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N-Tosyl Hydrazone Precursor for Diazo Compounds as Intermediates in the Synthesis of Aluminum Complexes

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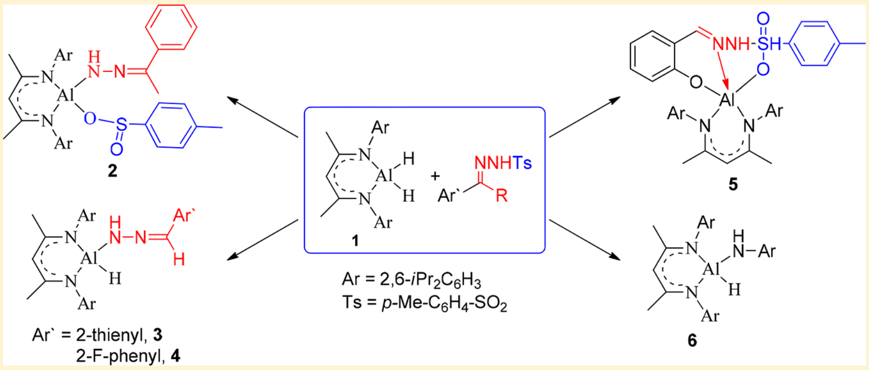
Supporting Information



ABSTRACT: The one-pot reaction of $LAlH_2$ (**1**; L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) with *N*-tosyl hydrazone as a precursor for preparing the diazo intermediate resulted in an aluminum compound with the composition LAl[OS(O)Ar]-NHN═CMePh, (Ar = 4-Me-phenyl (**2**); LAl(H)NHN═CHR, R = 2-thienyl (**3**), 2-F-phenyl (**4**)). This is the first example of utilizing *N*-tosyl hydrazone as precursor of diazo ligands for aluminum compounds. Compound **2** with Al−O−S(O)−C and the Al−N(H)N═C chains was obviously obtained via the reaction of $LAlH_2$ (**1**) with the intermediates given in Scheme 2. In contrast, compounds **3** and **4** exhibit only one Al−N(H)N═C chain due to the different behavior of the substituents R. It is worth mentioning that complex **5** with five-coordinate aluminum was obtained directly from the reaction of *N*-tosyl hydrazone with $LAlH_2$. In compound **5**, the aluminum atom functions as the center of three heterocycles. LAl(H)NHAr (Ar = 2,6-$i$$Pr_2C_6H_3$) (**6**) was obtained via the decomposition of the educts at 110 °C. Complexes **2**−**6** were characterized by NMR and single-crystal X-ray diffraction studies. Additionally, the hydroboration of benzaldehyde catalyzed by **1**−**6**, respectively, was studied, affording the corresponding product in high yield.

INTRODUCTION

In recent years diazo compounds have emerged as an important reagent in cross-coupling reactions catalyzed by transition metals, leading to the formation of various C−X bonds (e.g., X = C, N, O, Si, etc.).[1−11] Furthermore, diazo compounds are important starting materials to generate M−N bonds via the stoichiometric transformation of energetic organometallic compounds with diazo compounds.[12,13] In spite of the importance of diazo compounds, only a few stable diazo compounds, such as trimethyldiazomethane and α-diazocarbonyl derivatives, are usually applied in cross-coupling reactions or stoichiometric transformations.[14] Diazo compounds without electron-withdrawing groups are normally unstable and difficult to handle, significantly limiting the scope of diazo compounds in cross-coupling reactions or stoichiometric transformations.

Diazo compounds can be obtained in situ from the corresponding *N*-tosyl hydrazones via a Bamford−Stevens reaction in the presence of a base.[15,16] Morever, *N*-tosyl hydrazones are stable in air and can be easily obtained through the condensation of aldehydes or ketones with tosylhydrazides. These reactions determine the extensive application of *N*-tosyl hydrazones as precursors of diazo compounds in organic synthesis. The first application of *N*-tosyl hydrazone for preparing diazo compounds in a Pd-catalyzed cross-coupling reaction was carried out by Barluenga et al. in 2007.[17] Since then, many cross-coupling reactions starting from *N*-tosyl hydrazones have been reported catalyzed by transition metals.[18−28] Nevertheless, *N*-tosyl hydrazones are seldom applied as precursors for diazo compounds in stoichiometric transformations with energetic organometallic compounds.

The β-diketiminato aluminum dihydride $LAlH_2$ (**1**; L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) can react with small molecules,[29,30] unsaturated species,[13,31,32] amines,[33−35] and ionic compounds[36] to generate interesting aluminum com-

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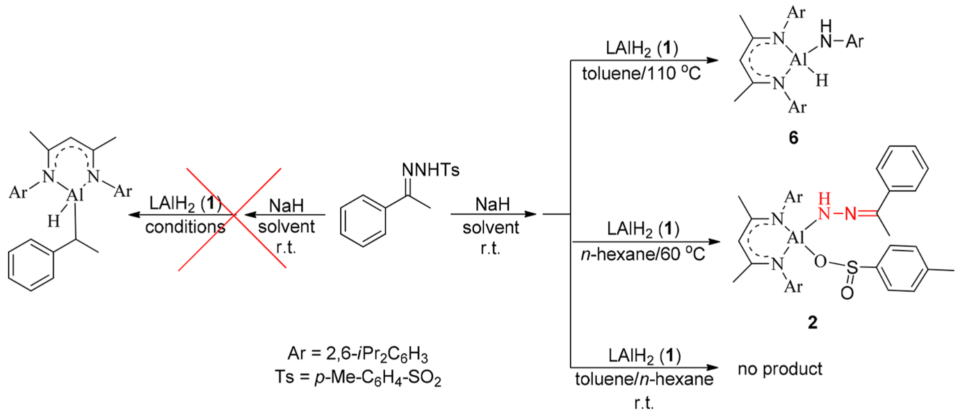
Scheme 1. Optimized Synthetic Route for Compound 2



pounds. So far, only LAl(NHN=CHSiMe$_3$)$_2$ has been prepared via the end-on insertion of the diazo group of N$_2$CHSiMe$_3$ into each Al−H bond of LAlH$_2$ (**1**).[13] Moreover, the aluminum(I) compound LAl^I was treated with 2 equiv of diphenyldiazomethane to yield the unexpected diiminylaluminum derivative L^{1}Al(N=CPh$_2$)$_2$.[12] Comparable diazo aluminum compounds have not been synthesized due to the limitation of diazo precursors. Herein, we report on three molecules bearing the Al−NH−N=CR moiety by the reaction of **1** with *N*-tosyl hydrazones in a one-pot reaction, respectively, which diminished the limited application of diazo compounds in stoichiometric reactions. Surprisingly, compound **5** with three heterocycles arranged at one Al atom was obtained when **1** was treated with a phenolic hydroxy-containing *N*-tosyl hydrazone directly. The high-temperature treatment of **1** with *N*-tosyl hydrazone in hexane resulted in the decomposition of the educts and formation of LAl(H)-NHAr (**6**; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$).

