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Alkaline Earth Metal Aluminates as Catalysts for Imine Hydrogenation

Holger Elsen, Jens Langer, Michael Wiesinger, and Sjoerd Harder*

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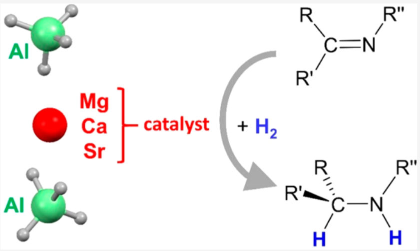

ABSTRACT: Alkaline earth (Ae) metal complexes with the alanate anion AlH_4^- have been prepared by salt metathesis between $NaAlH_4$ and $AeCl_2$ in THF and could be isolated as $Mg(AlH_4)_2\cdot(THF)_4$, $Ca(AlH_4)_2\cdot(THF)_4$, and $Sr(AlH_4)_2\cdot(THF)_5$. The previously reported crystal structure of the Mg alanate complex shows bonding of AlH_4^- with one bridging hydride, H_3Al-(μ-H)-Mg, while the Ca and Sr alanates show a combination of H_3Al-(μ-H)-Ae and H_2Al-(μ-H)$_2$-Ae bridging. The heteroleptic β-diketiminate complexes (^{DIPP}BDI)Mg(AlH_4)·THF and (^{DIPP}BDI)Ca(AlH_4)·(THF)$_2$ have been prepared by reaction of the corresponding Ae hydride complexes with $AlH_3\cdot(THF)_2$ [^{DIPP}BDI = DIPP-NC(Me)C(H)C(Me)N-DIPP, where DIPP = 2,6-diisopropylphenyl]. Crystal structures show H_2Al-(μ-H)$_2$-Ae bridging. The Ca complex decomposes at room temperature by reduction of the β-diketiminate anion. Density functional theory calculations (B3PW91/def2tzvpp) show that the formation of $Ae(AlH_4)_2$ from AeH_2 and AlH_3 is exothermic by Δ*H* (kilocalories per mole): Be, −68.8; Mg, −66.1; Ca, −95.4; Sr, −100.9; Ba, −112.3. Calculations of NPA charges on $LiAlH_4$ and the Ae alanate complexes (Ae = Mg, Ca, or Sr) show that these are highly ionic salts in which the charge on AlH_4^- of approximately −0.95 is hardly dependent on the countercation. Compared to $LiAlH_4$, the Ae alanates are very efficient catalysts for imine hydrogenation, clearly extending the substrate scope. In addition to aldimines RC(H)═NR′ (R/R′ = Ph/*t*Bu, *t*Bu/*t*Bu, *n*Pr/*t*Bu, or Ph/Ph), ketimine PhC(Me)═N*t*Bu could be reduced. The salt [Bu_4N^+][AlH_4^-] is catalytically not active, which shows that the *s*-block metal is crucial. The highest activities were found for the heterobimetallic Ca and Sr alanates.

■ INTRODUCTION

The simplest metal hydride, $(LiH)_\infty$, is a highly insoluble, essentially inert, salt that is stable in air and reportedly does not even react with hydrogen chloride.[1] This can be explained with its considerable lattice energy of 920 kJ mol^{-1}, which is the highest of those of the alkali metal hydrides.[2] However, in combination with AlH_3, it becomes soluble in organic ethereal solvents and represents one of the most powerful and versatile reducing agents. Schlesinger's synthesis of $Li^+AlH_4^-$ in the 1940s should be rated a milestone discovery.[3] Key to its fame is its fair solubility in ethereal solvents, rendering it highly reactive toward a large array of substrates.[4,5] Although old hat, at present $LiAlH_4$ is still one of the most potent reducing agents. This mixed metal hydride salt developed from a small scale laboratory reagent to industrial relevant bulk product.[6] $LiAlH_4$ is especially in the synthesis of alcohols or amines from polar double bonds like C═O or C═N bonds the reducing agent of choice. This synthetic approach, however, needs stoichiometric quantities of $LiAlH_4$ that after hydrolysis inherently generates copious amounts of Li/Al salts that complicate product workup and additionally pose fire and explosion hazards.

As part of our research activities in early main group metal catalysis,[7] we pioneered the reduction of C═C and C═N bonds using the simplest bulk reducing agent H_2.[8] The catalysts for these transformations can be surprisingly simple alkaline earth (Ae) metal amide complexes with a formula of $Ae[N(SiMe_3)_2]_2$ (Ae = Mg, Ca, Sr, or Ba). The latter are key reagents in group 2 metal chemistry and easily accessible at a larger scale.[9] Comprehensive calculations on the hydrogenation mechanism confirmed the intermediacy of metal hydride species. This recognition led to follow-up research using the even simpler, commercially available, bulk commodity $LiAlH_4$.[10] Screening a variety of imine substrates for hydrogenation, the researchers found that $LiAlH_4$ performed not as well as the Ae amide catalysts but for certain substrates, mild temperatures (85 °C), low catalyst loadings (2.5 mol %), and a conveniently low pressure of only 1 bar of H_2 could be applied (Scheme 1). The simplicity and mild conditions of this experiment found a broad interest[11] and stand in strong contrast with Slaugh's early attempt to hydrogenate alkenes under extreme conditions (35 mol % $LiAlH_4$, 190 °C, and 80 bar of H_2).[12] While Slaugh's experiences did not invite further research in this area, 50 years later $LiAlH_4$ catalysis is currently experiencing a revival (Scheme 1). The groups of Cowley and Thomas showed the hydro-

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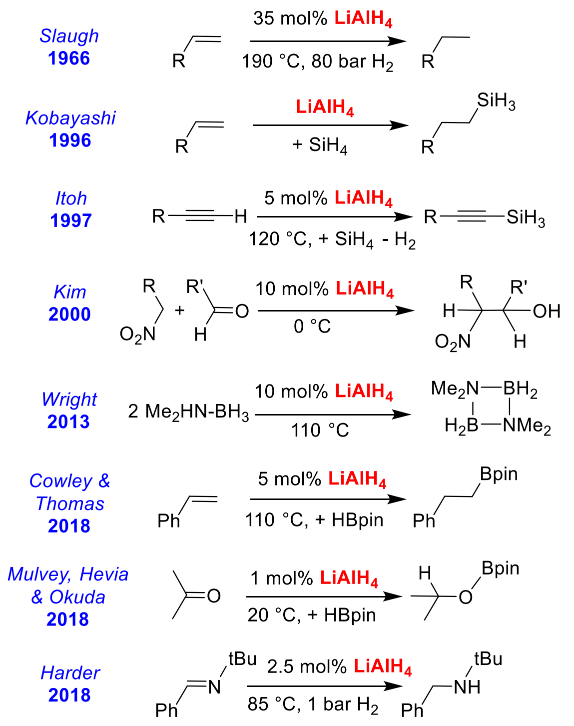
Scheme 1. Overview of $LiAlH_4$-Catalyzed Reactions



