RESEARCH ARTICLE

Three Oxidative Addition Routes of Group One Aluminyls to Dihydridoaluminates and Reactivity with CO_2

Sumanta Banerjee,*[a] Gerd M. Ballmann,[a] Matthew J. Evans,[b] Andrea O'Reilly,[b] Alan R. Kennedy,[a] J. Robin Fulton,[b] Martyn P. Coles,*[b] Robert E. Mulvey,*[a]

[a] Dr. S. Banerjee, Dr. G. M. Ballmann, Dr. A. R. Kennedy, Prof. R. E. Mulvey
     *West*CHEM, Department of Pure and Applied Chemistry
     University of Strathclyde
     Glasgow, G1 1XL, U.K
     E-mail: sumanta.banerjee@strath.ac.uk; r.e.mulvey@strath.ac.uk
[b] Dr. M. J. Evans, A. O'Reilly, Dr. J. R. Fulton, Prof. M. P. Coles
     School of Chemical and Physical Sciences
     Victoria University of Wellington
     P.O. Box 600, Wellington New Zealand
     E-mail: martyn.coles@vuw.ac.nz

     Supporting information for this article is given via a link at the end of the document.

Abstract: 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(SiMe$_2$NDipp)$_2$]$^{2-}$; Dipp = 2,6-iPr$_2$C$_6$H$_3$) starting from the alkali metal aluminyls, AM[Al(NON^{Dipp})]. Direct H$_2$ 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)(SiH$_2$Ph)]. Probing the reaction of Cs[Al(NON^{Dipp})] with 1,4-CHD provided access to a novel inverse sandwich complex, [{Cs(Et$_2$O)}$_2${Al(NON^{Dipp})(H)}$_2$(C$_6$H$_6$)], containing the 1,4-dialuminated [C$_6$H$_6$]$^{2-}$ 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 CO_2 under mild conditions to form the bis-formate AM[Al(NON^{Dipp})(O$_2$CH)$_2$] compounds, which exhibit a diverse series of eyecatching bimetallacyclic 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*BuC$_5$H$_5$N)AM (AM = Li – Cs) and AliBu$_2$(TMP) (TMP = 2,2,6,6-tetramethylpiperide) 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(SiMe$_2$NDipp)$_2$]$^{2-}$; Dipp = 2,6-iPr$_2$C$_6$H$_3$) (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.
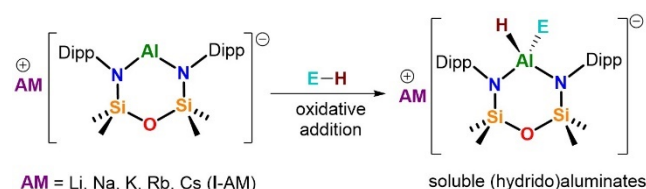
Figure 1. Oxidative addition of E–H bonds to furnish corresponding Al(III) (hydrido)aluminates, AM[Al(NON^{Dipp})(E)(H)] (Dipp = 2,6-iPr$_2$C$_6$H$_3$).

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

RESEARCH ARTICLE
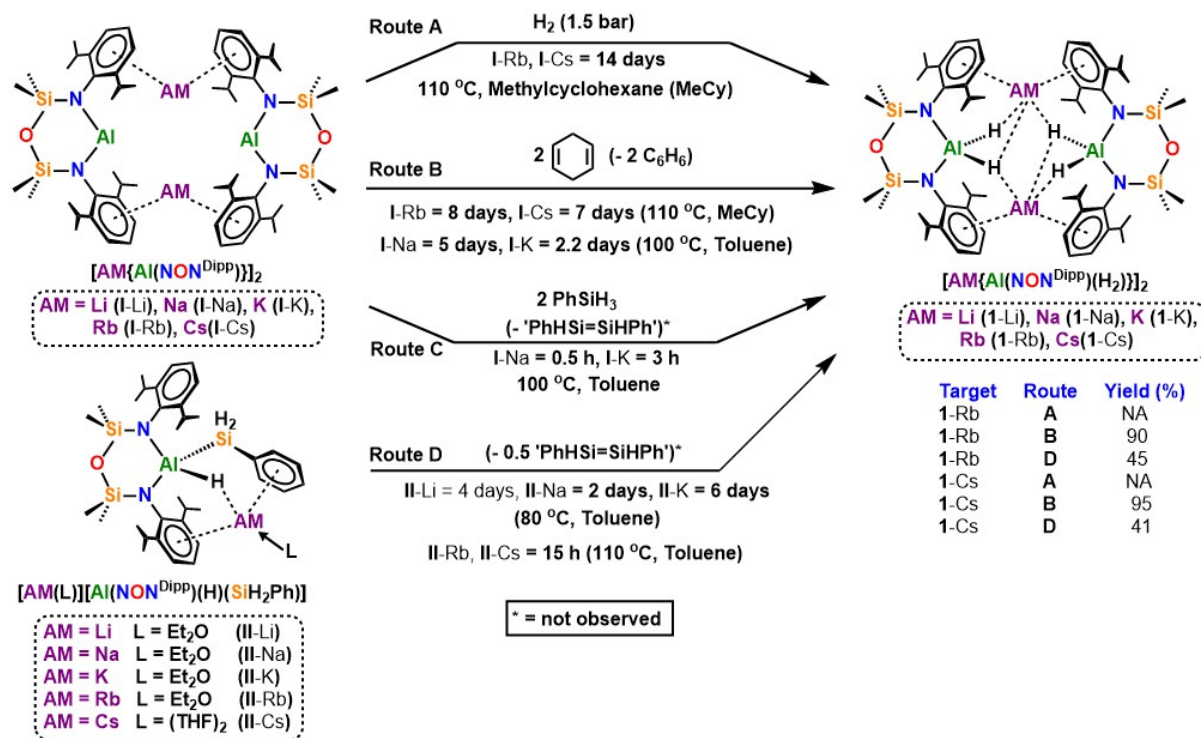
Scheme 1. Synthesis of [AM{Al(NON^{Dipp})(H)$_2$}]$_2$ {AM = Li (**1-Li**), Na (**1-Na**), K (**1-K**), Rb (**1-Rb**), Cs (**1-Cs**)} from low-valent [AM{Al(NON^{Dipp})}]$_2$ [AM = Li (**I-Li**), Na (**I-Na**), K (**I-K**), Rb (**I-Rb**), Cs (**I-Cs**)] and [AM(L)][Al(NON^{Dipp})(H)(SiH$_2$Ph)] (**II-Li**), (**II-Na**), (**II-K**), (**II-Rb**), (**II-Cs**) using three distinct H$_2$ sources (H$_2$, 1,4-CHD, PhSiH$_3$).

