

Three Oxidative Addition Routes of Alkali Metal Aluminyls to Dihydridoaluminates and Reactivity with CO₂

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Three distinct routes are reported to the soluble, dihydridoaluminate compounds, AM[Al(NON^{Dipp})(H)₂] (AM = Li, Na, K, Rb, Cs; [NON^{Dipp}]²⁻ = [O(SiMe₂NDipp)₂]²⁻; Dipp = 2,6-*i*Pr₂C₆H₃) starting from the alkali metal aluminyls, AM[Al(NON^{Dipp})]. Direct H₂ hydrogenation of the heavier analogues (AM = Rb, Cs) produced the first examples of structurally characterized rubidium and caesium dihydridoaluminates, although harsh conditions were required for complete conversion. Using 1,4-cyclohexadiene (1,4-CHD) as an alternative hydrogen source in transfer hydrogenation reactions provided a lower energy pathway to the full series of products for AM = Li–Cs. A further moderation in conditions was noted for the thermal decomposition of the

(silyl)(hydrido)aluminates, AM[Al(NON^{Dipp})(H)(SiH₂Ph)]. Probing the reaction of Cs[Al(NON^{Dipp})] with 1,4-CHD provided access to a novel inverse sandwich complex, [(Cs(Et₂O))₂{Al(NON^{Dipp})(H)₂(C₆H₆)}], containing the 1,4-dialuminated [C₆H₆]²⁻ dianion and representing the first time that an intermediate in the commonly utilized oxidation process of 1,4-CHD to benzene has been trapped. The synthetic utility of the newly installed Al–H bonds has been demonstrated by their ability to reduce CO₂ under mild conditions to form the bis-formate AM[Al(NON^{Dipp})(O₂CH)₂] compounds, which exhibit a diverse series of eye-catching bimetallic structures.

Introduction

The metal hydride bond (M–H) is a fundamental unit in inorganic and organometallic chemistry with an important role in a plethora of chemical transformations and catalysis.^[1] Compounds containing these bonds feature prominently in the chemistry of the *s*-, *p*-, *d*- and *f*-block elements, with the main group metal hydrides emerging as a key area of research for the development of new economically and environmentally robust chemical processes.^[2] This area is currently dominated by neutral, monometallic hydride systems. However, the extension to bimetallic main group hydrides that typically consist of a cation combined with an anionic metal hydride component allows for the modification of chemical and physical properties due in part to cooperative interactions between the two metal centres.^[3] In the context of the current study, we have demonstrated this principle through the combination of an

alkali metal (AM) dihydropyridyl unit (2-*t*Bu₃H₅N)AM (AM = Li–Cs) and Al*i*Bu₂(TMP) (TMP = 2,2,6,6-tetramethylpiperidide) to generate hydrocarbon soluble alkali-metal-aluminium hydride surrog[ATES].^[4]

The recently discovered class of aluminyls, consisting of an Al(I) containing anion that is charge balanced by an AM cation,^[5] are ideal sources of bimetallic main group metal complexes. Our progress in this area has focussed on the [Al(NON^{Dipp})]⁻ anion ([NON^{Dipp}]²⁻ = [O(SiMe₂NDipp)₂]²⁻; Dipp = 2,6-*i*Pr₂C₆H₃) (Figure 1), which we have successfully isolated as the full series of Li, Na, K, Rb, and Cs complexes.^[6] These low valent aluminium systems readily undergo oxidative addition of E–H bonds to furnish the corresponding Al(III) (hydrido)aluminates, AM[Al(NON^{Dipp})(E)(H)], with documented examples for E = H, C, N, O, P and Si.^[5b,6a,7] The resulting species offer soluble sources of the Al–H bond for useful onward reactivity.

With studies revealing the increasing diversity of roles and importance of Alkali Metals in Mediating (AMM) structure, reactivity, and catalytic profiles,^[6a,8] we stepped in to probe the reactivity of heavy-group-one aluminyl systems [AM{Al(NON^{Dipp})}]₂ [AM = Rb (I-Rb), Cs (I-Cs)] for the synthesis of their corresponding Al(III) hydrides. In an earlier study with the

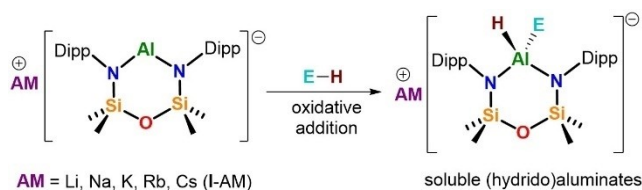


Figure 1. Oxidative addition of E–H bonds to furnish corresponding Al(III) (hydrido)aluminates, AM[Al(NON^{Dipp})(E)(H)] (Dipp = 2,6-*i*Pr₂C₆H₃).

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Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/chem.202301849>

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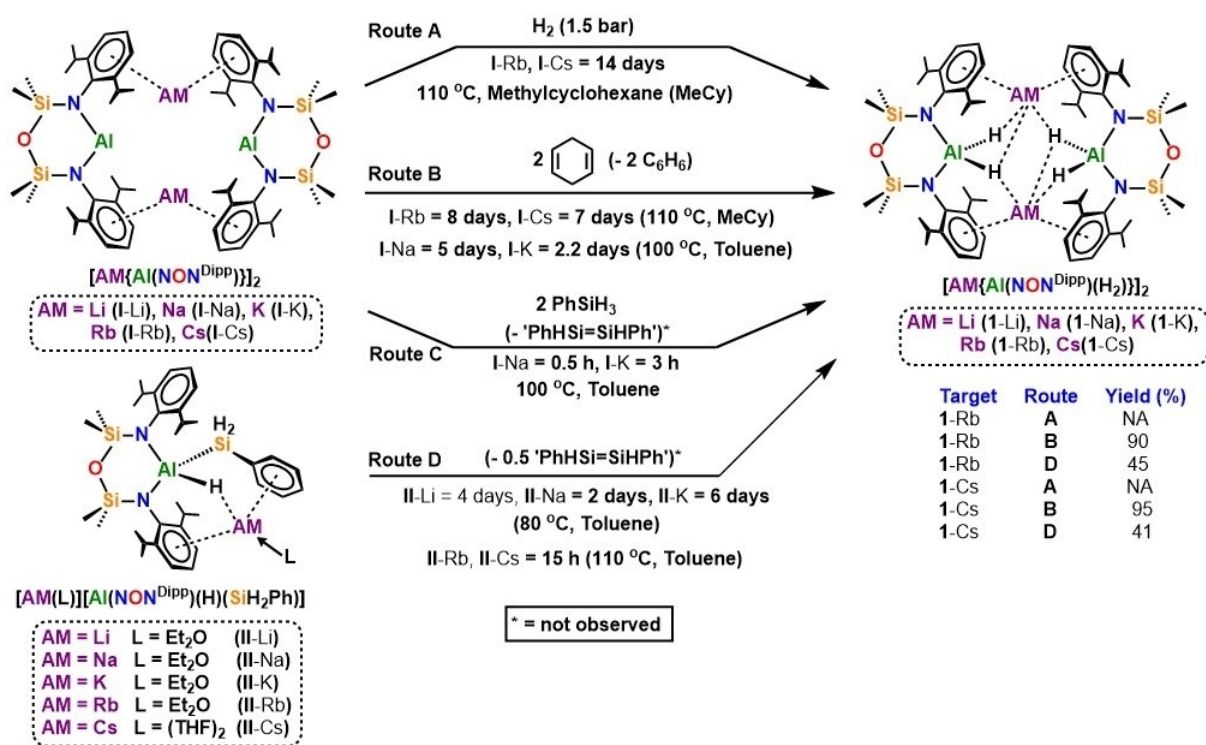
lighter alkali metal aluminyls $[AM\{Al(NON^{Dipp})\}_2]$ ($AM = Li$ (I-Li), Na (I-Na), K (I-K)),^[6b,c] the efficiency of dissociating the H–H bond at 1.5 bar pressure illustrated a diminishing trend on descending the group, requiring elevated temperatures (100 °C) and long reaction times ($Li = 3$ days, $Na = 14$ days, $K = 25$ days) to achieve complete conversion.^[6b] There are possibly several factors behind the harsher reaction conditions required on descending group one, but the stronger electronegativity at the top of the group is likely to be a factor in the higher reactivity of the lighter metal complexes with H_2 .^[8h,i] Hence, we postulated that alternative hydride sources containing breakable C–H and Si–H bonds such as in 1,4-cyclohexadiene (1,4-CHD) and phenylsilane ($PhSiH_3$) may provide other oxidative addition routes to the bimetallic hydrides. It should be mentioned that hydride synthesis using the above sources have the caveat that a M–R function (in which R = reactive group), is required such that oxidative addition of these sources is not expected to generate the dihydrides directly.^[2a]

1,4-CHD is an established viable alternative to H_2 in s-block chemistry as shown by the Harder and Mulvey groups in transfer hydrogenation catalysis of alkenes and imines using s-block metal amides in both mono- and bi-metallic scenarios.^[9] Reactions usually proceed via in-situ formation of homo- or bi-metallic hydride species that originate from putative M–Meisenheimer intermediates. In this regard $PhSiH_3$ has a longer established track record as a precursor to a range of main group metal hydrides, either through σ -bond metathesis or by adding a Si–H bond to an element in a lower oxidation state.^[2a] Recently we reported the outcomes of oxidative addition of

$PhSiH_3$ to the homologous series of alkali-metal aluminyls to give products of general formula $[AM(L)[Al(NON^{Dipp})(H)(SiH_2Ph)]]$ ($AM = Li - Cs$; $L = (Et_2O)$ for Li, Na, K, Rb ; $L = (THF)_2$ for Cs ; II-Li–Cs) and interrogated their unique structural characteristics.^[7a] In this contribution we describe the successful hydrogenation of the aluminyl series $[AM\{Al(NON^{Dipp})\}_2]$ for $AM = Na - Cs$ using three separate methods, and demonstrate the onwards reactivity of the Al–H bonds with CO_2 to generate compounds containing novel aluminium *bis*-formate anions. Note I-Li is poorly soluble in non-coordinating solvents, so it has been excluded from the hydrogenation studies.

