bond of  $1.9925(14)\text{ Å}$ . The two N–N bond lengths in the azido-fragment were  $1.258(2)$  and  $1.113(2)\text{ Å}$ , which are similar to those found in the known boron analogue  $[1.259(1)$  and  $1.117(2)\text{ Å}]$ .<sup>57,58</sup>

Heating **1** in a toluene solution at  $60\text{ °C}$  for 12 h led to the observation of two new sets of peaks at  $-124.3$ ,  $-146.7$  and  $-157.7$  ppm and  $-128.0$ ,  $-152.4$  and  $-161.7$  ppm in the  $^{19}\text{F}$  NMR spectrum. The latter signals affirm the generation of



Scheme 2 Synthesis of 1–6.

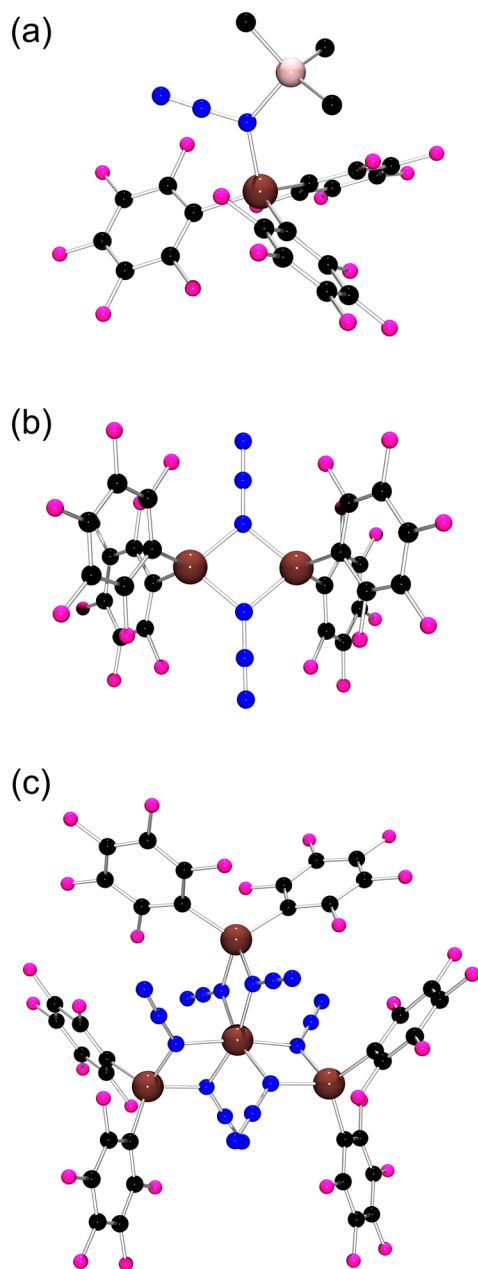
$\text{Me}_3\text{Si-C}_6\text{F}_5$ .<sup>59</sup> The remaining signals were attributed to **2** which was isolated as colorless crystals upon recrystallization from a toluene solution (Scheme 2). The persistence of IR absorptions at  $2174$  and  $1365\text{ cm}^{-1}$  suggests the retention of the azido-fragment. Upon redissolution, a  $^{19}\text{F}$ – $^{19}\text{F}$  DOSY NMR spectrum confirmed a single species in solution. In addition, compound **2** was found to be unstable in dichloromethane and chloroform giving a complex mixture of products. X-ray crystallography revealed **2** as the dimer  $[(\text{C}_6\text{F}_5)_2\text{Al}(\mu\text{-N}_3)]_2$  (Fig. 1b) structurally similar to the boron analog,<sup>25</sup> in which two azido groups bridge the two Al atoms. The four Al–N bond lengths are found to be  $1.914(2)$ ,  $1.918(2)$ ,  $1.918(2)$  and  $1.925(2)\text{ Å}$ .

The formation of **2** from **1** is thought to occur *via* a formal  $\beta$ -elimination of  $\text{Me}_3\text{SiC}_6\text{F}_5$ . This notion prompted us to probe the corresponding reaction of  $[\text{HAl}(\text{C}_6\text{F}_5)_2]_3$  with  $\text{Me}_3\text{SiN}_3$ . Indeed upon  $\beta$ -elimination of the silane,  $\text{HSiMe}_3$  was evidenced by the  $^1\text{H}$  NMR resonances at  $4.17$  (Si–H) and  $0.01$  ( $\text{SiCH}_3$ ) ppm and the product **2** could be isolated in 90% yield.

