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# A $\beta$ -diketiminato magnesium acetylide and formation of an imido aluminium magnesium hydride compound

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# ABSTRACT

The reaction of LiC=CMe with [(<sup>Dip</sup>nacnac)MgI(OEt<sub>2</sub>)] (<sup>Dip</sup>nacnac = [(DipNCMe)<sub>2</sub>CH], Dip = 2,6-diisopropylphenyl) afforded [{(<sup>Dip</sup>nacnac)MgC=CMe}<sub>2</sub>] **1** in good yield. Treatment of **1** with AlH<sub>3</sub>·NMe<sub>3</sub> in toluene under reflux afforded a low yield of the novel imido aluminium magnesium hydride compound [{(AlH)(AlH<sub>2</sub>)<sub>3</sub>(NDip)<sub>3</sub>]<sub>2</sub>Mg] **2**. The latter compound features a central Mg<sup>2+</sup> ion that is coordinated via hydride ligands to two monoanionic [(AlH)(AlH<sub>2</sub>)<sub>3</sub>(NDip)<sub>3</sub>]<sup>-</sup> fragments. The compounds have been characterised by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, IR spectroscopy and the crystal structures of **1** and **2**·4C<sub>7</sub>H<sub>8</sub> have been determined.

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## 1. Introduction

The chemistry of molecular compounds with polyanionic carbon or nitrogen ligands with multiple charges on one central atom is less developed compared with related monoanionic examples. For example, geminal organodimetallics with electropositive main group elements are less common in the synthetic laboratory, despite offering a unique reactivity and often feature interesting structural motifs [1]. An intriguing example is the tetralithiation of propyne using n-butylithium (nBuLi) in hexane that can afford a metastable hexane solution of  $C_3Li_4$  or an orange–red pyrophoric solid after precipitation [2]. These have previously been used to synthesize, for example, the substituted compounds (Me<sub>3</sub>E)<sub>2</sub>C=C=C(EMe<sub>3</sub>)<sub>2</sub> (E=Si, Ge, Sn) [2], however, the substitution chemistry of these and related complexes [1] remains underdeveloped.

# 2. Results and discussion

We carried out the reaction of propyne with four equivalents of nBuLi by adding a hexane solution of propyne to four equivalents of nBuLi at low temperature followed by heating under reflux to obtain an insoluble, highly pyrophoric orange–red solid. Unfortunately, this material could not be dissolved in coordinating solvents such as THF. This could indicate a highly polymeric nature of this solid. In order to prepare a soluble model complex of this system for further studies, we attempted to substitute one Li<sup>+</sup> cation with

a sterically demanding  $\beta$ -diketiminate magnesium fragment. Therefore, we prepared LiC=CMe from equimolar amounts of nBuLi and propyne and treated this with [(<sup>Dip</sup>nacnac)MgI(OEt<sub>2</sub>)] (<sup>Dip</sup>nacnac = [(DipNCMe)<sub>2</sub>CH], Dip = 2,6-diisopropylphenyl) [3] in toluene and diethyl ether to afford [{(<sup>Dip</sup>nacnac)MgC=CMe}<sub>2</sub>] **1** in good yield, see Fig. 1. Attempts to lithiate compound **1** using nBuLi or tBuLi in a range of hydrocarbon or donor solvents were unsuccessful so far and only yielded unaltered **1** back as the only isolated product.

A different concept to obtain compounds with polymetallated carbon atoms has been realised with hydrometallation reactivity [1]. For example, Uhl and Breher introduced the compound class of carbaalanes [4]. These aluminium carbon cluster compounds can be prepared by hydroalumination reactions of alkynyl aluminium compounds with small dialkyl aluminium hydrides [5] or similar reactions involving the alane adduct AlH<sub>3</sub>·NMe<sub>3</sub> [6]; the latter reactions can also form salt-like products. To investigate the reactivity of **1** towards aluminium hydrides, we treated [{(<sup>Dip</sup>nacnac)MgC $\equiv$ CMe}<sub>2</sub>] **1** with 7 equivalents of AlH<sub>3</sub>·NMe<sub>3</sub> in boiling toluene. This yielded large amounts of insoluble solid and a low yield of the mixed imido aluminium magnesium hydride compound [{(AlH)(AlH<sub>2</sub>)<sub>3</sub>(NDip)<sub>3</sub>}<sub>2</sub>Mg] **2** could be crystallised as a toluene solvate from the filtered reaction mixture as colourless blocks, Fig. 1. Furthermore, small amounts of [(<sup>Dip</sup>nacnac)AlH<sub>2</sub>] [7] could be detected in the reaction mixture by <sup>1</sup>H NMR spectroscopy. The formation of the imido complex 2 demonstrates that some of the β-diketiminate ligand in **1** has been cleaved under these conditions. The degradation of sterically demanding β-diketiminate complexes with hydride sources or low oxidation state species has previously been observed and involves the formation of a substituted