Results and Discussion

As predicted, oxidative addition of H_2 to the heavier group 1 metal aluminyls $[AM\{Al(NON^{Dipp})\}_2]$ (I-Rb) and (I-Cs) required elevated temperature and long reaction times. However, full conversion to the target dihydridoaluminates $[AM\{Al(NON^{Dipp})(H)_2\}_2]$ (1-Rb and 1-Cs) was achieved after 14 days under 1.5 atmosphere of H_2 at reflux conditions in methylcyclohexane (110 °C) (Scheme 1). Broad signals appearing at 114 and 115 ppm respectively in the ^{27}Al NMR spectra of the crude samples recorded in C_6D_6 indicated formation of a new species in solution (see Supporting Information for NMR details), unlike the aluminyl starting reagents I-Rb and I-Cs where no ^{27}Al signals were detected.^[6a] These chemical shifts are similar to those recorded for $[AM\{Al(NON^{Dipp})(H)_2\}_2]$ (I-Na, $\delta_{Al} = 122$ ppm; I-K, $\delta_{Al} = 118$ ppm). Akin to those of early group 1 dihydridoalu-



Scheme 1. Synthesis of $[AM\{Al(NON^{Dipp})(H)_2\}_2]$ ($AM = Li$ (1-Li), Na (1-Na), K (1-K), Rb (1-Rb), Cs (1-Cs)) from low-valent $[AM\{Al(NON^{Dipp})\}_2]$ ($AM = Li$ (I-Li), Na (I-Na), K (I-K), Rb (I-Rb), Cs (I-Cs)) and $[AM(L)[Al(NON^{Dipp})(H)(SiH_2Ph)]]$ (II-Li), (II-Na), (II-K), (II-Rb), (II-Cs) using three distinct H_2 sources (H_2 , 1,4-CHD, $PhSiH_3$).

minates, the AlH_2 resonances in 1-Rb and 1-Cs were also silent in the ^1H NMR spectrum and a symmetrical environment for the NON^{Dipp} ligand backbone was evident in solution (C_6D_6), in line with the lighter relatives.^[6b] The diffusion coefficients D obtained from diffusion-ordered NMR spectroscopy (DOSY, C_6D_6 , 294 K) are identical for 1-Rb and 1-Cs ($5.58 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) which is lower than the monomeric Al(III) iodide precursor $\text{Al}(\text{NON}^{\text{Dipp}})\text{I}$ ($6.14 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) used for synthesizing the alkali-metal aluminyls. This provided further evidence towards retention of the contacted dimeric pair (CDP) conformation of the heavy alkali metal dihydridoaluminates in aromatic solvents. Infra-red stretches at 1732 and 1724 cm^{-1} for 1-Rb and 1-Cs respectively lie in the same range as those for the corresponding sodium and potassium dihydridoaluminates (1714 and 1645 cm^{-1} respectively) and are characteristic of Al–H bonds.^[2a,b]

Colourless crystals grown from concentrated methylcyclohexane and benzene solutions revealed the solid-state structures which confirmed formation of the target hydrides $[\text{AM}\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2\}]_2$ (AM = Rb, Cs) 1-Rb and 1-Cs respectively (Figure 2). Residual electron density peaks in the X-ray diffraction data of 1-Rb and 1-Cs at positions consistent with Al–H bonds were located in the difference map and incorporated into the refined model. Compounds 1-Rb and 1-Cs crystallize as dimers in the $I2/a$ and $Pca2_1$ space groups, respectively. A clear asymmetry is discernible in the AM–Al (AM = Rb, Cs) distances of 1-Rb and 1-Cs when compared to those in their parent low-oxidation state systems (I-Rb and I-Cs). Alkali metals in I-Rb and I-Cs are approximately equidistant to each Al centre [AM–Al distances range: I-Rb = $3.7068(9)$ Å– $3.7678(8)$ Å; I-Cs = $3.8833(10)$ Å– $3.9145(10)$ Å], while in contrast in the dihydridoaluminates (1-Rb and 1-Cs) the AM cation is located closer to one aluminium (Table S1, Supporting Information). The Rb and Cs cations are supported by two AM–H(Al) hydride bridges, a feature also prominent in the monomeric Li and dimeric Na/K-dihydridoaluminates.^[6b] This coupled with the increased twist

angle θ , defined by the angle between the Al–N–Si–O–Si–N planes of the ' $\text{Al}(\text{NON}^{\text{Dipp}})$ ' groups [1-Rb: $74.20(2)^\circ$; 1-Cs: $77.09(6)/77.20(7)^\circ$ (in two independent molecules) > I-Rb: $66.55(4)^\circ$; I-Cs: $66.31(5)^\circ$] confirm the presence of the hydride bridges with distorted tetrahedral Al centres. Despite the larger θ values, the Dipp groups are still able to stabilise the large cationic sphere of the heavy group 1 metals with their π -cloud such that the distances between the centroids (C_i) and the corresponding metal are similar to those of the sub-valent aluminyl species [average M– C_i distance for 1-Rb = 3.0622 Å, 1-Cs = $3.2367/3.2247$ Å, I-Rb = 3.1195 Å, I-Cs = 3.2567 Å].

Treating the H atom positions with due caution, 1-Rb and 1-Cs are best interpreted as dimers of contacted ion pairs $[\text{AM}]^+ [\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2]^-$. Though there are no examples of a hydride bridged Rb or Cs aluminate in the literature for comparison, the average values of Al–H bonds for 1-Rb and 1-Cs (Al– H_{avg} in Å for 1-Rb = 1.585 , 1-Cs = $1.653/1.548$) lean towards those reported for the lighter (Li, Na, K) dihydridoaluminates,^[6b] thereby lending weight to the above interpretation. Interestingly, the Rb–H(Al) distances in 1-Rb [Rb–H(Al) $_{\text{avg}}$ = 2.945 Å] are comparable to the Rb–H(C) distances found in donor-free rubidium aluminate $[\text{Rb}(\text{tBuDHP})(\text{TMP})\text{Al}(\text{tBu})_2]_\infty$ [tBuDHP = 2-*t*-butyldihydropyridyl (2-*t*Bu $\text{C}_5\text{H}_5\text{N}$), TMP = 2,2,6,6-tetramethylpiperidide] where the alkali metal interacts with the saturated TMP ring (NC_9H_{18}) via electrostatic and dispersive interactions [Rb–H(C) $_{\text{avg}}$ = 2.827 Å].^[4]

The time taken for direct hydrogenation of the heavy set of alkali metal aluminyls (Na, Rb, Cs = 14 days) are identical except for K which takes 25 days for completion of reaction, although concentration and solvent effects (change in the medium from an aromatic toluene solution for Li, Na and K to a saturated methylcyclohexane solvent for Rb and Cs) cannot be discounted.^[10] Notably, Martinez carried out hydrogenation of a Cs-aluminyl monomer which equilibrates between a ligand separated and contacted ion pair, $[\text{Cs}(\text{crypt})][\text{Al}(\text{DippBDI-H})]$ and $[\text{Cs}(\text{crypt})-\text{Al}(\text{DippBDI-H})]$ (crypt = 2,2,2-cryptand; BDI–H =

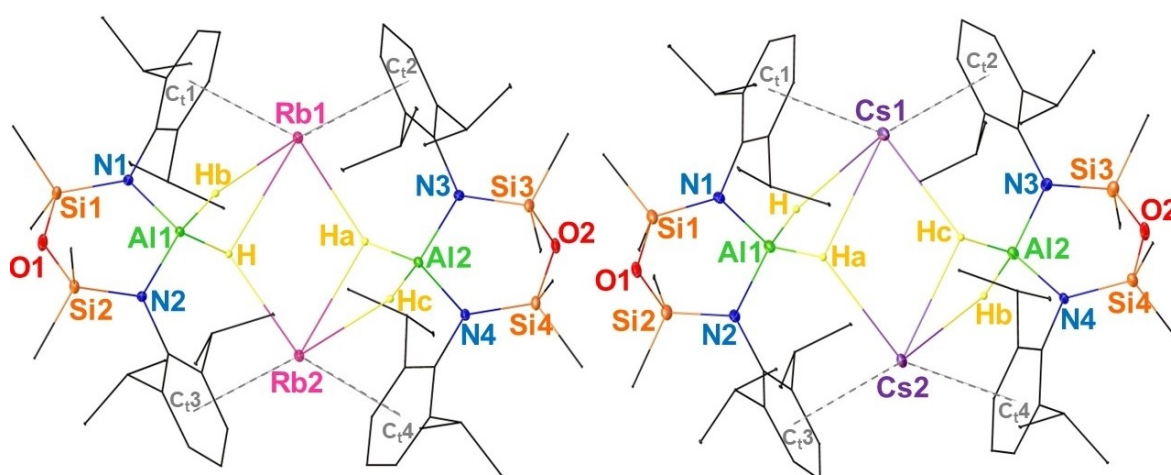
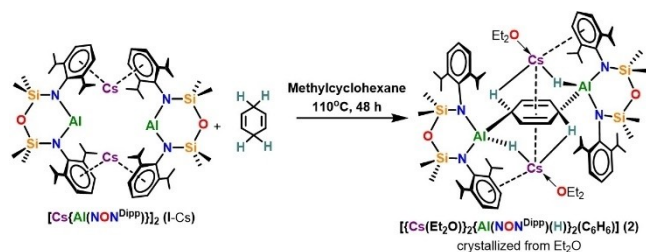


Figure 2. Molecular structures of $[\text{AM}\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2\}]_2$ (AM = Rb, Cs) 1-Rb and one independent molecule of 1-Cs respectively. Solvent of crystallization (benzene) has been removed from the depiction of 1-Cs for simplicity. Thermal ellipsoids of non-C/H atoms are displayed at 30% probability with those of C atoms reduced to 5% probability for clarity. H atoms other than in AlH_2 are omitted for a better view of the crystal structures. AM– π interactions are denoted by dashed lines to C_i where C_i depicts the aromatic ring centroid.

