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# The Monomeric Alanediyyl :AlAr<sup>iPr8</sup> (Ar<sup>iPr8</sup> = C<sub>6</sub>H-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>i</sup>)<sub>2</sub>-3,5-Pr<sup>i</sup>)<sub>2</sub>): An Organoaluminum(I) Compound with a One-Coordinate Aluminum Atom

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**ABSTRACT:** Reduction of the aluminum iodide AlI<sub>2</sub>Ar<sup>iPr8</sup> (**1**; Ar<sup>iPr8</sup> = C<sub>6</sub>H-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>i</sup>)<sub>2</sub>-3,5-Pr<sup>i</sup>) with 5% w/w Na/NaCl in hexanes gave a dark red solution from which the monomeric alanediyyl :AlAr<sup>iPr8</sup> (**2**) was isolated in ca. 28% yield as yellow-orange crystals. Compounds **1** and **2** were characterized by X-ray crystallography, electronic and NMR spectroscopy, and theoretical calculations. The Al atom in **2** is one-coordinate, and the compound displays two absorptions in its electronic spectrum at 354 and 455 nm. It reacts with H<sub>2</sub> under ambient conditions to give the aluminum hydride {AlH(μ-H)Ar<sup>iPr8</sup>}<sub>2</sub>, probably via a weakly bound dimer of **2** as an intermediate.

The chemistry of the group 13 elements is largely defined by the increasing stability of the +1 oxidation state as the group is descended from B to Tl.<sup>1</sup> For aluminum, low-oxidation-state compounds have generated much interest,<sup>2–11</sup> but they are more challenging to isolate in comparison to those of the other group 13 metals because of their higher reactivity and tendency to disproportionate.<sup>2</sup> The isolation of the landmark Al<sup>II</sup> compound R<sub>2</sub>Al-ALR<sub>2</sub> (R = -CH(SiMe<sub>3</sub>)<sub>2</sub>), the first Al–Al bonded molecular species, by Uhl<sup>12</sup> in 1988, and of the first organo Al<sup>I</sup> species Al<sub>4</sub>Cp\*<sub>4</sub> (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) by Schnöckel and co-workers<sup>13</sup> in 1991 as well as the icosahedral cluster K<sub>2</sub>[Al<sub>12</sub>Bu<sub>12</sub>]<sup>14</sup> were major breakthroughs. Continued advancement has been made via the synthesis of further Al<sub>4</sub>R<sub>4</sub> derivatives (R = alkyl, silyl, amide),<sup>15–18</sup> of dialuminenes RAl = ALR (R = large *m*-terphenyl, aryl, or silyl groups), which were trapped either as their cycloaddition products with aromatic species<sup>19,20</sup> or stabilized and isolated by complexation with NHC ligands,<sup>21,22</sup> and of the monomeric β-diketiminato complexes :Al(D<sup>iPr8</sup>Nacnac) (D<sup>iPr8</sup>Nacnac = [R{C=N(2,6-C<sub>6</sub>H<sub>3</sub>-iPr<sub>2</sub>)<sub>2</sub>}]<sub>2</sub>, R = CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>).<sup>23,24</sup>

Several anionic low-oxidation-state Al complexes have also been reported, such as the dialuminyne<sup>25</sup> Na<sub>2</sub>(AlAr<sup>iPr4</sup>)<sub>2</sub> (oxidation state Al<sup>0</sup>; Ar<sup>iPr4</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup>)<sub>2</sub>) with a nonclassical Al–Al triple bond and the metalloaromatic cycloalane Na<sub>2</sub>(AlAr<sup>Me6</sup>)<sub>3</sub> (oxidation state Al<sup>0.33</sup>; Ar<sup>Me6</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>)<sub>2</sub>), which are analogous to the corresponding Ga complexes Na<sub>2</sub>(GaAr<sup>iPr6</sup>)<sub>2</sub> (Ar<sup>iPr6</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>i</sup>)<sub>2</sub>) and Na<sub>2</sub>(GaAr<sup>Me6</sup>)<sub>3</sub> of Robinson and co-workers.<sup>26,27</sup> Treatment of the dialanes Trip<sub>2</sub>AlAlTrip<sub>2</sub> (Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>i</sup>)<sub>2</sub> and R<sub>2</sub>AlAIR<sub>2</sub> (R = CH(SiMe<sub>3</sub>)<sub>2</sub>) with alkali metals in donor solvents gave the radical anion complexes [Li(TMEDA)<sub>2</sub>][Trip<sub>2</sub>AlAlTrip<sub>2</sub>]<sup>28</sup> [Li(TMEDA)<sub>2</sub>][R<sub>2</sub>AlAIR<sub>2</sub>]<sup>29</sup> (TMEDA = *N,N,N',N'*-tetramethylethane-1,2-diamine), and [K(DME)<sub>3</sub>][R<sub>2</sub>AlAIR<sub>2</sub>]<sup>30</sup> (DME = 1,2-dimethoxyethane) with Al–Al bond orders of 1.5. The chelating NON/NON<sup>Dipp</sup> scaffolds (NON = 4,5-bis(2,6-