Heating compound **2** in the presence of additional  $\text{Me}_3\text{SiN}_3$  at  $80\text{ °C}$  for 3 days resulted in the formation of a new species **3** as evidenced by a new set of  $^{19}\text{F}$  NMR signals and the resonances attributable to  $\text{Me}_3\text{SiC}_6\text{F}_5$ . Species **3** was isolated in 73% yield (Scheme 2) and showed IR absorptions at  $2169$  and  $1360\text{ cm}^{-1}$ . An X-ray crystallographic study confirmed the formulation of **3** as  $[(\text{C}_6\text{F}_5)_2\text{Al}(\mu\text{-N}_3)]_3\text{Al}$  (Fig. 1c) featuring a pseudo-octahedral Al center surrounded by six azido fragments, each of which bridges three other Al centers. The twelve Al–N bond lengths range from  $1.893(2)$  to  $1.996(2)\text{ Å}$ . Each of the three  $\text{Al}_2\text{N}_2$  rings are nearly planar with the N–Al–N angles ranging from  $76.23(8)^\circ$  to  $80.8(1)^\circ$ . Compound **3** represents an unusual polyazido-alane, incorporating an unprecedented hexaazido-aluminum center.

The Lewis acidity of **2** was assessed by Gutmann–Beckett Lewis acidity test revealing an acceptor number (AN) of  $82.4$





**Fig. 1** POV-ray depiction of (a) **1**, (b) **2**, and (c) **3**; C: black, Al: brown, F: pink, N: blue, and Si: salmon. Hydrogen atoms have been omitted for clarity.

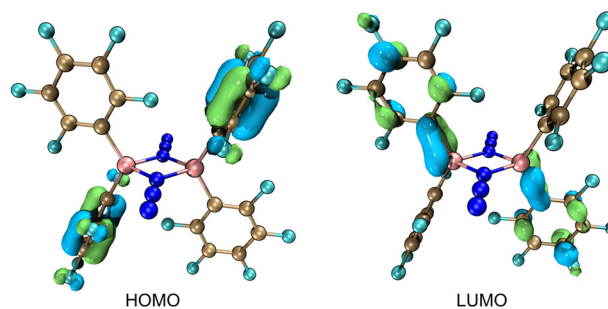
for **2**. This is significantly higher than that observed for  $B(C_6F_5)_3$  (AN = 76.0).<sup>55,60</sup> Density functional theory (DFT) calculations performed at the BP86-D3/def2-SVP level of theory revealed that the gas-phase/solvent-corrected (toluene) isodesmic fluoride ion affinity values (FIA) of 545.1 kJ mol<sup>-1</sup> and 387.6 kJ mol<sup>-1</sup> exceed those of  $SbF_5$  (FIA: 483.2 kJ mol<sup>-1</sup>; FIA<sub>toluene</sub>: 383.5 kJ mol<sup>-1</sup>). Similarly, the hydride ion affinities (HIA) of 487.7 kJ mol<sup>-1</sup> and 324.5 kJ mol<sup>-1</sup> for **2** are similar to those of  $B(C_6F_5)_3$  (HIA: 488.1 kJ mol<sup>-1</sup>; HIA<sub>toluene</sub>: 286.4 kJ mol<sup>-1</sup>). Collectively these data suggest that **2** is a Lewis superacid,<sup>61–63</sup> with the lowest unoccupied molecular orbital

(LUMO) of **2** partly associated with the empty p-orbital on Al (Fig. 2).

Treatment of **2** with  $Ph_2P(O)H$  afforded colorless crystals of **4** (Scheme 2) which exhibited a <sup>31</sup>P NMR doublet at –34.5 ppm, with a P–H coupling constant of 539.2 Hz. The molecular structure of **4** (Scheme 2 and Fig. 3a) confirmed the coordination of a phosphine-oxide to each of the Al centers of **2**, with  $[(C_6F_5)_2Al(OP(H)Ph_2)(\mu-N_3)]_2$  generating five coordinate Al centers. The analogous tetrahydrofuran adduct  $[(C_6F_5)_2Al(thf)(\mu-N_3)]_2$ , **5** was also isolated (Scheme 2, see the ESI†). In contrast, the reaction of **2** with the N-heterocyclic carbene [1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene] (IPr) gave the product **6** (Scheme 2) which was shown crystallographically to be the monomeric species  $(IPr)Al(N_3)(C_6F_5)_2$  (Fig. 3b). This contrasting reactivity is thought to result from both the strong donor ability and the steric demands of the IPr ligand.

