Preparation of Aluminum Hydrides with Chelating Anilido-Imine Ligands by Addition of an Al–H Bond to a C=N Bond

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Abstract. Reacting o-C₆H₄F(CH = NC₆H₃iPr₂-2,6) (L) with H₃Al·NMe₃ resulted in the aluminum dihydride with coordinated NMe₃ of composition [o-C₆H₄F(CH₂NC₆H₃iPr₂-2,6)]AlH₂(NMe₃)(1). Furthermore, the aluminum monohydride [o-C₆H₄N(C₆H₃iPr₂-2,6)](CH₂NC₆H₃iPr₂-2,6)]AlH(NMe₃) (2) was prepared by treatment of the anilido-imine ligand o-C₆H₄N(C₆H₃iPr₂-2,6)(CH = NC₆H₃iPr₂-2,6)

Introduction

Much attention was paid to the aluminum hydride family because of their scientific importance and numerous applications. They are well-known reducing agents for unsaturated molecules such as ketones, nitriles, alkenes, and alkines.^[1] In addition, aluminum hydrides are very effective precursors for preparing aluminum chalcogenides^[2] and alumoxanes by controlled hydrolysis.^[3] They can be used in the production of amidoalane clusters with organic nitriles,^[4] in the preparation of carbaalane clusters and chlorinated derivatives using alkines,^[5] in the generation of alkoxide and aryloxide complexes,^[6] and in preparing aluminum containing heterocycles^[7] by elimination of H₂.

In the past decade, bulky aryl-substituted β -diketimine has attracted much attention due to its strong electron donation and steric constraints that can stabilize main group metal complexes,^[8] although these β -diketiminate ligands are not easily modified. The bidentate salicylaldiminate chelate ligand possesses easily modified features and has been applied in olefin polymerization chemistry.^[9] Our current research interest is to select a kind of novel bulky anilido–imine ligand that combines the steric effect of the β -diketiminate ligand framework and the more easily modified feature of the salicyl-

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 (L^\ast) with $H_3Al\cdot NMe_3$ in high yield. The formations of the two complexes both involve aluminum hydride addition to the C=N double bond. Compounds 1 and 2 were characterized by 1H NMR and IR spectroscopic, elementary analysis, and single-crystal X-ray diffraction studies.

aldiminate ligand framework to stabilize the aluminum center. To date, some alkylaluminum,^[10] nickel,^[11] copper,^[12] zinc,^[13] yttrium,^[14] boron,^[15] iridium,^[16] and platinum^[17] complexes bearing such ligands have been prepared and their catalytic properties have also been investigated. To the best of our knowledge, there have been no reports on aluminum hydride species with anilido-imine ligands. Given the above situation, herein we report on the synthesis of $[o-C_6H_4F(CH_2NC_6H_3iPr_2-2,6)]AlH_2(NMe_3)$ (1) and $[o-C_6H_4N(C_6H_3iPr_2-2,6)(CH_2NC_6H_3iPr_2-2,6)]AlH(NMe_3)$ (2) by addition of aluminum hydride to L and L*, respectively.

Results and Discussion

L and L^{*} were synthesized by a literature procedure^[11] shown in Scheme 1. The imine L was obtained from the reaction of 2,6-diisopropylaniline and o-fluorobenzaldehyde. The anilido-imine L* can be prepared via a nucleophilic aromatic displacement reaction of fluorine using LiNHAr (Ar = 2,6 $iPr_2C_6H_3$). Compounds 1 and 2 were synthesized in reasonable yields by reaction of a small excess of H₃Al·NMe₃ with L and L*, respectively, in toluene at 0 °C. The reactions of aluminum hydride with L and L* are quite different, when compared with that of the β -diketiminate ligand. Their C=N double bonds are reduced to C-N single bonds. However, in the case of the β diketiminate ligand the C=N double bonds are not reduced.[18] The reason for this different behavior might be due to the conjugation of the C=N with the C=C double bond in the β diketiminate ligand. The additions of aluminum hydride to C=N double bonds are accompanied with the hydrides turning to protons. Meanwhile, the core structure of compound 2 turns to an aluminum containing six-membered ring under elimination of H₂. This is attributed to the sufficient reactivity of the second hydride at the same Al atom to interact with the



other proton of the ligand with elimination of H_2 . A similar migration reaction of a methyl group was not observed when AlMe₃ was used instead,^[10a] and the CH=N double bond was retained. We assume that this is due to the higher reactivity of the hydride compared to that of CH₃. In the two reactions only the mononuclear product was obtained when the reactions were conducted in the ratio of 1:1 or 1:2. We think that the 2,6-*i*Pr₂C₆H₃ groups on the nitrogen atoms prevent the dimerization of compounds **1** and **2**, respectively. The two compounds are well soluble in common solvents such as toluene, dichloromethane, and tetrahydrofuran, and they can be stored in the glove box for several months without any decomposition.