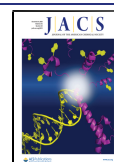
diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene; NON<sup>Dipp</sup> = O(SiMe<sub>2</sub>NDipp)<sub>2</sub>; Dipp = C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup>)<sub>2</sub>)<sup>31,32</sup> also stabilize the Al<sup>I</sup> compounds [KAl(NON)]<sub>2</sub> or [KAl(NON<sup>Dipp</sup>)]<sub>2</sub>, and the structurally related [KAl{N(Dipp)<sub>2</sub>-SiMe<sub>2</sub>CH<sub>2</sub>}<sub>2</sub>]<sub>2</sub> has also been reported.<sup>33</sup> In addition alkyl or alkyl amino ligands stabilize the cyclic Al<sup>I</sup> salts [K(toluenes)]<sub>2</sub>-[AlC(SiMe<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>]<sup>34</sup> and [K(12-crown-4)-[AlN(Ad)CHCHC(SiMe<sub>3</sub>)<sub>2</sub>]].<sup>35</sup> These “aluminum” complexes have nucleophilic Al centers that display a diverse reaction chemistry.<sup>36</sup>

Despite these advances, monomeric compounds of Al<sup>I</sup> remain especially rare, with the only well-characterized examples being the aforementioned :Al(D<sup>iPr8</sup>Nacnac) and the more recently reported :Al<sup>3t</sup>Cp (3tCp = C<sub>5</sub>H<sub>2</sub>-1,2,4-<sup>t</sup>Bu<sub>3</sub>),<sup>37</sup> although Al<sub>4</sub>Cp\*<sub>4</sub> had been shown earlier to dissociate into :AlCp\* monomers at elevated temperature.<sup>38</sup> Wiberg and co-workers have also shown that the dialane R<sub>2</sub>AlAIR<sub>2</sub> (R = Si<sup>t</sup>Bu<sub>3</sub>) dissociates into R<sub>2</sub>Al\* radicals upon heating to 50 °C.<sup>39,40</sup> These compounds have a rich chemistry<sup>5,6</sup> that involves oxidative additions,<sup>41</sup> reversible olefin coordination,<sup>42</sup> C–F and C–H bond activation,<sup>42,43</sup> and C–C bond coupling.<sup>44,45</sup>

However, no compound containing a singly coordinated Al atom has been isolated. A common theme among the low-oxidation-state aluminum compounds has been the use of chelating or π-bonding ligands to stabilize the reactive Al center. Although AlH and the monohalides AlX (X = F, Cl, Br, I) have been studied, they are only observed in the gas phase at high temperature and low pressure,<sup>46</sup> or as metastable

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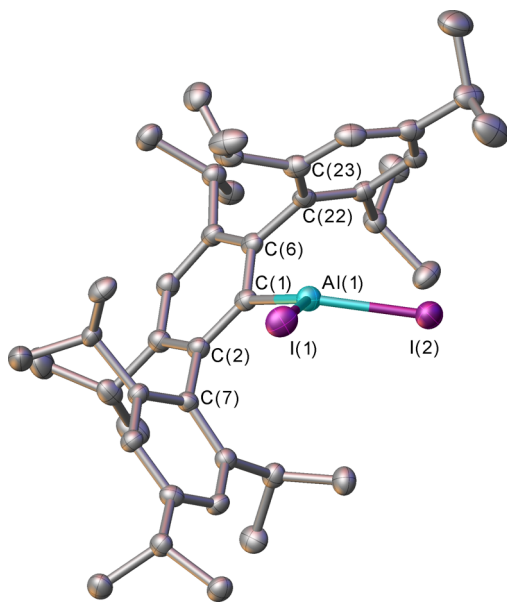
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solutions when condensed in toluene/ether at cryogenic temperatures.<sup>47,48</sup> Driess and co-workers characterized an AlBr moiety using a push–pull strategy by coordination of one Fe(CO)<sub>4</sub> and two NHC ligands to the Al atom.<sup>49</sup> Recently Braunschweig and co-workers characterized monomeric AlH trapped by two cyclic (alkyl)(amino)carbene (CAAC) ligands,<sup>50</sup> although a non-negligible resonance structure (36%) involving an Al(III) diradical centered on the two CAAC ligands contributes to its stability.

Our group has shown that the use of sterically demanding terphenyl ligands allowed the structural characterization of one-coordinate univalent compounds of Ga,<sup>51</sup> In,<sup>52</sup> and Tl<sup>53</sup> and transition-metal M(I) (M = Mn, Fe, Co) fragments, which form coordination complexes with arenes.<sup>54,55</sup> These results suggested that a similar stabilization of a one-coordinate compound of Al was feasible. However, numerous attempts to isolate such a compound via a reduction of aryl aluminum dihalides were unsuccessful owing to the extreme reactivity of the reduced aluminum species. We turned to the use of the extremely sterically crowding terphenyl ligand Ar<sup>iPr8</sup> (Ar<sup>iPr8</sup> = C<sub>6</sub>H-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>t</sup>)<sub>2</sub>-3,5-Pr<sup>t</sup>) in combination with the reducing agent Na/NaCl, which, upon reduction of the precursor AlI<sub>2</sub>Ar<sup>iPr8</sup>, afforded the monomeric alanedyl :AlAr<sup>iPr8</sup> containing a one-coordinate aluminum atom.

