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Dihydrogen Activation by Lithium- and Sodium-Aluminyls

Matthew J. Evans,^[a] Mathew D. Anker,^{*[a]} Claire L. McMullin,^{*[b]} Sam E. Neale,^[b] Martyn P. Coles^{*[a]}

[a] Mr M. J. Evans, Dr M. D. Anker, Professor Dr M. P. Coles
School of Chemical and Physical Sciences
Victoria University of Wellington
PO Box 600, Wellington 6012, New Zealand
E-mail: martyn.coles@vuw.ac.nz

[b] Dr C. L. McMullin, Dr S. E. Neale
Department of Chemistry
University of Bath
Bath, BA2 7AY, UK

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Abstract: To date, aluminyl anions have been exclusively isolated as their potassium salts. We report herein synthesis of the lithium and sodium aluminyls, $M[Al(NON^{Dipp})]$ ($M = Li, Na$, $NON^{Dipp} = [O(SiMe_2NDipp)_2]^{2-}$; $Dipp = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$). Both compounds crystallize from non-coordinating solvent as 'slipped' contacted dimeric pairs with strong $M \cdots \pi(\text{aryl})$ interactions. Isolation from Et_2O solution affords the monomeric ion pairs $(NON^{Dipp})Al-M(Et_2O)_2$, which contain discrete $Al-Li$ and $Al-Na$ bonds. The ability of the full series of Li , Na and K aluminyls to activate dihydrogen is reported.

In 2018 aluminyl compounds entered the arena of low-valent main group chemistry as a new class of aluminium(I) anion.^[1] The first aluminyl anion consisted of a three-coordinate $Al(I)$ centre supported by a xantheno-based diamido ligand, $[XanthNON^{Dipp}]^{2-}$.^[1] The crystal structure showed a contacted dimeric pair (CDP) in which the potassium cations were involved in $K \cdots \pi(\text{arene})$ interactions (Figure 1, $K_2[II]_2$). Shortly thereafter we reported the two-coordinate aluminyl anion $K_2[III]_2$ that also crystallized as a CDP,^[2] a motif that is common in aluminyl chemistry where $K \cdots \pi(\text{arene})$ contacts are possible (e.g. $K_2[III]_2$,^[3] and $K_2[IV]_2$).^[4]

In the absence of ligand substituents available for $K \cdots \pi(\text{arene})$ interactions, other aluminyl structures are observed. The dialkyl aluminyl $[K(L)_2][V]$ ($L = \text{toluene}$)^[5] exists as a monomeric ion pair (MIP) with an $Al-K$ bond considerably shorter than the $Al \cdots K$ contacts in the CDPs. Furthermore, compounds in which the potassium ion is segregated have been reported. The addition of [2.2.2]cryptand to $K_2[II]_2$ afforded the separated ion pair (SIP) $[K(2.2.2)\text{crypt}][Al(XanthNON^{Dipp})]$ $[K(\text{crypt})][I]$,^[6] and the two-coordinate SIP $[K(12\text{-c-}4)_2][VI]$ was isolated from reduction of the dialane precursor in the presence of 12-crown-4 (12-c-4).^[7]

Despite the chemistry of the aluminyl anions being governed by reactivity at aluminium,^[8] the potassium cation may also influence the reactivity through synergistic interactions in a protocol that is established for many bimetallic compounds incorporating group 1 metals.^[9] This is illustrated by the contrasting reactivity of $K_2[II]_2$ and $[K(\text{crypt})][I]$ with benzene, where the CDP showed the thermally promoted oxidative addition of a $C-H$ bond to Al ,^[11] whereas SIP $[K(\text{crypt})][I]$ underwent a reversible $C-C$ bond activation at room temperature.^[6] In addition, computational analysis showed that activation of substituted arenes with $K_2[II]_2$ and $[K(L)_2][V]$ involves coordination of the aromatic ring to K^+ , which lowered the π^* -orbital energy facilitating nucleophilic attack of Al in a *meta*-selective S_NAr reaction.^[10]