RESULTS AND DISCUSSION

From the previous literature,[24,37] diazo compounds can be obtained in situ from the corresponding *N*-tosyl hydrazones. Furthermore, they react with tin or germanium hydrides in the presence of transition metals or a PTC (phase transfer catalyst), leading to the formation of Sn−C or Ge−C bonds with elimination of one molecule of N$_2$. A similar synthesis of LAlH$_2$ (**1**) with *N*-tosyl hydrazones was investigated by our group, resulting in the end-on insertion of the N=N bond into Al−H, rather than the formation of the expected Al−C bond. The optimized synthetic route is shown in Scheme 1. According to previous literature,[24,37] a suspension of *N*-tosyl hydrazone and NaH in toluene was stirred at room temperature for 5 h, and then it was treated with 1 equiv of LAlH$_2$ (**1**) at 110 °C for 10 h, resulting in LAl(H)−NHAr (**6**; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) with an Al−N−C chain. This compound has already been obtained when a mixture of equal amounts of LAlH$_2$ (**1**) and 2,6-*i*Pr$_2$C$_6$H$_3$NH$_2$ was treated in the absence of solvent at 150 °C until H$_2$ evolution ceased.[40] It is proposed that heating the precursors to 110 °C in toluene resulted in decomposition and rearrangement to yield product **6**. X-ray-quality single crystals of **6** were obtained in toluene at low temperature. A comparison between the crystallographic data of **6** with those of LAl(H)NHAr (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)[38] confirmed the present structure (see the Supporting Information). To avoid the decomposition and rearrangement of precursors, the reaction temperature was reduced to 60 °C, but no crystals were obtained. Perhaps due to the excellent solubility within the multicomponent mixture, no suitable crystal formation was observed. Therefore, the toluene was replaced by *n*-hexane after the reaction.

A suspension of *N*-tosyl hydrazone and NaH in *n*-hexane was stirred at room temperature for 5 h, and then it was treated with 1 equiv of LAlH$_2$ (**1**) at 60 °C for 10 h, affording aluminum compound **2** in 71% yield via insertion of N=N and S=O bonds into both Al−H bonds of **1**. The insertion of a C=O bond into the Al−H bond has been reported before,[31] while the insertion of an S=O bond into an Al−H bond has been seldom explored. Compound **2** was isolated after growing colorless crystals from a concentrated *n*-hexane solution. An X-ray-quality single crystal of **2** was obtained in *n*-hexane solution at low temperature. The molecular structure and selected bond lengths and angles are given in Figure 1. The X-ray single-crystal structure of **2** shows that **2** belongs to the triclinic space

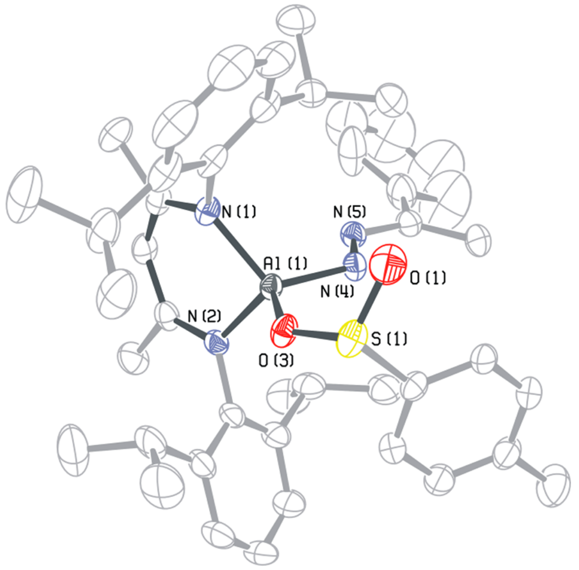


Figure 1. X-ray single-crystal structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al−N(1) 1.8785(19), Al−N(2) 1.8801(19), Al−N(4), 1.8017(19), Al−O(3) 1.7610(16), S−O(1) 1.476(2), S−O(3) 1.5807(16); N(2)−Al−N(1) 97.78(9), N(4)−Al−O(3) 109.55(8), N(1)−Al−N(4) 116.01(9), N(1)−Al−O(3) 110.37(8), N(2)−Al−O(3) 109.44(8), N(2)−Al−N(4) 113.14(9).

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group $P\bar{1}$ and exhibits an S−O−Al−N(H)−N═C framework. The Al(1)−O(3) bond length of **2** (average 1.761 Å) is close to the normal Al−OH bond distance (average 1.705 Å) in $LAl(OH)_2$,[39] and the S(1)−O(3) bond length (average 1.581 Å) is longer than the S(1)═O(1) bond length (average 1.476 Å), suggesting the formation of Al−O and S−O bonds via the insertion of an S═O moiety into the Al−H bond. The Al(1)−N(4) bond length (average 1.802 Å) is mostly close to the Al−N bond length (Al−N 1.807 Å or Al−N 1.816 Å) in $LAl(NHN{=}CHSiMe_3)_2$ reported by Zhu et al. in 2010.[13] This implies that an N═N bond inserts into the Al−H bond. In the ^1H NMR spectrum of **2** three singlet resonances appear for N═CMe, CMe in L, and *p*-Me (δ 1.6 to 2.2 ppm with a ratio of 1:2:1).

In addition, LAl(H)CH(Me)Ph was not obtained in the absence of transition metals or a PTC, and at room temperature no product was obtained in toluene or *n*-hexane due to its low reactivity. Finally, the optimized reaction conditions for the synthesis of aluminum compounds with Al−NHN═C chain structure were obtained: a suspension of *N*-tosyl hydrazones and NaH in *n*-hexane was stirred at room temperature for 5 h, and then it was treated with 1 equiv of $LAlH_2$ (**1**) at 60 °C for 10 h.