Note

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Fig. 1. Synthesis of compounds 1 and 2; (i) LiC=CMe, toluene, Et<sub>2</sub>O; (ii) 7 AlH<sub>3</sub>·NMe<sub>3</sub>, toluene, reflux.

azabutadiene and element imido fragments via a C–N cleavage reaction [8] and a similar process is believed to occur during the formation of the imido compound **2**.

The molecular structure of compound 1 (Fig. 2) shows that dimerisation of two (Dipnacnac)MgC=CMe fragments occur via contacts of the Mg atom to the acetylide  $\pi$ -system. The end on bound acetylide magnesium fragment Mg-C=C is almost linear (Mg1-C30-31 angle of 178.2(2)°) with a short Mg-C bond of 2.132(2) Å and longer Mg. C contacts (2.301(2) to C30 and 2.515(2) Å to C31) in the bridging  $\pi$  interaction. A number of related β-diketiminate calcium and strontium acetylides have recently been crystallographically characterised showing similar bridging coordination modes of the acetylide ligands [9]. Furthermore, interactions of acetylide ions with heavier group 2 metals have recently been investigated theoretically and experimentally [10]. The NMR and IR spectroscopic data of **1** is in accordance with its solid state structure. The comparison with data for related [{(<sup>Dip</sup>nacnac)CaC=CR}<sub>2</sub>] complexes [9a] suggest a less flexible solution behaviour for **1** at room temperature. In **1**, <sup>1</sup>H and <sup>13</sup>C NMR resonances for two different iPr groups of the (<sup>Dip</sup>nacnac) ligand can be detected, whereas only resonances for one iPr environment are found in  $[{(^{Dip}nacnac)CaC \equiv CR}_2]$  at room temperature. However, cooling of the latter complex (for R = tBu) leads to splitting of the iPr resonances [9a]. It is worth mentioning, that both 1 and  $[{(^{Dip}nacnac)CaC \equiv CR}_2]$  display six resonances in the aromatic region of the <sup>13</sup>C NMR spectrum for the Dip substituents at room temperature. The C $\equiv$ C stretch in the IR spectrum of **1** 



**Fig. 2.** ORTEP diagram of [{(<sup>Dip</sup>nacnac)MgC=CMe}<sub>2</sub>] **1** (30% ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-C30 2.132(2), Mg1<sup>····</sup>C30 2.301(2), Mg1<sup>····</sup>C31 2.515(2), C30-C31 1.234(3) Mg1-N1 2.0717(19), Mg1-N2 2.0613(18); N1-Mg1-N2 92.95(7), Mg1-C30-C31 178.2(2).

 $(2069 \text{ cm}^{-1})$  is at slightly higher wave numbers compared to those of  $[{(}^{\text{Dip}}\text{nacnac})\text{CaC} = \text{CR}]_2]$  (2029–2048 cm<sup>-1</sup>).