Scheme 1. Preparation of compounds 1 and 2.

In the ¹H NMR spectra of compounds **1** and **2**, the resonances ($\delta = 2.60$ for **1**) and ($\delta = 2.33$ for **2**) show the existence of the NMe₃ group, respectively. The resonances of protons on CH₂-N can be found at $\delta = 4.20$ for **1** and $\delta = 4.15$ for **2**, which indicate the conversion of hydrides to protons. The resonance for the hydride could not be observed in the ¹H NMR because of the quadrupolar broadening by the Al nucleus. The presence of Al–H bonds in **1** and **2** is evident from their IR spectra. The broad IR bands around 1835 cm⁻¹ in **1** and 1854 cm⁻¹ in **2** are assigned to the Al–H stretching frequency, which compares well with the known value of 1860 cm⁻¹.^[19] The absorptions for the C=N double bond and N–H group are absent in the IR spectrum of **2**.

Compounds 1 and 2 crystallize in the monoclinic system *C*2/*c* and in the monoclinic *P*2₁/*n* space group, respectively. The molecular structures of 1 and 2 are depicted in Figure 1 and Figure 2. Selected bond lengths and angles are listed in the captions of the figures The tetrahedral aluminum center in Figure 1 of compound 1 indicates the existence of two H atoms and the coordinate NMe₃ group. For the structure of 2, the aluminum atom also adopts a distorted tetrahedral geometry with one H atom, one nitrogen atom of the NMe₃ group and two nitrogen atoms of the anilido-imine ligand. The Al–H bond lengths (1.48(2) Å and 1.52(2) Å for 1, 1.53(2) Å for 2) are similar to that in [ArN(CH₂)₃NAr]AlHNMe₃ (Ar = 2,6-*i*Pr₂C₆H₃) (1.52 Å).^[20] The Al–N (amido) distances

(1.8214(15) Å for **1**, 1.8103(17) Å and 1.8591(17) Å for **2**) are much shorter than the coordinated Al–N (imine) distance (1.963(1) Å) in $[o-C_6H_4N(C_6H_3iPr_2-2,6)(CH = NC_6H_3iPr_2-2,6)]AlMe_2,^{[10a]}$ which shows the covalent nature of the Al–N bond in **1** and **2**, respectively. The Al–N_{NMe3} bond length (2.0188(17) Å in **1**, 2.0274 Å in **2**) is comparable to those in [ArN(CH₂)₃NAr]AlRNMe₃ (Ar = 2,6-*i*Pr₂C₆H₃, R = H, F) (2.024(2), 2.000(2) Å].^[20] The N(1)–C(13) bond length (1.47(2) Å] in **1** and N(1)–C(7) (1.481(2) Å] in **2** show a typical C–N single bond character than the corresponding retained C=N double bond in $[o-C_6H_4N(C_6H_3iPr_2-2,6)(CH = NC_6H_3iPr_2-2,6)]AlMe_2 (1.298(2) Å].^{[10a]}$



Figure 1. Molecular structure of 1. Thermal ellipsoids are drawn at the 50% level and the hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /deg: Al(1)–N(1) 1.8214(15), Al(1)–N(2) 2.0188(17), N(1)–C(13) 1.47(2) Å, N(1)–Al(1)–N(2) 111.78(7), C–N(1)–C(13) 113.62(13), C–N(1)–Al(1) 125.54(11), C(13)–N(1)–Al(1) 119.85(11), N(1)–C(13)–C 114.48(14).



Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level and the hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /deg: Al(1)–N(1) 1.8103(17), Al(1)–N(2) 1.8591(17), Al(1)–N(3) 2.0274(18), N(1)–Al(1)–N(2) 102.62(8), N(1)–Al(1)–N(3) 108.23(8), N(2)–Al(1)–N(3) 109.07(7), C–N(1)–C(7) 115.39(15), C–N(1)–Al(1) 128.44(13), C(7)–N(1)–Al(1) 111.94(12), N(1)–C(7)-C 113.70(15).

