

# Oxidative Addition of $\sigma$ Bonds to an Al(I) Center

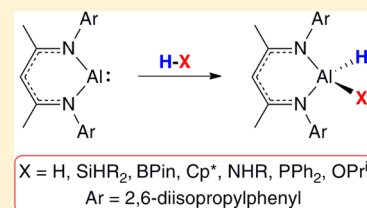
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## Supporting Information

**ABSTRACT:** The Al(I) compound NacNacAl (**1**, NacNac = [ArNC(Me)CHC(Me)-NAr]<sup>-</sup> and Ar = 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>) reacts with H-X (X = H, Si, B, Al, C, N, P, O)  $\sigma$  bonds of H<sub>2</sub>, silanes, borane (HBpin, pin = pinacolate), allane (NacNacAlH<sub>2</sub>), phosphine (HPPH<sub>2</sub>), amines, alcohol (Pr<sup>i</sup>OH), and Cp<sup>\*</sup>H (Cp<sup>\*</sup> = pentamethylcyclopentadiene) to give a series of hydride derivatives of the four-coordinate aluminum NacNacAlH(X), which are characterized herein by spectroscopic methods (NMR and IR) and X-ray diffraction. This method allows for the syntheses of the first boryl hydride of aluminum and novel silyl hydride and phosphido hydride derivatives. In the case of the addition of NacNacAlH<sub>2</sub>, the reaction is reversible, proving the possibility of reductive elimination from the species NacNacAlH(X).



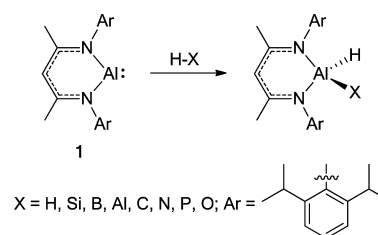
## INTRODUCTION

Main-group metal catalysis is of great current interest due to its potential to circumvent the high cost and toxicity of common transition metal catalysts.<sup>1,2</sup> However, its further development faces several obstacles, of which the lack of activation of robust  $\sigma$  bonds is one of the biggest problems. The success of transition metal catalysis is related to a great extent to the ease of activation of H-H, H-Si, H-B, H-C, etc. bonds, which proceeds either by the formation of  $\sigma$ -complexes, e.g., M-( $\sigma$ -H-X),<sup>3</sup> or, more commonly, by oxidative addition, e.g., MH(X).<sup>4</sup> Additions of H-X bonds to main-group centers are much less common.<sup>1,5</sup> Examples include the hydrogenations of digermene,<sup>6</sup> borole,<sup>7</sup> digallene (GaR)<sub>2</sub>,<sup>8</sup> NacNacGa (NacNac = [ArNC(Me)CHC(Me)NAr]<sup>-</sup> and Ar = 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>9</sup> and carbenes,<sup>10,11</sup> as well as heterolytic splitting of H<sub>2</sub> by frustrated Lewis pairs, i.e., a pair of a Lewis acid and base that cannot form an adduct for steric reasons,<sup>12-16</sup> which find many applications in catalytic hydrogenation.<sup>12,17</sup> The H-Si bond undergoes a similar heterolytic cleavage by a combination Lewis acids and bases,<sup>18</sup> allowing for ionic hydrosilylation of organic substrates.<sup>19</sup> Addition of B-H, C-H, Si-H, N-H, and P-H bonds to a single main-group element center has been observed for a few Group 14 carbenoids<sup>10,11,20</sup> and for a P(III) center supported by an ONO tridentate ligand.<sup>21</sup> Oxidative additions to a single Group 13 center have been studied for atomic reactions with H<sub>2</sub> and NH<sub>3</sub> in frozen matrixes,<sup>22</sup> whereas activation of the H-H bond has been demonstrated by Ga(I) aryls, via a 2+2 addition to the digallene RGe=GaR.<sup>8</sup> Most relevant to this study is the report by Linti et al.<sup>9</sup> on H-X bond addition to a low-valent gallium(I) complex, NacNacGa, and addition of aryl and alkyl halides to NacNacIn.<sup>23</sup> Here we report the first examples of oxidative additions of a series of robust  $\sigma$  H-X bonds (X = H, B, C, Si, N, P, O) to a single Al(I) center supported by the diiminoacetylacetonate ligand.

## RESULTS AND DISCUSSION

The Al(I) compound NacNacAl (**1**) was reported over a decade ago,<sup>24</sup> and its reactivity toward unsaturated molecules has been extensively studied by Roesky et al.<sup>25</sup> Compound **1** can be classified as an aromatically stabilized carbenoid, featuring an Al-based lone pair and an accessible antibonding  $\pi^*$ (Al-N) orbital. Such a situation, i.e., the presence of a metal-centered lone pair and an accessible vacant orbital, is reminiscent of transition metal centers amenable for activation of robust bonds.<sup>1</sup> This fact prompted our study of oxidative addition reactions to this Al(I) center (Scheme 1). Indeed,

**Scheme 1. Oxidative Additions to the Al(I) Compound 1**

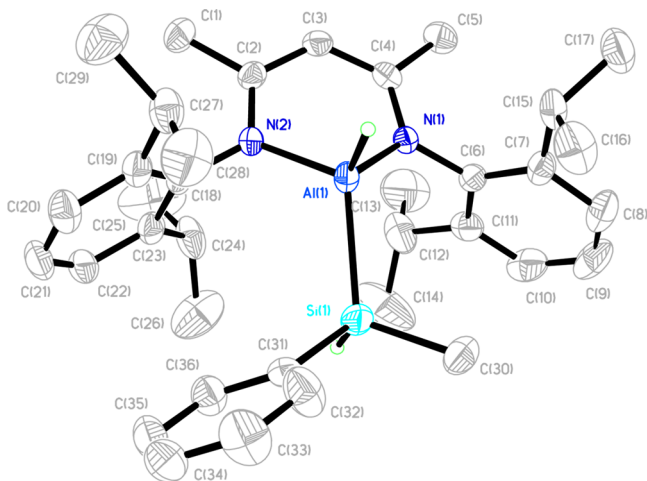


molecular hydrogen cleanly adds to complex **1** at 70 °C to furnish the known dihydride compound NacNacAlH<sub>2</sub> (**2**).<sup>26</sup> Encouraged by this result and given the analogy between H-H and Si-H bond activation,<sup>3</sup> we studied the addition of silanes to **1**. H<sub>3</sub>SiPh readily adds to **1** at room temperature after its mixture is stirred overnight to give the silyl hydride NacNacAlH(SiH<sub>2</sub>Ph) (**3**), whereas heating overnight at 70 °C was required for the bulkier silane H<sub>2</sub>SiMePh to produce NacNacAlH(SiHMePh) (**4**). Compounds **3** and **4** represent rare examples of silyl hydride derivatives of Al(III), with the only one other example being LSiH(AlH<sub>2</sub>(NMe<sub>3</sub>)) (**5**, L =

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(ArN)C(=CH<sub>2</sub>)CH=C(Me)(NAr)), reported by Driess et al.<sup>27</sup> The Si–H bonds in **3** and **4** give rise to the <sup>1</sup>H NMR signals at 3.87 (d, <sup>3</sup>J<sub>H–H</sub> = 2.8 Hz) and 4.20 ppm (dq, <sup>3</sup>J<sub>H–H</sub> = 5.1 Hz, <sup>3</sup>J<sub>H–H(Al)}</sub> = 6.6 Hz), respectively, which correlate with the upfield <sup>29</sup>Si NMR resonances at –74.0 and –48.0 ppm. The Al–H signals cannot be observed directly by <sup>1</sup>H NMR spectroscopy because of quadrupolar broadening on the <sup>27</sup>Al center (nuclear spin = 5/2), but the presence of the Al–H bond is confirmed by the IR stretches observed at 1785 cm<sup>–1</sup> both for **3** and **4**. The X-ray structure of **4** is shown in Figure 1.