The precursor aluminum iodide **1** (Figure 1) was prepared by treatment of the corresponding trihydridoaluminate salt



**Figure 1.** Thermal ellipsoid plot (50%) of AlI<sub>2</sub>Ar<sup>iPr8</sup> (**1**). Hydrogen atoms are not shown. Selected distances (Å) and angles (deg): Al(1)–I(1): 2.5125(18) Al(1)–I(2): 2.4840(18), Al(1)–C(1): 1.9653(57), Al(1)···C(7): 3.347(5) Al(1)···C(22): 2.745(5), Al(1)···C(23): 2.766(6), I(1)–Al(1)–I(2): 103.88(6), C(1)–Al(1)–I(1): 124.85(17), C(1)–Al(1)–I(2): 127.80(17), Al(1)–C(1)–C(2): 128.48(40), Al(1)–C(1)–C(6): 110.89(39).

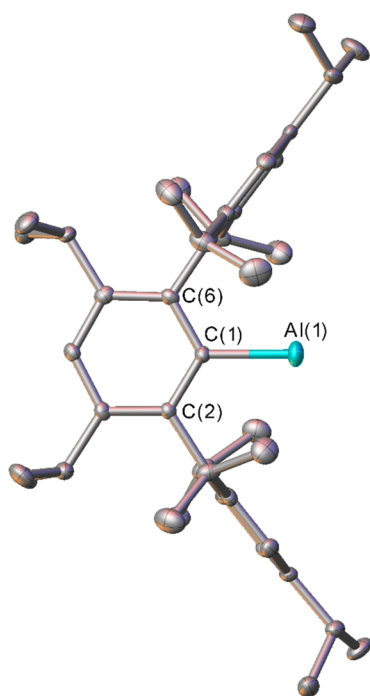
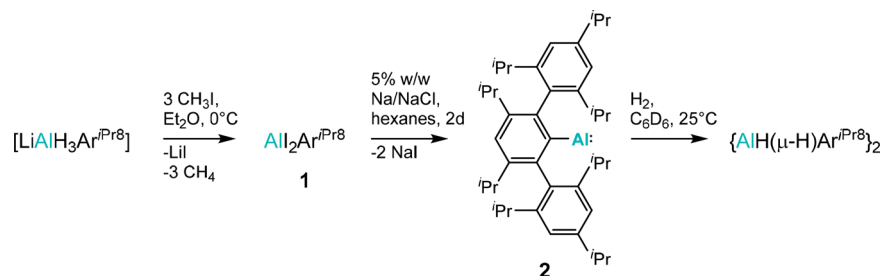
[LiAlH<sub>3</sub>Ar<sup>iPr8</sup>]<sup>56</sup> with an excess of methyl iodide in diethyl ether at 0 °C (Scheme 1). Crystallization from hexanes gave **1** as colorless blocks in 91% yield. Compound **1** is an uncommon example of a three-coordinate monomeric aluminum(III) halide.<sup>57,58</sup> The coordination environment of the Al atom is slightly pyramidalized (sum of the interligand angles at Al = 356.5(4)°), and the sterically demanding ligand prevents

dimerization or the coordination of Et<sub>2</sub>O solvent that is normally seen for similar compounds.<sup>59</sup> One of the flanking phenyl rings is bent toward the Al atom (Al–C(1)–C(6) = 110.89(39)° vs Al–C(1)–C(2) = 128.45(40)°, and two of the Al···C<sub>(ring)</sub> distances (Al–C(22) = 2.745(5) Å, Al–C(23) = 2.766(6) Å) are the closest Al···C approaches, indicating a weak attraction between the electron-rich  $\pi$ -system and the Lewis acidic Al atom. These are, however, much longer than, for example, the Al–C distances in Al<sub>4</sub>Cp\*<sub>4</sub> (Al–C = 2.29(1)–2.38(1) Å)<sup>13</sup> and are expected to be very weakly bonding at most.

The unusual monomeric structure of **1** suggested that the Ar<sup>iPr8</sup> ligand could be effective for the stabilization of other low-coordinate Al complexes. Attempts at a reductive dehalogenation of **1** with KC<sub>8</sub> or Na mirrors gave pale yellow-green solutions from which only Ar<sup>iPr8</sup>H could be isolated. A recent report by Jones and co-workers showed that alkali metals supported on their halide salts are effective reagents for the preparation of Mg(I) and Al(I)  $\beta$ -diketiminate complexes,<sup>60</sup> and we chose 5% weight Na on NaCl as a reducing agent for **1**. A hexanes solution of **1** stirred over an excess of freshly prepared Na/NaCl yielded a dark red solution after 2 d. Filtration and removal of the solvent, followed by recrystallization from benzene at ca. 8 °C, gave the compound :AlAr<sup>iPr8</sup> (**2**) as yellow crystals in ca. 28% yield, which were thermally stable up to their melting point of 228–231 °C. Upon isolation and drying under reduced pressure these crystals of **2** darkened to an orange color.