Conclusions

We describe the synthesis, characterization, and X-ray structure of two aluminum hydrides supported by the anilido-imine ligand. They are prepared by addition reactions of the Al–H bond to the unsaturated C=N bond. The resulting compounds are interesting precursors for the preparation of new aluminum compounds.

Experimental Section

General Procedures

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All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside an MBraun MB200 glove box. All solvents were distilled from Na/benzophenone ketyl prior to use. Commercially available chemicals were purchased from J&K chemical or VAS and used as received. ¹H NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer. The melting points were measured in sealed glass tubes and were not corrected. Elemental analyses were carried out by the Analytical Instrumentation Center of the Peking University. The IR spectra were recorded using KBr pellets with a Bio-Rad Digilab FTS-7 spectrometer from 4000 to 400 cm⁻¹.

$[o-C_6H_4F(CH_2NC_6H_3iPr_2-2,6)]AlH_2(NMe_3)$ (1)

To a toluene solution (20 mL) of o-C₆H₄F(CH = NC₆H₃iPr₂-2,6) (0.283 g, 1.0 mmol) at 0 °C was added drop by drop H₃Al·NMe₃ in toluene (1 M, 1.2 mL, 1.2 mmol). After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued for 12 h. The solution was evaporated to dryness in vacuo, and the residue was washed with cold *n*-hexane (10 mL) to yield crystalline **1** (0.326 g,87%); m.p. 89–92 °C. **IR** (KBr (cm⁻¹)): \tilde{v} = 1835 cm⁻¹ (m, Al-H). ¹H NMR (400MHz, CDCl₃, 25 °C, TMS): δ = 7.15–6.80(m, 7 H, Ph-H), 4.20(s, 2 H, CH₂N), 3.38(m, 2 H, CHMe₂), 2.60(s, 9 H, NMe₃), 1.19(d, 6 H, CHMe₂), 0.85(d, 6 H, CHMe₂); **Elemental Analysis** calcd. (%) for C₂₂H₃₄AlFN₂: C 70.94, H 9.20, N 7.52; Found: C 70.89, H 9.24, N 7.48.

$[o-C_6H_4N(C_6H_3iPr_2-2,6)(CH_2NC_6H_3iPr_2-2,6)]AlH(NMe_3)$ (2)

To a toluene solution (20 mL) of o-C₆H₄N(C₆H₃*i*Pr₂-2,6)(CH = NC₆H₃*i*Pr₂-2,6) (0.440 g, 1.0 mmol) at 0 °C was added drop by drop H₃Al·NMe₃ in toluene (1 M, 1.3 mL, 1.3 mmol). After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued for 24 h. The solution was filtered to remove any solid impurities and stored at room temperature for crystallization. Product **2** was isolated as colorless crystals. An additional crop of **2** was obtained from the mother liquor. Total yield: 0.437 g (82.9%); m.p. 140–142 °C. **IR** (KBr (cm⁻¹)): \tilde{v} = 1854 cm⁻¹ (m, Al-H). ¹H NMR (400MHz, CDCl₃, 25 °C, TMS): δ = 7.32–6.88(m, 4 H, Ph-*H*), 6.47–6.18 (d, 6 H, Ph-*H*), 4.15(s, 2 H, C*H*₂N), 3.76–3.20(m, 4 H, C*HM*e₂), 2.33(s, 9 H, N*M*e₃), 1.42–0.45(m, 24 H, CH*M*e₂); **Elemental Analysis** calcd. (%) for C₃₄H₅₀AlN₃: C 77.38, H 9.55, N 7.96; Found: C 77.28, H 9.52, N 8.01.

X-ray Structure Determination of 1 and 2

Suitable crystals of **1** and **2** were mounted on a glass fiber and coated with paraffin oil. They were collected on the Rigaku AFC10 Saturn724 + (2 × 2 bin mode) diffractometer equipped with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Empirical absorption correction was applied using the SADABS program.^[21] The structures were solved by direct methods^[22] and refined by full-matrix

least-squares on F^2 using the SHELXL-97 program.^[23] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms connected to carbon atoms were included at geometrically calculated positions and refined by using a riding model (Table 1).

Table 1. X-ray crystallographic data for 1 and 2.