Compound **2** crystallises with half a molecule in the asymmetric unit, with the Mg atom sitting on a centre of inversion, and can be described as a contact ion pair of two monoanionic [(AlH)(AlH<sub>2</sub>)<sub>2</sub> (NDip)<sub>3</sub>]<sup>-</sup> moieties coordinating solely via bridging hydrides to a central Mg<sup>2+</sup> cation, see Fig. 3. Each DipN imido ligand acts as a  $\mu^3$ cap between two AlH<sub>2</sub> and one AlH fragment with Al–N distances between ca. 1.92-1.94 Å. For comparison, some related anionic amino and/or imino alanate complexes incorporating Li or Na cations have been characterised by the groups of Roesky [11] and Henderson [12]. The latter work describes the structure of  $[Li(OEt_2)_3][(AIH)_4]$  $(NPh)_{6}$ {Li(OEt<sub>2</sub>)}<sub>3</sub>] and contains an anionic open cage fragment with solely four coordinate Al atoms with Al-N distances slightly shorter than those in 2. Also, a range of products from the reaction of DipNH<sub>2</sub> with AlH<sub>3</sub>·NMe<sub>3</sub> under various stoichiometries and conditions yielded amino and imino alanes that have been studied by Schulz and co-workers [13]. In compound 2, the two [(AlH)(AlH<sub>2</sub>)<sub>3</sub>  $(NDip)_3]^-$  half spheres coordinate via hydride bridges of the six AlH<sub>2</sub> units to the central Mg atom. The six Mg...H contacts range from ca. 1.87 to 2.00 Å giving a slightly distorted octahedral coordination sphere. Mixed element hydride bridges to Mg are not an uncommon structural motif. For example, a monoetherate complex of magnesium alanate has been crystallographically characterised and features a central Mg<sup>2+</sup> ion octahedrally coordinated to five hydrides and one diethyl ether ligand [14]. The mean Mg...H contact of 2.0 Å and the mean Al-H bond length of 1.55 Å in the alanate complex are similar to those in 2. The Mg environment in 2 is reminiscent of the Mg packing in solid MgH<sub>2</sub>, as determined from a neutron diffraction structure of rutil type MgD<sub>2</sub> with six Mg…D contacts of ca. 1.95 Å in a regular octahedral environment [15]. Accordingly, compound 2 can be viewed as a soluble model complex for the coordination of magnesium in solid MgH<sub>2</sub>. Very recently, hydride rich magnesium complexes with  $Mg_4H_6^{2+}$  and  $Mg_8H_{10}^{6+}$  cores supported by sterically demanding ligands have been prepared and structurally characterised that feature distorted tetrahedral coordination spheres around the Mg atoms [16].

The spectroscopic data for compound **2** is consistent with its solid state structure. The <sup>1</sup>H NMR spectrum shows two doublets and two septets for the protons of the iPr groups and, accordingly in its <sup>13</sup>C NMR spectrum, two resonances each for the methyl and methine carbon atoms of the iPr groups, as well as six resonances for the aromatic carbons. The IR spectrum displays two sharp stretches at 1999 and 1900 cm<sup>-1</sup>, the latter being the stronger one, and a broad one at around 1693 cm<sup>-1</sup> with a shoulder peak at around 1753 cm<sup>-1</sup>. The first two stretches are tentatively assigned to the terminal Al–H bonds and the latter ones to the bridging hydrides.

In summary, we have synthesised the first structurally characterised  $\beta$ -diketiminate magnesium acetylide and its reaction with AlH<sub>3</sub>·NMe<sub>3</sub> yielded a novel imido aluminium magnesium hydride compound with a central Mg<sup>2+</sup> ion solely coordinated to hydride ligands. The latter reaction involves some degradation of the  $\beta$ -diketiminate ligand.



**Fig. 3.** ORTEP diagram of [{(AlH)(AlH<sub>2</sub>)<sub>3</sub>(NDip)<sub>3</sub>]<sub>2</sub>Mg] **2** (30% ellipsoids). Four toluene molecules per formula unit and hydrogen atoms except hydride ligands have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.9410(19), Al1–N2 1.9374(18), Al1–N3 1.9368(18), Al2–N1 1.9254(18), Al2–N2 1.9301(19), Al3–N2 1.9250(18), Al3–N3 1.9265(18), Al4–N1 1.9318(18), Al4–N3 1.9220(19), Al1–H1 1.48(3), Al2–H2 1.48(2), Al2–H5 1.66(4), Al3–H3 1.49(3), Al3–H6 1.62(4), Al4–H4 1.56(3), Al4–H7 1.60(3), Mg1–H5 1.87(4), Mg1–H6 1.88(3), Mg1–H7 2.00(3); N1–Al1–N2 90.08(8), Al1–N1–Al2 88.59(8), Al2–N1–Al4 111.64(9).

