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One-step synthesis of new aluminum hydrides bearing a highly sterically hindered acenaphthene-1,2-diimine ligand

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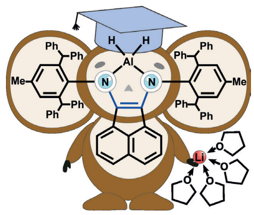
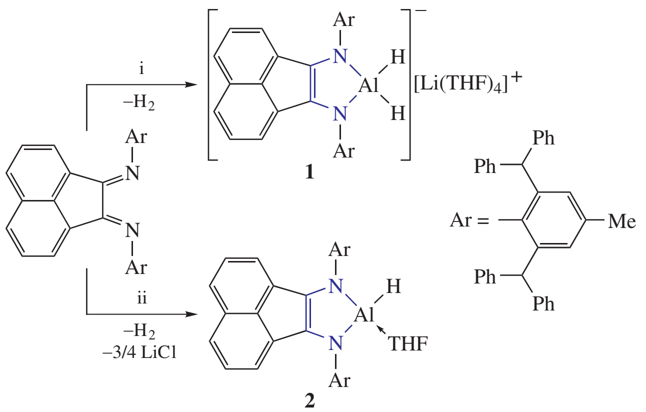
Treatment of a bulky dbhmp-bian ligand (dbhmp-bian = = 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)imino]acenaphthene) by 1 equiv. of $LiAlH_4$ or mixture of 3/4 equiv. $LiAlH_4$ and 1/3 eqiuv. $AlCl_3$ in tetrahydrofuran results in new hydrides $[(dbhmp\text{-}bian)AlH_2(THF)]^-[Li(THF)_4]^+$ and (dbhmp-bian)-AlH(THF), respectively. Both complexes were characterized by spectroscopic (IR, NMR) and X-ray diffraction methods.



Keywords: aluminum hydrides, imines, acenaphthenes, sterically hindered ligands, diimine ligands, redox-active ligands.

Aluminum hydrides chelated by bulky ligands attract attention as efficient reductants and hydride-ion sources in reactions with unsaturated compounds, EH-acids (E = C, N, O, P, S, *etc.*) and small molecules.[1–3] Some of these processes can be reconsidered as key steps of catalytic cycles of organic substrates transformations.[3] For instance, the detailed studies of aluminum hydride protonolysis with phenols,[4,5] amines and thiols,[4,6,7] or terminal alkynes[8] as well as hydroalumination of CO_2 or substrates containing C=O moieties[9,10] served for developing efficient catalysts based on β-diketiminato aluminum hydrides for dehydrocoupling,[11] hydroboration[11–14] and hydrosilylation[12] reactions. Generally, the mentioned catalytic cycles proceeds by involving the Al–H functionality only, while no structural transformations occur with N,N-ligands. However, several examples of N–H and O–H bond activation under aluminum–ligand cooperation using the bis(imino)pyridine aluminum complex $(I_2P)Al(THF)H$ [I_2P is 2,6-(2,6-$Pr^i_2C_6H_3N$=CPh)$_2C_5H_3N$] were reported[15–17] when both aluminum and ligand sites were involved to form new bonds with substrates (*e.g.*, amines, alcohols or phenols). In addition, owing to aluminum–ligand cooperative effect, compound $(I_2P)Al(THF)H$ exhibited catalytic activity in dehydrogenative coupling of benzylamine and dehydrogenation of formic acid.[17] The results achieved show high potential of these and related compounds in main group metal catalysts development. Obviously, it requires obtaining new aluminum hydride complexes as well as exploration, their reactivity depending on the kind and bulkiness of N-donor ligands. Recently we synthesized compounds with Al–H moiety stabilized by radical anion or dianion of redox-active dpp-bian ligand, *viz.* 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene, and studied their reductive potential towards some organic substrates.[18,19] Here we report on preparation of two new aluminum hydrides bearing a highly sterical hindered dbhmp-bian ligand $[(dbhmp\text{-}bian)AlH_2]^-[Li(THF)_4]^+$ **1** and (dbhmp-bian)AlH(THF) **2**, where dbhmp-bian is 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)imino]acenaphthene. This ligand was chosen because of easy accessibility[20] as well as better stabilization effect of 2,6-dibenzhydryl-4-methylphenyl *vs.* 2,6-diisopropylphenyl group. This ligand was also employed in transition metal-catalyzed olefin polymerization.[21] Moreover, to the best of our knowledge, there are no synthesized main group metal complexes of acenaphthene-1,2-diimine family with substituents bulkier than 2,6-$Pr^i_2C_6H_3$ substituents at N-atoms of ligand.