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 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 oxidation 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$_2$Ph)] [AM = Li – Cs; L = (Et$_2$O) 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$_6$D$_6$ indicated formation of a new species in solution (see ESI 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**, δ$_{Al}$ = 122 ppm; **I-K**, δ$_{Al}$ = 118 ppm). Akin to those of early group 1 dihydridoaluminates, the AlH_2 resonances in **1**-Rb and **1**-Cs were

RESEARCH ARTICLE
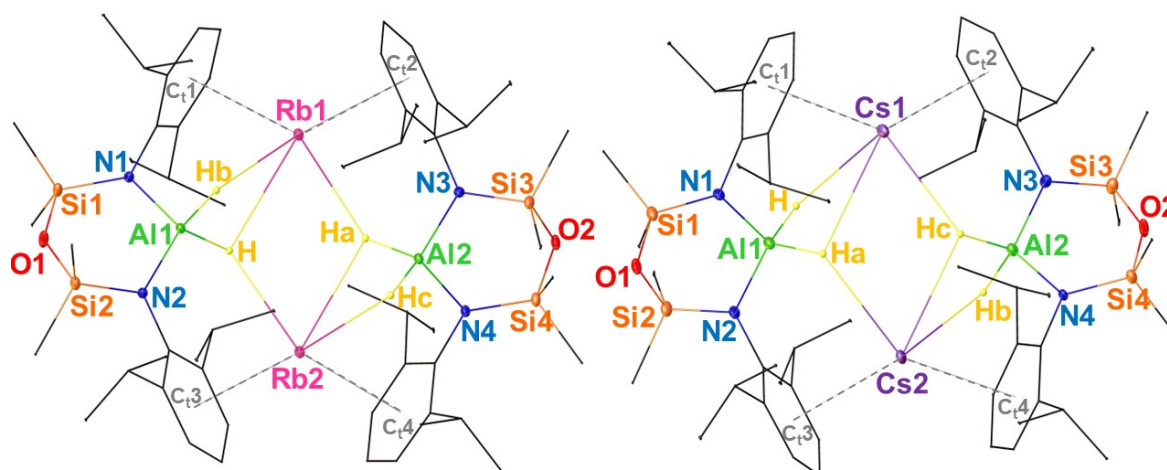
Figure 2. Molecular structures of [AM{Al(NON^{Dipp})(H)$_2$}]$_2$ (AM = Rb, Cs) **1**-Rb and one independent molecule of **1**-Cs respectively. Solvent of crystallization (benzene) has been removed from the depiction of **1**-Cs for simplicity. Thermal ellipsoids of non-C/H atoms are displayed at 30% 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$_t$ where C$_t$ depicts the aromatic ring centroid.

also silent in the ^{1}H NMR spectrum and a symmetrical environment for the NON^{Dipp} ligand backbone was evident in solution (C$_6$D$_6$), in line with the lighter relatives.[6b] The diffusion coefficients D obtained from diffusion-ordered NMR spectroscopy (DOSY, C$_6$D$_6$, 294 K) are identical for **1**-Rb and **1**-Cs (5.58 X 10^{-10} m^{2}s^{-1}) which is lower than the monomeric Al(III) iodide precursor Al(NON^{Dipp})I (6.14 X 10^{-10} m^{2}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 [AM{Al(NON^{Dipp})(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, ESI). 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 'Al(NON^{Dipp})' groups [**1**-Rb: 74.20(2)°; **1**-Cs: 77.09(6)/77.20(7)° (in two independent molecules) > **I**-Rb: 66.55(4)°; **I**-Cs: 66.31(5)°] 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$_t$) and the corresponding metal are similar to those of the sub-valent aluminyl species [average M---C$_t$ 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 [AM]$^+$[Al(NON^{Dipp})(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)$_{avg}$ = 2.945 Å] are comparable to the Rb---H(C) distances found in donor-free rubidium aluminate [Rb(tBuDHP)(TMP)Al(iBu)$_2$]$_\infty$ [tBuDHP =2-t-butyldihydropyridyl (2-tBuC$_5$H$_5$N), TMP = 2,2,6,6-tetramethylpiperidide] where the alkali metal interacts with the saturated TMP ring (NC$_9$H$_{18}$) via electrostatic and dispersive interactions [Rb---H(C)$_{avg}$ = 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

3

RESEARCH ARTICLE

separated and contacted ion pair, [Cs(crypt)][Al(^{Dipp}BDI-H)] and [Cs(crypt)---Al(^{Dipp}BDI-H) (crypt = 2,2,2-cryptand; BDI-H = [DippNC(Me)=C(H)C(=CH$_2$)(NDipp)]$^{2-}$), in 16 hours 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(SiMe$_3$)$_2$]$^-$). Significantly, these results highlight the utility of the large alkali metal cation in providing increased stability and reactivity towards H$_2$ 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(CMeNDep/Dipp)$_2$CH)]$^-$; Dep = 2,6-Et$_2$C$_6$H$_3$) 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 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 hour.

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(Et$_2$O)}$_2${Al(NON^{Dipp})(H)}$_2$(C$_6$H$_6$)] (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)}$_2$(C$_6$H$_6$)]$^{2-}$ 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 [C$_6$H$_6$]$^{2-}$ dianion, in addition to one aromatic Dipp group and one Et$_2$O 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···π(arene) analysis,[7a] the Cs cation is best described as η^4-coordinated to [C$_6$H$_6$]$^{2-}$, 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 iPr-CH protons in the ^{1}H 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 ^{27}Al peak at 72.8 ppm supports the reasoning that the reduced species has undergone oxidative addition.
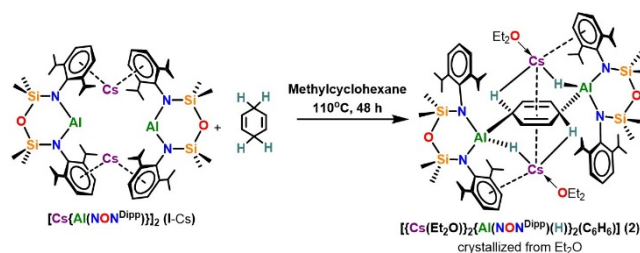
**Scheme 2.** Oxidative addition reaction of 1,4-cyclohexadiene with [Cs{Al(NON^{Dipp})}]$_2$ (I-Cs).