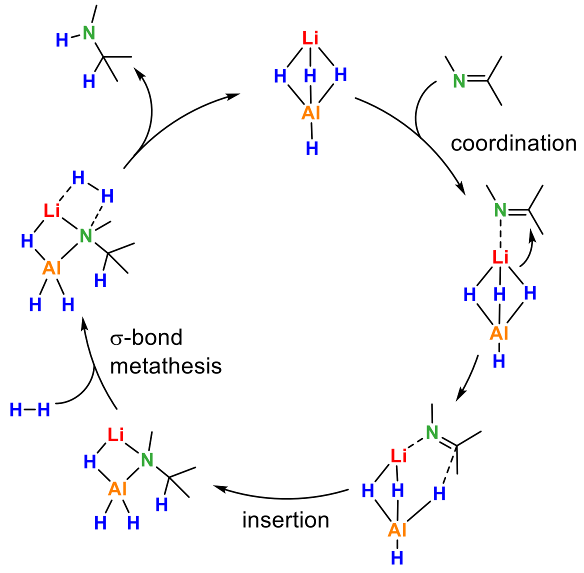
boration of alkenes (5−10 mol %, 110 °C, and 4 h),[13] while the groups of Mulvey, Hevia, and Okuda converted $LiAlH_4$ into the well-defined catalyst $LiAlH_2[N(SiMe_3)_2]_2$ for ketone/aldehyde hydroboration.[14] These hydroborations take advantage of the very polar $B^{\delta+}$—$H^{\delta-}$ bond that is substantially more reactive than apolar H_2. The $LiAlH_4$-catalyzed alkene hydrosilylation with SiH_4 by the Kobayashi group profits from a similar high reactivity of the polarized $Si^{\delta+}$—$H^{\delta-}$ bond.[15] Further niche applications of the $LiAlH_4$ catalyst are illustrated by Kim's nitroaldol condensation,[16] the dehydrogenation of HMe_2NBH_3 by Wright and co-workers,[17] and Itoh's dehydrogenative alkyne−silane coupling.[18]

There is strong evidence for heterobimetallic cooperativity in $LiAlH_4$-catalyzed reactions.[10,13,14] On the basis of the importance of both metals, a mechanism for $LiAlH_4$-catalyzed imine hydrogenation has been proposed (Scheme 2).[10] The heterobimetallic nature of the $LiAlH_4$ catalyst makes this system perfectly suitable for further optimization. Herein, we present the synthesis and compare the structures of a series of homoleptic group 2 metal aluminates $Ae(AlH_4)_2$ (Ae = Mg, Ca, or Sr). In addition, we present heteroleptic *β*-diketiminate Ae metal complexes with the AlH_4^- anion. Both homo- and heteroleptic complexes have been investigated in the catalytic reduction of various imines by H_2, and their performance was compared to that of $LiAlH_4$.

■ RESULTS AND DISCUSSION

Homoleptic Aluminate Complexes. The chemistry of the tetraalkylaluminates of group 2 metals is reasonably well developed. Westerhausen and co-workers describe $[Ca^{2+}\cdot(THF)_6][AlMe_4^-]_2$,[19] while the Anwander group reported the structure of the similar Mg salt $[Mg^{2+}\cdot(THF)_6][AlMe_4^-]_2$.[20] The latter group also published crystal structures of tetraethylaluminates $[Ca(AlEt_4)_2]_\infty$, $Ca(AlEt_4)_2\cdot(THF)_2$, and $Ca(AlEt_4)_2\cdot(phenanthroline)$.[20] Also, Mitzel and co-workers contributed to the field with structures of $Ca(AlEt_4)_2$ solvated by various N-ligands.[21] The solubilities of $Ae(AlR_4)_2$ compounds increase with an increase in alkyl chain length but decrease with an increase in Ae^{2+} ion size. The Anwander group reported the synthesis of $Ba(AlMe_4)_2$, which is insoluble in aromatic solvents, and $Ba(AlEt_4)_2$, which crystallized from toluene as a three-dimensional (3D) coordination polymer or toluene solvate.[22]

Scheme 2. Proposed Heterobimetallic Mechanism for $LiAlH_4$-Catalyzed Imine Hydrogenation