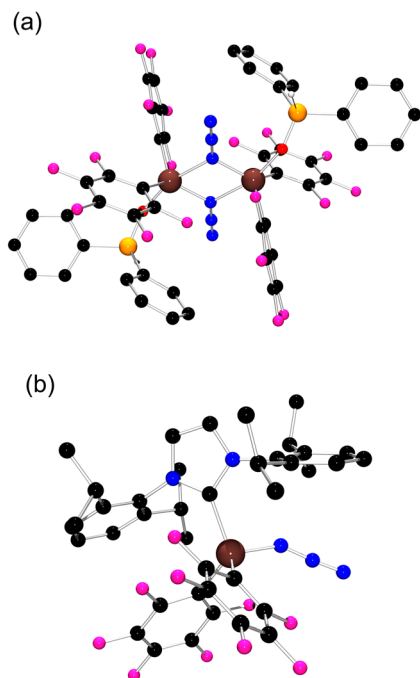
We speculated that alkynes react with **2** in a ‘click reaction’ and that the superacidity of **2** and the nature of the alkyne substitution would have an impact on the degree of aggregation. To probe this, **2** was reacted with ethyl phenylpropiolate in a toluene solution. The *in situ* <sup>19</sup>F NMR spectrum showed new resonances at –123.1, –153.6 and –161.5 ppm (Scheme 3). An X-ray crystallographic study of the product **7** showed it to be the dimeric species  $[(C_6F_5)_2Al(\mu-EtO_2CC_2PhN_3)]_2$  (Fig. 4a) in which two penta-coordinate Al centers are bridged by two triazole rings in a 1,3-fashion with Al–N bond lengths of 1.9547 (14) and 2.0337(15) Å.

The analogue reaction of **2** with dimethyl acetylenedicarboxylate in toluene solution led to the formation of a new species **8** which exhibited <sup>19</sup>F NMR signals at –139.1, –154.0 and –162.3 ppm. Colourless crystals of **8** (Scheme 3) suitable for single-crystal XRD analysis were obtained by storing a  $C_6H_6$ /hexane solution of **8** at –30 °C. The molecular structure showed **8** to be the trimeric species  $[(C_6F_5)_2Al((\mu-MeO_2C)_2C_2N_3)]_3$  (Fig. 4b). In this case, three triazole rings bridged three  $Al(C_6F_5)_2$  moieties with Al–N bond lengths ranging from 2.030(3) to 2.118(2) Å. The Al centers are also coordinated to C=O fragments of the ester with Al–O distances of 1.9804(19) to 2.155(2) Å generating a pseudo-octahedral Al coordination sphere.