Under the optimized conditions, the reaction of *N*-tosyl hydrazone with $LAlH_2$ (**1**) gave the corresponding product LAl(H)NHN═CHR (R = 2-thienyl (**3**), 68% yield; R = 2-F-phenyl (**4**), 83% yield) with the end-on insertion of the N═N bond into the Al−H bond. Obviously, the electronic properties of the substituent in *N*-tosyl hydrazone prevents the insertion of the S═O bond into the adjacent comparatively stable Al−H bond. X-ray-quality single crystals of **3** and **4** were obtained in *n*-hexane solution at low temperature. **3** and **4** both crystallized in the monoclinic space group $P2_1/n$ and have as a common characteristic an Al−NH−N═C chain. The Al−N bond lengths of **3** (average 1.814 Å) and **4** (average 1.814 Å) are close to the Al−N bond length (Al−N 1.807 Å or Al−N 1.816 Å) of $LAl(NHN{=}CHSiMe_3)_2$ reported by Zhu et al.[13] suggesting that the Al−N bonds in both compounds **3** and **4** are covalent bonds. The molecular structures of **3** and **4** are shown in Figures 2 and 3, respectively. The ^1H NMR spectra of **3** and **4** are in agreement with the single-crystal structure.

It is worth mentioning that compound **5** with three heterocycles arranged at one Al atom was obtained in 57% yield. Moreover, we found that *N*′-(2-hydroxybenzylidene)-4-methylbenzenesulfonohydrazide did not transform into the corresponding diazo compound via a Bamford−Stevens reaction at room or higher temperature. The reaction could proceed with insertion of the S═O bond into $LAlH_2$ (**1**) along with the coordination of an N atom to the central Al atom, resulting in the formation of compound **5**. An X-ray-quality single crystal of **5** was obtained in hexane solution at low temperature (triclinic space group $P\bar{1}$). In compound **5**, the S(1)−O(2) bond (average 1.499 Å) is longer than the S(1)−O(1) bond (average 1.429 Å). The Al−O(2) bond length (average 1.901 Å) is close to the Al−O covalent bond (1.8929 or 1.9376 Å) in ref 40, suggesting that there is an insertion of an S═O bond into an Al(1)−H bond with transformation from a double to a single bond. Another Al(1)−O(3) bond length (average 1.795 Å) is close to the normal Al−OH bond distance (average 1.705 Å) in $LAl(OH)_2$,[38] implying an Al−O covalent bond. According to the Al(1)−N(3) bond length (average 2.012 Å), it is obviously a coordinate bond in comparison with the Al−N covalent bond (Al−N 1.807 Å or Al−N 1.816 Å) of $LAl(NHN{=}CHSiMe_3)_2$.[13] The X-ray single-crystal structure of **5** is shown in Figure 4.

Compounds **3**−**5** were obtained after growing crystals from a concentrated *n*-hexane solution, and their synthetic route is shown in Scheme 2.

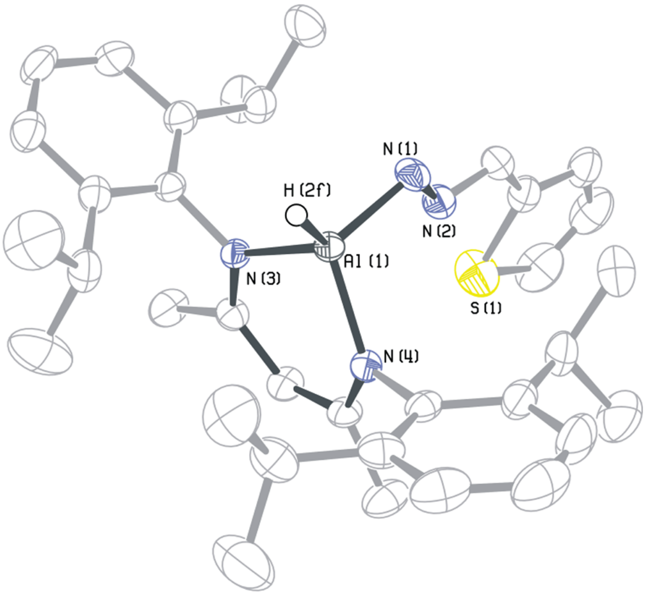

Figure 2. X-ray single-crystal structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity, except for that of the Al−H bond. Selected bond distances (Å) and angles (deg): Al−N(3) 1.884(3), Al−N(4) 1.889(3), Al−N(1), 1.814(3), Al−H(2f) 1.5434; N(3)−Al−N(4) 97.08(12), N(1)−Al−H(2f) 111.7, N(1)−Al−N(4) 110.04(13), N(4)−Al−H(2f) 116.0, N(1)−Al−N(3) 110.10(13), N(3)−Al−H(2f) 111.0.

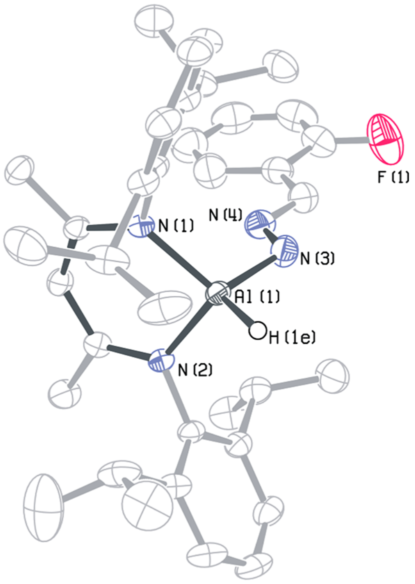

Figure 3. X-ray single-crystal structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity, except for that of the Al−H bond. Selected bond distances (Å) and angles (deg): Al−N(1) 1.8886(14), Al−N(2) 1.8883(14), Al−N(3), 1.8140(17), Al−H(1e) 1.562(12); N(1)−Al−N(2) 97.11(6), N(3)−Al−H(1e) 110.2(5), N(1)−Al−N(3) 110.79(7), N(1)−Al−H(1e) 115.1(5), N(2)−Al−N(3) 111.86(7), N(2)−Al−H(1e) 111.2(5).

