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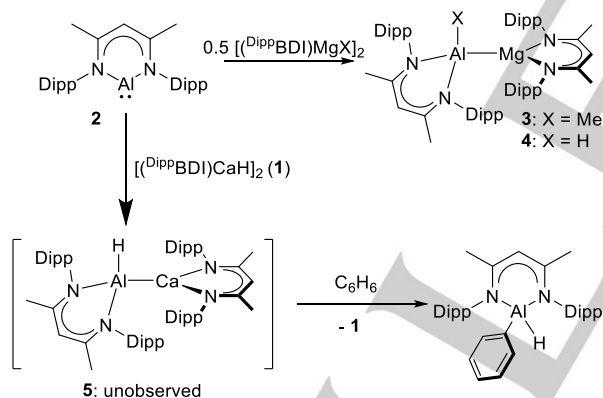
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# A Stable Calcium Alumanyl

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Alkaline earth (Ae = Be, Mg, Ca, Sr, Ba) compounds continue to provide unprecedented observations for stoichiometric and catalytic bond activation.<sup>[1]</sup> Some of the most notable advances have been provided by kinetically-stabilized hydride derivatives.<sup>[2]</sup> The  $\beta$ -diketiminato calcium complex,  $[(\text{DippBDI})\text{CaH}]_2$  (**1**,  $\text{DippBDI} = \text{HC}\{\text{Me}\}\text{CNDipp}\}_2$ ;  $\text{Dipp} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ), for example, reacts with alkenes to provide *n*-alkyl derivatives, which are sufficiently reactive to effect even the nucleophilic alkylation of benzene.<sup>[3]</sup> These observations also impel the exploration of a broader range of Ae-X bonded compounds. A topical case in point is provided by reports of the reactivity of  $\beta$ -diketiminato magnesium and calcium complexes with Roesky's similarly coordinated aluminium(I) species,  $[(\text{DippBDI})\text{Al}]$  (**2**).<sup>[4]</sup> Compound **2** reacts with  $[(\text{DippBDI})\text{MgMe}]$ ,  $[(\text{DippBDI})\text{MgH}]_2$  or  $[(\text{TMEDA})\text{Mg}]_2$  to provide the Mg-Al bonded oxidative addition products (e.g. **3** and **4**, Scheme 1).<sup>[5-7]</sup> In contrast, Harder has observed that addition of **2** to  $(\text{DippBDI})\text{Ca}$ -based reagents results in arene activation. While reaction with the ionic calcium complex  $[(\text{DippBDI})\text{Ca}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  provided two electron reduction of benzene,<sup>[8]</sup> addition of **1** to benzene or toluene solutions of **2** resulted in arene C-H activation and the production of  $[(\text{DippBDI})\text{Al}(\text{H})\text{Ar}]$  complexes (Scheme 1).<sup>[6]</sup> Density Functional Theory (DFT) calculations of this latter reactivity implicated an initial Ca-Al bonded oxidative addition product,  $[(\text{DippBDI})\text{Al}(\text{H})\text{Ca}(\text{DippBDI})]$  (**5**), which, although otherwise analogous to compound **4**, is unobservable due to its rapid nucleophilic activation of the arene solvent.