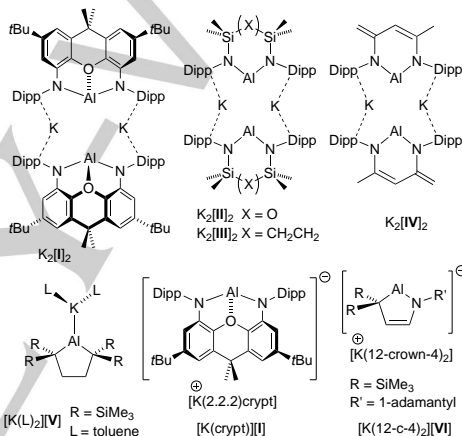
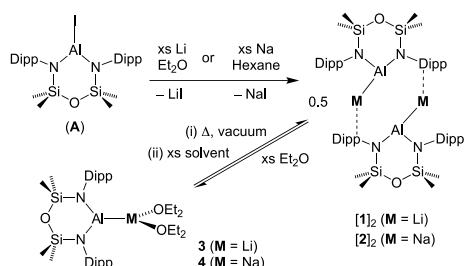


Figure 1. The family of potassium aluminyl species.

The exclusivity of potassium in aluminyl chemistry and its influence on small molecule activation prompted the question whether other group 1 metals could be exploited in this area. In this contribution we report isolation of the first sodium and lithium aluminyls and demonstrate differences in their activation of H_2 .

The reduction of $Al(NON^{Dipp})$ (**A**)^[2] with lithium in Et_2O afforded pale yellow crystals of $Li_2[Al(NON^{Dipp})_2]$ **[1]**₂ on work-up (Scheme 1). The analogous reduction of **A** with sodium metal proceeded in hexane to afford the sodium aluminyl, $Na_2[Al(NON^{Dipp})_2]$ **[2]**₂. Although no identifiable peak was observed in the ^{27}Al NMR spectra for either compound,^[11] a singlet at $\delta_{Li} -2.93$ was observed in the 7Li NMR spectrum of **[1]**₂, with a high field chemical shift consistent with the shielding effect of an aromatic ring current (*vide infra*). The diffusion coefficients D of **[1]**₂ ($5.32 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) and **[2]**₂ ($4.60 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) measured by 1H diffusion-ordered NMR spectroscopy (DOSY, toluene- D_6 , 298 K) are lower than the monomeric iodide **A**^[2] ($D = 6.14 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), indicating retention of the CDP in aromatic solvent.^[1,4]

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Scheme 1. Synthesis of $[1]_2$, $[2]_2$, **3** and **4**. (i) 60 °C, vacuum 10^{-2} mbar, solid-state; (ii) Solvent = toluene, benzene.

X-ray diffraction data show that $[1]_2$ and $[2]_2$ are best described as 'slipped' CDPs (Figure 2). Within each structure the shortest Al–M distance (Al–Li 2.746(3) Å and Al–Na 3.0305(6) Å) is greater than the sum of the covalent radii ($\Sigma_{cov}(Al, Li) = 2.49$ Å and $\Sigma_{cov}(Al, Na) = 2.87$ Å).^[12] The remaining Al...M distances are considerably longer (Al...Li' 3.364(3) Å; Al...Na' 3.5606(6) Å) generating a pronounced asymmetry within the dimer and contrasting with the symmetrical bonding in the potassium aluminyls. Such slippage has been observed in a Mg(0) compound and was attributed to Na... π (arene) interactions.^[13] This is supported by analogous contacts in $[1]_2$ and $[2]_2$, where short Li...Ct and Na...Ct distances^[14] suggest strongly held CDPs.