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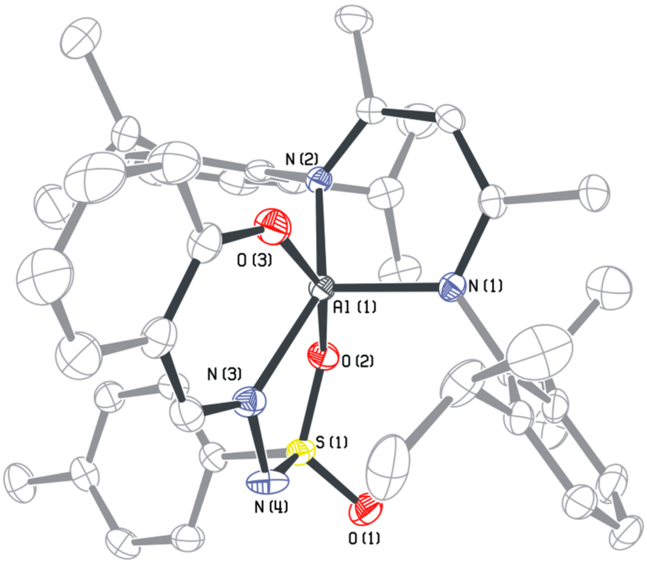
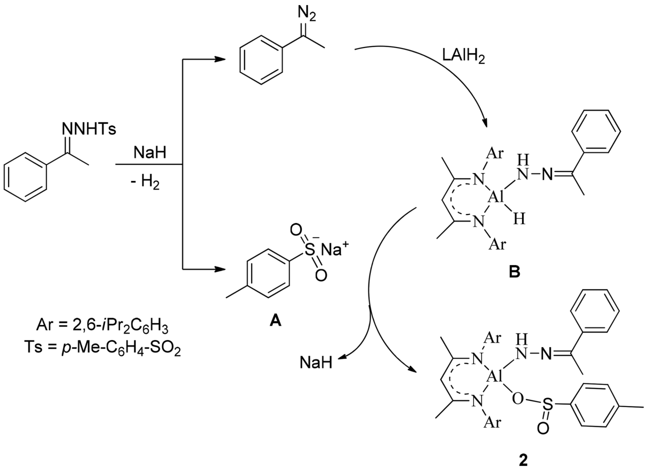


Figure 4. X-ray single crystal structure of **5**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al–N(1) 1.8967(14), Al–N(2) 1.9170(14), Al–N(3), 2.0119(15), Al–O(2) 1.9008(12), Al–O(3), 1.7952(13), S–O(1) 1.4292(13), S–O(2) 1.4993(12); N(1)–Al–N(2) 97.97(6), N(1)–Al–N(3) 116.17(6), N(1)–Al–O(2) 100.25(6), N(1)–Al–O(3) 101.10(6), N(2)–Al–N(3) 145.50(6), N(2)–Al–O(2) 90.05(6), N(2)–Al–O(3) 91.50(6), N(3)–Al–O(2) 79.64(6), N(3)–Al–O(3) 86.87(6), O(2)–Al–O(3) 158.16(6).

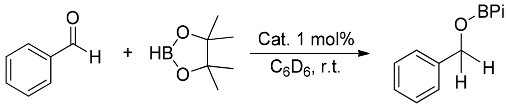
Scheme 3. Proposed Mechanism of the Synthesis of 2



From previous results and our recent work, a possible mechanism for the synthesis of **2** is shown in Scheme 3. The diazo compound along with the sodium salt **A** were obtained via treatment of *N*-tosyl hydrazone with NaH as strong base at room temperature.[15,16] This was followed by the end-on insertion of the diazo compound into the Al–H bond, resulting in the intermediate **B**. This step is supported by the similar insertion of an N═N bond into an Al–H bond reported by Zhu et al.[13] Finally, **B** reacted with the sodium salt **A**, affording the corresponding compound **2** via insertion of an S═O bond into the other Al–H bond with elimination of NaH.

The pioneering work of hydroboration of aldehydes and ketones catalyzed by aluminum hydride has been reported by Yang et al.,[41] and the catalytic activity of numerous aluminum compounds and other p-block compounds in hydroboration has been explored.[42−48] Herein, we carried out the reaction of HBpin (1 mmol) with benzaldehyde (1 mmol) by addition of **1**–**6** (1 mol %) in C_6D_6 (2 mL) at room temperature for 1 h. The results of catalytic hydroboration are summarized in Table 1. As shown in Table 1, the yields changed from 71% to 99% (Table 1, entries 2–7) and were obtained using compounds **1**–**6** as catalysts (Table 1). The yields of aluminum dihydride **1** (99%), aluminum monohydrides **3**, **4**, and **6** (87%, 78%, 90%), and **2** and **5** (75%, 71%) show a decrease in the catalytic activity, in comparison with $LAlH_2$ (**1**), due to the replacement of one or both hydrogens by other substituents. Probably, the steric hindrance of the substituents in complexes **3** and **4** results in lower yields of the corresponding products, although the electronegative element N may increase the Lewis acidic

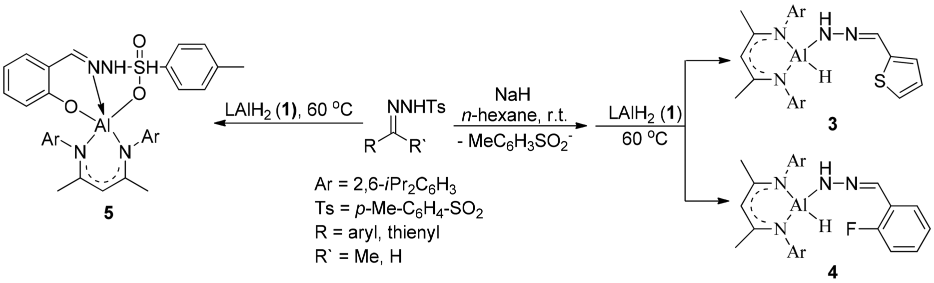
Table 1. Hydroboration of Benzaldehyde Catalyzed by 1–6[a]



entry	cat.	loading (mol %)	*t* (h)	yield (%)[b]
1	none	0	1	trace
2	**1**	1	1	99
3	**2**	1	1	75
4	**3**	1	1	87
5	**4**	1	1	78
6	**5**	1	1	71
7	**6**	1	1	90

[a] All reactions were carried out in C_6D_6 using 1 mmol of HBpin and 1 mmol of benzaldehyde at room temperature. [b] Conversion was determined by NMR spectroscopy on the basis of the consumption of the benzaldehyde, and the identity of the product was confirmed by the $PhCH_2OBpin$ signal in NMR spectra.

Scheme 2. Synthetic Route of Compounds 3–5



character. The mechanism for the reaction of aldehydes and ketones with HBpin was mentioned in previous literature.[41] In contrast, the catalytic cycle is not suitable for the hydroboration of CO_2 according to a recent paper by Aldridge and co-workers.[51] They proposed that the Al−O/B−H σ-bond metathesis is thermodynamically very unlikely without additional interaction of the strongly Lewis acidic borane in the hyboration of CO_2. Aluminum hydrides were applied to the hydroboration of benzaldehyde mainly due to the Lewis acidic character of the central aluminum and enhancement of the negative hydrogen, which was verified by the results of hydroboration. Furthermore, the yields of hydroborations catalyzed by **2**−**6** could be improved to 99% by increasing the reaction time or temperature (see the Supporting Information).