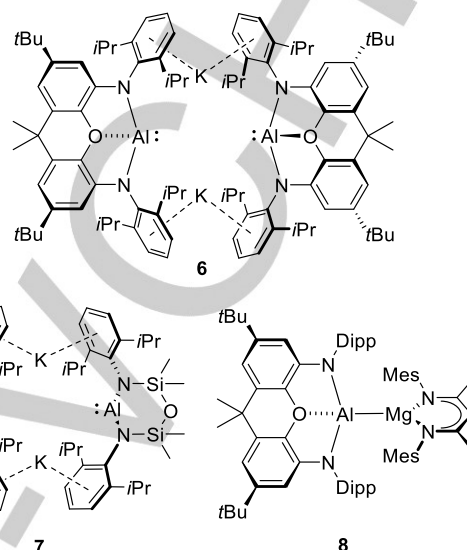


**Scheme 1:** Reactivity of compound **2** with  $(\text{DippBDI})\text{Ae}$  reagents.

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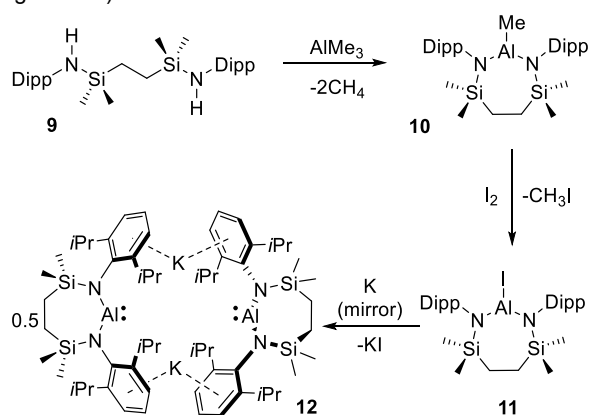
**Figure 1:** The potassium alumanyl derivatives, **6** and **7**, and the Al-Mg bonded species, **8**.

While Scheme 1 highlights how the reactivity of a neutral Al(I) nucleophile may be augmented by the presence of a calcium center, other recent advances have illuminated a further pathway to the formation of group 2 alumanyl derivatives. Building on the earlier development of boryl and gallyl nucleophiles,<sup>[9]</sup> the groups of Aldridge, Goicoechea and Coles have extended the range of *N*-heterocyclic group 13-centered anions to include the potassium alumanyl species, **6** and **7** (Figure 1).<sup>[10-14]</sup> The formally monovalent aluminum centers in both compounds can behave as potent reducing agents or as aluminum-centered nucleophiles. Of most relevance to these studies, the potassium reagent **6** can activate the C-H or C-C bonds of benzene, and reacts with  $[(\text{MesBDI})\text{Mg}(\text{OEt}_2)]$  ( $\text{MesBDI} = \text{HC}\{\text{Me}\}\text{CN-2,4,6-Me}_3\text{C}_6\text{H}_2\}_2$ ) to yield a further Mg-Al bonded complex, **8** (Figure 1).<sup>[10, 12]</sup> In contrast to this recent development of magnesium alumanyl chemistry, the gallyl derivatives of Jones and co-workers, *trans*- $[\text{Ca}\{\text{Ga}[(\text{DippNCR})_2]\}_2(\text{THF})_4]$  (R = H, Me) and *trans*- $[\text{Ca}\{\text{Ga}[(\text{DippNCH})_2]\}_2(\text{TMEDA})_2]$ ,<sup>[15]</sup> provide the only examples of isolable compounds containing calcium-group 13  $\sigma$ -bonds and no calcium alumanyls have been considered beyond the implied intermediacy of species **5**.<sup>[6]</sup> In this contribution, therefore, and as an extension to our recent interest in the reactivity of alkaline earth boryls,<sup>[16]</sup> we describe a seven-membered cyclic alumanyl anion and its use in the synthesis of a stable, yet highly reactive, calcium derivative.

Following an analogous procedure to that employed in the synthesis of compound **7**,<sup>[13]</sup> addition of the pre-ligand  $\{\text{SiN}^{\text{Dipp}}\}_2\text{H}_2$  (**9**,  $\{\text{SiN}^{\text{Dipp}}\} = \{\text{CH}_2\text{SiMe}_2\text{N}(\text{Dipp})\}_2$ ) to trimethylaluminum provided  $[(\text{SiN}^{\text{Dipp}})\text{AlMe}]$  (**10**) (Scheme 2). The slow conversion of **10** to  $[(\text{SiN}^{\text{Dipp}})\text{Al}]$  (**11**) was achieved by reaction with  $\text{I}_2$ , providing >95 % conversion after 5 days at 100 °C. The solid-