# 3. Experimental

# 3.1. General

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Toluene and hexane were distilled over molten potassium, whilst diethylether was distilled over Na/K alloy (1:3). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker DPX 300 spectrometer in deuterated benzene and were referenced to the residual <sup>1</sup>H or <sup>13</sup>C resonances of the solvent used. IR spectra were recorded using a Perkin–Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. LiC=CMe was prepared from nBuLi and propyne in hexane [2] and [(<sup>Dip</sup>nacnac)MgI(OEt<sub>2</sub>)] [3] was prepared according to the literature procedure.

# 3.2. Preparation of [{(<sup>Dip</sup>nacnac)MgC=CMe}<sub>2</sub>] 1

Toluene (40 mL) and Et<sub>2</sub>O (20 mL) were added to a mixture of  $[(^{Dip}nacnac)MgI(OEt_2)]$  (1.73 g, 2.69 mmol) and LiC=CMe (0.133 g, 2.90 mmol) at -80 °C. The mixture was slowly warmed to room temperature and stirred for 1 h. The mixture was filtered, concentrated to ca. 20 mL and cooled to 4 °C to afford a toluene solvate of 1. Further concentration of the supernatant solution and cooling afforded a second crop. The solid was dried under vacuum. Single crystals of 1 were obtained by crystallisation from hexane. Yield: 0.92 g (71%); Mp >300 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K):  $\delta$  0.57 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48 (d,  ${}^{3}J_{H-H}$  = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48 (s, 12H, NCCH<sub>3</sub>), 1.59 (s, 6H, C=CCH<sub>3</sub>), 3.00 (sept,  ${}^{3}J_{H-H}$  = 6.9 Hz, 4 H,  $CH(CH_3)_2$ ), 3.42 (sept,  ${}^3J_{H-H}$  = 6.9 Hz, 4H,  $CH(CH_3)_2$ ), 4.65 (s, 2H, *CH*), 6.97–7.22 (m, 12H, Ar*H*);  $^{13}C{}^{1}H$  NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K):  $\delta$  = 23.9, 24.3, 24.4, 24.5, 25.1, 25.9 (4 × CH(CH<sub>3</sub>)<sub>2</sub>, NCCH<sub>3</sub>, C=CCH<sub>3</sub>), 27.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 94.9 (CH), 112.8 (MgC=C), 115.8 (C=CCH<sub>3</sub>), 124.1 (Ar-C), 125.7 (Ar-C), 129.4 (Ar-C), 142.2 (Ar-C), 143.5 (Ar-C), 145.9 (Ar-C), 169.3 (NCCH<sub>3</sub>); IR (Nujol) v (cm<sup>-1</sup>): 2069w (C=C), 1623w, 1519m, 1365s, 1314m, 1261m, 1252m, 1174m, 1098m, 1057m, 1018m, 934m, 792s, 760s, 727m; *Anal.* Calc. for C<sub>64</sub>H<sub>88</sub>Mg<sub>2</sub>N<sub>4</sub>: C, 79.90; H, 9.22; N, 5.82. Found: C, 79.12; N, 9.04; H, 5.63%.