CONCLUSION

The three compounds **2**−**4** with the chain structure Al−NHN═CR have been obtained via the reactions of *N*-tosyl hydrazones as precursors for diazo compounds with $LAlH_2$ (**1**) through end-on insertion of the N═N bond into an Al−H bond, and this is the first example of utilizing *N*-tosyl hydrazones as precursors for diazo compounds in aluminum chemistry. We have developed an efficient method for the formation of aluminum compounds with the chain structure Al−NHN═CR, diminishing the limited application of diazo compounds in stoichiometric transformations, and the insertion of an S═O bond into an Al−H bond has been explored successfully. Additionally, the five-coordinated aluminum compound **5** with three heterocycles was obtained by serendipity. The hydroboration of benzaldehyde catalyzed by **1**−**6**, respectively, was explored, affording the corresponding product in moderate to high yield.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside an Etelux MB 200G glovebox. All solvents were refluxed over the appropriate drying agent and distilled prior to use. Commercially available chemicals were purchased from J&K chemical or VAS and used as received. LH,[49] $LAlH_2$,[50] and *N*-tosyl hydrazones[17] were prepared as described in the literature. Elemental analyses were performed by the Analytical Instrumentation Center of the Beijing Institute of Technology. NMR spectra were recorded on Bruker AM 400 spectrometers. Melting points were measured in sealed glass tubes.

Synthesis of LAl[OS(O)Ar]NHN═C(Me)Ph (Ar = 4-Me-phenyl) (2). A suspension of 4-methyl-*N*′-(1-phenylethylidene)-benzenesulfonohydrazide (0.145 g, 0.5 mmol) with NaH (60% dispersion in mineral oil; 0.040 g, 1.0 mmol) in *n*-hexane (15 mL) was stirred at room temperature. After the suspension was stirred for 5 h, $LAlH_2$ (**1**; 0.224g, 0.5 mmol) was loaded under a nitrogen atmosphere. The mixture was stirred at 60 °C for 10 h, and then the suspension was filtered. Colorless crystals of **2** were obtained upon cooling to −7 °C. An additional crop of **2** was obtained from the mother liquor. Total yield: 0.261 g (71%). Mp: 155−161 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 7.55 (d, 2 H, ArH), 7.30−7.16 (m, 9 H, ArH), 6.84 (d, 2 H, ArH), 6.71 (d, 2 H, ArH), 5.32 (s, 1 H, *N*H), 5.21 (s, 1 H, γ-H), 3.16−3.06 (sept, 2 H, $CHMe_2$), 3.04−2.95 (sept, 2 H, $CHMe_2$), 2.18 (S, 3 H, *p*-ArMe), 1.81 (S, 6 H, CMe), 1.64 (S, 3 H, N═CMe), 1.18 (d, J_{H-H} = 6.4 Hz, 6 H), 1.04 (d, *J* = 6.4 Hz, 6 H), 0.89 (d, *J* = 6.4 Hz, 6 H), 0.73 (d, *J* = 6.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 170.44 (s, N═C), 148.39 (s), 144.49 (s), 142.85 (s), 140.30 (s), 139.03 (s), 137.44 (s), 136.45 (s), 128.10 (s), 127.26 (s), 126.75 (s), 126.25 (s), 124.52 (d, *J* = 10.8 Hz), 123.62 (s), 123.12 (s), 122.89 (s), 122.62 (s), 96.88 (s, γ-C), 27.65 (s), 25.93 (s), 23.93 (s), 23.34 (d, *J* = 11.4 Hz), 22.84 (s), 22.46 (s), 20.23 (s), 7.61 (s). Anal. Calcd for $C_{44}H_{57}AlN_4O_2S$ (732.40): C, 72.10; H, 7.84; N, 7.64. Found: C, 72.56; H, 7.61; N, 7.89.

Synthesis of LAl(H)NHN═CH-2-thienyl (3). A suspension of 4-methyl-*N*′-(thiophen-2-ylmethylene)benzenesulfonohydrazide (0.141 g, 0.5 mmol) with NaH (60% dispersion in mineral oil; 0.040 g, 1.0 mmol) in *n*-hexane (15 mL) was stirred at room temperature. After the suspension was stirred for 5 h, $LAlH_2$ (**1**; 0.224 g, 0.5 mmol) was loaded under a nitrogen atmosphere. The mixture was stirred at 60 °C for 10 h, and then the suspension was filtered. Red crystals of **3** were obtained upon cooling to −7 °C. An additional crop of **3** was obtained from the mother liquor. Total yield: 0.194 g (68%). Mp: 165−171 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 7.20−7.09 (m, 7 H, ArH), 6.96−6.80 (m, 2 H, ArH), 5.70 (s, 1 H, *N*H), 5.25 (s, 1 H, γ-H), 3.18−3.05 (m, 4 H, $CHMe_2$), 1.77 (s, 6 H, CMe), 1.22 (d, *J* = 6.9 Hz, 6 H,), 1.08 (d, *J* = 6.9 Hz, 6 H), 1.01 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 169.31 (s, N═C), 144.81 (s), 143.75 (s), 143.31 (s), 142.97 (s), 142.51 (s), 138.30 (s), 138.05 (s), 126.07 (s), 125.51 (d, *J* = 5.6 Hz), 123.78−123.17 (m), 122.99 (d, *J* = 12.2 Hz), 121.50 (s), 120.56 (d, *J* = 6.3 Hz), 96.35 (s, γ-C), 27.67 (s), 27.34 (s), 26.01 (s), 25.45 (s), 23.46 (dd, *J* = 32.0, 13.6 Hz), 22.35 (s). Anal. Calcd for $C_{34}H_{47}AlN_4S$ (570.33): C, 71.54; H, 8.30; N, 9.82. Found: C, 71.79; H, 8.53; N, 9.97.