The structure of 2 resembles that of the neutral, homometallic dialuminated CHD derivative 1,4-{Al(NC$_3$N^{Dipp})(THF)}$_2$(C$_6$H$_6$) (NC$_3$N^{Dipp} = N,N'-bis(2,6-diisopropylphenyl)-1,3-propanediamide = [DippN(CH$_2$)$_3$NDipp]$^{2-}$). However, this compound is accessed via cooperative reduction of benzene by the bimetallic complex (NC$_3$N^{Dipp})Al—Sc(N^{i}Pr$_2$)$_2$(THF) in the presence of alkyl bromide (Ph$_2$CHBr),[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 [(BDI)Ca$^+$(C$_6$H$_6$)Al^{III}(BDI) where BDI=CH[C(CH$_3$)N-Dipp]$_2$, Dipp=2,6-diisopropylphenyl].by combining a Lewis acid/base mixture [{(BDI)Ca}$^+${B(C$_6$F$_5$)$_4$}$^-$] and {(BDI)Al^i}] in a benzene/fluorobenzene concoction.[13] The C—C bond distances of this (C$_6$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 atom giving it a puckered geometry, unlike the planar ring bridged by two Al centres in 2. While the above systems, and others by Braunschweig [{Fc*(NHC^{Me4})Al}$_2${2,5-C$_6$H$_5$CH$_3$}] [Fc* = 2,5-bis(3,5-di-tert-butylphenyl)-1-ferrocenyl; NHC^{Me4} = 1,3,4,5-tetramethylimidazol-2-ylidene][14] and another by Harder {[(BDI-H)AlH]$_2$(C$_6$H$_4$)}$^{2-}$[Cs$^+$·(THF)$_2$]$_2$ (BDI = β-diketiminate ligand HC[C(Me)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 [NaDA, where DA = diisopropylamide = (N^{i}Pr$_2$)] in THF, though this was performed at the extreme low temperature of −95 °C.[15]

RESEARCH ARTICLE
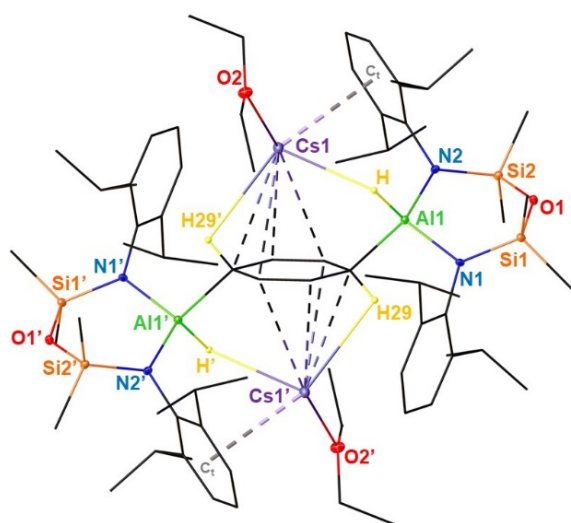
Figure 3. Molecular structure of $[\{Cs(Et_2O)\}_2\{Al(NON^{Dipp})(H)\}_2(C_6H_6)]$ (**2**). Thermal ellipsoids of non-C/H atoms are displayed at 30% probability with those of C atoms reduced to 5% probability for clarity. H atoms other than the ones having the following connectivity (Al—H and Al—C—H) have been omitted for clarity. Symmetry operation to generate equivalent atoms denoted: 1/2-x, 3/2-y, 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).
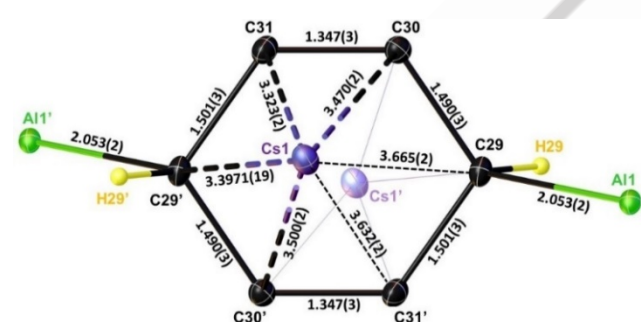

Figure 4. Selected bond lengths (Å) of the sandwiched cyclohexadienyl dialuminate section of **2** viewed from the top with Cs1 above the plane of paper (shaded in violet) and Cs1' below the plane (shaded in light violet). Thermal ellipsoids are displayed at 30% probability. H atoms on the sp² carbons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

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 $[AM(L)][Al(NON^{Dipp})(H)(SiH_2Ph)]$, (**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 mins and 3 h, respectively.

Studies have previously shown that Al–H bonds are active for the reduction of CO_2 to form 'Al(O_2CH)' 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, $AM[Al(NON^{Dipp})(O_2CH)_2]$ (**3**-AM, AM = 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, $[Na(Et_2O)_2][Al(NON^{Dipp})(O_2CH)_2]$ (**3**-Na·Et_2O) and the non-solvated $K[Al(NON^{Dipp})(O_2CH)_2]$ (**3**-K), respectively. The corresponding lithium etherate crystals rapidly desolvated and hence crystals were isolated from a TMEDA/Et_2O solution as TMEDA adduct, $[Li(TMEDA)][Al(NON^{Dipp})(O_2CH)_2]$ (**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: $^1J_{CH}$ = 212 Hz) and 7.40 (**3**-Na·Et_2O: $^1J_{CH}$ = 215 Hz) in C_6D_6 and δ_H 7.81 (**3**-K: $^1J_{CH}$ = 210 Hz) in 5:1 C_6D_6:THF-D_8. Carbon atoms of the $[OC(H)O]^-$ anion can be assigned in the $^{13}C\{^1H\}$ NMR spectra at δ_C 166.5 (**3**-Li·TMEDA), 168.2 (**3**-Na·Et_2O), 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.
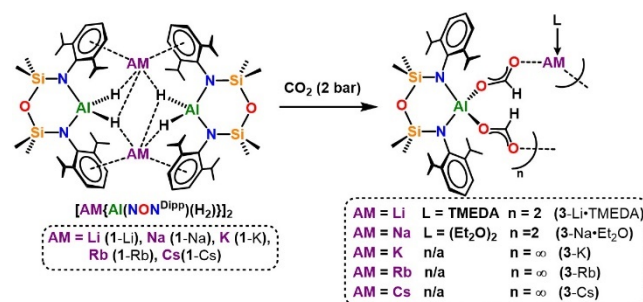
**Scheme 3.** Reactivity of **1**-AM (Li – Cs) with CO_2. ^{13}C enriched CO_2 was used for **1**-Li,Na,K.