Hydrides **1** and **2** have been synthesized by treatment of free dbhmp-bian with $LiAlH_4$ only (for **1**) or with addition of $AlCl_3$ (for **2**) in THF (Scheme 1). In both cases, the reduction of diimine moiety of dbhmp-bian to dianionic form occurred and hydrogen evolution was observed. Compounds **1** (81%) and **2** (86%) were isolated as green crystals grown from THF or Et_2O, respectively, and were characterized by elemental analysis, IR, NMR spectroscopy as well as X-ray diffraction method† (for synthetic procedures



Scheme 1 *Reagents and conditions*: i, $LiAlH_4$ (1 equiv.), THF; ii, $LiAlH_4$ (0.75 equiv.), $AlCl_3$ (0.25 equiv.), THF.

† *Crystallographic data for* **1**. Crystals of $C_{114}H_{134}AlLiN_2O_9$ (M = 1710.14) are monoclinic, space group Cc, at 100 K: a = 26.5917(7), b = 44.9008(12) and c = 16.7904(4) Å, β = 111.353(1)°, V = 18671.4(8) Å^3, Z = 8, d_{calc} = = 1.217 g cm^{-3}, μ(MoKα) = 0.084 mm^{-1}, F(000) = 7360. 105455 reflections were measured and 43909 independent reflections (R_{int} = 0.0370) were used in a further refinement. The refinement converged to wR_2 = 0.1255 and GOF = 1.035 for all independent reflections [R_1 = 0.0476 was calculated against F for 36894 observed reflections with $I > 2\sigma(I)$].

and detailed spectral information, see Online Supplementary Materials). It should be noted that reaction of dbhmp-bian with one equivalent of $LiAlH_4$ gives the only product **1**, while similar process for dpp-bian was accompanied by hydrogenation of C–C diimine bond.[18]

In the IR spectra of the complexes, Al–H bonds give rise to the absorption bands at 1757 and 1702 cm^{-1} for **1**, and 1816 cm^{-1} for **2** (Figures S1 and S2, Online Supplementary Materials), which are well comparable with IR spectra of aluminum hydrides coordinated to dianionic dpp-bian ligand.[18] Their ^{1}H NMR spectra in THF-d_8 (Figures S3 and S4) contain the expected set of signals. Because of dynamic processes in the solution of **1** in THF-d_8 caused probably by vibrations of –$CH(Ph)_2$ groups, the well resolved ^{1}H NMR spectrum has been recorded only at 213 K. Herein the hydride atoms appear as a broad singlet at δ 4.62 ppm, which is close to chemical shifts of hydride atoms in $(I_2P)Al(THF)H(THF)$ or $(I_2P)Al(THF)H$ complexes.[15] Unfortunately, a ^{1}H NMR signal appropriate to hydride atom in **2** could not be detected even at 223 K due to the quadrupolar effect of ^{27}Al nucleus.

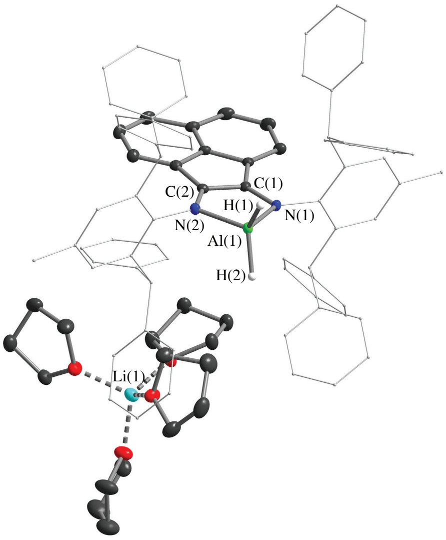


Figure 1 Molecular structure of one of two independent molecules of **1**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms with the exception of H(1) and H(2) are omitted. Aryl substituents at *N*-diimine atoms are represented schematically for clarity. Selected bond lengths (Å): Al(1)–N(1) 1.877(2), Al(1)–N(2) 1.886(2), Al(1)–H(1) 1.59(3), Al(1)–H(2) 1.51(3), C(1)–N(1) 1.402(3), C(2)–N(2) 1.382(3), C(1)–C(2) 1.380(4); selected angles (°): N(1)–Al(1)–N(2) 89.15(10), N(1)–Al(1)–H(1) 113.7(12), N(2)–Al(1)–H(1) 113.3(12), N(1)–Al(1)–H(2) 114.1(12), N(2)–Al(1)–H(2) 115.5(12), H(1)–Al(1)–H(2) 109.9(17).