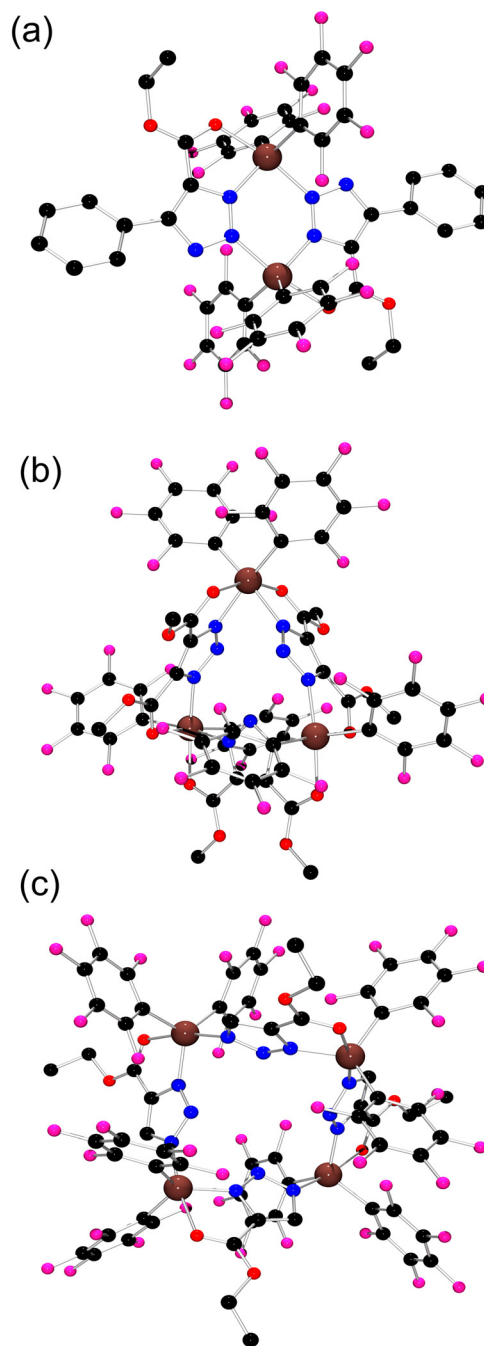


**Fig. 2** Selected molecular orbitals for **2** (dimer) at the M062X/def2-SVP level. Isovalue: 0.05.

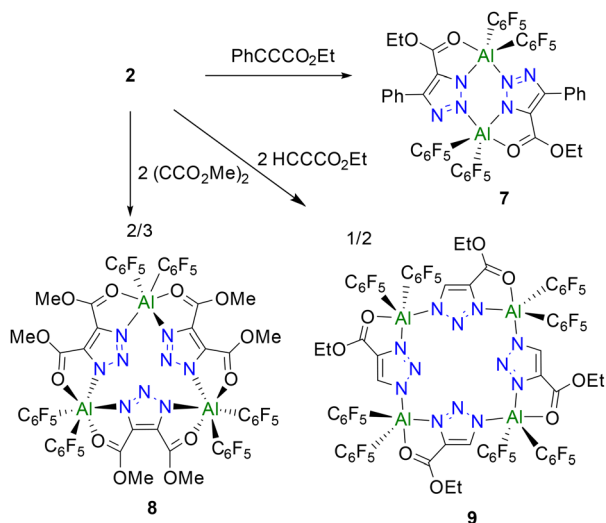




**Fig. 3** POV-ray depiction of (a) **4** and (b) **6**; C: black, Al: brown, F: pink, N: blue, O: red, and P: orange. Hydrogen atoms have been omitted for clarity.



**Fig. 4** POV-ray depiction of (a) **7**, (b) **8**, and (c) **9**; C: black, Al: brown, F: pink, N: blue, and O: red. Hydrogen atoms have been omitted for clarity.



**Scheme 3** Synthesis of **7–9**.

Compound **2** also reacted with an equivalent of ethyl propiolate in a benzene solution, affording colorless crystals of **9** in a yield of 76%. This species exhibited  $^{19}\text{F}$  NMR signals at  $-123.2$ ,  $125.3$ ,  $-151.7$ ,  $156.2$ ,  $-160.1$ , and  $162.9$ , inferring a tetra-coordinate Al center with the inequivalent  $\text{C}_6\text{F}_5$  groups. A single-crystal X-ray diffraction study of **9** (Scheme 3 and Fig. 4c) revealed a tetrameric formulation  $((\text{C}_6\text{F}_5)_2\text{Al}(\mu\text{-EtO}_2\text{CC}_2\text{HN}_3))_4$  in which the four triazole rings bridged four Al atoms in a 1, 3-fashion with Al–N bond lengths of  $1.936(3)$  and

$2.002(3)$  Å. Coordination of the ester's carbonyl fragment to Al affords penta-coordinate Al centers.

In contrast to boron azides which undergo “click reactions”, affording four coordinate boron centers,<sup>38–40</sup> the present reactions of superacidic aluminum centers incorporated in **7–9** provide interactions with the carbonyl substituents to give penta- or hexa-coordinate Al centers. As a consequence, the nature of the substituents on the alkyne determines the degree





of aggregation, permitting the formation of dimers, trimers and tetramers, 7–9. Thus, the super-Lewis acidity of the Al centers in **2** and the nature of the substitutions on the alkynes can be tuned to control the nature of aggregates formed.

## Conclusions

In summary, we have reported the synthesis of the aluminum azido derivative **1** and its thermal conversion to **2**. In addition, **2** was shown to react with excess  $\text{Me}_3\text{SiN}_3$  to give **3**, a species containing an unusual hexaazido-Al center. The superacidity of **2** was confirmed experimentally and computationally while reactions with donors revealed that steric demands have an impact on the nature of the resulting adducts. Exploiting compound **2** for click reactions with substituted alkynyl esters afforded oligomeric aluminum triazole derivatives 7–9. These findings demonstrate the ability of highly electron deficient aluminum-azides to access a range of structurally diverse aggregates, the nature of which is determined by the steric demands of the substitution on the alkyne. This provides a strategy to control the degree of aggregation. Further exploration of the utility of such Lewis superacidic aluminum azides in organic and materials chemistry is the subject of ongoing work.