[DippNC(Me)=C(H)C(=CH₂)(NDipp)]²⁻, in 16 h at room temperature (60% yield) in fluorobenzene solvent. This low-valent precursor was made by a different method of deprotonation of β -diketiminate supported Al(I) complex with CsHMDS (HMDS = 1,1,1,3,3,3-hexamethyldisilazide, [N(SiMe₃)₂]⁻). Significantly, these results highlight the utility of the large alkali metal cation in providing increased stability and reactivity towards H₂ through Cs–Al/Cs– π (arene) interactions.^[8d]

Jones has exploited 1,4-CHD to hydrogenate low-valent Mg species [(^{Dep/Dipp}Nacnac)Mg]₂ (^{Dep/Dipp}Nacnac = [HC(CM₂Dep/Dipp)₂CH]); Dep = 2,6-Et₂C₆H₃) to their respective hydrides.^[11] Accordingly, we report herein that employing two equivalents of this alternative hydrogen source significantly improved reaction times, and full conversions to the aluminium dihydrides were achieved (i.e., I-Na = 5 days and I-K = 2.2 days with 2 equiv. at 100 °C in toluene; I-Rb = 8 days and I-Cs = 7 days with 2.1 equiv. at 110 °C in MeCy, Scheme 1). Reaction of I-K to 1-K can also be completed in 1.5 days by using a threefold excess of 1,4-CHD. Furthermore, addition of 2 equiv. TMEDA to



Scheme 2. Oxidative addition reaction of 1,4-cyclohexadiene with [Cs{Al(NON^{Dipp})}]₂ (I-Cs).

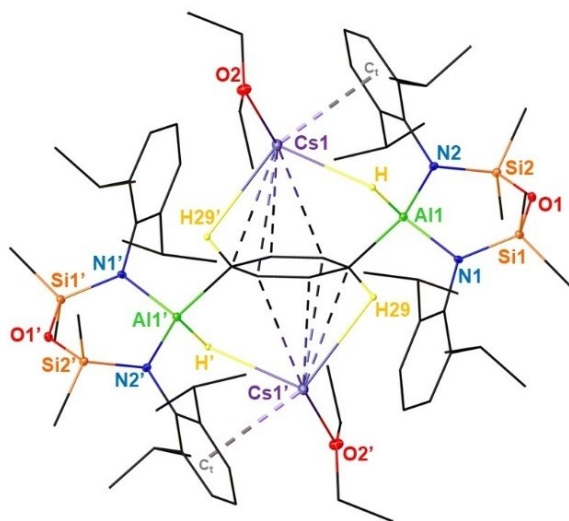


Figure 3. Molecular structure of [(Cs(Et₂O))₂{Al(NON^{Dipp})(H)}₂(C₆H₆)] (2). Thermal ellipsoids of non-C/H atoms are displayed at 30% probability with those of C atoms reduced to 5% probability for clarity. H atoms other than the ones having the following connectivity (Al–H and Al–C–H) have been omitted for clarity. Symmetry operation to generate equivalent atoms denoted: $\frac{1}{2}-x, \frac{3}{2}-y, \frac{3}{2}-z$. Selected bond distances (Å) and angles (°): Al1–N1 1.8868(16), Al1–N2 1.8849(15), N1–Si1 1.7176(15), Si1–O1 1.6393(14), O1–Si2 1.6438(14), Si2–N2 1.7231(15), Cs1–O2 2.923(2), Cs1–Al1 3.7958(5), Cs1–Al1' 5.2969(6); N2–Al1–N1 106.07(7), Al1–N1–Si1 121.09(8), N1–Si1–O1 107.08(7), Si1–O1–Si2 134.05(9), O1–Si1–N2 108.72(8).

I-K, which will form the monomeric ion pair (NON^{Dipp})Al–K(TMEDA)₂ in situ, and heating to 100 °C in the presence of just 1 equiv. 1,4-CHD effected full conversion after only 1 h.

Remarkably, reacting caesium aluminyl I-Cs with a stoichiometric amount of 1,4-CHD for 2 days (Scheme 2), yielded colourless X-ray quality crystals from diethyl ether, the structure of which revealed a hitherto unreported oxidative addition product of 1,4-CHD, [(Cs(Et₂O))₂{Al(NON^{Dipp})(H)}₂(C₆H₆)] (2, Figure 3). Compound 2 crystallizes in the I2/a space group as the centrosymmetric bimetallic dimer with two Cs atoms stabilising a dialuminated [1,4-{Al(NON^{Dipp})(H)}₂(C₆H₆)]²⁻ dianion that is present in an inverse sandwich complex. The pattern of short and long C–C bond lengths in Figure 4 prove the existence of a planar 1,4-cyclohexadienyl fragment with Cs preferentially shifted towards one of the unsaturated bonds. The coordination sphere of caesium is occupied by contacts with the [C₆H₆]²⁻ dianion, in addition to one aromatic Dipp group and one Et₂O molecule. The cation is located closer to the sandwiched cyclohexadienyl dianion with Cs–C distances ranging from 3.323(2) Å–3.665(2) Å (Figure 4) in comparison to the longer Cs–C^{Dipp} distances [3.4391(17) Å–3.650(3) Å]. According to our recent AM $\cdots\pi$ (arene) analysis,^[7a] the Cs cation is best described as η^4 -coordinated to [C₆H₆]²⁻, with ρ_1 (1.02)~ ρ_2 (1.04), and Δd_{4-3} (0.03 Å)~0. The Al–H bond length at 1.56(3) Å falls in a similar territory to those of 1-Rb and 1-Cs stated above.

A single septet signal for the *i*Pr-CH protons in the ¹H NMR spectrum of 2 in THF-*d*₈ suggests a symmetric arrangement in solution. However, the hydrogens for the sandwiched cyclohexadienyl dianion are silent in the NMR spectrum even at –35 °C, in contrast to the dialuminated species reported by Yamashita et al. (singlets at 1.52 ppm and 3.79 ppm).^[12] The presence of a broad ²⁷Al peak at 72.8 ppm supports the reasoning that the reduced species has undergone oxidative addition.

The structure of 2 resembles that of the neutral, homometallic dialuminated CHD derivative 1,4-{Al(NC₃N^{Dipp})(THF)}₂(C₆H₆) (NC₃N^{Dipp} = *N,N'*-bis(2,6-diisopropylphenyl)-1,3-propanediamide = [DippNC(CH₂)₃NDipp]²⁻). However, this compound is accessed via cooperative reduction of benzene by the bimetallic complex (NC₃N^{Dipp})Al–Sc(NⁱPr)₂(THF) in the presence of alkyl

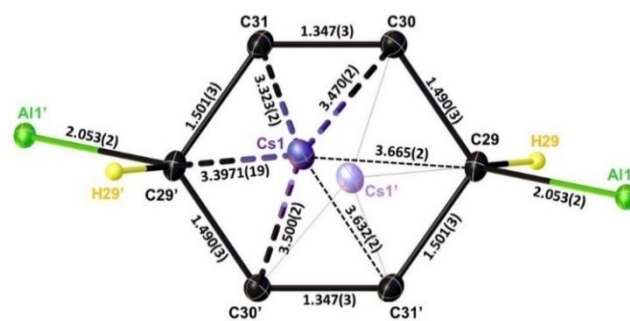
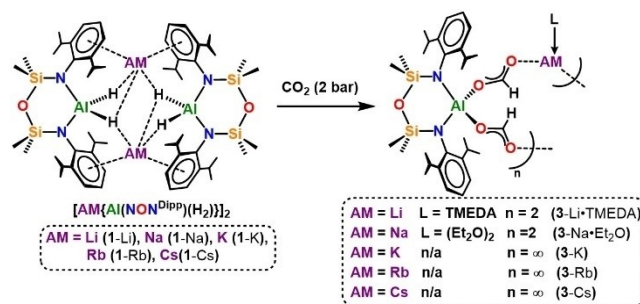


Figure 4. Selected bond lengths (Å) of the sandwiched cyclohexadienyl dialuminate section of 2 viewed from the top with Cs1 above the plane of paper (shaded in violet) and Cs1' below the plane (shaded in light violet). Thermal ellipsoids are displayed at 30% probability. H atoms on the sp² carbons have been omitted for clarity. Symmetry operation to generate equivalent atoms denoted: $\frac{1}{2}-x, \frac{3}{2}-y, \frac{3}{2}-z$.