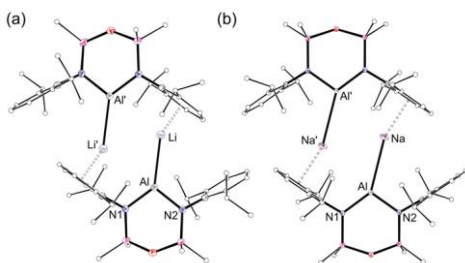


Figure 2. Displacement ellipsoid plots (30 %, C-atoms reduced for clarity, H-atoms omitted) of (a) $[1]_2$ ($\ell = \frac{1}{2}-x, \frac{1}{2}-y, -z$) and (b) $[2]_2$ ($\ell = -x, -y, 1-z$). Selected bond lengths (Å, Ct = centroid): $[1]_2$ Al–Li 2.746(3), Al...Li' 3.364(3), Li...Ct 2.008(4); $[2]_2$ Al–Na 3.0305(6), Al...Na' 3.5606(6), Na...Ct 2.4596(8).

Topological analyses of the bonding between the $[Al(NON^{Dipp})]^-$ anions and the group 1 metal cations **M** within $[1]_2$, $[2]_2$ and $K_2[III]_2$ were provided by DFT calculations via QTAIM. In all cases the Al...M (M = Li, Na, K) interactions can be comfortably classed as non-covalent, based on criteria where the absolute potential density is less than twice the kinetic potential density ($|V(r)| < 2G(r)^{[15]}$), and when the Laplacian is greater than zero ($\nabla^2\rho(r) > 0$). The degree of covalent character increases with the group 1 metal according to $Li > Na > K$, with $-G(r)/V(r)$ ratios $[1]_2 = 0.88$, $[2]_2 = 0.98$ and $K_2[III]_2 = 1.07$.^[16]

The asymmetry in the CDPs in $[1]_2$ and $[2]_2$ is evident from a single Al...M (M = Li, Na) bond critical point (BCP) above the

chosen threshold of 0.005 ($[1]_2$, Figure 3), whereas the more symmetrical $K_2[III]_2$ dimer has two analogous BCPs (Figure S57). This is also reflected in the calculated M... π (arene) interactions, where BCPs between K and both adjacent aryl rings are measured in $K_2[III]_2$, whereas $[1]_2$ and $[2]_2$ only qualify a single interaction.

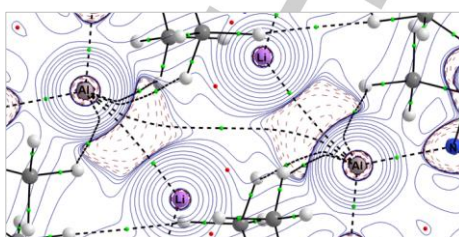


Figure 3. Contour plot of the Laplacian of the electron density for the DFT computed Al_2Li_2 core of $[1]_2$ in the (AINLi)-plane. Bond critical points (BCP) are shown in green and ring critical points (RCP) in red.

The reduced number of contacts between the monomeric $M[Al(NON^{Dipp})]$ units in $[1]_2$ and $[2]_2$, and the observed colour change of lithium aluminyl from colourless in Et_2O to pale yellow for the isolated CDP suggested a solvated form may be accessible in coordinating solvent. Accordingly, the relative energies of the CDPs were calculated and compared with the hypothetical $M[Al(NON^{Dipp})]$ monomers and the Et_2O solvated MIP forms $(NON^{Dipp})Al-M(Et_2O)_2$ (Table S3). For M = Li and Na, breaking the dimer into monomeric units results in a loss of stability amounting to 25.4 kcal mol⁻¹ and 15.9 kcal mol⁻¹, respectively. However, solvating the alkali metal with two equivalents of Et_2O stabilizes the MIPs, with overall energies of -7.0 kcal mol⁻¹ (M = Li) and -3.2 kcal mol⁻¹ (M = Na) relative to the respective CDPs. When M = K, a similar loss of stability is noted on monomer formation (24.0 kcal mol⁻¹). However, compensation of this energy loss is not achieved on solvation by ether and $(NON^{Dipp})Al-K(Et_2O)_2$ is less stable than $K_2[III]_2$ by 7.7 kcal mol⁻¹.