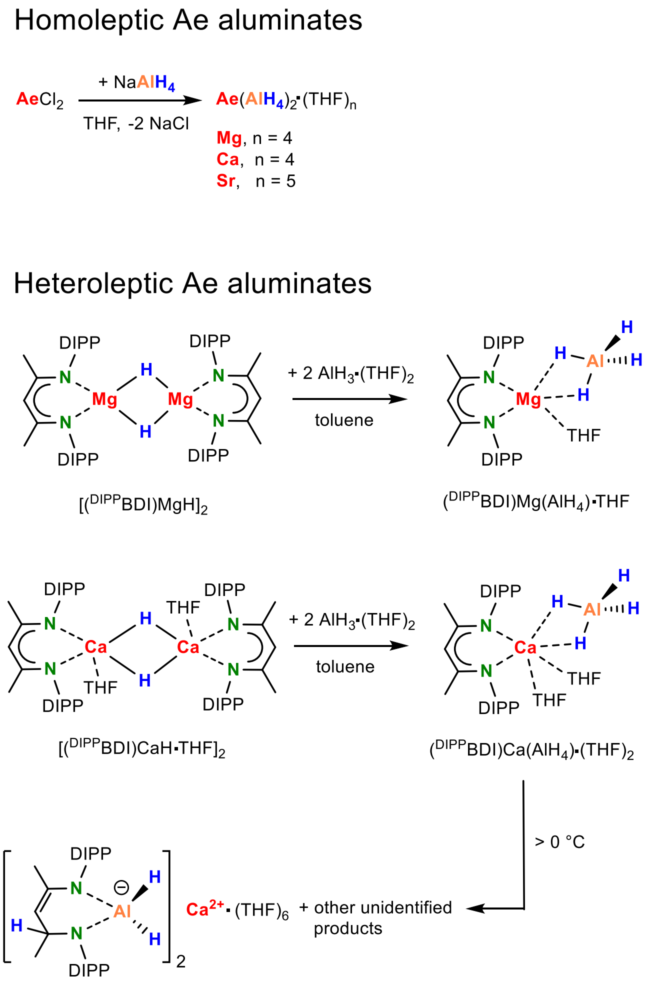


Much less is known of Ae metal complexes with the smallest aluminate anion AlH_4^-, which are expected to show lower solubilities. Fichtner et al. reported the synthesis of $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$ from the corresponding $AeCl_2$ and $NaAlH_4$ in ethereal solvents.[23,24] For $Sr(AlH_4)_2$, only a ball-milling route has been documented.[25] We prepared these aluminates using the salt metathesis route mixing $AeCl_2$ (Ae = Mg, Ca, or Sr) and $NaAlH_4$ in THF in a 1/2 ratio (Scheme 3). The mixtures were stirred in THF at 60 °C overnight and filtered hot to remove precipitates. All aluminates crystallize very well from THF and were isolated in the form of their THF adducts. ^1H NMR spectra of the Mg, Ca, and Sr alanate complexes in THF-d_8 show very broad resonances for AlH_4^- between 2 and 4 ppm. These signals are broadened due to substantial Al−H magnetic coupling and the very large quadrupole moment of ^{27}Al. The ^{27}Al NMR chemical shifts are in the range of 107−114 ppm. The ^1H NMR spectra also show considerable quantities of THF, which is very loosely bound and partially lost during crystal drying.

While wet synthetic methods successfully gave the Mg, Ca, and Sr alanates, $BaCl_2$ did not react with $NaAlH_4$. Alternatively, reaction of $Ba[N(SiMe_3)_2]_2$ with $PhSiH_3$, to generate BaH_2 *in situ* and addition of AlH_3 led to an insoluble white powder that could not be dissolved in various polar solvents. Due to its complete insolubility, the presumed $[Ba(AlH_4)_2]_\infty$ was not further characterized or used in catalysis.

The crystal structure of $Mg(AlH_4)_2\cdot(THF)_4$ is known and described as a complex in which both aluminate anions are bound to Mg^{2+} in a H_3Al-(μ-H)-Mg fashion (Figure 1a and Table 1).[23] The crystal structure of $Ca(AlH_4)_2\cdot(THF)_4$ is reported to be isostructural but of very poor quality, and hydride positions are uncertain.[24] A high-quality structure, including refined hydride positions, is shown in Figure 1b. While one of the AlH_4^- anions is bound in a H_3Al-(μ-H)-Ca fashion, the other should be described as H_2Al-(μ-H)$_2$-Ca. Moreover, there

Scheme 3. Synthesis of Homoleptic and Heterolepic Alkaline Earth Metal Alanate Complexes



is an additional H_3Al-(μ-H)-Ca contact to a neighboring molecule, and the complex should more appropriately be described as a dimer; however, due to the weakness of the Ae···AlH_4 and Ae···THF bonds, these complexes will be extremely dynamic in solution. For strontium alanate, only an inaccurate powder X-ray diffraction structure for the 3D coordination polymer of THF-free $[Sr(AlH_4)_2]_\infty$ is known.[25] Crystallization from THF gave the complex $Sr(AlH_4)_2\cdot(THF)_5$, and the crystal structure is shown in Figure 1c. The five THF ligands coordinate approximately in an equatorial plane that deviates from planarity

Table 1. Selected Bond Lengths (angstroms) and Angles (degrees) for $Ae(AlH_4)_2$ Complexes[a]

complex	$Mg(AlH_4)_2\cdot(THF)_4$[23]	$Ca(AlH_4)_2\cdot(THF)_4$	$Sr(AlH_4)_2\cdot(THF)_5$
Ae-(μ-H)	1.977(18)	H_3Al(μ-H): 2.33(2), 2.43(2)[b]	H_3Al(μ-H): 2.45(3)
		H_2Al(μ-H)$_2$: 2.44(2), 2.68(3)	H_2Al(μ-H)$_2$: 2.60(3), 2.65(3)
Al-(μ-H)	1.573(18)	H_3Al(μ-H): 1.54(2)	H_3Al(μ-H): 1.59(3)
		H_2Al(μ-H)$_2$: 1.49(2), 1.57(3)	H_2Al(μ-H)$_2$: 1.58(3), 1.58(3)
Al-H_t	1.52(2), 1.50(2), 1.55(2)	H_3Al(μ-H): 1.50(3), 1.54(3), 1.54(3)	H_3Al(μ-H): 1.51(3), 1.52(3), 1.54(3)
		H_2Al(μ-H)$_2$: 1.49(3), 1.52(3)	H_2Al(μ-H)$_2$: 1.50(3), 1.53(3)
Ae···Al	3.5383(5)	H_3Al(μ-H): 3.8467(6)	H_3Al(μ-H): 4.0044(8)
		H_2Al(μ-H)$_2$: 3.2705(6)	H_2Al(μ-H)$_2$: 3.3467(9)
Al···Ae···Al′	180	173.41(2)	167.15(2)

[a] (μ-H) = bridging hydride, and H_t = terminal hydride. [b] Contact to the neighboring molecule.

as shown by O−Sr−O′ angles that are larger than 72° [range of 72.50(5)−77.81(5)°, average of 75.69°]. The aluminate anions are bound in axial positions [Al···Sr···Al′, 167.15(2)°] either in a H_3Al-(μ-H)-Sr or in a H_2Al-(μ-H)$_2$-Sr fashion. The aluminate anions in these crystal structure show no deviation from a tetrahedral geometry, but the Al−H distances for bridging hydrides are somewhat larger than those for terminal hydrides (Table 1).

To evaluate the influence of the group 2 metal in catalysis, additionally an *s*-block metal-free aluminate complex was synthesized. Reaction of $[Bu_4N^+][Cl^-]$ with $NaAlH_4$ in THF gave after workup $[Bu_4N^+][AlH_4^-]$ in 54% yield. This salt dissolves well in THF-d_8, and the highly symmetric free AlH_4^- anion showed in ^1H NMR a well-resolved sextet (1/1/1/1/1/1) at 2.27 ppm ($^1J_{Al-H}$ = 174 Hz) and a ^{27}Al NMR signal at 100.0 ppm.

Heteroleptic Aluminate Complexes. Large spectator ligands like N,N-chelating β-diketiminate ligands will enhance the solubility of alanate complexes. Jones and co-workers reported the synthesis of $[(^{DEP}BDI)Mg(AlH_4)\cdot Et_2O]_2$ [^{DEP}BDI = DEP-NC(Me)C(H)C(Me)N-DEP, where DEP = 2,6-diethylphenyl], but due to poor crystal quality, the exact bridging mode of AlH_4^- ions could not be established.