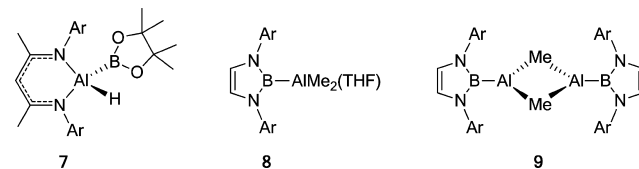


**Figure 1.** Molecular structure of **4** (thermal ellipsoids are shown at 50%; hydrogen atoms except the hydride are omitted for clarity). Selected bond lengths (Å) and angles (deg): Al(1)–Si(1) 2.4551(8), Al(1)–N(1) 1.9043(15), Al(1)–N(2) 1.9084(15), N(1)–Al(1)–N(2) 95.66(7), N(1)–Al(1)–Si(1) 111.94(5), N(2)–Al(1)–Si(1) 115.08(5).

The NacNac fragment is nearly planar (mean deviation of 0.029 Å), with the Al atom sitting above the N1–C4–C3–C2–N2 plane by 0.751 Å. The Al(1)–Si(1) bond distance of 2.4551(8) Å is comparable with the corresponding distance in **5**, 2.487(1) Å,<sup>27</sup> and the average Al–Si distance on a four-coordinate Al center (2.466 Å).<sup>28</sup> The Al–N distances of 1.9043(15) and 1.9084(15) Å are shorter than in the parent NacNac complex **1** having a two-coordinate aluminum (1.957(2) Å),<sup>24</sup> but comparable with the related compound NacNacAl(η<sup>2</sup>(F,B)–B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) (**6**) with a four-coordinate aluminum (1.885(4) and 1.900(3) Å).<sup>29</sup> Another prominent feature of **4** and its analogues discussed below is the significant distortion of the N<sub>2</sub>AlHX (X = Si, B, C, P, etc.) fragment from tetrahedral geometry in that the N–Al–N bond angle is significantly smaller than the N–Al–X angle (in **4**: 95.66(7)° vs 111.94(5)° and 115.08(5)° for X = Si).

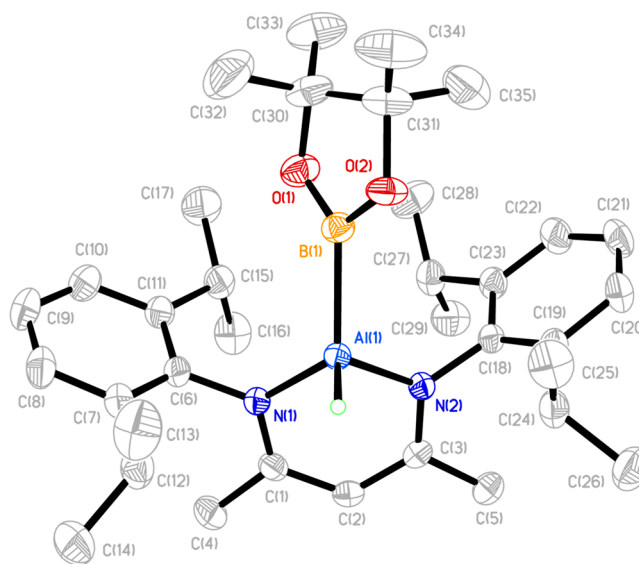
Given the diagonal analogy between silicon and boron, we then studied the reactions of boranes with **1**. HBpin (pin = pinacolate) adds to **1** at room temperature in the course of 3 h to furnish cleanly the first boryl hydride derivative of aluminum, NacNacAlH(Bpin) (**7**, Scheme 2). Complex **7** was characterized by multinuclear NMR spectroscopy, IR spectroscopy, and X-ray analysis. Similar to those for complexes **3** and **4**, <sup>1</sup>H NMR data are indicative of C<sub>s</sub> symmetry in solution.<sup>30</sup> The boryl ligand gives rise to the <sup>11</sup>B NMR resonance at 34.9 ppm, consistent with a three-coordinate boron, and the presence of the Al–H bond is evidenced by the observation of an IR stretch at 1795 cm<sup>–1</sup>. The chemistry of boron-substituted compounds

## Scheme 2. Examples of Boryl Aluminum Compounds<sup>a</sup>



<sup>a</sup>Ar = 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

of aluminum is mainly represented by carborane and borohydride derivatives. The first boryl-substituted aluminum compounds, (THF)Me<sub>2</sub>Al–B(NArCH–)<sub>2</sub> and ((*μ*-Me)MeAl–B(NArCH–)<sub>2</sub>)<sub>2</sub> (**8** and **9**, Scheme 2), have been obtained only recently by Anwender et al.<sup>31</sup> by reacting AlMe<sub>3</sub> with Yamashita's borylide [Li(THF)<sub>2</sub>][B(NArCH–)<sub>2</sub>]. The molecular structure of **7** (Figure 2) closely resembles that of **4**. The

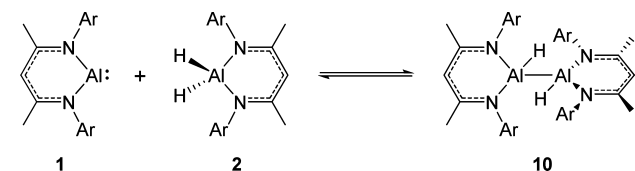


**Figure 2.** Molecular structure of **7** (thermal ellipsoids are shown at 50%; hydrogen atoms except the hydride are omitted for clarity). The oxygen atoms are disordered, but only one pair is shown for clarity. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 1.9095(11), Al(1)–N(2) 1.9103(11), Al(1)–B(1) 2.1232(15), N(1)–Al(1)–N(2) 95.12(5), N(1)–Al(1)–B(1) 119.18(6), N(2)–Al(1)–B(1) 110.65(5).