The crystal structure of **2** (Figure 2) revealed two crystallographically independent molecules in which the Al atoms are bound only to the ipso carbon of the central ring of the Ar<sup>iPr8</sup> ligand. The Al–C distances of 1.988(4) and 2.003(4) Å (calculated value 2.023 Å at the PBE1PBE-G3BJ/def2-TZVP level) are only slightly longer than the Al–C single bond in **1**. It crystallizes from benzene in the space group *Pc* and is packed in a head-to-tail fashion (Figure S7 in Supporting Information) preventing any Al–Al bonding in the crystal structure. The long Al···H and Al···C separations for atoms in the nearby methyl groups (>2.9 Å), flanking rings (>3.0 Å), or benzene molecules of crystallization (>4.8 Å) indicate no strong secondary bonding interactions in the crystal structure. An analysis of generalized compliance constants calculated for the optimized structure of **2** supports this conclusion. However, the Quantum Theory of Atoms in Molecules shows a bond path and a bond critical point between the C–H atoms and the aluminum center with very low electron density value of 0.006 e bohr<sup>-3</sup>. An examination of the Natural Bond Orbitals further revealed that the C–H···Al donor–acceptor interactions, calculated at the second-order perturbation level, have a stabilization energy of only 7–8 kJ mol<sup>-1</sup>, that is, considerably less than that typically found for C–H···metal agostic interactions.<sup>61</sup> Thus, **2** is an example of a compound containing a singly coordinated aluminum atom. The Al atom lies almost symmetrically between the two flanking rings, and nearly in the extended plane of the central ring of the terphenyl ligand. This is similar to its Ga congener but not to the related In and Tl compounds :MAr<sup>iPr6</sup> (M = In, Tl),<sup>52,53</sup> where the metal atoms lie 0.23 and 0.28 Å from the extended plane.

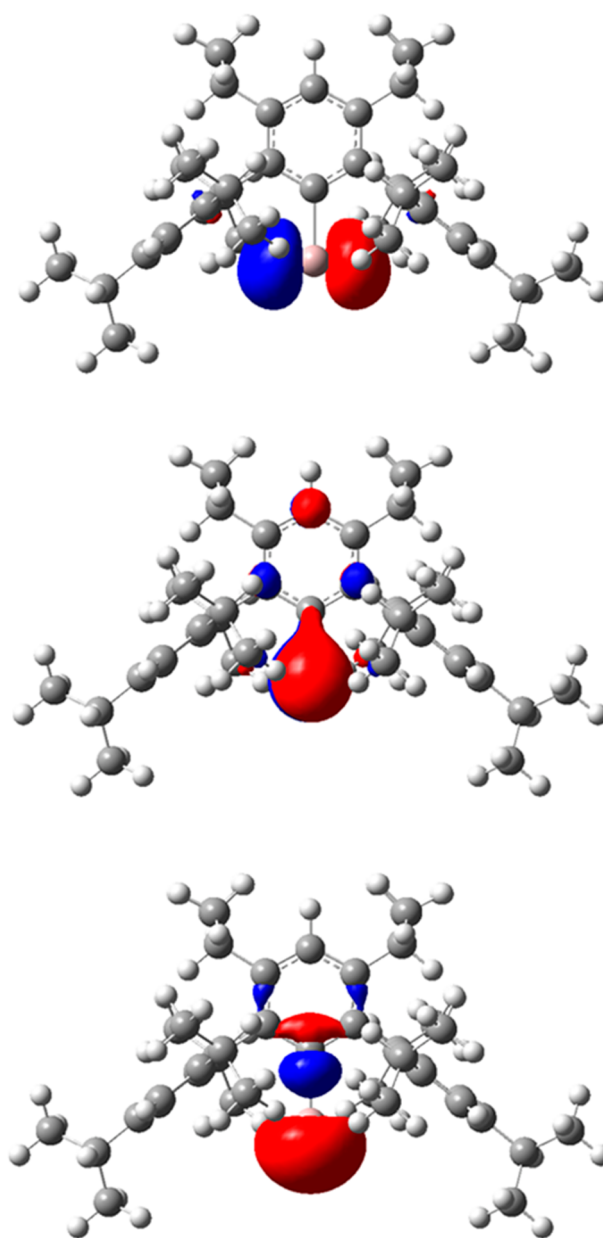
The frontier molecular orbitals of **2** are the n-type highest occupied molecular orbital (HOMO) occupied by the Al nonbonding lone pair, while the lowest unoccupied molecular orbital (LUMO) ( $\pi_{\text{out-of-plane}}$ ) and LUMO+1 ( $\pi_{\text{in-plane}}$ ) orbitals

Scheme 1. Synthesis of Compounds 1 and 2 and the Reaction of 2 with H<sub>2</sub>

**Figure 2.** Thermal ellipsoid plot (50%) of one of the crystallographically independent molecules of :AlAr<sup>iPr8</sup> (2). Hydrogen atoms and solvent benzene molecules are not shown (cf. Figure S7). Selected bond lengths (Å) and angles (deg) {values in braces correspond to the other crystallographically independent molecule of 2}: Al(1)–C(1): 1.9883(36) {2.0028(37)}, Al(1)–C(1)–C(2): 121.29(28) {121.22(29)}, Al(1)–C(1)–C(6): 119.41(30) {119.46(31)} C(2)–C(1)–C(6): 119.27(29) {119.31(31)}.

are mainly composed of the Al 3p orbitals (Figure 3). The electronic spectrum of 2 shows two absorptions at 455 and 354 nm (calculated values 467 and 351 nm), which are responsible for its yellow-orange color. These are calculated to correspond to the lone pair  $n \rightarrow \pi_{\text{out-of-plane}}$  and  $n \rightarrow \pi_{\text{in-plane}}$  transitions, respectively, both of which are symmetry-allowed. The absorptions are slightly lower in energy than those of the gallium congener :GaAr<sup>iPr8</sup> (437 and 351 nm).<sup>51</sup>