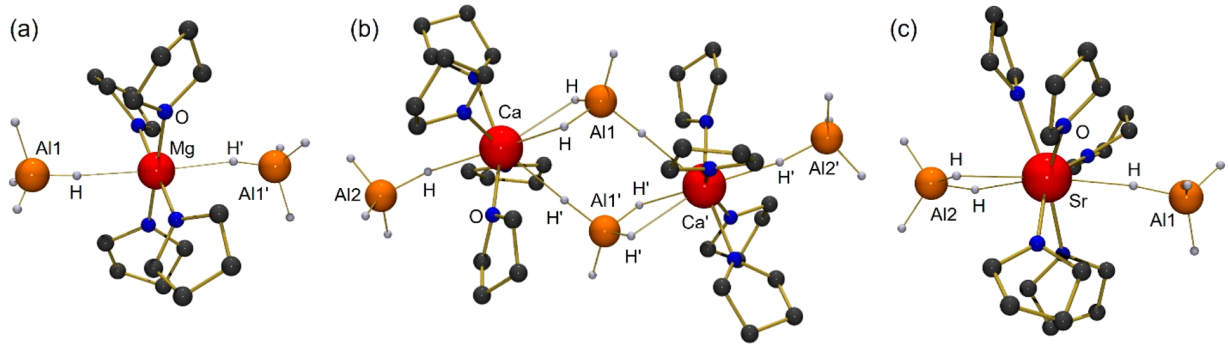


Figure 1. Crystal structures of (a) $Mg(AlH_4)_2\cdot(THF)_4$,[23] (b) $[Ca(AlH_4)_2\cdot(THF)_4]_2$, and (c) $Sr(AlH_4)_2\cdot(THF)_5$. H atoms, except those of AlH_4^-, have been omitted for the sake of clarity.

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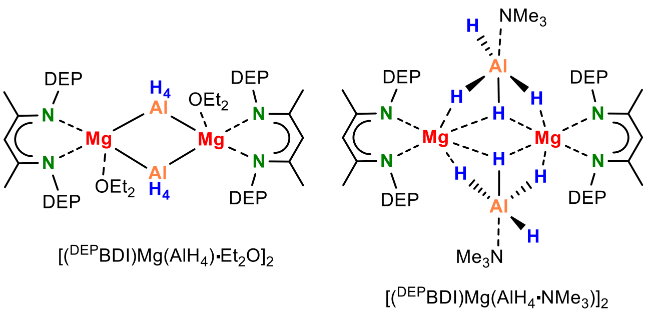
Interestingly, exchanging the Lewis base Et_2O for Me_3N gave a product with Al-amine coordination (Scheme 4).

Scheme 4. β-Diketiminate Magnesium Alanate Complexes[26]



We here report the synthesis of Mg and Ca alanate complexes with the bulkier β-diketiminate ligand ^{DIPP}BDI [DIPP-NC-(Me)C(H)C(Me)N-DIPP, where DIPP = 2,6-diisopropylphenyl] (Scheme 3). Reaction of $[(^{DIPP}BDI)MgH]_2$ with $AlH_3\cdot(THF)_2$ in toluene gave after recrystallization $(^{DIPP}BDI)Mg(AlH_4)\cdot THF$ in 69% yield. The complex crystallizes as a monomer with a $H_2Al(\mu\text{-}H)_2$-bound aluminate anion (Figure 2a and Table 2). The product dissolves well in C_6D_6 and shows a broad AlH_4^- resonance at 3.20 ppm and a ^{27}Al NMR signal at 97.4 ppm.

The synthesis of the analogue Ca complex was considerably more problematic due to the instability of the product, which requires synthesis at a lower temperature. Reaction of $[(^{DIPP}BDI)CaH\cdot THF]_2$ with AlH_3 in toluene at 0 °C gave after crystallization $(^{DIPP}BDI)Ca(AlH_4)\cdot(THF)_2$ in 64% yield. The complex crystallizes as a monomer with a $H_2Al(\mu\text{-}H)_2$-bound aluminate anion (Figure 2b and Table 2). The product dissolves well in C_6D_6 and shows a broad AlH_4^- resonance at 2.88 ppm and a ^{27}Al signal at 120.4 ppm. It decomposes slowly at temperatures above 0 °C. Although we could not isolate higher yields of a defined decomposition product, we obtained in one case a few crystals. Due to severe disorder, the crystal structure was partially determined (see the Supporting Information) and suggests that decomposition proceeds by reduction of the β-diketiminate anion by the AlH_4^- anion and a Ca/Al exchange reaction (Scheme 3).

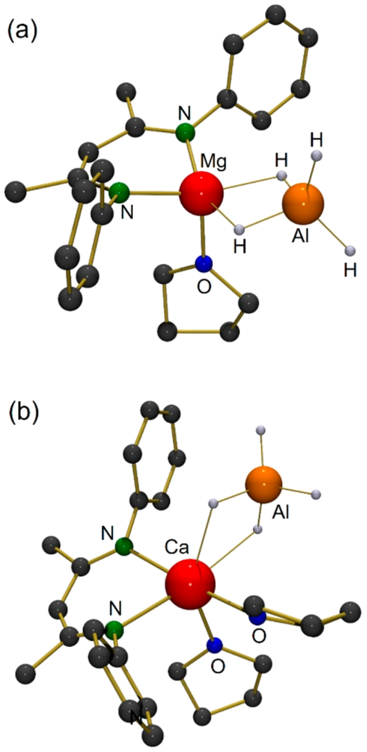


Figure 2. Crystal structures of (a) $(^{DIPP}BDI)Mg(AlH_4)\cdot THF$ and (b) $(^{DIPP}BDI)Ca(AlH_4)\cdot(THF)_2$. The *i*Pr substituent of ^{DIPP}BDI and the H atoms, except those of AlH_4^-, have been omitted for the sake of clarity.

Table 2. Selected Bond Lengths (angstroms) and Angles (degrees) for $(^{DIPP}BDI)Mg(AlH_4)\cdot THF$ and $(^{DIPP}BDI)Ca(AlH_4)\cdot(THF)_2$[a]

complex	$(^{DIPP}BDI)Mg(AlH_4)\cdot THF$	$(^{DIPP}BDI)Ca(AlH_4)\cdot(THF)_2$
Ae-N	2.056(2), 2.048(2)	2.395(2), 2.388(1)
Ae-O	2.036(2)	2.358(1), 2.406(1)
Ae-(μ-H)	1.91(3), 2.03(3)	2.39(2), 2.38(2)
Al-(μ-H)	1.54(3), 1.55(3)	1.58(2), 1.59(2)
Al-H_t	1.55(3), 1.57(3)	1.54(2), 1.49(2)
Ae···Al	2.768(1)	3.1502(7)
N-Ae···Al	125.57(7), 124.47(7)	143.60(4), 100.00(3)
O-Ae···Al	99.48(6)	76.42(3), 118.04(3)

