

Incorporating Trimethylaluminium into the Structures of Alkali Metal (Li, Na, K, Cs) dihydropyridines

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In celebration of the 60th birthday of Professor Sjoerd Harder, a maestro of main group chemistry

Abstract

Co-complexation of equimolar amounts of 1-alkali-metal-2-*tert*butyldihydropyridines with AlMe_3 in the presence of a polydentate *N*-donor ligand has delivered four crystallographically verified alkali-metal aluminates $[\text{donor}\cdot\text{AM}(\mu\text{-}t\text{BuDHP})\text{AlMe}_3]_n$ (**1**, AM = Li, donor = TMEDA, $n = 1$; **2**, AM = Na, donor = PMDETA, $n = 1$; **3**, AM = K, donor = PMDETA, $n = 2$; **4**, AM = Cs, donor = PMDETA, $n = \infty$; TMEDA = *N,N,N',N'*-tetramethylethylenediamine; PMDETA = *N,N,N',N'',N''*-pentamethyldiethylenetriamine). While the monomeric complexes (**1**, **2**) and the polymeric complex (**4**) are thermally stable, the dimeric complex (**3**) undergoes a disproportionation process yielding the known ion-separated homoanionic complex $[\text{K}\cdot(\text{PMDETA})_2]^+ [\text{AlMe}_4]^-$ (**3a**). Utilizing TMEDA as the *N*-donor resulted in the same disproportionation, but gave rise to two distinct solid-state aggregated forms of aluminate $[\text{K}\cdot(\text{TMEDA})_2]^+ [\text{AlMe}_4]^-$, namely monomeric (**3b**) and polymeric (**3b'**) polymorphs, in which the anionic moiety acts as a bidentate chelator or monodentate bridge respectively to the potassium cationic moieties.

Introduction

The recent comprehensive review article by Hill, Aldridge, Rivard *et al* on “molecular main group hydrides”,^[1] building in part on Harder’s earlier feature article “molecular early main group metal hydrides: synthetic challenge, structures and applications”,^[2] has flagged up to the community the escalating importance and future potential of such hydride species. Our own contributions to molecular *s*-block hydride chemistry date back to 2002 with reports of the first well-defined molecular magnesium hydride complexes, bimetallic “inverse crown” $(\text{AM-N-Mg-N})_2$ ring species (AM = Na, K) featuring $(\text{Mg}-\mu\text{H})_2$ bridges and AM–arene π -interactions (Figure 1).^[3] As the aforementioned review bears testimony to, molecular main group hydride chemistry is diversifying quickly and as a

consequence opening a gateway to new applications in both stoichiometric and catalytic bond forming reactions. Aluminium hydrides occupy an imposing large plot within this chemical pastureland with chemists attracted to the high earth abundance of aluminium, as well as to the beneficial economical and eco-benign factors that it holds over precious transition metals which have long dominated the application market. New molecular aluminium hydride complexes span the whole gamut of neutral,^[4] anionic^[5] and cationic^[6] varieties. Even old varieties such as lithium aluminium hydride (LiAlH₄), formally a mixed bimetallic complex of lithium hydride and aluminium trihydride, are finding new employment, as *Harder* demonstrated in the direct hydrogenation of imine substrates to amines,^[5b, 5f] where it acts as a pre-catalyst to bis-hydrido–bis-amido aluminate catalysts.^[5a] Hydroboration is an area in which aluminium complexes of many diverse types including hydrides have excelled, as recently discussed in a frontier article.^[7]