## Author contributions

S. J., J. T. and T. C. performed the experiments; S. J. performed DFT calculations; T. C., W. Y and N. X. assisted S. J. and J. T. with data collection; D. W. S. and Y. W. prepared the manuscript and managed the project.

## Data availability

The data supporting this article have been included as part of the ESI.† Deposition numbers 2164107 (2), 2329987 (3), 2329988 (1), 2329989 (8), 2329990 (5), 2329991 (6), 2329992 (4), 2356544 (7), and 2359713 (9) contain the supplementary crystallographic data for this paper.†

## Conflicts of interest

The authors declare no competing financial interests.

## Acknowledgements

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## References

- 1 J. P. Griess and A. W. V. Hofmann, XVIII. On a new series of bodies in which nitrogen is substituted for hydrogen, *Philos. Trans. R. Soc. London*, 1864, **154**, 667–731.
- 2 J. P. Griess and A. W. V. Hofmann, XX. On a new class of compounds in which nitrogen is substituted for hydrogen, *Proc. R. Soc. London*, 1864, **13**, 375–384.
- 3 E. F. V. Scriven and K. Turnbull, Azides: their preparation and synthetic uses, *Chem. Rev.*, 1988, **88**, 297–368.
- 4 L.-H. Liu and M. Yan, Perfluorophenyl Azides: New Applications in Surface Functionalization and Nanomaterial Synthesis, *Acc. Chem. Res.*, 2010, **43**, 1434–1443.
- 5 C. Wentrup, Flash Vacuum Pyrolysis of Azides, Triazoles, and Tetrazoles, *Chem. Rev.*, 2017, **117**, 4562–4623.
- 6 J. C. Jewett and C. R. Bertozzi, Cu-free click cycloaddition reactions in chemical biology, *Chem. Soc. Rev.*, 2010, **39**, 1272–1279.
- 7 P. Thirumurugan, D. Matosiuk and K. Jozwiak, Click Chemistry for Drug Development and Diverse Chemical-Biology Applications, *Chem. Rev.*, 2013, **113**, 4905–4979.
- 8 G. C. Tron, T. Pirali, R. A. Billington, P. L. Canonico, G. Sorba and A. A. Genazzani, Click chemistry reactions in medicinal chemistry: Applications of the 1,3-dipolar cycloaddition between azides and alkynes, *Med. Res. Rev.*, 2008, **28**, 278–308.
- 9 J. Lahann, *Click chemistry for biotechnology and materials science*, John Wiley & Sons, 2009.
- 10 M. F. Debets, C. W. J. van der Doelen, F. P. J. T. Rutjes and F. L. van Delft, Azide: A Unique Dipole for Metal-Free Bioorthogonal Ligations, *ChemBioChem*, 2010, **11**, 1168–1184.
- 11 S. Xie, M. Sundhoro, K. N. Houk and M. Yan, Electrophilic Azides for Materials Synthesis and Chemical Biology, *Acc. Chem. Res.*, 2020, **53**, 937–948.
- 12 S. Chiba, Application of Organic Azides for the Synthesis of Nitrogen-Containing Molecules, *Synlett*, 2012, 21–44.
- 13 S. Bräse, C. Gil, K. Knepper and V. Zimmermann, Organic Azides: An Exploding Diversity of a Unique Class of Compounds, *Angew. Chem., Int. Ed.*, 2005, **44**, 5188–5240.
- 14 O. T. O'Sullivan and M. J. Zdzilla, Properties and Promise of Catenated Nitrogen Systems As High-Energy-Density Materials, *Chem. Rev.*, 2020, **120**, 5682–5744.
- 15 I. C. Tornieporth-Oetting and T. M. Klapötke, Covalent Inorganic Azides, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 511–520.
- 16 R. P. Singh, R. D. Verma, D. T. Meshri and J. N. M. Shreeve, Energetic Nitrogen-Rich Salts and Ionic Liquids, *Angew. Chem., Int. Ed.*, 2006, **45**, 3584–3601.
- 17 G. Zhang, G. Chen, J. Li, S. Sun, Y. Luo and X. Li, High Azide Content Hyperbranched Star Copolymer as Energetic Materials, *Ind. Eng. Chem. Res.*, 2018, **57**, 13962–13972.