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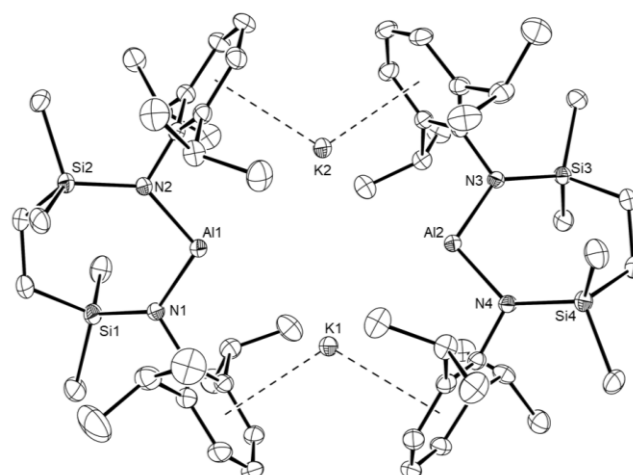
state structure of **11** was investigated by single crystal X-ray diffraction, confirming the formation of a 7-membered metallacycle via *N,N*-chelation to a planar three-coordinate aluminum center [Al-N, 1.782(1) and 1.790(1); Al-I, 2.4690(5) Å] (Figure S10).



**Scheme 2:** Synthesis of compounds **10**–**12**.

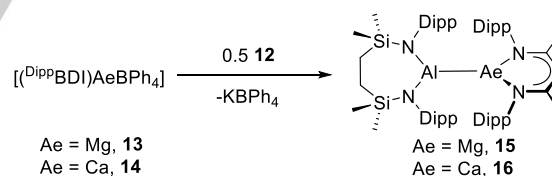
Stirring a solution of **11** in hexane over a potassium mirror resulted in a gradual change from colorless to yellow and the deposition of a grey solid. Filtration of the reaction mixture after 3 days at room temperature and removal of the volatile components gave a yellow powder, which crystallized from  $\text{Et}_2\text{O}$  to provide crystals of  $[\text{Al}\{\text{SiN}^{\text{Dipp}}\}\text{K}]_2$  (**12**). The resultant  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were consistent with a symmetrical *N,N*-chelated disposition of the diamide ligand about aluminum, a deduction confirmed by a subsequent single crystal X-ray diffraction analysis (Figure 2). Like both the previously reported derivatives, **6** and **7**,<sup>[10, 13]</sup> the asymmetric unit of compound **12** comprises two ' $\text{Al}\{\text{SiN}^{\text{Dipp}}\}\text{K}$ ' entities linked through flanking  $\eta^6\text{-K}\cdots\text{Ar}$  interactions [range 2.945(1)–3.026(1) Å]. As expected for a lower oxidation state aluminum species, the Al-N bond distances [range 1.887(2)–1.892(2) Å] are significantly longer than those of **11**. Despite the larger bite angles imposed by chelation of the  $\{\text{SiN}^{\text{Dipp}}\}$  ligand [**12**: N1-Al1-N2 108.84(9), N3-Al2-N4 108.77(9)° versus **7**: 103.89(8), 105.05(8)°], the Al $\cdots$ Al distance [5.721(1) Å] and Al $\cdots$ K distances [range 3.584(1)–3.625(1) Å] are also comparable to the analogous measurements within compound **7** [Al $\cdots$ Al 5.673(1); Al $\cdots$ K 3.5916(8) Å].

Although the implications of any metrical adjustments on the electronic structure of compound **12** will be addressed elsewhere, the similarity of its gross features to both compounds **6** and **7** advocates that **12** should display comparable reactivity. Mindful of Evans' use of tetraphenylborate derivatives of similarly electropositive rare earth elements as hydrocarbon-soluble reagents in further synthesis,<sup>[17]</sup> we prepared  $[(^{\text{Dipp}}\text{BDI})\text{AeBPh}_4]$  (**13**, Ae = Mg; **14**, Ae = Ca) by the respective reactions of  $[(^{\text{Dipp}}\text{BDI})\text{Mg}n\text{-Bu}]$  and  $[(^{\text{Dipp}}\text{BDI})\text{CaN}(\text{SiMe}_3)_2]$  with  $[\text{HNEt}_3][\text{BPh}_4]$ . Both compounds **13** and **14** were isolated in high yields and their solid-state structures were confirmed by X-ray diffraction analysis (Figures S16 and S20) as mononuclear species in which the tetraphenylborate anions interact with the Ae centers via polyhaptic Ae $\cdots\mu\text{-Ph-B}$  interactions.