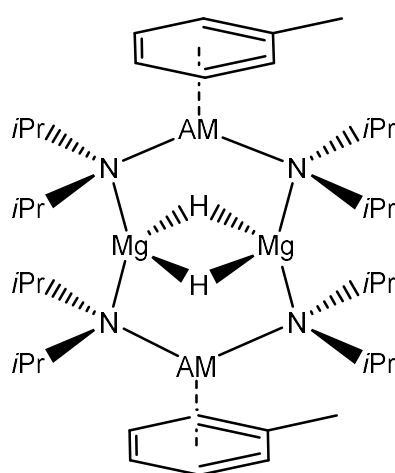


Figure 1 The first molecular magnesium hydride [AMMg(NiPr₂)₂H·C₇H₈]₂

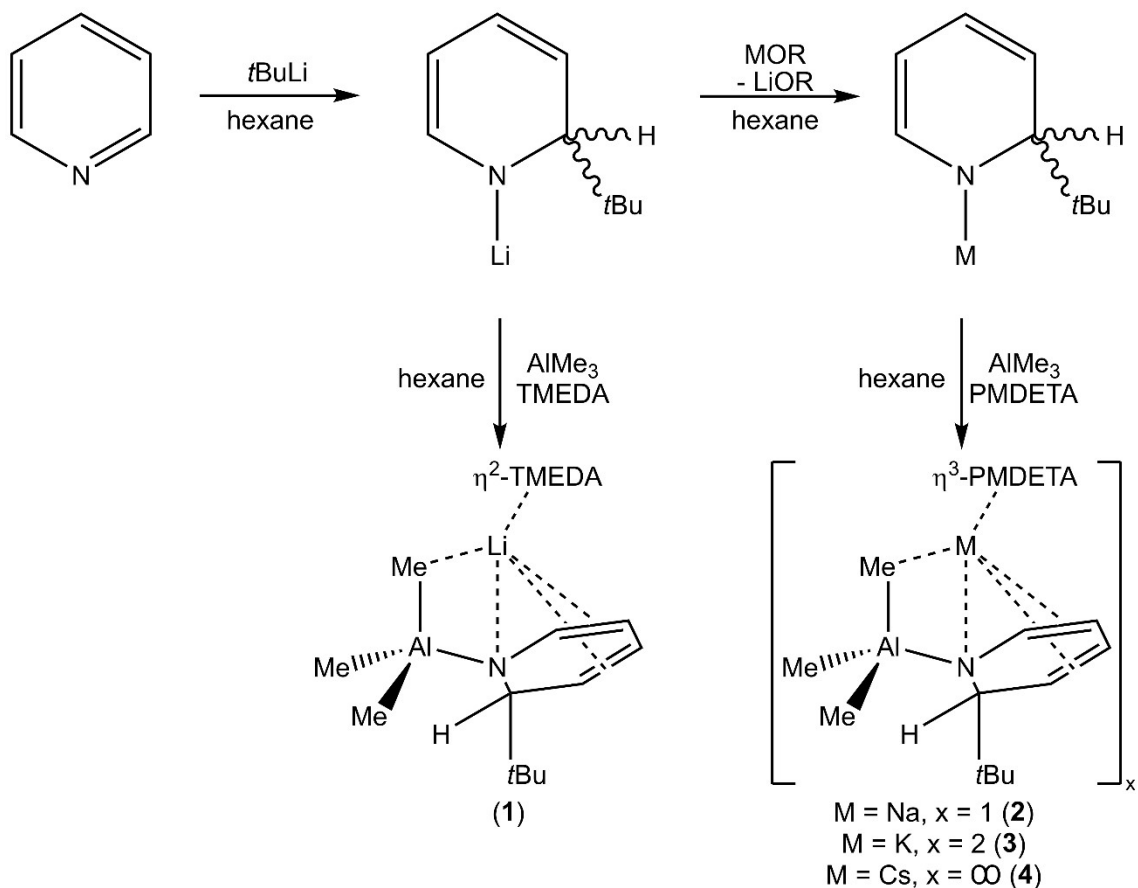
In our latest contribution to expanding the variety of aluminium hydride species, we reported the synthesis and crystal structures of the alkali metal aluminate complexes [AM(*t*BuDHP)(TMP)Al(*i*Bu)₂] (AM = Li, Na, K, Rb), where *t*BuDHP is the 2-*tert*-butyl-1,2-dihydropyridyl anion (TMP is 2,2,6,6-tetramethylpiperidide).^[8] Formally, the AM(*t*BuDHP) moieties represent the product of the addition of the corresponding metal alkyls AM*t*Bu across the azomethine bond of pyridine, an action which destroys the aromaticity of pyridine in forming a dihydropyridyl anion that contains an aza-dienyl unit. In practice, that reaction only works efficiently with lithium,^[9] as the lower stability of the heavier AM*t*Bu complexes require that the AM(*t*BuDHP) (AM = Na, K, Rb, Cs) complexes are best prepared by transmetallation from the lithium congener and heavier alkali *tert*-alkoxides.^[8, 10] These monometallic alkali metal complexes, though formally a special category of alkali metal amide, have shown promise in several catalytic applications as hydride surrogates including hydroboration of aldehydes and ketones, dehydrogenation of diamine boranes and dehydrocoupling of amine boranes.^[11] The hydride