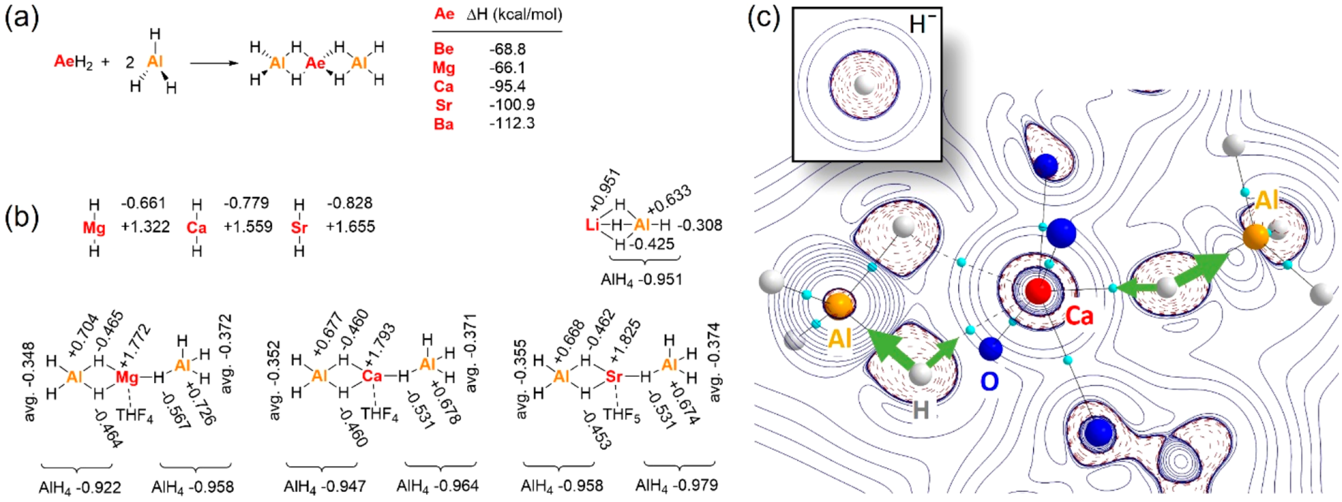
[a] (μ-H) = bridging hydride, and H_t = terminal hydride.

Density Functional Theory (DFT) Calculations. The stability of alkaline earth metal aluminates was investigated by calculation (B3PW91/def2tzvpp) of a simple model reaction in which AeH_2 is reacted with AlH_3. While for Be and Mg similar ΔH values of −68.8 and −66.1 kcal/mol, respectively, have been calculated, the reaction becomes considerably more exothermic for the heavier Ae metals (Scheme 5a), i.e., with increasing ionicity of AeH_2.

The DFT-optimized structures of $Ca(AlH_4)_2\cdot(THF)_4$ and $Sr(AlH_4)_2\cdot(THF)_4$ compare fairly well to the crystal structures, but for $Mg(AlH_4)_2\cdot(THF)_4$, there is a different minimum in which one AlH_4^- ligand binds to Mg^{2+} in a monodentate fashion while the other coordinates in a bidentate fashion (see Figures S37−S39). Upon comparison of the NPA charges of AeH_2 with those in $Ae(AlH_4)_2\cdot(THF)_n$ complexes, the saline nature of the alkaline earth aluminates becomes apparent (Scheme 5b). For AeH_2, the ionic character of the Ae-H bond increases from 66% (Mg) to 83% (Sr). However, in the alanate complexes, the negative charge on AlH_4^- is relatively constant and hardly dependent on the *s*-block metal (range of −0.922 to −0.979). Consequently, there is also hardly any variation in the positive charge of Mg^{2+}, Ca^{2+}, and Sr^{2+} ions, and these alanates should be considered salt-like species with ∼95% ionic bond character. For $LiAlH_4$, a similar charge distribution is found. The bridging hydrides are considerably more negatively charged than the terminal ones. The negative charge on the hydrides increases in the following order: terminal H^- < double bridging H^- < single bridging H^-. This is most likely due to the very good polarizability of the AlH_4^- anion and the hydride anion itself. This electrostatic polarization can be visualized by the Laplacian of the electron density according to AIM theory (Scheme 5c). The spherical electron density in an isolated hydride anion (see the inset) is strongly polarized toward the hard and highly charged Al^{3+} cation (thick green arrow) and only weakly attracted by Ca^{2+} (thin green arrow).

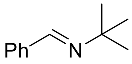
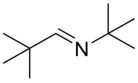
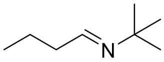
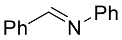
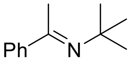
Catalytic Imine Hydrogenation. Homo- and heteroleptic Ae metal alanate complexes have been investigated as catalysts in imine hydrogenation under standard conditions (neat imine, 20

Scheme 5. DFT Calculations (B3PW91/def2tzvpp), Including (a) Calculated Enthalpies for Formation of Metal Alanates from Their Metal Hydrides, (b) Calculated NPA Charges, and (c) the Laplacian of the Electron Density in $Ca(AlH_4)_2·(THF)_4$ in the Plane of Mg and the Bridging Hydrides[a]



[a]THF molecules have been omitted for the sake of clarity, and bond critical points are colored light blue. Green arrows represent polarization of the hydrides as compared to an unperturbed hydride anion (see the inset).

Table 3. Catalytic Hydrogenation of Imines[a]

Entry	Catalyst (mol%)	Substrate	Pressure [bar]	T [°C]	Time [h]	Conversion (%)
1	$LiAlH_4$ (5)		20	85	2.5	85[10]
2	$Mg(AlH_4)_2·(THF)_4$ (2.5)		20	85	2.5	19
3	$Ca(AlH_4)_2·(THF)_4$ (2.5)		20	85	2.5	87
4	$Sr(AlH_4)_2$ (2.5)		20	85	2.5	99
5	$n\mathrm{Bu_4NAlH_4}$ (5)		20	85	24	8
6	$n\mathrm{Bu_4NAlH_4}$ (5) + MgI_2 (5)		20	85	24	29
7	$n\mathrm{Bu_4NAlH_4}$ (5) + CaI_2 (5)		20	85	24	63
8	$n\mathrm{Bu_4NAlH_4}$ (5) + SrI_2 (5)		20	85	24	36
9	$n\mathrm{Bu_4NAlH_4}$ (5) + BaI_2 (5)		20	85	24	9
10	$LiAlH_4$ (5)		1	85	2.5	55[10]
11	$Ca(AlH_4)_2·(THF)_4$ (2.5)		1	85	2.5	60
12	$Ca(AlH_4)_2·(THF)_4$ (2.5)		20	60	2.5	42
13	$Sr(AlH_4)_2$ (2.5)		20	60	2.5	54
14	$(^{DIPP}BDI)Mg(AlH_4)·THF$ (5)		20	85	2.5	43
15	$(^{DIPP}BDI)Ca(AlH_4)·(THF)_2$ (5)		20	85	2.5	94
16	$LiAlH_4$ (5)		6	85	96	66[10]
17	$Ca(AlH_4)_2·(THF)_4$ (2.5)		20	85	24	99
18	$Sr(AlH_4)_2$ (2.5)		20	85	24	99
19	$LiAlH_4$ (5)		20	85	24	20
20	$Ca(AlH_4)_2·(THF)_4$ (2.5)		20	85	24	99
21	$LiAlH_4$ (5)		6	85	24	13[10]
22	$Ca(AlH_4)_2·(THF)_4$ (2.5)		20	85	24	43[b]
23	$Sr(AlH_4)_2$ (2.5)		20	85	24	46[b]
24	$LiAlH_4$ (5)		6	85	24	4
25	$Ca(AlH_4)_2·(THF)_4$ (2.5)		20	85	24	43
26	$Sr(AlH_4)_2$ (2.5)		20	85	24	94
27	$Ca(AlH_4)_2·(THF)_4$ (0.5)	PhC(H)=N*t*Bu	50	85	24	98