**Figure 2:** ORTEP representation of compound **12** (30% probability ellipsoids). Hydrogen atoms and occluded molecule of diethyl ether solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Al1-N1 1.887(2), Al1-N2 1.8889(19), Al2-N3 1.890(2), Al2-N4 1.892(2), Si1-N1 1.729(2), Si2-N2 1.7333(19), Si3-N3 1.731(2), Si4-N4 1.731(2), N1-Al1-N2 108.84(9), N3-Al2-N4 108.77(9).

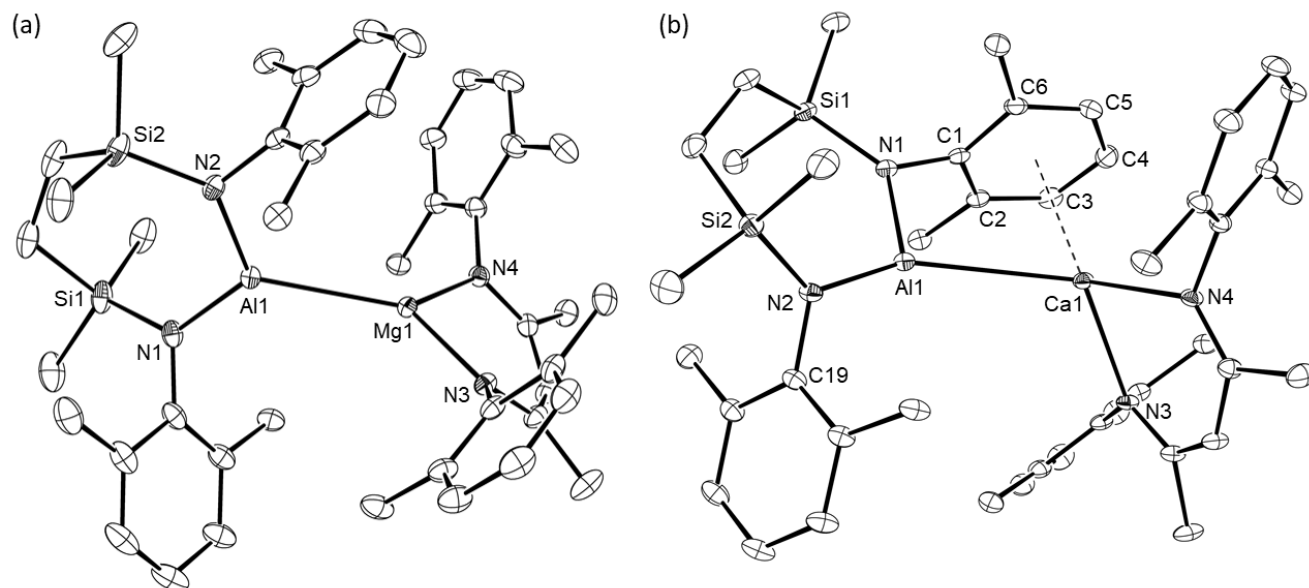
Addition of toluene solutions of compound **12** to either compound **13** or **14** resulted in a colorless suspension of  $\text{KBPh}_4$  and, after crystallization from *n*-hexane and benzene, respectively, the formation of the magnesium and calcium aluminyl species,  $[(^{\text{Dipp}}\text{BDI})\text{Al-Mg}^{\text{Dipp}}\text{BDI}]$  (**15**) and  $[(^{\text{Dipp}}\text{BDI})\text{Al-Ca}^{\text{Dipp}}\text{BDI}]$  (**16**), as colorless and yellow crystals (Scheme 3). The solid-state structures of both compounds **15** and **16** were determined by X-ray diffraction analysis, which confirmed them as magnesium and calcium derivatives comprising aluminum to alkaline earth interactions.