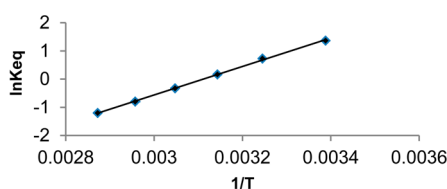
Al–B single bond of 2.1232(15) Å in **7** is comparable with the corresponding distances in **8** (2.150(2) Å) and **9** (2.119(3) Å). There are also a few structurally characterized Lewis adducts between nucleophilic Al(I) species<sup>32</sup> and electrophilic boranes which feature donor–acceptor Al→B bonds in the range of 2.115(2)–2.183(5) Å, with the longest value found in the four-coordinate Al complex **6**.<sup>29,33</sup>

Related oxidative addition of the Al–H bond of **2** to **1** results in the formation of an equilibrium mixture of the starting compounds and the dimer (NacNacAl(H)–)<sub>2</sub> (**10**, Scheme 3). At room temperature, complex **10** forms in about 50% yield. The <sup>1</sup>H NMR spectrum of **10** displays four septets for the methine protons and eight doublets for the methyls of the Pr<sup>i</sup> groups on the aryl rings, consistent with the effective C<sub>2</sub> or C<sub>i</sub> symmetry in solution. The IR spectrum of the mixture displays new bands at 1778 and 1772 cm<sup>–1</sup>, attributed to the Al–H bond and similar to the Al–H stretches at 1832 and 1795 cm<sup>–1</sup> observed for **2**.<sup>26,34</sup> Upon heating of the reaction mixture to 50

## Scheme 3. Equilibrium between 1 and 2 To Give 10



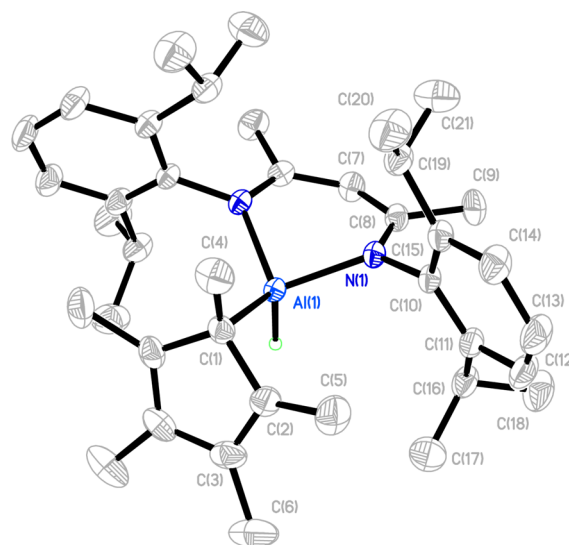
°C, complex **10** disproportionates back to a mixture of the starting compounds **1** and **2**, indicating an entropy-driven reaction. However, returning to room temperature results in clean reproduction of the original equilibrium mixture without any side reactions. The equilibrium between **1**, **2**, and **10** was studied by  $^1\text{H}$  NMR spectroscopy and the thermodynamic parameters ( $\Delta H = -42.0 \pm 0.7 \text{ kJ mol}^{-1}$ ;  $\Delta S = -130.8 \pm 2.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ) were extracted from the van't Hoff plot in the range from 295 to 348 K (Figure 3). This dynamic process is of



**Figure 3.** van't Hoff plot of the equilibrium between **1**, **2**, and **10** ( $R^2 = 0.999$ ).

interest as a proof of principle of reductive elimination from an aluminum center. Reductive elimination of H–X bonds is a key step in many transition-metal-catalyzed reactions but is uncommon for main-group complexes. Previously, Beachley and co-workers reported the synthesis of organometallic Ga(I)<sup>35</sup> and In(I)<sup>36</sup> compounds via elimination of  $\text{SiMe}_4$  from  $\text{KM}(\text{CH}_2\text{SiMe}_3)_3\text{H}$  ( $M = \text{Ga}$  or  $\text{In}$ ). However, the results were not reproducible and the proposed decomposition likely follows a more complicated pathway rather than a simple reductive elimination.<sup>37</sup> More recently, Fischer et al. has reported the reductive elimination of  $\text{Cp}^*\text{H}$  from  $\text{Cp}^*\text{AlH}_2$  to furnish the Al(I) compound  $\text{Cp}^*\text{Al}$ , with the three species being in equilibrium in toluene at 110 °C.<sup>38</sup>

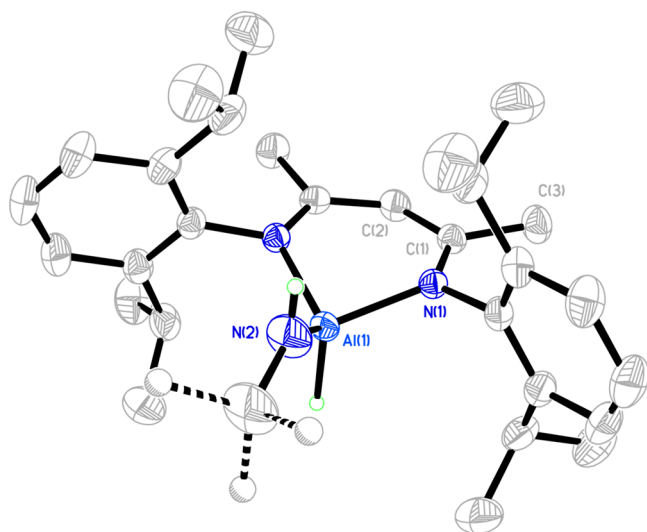
Complex **1** does not react with the  $\text{sp}^2$  C–H bonds of benzene, toluene, or terminal alkene, nor with the  $\text{sp}$  C–H bonds of alkynes. In the latter two cases, addition to the  $\pi$ -system takes place.<sup>25</sup> Similar  $\pi$ -complexation occurs for the C–H acidic cyclopentadiene. However, for the sterically encumbered pentamethylcyclopentadiene, oxidative addition of the C–H bond takes place at 70 °C in the course of 3 days to give the hydride alkyl derivative  $\text{NacNacAlH}(\text{Cp}^*)$  (**11**,  $\text{Cp}^* = \text{C}_5\text{Me}_5$ ). Compound **11** was characterized by multinuclear NMR and IR spectroscopy and its structure was confirmed by X-ray crystallography. In particular, two types of  $\text{Pr}^t$  groups are observed by  $^1\text{H}$  NMR spectroscopy at 3.57 (hept,  $^3J_{\text{H-H}} = 6.8 \text{ Hz}$ ) and 3.16 ppm (hept,  $^3J_{\text{H-H}} = 6.9 \text{ Hz}$ ), consistent with  $C_s$  symmetry. The methyl groups of the  $\text{Cp}^*$  ligand gives rise to a singlet at 1.48 ppm indicating the occurrence of a fast haptotropic shift. Like the other aluminum hydrides discussed above, the Al–H signal is not observed by  $^1\text{H}$  NMR spectroscopy but the presence of the Al–H bond is supported by the IR stretch at  $1802 \text{ cm}^{-1}$ . The molecular structure of **11** is shown in Figure 4. The molecule lies on a special position, with a crystallographically imposed symmetry plane running through atoms C(7), Al(1), C(1), and C(4). The Al(1) center is