[a]Runs in neat imine (except for entries 21–23, in which case the solid imine was dissolved in THF, 2.8 M) and conversion followed by ^1H NMR. [b]Due to the severe overlap of product/substrate ^1H NMR signals, the conversion was determined by GC/MS.

bar of H_2, 85 °C), and conversion was followed by ^1H NMR (Table 3). To evaluate the metal effects, their performance is compared to that of $LiAlH_4$ and $[Bu_4N^+][AlH_4^-]$. Because the $Ae(AlH_4)_2$ complexes contain two alanate anions, their catalyst loading was halved in comparison to that of $LiAlH_4$. As catalysis with these alanates is thought to be a heterobimetallic process, this comparison is debatable. Therefore, the performances of the $Ae(AlH_4)_2$ catalysts described herein are conservative estimates.

Screening studies using the benchmark substrate PhC(H)═N*t*Bu show that Mg alanate is clearly less active than $LiAlH_4$ but activities increase with the size of the Ae metal (Mg < Ca < Sr; entries 1−4). Using the $Sr(AlH_4)_2{\cdot}(THF)_5$ complex as a catalyst, essentially full conversion was achieved within 2.5 h. This clearly shows that the nature of the second metal in alanate complexes is important. This conclusion is especially supported by attempts to catalyze imine hydrogenation with $[Bu_4N^+][AlH_4^-]$ (entry 5). As there is hardly any conversion, the presence of a second metal is crucial for catalysis. This hypothesis was tested by addition of the metal salts. While combinations of $[Bu_4N^+][AlH_4^-]$ with LiI, NaI, or KI are not active, the addition of group 2 salts AeI_2 (Ae = Mg, Ca, Sr, or Ba) led to a considerable increase in activities (entries 6−9). A maximum in activity was found for the addition of CaI_2. This may be due to differences in solubility (in all cases, the AeI_2 salt did not completely dissolve).

In previous studies of $LiAlH_4$-catalyzed imine hydrogenation, it was found that pressure only slightly affects conversion rates: decreasing the pressure from 20 to 1 bar led to only a small decrease in activity (cf. entries 1 and 10).[10] Also, imine hydrogenation with $Ca(AlH_4)_2{\cdot}(THF)_4$ could be performed conveniently at atmospheric pressure (entry 11). A slight temperature decrease from 85 to 60 °C had larger consequences (entries 12 and 13). The activities with heteroleptic catalysts $(^{DIPP}BDI)Mg(AlH_4){\cdot}THF$ and $(^{DIPP}BDI)Ca(AlH_4){\cdot}(THF)_2$ were higher than those of the corresponding homoleptic salts (entries 14 and 15, respectively), and for the Ca complex, nearly full conversion could be achieved within 2.5 h. Due to the facile decomposition of the *β*-diketiminate Ca alanate complex (Scheme 3), the nature of the catalyst is not exactly clear.

Earlier studies of $LiAlH_4$-catalyzed imine hydrogenation showed that slight variations in the substrate led to problems. Exchanging the Ph group in PhC(H)═N*t*Bu for a *t*Bu substituent impedes conversion by steric hindrance and electronic effects: the electron-releasing alkyl group makes the imine C less electrophilic. Hence, for $LiAlH_4$, long reaction times of ≤4 days gave only incomplete conversion (entry 16). Using the Ae alanates, however, solved this problem, and full conversion was obtained within 24 h (entries 17 and 18).

The substrate *n*PrC(H)═N*t*Bu represents an imine that potentially could be deprotonated to form an aza-allyl anion. This complication was previously encountered in the mechanistically related imine hydrosilylation with early main group metal catalysts.[27] Although we could not isolate defined products from stoichiometric reactions between $Ca(AlH_4)_2{\cdot}(THF)_4$ and *n*PrC(H)═N*t*Bu, reaction of the Ca hydride complex $[(^{DIPP}BDI)CaH{\cdot}THF]_2$ indeed gave deprotonation and formation of an aza-allyl product that could be characterized by NMR and X-ray diffraction (see Figure S35). Such side reactions potentially impede imine hydrogenation. It could, however, be shown that the catalyst $Ca(AlH_4)_2{\cdot}(THF)_4$ is clearly superior to $LiAlH_4$ (entries 19 and 20).

The imine with Ph substituents at C and N, PhC(H)═NPh, is a challenging substrate. The addition of hydride to this highly activated (conjugated) C═N bond should be unproblematic, but subsequent reaction of the resulting amide anion $PhCH_2(Ph)N^-$ with H_2 is difficult due to stabilization of this anion by charge delocalization. Although more active than $LiAlH_4$, the Ae alanate catalysts also gave only partial conversion (entries 21−23).

In contrast, Ae alanates were found to be very effective catalysts for the hydrogenation of a ketimine, which is known to be much more challenging than aldimine reduction. While $LiAlH_4$ is essentially not active, nearly quantitative conversion could be achieved with the catalyst $Sr(AlH_4)_2{\cdot}(THF)_5$ (entries 24−26).

This study shows that Ae metal alanates are considerably more active in imine hydrogenation than $LiAlH_4$. While $LiAlH_4$ is conveniently commercially available, the catalyst loadings could not be decreased below 2.5 mol %.[10] The more active catalyst $Ca(AlH_4)_2{\cdot}(THF)_4$ is still active at catalyst loadings down to 0.5 mol %, but a higher H_2 pressure was needed (entry 27).