	1	2
Empirical formula	C ₂₂ H ₃₄ AlFN ₂	C ₃₄ H ₅₀ AlN ₃
Formula weight	372.49	527.75
Temperature /K	153(2)	163(2)
Wavelength /Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/c$
a /Å	22.737(4)	14.637(3)
b /Å	11.294(2)	11.112(2)
c /Å	18.035(4)	20.129(5)
a /°	90	90
β /°	102.949	105.962
γ /°	90	90
$V/Å^3$	4513.7(15)	3147.7(12)
Z	8	4
D _{calcd.} /Mg·m ⁻³	1.096	1.114
Absorption coefficient /mm ⁻¹	0.105	0.090
F(000)	1616	1152
θ range for data collection /°	2.92 to 29.13	2.39 to 28.50
Index ranges	$-27 \le h \le 31$	$-17 \le h \le 19$
	$-14 \le k \le 15$	$-10 \le k \le 14$
	$-24 \le l \le 24$	$-27 \le l \le 27$
Reflections collected	23531	26652
R (int)	0.0456	0.0437
Data / restraints / parameters	6047 / 0 / 250	7872 / 0 / 359
Goodness-of-fit on F^2	1.003	1.0002
Final Rint $[I > 2\sigma(I)]$	R1 = 0.0664	R1 = 0.0676
	wR2 = 0.1450	wR2 = 0.1810
Rint (all data)	R1 = 0.0820	R1 = 0.0781
8 a	wR2 = 0.1563	wR2 = 0.1897
Largest diff. peak /e·Å ⁻³	0.233 and	0.238 and
	-0.280	-0.268

CCDC-1030540 (1) and -1030541 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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References

- J. J. Eisch, Comprehensive Organometallic Chemistry II (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Elsevier, Oxford, 1995, Vol. II, pp. 557–569.
- [2] a) V. Jancik, Y. Peng, H. W. Roesky, J. Li, D. Neculai, A. M. Neculai, R. Herbst-Irmer, J. Am. Chem. Soc. 2003, 125, 1452–1453; b) Z. Yang, X. Ma, V. Jancik, Z. Zhang, H. W. Roesky, J. Magull, M. Noltemeyer, H.-G. Schmidt, R. Cea-Olivares, R. A. Toscano, Inorg. Chem. 2006, 45, 3312–3315; c) Z. Yang, X. Ma, R. B. Oswald, H. W. Roesky, C. Cui, H.-G. Schmidt, M. Noltemeyer, Angew. Chem. 2006, 118, 2335–2338; Angew. Chem. Int.

Ed. **2006**, *45*, 2277–2280; d) Z. Yang, X. Ma, H. W. Roesky, Y. Yang, J. Magull, A. Ringe, *Inorg. Chem.* **2007**, *46*, 7903–7906.

[3] Y. Peng, G. Bai, H. Fan, D. Vidovic, H. W. Roesky, J. Magull, *Inorg. Chem.* 2004, 43, 1217–1219.