Synthesis of LAl(H)NHN═CH-2-F-phenyl (4). A suspension of *N*′-(2-fluorobenzylidene)-4-methylbenzenesulfonohydrazide (0.147 g, 0.5 mmol) with NaH (60% dispersion in mineral oil; 0.040 g, 1.0 mmol) in *n*-hexane (15 mL) was stirred at room temperature. After the suspension was stirred for 5 h, $LAlH_2$ (**1**; 0.224 g, 0.5 mmol) was loaded under a nitrogen atmosphere. The mixture was stirred at 60 °C for 10 h, and then the suspension was filtered. Colorless crystals of **4** were obtained upon cooling to −7 °C. An additional crop of **4** was obtained from the mother liquor. Total yield: 0.242 g (83%). Mp: 160−164 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 7.27−7.16 (m, 8 H, ArH), 7.03−6.87 (m, 2 H, ArH), 5.43 (s, 1 H, *N*H), 5.24 (s, 1 H, γ-H), 3.25−3.12 (m, 4 H, $CHMe_2$), 1.84 (s, 6 H, CMe), 1.29 (d, *J* = 6.9 Hz, 6 H), 1.15 (d, *J* = 6.9 Hz, 6 H), 1.00 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 169.77 (s), 169.37 (s, N═C), 144.69 (s), 143.95−143.66 (m), 143.47 (d, *J* = 30.0 Hz), 142.51 (s), 138.26 (s), 138.05 (s), 126.11 (s), 123.63 (s), 123.44 (s), 123.43−122.45 (m), 114.16 (s), 113.95 (s), 96.34 (s, γ-C), 27.69 (s), 25.51 (s), 23.69 (s), 23.66−23.11 (m), 22.36 (s), 21.63 (s). Anal. Calcd for $C_{36}H_{48}AlFN_4$ (582.37): C, 74.19; H, 8.30; N, 9.61. Found: C, 74.54; H, 8.11; N, 9.86.

Synthesis of LAl[(*μ*-O)(*o*-C_6H_4)][(*μ*-O)(H)S(O)(*p*-Me-C_6H_4)NH]-(NCH) (5). A suspension of *N*′-(2-hydroxybenzylidene)-4-methylbenzenesulfonohydrazide (0.145 g, 0.5 mmol) with $LAlH_2$ (**1**; 0.224 g, 0.5 mmol) in *n*-hexane (15 mL) was stirred at 60 °C for 10 h, and then the suspension was filtered. Colorless crystals of **5** were obtained upon cooling to −7 °C. An additional crop of **5** was obtained from the mother liquor. Total yield: 0.209 g (57%). Mp: 198−206 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 8.04 (s, 1 H, HC = N), 7.24−7.10 (m, 4 H, ArH), 7.01 (dd, *J* = 19.0, 8.1 Hz, 3 H, ArH), 6.81 (d, *J* = 8.3 Hz, 1 H, ArH), 6.67 (t, *J* = 8.0 Hz, 3 H, ArH), 6.55 (d, *J* = 7.8 Hz, 2 H, ArH), 5.29 (s, 1 H, γ-H), 3.64 (dt, *J* = 13.1, 6.7 Hz, 1 H, $CHMe_2$), 3.28 (tt, *J* = 13.7, 6.7 Hz, 2 H, $CHMe_2$), 2.57−2.46 (m, 1 H, $CHMe_2$), 2.15 (s, 3 H, *p*-ArMe), 1.81 (s, 3 H, CMe), 1.71 (s, 3 H, CMe), 1.35 (d, *J* = 6.5 Hz, 3 H), 1.20 (s, 1 H, NH), 1.06 (t, *J* = 6.5 Hz, 12 H), 0.78 (d, *J* = 6.5 Hz, 3 H), 0.70 (d, *J* = 6.5 Hz, 3 H), 0.39 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 168.86 (d, *J* = 8.2 Hz, N═C), 160.61 (s), 153.96 (s), 143.91 (d, *J* = 4.0 Hz), 143.23 (d, *J* = 10.5 Hz), 140.54 (d, *J* = 19.8 Hz), 139.27 (s), 137.48 (s), 124.40 (s), 123.92−123.79 (m), 123.56 (d, *J* = 25.1 Hz), 122.94 (d, *J* = 8.2 Hz), 119.36 (s), 117.63 (s), 116.10 (s), 97.59 (s, γ-C), 27.29 (d, J = 6.6 Hz), 26.33 (s), 26.05 (s), 24.18−23.46 (m), 23.27 (d, *J* = 5.2 Hz), 22.96 (s), 22.75 (s), 20.26 (s). Anal. Calcd for $C_{43}H_{54}AlN_4O_3S$ (733.37): C, 70.37; H, 7.42; N, 7.63. Found: C, 70.86; H, 7.23; N, 7.86.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00518.

Experimental details, analytical and crystallographic data of **2**−**6**, details of the crystal structure refinements, and NMR spectra (PDF)

Accession Codes

CCDC 1836601−1836605 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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■ REFERENCES

(1) Greenman, K. L.; Carter, D. S.; Van Vranken, D. L. Palladium-Catalyzed Insertion Reactions of Trimethylsilyldiazomethane. *Tetrahedron* **2001**, *57*, 5219−5225.

(2) Greenman, K. L.; Van Vranken, D. L. Palladium-Catalyzed Carbene Insertion into Benzyl Bromides. *Tetrahedron* **2005**, *61*, 6438−6441.

(3) Devine, S. K.; Van Vranken, D. L. Palladium-Catalyzed Carbene Insertion into Vinyl Halides and Trapping with Amines. *Org. Lett.* **2007**, *9*, 2047−2049.

(4) Peng, C.; Cheng, J.; Wang, J. Palladium-Catalyzed Cross-Coupling of Aryl or Vinyl Iodides with Ethyl Diazoacetate. *J. Am. Chem. Soc.* **2007**, *129*, 8708−8709.

(5) Devine, S. K.; Van Vranken, D. L. Palladium-Catalyzed Carbene Insertion and Trapping with Carbon Nucleophiles. *Org. Lett.* **2008**, *10*, 1909−1911.

(6) Chen, S.; Wang, J. Palladium-Catalyzed Reaction of Allyl Halides with α-Diazocarbonyl Compounds. *Chem. Commun.* **2008**, 4198−4200.

(7) Peng, C.; Wang, Y.; Wang, J. Palladium-Catalyzed Cross-Coupling of α-Diazocarbonyl Compounds with Arylboronic Acids. *J. Am. Chem. Soc.* **2008**, *130*, 1566−1567.

(8) Kudirka, R.; Devine, S. K.; Adams, C. S.; Van Vranken, D. L. Palladium-Catalyzed Insertion of α-Diazoesters into Vinyl Halides to Generate α, β-Unsaturated γ-Amino Esters. *Angew. Chem., Int. Ed.* **2009**, *48*, 3677−3680.

(9) Yu, W. Y.; Tsoi, Y. T.; Zhou, Z.; Chan, A. S. Palladium-Catalyzed Cross Coupling Reaction of Benzyl Bromides with Diazoesters for Stereoselective Synthesis of (E)-α, β-Diarylacrylates. *Org. Lett.* **2009**, *11*, 469−472.

(10) Tsoi, Y. T.; Zhou, Z.; Chan, A. S.; Yu, W. Y. Palladium-Catalyzed Oxidative Cross-Coupling Reaction of Arylboronic Acids with Diazoesters for Stereoselective Synthesis of (E)-α, β-Diarylacrylates. *Org. Lett.* **2010**, *12*, 4506−4509.