**Figure 4.** Molecular structure of **11** (thermal ellipsoids are shown at 50%; hydrogen atoms except the hydride are omitted for clarity). Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 1.9534(11), Al(1)–C(1) 2.0901(19), N(1)–C(8) 1.3387(17), N(1)–Al(1)–N(1a) 93.64(7), N(1)–Al(1)–C(1) 117.78(5), C(4)–C(1)–Al(1) 118.50(14), C(2)–C(1)–Al(1) 97.07(10).

attached to the C(1) atom of the  $\text{Cp}^*$  ligand with a distance of 2.0901(19) Å, which is 0.109 Å longer than the average Al–C distance in four-coordinate hydrido alkyl aluminum compounds (1.981 Å).<sup>39</sup> Such an elongated Al–C bond and the acute C(2)–C(1)–Al(1) bond angle of 97.07(10)° indicate that bonding of Al(1) to the  $\text{Cp}^*$  ring has a significant p-character on carbon, which is consistent with the facile haptotropic shift of the  $\text{Cp}^*$  ligand observed by  $^1\text{H}$  NMR. Unlike the related structures of **4** and **7**, the NacNac ligand is slightly folded, with the dihedral angle between the N(1)–C(8)–C(7) and N(1a)–C(8a)–C(7) planes being 13.3°. Another telling feature is the very significant elongation of the Al(1)–N(1) bond (1.9534(11) Å) versus the range found for other  $\text{NacNacAlH}(\text{X})$  species discussed herein (1.9043(15)–1.9095(11) Å), which can be accounted for by the significant steric strain imposed by the bulky Ar and  $\text{Cp}^*$  groups.

Amines add readily to the Al(I) precursor **1** at room temperature. Thus, the addition of  $\text{H}_2\text{NBu}^t$  is completed after the mixture is stirred for 3 days, whereas the more acidic aniline  $\text{H}_2\text{NPh}$  requires only 16 h. The formation of amido hydride products **12** and **13**, respectively, was established by multinuclear NMR and IR spectroscopy, X-ray studies, and comparison with the related compound  $\text{NacNacAlH}(\text{NHAr})$  (**14**) obtained by the reaction of  $\text{NacNacAlH}_2$  with  $\text{H}_2\text{NAr}$ .<sup>40</sup> In particular, the presence of Al–H bonds in **12** and **13** is evidenced from the IR stretches at 1812 and 1854  $\text{cm}^{-1}$ , respectively. Both compounds show two sets of signals in the  $^1\text{H}$  NMR spectrum for the methine CHs of the  $\text{Pr}^t$  groups on the aryl rings consistent with  $C_s$  symmetry. The N–H signals were observed as broad signals at –0.03 and 3.27 ppm for **12** and **13**, respectively. The molecular structure of compound **12** is shown in Figure 5. The structure of **13** is very similar and is given in the Supporting Information.<sup>30</sup> The molecule of **12** is bisected by a crystallographically imposed symmetry plane running through atoms Al(1), N(2) and C(2). The  $\text{Bu}^t$  group on the amido center N(2) is rotationally disordered. The N–H and Al–H protons are in transoid arrangement, which results in

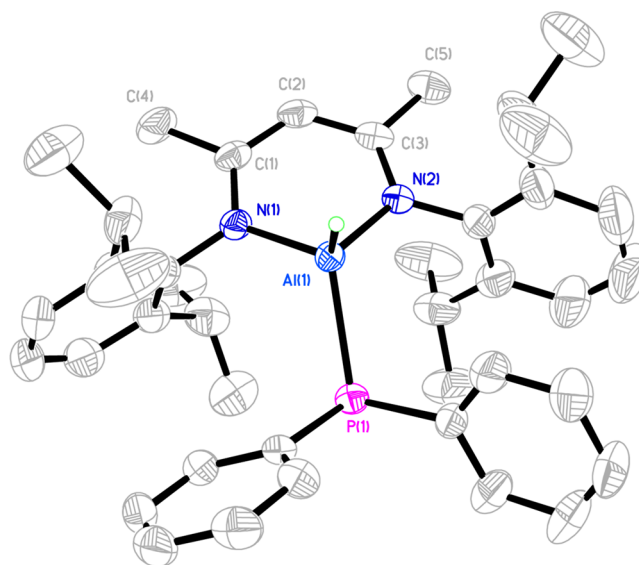


**Figure 5.** Molecular structure of **12** (thermal ellipsoids are shown at 50%; hydrogen atoms except the hydride are omitted for clarity). Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 1.9069(11), Al(1)–N(2) 1.7859(19), N(1)–C(1) 1.3324(15), N(2)–C(16) 1.450(3), N(1)–Al(1)–N(1a) 94.63(6), N(2)–Al(1)–N(1) 112.00(5).

the alignment of the amide lone pair in parallel with the N(1)–N(1a) vector and hence leads to the possibility of partial electron transfer on the antibonding orbitals of the Al(1)–N(1) and Al(1)–N(1a) bonds. Although the short Al(1)–N(2) distance of 1.7859(19) Å (cf. with the average Al–N distance on a four-coordinate aluminum of 1.927 Å) appear to support this notion, the Al(1)–N(1) distance, 1.9069(1) Å, is quite normal.

Related addition of a less polar but weaker P–H bond of HPPH<sub>2</sub> also occurs at room temperature and affords a phosphide hydride derivative of aluminum, NacNacAlH(PPh<sub>2</sub>) (**15**). The <sup>1</sup>H and <sup>13</sup>C NMR features for **15** are similar to those of other NacNacAlH(X) complexes reported above. The presence of the phosphide ligand is supported by the upfield <sup>31</sup>P NMR signal at –67.9 ppm. The hydride gives rise to the Al–H stretch at 1778 cm<sup>–1</sup> in the IR spectrum. The molecular structure of **15** found by X-ray diffraction is shown in Figure 6. The Al–P distance of 2.3971(6) Å is comparable to the average Al–P bond found on neutral four-coordinate aluminum hydrido phosphides (2.375 Å)<sup>41</sup> and four-coordinate phosphide hydride aluminates (2.403 Å).<sup>42</sup> Given the small size of the hydride ligand, it appears that the Al–P bond length is primarily controlled by steric factors. The phosphide center is pyramidal, with the sum of bond angles equal to 308.72(7)°.

Finally, the reaction of complex **1** with HOPr<sup>t</sup> occurs smoothly at room temperature in the course of 16 h to furnish the hydrido alkoxy product NacNacAlH(OPr<sup>t</sup>) (**16**). Compound **16** was characterized by spectroscopic data and X-ray analysis.<sup>30</sup> Although many hydrido alkoxides of four-coordinate aluminum are known, most of them are aluminate compounds with bulky aryloxy ligands.<sup>43</sup> Therefore, compound **16** represents a rare example of a neutral, monomeric hydrido alkoxy species. The structural features of **16** are very close to those of the related hydrido amides **12** and **13**. The Al–O bond distance of 1.6969(15) Å is shorter than the average Al–O distance in neutral, monomeric four-coordinate hydrido aryloxy aluminum compounds (1.723 Å),<sup>44</sup> but comparable with the



**Figure 6.** Molecular structure of **15** (thermal ellipsoids are shown at 50%; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Al(1)–P(1) 2.3971(6), Al(1)–N(1) 1.8963(13), Al(1)–N(2) 1.9070(13), N(1)–Al(1)–N(2) 95.42(6), N(1)–Al(1)–P(1) 112.02(4), N(2)–Al(1)–P(1) 111.55(4).