bromide (Ph_2CHBr),^[12] which is the opposite redox pathway to that forming **2**. In another related study, Harder and co-workers isolated a doubly reduced benzene moiety in $[(\text{BDI})\text{Ca}^+(\text{C}_6\text{H}_6)\text{Al}^{\text{III}}(\text{BDI})]$ where $\text{BDI} = \text{CH}[\text{C}(\text{CH}_3)\text{N-Dipp}]_2$, $\text{Dipp} = 2,6$ -diisopropylphenyl, by combining a Lewis acid/base mixture $[(\text{BDI})\text{Ca}]^+\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ and $[(\text{BDI})\text{Al}^{\text{I}}]$ in a benzene/fluorobenzene concoction.^[13] The C–C bond distances of this $(\text{C}_6\text{H}_6)^{2-}$ fragment in the heterobimetallic compound are very much alike in comparison to **2**, although in this case the carbon atoms in para-position are bound to the same Al centres in **2**. While the above systems, and others by Braunschweig $[\{\text{Fc}^*(\text{NHC}^{\text{Me}_4})\text{Al}\}]_2\{2,5\text{-C}_6\text{H}_3\text{CH}_3\}$ [$\text{Fc}^* = 2,5$ -bis(3,5-di-tert-butylphenyl)-1-ferrocenyl; $\text{NHC}^{\text{Me}_4} = 1,3,4,5$ -tetramethylimidazol-2-ylidene]^[14] and another by Harder $[(\text{BDI-H})\text{AlH}]_2(\text{C}_6\text{H}_4)^{2-}[\text{Cs}^+(\text{THF})_2]$ ($\text{BDI} = \beta$ -diketiminato ligand $\text{HC}[\text{C}(\text{Me})\text{N-Dipp}]_2$)^[8c] infer formation of a Meisenheimer intermediate during the Birch-type process of benzene reduction, significantly compound **2** can be uniquely regarded as the first sighting of an intermediate in the *reverse* and more common oxidation process, where 1,4-CHD converts to benzene. Note that Collum found indirect evidence of a short-lived sodium-Meisenheimer intermediate in solution formed by deprotonation of 1,4-CHD with a Brønsted base $[\text{NaDA}]$, where $\text{DA} =$ diisopropylamide $= (\text{N}^i\text{Pr}_2)_2$ in THF, though this was performed at the extreme low temperature of -95°C .^[15]

Next, we discovered that access to the series of alkali metal dihydridoaluminates (1-AM) could be readily achieved by heating the (silyl)(hydrido) oxidative addition products $[\text{AM}(\text{L})][\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})(\text{SiH}_2\text{Ph})]$, (II-AM, Scheme 1). Monitoring the reactions by ^1H NMR spectroscopy showed the disappearance of the characteristic SiH_2 resonances and appearance of peaks identical to the corresponding 1-AM compounds. These data implied a thermal decomposition pathway, presumably accompanied by formation of dehydrocoupled silane derivative 'PhHSi=SiHPh' (or oligomers thereof), though this was not observed in the reaction. This reaction may therefore be considered as a type of silane coupling reaction, which is achieved typically through Wurtz-type coupling of halo-silanes promoted by alkali metals^[16] or by transition metal complexes.^[17] After removal of volatiles and crystallization of the crude sample in Et_2O , colourless crystals of identical unit cell parameters to that of 1-Rb and 1-Cs were obtained. For the sodium and potassium systems, we also showed this conversion may also be achieved in a one-pot process directly by reacting the I-Na and I-K aluminyls with PhSiH_3 at elevated temperatures, showing complete conversion to the dihydridoaluminates 1-Na and 1-K after 30 min and 3 h, respectively.

Studies have previously shown that Al–H bonds are active for the reduction of CO_2 to form 'Al(O₂CH)' formates.^[18] Therefore, to probe the reactivity of the newly installed Al–H bonds, the alkali-metal dihydridoaluminates were treated with CO_2 at approximately 2 bar pressure in C_6D_6 at 25°C , affording the bis-formates, $\text{AM}[\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2]$ (**3-AM**, $\text{AM} = \text{Li–Cs}$) (Scheme 3). Single crystals **3-Na** and **3-K** were obtained by slow evaporation of a Et_2O solution, affording the bis-ether adduct, $[\text{Na}(\text{Et}_2\text{O})_2][\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2]$ (**3-Na·Et₂O**) and the non-sol-



Scheme 3. Reactivity of 1-AM (Li–Cs) with CO_2 . ^{13}C enriched CO_2 was used for 1-Li, Na, K.

ated $\text{K}[\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2]$ (**3-K**), respectively. The corresponding lithium etherate crystals rapidly desolvated and hence crystals were isolated from a TMEDA/ Et_2O solution as TMEDA adduct, $[\text{Li}(\text{TMEDA})][\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2]$ (**3-Li·TMEDA**). Crystals of the Rb and Cs analogues were grown directly from the benzene reaction solvent. ^1H NMR spectra of the isolated crystals **3-Rb** and **3-Cs** recorded in THF-d_8 , show a low field singlet for the formyl proton at δ_{H} 7.64 (**3-Rb**) and 7.63 (**3-Cs**) indicative of CO_2 reduction. Further evidence for formate formation was obtained using ^{13}C -labelled carbon dioxide with 1-Li, 1-Na and 1-K, resulting in doublet resonances at δ_{H} 7.75 (**3-Li·TMEDA**: $^1J_{\text{CH}} = 212$ Hz) and 7.40 (**3-Na·Et₂O**: $^1J_{\text{CH}} = 215$ Hz) in C_6D_6 and δ_{H} 7.81 (**3-K**: $^1J_{\text{CH}} = 210$ Hz) in 5:1 C_6D_6 : THF-d_8 . Carbon atoms of the $[\text{OC}(\text{H})\text{O}]^-$ anion can be assigned in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at δ_{C} 166.5 (**3-Li·TMEDA**), 168.2 (**3-Na·Et₂O**), 165.1 (**3-K**), 164.9 (**3-Rb**) and 162.6 (**3-Cs**). In all cases a singlet resonance for SiMe_2 peaks indicates a symmetric arrangement of ligand at Al.

Single crystal XRD analysis of **3-Li·TMEDA** and **3-Na·Et₂O** revealed dimers, with **3-Li·TMEDA** forming an unusual 16-membered macrocycle (nodal descriptor [016]),^[19] (Figure 5; bottom) and **3-Na·Et₂O** best described as the $[016.0^{1,8,9,16}]$ tricycle, consisting of two 8-membered $\text{AlC}_2\text{O}_4\text{Na}$ metallacycles fused by a central Na_2O_2 -ring (Figures 5 and 6). In the absence of coordinating solvents, **3-(K/Rb/Cs)** adopted a polymeric arrangement of alkali-metal (K, Rb, Cs) aluminium formates (Figures 5 and 6 for **3-Cs**; see Figure S61 in Supporting Information for crystal structures of **3-K** and **3-Rb**). The geometries of **3-K**, **3-Rb** and **3-Cs** look to be a hybrid of **3-Li** and **3-Na**, where a repeating order of 16-membered macrocycle is fused together by AM_2O_2 -rings on both sides forming an infinite chain, $[032.0^{1,16,17,32}]_{\infty}$ revealing structural diversity at the Li–Na and Na–K junctions, though this may be influenced by solvation non-solvation distinctions. While both **3-Rb/Cs** contain benzene in their crystal lattice, only the large Cs cation in **3-Cs** shows interactions with it in an η^1 -bonding mode (Figure 6).

In all cases the formate ligands adopt a bridging $\text{Al}(\mu\text{-O}_2\text{CH})\text{AM}$ mode between Al and one or more AMs. With **3-Li·TMEDA** each formate joins the Al to different Li atoms via the oxygen atom, whereas in **3-Na·Et₂O** both formates link to the same AM cation, with one oxygen atom engaging in bonding to the symmetry generated cation within the AM_2O_2 core. In the extended **3-(K/Rb/Cs)** structures, one of the formates appears to

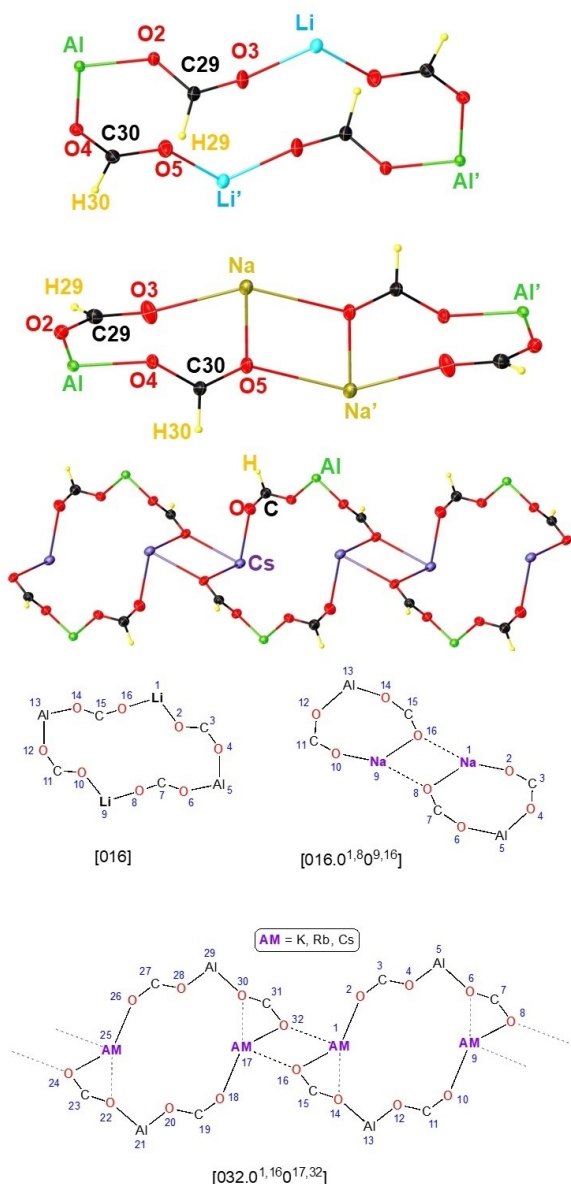


Figure 5. (Top) Structural diversity in a series of alkali-metal aluminium formates (**3**), depicting formation of unusual metallacyclic cores: **3**-Li·TMEDA = [016], **3**-Na·Et₂O = [016.0^{1,8,9,16}], **3**-(K/Rb/Cs) = [032.0^{1,16,17,32}]; (Bottom) Nodal descriptor for metallacycles.