Single crystal XRD analysis of **3**-Li·TMEDA and **3**-Na·Et_2O revealed dimers, with **3**-Li·TMEDA forming an unusual 16-membered macrocycle (nodal descriptor [016]),[19] (Figure 5; bottom) and **3**-Na·Et_2O best described as the $[016.0^{1,8}0^{9,16}]$ tricycle, consisting of two 8-membered AlC_2O_4Na metallacycles

5
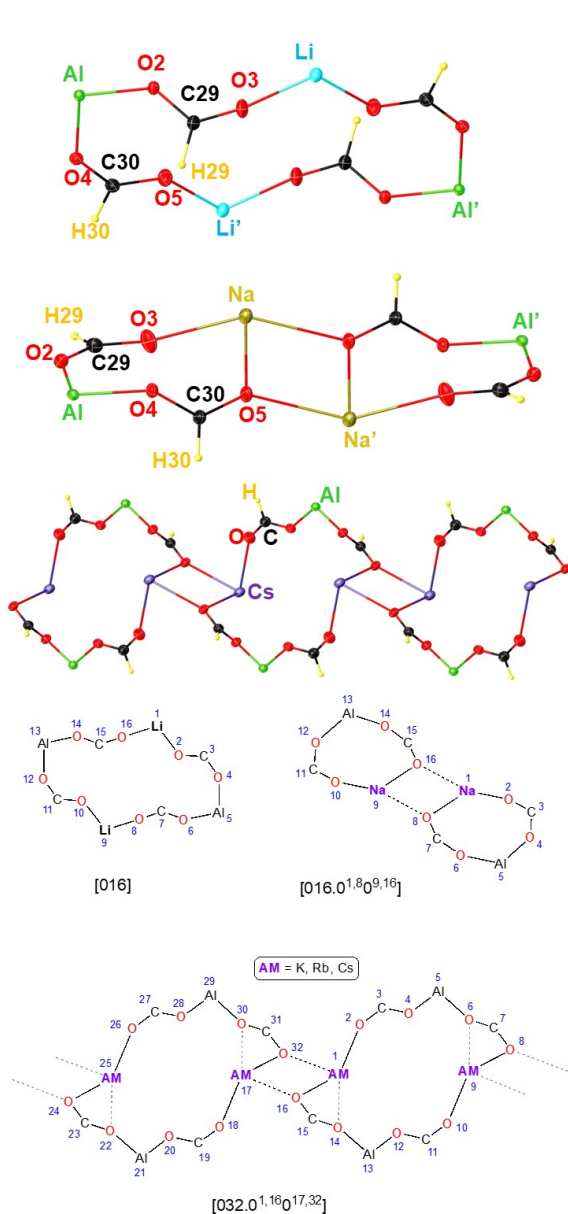
Figure 5. (Top) Structural diversity in a series of alkali-metal aluminium formates (**3**), depicting formation of unusual metallacyclic cores: **3**-Li·TMEDA = [016], **3**-Na·Et$_2$O = [016.0^{1,8}0^{9,16}], **3**-(K/Rb/Cs) = [032.0^{1,16}0^{17,32}]$_\infty$; (Bottom) Nodal descriptor for metallacycles.

fused by a central Na$_2$O$_2$-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 Fig. S61 in ESI 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$_2$O$_2$-rings on both sides forming an infinite chain, [032.0^{1,16}0^{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).
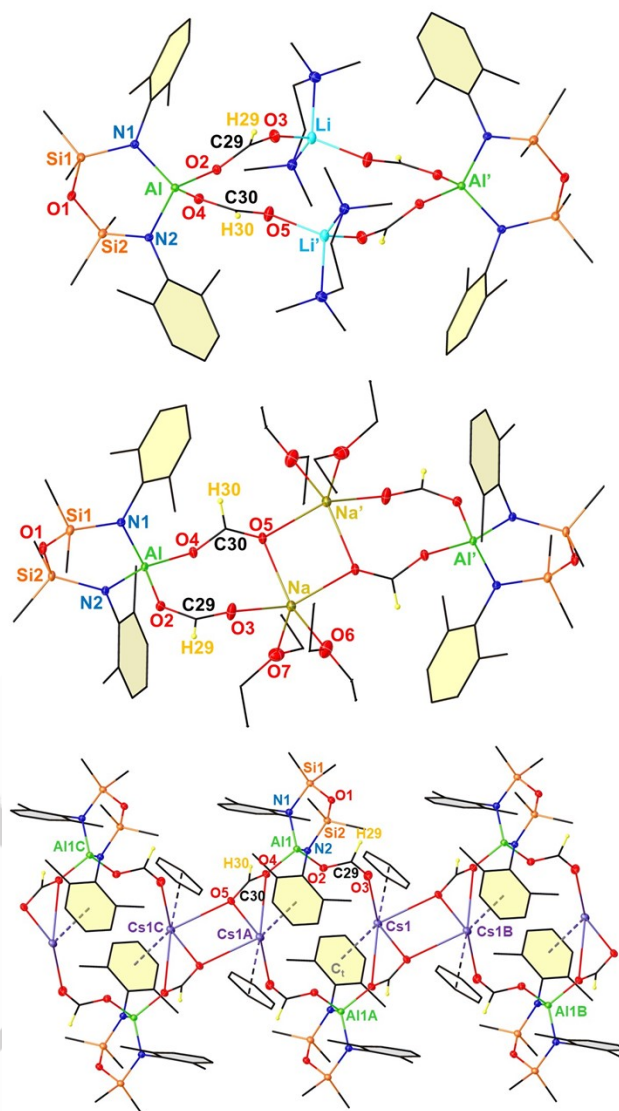
Figure 6. Solid-state structures of [{Li(TMEDA)}{Al(NON^{Dipp})(O$_2$CH)$_2$}]$_2$ (**3**-Li·TMEDA), [{Na(Et$_2$O)$_2$}{Al(NON^{Dipp})(O$_2$CH)$_2$}]$_2$ (**3**-Na·Et$_2$O), and section of polymeric [{Cs(η^1-C$_6$H$_6$)}$_2${Al(NON^{Dipp})(O$_2$CH)$_2$}$_2$]$_\infty$ (**3**-Cs) are shown for comparison. Solid-state structures of **3**-K and **3**-Rb are included in the ESI 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·Et$_2$O): 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.