■ CONCLUSIONS

Synthetic procedures and crystal structures for homo- and heteroleptic Ae metal complexes of the alanate anion AlH_4^- have been presented. While the complex with the smaller Ae metal $Mg(AlH_4)_2{\cdot}(THF)_4$ shows bonding of the aluminate anion with one bridging hydride, H_3Al-(μ-H)-Mg, complexes with the larger Ae metals Ca and Sr show a combination of H_3Al-(μ-H)-Ae and H_2Al-$(\mu\text{-H})_2$-Ae bridging.

Heteroleptic *β*-diketiminate complexes with AlH_4^- anions have been isolated for Mg and Ca. The Ca complex is so reactive that already at room temperature the *β*-diketiminate anion is reduced to a dianionic bis-amide ligand.

DFT calculations demonstrate that the formation of $Ae(AlH_4)_2$ from AeH_2 and AlH_3 is increasingly exothermic from Be to Ba. Like $LiAlH_4$, all $Ae(AlH_4)_2$ complexes should be considered highly ionic salts in which the charge on the AlH_4^- anions (approximately −0.95) is hardly dependent on the countercation.

The $Ae(AlH_4)_2$ salts are very efficient catalysts for imine hydrogenation. Compared to $LiAlH_4$, not only higher activities but also an extended substrate scope could be demonstrated. The nature of the *s*-block metal strongly influences catalytic activity. While Mg aluminate is less active than $LiAlH_4$, the catalyst performance generally increased with metal size, and for most substrates, the Sr alanate performed best. As the salt $[Bu_4N^+][AlH_4^-]$ is catalytically not active, the *s*-block metal is crucial. This is a strong argument for heterobimetallic catalysis. A comprehensive, combined experimental and theoretical, study of the exact mechanisms for imine hydrogenation with heterobimetallic catalysts will be reported in due course.

■ EXPERIMENTAL SECTION

All experiments were carried out in dry glassware under N_2 using standard Schlenk techniques and freshly dried and degassed solvents (all solvents were dried over a column except for THF, which was dried over sodium benzophenone and redistilled). Commercially available $LiAlH_4$ was extracted with diethyl ether and after removal of all solvents dried in vacuo to give a white fluffy material. Commercially available $NaAlH_4$ was purified via a similar method using THF. Ph(H)C═N*t*Bu was obtained commercially from Sigma-Aldrich (97%). The following imine substrates were prepared according to literature procedures: PhC(H)═NPh,[28] *t*BuC(H)═N*t*Bu,[29] *n*PrC(H)═N*t*Bu,[30] and PhC(Me)═N*t*Bu.[31] $AlH_3{\cdot}(THF)_2$ was prepared according to Smith.[32] Complexes $Mg(AlH_4)_2{\cdot}THF_4$[33] and $Ca(AlH_4)_2{\cdot}THF_4$[34] were prepared according to Fichtner, but both could also be prepared by a similar procedure as described below for $Sr(AlH_4)_2{\cdot}THF_5$. All complexes decomposed rapidly on contact with air but did not ignite. **Caution!** *The presumed* $Ba(AlH_4)_2$ *powder was found to be very pyrophoric in air.* Hydrogen of quality N5 has been used for catalytic hydrogenation. Deuterated solvents were dried over molecular sieves (3 Å) and stored in a glovebox. All substrates were dried by being stirred over freshly powdered CaH_2 at 60 °C and then distilled. In the case of PhC(H)═NPh, which is a solid, the substrate was first dissolved in hexane and then dried over CaH_2, and after filtration, all volatiles were removed under vacuum. Stainless steel pressure reactors were dried by being heated overnight in an oven at 70 °C. The products from catalytic reactions have been analyzed by NMR and GC-MS. NMR spectra were recorded on Bruker Avance III HD 400 MHz and Bruker Avance III HD 600 MHz spectrometers. Elemental analysis was performed with a Hekatech Eurovector EA3000 analyzer. Crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications 1993706−1993710.

Synthesis of $Sr(AlH_4)_2$·THF_5. The salt $SrCl_2$ (500 mg, 3.15 mmol) and $NaAlH_4$ (341 mg, 6.31 mmol) were suspended in THF (10 mL), and the mixture was stirred at room temperature for 16 h. The solution was filtered hot, reduced to half of its volume, and kept at −30 °C to grow crystals. The product was isolated as colorless crystals (481 mg, 0.942 mmol, 30%). Elemental analysis is complicated by the large amounts of loosely bound THF that is partially lost during product isolation but cannot be removed completely under high vacuum. Similar problems have been described for the isolation and characterization of $[Ca^{2+}\cdot(THF)_6][Me_4Al^-]_2$ by Westerhausen et al.:[35] ^{1}H NMR (THF-d_8, 600 MHz, 298 K) δ 4.0−2.1 extremely broad due to ^{27}Al coupling, AlH_4, 3.58 (m, THF), 1.73 (m, THF); ^{27}Al NMR (THF-d_8, 233 MHz, 298 K) δ 109.5.

Synthesis of $[n\mathrm{Bu}_4N^+][AlH_4^-]$. The salt $n\mathrm{Bu}_4N^+Cl^-$ (834 mg, 3.00 mmol) and $NaAlH_4$ (162 mg, 3.00 mmol) were stirred in THF (20 mL) at room temperature for 16 h. The suspension was filtered, and the solvent was removed under reduced pressure. The residue was washed twice with cold pentane (8 mL) and dried under vacuum. The product was isolated as a white powder (444 mg, 1.62 mmol, 54%): ^{1}H NMR (THF-d_8, 600 MHz, 298 K) δ 3.72, 3.44, 3.14, 2.85, 2.56, 2.27 (sextet, $^{1}J_{\mathrm{Al-H}}$ = 174 Hz, 4H, AlH_4), 3.36 (m, 8H, N-C*H*$_2$), 1.72 (m, 8H, NCH_2-C*H*$_2$), 1.43 (sextet, $^{3}J_{\mathrm{H-H}}$ = 7.5 Hz, 8H, CH_3-C*H*$_2$), 1.00 (t, $^{3}J_{\mathrm{H-H}}$ = 7.5 Hz, 12H, C*H*$_3$); ^{13}C NMR (THF-d_8, 150 MHz, 298 K) δ 58.5, 23.9, 19.6, 13.1; ^{27}Al NMR (THF-d_8, 233 MHz, 298 K) δ 100.0 (quint, $^{1}J_{\mathrm{Al-H}}$ = 258.4 Hz). Elemental Anal. Calcd for $C_{16}H_{40}NAl$: N, 5.12%; C, 70.27%; H, 14.74%. Found: N, 4.78%; C, 69.60%; H, 14.62%.