**Scheme 3:** Synthesis of the magnesium and calcium aluminyl compounds, **15** and **16**.

Both the Mg1 and Al1 centers of compound **15** are unambiguously three-coordinate (closest Al-C separation 4.965 Å) and the two *N*-donor ligand systems are almost orthogonal (Figure 3a), such that the dihedral angle subtended by the N1-Al1-N2 and N3-Mg1-N4 mean planes is 84.1°. Although the Mg1-Al1 bond in **15** [2.7980(6) Å] is longer than the comparable length in compound **8** [2.696(1) Å],<sup>[10]</sup> it is commensurate with the corresponding distances observed in compounds **3** [2.7687(8) Å] and **4** [2.7687(5) Å],<sup>[5, 6]</sup> which also comprise magnesium coordinated by the  $^{\text{Dipp}}\text{BDI}$  ligand, and in Jones' derivative,  $[(\text{TMEDA})(1)\text{Mg-Al}(1)(^{\text{Dipp}}\text{BDI})]$  [2.727(2) Å].<sup>[7]</sup>

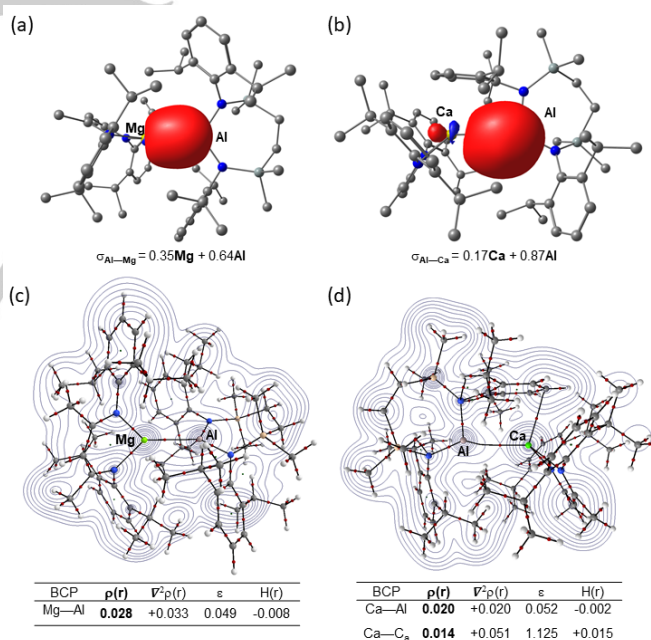
Like **15**, compound **16** contains a direct alkaline earth to aluminum bond (Figure 3b). Although the Al-Ca bond length [3.1664(4) Å] is 6.6% longer than the sum of covalent radii of the metal centers, this distance is closely comparable with that calculated for the analogous intermetallic separation [3.120 Å] in the unobservable intermediate **5** (Scheme 1).



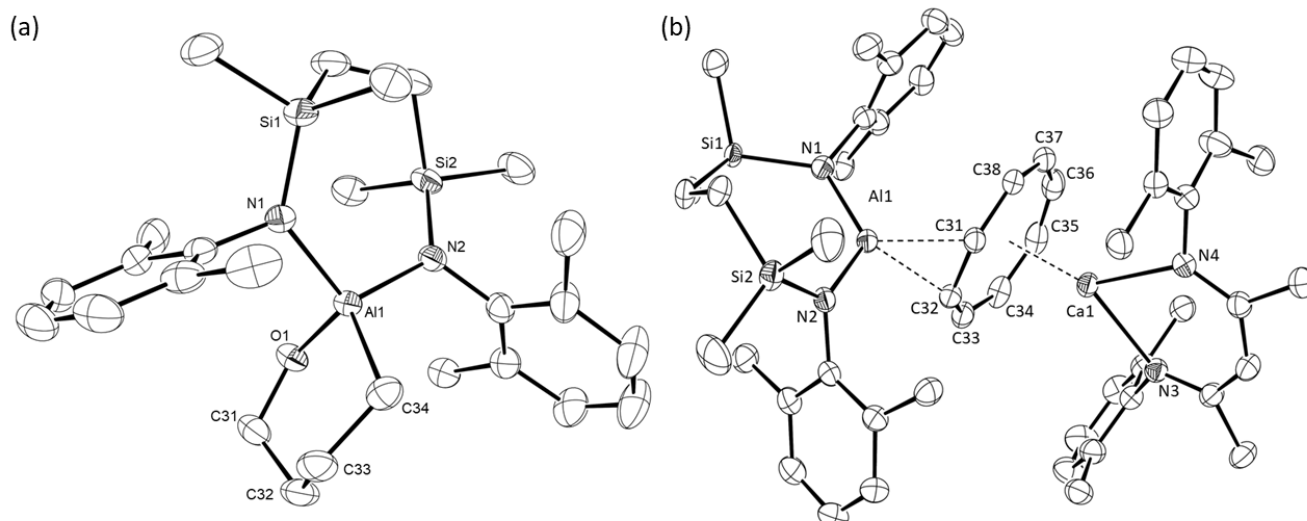
**Figure 3:** ORTEP representations of (a) compound **15** and (b) compound **16** (30% probability ellipsoids). Hydrogen atoms, *iso*-propyl carbon atoms and disordered molecules of solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): (**15**) Al1-Mg1 2.7980(6), Al1-N1 1.8482(13), Al1-N2 1.8402(13), Mg1-N3 2.0528(12), Mg1-N4 2.0721(12), N1-Al1-Mg1 125.94(5), N2-Al1-Mg1 121.91(4), N2-Al1-N1 111.87(6), N3-Mg1-Al1 132.59(4), N3-Mg1-N4 93.77(5), N4-Mg1-Al1 132.94(4); (**16**) Ca1-Al1 3.1229(5), Al1-N1 1.8973(13), Al1-N2 1.8544(14), Ca1-N3 2.3538(12), Ca1-N4 2.3682(13), Ca1-C1 3.1735(15), Ca1-C2 3.1333(16), Ca1-C3 3.0213(17), Ca1-C4 2.9790(17), Ca1-C5 3.0884(16), Ca1-C6 3.2215(15), N2-Al1-N1 111.08(6), N3-Ca1-N4 81.10(4), N1-Al1-Ca1 98.14(4), N2-Al1-Ca1 150.30(5), N3-Ca1-Al1 118.99(3), N4-Ca1-Al1 123.45(3).