Compound 2 was found to react rapidly with H<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>, giving the known compound {AlH(μ-H)Ar<sup>iPr8</sup>}<sub>2</sub>,<sup>56</sup> identified by its <sup>1</sup>H NMR spectrum, in high yield. The facile formation of {AlH(μ-H)Ar<sup>iPr8</sup>}<sub>2</sub> is surprising, considering that its gallium congener :GaAr<sup>iPr8</sup> shows no such reactivity.<sup>62</sup> In contrast, the related digallene Ar<sup>iPr4</sup>GaGaAr<sup>iPr4</sup> readily reacts with H<sub>2</sub> to afford {GaH(μ-H)Ar<sup>iPr4</sup>}<sub>2</sub>, suggesting that the metal–metal bonded dimer Ar<sup>iPr8</sup>AlAlAr<sup>iPr8</sup> is the reactive species in solution. Similar reactivity was seen for the dialuminene-benzene cycloaddition products reported by Tokitoh and co-



**Figure 3.** LUMO+1 (top), LUMO (middle), and HOMO (bottom) of AlAr<sup>iPr8</sup> (2) ( $\pm 0.05$  isovalue).

workers.<sup>63</sup> Upon retro-cycloaddition, free dialuminene is liberated in solution and was further found to react with H<sub>2</sub> to give the corresponding aluminum dihydride product. Inoue and co-workers also demonstrated that H<sub>2</sub> adds to the classical double bond in the dialuminene Trip(NHC)AlAl(NHC)Trip

to give the dialane Trip(NHC)HAl-AIH(NHC)Trip.<sup>22</sup> Analysis of the frontier orbitals of **2** indicates that its direct reactivity with H<sub>2</sub> is likely to involve a very high-energy transition state, and all attempts to follow this reaction path computationally were met with steep increases in energy with no identifiable transition state. Consequently, a weak association of 2 equiv of **2** to form the corresponding dialuminene could be crucial for the observed reactivity by lowering the activation energy. Calculations probing the energetics of this process indicated that dimerization of **2** is energetically slightly favored ( $\Delta G = -20 \text{ kJ mol}^{-1}$ ) in the gas phase. Thus, a judicious choice of solvent may allow the characterization of the dialuminene Ar<sup>iPr8</sup>AlAlAr<sup>iPr8</sup>.

In conclusion, we have isolated the monomeric alanediyli :AlAr<sup>iPr8</sup> (**2**) containing a one-coordinate aluminum atom by reduction of the precursor arylaluminum diiodide AlI<sub>2</sub>Ar<sup>iPr8</sup> (**1**) with excess 5% w/w Na/NaCl in hexanes. Two absorbances at 455 and 354 nm in the electronic spectrum of **2** correspond to the Al lone pair  $n \rightarrow \pi_{\text{out-of-plane}}$  and  $n \rightarrow \pi_{\text{in-plane}}$  transitions. Compound **2** appears to have good thermal stability and reacts with H<sub>2</sub> to give the aluminum hydride complex {AlH( $\mu$ -H)Ar<sup>iPr8</sup>}<sub>2</sub> in contrast with its heavier congener :GaAr<sup>iPr8</sup>. Further reactivity studies of **2** with small molecules and the preparation of other low-coordinate aluminum complexes are in hand along with computational investigations of the mechanisms involved.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c10222>.

Experimental details for compounds **1** and **2**, NMR and electronic spectral data, and computational details (PDF)

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### Notes

The authors declare no competing financial interest.

CCDC 2026033–2026034 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](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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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## REFERENCES