- 18 Y. Huang, J. Gao, H. Gao, Y. Chen, Y. Zang, J. Sun and C. Zhang, Azide Polyether with a Highly Flexible Main Chain as Energetic Materials, *ACS Appl. Polym. Mater.*, 2023, **5**, 3096–3103.
- 19 P. Portius and M. Davis, Recent developments in the chemistry of homoleptic azido complexes of the main group elements, *Coord. Chem. Rev.*, 2013, **257**, 1011–1025.
- 20 T. M. Klapötke and B. Krumm, Azide-Containing High Energy Materials, in *Organic Azides*, ed. K. B. Stefan Bräse, 2009, pp. 389–411.
- 21 C. Zhang, X. Liu, J. Wang and Q. Ye, A Three-Dimensional Inorganic Analogue of 9,10-Diazido-9,10-Diboraanthracene: A Lewis Superacidic Azido Borane with Reactivity and Stability, *Angew. Chem., Int. Ed.*, 2022, **61**, e202205506.
- 22 L. Zhu and R. Kinjo, Reactions of main group compounds with azides forming organic nitrogen-containing species, *Chem. Soc. Rev.*, 2023, **52**, 5563–5606.
- 23 F. A. Carey and R. J. Sundberg, Structural Effects on Stability and Reactivity, in *Advanced Organic Chemistry: Part A: Structure and Mechanisms*, Springer US, Boston, MA, 2007, pp. 253–388.
- 24 W. Fraenk, T. M. Klapötke, B. Krumm, H. Nöth, M. Suter and M. Warchhold, Oligomeric pentafluorophenylboron azides, *J. Chem. Soc., Dalton Trans.*, 2000, 4635–4638.
- 25 W. Fraenk, T. M. Klapötke, B. Krumm and P. Mayer, Bis (pentafluorophenyl)boron azide: synthesis and structural characterization of the first dimeric boron azide, *Chem. Commun.*, 2000, 667–668.
- 26 W. Fraenk and T. M. Klapötke, Theoretical studies on the thermodynamic stability and trimerization of  $\text{BF}_2\text{N}_3$ , *J. Fluorine Chem.*, 2001, **111**, 45–47.
- 27 M. F. Lappert and H. Pyszora, Pseudohalides of Group IIIB and IVB Elements, in *Advances in Inorganic Chemistry and Radiochemistry*, ed. H. J. Emeléus and A. G. Sharpe, Academic Press, 1966, vol. 9, pp. 133–184.
- 28 F. Lindl, F. Fantuzzi, L. Mailänder, C. Hörl, G. Bélanger-Chabot and H. Braunschweig, Azidoborolate anions and azidoborole adducts: isolable forms of an unstable borole azide, *Chem. Commun.*, 2022, **58**, 4735–4738.
- 29 A. K. Swarnakar, C. Hering-Junghans, K. Nagata, M. J. Ferguson, R. McDonald, N. Tokitoh and E. Rivard, Encapsulating Inorganic Acetylene, HBNH, Using Flanking Coordinative Interactions, *Angew. Chem., Int. Ed.*, 2015, **54**, 10666–10669.
- 30 A. K. Swarnakar, C. Hering-Junghans, M. J. Ferguson, R. McDonald and E. Rivard, Reactivity of a coordinated inorganic acetylene unit, HBNH, and the azidoborane cation  $[\text{HB}(\text{N}_3)]^+$ , *Chem. Sci.*, 2017, **8**, 2337–2343.
- 31 E. Merling, V. Lamm, S. J. Geib, E. Lacôte and D. P. Curran,  $[3 + 2]$ -Dipolar Cycloaddition Reactions of an N-Heterocyclic Carbene Boryl Azide, *Org. Lett.*, 2012, **14**, 2690–2693.
- 32 P. I. Paetzold, Beiträge zur Chemie der Bor-Azide. I. Zur Kenntnis von Dichlorborazid, *Z. Anorg. Allg. Chem.*, 1963, **326**, 47–52.
- 33 P. I. Paetzold, M. Gayoso and K. Dehnicke, Darstellung, Eigenschaften und Schwingungsspektren der trimeren Bordihalogenidazide  $(\text{BCl}_2\text{N}_3)_3$  und  $(\text{BBr}_2\text{N}_3)_3$ , *Chem. Ber.*, 1965, **98**, 1173–1180.