The coordination sphere of Ca1 is augmented by a pronounced  $\eta^6$ -interaction with the C1-C6-containing Dipp substituent [Ca1-C range; 2.9790(17)-3.2215(15) Å] of the aluminum-coordinated diamide ligand. The consequent asymmetry in the relative orientation of the {SiN<sup>Dipp</sup>}Al and (DippBDI)Ca units is particularly reflected by the N1-Al-Ca1 [98.14(4)°] and N2-Al1-Ca1 [150.30(5)°] angles.

Insight into the contrasting structures of **15** and **16** was provided by DFT calculations.<sup>[18]</sup> Both structures optimized to geometries close to those in the solid state, albeit with slightly overestimated metal-metal bond lengths (**15**, Mg-Al 2.85; **16**, Ca-Al 3.25 Å). Inspection of the localised Pipek-Mezey orbitals for compounds **15** and **16** (Figures 4a,b) emphasizes the polarization intrinsic to both the Al-Mg and Al-Ca  $\sigma$ -bonds. Although contributions from the aluminum centers dominate both orbitals, the charge distributions clearly reflect the greater ionic character of the Al-Ca interaction, an observation further underscored by the calculated NBO charges (**15**, Mg +1.45 Al +0.83; **16** Ca +1.65, Al +0.72 a.u.). Similarly, QTAIM plots of **15** and **16** identify bond critical points (BCPs) on both Ae-Al bond paths (Figures 4c,d). The attributes of the BCP associated with the Al-Mg bond path [higher  $\rho(r)$ , 0.028 a.u. (**15**) versus 0.020 (**16**) and more negative  $H(r)$ , -0.008 a.u. (**15**) versus -0.002 a.u. (**16**)], however, are indicative of a marginally higher covalency between magnesium and aluminum than for the equivalent Al-Ca interaction. Although compound **16** features a further bond path between the Ca center and a Dipp substituent of the {SiN<sup>Dipp</sup>}Al unit, this BCP is characterized by a very small  $\rho(r)$  and small positive  $H(r)$ . Similarly, analysis of the relevant NBOs of **16** (HOMO-8 and HOMO-10, Figure S37) and visualization of the analogous Non Covalent Interaction (NCI) index (Figure S39) are indicative that this interaction is non-covalent in origin and only weakly stabilizing of the structure as a whole.