In all cases the formate ligands adopt a bridging Al(μ-O$_2$CH)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·Et$_2$O both formates link to the same AM cation, with one oxygen atom engaging in bonding to the symmetry generated cation within the AM$_2$O$_2$ core. In the extended **3**-(K/Rb/Cs) structures, one of the formates appears to 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

6

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}0^{9,16}], 103.71(5)°; [032.0^{1,16}0^{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 from the different O—C bond lengths (one short and one long) in the crystal structures.

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}0^{9,16}], 103.71(5)°; [032.0^{1,16}0^{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 from the different O—C bond lengths (one short and one long) in the crystal structures.

Conclusion

In the quest for completing the homologous series of group 1 dihydridoaluminates [AM{Al(NON^{Dipp})(H)$_2$}]$_2$ (AM = Li – Cs; 1), three distinct hydrogen sources were investigated in H$_2$, 1,4-CHD, and PhSiH$_3$. The studies culminated in the isolation of novel Rb and Cs dihydridoaluminates from their parent Al(I) compounds [AM{Al(NON^{Dipp})}]$_2$ (AM = Rb, Cs; 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 [AM{Al(NON^{Dipp})(H)$_2$}]$_2$ (AM = Na – Cs; 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 [{Cs(Et$_2$O)}$_2${Al(NON^{Dipp})(H)}$_2$(C$_6$H$_6$)] (2), resulting from an oxidative addition reaction. Its crystal structure shows two Cs atoms stabilising a dialuminated [1,4-{Al(NON^{Dipp})}$_2$C$_6$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, [C$_6$H$_7$]$^-$ before releasing a hydride ion, whereas here it is doubly deprotonated in generating a trapped [C$_6$H$_6$]$^{2-}$ dianion. Cooperativity of soft Cs cation and a bulky Al anion with NON^{Dipp} scaffold helps in stabilising this [C$_6$H$_6$]$^{2-}$ unit effectively.

The alkali-metal dihydridoaluminates (1) also succeeded in reducing CO$_2$ to form the respective formates of general formula AM[Al(NON^{Dipp})(O$_2$CH)$_2$] (3-AM, AM = Li – Cs). While the structures of Li and Na formates were isolated as dimers of solvated TMEDA and Et$_2$O, respectively (3-Li·TMEDA, 3-Na·Et$_2$O), 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 [Al$_2$C$_4$O$_8$Li$_2$] ([016]), 3-Na·Et$_2$O forming two fused 8-membered metallacycles [AlC$_2$O$_4$Na] ([016.0^{1,8}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 <url href="https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.202201849"> 2260051 (for 1-Rb), 2260052 (for 1-Cs), 2260053 (for 2), 2260054 (for 3-Li·TMEDA), 2260055 (for 3-Na·Et$_2$O), 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 <url href="http://www.ccdc.cam.ac.uk/structures">Access Structures service</url>.

General experimental procedures

All manipulations were performed under dry argon or nitrogen using standard Schlenk-line techniques, or in a conventional nitrogen-filled glovebox. Starting materials and research chemicals were obtained from commercial suppliers where appropriate and used without further purification. [Al(NON^{Dipp})(I)],[6c] [Li{Al(NON^{Dipp})}]$_2$ (I-Li),[6b] [Na{Al(NON^{Dipp})}]$_2$ (I-Na),[6b] [K{Al(NON^{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 [Rb{Al(NON^{Dipp})}]$_2$ (I-Rb),[6a] [Cs{Al(NON^{Dipp})}]$_2$ (I-Cs),[6a] was followed but instead of aromatic solvents the reaction was conducted in methylcyclohexane. [Rb(Et$_2$O)][Al(NON^{Dipp})(H)(SiH$_2$Ph)] (II-Rb),[7a] and [Cs(THF)$_2$][Al(NON^{Dipp})(H)(SiH$_2$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

7

RESEARCH ARTICLE

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_8 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 ^{1}H, 100.62 MHz for ^{13}C. All ^{13}C spectra were proton decoupled. ^{1}H and ^{13}C{^{1}H} 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 were 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−Kα (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 Et$_2$O. 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 Å^3 of unit cell volume. This equates to approximately 2 molecules of Et$_2$O per unit cell. The benzene solvent of **1**-Rb and the Et$_2$O 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 (Et$_2$O), and tetrahydrofuran (THF) were obtained from a PureSolv MD 5 system and stored over activated 5 Å molecular sieves for 24 hours 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 (^{1}H), 194.4 (^{7}Li), 130.3 (^{27}Al), 125.8 (^{13}C) and 99.3 (^{29}Si) 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 (FT-IR) spectra were recorded on solid samples using a Bruker Tensor 27 FT-IR spectrometer. Crystallographic data for complexes **3**-Li·TMEDA, **3**-Na·Et$_2$O and **3**-K were collected 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 Kα 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 F^2 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 $\Sigma w(F^2_{obs} - F^2_{calc})$, with $w = [\sigma^2(F^2_{obs}) + aP^2 + bP]$-1, where $P = [max(F_{obs})^2 + 2F^2_{calc}]/3$. 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 d$_8$-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 PhSiH$_3$ route

A solution of [Na{Al(NON^{Dipp})}]$_2$ (**I**-Na)[6b] (53.3 mg, 0.05 mmol) in d$_8$-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 minutes at 100 °C.

^{1}H NMR (500 MHz, C$_7$D$_8$) δ 6.86 (d, J = 7.6 Hz, 4H, C$_6$H$_3$),), 6.74 (t, J = 7.6 Hz, 2H, C$_6$H$_3$), 3.89 (sept, J = 6.8 Hz, 4H, CHMe$_2$), 1.23 (d, J = 6.8 Hz, 12H, CHMe$_2$), 1.16 (d, J = 6.8 Hz, 12H, CHMe$_2$) 0.33 (br. s, 12H, SiMe$_2$).

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 d$_8$-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

RESEARCH ARTICLE

NMR spectroscopy. Complete conversion was achieved after 52 hrs 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 hrs at 100 °C.
¹H NMR (500 MHz, C₇D₈) δ 6.86 (d, *J* = 7.5 Hz, 4H, C₆*H*₃), 6.75 (t, *J* = 7.5 Hz, 2H, C₆*H*₃), 4.00 (sept, *J* = 6.8 Hz, 4H, C*H*Me₂), 1.20 (d, *J* = 6.8 Hz, 12H, CH*Me*₂), 1.15 (d, *J* = 6.8 Hz, 12H, CH*Me*₂), 0.33 (s, 12H, Si*Me*₂).