- (1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.
- (2) Aldridge, S.; Downs, A. J. *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*; Wiley: Chichester, UK, 2011.
- (3) Downs, A. J. Recent Advances in the Chemistry of the Group 13 Metals: Hydride Derivatives and Compounds Involving Multiply Bonded Group 13 Metal Atoms. *Coord. Chem. Rev.* **1999**, *189*, 59–100.
- (4) Bag, P.; Weetman, C.; Inoue, S. Experimental Realisation of Elusive Multiple-Bonded Aluminium Compounds: A New Horizon in Aluminium Chemistry. *Angew. Chem., Int. Ed.* **2018**, *57*, 14394–14413.
- (5) Roesky, H. W.; Kumar, S. S. Chemistry of Aluminium(I). *Chem. Commun.* **2005**, 4027–4038.
- (6) Zhong, M.; Sinhababu, S.; Roesky, H. W. The Unique  $\beta$ -Diketiminato Ligand in Aluminum(I) and Gallium(I) Chemistry. *Dalton Trans.* **2020**, *49*, 1351–1364.
- (7) Wang, Y.; Robinson, G. H. Unique Homonuclear Multiple Bonding in Main Group Compounds. *Chem. Commun.* **2009**, 5201–5213.
- (8) Wang, Y.; Robinson, G. H. Organometallics of the Group 13 M–M Bond (M = Al, Ga, In) and the Concept of Metalloaromaticity. *Organometallics* **2007**, *26*, 2–11.
- (9) Robinson, G. H. Multiple Bonds Involving Aluminum and Gallium Atoms. *Adv. Organomet. Chem.* **2001**, *47*, 283–294.
- (10) (a) Brothers, P. J.; Power, P. P. Multiple Bonding Involving the Heavier Main Group 3 Elements. *Adv. Organomet. Chem.* **1996**, *39*, 1–69. (b) Power, P. P. Multiple Bonding Between Heavier Group 13 Elements. *Struct. Bonding (Berlin, Ger.)* **2002**, *103*, 57–84.
- (11) Hobson, K.; Carmalt, C. J.; Bakewell, C. Recent Advances in Low Oxidation State Aluminium Chemistry. *Chem. Sci.* **2020**, *11*, 6942–6956.
- (12) Uhl, W. Tetrakis[Bis(Trimethylsilyl)methyl]Dialan(4), Eine Verbindung Mit Aluminium–Aluminium-Bindung. *Z. Naturforsch., B: J. Chem. Sci.* **1988**, *43*, 1113–1118.
- (13) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. The Tetrameric Aluminum(I) Compound [ $\{\text{Al}(\eta^5\text{-C}_5\text{Me}_5)\}_4$ ]. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564–565.
- (14) Klinkhammer, K.-W.; Uhl, W.; Wagner, J.; Hiller, W. K<sub>2</sub>[Al<sub>12</sub>iBu<sub>12</sub>], a Compound with Al<sub>12</sub> Icosahedra. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 179–180.
- (15) Purath, A.; Dohmeier, C.; Ecker, A.; Schnöckel, H.; Amelunxen, K.; Passler, T.; Wiberg, N. Synthesis and Crystal Structure of the Tetraaluminatetrahedrane Al<sub>4</sub>[Si(t-Bu)<sub>3</sub>]<sub>4</sub>, the Second Al<sub>4</sub>R<sub>4</sub> Compound. *Organometallics* **1998**, *17*, 1894–1896.