(11) Zhang, Y.; Wang, J. Recent Developments in Pd-Catalyzed Reactions of Diazo Compounds. *Eur. J. Org. Chem.* **2011**, *2011*, 1015−1026.

(12) Zhu, H.; Chai, J.; Stasch, A.; Roesky, H. W.; Blunck, T.; Vidovic, D.; Magull, J.; Schmidt, H. G.; Noltemeyer, M. Reactions of the Aluminum(I) Monomer LAl [L = HC{(CMe)(NAr)}$_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$] with Imidazol-2-ylidene and Diphenyldiazomethane. A Hydrogen Transfer from the Ligand to the Central Aluminum Atom and Formation of the Diiminylaluminum Compound LAl(N=CPh$_2$)$_2$. *Eur. J. Inorg. Chem.* **2004**, *2004*, 4046−4051.

(13) Chu, C.; Yang, Y.; Zhu, H. Hydroalumination of Diazo and Azido Compounds: An Al-H Addition to End-on Nitrogen of Substrates. *Sci. China: Chem.* **2010**, *53*, 1970−1977.

(14) Zhang, Z.; Wang, J. Recent Studies on the Reactions of α-Diazocarbonyl Compounds. *Tetrahedron* **2008**, *64*, 6577−6605.

(15) Bamford, W.; Stevens, T. The Decomposition of Toluene-*p*-Sulphonylhydrazones by Alkali. *J. Chem. Soc.* **1952**, 4735−4740.

(16) Fulton, J. R.; Aggarwal, V. K.; de Vicente, J. The Use of Tosylhydrazone Salts as a Safe Alternative for Handling Diazo Compounds and Their Applications in Organic Synthesis. *Eur. J. Org. Chem.* **2005**, *2005*, 1479−1492.

(17) Barluenga, J.; Moriel, P.; Valdés, C.; Aznar, F. *N*-Tosylhydrazones as Reagents for Cross-Coupling Reactions: A Route to Polysubstituted Olefins. *Angew. Chem., Int. Ed.* **2007**, *46*, 5587−5590.

(18) Brachet, E.; Hamze, A.; Peyrat, J. F.; Brion, J. D.; Alami, M. Pd-Catalyzed Reaction of Sterically Hindered Hydrazones with Aryl Halides: Synthesis of Tetra-Substituted Olefins Related to Isocombretastatin A4. *Org. Lett.* **2010**, *12*, 4042−4045.

(19) Ganapathy, D.; Sekar, G. Efficient Synthesis of Polysubstituted Olefins Using Stable Palladium Nanocatalyst: Applications in Synthesis of Tamoxifen and Isocombretastatin A4. *Org. Lett.* **2014**, *16*, 3856−3859.

(20) Tréguier, B.; Hamze, A.; Provot, O.; Brion, J. D.; Alami, M. Expeditious Synthesis of 1,1-Diarylethylenes Related to Isocombretastatin A-4 (isoCA-4) via Palladium-Catalyzed Arylation of *N*-Tosylhydrazones with Aryl Triflates. *Tetrahedron Lett.* **2009**, *50*, 6549−6552.

(21) Barluenga, J.; Florentino, L. A.; Aznar, F.; Valdés, C. Synthesis of Polysubstituted Olefins by Pd-Catalyzed Cross-Coupling Reaction of Tosylhydrazones and Aryl Nonaflates. *Org. Lett.* **2011**, *13*, 510−513.

(22) Zhao, X.; Jing, J.; Lu, K.; Zhang, Y.; Wang, J. Pd-Catalyzed Oxidative Cross-Coupling of *N*-Tosylhydrazones with Arylboronic Acids. *Chem. Commun.* **2010**, *46*, 1724−1726.

(23) Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P. Asymmetric Radical Cyclopropanation of Alkenes with In Situ-Generated Donor-Substituted Diazo Reagents via Co(II)-Based Metalloradical Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 1049−1052.

(24) Liu, Z.; Li, Q.; Yang, Y.; Bi, X. Silver(I)-Promoted Insertion into X−H (X = Si, Sn, and Ge) Bonds with *N*-Nosylhydrazones. *Chem. Commun.* **2017**, *53*, 2503−2506.

(25) Hamze, A.; Tréguier, B.; Brion, J. D.; Alami, M. Copper-Catalyzed Reductive Coupling of Tosylhydrazones with Amines: A Convenient Route to α-Branched Amines. *Org. Biomol. Chem.* **2011**, *9*, 6200−6204.

(26) Aziz, J.; Brion, J. D.; Hamze, A.; Alami, M. Copper Acetoacetonate [Cu(acac)$_2$]/BINAP-Promoted Csp^3−N Bond Formation via Reductive Coupling of *N*-Tosylhydrazones with Anilines. *Adv. Synth. Catal.* **2013**, *355*, 2417−2429.

(27) Ye, F.; Ma, X.; Xiao, Q.; Li, H.; Zhang, Y.; Wang, J. C(sp)−C(sp^3) Bond Formation through Cu-Catalyzed Cross-Coupling of *N*-Tosylhydrazones and Trialkylsilylethynes. *J. Am. Chem. Soc.* **2012**, *134*, 5742−5745.

(28) Arredondo, V.; Hiew, S. C.; Gutman, E. S.; Premachandra, I. D. U. A.; Van Vranken, D. L. Enantioselective Palladium-Catalyzed Carbene Insertion into the N−H Bonds of Aromatic Heterocycles. *Angew. Chem., Int. Ed.* **2017**, *56*, 4156−4159.

(29) Jancik, V.; Moya Cabrera, M. M.; Roesky, H. W.; Herbst-Irmer, R.; Neculai, D.; Neculai, A. M.; Noltemeyer, M.; Schmidt, H. G. Phosphane-Catalyzed Reactions of $LAlH_2$ with Elemental Chalcogens; Preparation of $[LAl(\mu\text{-}E)_2AlL][E = S, Se, Te, L = HC\{C(Me)N(Ar)\}_2$, $Ar = 2,6\text{-}iPr_2C_6H_3]$. *Eur. J. Inorg. Chem.* **2004**, *2004*, 3508−3512.

(30) González-Gallardo, S.; Jancik, V.; Cea-Olivares, R.; Toscano, R. A.; Moya-Cabrera, M. Preparation of Molecular Alumoxane Hydrides, Hydroxides, and Hydrogensulfides. *Angew. Chem., Int. Ed.* **2007**, *46*, 2895−2898.