Al–O distance in monomeric four-coordinate aryloxy hydride aluminates (1.712 Å)<sup>45</sup> and three-coordinate Al compounds.<sup>46</sup> Thus, like the related amide derivatives we can conclude that this metric is primarily determined by the steric hindrance around the aluminum center.

## CONCLUSION

In conclusion, we have found that the Al(I) compound NacNacAl shows transition-metal-like reactivity toward the oxidative addition of robust H–X bonds, leading to a series of aluminum hydrides, NacNacAlH(X), substituted by silyl, boryl, alumanyl, alkyl, amido, phosphido, and alkoxy groups. Investigations into the application of these species toward catalytic processes are in progress and will be reported in due course.

## EXPERIMENTAL SECTION

Unless stated otherwise, all manipulations were performed using standard inert atmosphere (N<sub>2</sub> gas) glovebox and Schlenk techniques. Benzene, toluene, and hexanes were dried using a Grubbs-type solvent purification system. C<sub>6</sub>D<sub>6</sub> was dried by distillation from K/Na alloy. NMR spectra were obtained with a Bruker DPX-300 and DPX-600 instruments (<sup>1</sup>H, 300 and 600 MHz; <sup>13</sup>C, 75 and 151 MHz; <sup>11</sup>B, 96 and 193 MHz; <sup>29</sup>Si, 60 and 119 MHz; <sup>31</sup>P, 121 and 243 MHz) at room temperature, unless specified otherwise. IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analysis was performed by the ANALEST laboratories (University of Toronto) or the analytical laboratory of McMaster University. Analyses were done in quadruplicate, but were generally found to be low in carbon, regardless if a single crystal or a well ground powder was submitted. Methylphenylsilane (MePhSiH<sub>2</sub>), pinacolborane (HBPin), *tert*-butylamine (H<sub>2</sub>NBu<sup>t</sup>), aniline (H<sub>2</sub>NPh), and isopropanol (Pr<sup>t</sup>OH) were purchased from Sigma-Aldrich. Pentamethylcyclopentadiene (Cp\*H) was purchased from Strem Chemicals. Phenylsilane (PhSiH<sub>3</sub>) and diphenylphosphine (Ph<sub>2</sub>PH) were prepared by the reduction of PhSiCl<sub>3</sub> and Ph<sub>2</sub>PCl with LiAlH<sub>4</sub>, respectively. Compound **1** was prepared according to a literature procedure.<sup>24</sup>

**Reaction of **1** with Hydrogen.** An NMR tube was charged with **1** (0.007 g, 0.016 mmol) dissolved in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. Hydrogen gas (4

atm) was introduced into the sample and heated at 70 °C overnight to cleanly furnish **2**. The spectroscopic data are consistent with previously published data.<sup>26</sup>

**NacNacAlH(SiH<sub>2</sub>Ph) (3)**. A solution of **1** (0.118 g, 0.265 mmol) in benzene (6 mL) was added to a flask followed by the addition of PhSiH<sub>3</sub> (0.033 mL, 0.265 mmol). The reaction was stirred overnight at room temperature to yield a dark yellow solution. Volatiles were removed under vacuo and taken up in hexanes. Colorless crystals of **3** were obtained upon cooling to -30 °C (0.092 g, 0.166 mmol, 63%). <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.13 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.08 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 6.96 (m, 7H, C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>), 4.93 (s, 1H, CH), 3.87 (d, 2H, SiH<sub>2</sub>Ph, <sup>3</sup>J<sub>H-H</sub> = 2.8 Hz), 3.42 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 3.35 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 1.54 (s, 6H, NCCH<sub>3</sub>), 1.43 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.17 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 1.13 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 1.11 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 171.0 (NCCH<sub>3</sub>), 145.6, 143.0, 134.7, 128.3, 127.7, 127.5, 127.4, 125.2, 124.4 (C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>), 140.5 (C<sub>ipso</sub>), 136.3 (o-C Ph), 97.8 (CH), 29.4, 28.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.2, 24.8, 24.3, 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.0 (NCCH<sub>3</sub>). <sup>29</sup>Si INEPT+ NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>, J = 200 Hz): δ -74.3 (m, SiH<sub>2</sub>Ph). IR (Nujol): ν = 2065 cm<sup>-1</sup> (Si-H), 1785 cm<sup>-1</sup> (Al-H). Anal. Calcd for C<sub>35</sub>H<sub>49</sub>AlN<sub>2</sub>Si: C, 76.04; H, 8.93; N, 5.07. Found: C, 74.71; H, 9.10; N, 5.01.

**NacNacAlH(SiHMePh) (4)**. A flask containing **1** (0.120 g, 0.270 mmol) in benzene (8 mL) was charged with MePhSiH<sub>2</sub> (0.037 mL, 0.270 mmol) and heated with stirring for 16 h at 70 °C. Solvent was removed from the resulting yellow solution and the residue was dissolved in a 1:2 mixture of toluene and hexanes. Cooling the solution to -30 °C afforded colorless crystals of **4** (0.107 g, 0.189 mmol, 70%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 7.05 (m, 9H, C<sub>6</sub>H<sub>3</sub>, *m*-H Ph and *p*-H Ph), 6.90 (m, 2H, *o*-H Ph), 4.93 (s, 1H, CH), 4.20 (dq, 1H, SiH(CH<sub>3</sub>)Ph, <sup>3</sup>J<sub>H(Si)-H(C)} = 5.1 Hz, <sup>3</sup>J<sub>H(Si)-H(Al)} = 6.6 Hz), 3.46 (m, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.23 (hept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 1.56 (s, 3H, NCCH<sub>3</sub>), 1.53 (s, 3H, NCCH<sub>3</sub>), 1.52 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.44 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.39 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 1.16 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 1.13 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.09 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 0.82 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), -0.14 (d, 3H, SiH(CH<sub>3</sub>)Ph, <sup>3</sup>J<sub>H-H</sub> = 5.1 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 170.9, 170.6 (NCCH<sub>3</sub>), 145.6, 143.1, 142.8, 127.6, 127.5, 127.3, 127.1, 125.4, 125.2, 124.4 (C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>), 140.9, 140.9 (C<sub>ipso</sub>), 140.1 (C<sub>ipso</sub> Ph), 134.9 (o-C Ph), 97.6 (CH), 29.5, 29.3, 28.2, 28.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.4, 25.5, 24.8, 24.8, 24.4, 24.2, 24.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.1, 22.9 (NCCH<sub>3</sub>), -7.3 (SiH(CH<sub>3</sub>)Ph). <sup>29</sup>Si INEPT+ NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>, J = 200 Hz): δ -47.2 (m, SiH(CH<sub>3</sub>)Ph). IR (Nujol): ν = 2065 cm<sup>-1</sup> (Si-H), 1785 cm<sup>-1</sup> (Al-H). Anal. Calcd for C<sub>36</sub>H<sub>51</sub>AlN<sub>2</sub>Si: C, 76.28; H, 9.07; N, 4.94. Found: C, 75.64; H, 9.31; N, 4.84.</sub></sub>