be bidentate and the other is monodentate with respect to the AM (e.g. Cs1...O3 = 2.912(3) Å while Cs1A...O4 = 3.206(3) Å and Cs1A...O5 = 3.167(3) Å). The Al centre has a distorted tetrahedral geometry consistent with O–Al–O angles that reflect the different orientations of the formate ligands in the extended cyclic structures ([016], 107.69(11)°; [016.0^{1,8,9,16}], 103.71(5)°; [032.0^{1,16,17,32}], 97.82(5)°, 98.34(6)° and 98.97(12)°). In the absence of coordinating solvent at the AM in **3**-(K/Rb/Cs), one Dipp group of the NON ligand stabilises the alkali metal with its π -cloud [K–C_t = 3.0116(7) Å; Rb–C_t = 3.1135(3) Å, Cs–C_t = 3.2594(7) Å; C_t = centroid of Dipp group], while the other aromatic handle turns vestigial and now provides steric bulk. Evidence for the presence of formate species can be confirmed

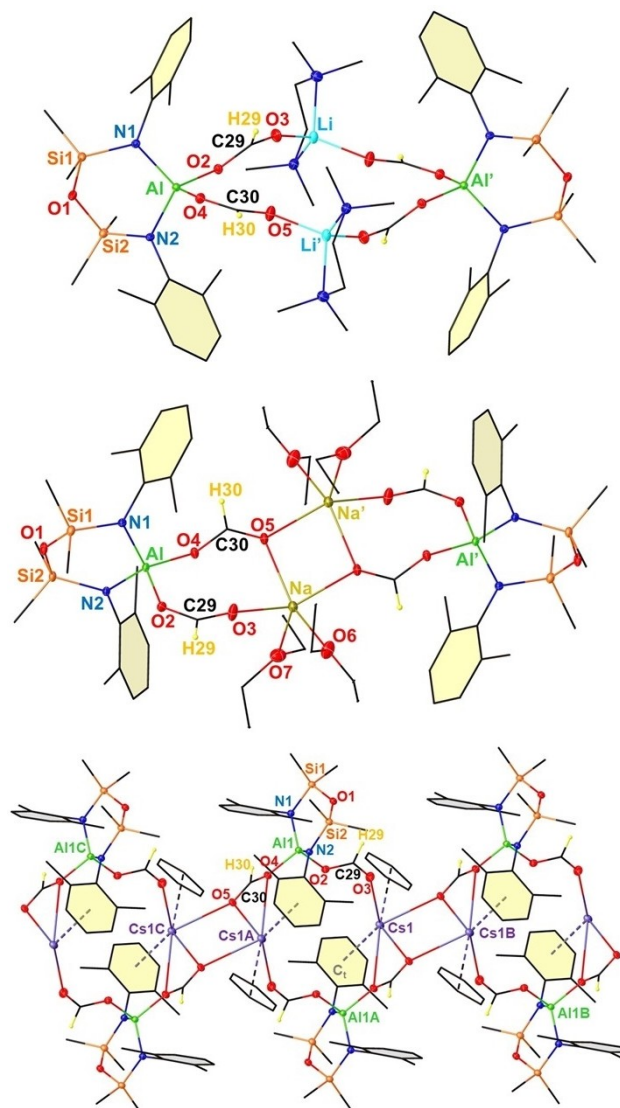


Figure 6. Solid-state structures of $\{[\text{Li}(\text{TMEDA})]\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2\}_2\}$ (**3**-Li·TMEDA), $\{[\text{Na}(\text{Et}_2\text{O})_2]\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2\}_2\}$ (**3**-Na·Et₂O), and section of polymeric $\{[\text{Cs}(\eta^1\text{-C}_6\text{H}_6)_2]\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2\}_2\}_\infty$ (**3**-Cs) are shown for comparison. Solid-state structures of **3**-K and **3**-Rb are included in the Supporting Information since they have similar bonding motif to that of **3**-Cs. Thermal ellipsoids of non-C/H atoms are displayed at 30% probability with those of C atoms reduced to 5% probability for better view. H atoms other than the formate ones have been omitted for clarity. iPr methyl groups have not been displayed for clarity. Symmetry operation to generate equivalent atoms for (**3**-Li·TMEDA): 2–x, 1–y, –z; (**3**-Na·Et₂O): 1–x, –y, –z; (**3**-Cs): A = 1–x, 1–y, 1–z; B = 2–x, 1–y, 1–z; C = –1+x, +y, +z.

from the different O–C bond lengths (one short and one long) in the crystal structures.

Conclusions

In the quest for completing the homologous series of group 1 dihydroaluminates $[\text{AM}\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2\}_2]$ (AM = Li–Cs; **1**), three distinct hydrogen sources were investigated in H₂, 1,4-CHD, and PhSiH₃. The studies culminated in the isolation of novel Rb and Cs dihydroaluminates from their parent Al(I)

compounds $[\text{AM}\{\text{Al}(\text{NON}^{\text{Dipp}})\}_2]$ ($\text{AM} = \text{Rb}, \text{Cs}; \text{I-Rb/Cs}$). In their crystalline form, they resemble their lighter Na and K siblings by stabilising a dimeric arrangement with aromatic Dipp groups in the ligand backbone providing stability to the large alkali metal cations.

Comparing the reactivity of group 1 aluminyls with alternative reservoirs of H_2 uncovered that PhSiH_3 provides the most effective path to reach destination hydrides $[\text{AM}\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2\}_2]$ ($\text{AM} = \text{Na-Cs}; \text{1-Na-Cs}$) with 1,4-CHD being the second best. The trail taken by 1,4-CHD to achieve the target hydrides led to the first sighting of an extraordinary intermediate $[\{\text{Cs}(\text{Et}_2\text{O})\}_2\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})\}_2(\text{C}_6\text{H}_6)]$ (**2**), resulting from an oxidative addition reaction. Its crystal structure shows two Cs atoms stabilising a dialuminated $[\text{1,4-}\{\text{Al}(\text{NON}^{\text{Dipp}})\}_2\text{C}_6\text{H}_6]^{2-}$ dianion, in a centrosymmetric inverse sandwich. The isolation of this compound highlights the flexible reactivity of 1,4-CHD, since in transfer hydrogenation it is generally assumed to be deprotonated by a reactive M-R reagent, to form an unstable Meisenheimer intermediate, $[\text{C}_6\text{H}_7]^-$ before releasing a hydride ion, whereas here it is doubly deprotonated in generating a trapped $[\text{C}_6\text{H}_6]^{2-}$ dianion. Cooperativity of soft Cs cation and a bulky Al anion with NON^{Dipp} scaffold helps in stabilising this $[\text{C}_6\text{H}_6]^{2-}$ unit effectively.

The alkali-metal dihydroaluminates (**1**) also succeeded in reducing CO_2 to form the respective formates of general formula $\text{AM}[\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2]$ (**3-AM**, $\text{AM} = \text{Li-Cs}$). While the structures of Li and Na formates were isolated as dimers of solvated TMEDA and Et_2O , respectively (**3-Li-TMEDA**, **3-Na-Et₂O**), the heavy alkali metal formates could be isolated as donor free polymers (**3-K/Rb/Cs**) with **3-Cs** featuring η^1 -coordination of benzene to the large Cs ion. Interestingly, the formates show unique structural features, with **3-Li-TMEDA** adopting an unusual 16-membered macrocycle $[\text{Al}_2\text{C}_4\text{O}_8\text{Li}_2]$ ([016]), **3-Na-Et₂O** forming two fused 8-membered metallacycles $[\text{AlC}_2\text{O}_4\text{Na}]$ ([016.0^{1.80}0^{9.16}]), and **3-K/Rb/Cs** revealing a hybrid of the two with fused 16-membered macrocycles in a repeating arrangement ([032.0^{1.16}0^{17.32}]_∞).

Collectively, the results of this study exemplify the profound influence that alkali metal mediation can exert on anionic aluminium chemistry, with the distinctions found in reactions and their structural outcomes showing that it is important to consider each alkali metal separately in such studies instead of viewing them as mere generic counter cations.