Allowing Et_2O solutions of $[1]_2$ and $[2]_2$ to evaporate gave colourless crystals $(NON^{Dipp})Al-Li(Et_2O)_2$ (**3**) and $(NON^{Dipp})Al-Na(Et_2O)_2$ (**4**), respectively (Scheme 1). Performing the procedure with $K_2[III]_2$ did not give the analogous potassium compound, in agreement with the calculated CDP and MIP energies. The ¹H NMR spectrum of **3** (C₇D₈, 298 K) shows peaks for a new ligand environment and confirms the presence of 2 equivalents of Et_2O . Intriguingly, resonances for the dimer $[1]_2$ were consistently observed in the ¹H, ¹³C, ⁷Li and DOSY NMR spectra of isolated **3**. A ⁷Li NMR resonance at δ_{Li} 2.68, congruent with disruption of the Li... π (arene) interactions, and a low molecular weight species ($D = 6.21 \times 10^{-10}$ m² s⁻¹) in the DOSY were assigned to $(NON^{Dipp})Al-Li(Et_2O)_2$. In contrast, the ¹H and ¹³C NMR spectra of **4** showed only peaks for $[2]_2$ and non-coordinated Et_2O at 298 K. These data indicate an equilibrium between the CDPs and the solvated MIPs, with the CDP dominating at high temperature. This was confirmed by a van't Hoff analysis of variable temperature NMR data, giving $\Delta H = -34$ kJ mol⁻¹ and $\Delta S = -78$ J K⁻¹ mol⁻¹ (M = Li) and $\Delta H = -40$ kJ mol⁻¹ and $\Delta S = -141$ J K⁻¹ mol⁻¹ (M = Na). These data correspond to $\Delta G(253$ K) values of -15.2 kJ mol⁻¹ and -1.5 kJ

Commented [CM1]: I think these symbols are the wrong way round? Should be increasing to K so: Li < Na < K

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mol⁻¹ for Li and Na, respectively, consistent with a smaller energy difference between the CDP and MIP forms for the sodium alumynyls and in agreement with results from DFT studies.

The crystal structures of **3** and **4** confirmed formation of the monomeric ion pairs (NON^{Dipp})Al–M(Et₂O)₂ (Figure 4), containing unsupported Al–Li and Al–Na bonds. In both cases the aluminium is distorted trigonal planar defined by the chelating NON^{Dipp}-ligand and a solvated alkali metal atom. The Al–Li bond length in **3** is 2.767(2) Å is slightly longer than that in [1]₂ and 11.1 % greater than Σ_{cov}(Al, Li). The corresponding Al–Na bond in **4** (3.0137(8) Å) is shorter than in [2]₂ and is only 5.0 % greater than Σ_{cov}(Al, Na).

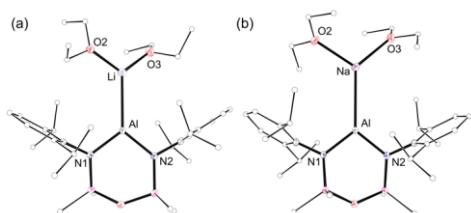


Figure 4. Displacement ellipsoid plot (30 %, C-atoms reduced for clarity, H-atoms and disordered atoms omitted) of **3** and **4**. Selected bond lengths (Å): **3** Al–Li 2.767(2), **4** Al–Na 3.0137(8)