**NacNacAlH(BPin) (7)**. To a dark red solution of **1** (0.119 g, 0.268 mmol) in benzene (5 mL) was added HBPin (0.039 mL, 0.268 mmol) at room temperature. The mixture was stirred for 3 h to afford a yellow solution. Solvent was removed to give a pale yellow solid. Colorless crystals of **7** were obtained upon cooling a hexanes solution to -30 °C (0.080 g, 0.152 mmol, 57%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.13 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 5.00 (s, 1H, CH), 3.50 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.59 (s, 6H, NCCH<sub>3</sub>), 1.53 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.43 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 1.19 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 0.73 (s, 12H, OC(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 170.3 (NCCH<sub>3</sub>), 145.7, 143.5, 126.8, 124.5, 123.9 (C<sub>6</sub>H<sub>3</sub>), 141.4 (C<sub>ipso</sub>), 97.7 (CH), 81.2 (OC(CH<sub>3</sub>)<sub>2</sub>), 29.1, 28.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.7, 24.8, 24.4, 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.1 (OC(CH<sub>3</sub>)<sub>2</sub>), 23.1 (NCCH<sub>3</sub>). <sup>11</sup>B NMR (96 MHz, C<sub>6</sub>D<sub>6</sub>): δ 34.9 (br s, B-Pin). IR (Nujol): ν = 1795 cm<sup>-1</sup> (Al-H). Anal. Calcd for C<sub>35</sub>H<sub>54</sub>AlBN<sub>2</sub>O<sub>2</sub>: C, 73.41; H, 9.51; N, 4.89. Found: C, 72.70; H, 9.77; N, 4.88.

**Generation of (NacNacAlH)<sub>2</sub> (10)**. A solution of **1** (0.012 g, 0.027 mmol) in C<sub>6</sub>D<sub>6</sub> (0.6 mL) was added to **2** (0.012 g, 0.027 mmol), and the mixture was charged into an NMR tube. The tube was allowed to stand for 4 h at room temperature, and the resulting solution contained a mixture of **1**, **2**, and **10**. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): 7.17 (m, 8H, C<sub>6</sub>H<sub>3</sub>) 7.01 (t, 2H, *m*-H Ar, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz), 6.85 (d, 2H, *p*-H

Ar, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz), 4.69 (s, 2H, CH), 3.77 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.1 Hz), 3.67 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 3.53 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 2.95 (sp, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz), 1.74 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.50 (m, 12H, NCCH<sub>3</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (s, 6H, NCCH<sub>3</sub>), 1.21 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 1.12 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.09 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz), 0.90 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz), 0.84 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 169.8, 168.4 (NCCH<sub>3</sub>), 145.8, 145.6, 144.5, 143.8, 143.0, 127.7, 127.4, 127.0, 126.9, 125.5, 125.1, 124.4, 124.0 (C<sub>6</sub>H<sub>3</sub>), 98.1 (CH), 29.9, 28.4, 28.1, 27.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.8, 26.0, 25.6, 25.3, 25.1, 25.1, 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.4, 23.4 (NCCH<sub>3</sub>). IR (Nujol): ν = 1778, 1772 cm<sup>-1</sup> (Al-H).

**NacNacAlH(Cp\*) (11)**. Cp\*H (0.043 mL, 0.277 mmol) was added to a flask containing **1** (0.123 g, 0.277 mmol) in benzene (8 mL). The mixture was heated with stirring at 70 °C for 3 days to give a pale orange solution. Removal of the solvent in vacuo yielded a yellow solid. The product was recrystallized in a 1:2 mixture of toluene and hexanes at -30 °C to give yellow crystals of **11** (0.099 g, 0.170 mmol, 61%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.15 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 4.90 (s, 1H, CH), 3.57 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 3.16 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 1.48 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.44 (m, 18H, NCCH<sub>3</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.03 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 170.3 (NCCH<sub>3</sub>), 145.7, 142.8, 127.5, 125.7, 123.9 (C<sub>6</sub>H<sub>3</sub>), 144.0 (C<sub>ipso</sub>), 121.5 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 98.0 (CH), 29.9, 28.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.4, 24.9, 24.5, 24.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.5 (NCCH<sub>3</sub>), 12.3 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). IR (Nujol): ν = 1802 cm<sup>-1</sup> (Al-H). Anal. Calcd for C<sub>39</sub>H<sub>57</sub>AlN<sub>2</sub>: C, 80.64; H, 9.89; N, 4.82. Found: C, 82.39; H, 10.33; N, 4.93.

**NacNacAlH(NHBu<sup>t</sup>) (12)**. To a dark red solution of **1** (0.120 g, 0.270 mmol) in benzene (6 mL) was added H<sub>2</sub>NBu<sup>t</sup> (0.028 mL, 0.270 mmol) at room temperature. The mixture was stirred for 3 days to afford a dark yellow solution. Solvent was removed, and the solid was dissolved in hexanes, which afforded colorless crystals of **12** upon cooling to -30 °C (0.070 g, 0.135 mmol, 50%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.12 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 4.86 (s, 1H, CH), 3.46 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 3.31 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 1.57 (s, 6H, NCCH<sub>3</sub>), 1.45 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 1.11 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 0.90 (s, 9H, NH-C(CH<sub>3</sub>)<sub>3</sub>), -0.03 (s, 1H, NH-C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 169.7 (NCCH<sub>3</sub>), 144.9, 143.6, 127.1, 124.8, 123.9 (C<sub>6</sub>H<sub>3</sub>), 140.8 (C<sub>ipso</sub>), 96.3 (CH), 48.6 (NH-C(CH<sub>3</sub>)<sub>3</sub>), 35.5 (NH-C(CH<sub>3</sub>)<sub>3</sub>), 28.9, 28.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.8, 24.9, 24.8, 24.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.3 (NCCH<sub>3</sub>). IR (Nujol): ν = 1812 cm<sup>-1</sup> (Al-H). Anal. Calcd for C<sub>33</sub>H<sub>52</sub>AlN<sub>3</sub>: C, 76.55; H, 10.12; N, 8.12. Found: C, 71.94; H, 9.87; N, 8.54.