Crystallographic data for **2**. Crystals of $C_{90}H_{85}AlN_2O_3$ (M = 1269.57) are monoclinic, space group $C2/c$, at 150 K: a = 16.2502(10), b = 17.6946(12) and c = 48.256(4) Å, β = 92.562(6)°, V = 13861.7(17) Å^3, Z = 8, d_{calc} = = 1.217 g cm^{-3}, μ(CuKα) = 0.671 mm^{-1}, F(000) = 5408. 27266 reflections were measured and 13524 independent reflections (R_{int} = 0.0863) were used in a further refinement. The refinement converged to wR_2 = 0.2352 and GOF = 1.043 for all independent reflections [R_1 = 0.0916 was calculated against F for 6835 observed reflections with $I > 2\sigma(I)$].

The measurements were performed on Bruker D8 Quest (MoKα radiation, λ = 0.71073 Å, **1**) and SuperNova Atlas (CuKα radiation, λ = 1.5406 Å, **2**) diffractometers. The structures were solved by dual-space method using the SHELXT.[22] All non-hydrogen atoms in **1** and **2**, H(1A), H(2A), H(1B), H(2B) atoms in **1** and H(1) atom in **2** were found from Fourier syntheses of electron density and were refined anisotropically using the SHELXTL (**1**, **2**)[23] and OLEX2 (**2**)[24] software packages. All other hydrogen atoms in **1** and **2** were placed in calculated positions and were refined using the riding model with $U_{iso}(H) = 1.2U_{eq}$ [$U_{iso}(H) = 1.5U_{eq}$ for the hydrogen atoms in Me groups] of their parent atoms.

CCDC 1922849 and 1922850 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

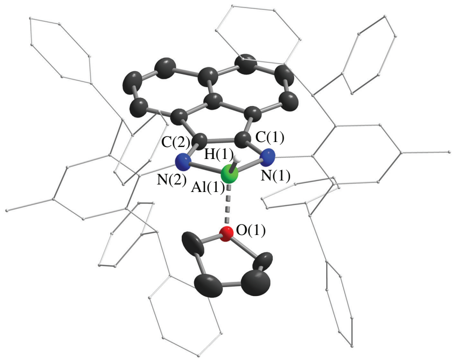


Figure 2 Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms with the exception of H(1) are omitted. Aryl substituents at *N*-diimine atoms are represented schematically for clarity. Selected bond lengths (Å): Al(1)–N(1) 1.847(4), Al(1)–N(2) 1.839(4), Al(1)–H(1) 1.58(4), Al(1)–O(1) 1.932(18), C(1)–N(1) 1.405(5), C(2)–N(2) 1.405(5), C(1)–C(2) 1.376(6); selected angles (°): N(1)–Al(1)–N(2) 92.87(15), N(1)–Al(1)–H(1) 119.0(14), N(2)–Al(1)–H(1) 126.8(14), N(1)–Al(1)–O(1) 116.4(5), N(2)–Al(1)–O(1) 105.5(6), H(1)–Al(1)–O(1) 97.0(15).

Molecular structures of hydrides **1** and **2** (Figures 1 and 2) have been determined by single crystal X-ray analysis.† The unit cell of **1** contains two crystallographically independent molecules with similar geometry, therefore only one of these is represented (both molecules are shown in Figure S8). In both monomeric complexes **1** and **2**, a four-coordinated aluminum atom has distorted tetrahedral geometry. Interatomic distances of diimine moieties in **1** and **2** are close to those in bis-amides $[(dpp\text{-}bian)AlH_2]^-[Li(THF)_3]^+$ and (dpp-bian)AlH(THF), respectively,[18] which confirms dianionic character of dbhmp-bian. Despite of high bulkiness of 2,6-dibenzhydryl-4-methylphenyl groups in **1** and **2**, one significant structural feature compared to mentioned above dpp-bian hydrides was established, namely, compound **1** exists as a discrete ionic pair, while in salt $[(dpp\text{-}bian)AlH_2]^-[Li(THF)_3]^+$ the counterions are connected *via* µ-H bridge.[18]

In summary, two new aluminum hydrides bearing a highly hindered dbhmp-bian ligand have been synthesized by a simple reduction of the ligand with $LiAlH_4$. These compounds can be of a great application potential in both ligand-promoted and catalytic transformations of organic and small molecules.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.031.

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