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 µL, 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 (3x) 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-C*H*), 6.79 – 6.70 (m, 4H, Ar-C*H*), 4.10 (sept, *J* = 6.7 Hz, 8H, C*H*(CH₃)₂), 1.25 (d, *J* = 6.9 Hz, 24H, CH(C*H*₃)₂), 1.18 (d, *J* = 6.8 Hz, 24H, CH(C*H*₃)₂), 0.41 (s, 24H, Si(C*H*₃)₂); ¹³C{¹H} NMR (101 MHz, C₆D₆, 25°C): δ = 149.4 (*C*arom), 147.6 (*C*arom), 124.1 (*C*arom), 122.4 (*C*aromH), 27.4 (*C*aliphH), 25.5 (*C*aliphH₃), 25.4 (*C*aliphH₃), 2.6 (Si(*C*H₃)₂); ²⁷Al NMR (104 MHz, C₆D₆ 25 °C): δ = 114.6 (*Al*H); ²⁹Si NMR (80 MHz, C₆D₆ 25 °C): δ = -11.0 (*Si*CH₃); m.p.: 262 °C – 266 °C (dec.); IR (Nujol, cm⁻¹): 1\λ= 1732 (w), 1668 (w), 1588 (w), 1312 (w), 1248 (w), 1190 (w), 1122 (w), 1106 (w), 1008 (w), 938 (w), 800 (w).

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

Via 1,4-CHD route
In a J. Young ampoule [Cs{Al(NON^{Dipp})}]₂ (**I**-Cs)[6a] (511mg, 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 H₂ route
In a J. Young NMR tube [Cs{Al(NON^{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 (3x) 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 [Cs(THF)₂][Al(NON^{Dipp})(H)(SiH₂Ph)] (**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 Et₂O. Yield: 18 mg, 41%.

RESEARCH ARTICLE

A satisfactory elemental analysis for the bulk material of [Cs{Al(NON^{Dipp})(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 C$_{56}$H$_{96}$Al$_2$Cs$_2$N$_4$O$_2$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; ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 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, CH(CH$_3$)$_2$), 1.26 (d, J = 6.9 Hz, 24H, CH(CH_3)$_2$), 1.21 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$), 0.41 (s, 24H, Si(CH_3)$_2$); ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 25°C): δ = 149.4 (C_{arom}), 148.6 (C_{arom}), 124.4 (C_{arom}), 122.3 (C_{arom}H), 27.4 (C_{aliph}H), 25.5 (C_{aliph}H$_3$), 25.3 (C_{aliph}H$_3$), 2.5 (Si(CH$_3$)$_2$); ^{27}Al NMR (104 MHz, C$_6$D$_6$ 25 °C): δ = 115.3 (*Al*H); ^{29}Si NMR (80 MHz, C$_6$D$_6$ 25 °C): δ = -11.0 (*Si*CH$_3$)$_2$); m.p.: 239 °C – 243 °C (dec.); IR (Nujol, cm^{-1}): 1\λ= 1724 (w), 1648 (w), 1584 (w), 1314 (w), 1248 (w), 1186 (w), 1106 (w), 1042 (w), 1013 (w), 938 (w), 800 (w).

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

In a J. Young NMR tube [Cs{Al(NON^{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%.

^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 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, CH(CH$_3$)$_2$), 1.24 (d, J = 6.7 Hz, 24H, CH(CH_3)$_2$), 1.14 (d, J = 6.9 Hz, 24H, CH(CH_3)$_2$), 0.96 (s, 24H, Si(CH_3)$_2$); ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 25°C): δ = 146.6 (C_{arom}), 121.9 (C_{arom}), 119.8 (C_{arom}H), 26.0 (C_{aliph}H), 22.4 (C_{aliph}H$_3$), 0.90 (Si(CH$_3$)$_2$); ^{27}Al NMR (104 MHz, C$_6$D$_6$ 25 °C): δ = 72.7; ^{29}Si NMR (80 MHz, C$_6$D$_6$ 25 °C): δ = not detected.

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

A solution of [Li(OEt$_2$)$_2$][Al(NON^{Dipp})(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}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. ^{1}H NMR (500 MHz, C$_6$D$_6$): 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}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ 166.5 (O^{13}CHO), 157.6, 147.1, 123.9, 123.1 (C_6H3), 56.9, 46.7 (TMEDA), 27.5 (CHMe_2), 26.0, 25.9 (CHMe_2), 2.8 (SiMe_2); ^{7}Li{^{1}H} NMR (194 MHz, C$_6$D$_6$): δ 4.4.

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

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

3-Na·Et$_2$O was prepared according to the procedure described for 3-Li·TMEDA using 80 mg (0.15 mmol) of Na[Al(NON^{Dipp})(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 C$_{30}$H$_{48}$AlN$_2$NaO$_5$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$_2$O

^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.40 (d, J = 214.8, 2H, O^{13}CHO), 7.04 (d, J = 7.6, 4H, C$_6$H$_3$), 6.93 (t, J = 7.6, 2H, C$_6$H$_3$), 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$_2$CH_3), 0.47 (s, 12H, SiMe_2); ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): 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 (C_6H$_3$), 65.9 (OCH_2), 27.5 (CHMe_2), 26.4, 25.2 (CHMe_2), 15.5 (CH$_2$CH_3), 2.8 (SiMe_2).

* integration of the ^{1}H resonances for Et$_2$O indicate ~1 equivalent present in the sample consistent with partial loss of coordinated Et$_2$O during sample preparation.

Preparation of K[Al(NON^{Dipp})(O$_2$CH)$_2$] (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 C$_{30}$H$_{48}$AlKN$_2$O$_5$Si$_2$* (*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 Et$_2$O solvent). ^{1}H NMR (500 MHz, 5:1 C$_6$D$_6$:D$_8$-THF): δ 7.81 (d, J = 210.0, 2H, O^{13}CHO), 7.01 (d, J = 7.6, 4H, C$_6H_3$), 6.89 (t, J = 7.6, 2H, C$_6H_3$), 4.08 (sept, J = 6.7, 4H, CHMe$_2$), 1.25 (t, J = 6.7, 24H, CHMe_2), 0.30 (s, 12H, SiMe_2); ^{13}C{^{1}H} NMR (126 MHz, 5:1 C$_6$D$_6$:D$_8$-THF): δ 165.1 (O^{13}CHO), 147.4, 144.1, 123.7, 122.7 (C_6H_3), 27.5 (CHMe_2), 26.0, 25.6 (CHMe_2), 2.8 (SiMe_2).