- (16) Purath, A.; Schnöckel, H. Tetrakis[Tris(Trimethylsilyl)-Silylaluminum(I)]  $Al_4[Si(SiMe_3)_3]_4$ —Eine Siliziumreiche Verbindung Mit Zentralem Tetraedrischem  $Al_4$ -Kern. *J. Organomet. Chem.* **1999**, *579*, 373–375.
- (17) 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.
- (18) Schmitter, C.; Roesky, H. W.; Röpken, C.; Herbst-Imer, R.; Schmidt, H.-G.; Noltemeyer, M. The Behavior of  $[RALX_2 \cdot THF]$  Compounds under Reductive Conditions: Tetrakis[Tris-(Trimethylsilyl)methylaluminum(I)]—A Neutral Aluminum(I) Compound with  $\sigma$ -Bound Alkyl Groups and a Tetrahedral Structure. *Angew. Chem., Int. Ed.* **1998**, *37*, 1952–1955.
- (19) Wright, R. J.; Phillips, A. D.; Power, P. P. The  $[2 + 4]$  Diels–Alder Cycloaddition Product of a Probable Dialuminene,  $Ar'AlAlAr'$  ( $Ar' = C_6H_3-2,6-Dipp_2$ ;  $Dipp = C_6H_3-2,6-Pr_2^t$ ), with Toluene. *J. Am. Chem. Soc.* **2003**, *125*, 10784–10785.
- (20) Agou, T.; Nagata, K.; Tokitoh, N. Synthesis of a Dialumene-Benzene Adduct and Its Reactivity as a Synthetic Equivalent of a Dialumene. *Angew. Chem., Int. Ed.* **2013**, *52*, 10818–10821.
- (21) Bag, P.; Porzelt, A.; Altmann, P. J.; Inoue, S. A Stable Neutral Compound with an Aluminum–Aluminum Double Bond. *J. Am. Chem. Soc.* **2017**, *139*, 14384–14387.
- (22) Weetman, C.; Porzelt, A.; Bag, P.; Hanusch, F.; Inoue, S. Dialumenes – Aryl vs. Silyl Stabilization for Small Molecule Activation and Catalysis. *Chem. Sci.* **2020**, *11*, 4817–4827.
- (23) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. Synthesis and Structure of a Monomeric Aluminum(I) Compound  $[\{HC(CMeNAr)_2\}Al]$  ( $Ar = 2,6-iPr_2C_6H_3$ ): A Stable Aluminum Analogue of a Carbene. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274–4276.
- (24) Li, X.; Cheng, X.; Song, H.; Cui, C. Synthesis of  $HC[(CBut)(NAr)]_2Al$  ( $Ar = 2,6-Pr_2C_6H_3$ ) and Its Reaction with Isocyanides, a Bulky Azide, and  $H_2O$ . *Organometallics* **2007**, *26*, 1039–1043.
- (25) Wright, R. J.; Brynda, M.; Power, P. P. Synthesis and Structure of the “Dialuminyne”  $Na_2[Ar'AlAlAr']$  and  $Na_2[(Ar'Al)_3]$ : Al–Al Bonding in  $Al_2Na_2$  and  $Al_3Na_2$  Clusters. *Angew. Chem., Int. Ed.* **2006**, *45*, 5953–5956.
- (26) Su, J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. How Short Is a Ga–Ga Triple Bond? Synthesis and Molecular Structure of  $Na_2[Mes^*_2C_6H_3-Ga-Ga-C_6H_3Mes^*_2]$  ( $Mes^* = 2,4,6-i-Pr_3C_6H_2$ ): The First Gallyne. *J. Am. Chem. Soc.* **1997**, *119*, 5471–5472.
- (27) Li, X.-W.; Pennington, W. T.; Robinson, G. H. Metallic System with Aromatic Character. Synthesis and Molecular Structure of  $Na_2[(2,4,6-Me_3C_6H_2)_2C_6H_3Ga]_3$  The First Cyclogallane. *J. Am. Chem. Soc.* **1995**, *117*, 7578–7579.
- (28) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. Reduction of a Tetraaryldialane to Generate Al–Al  $\pi$ -Bonding. *Inorg. Chem.* **1993**, *32*, 2983–2984.
- (29) Pluta, C.; Pörschke, K.-R.; Krüger, C.; Hildenbrand, K. An Al–Al One-Electron  $\pi$  Bond. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 388–390.
- (30) Uhl, W. Organoelement Compounds with Al–Al, Ga–Ga, and In–In Bonds. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386–1397.
- (31) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. Synthesis, Structure and Reaction Chemistry of a Nucleophilic Aluminyl Anion. *Nature* **2018**, *557*, 92–95.
- (32) Schwamm, R. J.; Anker, M. D.; Lein, M.; Coles, M. P. Reduction vs. Addition: The Reaction of an Aluminyl Anion with 1,3,5,7-Cyclooctatetraene. *Angew. Chem., Int. Ed.* **2019**, *58*, 1489–1493.
- (33) Schwamm, R. J.; Coles, M. P.; Hill, M. S.; Mahon, M. F.; McMullin, C. L.; Rajabi, N. A.; Wilson, A. S. S. A Stable Calcium Aluminyl. *Angew. Chem., Int. Ed.* **2020**, *59*, 3928–3932.
- (34) Kurumada, S.; Takamori, S.; Yamashita, M. An Alkyl-Substituted Aluminium Anion with Strong Basicity and Nucleophilicity. *Nat. Chem.* **2020**, *12*, 36–39.
- (35) Koshino, K.; Kinjo, R. Construction of  $\sigma$ -Aromatic  $AlB_2$  Ring via Borane Coupling with a Dicoordinate Cyclic (Alkyl)(Amino)-Aluminyl Anion. *J. Am. Chem. Soc.* **2020**, *142*, 9057–9062.
- (36) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. The Aluminyl Anion: A New Generation of Aluminium Nucleophile. *Angew. Chem., Int. Ed.* **2020**, *59*, 2–14.
- (37) Hofmann, A.; Tröster, T.; Kupfer, T.; Braunschweig, H. Monomeric  $Cp^3Al(I)$ : Synthesis, Reactivity, and the Concept of Valence Isomerism. *Chem. Sci.* **2019**, *10*, 3421–3428.
- (38) Sitzmann, H.; Lappert, M. F.; Dohmeier, C.; Üffing, C.; Schnöckel, H. Cyclopentadienyl-derivate von Aluminium(I). *J. Organomet. Chem.* **1998**, *561*, 203–208.
- (39) Wiberg, N.; Amelunxen, K.; Blank, T.; Nöth, H.; Knizek, J. Tetrasupersilyldialuminum  $[(t-Bu)_3Si]_2Al-Al[Si(t-Bu)_3]_2$ : The Dialane(4) with the Longest Al–Al Bond to Date. *Organometallics* **1998**, *17*, 5431–5433.
- (40) Wiberg, N.; Blank, T.; Kaim, W.; Schwederski, B.; Linti, G. Tri(Supersilyl)Dialanyl  $(tBu_3Si)_3Al_2$  and Tetra(Supersilyl)-Cyclotrialanyl  $(tBu_3Si)_4Al_3$  – New Stable Radicals of a Group 13 Element from Thermolysis of  $(tBu_3Si)_4Al_2$ . *Eur. J. Inorg. Chem.* **2000**, *2000*, 1475–1481.
- (41) Chu, T.; Korobkov, I.; Nikonov, G. I. Oxidative Addition of  $\sigma$  Bonds to an Al(I) Center. *J. Am. Chem. Soc.* **2014**, *136*, 9195–9202.
- (42) Bakewell, C.; White, A. J. P.; Crimmin, M. R. Reversible Alkene Binding and Allylic C–H Activation with an Aluminium(I) Complex. *Chem. Sci.* **2019**, *10*, 2452–2458.
- (43) Bakewell, C.; White, A. J. P.; Crimmin, M. R. Reactions of Fluoroalkenes with an Aluminium(I) Complex. *Angew. Chem., Int. Ed.* **2018**, *57*, 6638–6642.
- (44) Urwin, S. J.; Nichol, G. S.; Cowley, M. J. Aluminium-Mediated Carbon–Carbon Coupling of an Isonitrile. *Chem. Commun.* **2018**, *54*, 378–380.
- (45) Kong, R. Y.; Crimmin, M. R. Reversible Insertion of CO into an Aluminium–Carbon Bond. *Chem. Commun.* **2019**, *55*, 6181–6184.
- (46) Nagendran, S.; Roesky, H. W. The Chemistry of Aluminum(I), Silicon(II), and Germanium(II). *Organometallics* **2008**, *27*, 457–492.
- (47) Tacke, M.; Schnöckel, H. Metastable Aluminum Chloride,  $AlCl$ , as a Solid and in Solution. *Inorg. Chem.* **1989**, *28*, 2895–2896.
- (48) Dohmeier, C.; Loos, D.; Schnöckel, H. Aluminium(I) and Gallium(I) Compounds: Syntheses, Structures, and Reactions. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129–149.
- (49) Tan, G.; Szilvási, T.; Inoue, S.; Blom, B.; Driess, M. An Elusive Hydridoaluminum(I) Complex for Facile C–H and C–O Bond Activation of Ethers and Access to Its Isolable Hydridogallium(I) Analogue: Syntheses, Structures, and Theoretical Studies. *J. Am. Chem. Soc.* **2014**, *136*, 9732–9742.
- (50) Mellerup, S. K.; Cui, Y.; Fantuzzi, F.; Schmid, P.; Goettel, J. T.; Bélanger-Chabot, G.; Arrowsmith, M.; Krummenacher, L.; Ye, Q.; Engel, V.; Engels, B.; Braunschweig, H. Lewis-Base Stabilization of the Parent Al(I) Hydride under Ambient Conditions. *J. Am. Chem. Soc.* **2019**, *141*, 16954–16960.
- (51) Zhu, Z.; Fischer, R. C.; Ellis, B. D.; Rivard, E.; Merrill, W. A.; Olmstead, M. M.; Power, P. P.; Guo, J. D.; Nagase, S.; Pu, L. Synthesis, Characterization and Real Molecule DFT Calculations for Neutral Organogallium(I) Aryl Dimers and Monomers: Weakness of Gallium–Gallium Bonds in Digallenes and Digallynes. *Chem. - Eur. J.* **2009**, *15*, 5263–5272.
- (52) Haubrich, S. T.; Power, P. P. Monomeric  $InC_6H_3-2,6-Trip_2$  ( $Trip = -C_6H_2-2,4,6-i-Pr_3$ ) and Its Manganese Complex  $(\eta^5-C_5H_5)(CO)_2MnInC_6H_3-2,6-Trip_2$ : One-Coordinate Indium in the Solid State. *J. Am. Chem. Soc.* **1998**, *120*, 2202–2203.
- (53) Niemeyer, M.; Power, P. P. Synthesis and Solid-State Structure of 2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Tl ( $Trip = 2,4,6-iPr_3C_6H_2$ ): A Monomeric Arylthallium(I) Compound with a Slightly Coordinated Thallium Atom. *Angew. Chem., Int. Ed.* **1998**, *37*, 1277–1279.
- (54) Ni, C.; Ellis, B. D.; Fettingner, J. C.; Long, G. J.; Power, P. P. Univalent Transition Metal Complexes of Arenes Stabilized by a Bulky Terphenyl Ligand: Differences in the Stability of Cr(I), Mn(I) or Fe(I) Complexes. *Chem. Commun.* **2008**, 1014–1016.