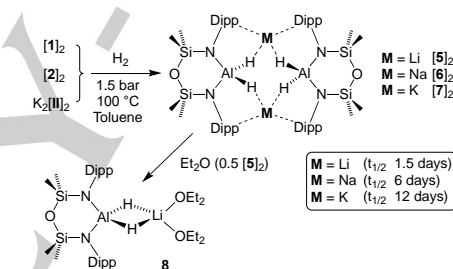
Natural Bond Order (NBO) analysis of **3** and **4** located no covalent bonds between aluminium and the alkali metals, although substantial 'donor-acceptor' interactions were found (stabilisation energies of **3** = 40.5 kcal mol⁻¹ and **4** = 25.2 kcal mol⁻¹). In both cases the HOMO depicts lone pair character retained at Al, composed of 80.2 % s and 19.8 % p for **3** and 79.3 % s and 20.7 % p for **4**. The orbital lobes are directed towards Li/Na, with the extension less pronounced for **4** (Figures S58–S61). QTAIM analysis of the Al–M bond confirmed non-covalent character with a low electron density at the BCP ($\rho(r)$: **3** 0.0182; **4** 0.0164) and a positive Laplacian ($\nabla^2\rho(r)$ = 0.0340 for **3** and **4**).

Comparison of the Al–M bonds in the CDP and MIP structure types was performed by analysis of the Wiberg bond indices (WBIs, Table S4). The WBI for the Al–Li bond in **3** is 0.2259, denoting less electron sharing between the two metals than the major interactions in the CDP (WBI = 0.2681 / 0.2664). However, considering the sum of both the major and minor Al–Li interactions in [1]₂ (0.3626 / 0.3706), we note a greater overall sharing in the dimer. Comparing these values with the sodium species, the Al–Na WBI in **4** (0.2506) is greater than the stronger interaction in [2]₂ (0.1712) but less than the sum (0.2638). This trend is also reflected in the delocalization indices (Dis) for each structure, with [1]₂ (0.1114) > **3** (0.1085) and [2]₂ (0.1684) < **4** (0.1873), consistent with greater overall WBIs in the CDP for M = Li, whereas for M = Na this occurs for the MIP.

The K₂[1]₂ alumynyl system reacted with dihydrogen under ambient conditions (2.0 bar, 5 days, room temperature) to afford K₂[Al(NON^{Dipp})(H)₂]₂.^[11] Using this reaction as a benchmark, we examined the hydrogenation of the series of M₂[Al(NON^{Dipp})₂]₂ alumynyls for M = Li, Na, K.^[17] All reactions require heating to proceed, and data were collected for 0.083 M solutions in C₇D₈ with 1.5 bar H₂ at 100 °C. Using the time taken for 50% conversion

(t_{1/2}) as an approximate measure of the rate of the reaction, we observe that the hydrogenation proceeds in the order Li (t_{1/2} = 1.5 days) >> Na (t_{1/2} = 6 days) > K (t_{1/2} = 12 days). Allowing reaction to go to completion allowed isolation of the dihydroaluminate M₂[Al(NON^{Dipp})(H)₂]₂ (Scheme 2, M = Li [5]₂, M = Na [6]₂, M = K [7]₂). The low solubility of [5]₂ in non-coordinating solvents prevented spectroscopic analysis, and the crude solid was therefore crystallized from Et₂O, affording (NON^{Dipp})Al(μ-H)₂Li(OEt)₂ (**8**).

Although the AlH₂ resonances of the dihydroaluminate salts are not observed in the ¹H NMR spectra,^[18] resolved peaks in ²⁷Al NMR spectra of [6]₂ (δ_{Al} 122) and [7]₂ (δ_{Al} 118) indicate a change in the coordination environment at aluminium compared with [1]₂ and [2]₂, for which no ²⁷Al NMR signals were observed. The full-width half-maximum (FWHM) of these peaks are significantly reduced in the ²⁷Al{¹H} spectra, indicating the presence of ²⁷Al{¹H} interactions. Furthermore, the infrared spectra show stretches between 1714 and 1645 cm⁻¹, characteristic for Al–H bonds.^[19] Compound **8** shows an analogous ²⁷Al{¹H} resonance at δ_{Al} 117, which resolves into a broad triplet in the proton-coupled ²⁷Al NMR spectrum (Figure S51).^[20]



Scheme 2. Synthesis of [5]₂, [6]₂, [7]₂ and **8**.