- 34 M. Müller, C. Maichle-Mössmer and H. F. Bettinger, BN-Phenanthryne: Cyclotetramerization of an 1,2-Azaborine Derivative, *Angew. Chem., Int. Ed.*, 2014, **53**, 9380–9383.
- 35 S. Biswas, I. M. Oppel and H. F. Bettinger, Synthesis and Structural Characterization of 9-Azido-9-Borafluorene: Monomer and Cyclootrimer of a Borole Azide, *Inorg. Chem.*, 2010, **49**, 4499–4506.
- 36 T. Thiess, G. Bélanger-Chabot, F. Fantuzzi, M. Michel, M. Ernst, B. Engels and H. Braunschweig, Diborane(4) Azides: Surprisingly Stable Sources of Transient Iminoboranes, *Angew. Chem., Int. Ed.*, 2020, **59**, 15480–15486.
- 37 D. Prieschl, G. Bélanger-Chabot, X. Guo, M. Dietz, M. Müller, I. Krummenacher, Z. Lin and H. Braunschweig, Synthesis of Complex Boron–Nitrogen Heterocycles Comprising Borylated Triazenes and Tetrazenes Under Mild Conditions, *J. Am. Chem. Soc.*, 2020, **142**, 1065–1076.
- 38 R. L. Melen, A. J. Lough and D. W. Stephan, Boron azides in Staudinger oxidations and cycloadditions, *Dalton Trans.*, 2013, **42**, 8674–8683.
- 39 R. L. Melen and D. W. Stephan, Cycloaddition reactions between dicyclohexylboron azide and alkynes, *Dalton Trans.*, 2013, **42**, 4795–4798.
- 40 R. L. Melen and D. W. Stephan, Cycloaddition reactions of  $(\text{C}_6\text{F}_5)_2\text{BN}_3$  with dialkyl acetylenedicarboxylates, *Dalton Trans.*, 2015, **44**, 5045–5048.
- 41 T.-T. Liu, J. Chen, B.-T. Guan, Z. Lin and Z.-J. Shi, Distance-Triggered Distinct Aryl Migrations on Azidodiboranes, *Chem. – Eur. J.*, 2023, **29**, e202203676.
- 42 R. Haiges, J. A. Boatz, J. M. Williams and K. O. Christe, Preparation and Characterization of the Binary Group 13 Azides  $\text{M}(\text{N}_3)_3$  and  $\text{M}(\text{N}_3)_3\cdot\text{CH}_3\text{CN}$  ( $\text{M}=\text{Ga}$ ,  $\text{In}$ ,  $\text{Tl}$ ),  $[\text{Ga}(\text{N}_3)_5]^{2-}$ , and  $[\text{M}(\text{N}_3)_6]^{3-}$  ( $\text{M}=\text{In}$ ,  $\text{Tl}$ ), *Angew. Chem., Int. Ed.*, 2011, **50**, 8828–8833.
- 43 N. Emig, F. P. Gabbaï, H. Krautscheid, R. Réau and G. Bertrand, The Azide-Nitrilimine Analogy in Aluminum Chemistry, *Angew. Chem., Int. Ed.*, 1998, **37**, 989–992.
- 44 J. D. Queen, S. Irvankoski, J. C. Fettinger, H. M. Tuononen and P. P. Power, A Monomeric Aluminum Imide (Iminoalane) with Al–N Triple-Bonding: Bonding Analysis and Dispersion Energy Stabilization, *J. Am. Chem. Soc.*, 2021, **143**, 6351–6356.
- 45 W. Uhl, R. Gerding, S. Pohl and W. Saak, Reaktionen von  $\text{R}_2\text{Al-AlR}_2$  ( $\text{R}=\text{CH}(\text{SiMe}_3)_2$ ) mit Trimethylsilylazid—Insertion in die Al–Al-Bindung und Abbau zum trimeren Dialkylaluminiumazid, *Chem. Ber.*, 1995, **128**, 81–85.
- 46 R. A. Fischer, A. Miehr, H. Sussek, H. Pritzkow, E. Herdtweck, J. Müller, O. Ambacher and T. Metzger, Structures of  $(\text{C}_5\text{H}_5\text{N})_3\text{Al}(\text{N}_3)_3$ ,  $[\text{Me}_2\text{N}(\text{CH}_2)_3]_2\text{Al}(\text{N}_3)$  and  $\text{Me}_2(\text{N}_3)\text{Al}(\text{H}_2\text{NBut})$ . Low-temperature OMVPE of AlN in the absence of ammonia, *Chem. Commun.*, 1996, 2685–2686.