Experimental Section

Deposition Numbers 2260051 (for 1-Rb), 2260052 (for 1-Cs), 2260053 (for **2**), 2260054 (for 3-Li-TMEDA), 2260055 (for 3-Na-Et₂O), 2260056 (for 3-K), 2260057 (for 3-Rb), and 2260058 (for 3-Cs) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

General experimental procedures: All manipulations were performed under dry argon or nitrogen using standard Schlenk-line techniques, or in a conventional argon-filled glovebox. Starting materials and research chemicals were obtained from commercial

suppliers where appropriate and used without further purification. $[\text{Al}(\text{NON}^{\text{Dipp}})(\text{I})]$,^[6c] $[\text{Li}\{\text{Al}(\text{NON}^{\text{Dipp}})\}_2]$ (I-Li),^[6b] $[\text{Na}\{\text{Al}(\text{NON}^{\text{Dipp}})\}_2]$ (I-Na),^[6b] $[\text{K}\{\text{Al}(\text{NON}^{\text{Dipp}})\}_2]$ (I-K),^[6c] RbC_8 ^[20] and CsC_8 ^[20] were synthesized according to literature procedures. The literature known methodology for the synthesis of $[\text{Rb}\{\text{Al}(\text{NON}^{\text{Dipp}})\}_2]$ (I-Rb),^[6a] $[\text{Cs}\{\text{Al}(\text{NON}^{\text{Dipp}})\}_2]$ (I-Cs),^[6a] was followed but instead of aromatic solvents the reaction was conducted in methylcyclohexane. $[\text{Rb}(\text{Et}_2\text{O})][\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})(\text{SiH}_2\text{Ph})]$ (II-Rb),^[7a] and $[\text{Cs}(\text{THF})_2][\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})(\text{SiH}_2\text{Ph})]$ (II-Cs)^[7a] were synthesized using literature procedures.

For compounds prepared at the University of Strathclyde:

Hexane, THF and diethyl ether were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. Pentane, benzene, and toluene were degassed with nitrogen, dried over activated aluminium oxide (Innovative Technology, Pure Solv 400-4-MD, Solvent Purification System), and then stored under inert atmosphere over activated 4 Å molecular sieves. Benzene-*d*₆, toluene-*d*₈ and THF-*d*₆ were degassed by freeze-pump-thaw methods and stored over activated 4 Å molecular sieves. NMR spectra were recorded on a Bruker AV3 or AV 400 MHz spectrometer operating at 400.13 MHz for ¹H, 100.62 MHz for ¹³C. All ¹³C spectra were proton decoupled. ¹H and ¹³C{¹H} chemical shifts are expressed in parts per million (δ , ppm) and referenced to residual solvent peaks. Coupling constants (*J*) are given in Hertz (Hz). For describing signal multiplicities common abbreviations have been used: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet) and br (broad). Elemental analyses (for compounds 1-Rb,Cs) were performed by the Elemental Analysis Service at London Metropolitan University. Infrared spectra of starting materials and selected products were obtained as Nujol mulls on NaCl plates. Mulls were prepared in the glove box using anhydrous Nujol, which was dried and stored over activated 4 Å molecular sieves under argon, and then transferred to the spectrometer in a desiccator. Spectra were recorded on a Nicolet 360 FTIR spectrometer spanning 4000–400 cm⁻¹. The melting points of selected products and starting materials were determined as follows. A small sample of crystalline/powdered material was loaded into a melting point tube in the glove box. This tube was then sealed with Plasticine[®] before removal from the glove box. The melting point was then determined in the usual manner using a Buchi Melting Point B-545 apparatus. Crystallographic data for complexes 1-Rb, 1-Cs, **2**, 3-Rb, and 3-Cs were measured with a Rigaku Synergy-i instrument with monochromated Cu-K α (λ 1.54184 Å) radiation. The measured data was processed with the CrysAlisPro^[21] software package. The structures were solved with the ShelXT^[22] structure solution program and refined to convergence against *F*² and using all reflections with the ShelXL-2018^[23] refinement package as implemented within OLEX^[24] or WINGX.^[25] Structure **2** contained disordered solvent believed to be Et₂O. This could not be modelled satisfactorily and so was dealt with using the SQUEEZE routine of PLATON.^[26] A total of 154 electron equivalents were removed from 920 Å³ of unit cell volume. This equates to approximately 2 molecules of Et₂O per unit cell. The benzene solvent of 1-Rb and the Et₂O ligand of **2** were modelled as disordered. Appropriate restraints and constraints were applied to the displacement behaviour and to the geometry of these disordered groups to ensure that these approximated normal behaviour.

For compounds prepared at Victoria University of Wellington: Hexane, toluene, diethyl ether (Et₂O), and tetrahydrofuran (THF) were obtained from a PureSolv MD 5 system and stored over activated 5 Å molecular sieves for 24 h prior to use. NMR spectra were recorded using a Jeol JNM-ECZ500S 500 MHz (11.747 Tesla) spectrometer equipped with a ROYAL digital auto tune probe S, operating at 500.1 (¹H), 194.4 (⁷Li), 130.3 (²⁷Al), 125.8 (¹³C) and 99.3 (²⁹Si) MHz. Spectra were recorded at 294 K (unless stated otherwise) and proton and carbon chemical shifts were referenced internally

to residual solvent resonances. Coupling constants are quoted in Hz. Elemental analyses (for compounds 3-Li, Na, K) were performed by the Elemental Analysis Service at London Metropolitan University. Fourier transform infrared (FTIR) spectra were recorded on solid samples using a Bruker Tensor 27 FTIR spectrometer. Crystallographic data for complexes 3-Li·TMEDA, 3-Na·Et₂O and 3-K were collected on an Agilent SuperNova diffractometer fitted with an EOS S2 detector. Crystals were covered in inert oil and mounted. Data were collected at the temperature indicated (120 K or 150 K)^[27] using focused micro-source Cu K α radiation at 1.54184 Å. Intensities were corrected for Lorentz and polarisation effects and for absorption using multi-scan methods.^[28] Space groups were determined from systematic absences and checked for higher symmetry. All structures were solved using direct methods with SHELXS,^[23] refined on F² using all data by full matrix least-squares procedures with SHELXL-97,^[21,29] within the WinGX13 program. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions or manually assigned from residual electron density where appropriate, unless otherwise stated. The functions minimized were $\Sigma w(F_{\text{obs}}^2 - F_{\text{calc}}^2)$, with $w = [\sigma^2(F_{\text{obs}}^2) + aP^2 + bP]^{-1}$, where $P = [\max(F_{\text{obs}})^2 + 2F_{\text{calc}}^2]/3$. The isotropic displacement parameters are 1.2 or 1.5 times the isotropic equivalent of their carrier atoms.

Complex syntheses

Preparation of [Na{Al(NON^{Dipp})(H)₂}]₂ (1-Na)

Via 1,4-CHD route

A solution of [Na{Al(NON^{Dipp})}]₂ (I-Na)^[6b] (53.3 mg, 0.05 mmol) in d₈-toluene (0.6 mL) was added to 1,4-Cyclohexadiene (8.0 mg, 0.10 mmol). The reaction mixture was transferred to a J Youngs NMR tube and heated to 100 °C. Reaction progress was monitored via NMR spectroscopy. Complete conversion was achieved after 5 days at 100 °C.

Via PhSiH₃ route

A solution of [Na{Al(NON^{Dipp})}]₂ (I-Na)^[6b] (53.3 mg, 0.05 mmol) in d₈-toluene (0.6 mL) was added to phenylsilane (10.8 mg, 0.10 mmol). The reaction mixture was transferred to a J Youngs NMR tube and heated to 100 °C. Reaction progress was monitored via NMR spectroscopy. A bright red colour was observed upon heating. Complete conversion was achieved after 30 min at 100 °C.

¹H NMR (500 MHz, C₇D₈) δ 6.86 (d, $J = 7.6$ Hz, 4H, C₆H₃), 6.74 (t, $J = 7.6$ Hz, 2H, C₆H₃), 3.89 (sept, $J = 6.8$ Hz, 4H, CHMe₂), 1.23 (d, $J = 6.8$ Hz, 12H, CHMe₂), 1.16 (d, $J = 6.8$ Hz, 12H, CHMe₂) 0.33 (br. s, 12H, SiMe₂).

Preparation of [K{Al(NON^{Dipp})(H)₂}]₂ (1-K)

Via 1,4-CHD route

A solution of [K{Al(NON^{Dipp})}]₂ (I-K)^[6c] (54.9 mg, 0.05 mmol) in d₈-toluene (0.6 mL) was added to 1,4-Cyclohexadiene (8.0 mg, 0.10 mmol). The reaction mixture was transferred to a J Youngs NMR tube and heated to 100 °C. Reaction progress was monitored via NMR spectroscopy. Complete conversion was achieved after 52 h at 100 °C to afford a colourless solution.

Via PhSiH₃ route

A solution of [K{Al(NON^{Dipp})}]₂ (I-K)^[6c] (54.9 mg, 0.05 mmol) in d₈-toluene (0.6 mL) was added to phenylsilane (10.8 mg, 0.10 mmol). The reaction mixture was transferred to a J Youngs NMR tube and heated to 100 °C. Reaction progress was monitored via NMR spectroscopy. Complete conversion was achieved after 3 h at 100 °C.

¹H NMR (500 MHz, C₇D₈) δ 6.86 (d, $J = 7.5$ Hz, 4H, C₆H₃), 6.75 (t, $J = 7.5$ Hz, 2H, C₆H₃), 4.00 (sept, $J = 6.8$ Hz, 4H, CHMe₂), 1.20 (d, $J = 6.8$ Hz, 12H, CHMe₂), 1.15 (d, $J = 6.8$ Hz, 12H, CHMe₂), 0.33 (s, 12H, SiMe₂).

Preparation of [Rb{Al(NON^{Dipp})(H)₂}]₂ (1-Rb)

Via 1,4-CHD route

In a J. Young ampoule [Rb{Al(NON^{Dipp})}]₂ (I-Rb)^[6a] (502 mg, 0.843 mmol) was dissolved in methylcyclohexane (10 mL) to give a yellow solution. 1,4-Cyclohexadiene (158 μ L, 1.77 mmol, 2.1 equiv.) was added and the sealed reaction vessel was heated to 110 °C for 8 days. Evaporation of all volatiles of the resulting colourless solution under reduced pressure and subsequent drying at 60 °C for 4 h gave a white solid, sufficiently pure according to NMR in 90% (452 mg, 0.757 mmol) yield. Crystals suitable for single X-ray diffraction analysis can be grown from slow evaporation of a benzene solution at room temperature or by crystallisation from a diethyl ether solution at –20 °C.