X-ray crystallographic analysis of [6]₂ and [7]₂ confirm their structures as the M₂[Al(NON^{Dipp})(H)₂]₂ dimers (M = Na, [6]₂; M = K, [7]₂). Evidence for the formation of the AlH₂ groups is inferred from changes to the gross structural features of the dimer compared with the alumynyl starting materials (Figure 5). Additionally, residual electron density peaks in the X-ray diffraction data of [6]₂ and [7]₂ at positions consistent with Al–H bonds were located in the difference map and incorporated into the refined model.

Comparison of the crystal structure of **8** (Figure S54) with that of **3** also shows significant changes to the overall structure, with a reduction in the interplanar N₂Al / LiO₂ angle from 26.30(4)° in **3** to 11.10(6)° in **8**. We note that the incorporation of two hydride ligands decreases the Al...Li distance from 2.767(2) Å (**3**) to 2.640(3) Å in **8**, resulting in a value similar to that in the structurally related compound, ((Me₃Si)₂N)₂Al(μ-H)₂Li(OEt)₂ (2.621(5) Å).^[21]

In summary we have demonstrated that the alumynyl anion [Al(NON^{Dipp})₂]⁻ is not exclusive to its potassium salt but can be accessed as the lithium and sodium complexes via standard reduction procedures. All three members of the series activate

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dihydrogen to form the corresponding dihydroaluminate salts with the rate of conversion $\text{Li} > \text{Na} > \text{K}$.

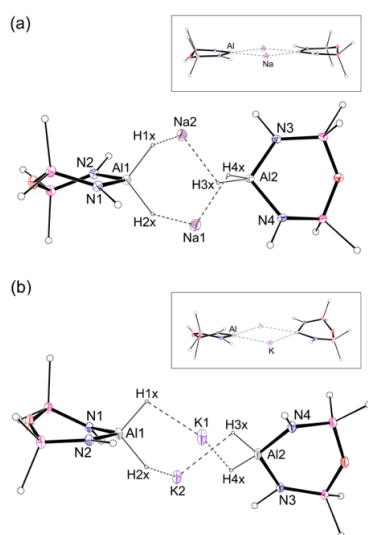


Figure 5. Displacement ellipsoid plots (30 %, C-atoms reduced for clarity, H-atoms except AlH₂ omitted) of the core structures of (a) [6]₂ (inset: core [2]₂) and (b) [7]₂ (inset: core [1]₂). Selected bond lengths (Å) and angles (°): (a) Al1...Al2 4.5357(4), Na1...Na2 5.0749(8). (b) Al1...Al2 5.4512(6), K1...K2 4.7347(6).

Acknowledgements

Ian Vorster is thanked for acquiring the DOSY data. This research made use of the Rāpoi High Performance Computing (HPC) Service at Victoria University of Wellington.

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Keywords: alumanyl anion • sodium alumanyl • lithium alumanyl • dihydrogen activation

Entry for the Table of Contents



It turns out there is nothing special about potassium after all. Sodium and lithium metal reduce Al(III) iodide precursors to the $\text{M}_2[\text{Al}(\text{NON}^{\text{Dipp}})]_2$ aluminyls ($\text{M} = \text{Li}, \text{Na}$). The crystal structures show non-symmetrical dimers held by $\text{M} \cdots \pi(\text{arene})$ interactions. Addition of Et_2O afforded the monomeric ion pairs $(\text{NON}^{\text{Dipp}})\text{Al}-\text{M}(\text{Et}_2\text{O})_2$ containing unsupported Al–Li and Al–Na bonds. All species activate dihydrogen, albeit at significantly different rates of reaction.

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