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- [4] N. D. Reddy, S. S. Kumar, H. W. Roesky, D. Vidovic, J. Magull, M. Noltemeyer, H. G. Schmidt, *Eur. J. Inorg. Chem.* 2003, 442– 448.
- [5] a) A. Stasch, M. Ferbinteanu, J. Prust, W. Zheng, F. Cimpoesu, H. W. Roesky, J. Magull, H. G. Schmidt, M. Noltemeyer, J. Am. Chem. Soc. 2002, 124, 5441–5448; b) S. S. Kumar, J. Rong, S. Singh, H. W. Roesky, D. Vidovic, J. Magull, D. Neculai, Organometallics 2004, 23, 3496–3500.
- [6] J. P. Campbell, W. L. Gladfelter, *Inorg. Chem.* 1997, 36, 4094– 4098.
- [7] a) X. Ma, Z. Yang, X. Wang, H. W. Roesky, F. Wu, H. Zhu, *Inorg. Chem.* 2011, 50, 2010–2014; b) Z. Yang, P. Hao, Z. Liu, X. Ma, H. W. Roesky, K. Sun, J. Li, *Organometallics* 2012, 31, 6500–6503; c) P. Hao, Z. Yang, X. Ma, X. Wang, Z. Liu, H. W. Roesky, K. Sun, J. Li, M. Zhong, *Dalton Trans.* 2012, 41, 13520–13524; d) X. Ma, P. Hao, J. Li, H. W. Roesky, Z. Yang, Z. Anorg. Allg. Chem. 2013, 639, 493–496; e) Z. Yang, P. Hao, Z. Liu, H. W. Roesky, Y. Yang, J. Li, Z. Anorg. Allg. Chem. 2013, 639, 2618–2622.
- [8] a) M. Cheng, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc. 1998, 120, 11018–11019; b) P. L. Holland, W. B. Tolman, J. Am. Chem. Soc. 1999, 121, 7270–7271; c) C. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, Angew. Chem. Int. Ed. 2000, 39, 4274–4276.
- [9] T. Xu, H. An, W. Gao, Y. Mu, *Eur. J. Inorg. Chem.* **2010**, 3360–3364.
- [10] a) X. Liu, W. Gao, Y. Mu, G. Li, L. Ye, H. Xia, Y. Ren, S. Feng, *Organometallics* 2005, 24, 1614–1619; b) X. Liu, H. Xia, W. Gao, L. Ye, Y. Mu, Q. Su, Y. Ren, *Eur. J. Inorg. Chem.* 2006, 1216– 1222; c) W. Yao, Y. Mu, A. Gao, Q. Su, Y. Liu, Y. Zhang, *Polymer* 2008, 49, 2486–2491.
- [11] a) H. Gao, W. Guo, F. Bao, G. Gui, J. Zhang, F. Zhu, Q. Wu, Organometallics 2004, 23, 6273–6280; b) H. Wang, X. Meng, G.

Jin, Dalton Trans. 2006, 2579–2585; c) H. Gao, Z. Ke, L. Pei, K. Song, Q. Wu, Polymer 2007, 48, 7249–7254.

- [12] a) E. C. Brown, N. W. Aboelella, A. M. Reynolds, G. Aullon, S. Alvarez, W. B. Tolman, *Inorg. Chem.* 2004, 43, 3335–3337; b)
 A. M. Reynolds, B. F. Gherman, C. J. Cramer, W. B. Tolman, *Inorg. Chem.* 2005, 44, 6989–6994; c)
 Y. M. Badiei, A. Krishnaswamy, M. M. Melzer, T. H. Warren, *J. Am. Chem. Soc.* 2006, 128, 15056–15057; d)
 B. F. Gherman, W. B. Tolman, C. J. Cramer, *J. Comput. Chem.* 2006, 27, 1950–1961; e)
 E. C. Brown, I. BarNahum, J. T. York, N. W. Aboelella, W. B. Tolman, *Inorg. Chem.* 2007, 46, 486–496.
- [13] a) B. Y. Lee, H. Y. Kwon, S. Y. Lee, S. J. Na, S. I. Han, H. Yun, H. Lee, Y. W. Park, J. Am. Chem. Soc. 2005, 127, 3031–3037; b) T. Bok, H. Yun, B. Lee, Inorg. Chem. 2006, 45, 4228–4237; c) Q. Su, W. Gao, Q. L. Wu, L. Ye, G. H. Li, Y. Mu, Eur. J. Inorg. Chem. 2007, 4168–4175.
- [14] P. G. Hayes, G. C. Welch, D. J. H. Emslie, C. L. Noack, W. E. Piers, M. Parvez, *Organometallics* **2003**, *22*, 1577–1579.
- [15] Y. Ren, X. Liu, W. Gao, H. Xia, L. Ye, Y. Mu, Eur. J. Inorg. Chem. 2007, 1808–1814.
- [16] X. Meng, Y. Lin, G. Jin, J. Organomet. Chem. 2008, 693, 2597– 2602.
- [17] S. M. Kloek, K. I. Goldberg, J. Am. Chem. Soc. 2007, 129, 3460– 3461.
- [18] C. Cui, H. W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, Angew. Chem. Int. Ed. 2000, 39, 1815–1817; Angew. Chem. 2000, 112, 1885–1887.
- [19] J. L. Atwood, S. M. Lawrence, C. L. Raston, J. Chem. Soc., Chem. Commun. 1994, 73–74.
- [20] H. Zhu, J. Chai, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, D. Vidovic, J. Magull, *Eur. J. Inorg. Chem.* **2003**, 3113–3119.
- [21] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1997.
- [22] G. M. Sheldrick, SHELXS-90, Program for Structure Solution, Acta Crystallogr, Sect. A 1990, 46, 467–473.
- [23] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

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