(55) Lei, H.; Ellis, B. D.; Ni, C.; Grandjean, F.; Long, G. J.; Power, P. P. An Arene-Stabilized Cobalt(I) Aryl: Reactions with CO and NO. *Inorg. Chem.* **2008**, *47*, 10205–10207.

(56) Melton, C. E.; Dube, J. W.; Ragogna, P. J.; Fetting, J. C.; Power, P. P. Synthesis and Characterization of Primary Aluminum Parent Amides and Phosphides. *Organometallics* **2014**, *33*, 329–337.

(57) Wehmschulte, R. J.; Power, P. P. New Routes to Synthetically Useful, Sterically Encumbered Arylaluminum Halides and Hydride Halides. *Inorg. Chem.* **1996**, *35*, 3262–3267.

(58) Petrie, M. A.; Power, P. P.; Dias, H. V. R.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. Synthesis and Characterization of Bulky Aryl Derivatives of the Heavier Main Group 3 Elements. *Organometallics* **1993**, *12*, 1086–1093.

(59) Wehmschulte, R. J.; Grigsby, W. J.; Schiemenz, B.; Bartlett, R. A.; Power, P. P. Synthesis and Characterization of Sterically Encumbered Derivatives of Aluminum Hydrides and Halides: Assessment of Steric Properties of Bulky Terphenyl Ligands. *Inorg. Chem.* **1996**, *35*, 6694–6702.

(60) Hicks, J.; Juckel, M.; Paparo, A.; Dange, D.; Jones, C. Multigram Syntheses of Magnesium(I) Compounds Using Alkali Metal Halide Supported Alkali Metals as Dispersible Reducing Agents. *Organometallics* **2018**, *37*, 4810–4813.

(61) Lein, M. Characterization of Agostic Interactions in Theory and Computation. *Coord. Chem. Rev.* **2009**, *253*, 625–634.

(62) Caputo, C. A.; Koivistoinen, J.; Moilanen, J.; Boynton, J. N.; Tuononen, H. M.; Power, P. P. Counterintuitive Mechanisms of the Addition of Hydrogen and Simple Olefins to Heavy Group 13 Alkene Analogues. *J. Am. Chem. Soc.* **2013**, *135*, 1952–1960.

(63) Nagata, K.; Murosaki, T.; Agou, T.; Sasamori, T.; Matsuo, T.; Tokitoh, N. Activation of Dihydrogen by Masked Doubly Bonded Aluminum Species. *Angew. Chem., Int. Ed.* **2016**, *55*, 12877–12880.