**NacNacAlH(NHPh) (13)**. H<sub>2</sub>NPh (0.025 mL, 0.270 mmol) was added to a flask containing **1** (0.120 g, 0.270 mmol) in benzene (6 mL). The mixture was stirred for 16 h at room temperature to give a yellow solution. Removal of the solvent in vacuo yielded a pale yellow solid. The product was recrystallized in hexanes at -30 °C to give colorless crystals of **13** (0.095 g, 0.177 mmol, 66%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.12 (m, 8H, C<sub>6</sub>H<sub>3</sub> and *o*-H Ph), 6.68 (t, 1H, *p*-H Ph, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz), 6.38 (br d, 2H, *m*-H Ph, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz) 5.07 (s, 1H, CH), 3.36 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz), 3.27 (s, 1H, NH-Ph), 3.17 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 1.56 (s, 6H, NCCH<sub>3</sub>), 1.44 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.14 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 1.03 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz), 0.96 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 170.5 (NCCH<sub>3</sub>), 152.1, 146.4, 143.7, 125.0, 124.4 (C<sub>6</sub>H<sub>3</sub>), 140.0 (C<sub>ipso</sub>), 128.8 (o-C Ph), 117.8 (*m*-C Ph), 115.4 (*p*-C Ph), 97.5 (CH), 29.1, 27.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.1, 24.9, 24.8, 24.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.4 (NCCH<sub>3</sub>). IR (Nujol): ν = 1854 cm<sup>-1</sup> (Al-H). Anal. Calcd for C<sub>33</sub>H<sub>48</sub>AlN<sub>3</sub>: C, 78.17; H, 9.00; N, 7.81. Found: C, 77.74; H, 8.72; N, 7.63.

**NacNacAlH(PPh<sub>2</sub>) (15)**. A solution of **1** (0.120 g, 0.270 mmol) in benzene (6 mL) was added to a flask followed by the addition of Ph<sub>2</sub>PH (0.047 mL, 0.270 mmol). The reaction was stirred for 24 h at room temperature to yield a yellow solution. Volatiles were removed

Table 1. Crystal and Structure Refinement Data

	compound							
	3	4	7	11	12	13	15	
empirical formula	$C_{35}H_{99}AlN_2O_{0.25}Si$	$C_{18}H_{25.5}Al_{0.5}NSi_{0.5}$	$C_{35}H_{54}AlBN_2O_2$	$C_{80}H_{100}Al_2N_2$	$C_{30}H_{30}AlN_3$	$C_{72}H_{100}Al_2N_6O_{0.50}$	$C_{27.33}H_{34.67}Al_{0.67}N_{1.33}P_{0.67}$	
formula weight	556.83	283.43	572.59	1143.58	459.55	1111.54	420.53	
crystal habit	block	block	block	Block	Block	block	block	
crystal color	colorless	colorless	colorless	colorless	Colorless	colorless	colorless	
temperature, K	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	
wavelength, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	
crystal system	monoclinic	triclinic	triclinic	orthorhombic	monoclinic	triclinic	monoclinic	
space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$Ibam$	$P2(1)/m$	$P\bar{1}$	$P2(1)/c$	
unit cell dimensions:								
$a$ , Å	9.6330(5)	12.0366(12)	9.3319(3)	16.3923(4)	8.9717(3)	11.9759(9)	17.2991(7)	
$b$ , Å	16.9749(8)	12.3508(13)	11.6691(3)	19.8520(6)	19.8654(7)	12.3948(8)	12.1331(6)	
$c$ , Å	20.9503(10)	12.6164(13)	17.0064(5)	21.4153(6)	10.1194(4)	24.9637(17)	18.0903(8)	
$\alpha$ , °	90	70.633(6)	80.3490(10)	90	90	104.188(3)	90	
$\beta$ , °	93.418(3)	87.367(6)	75.2380(10)	90	113.658(2)	93.639(4)	100.282(2)	
$\gamma$ , °	90	79.059(6)	88.0350(10)	90	90	90.242(4)	90	
volume, Å <sup>3</sup>	3419.7(3)	1737.0(3)	1765.37(9)	6969.0(3)	1651.97(10)	3584.6(4)	3736.0(3)	
$Z$	4	4	2	4	4	2	6	
density (calc), Mg/m <sup>3</sup>	1.082	1.084	1.077	1.090	1.848	1.030	1.121	
absorption coeff., mm <sup>-1</sup>	0.119	0.118	0.088	0.085	0.158	0.083	0.127	
$F(000)$	1208	616	624	2480	976	1208	1360	
crystal size, mm <sup>3</sup>	$0.190 \times 0.140 \times 0.120$	$0.24 \times 0.15 \times 0.14$	$0.22 \times 0.17 \times 0.15$	$0.23 \times 0.19 \times 0.16$	$0.19 \times 0.15 \times 0.10$	$0.18 \times 0.13 \times 0.11$	$0.23 \times 0.17 \times 0.13$	
$\theta$ range for data collection	2.28–28.31	1.71–26.43	1.77–28.32	1.61–28.32	2.05–28.32	2.38–24.81	2.03–28.33	
index ranges	$-12 \leq h \leq 12$ , $-22 \leq k \leq 22$ , $-27 \leq l \leq 27$	$-15 \leq h \leq 14$ , $-15 \leq k \leq 15$ , $-15 \leq l \leq 15$	$-12 \leq h \leq 12$ , $-15 \leq k \leq 15$ , $-22 \leq l \leq 22$	$-21 \leq h \leq 21$ , $-26 \leq k \leq 23$ , $-28 \leq l \leq 27$	$-11 \leq h \leq 11$ , $-25 \leq k \leq 26$ , $-13 \leq l \leq 13$	$-14 \leq h \leq 14$ , $-14 \leq k \leq 14$ , $-29 \leq l \leq 23$	$-23 \leq h \leq 23$ , $-16 \leq k \leq 15$ , $-24 \leq l \leq 23$	
reflections collected	26 467	22 062	26 594	47 830	22 744	24 915	52 628	
independent reflections	8338 [R(int) = 0.0406]	7090 [R(int) = 0.0251]	8702 [R(int) = 0.0197]	4465 [R(int) = 0.0485]	4213 [R(int) = 0.0299]	12063 [R(int) = 0.0516]	9241 [R(int) = 0.0242]	
absorption correction	semiempirical from equivalents	none	semiempirical from equivalents	none	none	semiempirical from equivalents	semiempirical from equivalents	
max. and min. transmissions	0.7457 and 0.6834	0.9837 and 0.9723	0.9869 and 0.9809	0.9865 and 0.9807	0.9844 and 0.9706	0.9910 and 0.9853	0.9837 and 0.9715	
refinement method				full-matrix least-squares on $F^2$				
data/restraints/parameters	8338/26/377	7090/0/369	8702/0/371	4465/0/209	4213/0/204	12063/18/746	9241/0/407	
goodness-of-fit on $F^2$	1.039	1.064	1.032	1.042	1.043	1.011	1.012	
final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0488$ , $wR2 = 0.1168$	$R1 = 0.0507$ , $wR2 = 0.1247$	$R1 = 0.0506$ , $wR2 = 0.1412$	$R1 = 0.0447$ , $wR2 = 0.1171$	$R1 = 0.0456$ , $wR2 = 0.1204$	$R1 = 0.0689$ , $wR2 = 0.1628$	$R1 = 0.0500$ , $wR2 = 0.1387$	
$R$ indices (all data)	$R1 = 0.0898$ , $wR2 = 0.1326$	$R1 = 0.0672$ , $wR2 = 0.1344$	$R1 = 0.0641$ , $wR2 = 0.1532$	$R1 = 0.0644$ , $wR2 = 0.1323$	$R1 = 0.0624$ , $wR2 = 0.1308$	$R1 = 0.1329$ , $wR2 = 0.1955$	$R1 = 0.0631$ , $wR2 = 0.1516$	
largest diff. peak and hole, e. Å <sup>-3</sup>	0.306 and -0.173	0.413 and -0.314	0.555 and -0.354	0.456 and -0.254	0.258 and -0.219	0.418 and -0.316	0.525 and -0.364	