## 3.3. Preparation of [{(AlH)(AlH<sub>2</sub>)<sub>3</sub>(NDip)<sub>3</sub>}<sub>2</sub>Mg] 2

A solution of AlH<sub>3</sub>·NMe<sub>3</sub> (2.4 mL of a 0.67 m solution in toluene, 1.61 mmol) was added to a mixture of [{(<sup>Dip</sup>nacnac)MgC=CMe}<sub>2</sub>] 1 (0.22 g, 0.23 mmol) and toluene (10 mL). The mixture was heated under reflux for 1 h (forming a large amount of a solid), filtered hot, concentrated to ca. 3 mL and cooled to 4 °C to afford colourless blocks of 2.4C7H8. Yield: 30 mg (12%, based on DipN); Mp: slow decomp. above ca. 190 °C; <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 303 K):  $\delta$  1.28 (d,  ${}^{3}J_{H-H} = 6.9 \text{ Hz}, 36\text{H}, CH(CH_{3})_{2}), 1.39 \text{ (d, }{}^{3}J_{H-H} = 6.9 \text{ Hz}, 36\text{H}, CH(CH_{3})_{2}), 2.93 \text{ (sept, }{}^{3}J_{H-H} = 6.9 \text{ Hz}, 6\text{ H}, CH(CH_{3})_{2}), 3.19 \text{ (sept, }{}^{3}J_{H-H} = 6.9 \text{ Hz}, 6\text{ H}, CH(CH_{3})_{2}), 3.19 \text{ (sept, }{}^{3}J_{H-H} = 6.9 \text{ Hz}, 6\text{ Hz$  ${}^{3}J_{H-H}$  = 6.9 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.52 (br, with shoulder at ca. 4.3, ca. 12H, AlH), 5.1 (vbr, ca. 2H, AlH), 6.84-7.20 (m, 18H, ArH); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K):  $\delta$  = 26.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 33.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 33.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 124.0 (Ar-C), 124.9 (Ar-C), 126.4 (Ar-C), 141.6 (Ar-C), 141.7 (Ar-C), 142.3 (Ar-C); IR (Nujol) v (cm<sup>-1</sup>): 1999w (AlH), 1901m (AlH), 1693s (br, with shoulder at 1753, AlH), 1426m, 1366s, 1314m, 1225m, 1163s, 1101s, 1032m, 946s, 888s, 853s, 758s, 729m, 696s.

# 3.4. X-ray crystallography

Suitable crystals were mounted in silicone oil and were measured with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at T = 123(2) K using a Nonius Kappa CCD (**1**) or a Bruker X8 Apex II (**2**·4C<sub>7</sub>H<sub>8</sub>) diffractometer and were refined using SHELX [17]. All non-hydrogen atoms were refined anisotropically. The hydride ligands in **2**·4C<sub>7</sub>H<sub>8</sub> were located from difference maps and their positions were freely refined, all other hydrogen atoms were included in calculated positions. Crystal data for **1**: C<sub>64</sub>H<sub>88</sub>Mg<sub>2</sub>N<sub>4</sub>; M = 962.00 g/mol; monoclinic space group  $P2_1/n$ ; a = 11.028(2) Å, b = 14.289(3) Å, c = 18.326(4) Å,  $\beta = 95.07(3)^\circ$ , V = 2876.5(10) Å<sup>3</sup>; Z = 2,  $\rho = 1.111$  g/cm<sup>3</sup>,  $\mu = 0.083$  mm<sup>-1</sup>,  $-13 \le h \le 13$ ,  $-16 \le k \le 16$ ,  $-21 \le l \le 21$ ,

refl. collected: 8877, refl. unique: 5050, Goodness-of-fit = 1.022, *R1* ( $I > 2\sigma(I)$ ) = 0.0520,  $wR_2$  (all data) = 0.1352, completeness to theta (25.00°): 99.6%, largest difference peak/hole: 0.449/-0.220 e Å<sup>-3</sup>. Crystal data for **2**·4C<sub>7</sub>H<sub>8</sub>: C<sub>100</sub>H<sub>148</sub>Al<sub>8</sub>MgN<sub>6</sub>; *M* = 1674.39 g/mol; monoclinic space group *P*2<sub>1</sub>/n; *a* = 15.2559(16) Å, *b* = 19.292(2) Å, *c* = 16.8874(17) Å,  $\beta$  = 94.294(4)°, *V* = 4956.3(9) Å<sup>3</sup>; *Z* = 2,  $\rho$  = 1.122 g/cm<sup>3</sup>,  $\mu$  = 0.135 mm<sup>-1</sup>, -19  $\leq$  *h*  $\leq$  18, -24  $\leq$  *k*  $\leq$  24, -21  $\leq$  *l*  $\leq$  21, refl. collected: 50507, refl. unique: 10811, Goodness-of-fit = 1.088, *R1* (*I* > 2 $\sigma(I)$ ) = 0.0535, *wR*<sub>2</sub> (all data) = 0.1439, completeness to theta (27.00°): 99.9%, largest difference peak/hole: 0.474/-0.279 e Å<sup>-3</sup>.

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#### Appendix A. Supplementary data

CCDC-793605 (1) and CCDC-793606 ( $2.4C_7H_8$ ) contains 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/data\_request/ cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.06.047.

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