Preparation of Rb[Al(NON^{Dipp})(O$_2$CH)$_2$] (3-Rb)

[Rb{Al(NON^{Dipp})(H)$_2$}]$_2$ (**1**-Rb) (80 mg, 0.13 mmol) was dissolved in C$_6$D$_6$ (400 µL) in a J. Young NMR tube and pressurised with carbon dioxide (2 atm) at 25ºC. Colourless crystals emerged after standing the solution in the NMR tube for 10 mins. Yield = 68 mg, 73%.

^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 7.64 (s, 3H, O$_2$CH), 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(CH$_3$)$_2$), 1.18 (t, J = 6.1 Hz, 48H, CH(CH_3)$_2$), 0.13 (s, 24H, Si(CH_3)$_2$); ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 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}H$_3$), 25.9 (C_{aliph}H$_3$), 2.9 (Si(CH$_3$)$_2$); ^{27}Al NMR (104 MHz, C$_6$D$_6$ 25 °C): not detected; ^{29}Si NMR (80 MHz, C$_6$D$_6$ 25 °C): δ = -8.61 (*Si*CH$_3$)$_2$).

Preparation of [Cs(η^1-C$_6$H$_6$)][Al(NON^{Dipp})(O$_2$CH)] (3-Cs)

10

RESEARCH ARTICLE

[Cs{Al(NON^{Dipp})(H)$_2$}]$_2$ (1-Cs) (80 mg, 0.12 mmol) was dissolved in C$_6$D$_6$ (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 mins. Yield = 80 mg, 79%.

^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 7.63 (s, 3H, O$_2$CH), 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(CH$_3$)$_2$), 1.17 (q, J = 6.8 Hz, 48H, CH(CH_3)$_2$), 0.13 (s, 24H, Si(CH_3)$_2$); ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 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$_{aliph}$H$_3$), 23.8 (C$_{aliph}$H$_3$), 0.9 (Si(CH_3)$_2$); ^{27}Al NMR (104 MHz, C$_6$D$_6$ 25 °C): δ = not detected; ^{29}Si NMR (80 MHz, C$_6$D$_6$ 25 °C): δ = -8.69 (SiCH$_3$)$_2$).

Supporting Information

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

Acknowledgements

[1] J. R. Norton, J. Sowa, *Chem. Rev.* **2016**, *116*, 8315-8317.

[2] a) M. M. D. Roy, A. A. Omaña, A. S. S. Wilson, M. S. Hill, S. Aldridge, E. Rivard, *Chem. Rev.* **2021**, *121*, 12784-12965; b) S. Aldridge, A. J. Downs, *Chem. Rev.* **2001**, *101*, 3305–3366; c) L. Fohlmeister, A. Stasch, *Aust. J. Chem.* **2015**, *68*, 1190-1201; d) D. Mukherjee, J. Okuda, *Angew. Chem. Int. Ed.* **2018**, *57*, 1458-1473; e) D. Mukherjee, D. Schuhknecht, J. Okuda, *Angew. Chem. Int. Ed.* **2018**, *57*, 9590-9602; f) T. J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.* **2018**, *47*, 4176-4197; g) S. K. Mandal, H. W. Roesky, *Acc. Chem. Res.* **2012**, *45*, 298-307;

[3] a) S. D. Robertson, M. Uzelac, R. E. Mulvey, *Chem. Rev.* **2019**, *119*, 8332-8405; b) J. M. Gil-Negrete, E. Hevia, *Chem. Sci.* **2021**, *12*, 1982-1992.

[4] S. Banerjee, P. A. Macdonald, S. A. Orr, A. R. Kennedy, A. van Teijlingen, S. D. Robertson, T. Tuttle, R. E. Mulvey, *Chem. Eur. J.* **2022**, *28*, e202201085.

[5] a) M. P. Coles, M. J. Evans, *Chem. Commun.* **2023**, *59*, 503-519; b) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2021**, *60*, 1702-1713.

[6] a) T. X. Gentner, M. J. Evans, A. R. Kennedy, S. E. Neale, C. L. McMullin, M. P. Coles, R. E. Mulvey, *Chem. Commun.* **2022**, *58*, 1390-1393; b) M. J. Evans, M. D. Anker, C. L. McMullin, S. E. Neale, M. P. Coles, *Angew.*

Chem. Int. Ed. **2021**, *60*, 22289-22292; c) R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles, *Angew. Chem. Int. Ed.* **2019**, *58*, 1489-1493.

[7] a) G. M. Ballmann, M. J. Evans, T. X. Gentner, A. R. Kennedy, J. R. Fulton, M. P. Coles, R. E. Mulvey, *Inorg. Chem.* **2022**, *61*, 19838-19846; b) M. J. Evans, M. D. Anker, M. P. Coles, *Inorg. Chem.* **2021**, *60*, 4772-4778.

[8] a) T. X. Gentner, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2021**, *60*, 9247-9262; b) G. M. Ballmann, T. X. Gentner, A. R. Kennedy, E. Hevia, R. E. Mulvey, *Chem. Eur. J.* **2022**, *28*, e202201716; c) S. Grams, J. Mai, J. Langer, S. Harder, *Dalton Trans.* **2022**, *51*, 12476-12483; d) H. Videa, A. J. Martinez-Martinez, **2022**, DOI:10.26434/chemrxiv-2022-wjs4l-v2; e) N. R. Judge, L. J. Bole, E. Hevia, *Chem. Eur. J.* **2022**, *28*, e202104164; f) Y. Gu, Z. Zhang, Y. Wang, Z. Dai, Y. Yuan, D. Xiong, J. Li, P. J. Walsh, J. Mao, *J. Org. Chem.* **2022**, *87*, 406-418; g) L. Brieger, C. Unkelbach, C. Strohmann, *Chem. Eur. J.* **2021**, *27*, 17780–17784; h) N. Villegas-Escobar, A. Toro-Labbé, H. F. Schaefer III, *Chem. Eur. J.* **2021**, *27*, 17369-17378; i) N. Villegas-Escobar, P. R. Hoobler, A. Toro-Labbé, H. F. Schaefer III, *J. Phys. Chem. A* **2023**, *127*, 956−965.

[9] a) P. A. Macdonald, S. Banerjee, A. R. Kennedy, A. van Teijlingen, S. D. Robertson, T. Tuttle, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304966; b) T. X. Gentner, A. R. Kennedy, E. Hevia, R. E. Mulvey, *ChemCatChem* **2021**, *13*, 2371-2378. c) H. Bauer, K. Thum, M. Alonso, C. Fischer, S. Harder, *Angew. Chem. Int. Ed.* **2019**, *58*, 4248-4253.