Synthesis of $(^{\mathrm{DIPP}}BDI)Mg(AlH_4)$·THF. Complex $[(^{\mathrm{DIPP}}BDI)MgH]_2$ (143 mg, 0.162 mmol) was dissolved in toluene (5 mL) and cooled to −80 °C. $AlH_3\cdot(THF)_2$ (56.2 mg, 0.323 mmol) was dissolved in toluene (5 mL) and added dropwise to the solution of $[(^{\mathrm{DIPP}}BDI)MgH]_2$. The reaction mixture was allowed to warm to room temperature. The solvent was removed under reduced pressure. The product was washed with cold pentane (2 mL) and isolated as a white powder. Recrystallization from cold toluene yielded crystals suitable for X-ray diffraction (121 mg, 0.222 mmol, 69%): ^{1}H NMR (600 MHz, C_6D_6, 298 K) δ 7.17−7.15 (m, 6H, *H*-Ph), 4.80 [s, 1H, CC(*H*)C], 3.67 (m, 4H, THF), 3.20 (br. 4H, Al*H*$_4$), 3.16 (septet, $^{3}J_{\mathrm{H-H}}$ = 6.6 Hz, 4H, CH_3C*H*CH_3), 1.63 (s, 6H, C*H*$_3$), 1.29 (d, *J* = 6.6 Hz, 12H, C*H*$_3$$CHCH_3$), 1.21 (d and m, $^{3}J_{\mathrm{H-H}}$ = 6.6 Hz, 16H, C*H*$_3$$CHCH_3$ and THF); ^{13}C NMR (151 MHz, C_6D_6, 298 K) δ 169.4, 145.3, 142.5, 125.7, 124.0, 95.1, 70.6, 28.5, 25.3, 25.1, 24.7, 24.5; ^{27}Al NMR (156 MHz, C_6D_6, 298 K) δ 97.43 (br). Elemental Anal. Calcd for $C_{33}H_{53}N_2OAlMg$: N, 5.14%; C, 72.72%; H, 9.80%. Found: N, 5.11%; C, 72.77%; H, 9.60%.

Synthesis of $(^{\mathrm{DIPP}}BDI)Ca(AlH_4)$·$THF_2$. Complex $[(^{\mathrm{DIPP}}BDI)CaH\cdot(THF)]_2$ (116.4 mg, 0.110 mmol) was dissolved in toluene (7 mL) and cooled to −80 °C. $AlH_3\cdot(THF)_2$ (38.2 mg, 0.219 mmol) was dissolved in toluene (5 mL) and added dropwise to the solution of $[(^{\mathrm{DIPP}}BDI)CaH\cdot(THF)]_2$. The reaction mixture was allowed to warm to 0 °C. The solvent was removed under reduced pressure while the temperature was kept at approximately 0 °C. The product was isolated as a white powder. The crude product was washed with 3 mL of cold pentane. Recrystallization from cold toluene yielded crystals suitable for X-ray diffraction (89.2 mg, 0.141 mmol, 64%): ^{1}H NMR (600 MHz, C_6D_6, 298 K) δ 7.14 (m, 6H, *H*-Ph), 4.78 [s, 1H, CC(*H*)C], 3.59 (m, 8H, THF), 3.20 (septet, $^{3}J_{\mathrm{H-H}}$ = 6.8 Hz, 4H, CH_3C*H*CH_3), 2.88 (br, 4H, Al*H*$_4$), 1.66 (s, 6H, C*H*$_3$), 1.34 (d and m, 6.8 Hz, 20H, C*H*$_3$$CHCH_3$ and THF), 1.22 (d, $^{3}J_{\mathrm{H-H}}$ = 6.8 Hz, 12H, C*H*$_3$$CHCH_3$); ^{13}C NMR ($C_6D_6$, 151 MHz, 298 K) δ 165.5, 146.2, 141.4, 124.4, 123.7, 93.9, 68.9, 28.1, 25.1, 24.6, 24.3; ^{27}Al NMR (C_6D_6, 233 MHz, 298 K) δ 120.4 (br). Elemental Anal. Calcd for $C_{37}H_{61}N_2O_2AlCa$: N, 4.43%; C, 70.21%; H, 9.71%. Found: N, 4.40%; C, 70.55%; H, 9.34%.

Synthesis of $(^{\mathrm{DIPP}}BDI)Ca[N(t\mathrm{Bu})(HC{=}C(H)Et)]$·THF. Complex $[(^{\mathrm{DIPP}}BDI)CaH\cdot THF]_2$ (62.6 mg, 0.0590 mmol) was dissolved in 2 mL of benzene. *n*PrC(H)=N*t*Bu (15.0 mg, 20.0 μL, 0.118 mmol) was added, and the solution was heated to 60 °C for 1 h. The solution was concentrated under reduced pressure and held at 8 °C. The product was isolated as yellow crystals (47.2 mg, 0.0720 mmol, 61%): ^{1}H NMR (600 MHz, C_6D_6) δ 7.28−7.14 (m, 6H, H-Ph), 4.80 [s, 1H, CC(*H*)C], 3.53 (m, 4H, THF), 3.28 [m (br), 4H, CH_3C*H*CH_3], 3.08 (m, 1H, CHC*H*N), 1.69 (s, 6H, C*H*$_3$), 1.57 (m, 2H, CH_3C*H*$_2$CH), 1.31 (br, 12H, C*H*$_3$$CHCH_3$), 1.26 (d, $^{3}J_{\mathrm{H-H}}$ = 6.60 Hz, 12H, CH_3CHC*H*$_3$), 1.21 (m, 5H, THF and NCHC*H*CH_2), 0.98 (s, 9H, *t*Bu) 0.94 (t, $^{3}J_{\mathrm{H-H}}$ = 7.32 Hz, 3H, C*H*$_3$$CH_2$CH); ^{13}C NMR (151 MHz, C_6D_6) δ 165.5, 151.1, 147.3, 141.2, 124.1, 123.7, 93.4, 84.2, 68.8, 51.8, 31.7, 29.0, 28.1, 24.9, 24.7, 24.5, 24.33, 23.8, 18.0. Elemental Anal. Calcd for $C_{41}H_{65}N_3OCa$: C, 75.06%; H, 9.99%; N, 6.40%. Found: C, 74.59%; H, 10.03%; N, 6.35%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00226.

Crystallographic details, including ORTEP plots, selected ^{1}H and ^{13}C NMR spectra, and details for the DFT calculations (PDF)

XYZ files (XYZ)

Accession Codes

CCDC 1993706−1993710 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.

■ AUTHOR INFORMATION

Corresponding Author

Sjoerd Harder − *Inorganic and Organometallic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany;* orcid.org/0000-0002-3997-1440; Email: sjoerd.harder@fau.de

Authors

Holger Elsen − *Inorganic and Organometallic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany*

Jens Langer − *Inorganic and Organometallic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany;* orcid.org/0000-0002-2895-4979

Michael Wiesinger − *Inorganic and Organometallic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00226

Notes

The authors declare no competing financial interest.

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