under vacuo to afford a yellow solid. Yellow crystals of **15** were obtained upon cooling a toluene solution layered with hexanes to  $-30\text{ }^{\circ}\text{C}$  (0.133 g, 0.211 mmol, 78%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.91 (m, 16H,  $\text{C}_6\text{H}_3$  and  $\text{C}_6\text{H}_5$ ), 4.92 (s, 1H, CH), 3.69 (hept, 2H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.9$  Hz), 3.21 (hept, 2H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.8$  Hz), 1.64 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.8$  Hz), 1.51 (s, 6H,  $\text{NCCH}_3$ ), 1.12 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.9$  Hz), 1.08 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.8$  Hz), 1.00 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.7$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  171.0 ( $\text{NCCH}_3$ ), 144.9, 143.5, 139.5, 139.2, 136.0, 135.7, 127.9, 127.8, 125.6, 125.4, 124.6 ( $\text{C}_6\text{H}_3$  and  $\text{C}_6\text{H}_5$ ), 140.8 ( $\text{C}_{\text{ipso}}$ ), 97.6 (CH), 29.6, 28.2 ( $\text{CH}(\text{CH}_3)_2$ ), 25.0, 24.7, 24.2, 24.1 ( $\text{CH}(\text{CH}_3)_2$ ), 23.3 ( $\text{NCCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$   $-67.85$  (s,  $\text{P-Ph}_2$ ). IR (Nujol):  $\nu = 1778\text{ cm}^{-1}$  (Al-H). Anal. Calcd for  $\text{C}_{41}\text{H}_{52}\text{AlN}_2\text{P}$ : C, 78.06; H, 8.31; N, 4.44. Found: C, 77.38; H, 8.42; N, 4.42.

**NacNacAl(H)OPr<sup>i</sup> (16)**. A flask containing **1** (0.120 g, 0.270 mmol) in benzene (6 mL) was charged with  $\text{PrOH}$  (0.020 mL, 0.270 mmol) and stirred for 16 h at room temperature. Solvent was removed from the resulting yellow solution and the residue was dissolved hexanes. Cooling the solution to  $-30\text{ }^{\circ}\text{C}$  afforded colorless crystals of **16** (0.070 g, 0.139 mmol, 51%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.11 (m, 6H,  $\text{C}_6\text{H}_3$ ), 4.87 (s, 1H, CH), 3.90 (hept, 1H,  $\text{O-CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.1$  Hz), 3.40 (m, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.57 (s, 6H,  $\text{NCCH}_3$ ), 1.52 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.8$  Hz), 1.41 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.7$  Hz), 1.15 (m, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 0.72 (d, 6H,  $\text{O-CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H-H}} = 6.0$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  170.0 ( $\text{NCCH}_3$ ), 144.8, 144.4, 127.3, 124.5, 124.3 ( $\text{C}_6\text{H}_3$ ), 139.6 ( $\text{C}_{\text{ipso}}$ ), 96.2 (CH), 64.0 ( $\text{O-CH}(\text{CH}_3)_2$ ), 28.8, 28.3 ( $\text{CH}(\text{CH}_3)_2$ ), 27.6 ( $\text{O-CH}(\text{CH}_3)_2$ ), 26.0, 24.7, 24.7, 24.5 ( $\text{CH}(\text{CH}_3)_2$ ), 23.0 ( $\text{NCCH}_3$ ). IR (Nujol):  $\nu = 1824\text{ cm}^{-1}$  (Al-H). Anal. Calcd for  $\text{C}_{32}\text{H}_{49}\text{AlN}_2\text{O}$ : C, 76.15; H, 9.79; N, 5.55. Found: C, 76.37; H, 10.18; N, 5.60.

**X-ray Crystallography.** The crystals were mounted on thin glass fibers using paraffin oil. Prior to data collection crystals were cooled to 200 K. Data were collected on a Bruker AXS SMART single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. The data collection results for compounds **3**, **4**, **7**, **11**, **12**, **13**, **15**, and **16** represent the best data sets obtained in several trials for each sample. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.<sup>47</sup> Diffraction data for crystals of **3**, **11**, **12**, **15**, and **16** were collected with a sequence of  $0.5^{\circ}$   $\omega$  scans at 0, 120, and  $240^{\circ}$  in  $\varphi$ . Due to a lower symmetry and in order to ensure adequate data redundancy, the diffraction data for **4**, **7**, and **13** were collected with a sequence of  $0.3^{\circ}$   $\omega$  scans at 0, 90, 180, and  $270^{\circ}$  in  $\varphi$ . Initial unit cell parameters were determined from 60 data frames with  $0.3^{\circ}$   $\omega$  scan each collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.<sup>48</sup> Unit-cell parameters and diffraction peak intensities were consistent with triclinic  $\text{P}\bar{1}$  (No. 2) symmetry space group for compounds **4**, **7**, and **13**. Presence of systematic absences in the diffraction data set together with unit cell parameters suggested the following symmetry space groups for the remaining compounds: monoclinic  $\text{P}2_1/c$  (No. 14) for compound **15**, monoclinic  $\text{P}2_1/n$  (No. 14, alternative settings) for compounds **3** and **16**, monoclinic  $\text{P}2_1/m$  (No. 11) for compound **12**, and orthorhombic  $\text{Ibam}$  (No. 72) for compound **11**. Solutions in the centrosymmetric space groups for all compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on  $F^2$ . For all structures the positions hydrogen atoms attached to non-carbon atoms (Al, N, or Si) were found as residual electron density peaks from the Fourier maps. The hydrogen atoms directly attached to carbon atoms were restrained to riding models and were consecutively treated as idealized contributions during the refinement. During the course of refinement of structure **3** a strong residual peak was observed in the vicinity of the Al-bound hydride which was successfully modeled as a hydroxyl impurity (occupancy factor of 25%). We believe that this impurity stems from partial hydrolysis by adventitious water during crystallization. All scattering factors are contained in several versions

of the SHELXTL program library, with the latest version used being v.6.12.<sup>49</sup> Crystal and structure refinement data are given in Table 1, except for compound **16**, whose parameters are given in the Supporting Information. Molecular structure of compounds **3**, **13**, and **16** are given in Figure S124, Figure S125, and Figure S126, respectively. Other structures are presented in the main text.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Further characterization data; molecular structures of **3**, **13**, and **16**; X-ray data files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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