Via H₂ route

In a J. Young ampoule [Rb{Al(NON^{Dipp})}]₂ (I-Rb)^[6a] (98 mg, 0.164 mmol) was dissolved in methylcyclohexane (6 mL) to give a yellow solution. The solution was degassed by freeze-pump-thawing (3 \times) and subsequently pressurized with 1.5 bar of elemental hydrogen H₂ (99.99%). The sealed reaction vessel was heated to 110 °C for 14 days. Evaporation of all volatiles of the resulting colourless solution and subsequent drying at 60 °C for 4 h gave a white solid, which was identified as the target compound by NMR techniques. Crystals suitable for single X-ray diffraction analysis, which match the cell parameters of the structural data reported can be grown from slow evaporation of this methylcyclohexane solution. The yield was not determined.

Via PhSiH₃ route

A J. Young NMR tube was charged with [Rb{(NON^{Dipp})Al(H)SiH₂Ph}(Et₂O)](II-Rb)^[7a] (60 mg, 0.078 mmol) and toluene was added to give a colourless suspension. After the reaction mixture was heated in the sealed NMR tube to reflux overnight, a colourless solution was obtained. Evaporation of all volatiles of the reaction mixture and subsequent drying at 60 °C for 2 h gave a white solid, which was identified as the target compound by NMR techniques. Crystals suitable for single X-ray diffraction analysis, which match the cell parameters of the structural data reported can be grown from recrystallization in Et₂O. Yield: 21 mg, 45%.

A satisfactory elemental analysis for the bulk material of [Rb{Al(NON^{Dipp})(H)₂}]₂ (1-Rb) was not obtained, which may be attributed to decomposition during shipping and/or sample preparation. Best values are given, nevertheless. Elemental analysis: Calculated values for C₅₆H₉₆Al₂N₄O₂Rb₂Si₄ (1194.265 g/mol): C 56.30, H 8.10, N 4.69; Found: C 57.72, H 8.07, N 4.00. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 6.88 (d, $J = 7.6$ Hz, 8H, Ar-CH), 6.79–6.70 (m, 4H, Ar-CH), 4.10 (sept, $J = 6.7$ Hz, 8H, CH(CH₃)₂), 1.25 (d, $J = 6.9$ Hz, 24H, CH(CH₃)₂), 1.18 (d,

$J=6.8$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$, 0.41 (s, 24H, $\text{Si}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 25 °C): $\delta=149.4$ (C_{arom}), 147.6 (C_{arom}), 124.1 (C_{arom}), 122.4 ($\text{C}_{\text{arom}}\text{H}$), 27.4 ($\text{C}_{\text{aliph}}\text{H}$), 25.5 ($\text{C}_{\text{aliph}}\text{H}_3$), 25.4 ($\text{C}_{\text{aliph}}\text{H}_3$), 2.6 ($\text{Si}(\text{CH}_3)_2$); ^{27}Al NMR (104 MHz, C_6D_6 , 25 °C): $\delta=114.6$ (A/H); ^{29}Si NMR (80 MHz, C_6D_6 , 25 °C): $\delta=-11.0$ ($\text{Si}(\text{CH}_3)_2$); m.p.: 262 °C–266 °C (dec.); IR (Nujol, cm^{-1}): $1\lambda=1732$ (w), 1668 (w), 1588 (w), 1312 (w), 1248 (w), 1190 (w), 1122 (w), 1106 (w), 1008 (w), 938 (w), 800 (w).

Preparation of $[\text{Cs}\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2\}]_2$ (1-Cs)

Via 1,4-CHD route

In a J. Young ampoule $[\text{Cs}\{\text{Al}(\text{NON}^{\text{Dipp}})\}]_2$ (I-Cs)^[6a] (511 mg, 0.795 mmol) was dissolved in methylcyclohexane (10 mL) to give a yellow solution. 1,4-Cyclohexadiene (149 μL , 1.67 mmol, 2.1 equiv.) was added and the sealed reaction vessel was heated to 110 °C for 7 days. Evaporation of all volatiles of the resulting colourless solution under reduced pressure and subsequent drying at 60 °C for 4 h gave a white solid, sufficiently pure according to NMR in 95% (488 mg, 0.757 mmol) yield. Crystals suitable for single X-ray diffraction analysis can be grown from slow evaporation of a benzene solution at room temperature or by crystallisation from a diethyl ether solution at –20 °C.

Via H_2 route

In a J. Young NMR tube $[\text{Cs}\{\text{Al}(\text{NON}^{\text{Dipp}})\}]_2$ (I-Cs)^[6a] (103 mg, 0.160 mmol) was dissolved in methylcyclohexane (6 mL) to give a yellow solution. The solution was degassed by freeze-pump-thawing (3 \times) and subsequently pressurized with 1.5 bar of elemental hydrogen H_2 (99.99%). The sealed reaction vessel was heated to 110 °C for 14 days. Evaporation of all volatiles of the resulting colourless solution and subsequent drying at 60 °C for 4 h gave a white solid, which was identified as the target compound by NMR techniques. Crystals suitable for single X-ray diffraction analysis, which match the cell parameters of the structural data reported can be grown from slow evaporation of this methylcyclohexane solution. The yield was not determined.

Via PhSiH_3 route

A J. Young NMR tube was charged with $[\text{Cs}(\text{THF})_2][\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})(\text{SiH}_2\text{Ph})]_2$ (II-Cs)^[7a] (60 mg, 0.067 mmol) and toluene was added. After the reaction mixture was heated in the sealed NMR tube to reflux overnight, a colourless solution was obtained. Evaporation of all volatiles of the reaction mixture and subsequent drying at 60 °C for 2 h gave a white solid, which was identified as the target compound by NMR techniques. Crystals suitable for single X-ray diffraction analysis, which match the cell parameters of the structural data reported can be grown from recrystallization in Et_2O . Yield: 18 mg, 41 %.

A satisfactory elemental analysis for the bulk material of $[\text{Cs}\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2\}]_2$ (1-Cs) was not obtained, which may be attributed to decomposition during shipping and/or sample preparation. Best values are given, nevertheless. Elemental analysis: Calculated values for $\text{C}_{56}\text{H}_{96}\text{Al}_2\text{Cs}_2\text{N}_4\text{O}_2\text{Si}_4$ (1288.44 g/mol): C 52.16, H 7.50, N 4.34; Found: C 54.20, H 7.47, N 3.74; ^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta=6.87$ (d, $J=7.5$ Hz, 8H, Ar-CH), 6.72 (t, $J=7.5$ Hz, 4H, Ar-CH), 4.17 (sept, $J=6.8$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $J=6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, $J=6.8$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 0.41 (s, 24H, $\text{Si}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 25 °C): $\delta=149.4$ (C_{arom}), 148.6 (C_{arom}), 124.4 (C_{arom}), 122.3 ($\text{C}_{\text{arom}}\text{H}$), 27.4 ($\text{C}_{\text{aliph}}\text{H}$), 25.5 ($\text{C}_{\text{aliph}}\text{H}_3$), 25.3 ($\text{C}_{\text{aliph}}\text{H}_3$), 2.5 ($\text{Si}(\text{CH}_3)_2$); ^{27}Al NMR (104 MHz, C_6D_6 , 25 °C): $\delta=115.3$ (A/H); ^{29}Si NMR (80 MHz, C_6D_6 , 25 °C): $\delta=-11.0$ ($\text{Si}(\text{CH}_3)_2$); m.p.: 239 °C–243 °C (dec.);

IR (Nujol, cm^{-1}): $1\lambda=1724$ (w), 1648 (w), 1584 (w), 1314 (w), 1248 (w), 1186 (w), 1106 (w), 1042 (w), 1013 (w), 938 (w), 800 (w).

Preparation of $[\text{Cs}(\text{Et}_2\text{O})_2][\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2](\text{C}_6\text{H}_6)$ (2)

In a J. Young NMR tube $[\text{Cs}\{\text{Al}(\text{NON}^{\text{Dipp}})\}]_2$ (I-Cs)^[6a] (133 mg, 0.1 mmol, calculated as a dimer) was dissolved in methylcyclohexane (500 μL) to give a yellow solution. 1,4-Cyclohexadiene (9 μL , 0.1 mmol, 1 equiv.) was added and the sealed NMR tube was heated to 110 °C for 2 days. Evaporation of all volatiles of the resulting solution under reduced pressure and subsequent drying under vacuum gave a white solid. Crystals suitable for single X-ray diffraction analysis can be grown from a concentrated diethyl ether solution at –20 °C. Yield = 68 mg, 44 %.

^1H NMR (400 MHz, C_6D_6 , 25 °C): $\delta=6.94$ (d, $J=7.4$ Hz, 8H, Ar-CH), 6.78 (t, $J=7.4$ Hz, 4H, Ar-CH), 4.10 (sept, $J=7.1$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 1.24 (d, $J=6.7$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, $J=6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 0.96 (s, 24H, $\text{Si}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 25 °C): $\delta=146.6$ (C_{arom}), 121.9 (C_{arom}), 119.8 ($\text{C}_{\text{arom}}\text{H}$), 26.0 ($\text{C}_{\text{aliph}}\text{H}$), 22.4 ($\text{C}_{\text{aliph}}\text{H}_3$), 0.90 ($\text{Si}(\text{CH}_3)_2$); ^{27}Al NMR (104 MHz, C_6D_6 , 25 °C): $\delta=72.7$; ^{29}Si NMR (80 MHz, C_6D_6 , 25 °C): δ = not detected.