- 47 J. Müller and K. Dehnicke, Darstellung, eigenschaften und schwingungsspektren von dialkylmetall-aziden der elemente aluminum, gallium, indium und thallium, *J. Organomet. Chem.*, 1968, **12**, 37–47.
- 48 K. Haraguchi, Y. Kubota and H. Tanaka, Ring Opening of Nucleoside 1',2'-Epoxides with Organoaluminum Reagents: Stereoselective Entry to Ribonucleosides Branched at the Anomeric Position, *J. Org. Chem.*, 2004, **69**, 1831–1836.
- 49 H. L. Ricks-Laskoski, B. L. Chaloux, S. M. Deese, M. Laskoski, J. B. Miller, M. A. Buckley, J. W. Baldwin, M. A. Hickner, K. M. Saunders and C. M. Christensen, Tetrazolization of Side Chains and Anhydrous Conductivity in a Hydrophobic Polymer, *Macromolecules*, 2014, **47**, 4243–4250.
- 50 S. Monticelli and V. Pace, Diethylaluminium Azide: A Versatile Reagent in Organic Synthesis, *Aust. J. Chem.*, 2015, **68**, 703–706.
- 51 V. Aureggi and G. Sedelmeier, 1,3-Dipolar Cycloaddition: Click Chemistry for the Synthesis of 5-Substituted Tetrazoles from Organoaluminum Azides and Nitriles, *Angew. Chem., Int. Ed.*, 2007, **46**, 8440–8444.
- 52 V. H. Rawal and H. M. Zhong, One-step conversion of esters to acyl azides using diethylaluminum azide, *Tetrahedron Lett.*, 1994, **35**, 4947–4950.
- 53 J. M. Blackwell, W. E. Piers and M. Parvez, Mechanistic Studies on Selectivity in the  $B(C_6F_5)_3$ -Catalyzed Allylstannation of Aldehydes: Is Hypercoordination at Boron Responsible?, *Org. Lett.*, 2000, **2**, 695–698.
- 54 W. E. Piers, The chemistry of perfluoroaryl boranes, *Adv. Organomet. Chem.*, 2005, **52**, 1–76.
- 55 T. Beringhelli, D. Donghi, D. Maggioni and G. D'Alfonso, Solution structure, dynamics and speciation of perfluoroaryl boranes through  $^1H$ ,  $^{11}B$  and  $^{19}F$  NMR spectroscopy, *Coord. Chem. Rev.*, 2008, **252**, 2292–2313.
- 56 D. Volz, T. Baumann, H. Flügge, M. Mydlak, T. Grab, M. Bächle, C. Barner-Kowollik and S. Bräse, Auto-catalysed crosslinking for next-generation OLED-design, *J. Mater. Chem.*, 2012, **22**, 20786–20790.
- 57 K. Bläsing, J. Bresien, R. Labbow, D. Michalik, A. Schulz, M. Thomas and A. Villinger, Borane Adducts of Hydrazoic Acid and Organic Azides: Intermediates for the Formation of Aminoboranes, *Angew. Chem., Int. Ed.*, 2019, **58**, 6540–6544.
- 58 K. Bläsing, J. Bresien, S. Maurer, A. Schulz and A. Villinger, Trimethylsilyl Pseudohalide Adducts of  $GaCl_3$  and  $B(C_6F_5)_3$ , *Eur. J. Inorg. Chem.*, 2021, **2021**, 1913–1920.
- 59 M. R. Elsbey and S. A. Johnson, Nickel-Catalyzed C–H Silylation of Arenes with Vinylsilanes: Rapid and Reversible  $\beta$ -Si Elimination, *J. Am. Chem. Soc.*, 2017, **139**, 9401–9407.
- 60 M. Mewald, R. Fröhlich and M. Oestreich, An Axially Chiral, Electron-Deficient Borane: Synthesis, Coordination Chemistry, Lewis Acidity, and Reactivity, *Chem. – Eur. J.*, 2011, **17**, 9406–9414.
- 61 K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy and J. A. Boatz, On a quantitative scale for Lewis acidity and recent progress in polynitrogen chemistry, *J. Fluorine Chem.*, 2000, **101**, 151–153.
- 62 H. Böhrer, N. Trapp, D. Himmel, M. Schleep and I. Krossing, From unsuccessful  $H_2$ -activation with FLPs containing  $B(Ohfip)_3$  to a systematic evaluation of the Lewis acidity of 33 Lewis acids based on fluoride, chloride, hydride and methyl ion affinities, *Dalton Trans.*, 2015, **44**, 7489–7499.
- 63 L. Greb, Lewis Superacids: Classifications, Candidates, and Applications, *Chem. – Eur. J.*, 2018, **24**, 17881–17896.