(31) Peng, Y.; Bai, G.; Fan, H.; Vidovic, D.; Roesky, H. W.; Magull, J. Synthesis and Structural Characterization of a Terminal Hydroxide Containing Alumoxane via Hydrolysis of Aluminum Hydrides. *Inorg. Chem.* **2004**, *43*, 1217−1219.

(32) Chai, J.; Jancik, V.; Singh, S.; Zhu, H.; He, C.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M.; Hosmane, N. S. Synthesis of a New Class of Compounds Containing a Ln-O-Al Arrangement and Their Reactions and Catalytic Properties. *J. Am. Chem. Soc.* **2005**, *127*, 7521−7528.

(33) Yang, Z.; Hao, P.; Liu, Z.; Ma, X.; Roesky, H. W.; Sun, K.; Li, J. Reactivity Studies of $LAlH_2$ ($L = HC(CMeNAr)_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$) with 2-Aminobenzenethiol, 2-Aminophenol, and 1,4-Dithiane-2,5-diol. *Organometallics* **2012**, *31*, 6500−6503.

(34) Ma, X.; Hao, P.; Li, J.; Roesky, H. W.; Yang, Z. Reactivity Studies of $LAlH_2$ [$L = HC(CMeNAr)_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$] with 2-[(2-Hydroxybenzylidene)amino]-3-mercaptopropionic Acid and Benzene-1,2-diamine. *Z. Anorg. Allg. Chem.* **2013**, *639*, 493−496.

(35) Kumar, S. S.; Singh, S.; Hongjun, F.; Roesky, H. W.; Vidović, D.; Magull, J. Planar Dimeric Six-Membered Spirane Aluminum Hydrazide: Synthesis and X-ray Crystal Structure of $[LAlN(Me)NH]_2$ ($L = HC\{(2,6\text{-}iPr_2C_6H_3N)(CMe)\}_2$). *Organometallics* **2004**, *23*, 6327−6329.

(36) Singh, S.; Ahn, H. J.; Stasch, A.; Jancik, V.; Roesky, H. W.; Pal, A.; Biadene, M.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H. G. Syntheses, Characterization, and X-ray Crystal Structures of *β*-Diketiminate Group 13 Hydrides, Chlorides, and Fluorides. *Inorg. Chem.* **2006**, *45*, 1853−1860.

(37) Qiu, D.; Wang, S.; Meng, H.; Tang, S.; Zhang, Y.; Wang, J. Synthesis of Benzyltributylstannanes by the Reaction of *N*-Tosylhydrazones with Bu_3SnH. *J. Org. Chem.* **2017**, *82*, 624−632.

(38) Zhu, H.; Yang, Z.; Magull, J.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M. Syntheses and Structural Characterization of a $LAl(N_3)N[\mu\text{-}Si(N_3)(t\text{-}Bu)]_2NAl(N_3)L$ and a Monomeric Aluminum Hydride Amide LAlH(NHAr) ($L = HC[(CMe)(NAr)]_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$). *Organometallics* **2005**, *24*, 6420−6425.

(39) Bai, G.; Roesky, H. W.; Li, J.; Noltemeyer, M.; Schmidt, H. G. Synthesis, Structural Characterization, and Reaction of the First Terminal Hydroxide-Containing Alumoxane with an $[\{Al\ (OH)\}_2(\mu\text{-}O)]$ Core. *Angew. Chem., Int. Ed.* **2003**, *42*, 5502−5506.

(40) Hao, P.; Yang, Z.; Ma, X.; Wang, X.; Liu, Z.; Roesky, H. W.; Sun, K.; Li, J.; Zhong, M. Synthesis and Characterization of Compounds with the Al−O−X (X = Si, P, C) Structural Motify. *Dalton Trans.* **2012**, *41*, 13520−13524.

(41) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. An Aluminum Hydride That Functions like a Transition-Metal Catalyst. *Angew. Chem., Int. Ed.* **2015**, *54*, 10225−10229.

(42) Bismuto, A.; Thomas, S. P.; Cowley, M. J. Aluminum Hydride Catalyzed Hydroboration of Alkynes. *Angew. Chem., Int. Ed.* **2016**, *55*, 15356−15359.

(43) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. An Aluminum Dihydride Working as a Catalyst in Hydroboration and Dehydrocoupling. *J. Am. Chem. Soc.* **2016**, *138*, 2548−2551.

(44) Jakhar, V. K.; Barman, M. K.; Nembenna, S. Aluminum Monohydride Catalyzed Selective Hydroboration of Carbonyl Compounds. *Org. Lett.* **2016**, *18*, 4710−4713.

(45) Lawson, J. R.; Wilkins, L. C.; Melen, R. L. Tris(2,4,6-trifluorophenyl)borane: An Efficient Hydroboration Catalyst. *Chem. - Eur. J.* **2017**, *23*, 10997−11000.

(46) Bisai, M. K.; Pahar, S.; Das, T.; Vanka, K.; Sen, S. S. Transition Metal Free Catalytic Hydroboration of Aldehydes and Aldimines by Amidinato Silane. *Dalton Trans.* **2017**, *46*, 2420−2424.

(47) Chong, C. C.; Hirao, H.; Kinjo, R. Metal-Free *σ*-Bond Metathesis in 1, 3, 2-Diazaphospholene-Catalyzed Hydroboration of Carbonyl Compounds. *Angew. Chem., Int. Ed.* **2015**, *54*, 190−194.

(48) Pollard, V. A.; Fuentes, M. A.; Kennedy, A. R.; McLellan, R.; Mulvey, R. E. Comparing Neutral (Monometallic) and Anionic (Bimetallic) Aluminium Complexes in Hydroboration Catalysis: Influences of Lithium Cooperation and Ligand Set. *Angew. Chem., Int. Ed.* **2018**, *57*, 10651.

(49) Qian, B.; Ward, D. L.; Smith, M. R. Synthesis, Structure, and Reactivity of *β*-Diketiminato Aluminum Complexes. *Organometallics* **1998**, *17*, 3070−3076.

(50) Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H. G.; Noltemeyer, M. The First Structurally Characterized Metal-SeH Compounds: $[LAl(SeH)_2]$ and $[L(HSe)AlSeAl(SeH)L]$. *Angew. Chem., Int. Ed.* **2000**, *39*, 1815−1817.

(51) Caise, A.; Jones, D.; Kolychev, E. L.; Hicks, J.; Goicoechea, J. M.; Aldridge, S. On the Viability of Catalytic Turnover via Al−O/B−H Metathesis: The Reactivity of *β*-Diketiminate Aluminium Hydrides towards CO_2 and Boranes. *Chem. - Eur. J.* **2018**, *24*, 13624.

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