Preparation of $[\text{Li}(\text{TMEDA})][\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2]$ (3-Li·TMEDA)

A solution of $[\text{Li}(\text{OEt})_2][\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2]$ ^[6b] (30 mg, 0.04 mmol) in benzene- D_6 (~0.6 mL) was transferred to a J Youngs NMR tube and degassed (freeze-pump-thaw, 3 times). $^{13}\text{CO}_2$ (~1 atm) was condensed into the NMR tube and sealed. The resulting mixture was transferred to a scintillation vial and the solvent removed in vacuo. Crystallisation was achieved via slow evaporation from a saturated diethyl ether/TMEDA (1:50) mixture stored at room temperature. Yield 24 mg, 74 %.

We were unable to obtain meaningful elemental analysis on this compound, likely due to facile decomposition during sample preparation/handling/analysis. ^1H NMR (500 MHz, C_6D_6): δ 7.75 (d, $J=212.0$, 2H, O^{13}CHO), 7.13 (d, $J=7.6$, 4H, C_6H_3), 7.03 (t, $J=7.6$, 2H, C_6H_3), 4.23 (sept, $J=6.8$, 4H, CHMe_2), 2.05 (s, 28H*, TMEDA), 1.88 (s, 8H*, TMEDA), 1.41 (d, $J=6.8$, 12H, CHMe_2), 1.35 (d, $J=6.8$, 12H, CHMe_2), 0.53 (s, 12H, SiMe_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): δ 166.5 (O^{13}CHO), 157.6, 147.1, 123.9, 123.1 (C_6H_3), 56.9, 46.7 (TMEDA), 27.5 (CHMe_2), 26.0, 25.9 (CHMe_2), 2.8 (SiMe_2); $^7\text{Li}\{^1\text{H}\}$ NMR (194 MHz, C_6D_6): δ 4.4.

* integration of the ^1H resonances for TMEDA indicate ~2 equivalents present in the sample consistent with residual TMEDA from the crystallization solvent mixture.

Preparation of $[\text{Na}(\text{Et}_2\text{O})][\text{Al}(\text{NON}^{\text{Dipp}})(\text{O}_2\text{CH})_2]$ (3-Na·Et₂O)

3-Na·Et₂O was prepared according to the procedure described for 3-Li·TMEDA using 80 mg (0.15 mmol) of $[\text{Na}\{\text{Al}(\text{NON}^{\text{Dipp}})(\text{H})_2\}]$. The product was crystallised by slow evaporation from a diethyl ether solution stored at room temperature. Yield 60 mg, 58 %.

Anal. Calcd. for $\text{C}_{30}\text{H}_{48}\text{AlN}_2\text{NaO}_5\text{Si}_2$ (622.86 g mol⁻¹): C, 57.85; H, 7.77; N, 4.50 %. Found: C, 59.48; H, 7.63; N, 4.50 %.

* calculated for the desolvated form with loss of Et_2O

^1H NMR (500 MHz, C_6D_6): δ 7.40 (d, $J=214.8$, 2H, O^{13}CHO), 7.04 (d, $J=7.6$, 4H, C_6H_3), 6.93 (t, $J=7.6$, 2H, C_6H_3), 4.04 (sept, $J=6.8$, 4H, CHMe_2), 3.25 (q, $J=7.0$, 4H*, OCH_2), 1.30 (d, $J=6.8$, 12H, CHMe_2), 1.19 (d, $J=6.8$, 12H, CHMe_2), 1.10 (t, $J=7.0$, 6H*, CH_2CH_3), 0.47 (s, 12H, SiMe_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): δ 174.9 (C_6H_3), 168.2 (O^{13}CHO), 167.1, 166.7, 166.1, 159.4, 157.9, 147.5, 143.6, 124.0, 123.3

(C₆H₃), 65.9 (OCH₂), 27.5 (CHMe₂), 26.4, 25.2 (CHMe₂), 15.5 (CH₂CH₃), 2.8 (SiMe₂).

* integration of the ¹H resonances for Et₂O indicate ~1 equivalent present in the sample consistent with partial loss of coordinated Et₂O during sample preparation.

Preparation of K[Al(NON^{Dipp})(O₂CH)₂] (3-K)

3-K was prepared according to the procedure described for 3-Li·TMEDA using 56 mg (0.10 mmol) of K[Al(NON^{Dipp})(H)₂]. The product was crystallised by slow evaporation from a diethyl ether solution stored at room temperature. Yield 55 mg, 86%.

Anal. Calc'd for C₃₀H₄₈AlKN₂O₅Si₂* (638.97 g mol⁻¹): C, 56.39; H, 7.57; N, 4.38%. Found C, 55.61; H, 7.60; N, 3.90%. (* calculated for loss of Et₂O solvent). ¹H NMR (500 MHz, 5:1 C₆D₆:D₈-THF): δ 7.81 (d, *J* = 210.0, 2H, O¹³CHO), 7.01 (d, *J* = 7.6, 4H, C₆H₃), 6.89 (t, *J* = 7.6, 2H, C₆H₃), 4.08 (sept, *J* = 6.7, 4H, CHMe₂), 1.25 (t, *J* = 6.7, 24H, CHMe₂), 0.30 (s, 12H, SiMe₂); ¹³C{¹H} NMR (126 MHz, 5:1 C₆D₆:D₈-THF): δ 165.1 (O¹³CHO), 147.4, 144.1, 123.7, 122.7 (C₆H₃), 27.5 (CHMe₂), 26.0, 25.6 (CHMe₂), 2.8 (SiMe₂).

Preparation of Rb[Al(NON^{Dipp})(O₂CH)₂] (3-Rb)

[Rb{Al(NON^{Dipp})(H)₂}]₂ (1-Rb) (80 mg, 0.13 mmol) was dissolved in C₆D₆ (400 μL) in a J. Young NMR tube and pressurised with carbon dioxide (2 atm) at 25 °C. Colourless crystals emerged after standing the solution in the NMR tube for 10 min. Yield = 68 mg, 73%.

¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.64 (s, 3H, O₂CH), 6.97 (d, *J* = 7.5 Hz, 8H, Ar-CH), 6.86 (t, *J* = 7.4 Hz, 4H, Ar-CH), 3.96 (sept, *J* = 6.8 Hz, 8H, CH(CH₃)₂), 1.18 (t, *J* = 6.1 Hz, 48H, CH(CH₃)₂), 0.13 (s, 24H, Si(CH₃)₂); ¹³C{¹H} NMR (101 MHz, C₆D₆, 25 °C): δ = 164.9 (C_{formate}), 147.9 (C_{arom}), 144.9 (C_{arom}), 124.1 (C_{arom}), 123.0 (C_{arom}H), 27.9 (C_{aliph}H), 26.4 (C_{aliph}H₃), 25.9 (C_{aliph}H₃), 2.9 (Si(CH₃)₂); ²⁷Al NMR (104 MHz, C₆D₆, 25 °C): not detected; ²⁹Si NMR (80 MHz, C₆D₆, 25 °C): δ = -8.61 (Si(CH₃)₂).

Preparation of [Cs(η¹-C₆H₅)]₂[Al(NON^{Dipp})(O₂CH)] (3-Cs)

[Cs{Al(NON^{Dipp})(H)₂}]₂ (1-Cs) (80 mg, 0.12 mmol) was dissolved in C₆D₆ (400 μL) in a J. Young NMR tube and pressurised with carbon dioxide (2 atm) at 25 °C. Colourless crystals emerged after standing the solution in the NMR tube for 10 min. Yield = 80 mg, 79%.

¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.63 (s, 3H, O₂CH), 6.98 (d, *J* = 7.4 Hz, 8H, Ar-CH), 6.87 (t, *J* = 7.2 Hz, 4H, Ar-CH), 3.96 (sept, *J* = 6.7 Hz, 8H, CH(CH₃)₂), 1.17 (q, *J* = 6.8 Hz, 48H, CH(CH₃)₂), 0.13 (s, 24H, Si(CH₃)₂); ¹³C{¹H} NMR (101 MHz, C₆D₆, 25 °C): δ = 162.6 (C_{formate}), 145.9 (C_{arom}), 143.1 (C_{arom}), 122.2 (C_{arom}), 121.1 (C_{arom}H), 25.9 (C_{aliph}H), 24.4 (C_{aliph}H₃), 23.8 (C_{aliph}H₃), 0.9 (Si(CH₃)₂); ²⁷Al NMR (104 MHz, C₆D₆, 25 °C): δ = not detected; ²⁹Si NMR (80 MHz, C₆D₆, 25 °C): δ = -8.69 (Si(CH₃)₂).

Supporting Information

Detailed characterisation of compounds can be found in the Supporting Information.

Acknowledgements

This work was generously sponsored by the Leverhulme Trust (award no: RPG-2019-264), the Royal Society Te Apārangi (Grant Number: MFP-VUW2020) and the MacDiarmid Institute for Advanced Materials and Nanotechnology.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in PUREportal.strath.ac.uk at <https://doi.org/10.15129/ebd1459f-9d20-4806-b384-a2f116d5b61e>, reference number 161853396.

Keywords: alkali-metals · CO₂ reduction · dihydridoaluminates · Meisenheimer intermediate · oxidative addition

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Manuscript received: June 22, 2023

Accepted manuscript online: July 10, 2023

Version of record online: September 4, 2023