[10] Methylcyclohexane was chosen as the solvent for heavy alkali metal aluminyls because I-Cs was found to activate benzene.[6a]

[11] R. Lalrempuia, C. E. Kefalidis, S. J. Bonyhady, B. Schwarze, L. Maron, A. Stasch, C. Jones, *J. Am. Chem. Soc.* **2015**, *137*, 8944-8947

[12] G. Feng, K. L. Chan, Z. Lin, M. Yamashita, *J. Am. Chem. Soc.* **2022**, *144*, 22662-22668.

[13] S. Brand, H. Elsen, J. Langer, W. A. Donaubauer, F. Hampel, S. Harder, *Angew. Chem. Int. Ed.* **2018**, *57*, 14169 -14173.

[14] D. Dhara, F. Fantuzzi, M Härterich, R. D. Dewhurst, I. Krummenacher, M. Arrowsmith, C. Pranckeviciusab, H. Braunschweig, *Chem. Sci.* **2022**, *13*, 9693-9700.

[15] R. F. Algera, Y. Ma, D. B. Collum, *J. Am. Chem. Soc.* **2017**, *139*, 11544-11549.

[16] a) S. J. Holder, M. Achilleos, R. G. Jones, *Macromolecules* **2005**, *38*, 1633-1639; b) A. Saxena, K. Okoshi, M. Fujiki, M. Naito, G. Guo, T. Hagihara, M. Ishikawa, *Macromolecules* **2004**, *37*, 367-370; c) R. G. Jones, S. J. Holder, *Polym. Int.* **2006**, *55*, 711-718.

[17] a) C. T. Aitken, J. F. Harrod, E. Samuel, *J. Am. Chem. Soc.* **1986**, *108*, 4059-4066; b) J. Koe, M. Fujiki, Polysilanes, *Elsevier eBooks*, **2017**, pp. 219-300; c) J. Y. Corey, X. H. Zhu, T. C. Bedard, L. D. Lange, *Organometallics* **1991**, *10*, 924-930; d) L. Rosenberg, C. W. Davis, J. Yao, *J. Am. Chem. Soc.* **2001**, *123*, 5120-5121; e) E. E. Smith, G. Du, P. E. Fanwick, M. M. Abu-Omar, *Organometallics* **2010**, *29*, 6527-6533; f) C. L. Rock, T. L. Groy, R. J. Trovitch, *Dalton Trans.* **2018**, *47*, 8807-8816; g) J. E. Stevens, C. E. Moore, C. M. Thomas, *J. Am. Chem. Soc.* **2023**, *145*, 794-799.

[18] a) P. Kuo, I. Chen, J. Chang, M. Lee, C. Hu, C. Hung, H. M. Lee, J. Huang, *Eur. J. Inorg. Chem.* **2004**, *24*, 4898-4906; b) D. Franz, C. Jandl, C. Stark, S. Inoue, *Chemcatchem*, **2019**, *11*, 5275-5281; c) M. V. Moskalev, V. G. Sokolov, T. S. Koptseva, A. A. Skatova, A. A. Bazanov, E. V. Baranov, I. L. Fedushkin, *J. Organomet. Chem.* **2021**, *949*, 121972; d) T. W. Myers, L. A. Berben, *Chem. Sci.* **2014**, *5*, 2771-2777; e) G. Ménard, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 5447-5453; f) A. Caise, D. Jones, E. L. Kolychev, J. Hicks, J. M. Goicoechea, S. Aldridge, *Chem.*

Eur. J. **2018**, *24*, 13624-13635; g) S. González-Gallardo, V. Jancik, D. G. Díaz-Gómez, F. Cortés-Guzmán, U. Hernández-Balderas, M. Moya-Cabrera, *Dalton Trans.* **2019**, *48*, 5595-5603; h) T. S. Koptseva, M. V. Moskalev, A. A. Skatova, R. V. Rumyantcev, I. L. Fedushkin, *Inorg. Chem.* **2022**, *61*, 206-213.

[19]   E. O. Fluck, R. S. Laitinen, *Pure Appl. Chem.* **1997**, *69*, 1659-1692.

[20]   K. Grubel, W. W. Brennessel, B. Q. Mercado, P. L. Holland, *J. Am. Chem. Soc.* **2014**, *136*, 16807−16816.

[21]   CrysAlisPro Software system, version 1.171.39.46, Rigaku Corporation, Oxford UK, **2018**.

[22]   O. v. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339–341.

[23]   G. M. Sheldrick, *Acta Cryst. Sect. C* **2015**, *71*, 3–8.

[24]   G. M. Sheldrick, *Acta Cryst. Sect. C* **2008**, *64*, 112–122.

[25]   L. J. Farrugia, *J. Appl. Cryst.* **2012**, *45*, 849–854.

[26]   A. L. Spek, *Acta Cryst. Sect. D.* **2009**, *65*, 148–155.

[27]   J. Cosier, A. M. Glazer, *J. Appl. Cryst.* **1986**, *19*, 105–107.

[28]   R. H. Blessing, *Acta Cryst. Sect. A* **1995**, *51*, 33–38.

[29]   G. M. Sheldrick, SHELXL-97, **1997**.

RESEARCH ARTICLE

Entry for the Table of Contents
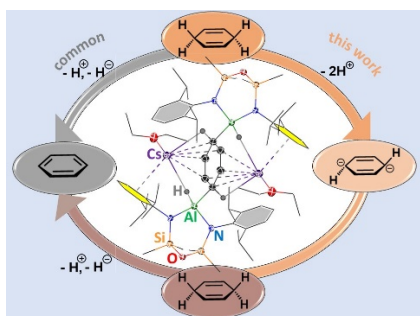
Three distinct methods have been studied to convert alkali metal aluminyls, AM[Al(NON^{Dipp})] (AM = Li-Cs) to dihydridoaluminates AM[Al(NON^{Dipp})(H)$_2$], which in turn reduce CO_2 to bis-formates AM[Al(NON^{Dipp})(O$_2$CH)$_2$]. Diverting from its usual proton-hydride releasing behaviour, 1,4-cyclohexadiene undergoes a remarkable oxidative addition in a 1:1 stoichiometric reaction with Cs[Al(NON^{Dipp})] yielding the inverse sandwich compound [{Cs(Et$_2$O)}$_2${Al(NONDipp)(H)}$_2$(C$_6$H$_6$)] (pictured).

Institute and/or researcher Twitter usernames: @Coles_lab @remulveygroup @mynameissumanta