**Figure 4:** Localized Pipek-Mezey orbitals of (a) **15** and (b) **16** showing Al-Ca and Al-Mg  $\sigma$ -bonding orbitals, respectively. QTAIM molecular graphs of (c) **15** and (d) **16**. The electron density contours are computed in the {Mg/Al/Si} planes with bond critical points (BCPs) shown as small red spheres. BCP electron densities ( $\rho(r)$  in eÅ<sup>-3</sup>), values of the Laplacian of the electron density ( $\nabla^2\rho(r)$  in eÅ<sup>-5</sup>), ellipticities ( $\epsilon$ ) and total energy densities ( $H(r)$  in a.u.) are tabulated beneath the relevant figures.



**Figure 5:** ORTEP representations of (a) the aluminate component of compound **17** and (b) compound **18** (30% probability ellipsoids). Hydrogen atoms and *iso*-propyl carbon atoms, in both structures, and a disordered molecule of benzene solvent in **18** are omitted for clarity. Selected bond lengths (Å) and angles (°): (**17**) Al1-O1 1.7637(16), Al1-N1 1.8997(18), Al1-N2 1.889(2), Al1-C34 1.984(3), O1-Al1-N1 109.88(8), O1-Al1-N2 106.51(8), O1-Al1-C34 102.23(10), N1-Al1-C34 113.76(10), N2-Al1-N1 110.75(8), N2-Al1-C34 113.10(10); (**18**) Al1-N1 1.8085(17), Al1-N2 1.8200(16), Al1-C31 2.125(2), Al1-C32 2.123(2), Ca1-N3 2.3437(17), Ca1-N4 2.3831(18), Ca1-C31 2.7107(19), Ca1-C32 2.804(2), Ca1-C33 2.818(2), Ca1-C34 2.753(2), Ca1-C35 2.693(2), Ca1-C36 2.695(2), Ca1-C37 2.706(2), Ca1-C38 2.698(2), N1-Al1-N2 119.27(8), N3-Ca1-N4 79.34(6).

Preliminary investigations indicate that compound **16** provides a significantly enhanced source of reactivity in comparison to its lighter congener. While neither compound displays any observable reaction with benzene or toluene, and compound **15** is stable in ether solvents, addition of THF to a solution of compound **16** in methylcyclohexane resulted in the immediate decoloration of the yellow solution and the formation of a single new compound (**17**). The ionic complex **17** comprises a charge separated  $[(\text{D}^{\text{ipp}}\text{BDI})\text{Ca}(\text{THF})_3]^+$  cation and an aluminate anion (Figure 5a), which may be considered as the formal product of oxidative addition of a THF C-O bond to the aluminium(I) center of the  $[\{\text{SiN}^{\text{Dipp}}\}\text{Al}]^-$  anion.<sup>[19]</sup> Similarly, compound **15** is unreactive toward 1,3,5,7-cyclooctatetraene (COT), whilst addition of COT to compound **16** results in its two-electron aromatization and production of the asymmetric and heterobimetallic inverse sandwich species, compound **18** (Figure 5b). Although the chemistry of compounds **17**, **18** and related derivatives will be discussed in detail elsewhere, these initial observations confirm that such heavier alkaline earth aluminyls, like heavier group 2 organo-derivatives, may provide a source of striking and unprecedented reactivity. We are continuing elaborate these possibilities.

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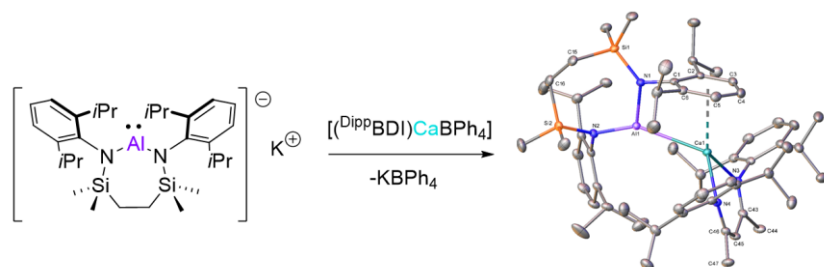
#### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** magnesium • calcium • potassium • aluminyl • density functional theory

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**A Stable Calcium Alumanyl**

**AlCan Wrap:** Reaction of a seven-membered cyclic alumanyl anion with a  $\beta$ -diketiminato calcium tetraphenylborate provides facile access to a stable, but highly reactive, calcium alumanyl.