comes from *in situ* elimination of an alkali metal hydride unit facilitated by aromatisation of the metal dihydropyridine to a neutral pyridine. Co-complexation reactions of the set of AM(*t*BuDHP) complexes with the bulky dialkylaluminium amide *i*Bu₂Al(TMP) generated the [AM(*t*BuDHP)(TMP)Al(*i*Bu)₂] aluminate complexes (AM = Li, Na, K, Rb) though the caesium congener could not be obtained in a pure solid form.^[8]

The aim of this present study was to attempt to prepare and fully characterize a complementary series of alkali metal dihydropyridyl aluminates using the commercial alkylaluminium compound Me₃Al in place of non-commercial *i*Bu₂Al(TMP), which needs to be synthesised from *i*Bu₂AlCl and LiTMP.^[12] As now outlined, this study has been successful with the characterization of four alkali-metal aluminate complexes. While the monomeric and polymeric examples appear to be thermally stable, in contrast the dimeric potassium congener undergoes a disproportionation process.

Results and Discussion

The family of alkali-metal dihydropyridyl starting materials were prepared as previously reported. Specifically, the lithium complex was prepared by the stoichiometric 1,2-addition of *t*BuLi to pyridine in hexane solution,^[9a] with the heavier complexes formed by transmetallation of this lithium complex using an appropriate alkali-metal alkoxide (scheme 1).^[8, 10] The resulting homometallic complexes were then co-complexed with AlMe₃ in hexane followed by the addition of a polydentate *N*-donor until a homogeneous solution was obtained, with crystals being obtained for four complexes (specifically containing the alkali-metals Li, Na, K and Cs; **1-4** respectively) upon standing the solutions at -26°C. Determined by X-ray diffraction studies, the crystal structures of these complexes are displayed in figures 1-4 with pertinent bond parameters listed collectively in table 1.



Scheme 1

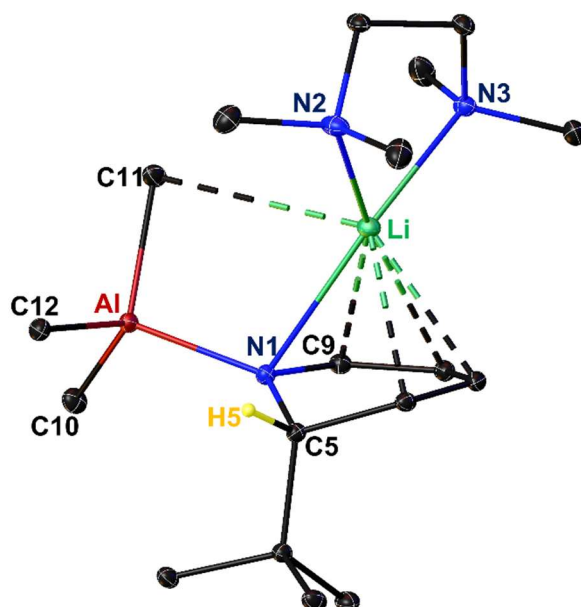


Figure 2 Molecular structure of $\text{TMEDA} \cdot \text{Li}(\mu\text{-}t\text{BuDHP})\text{AlMe}_3$ (1) with ellipsoids drawn at 30% probability and all hydrogen atoms (other than H5) and disordered component of TMEDA ligand removed for clarity

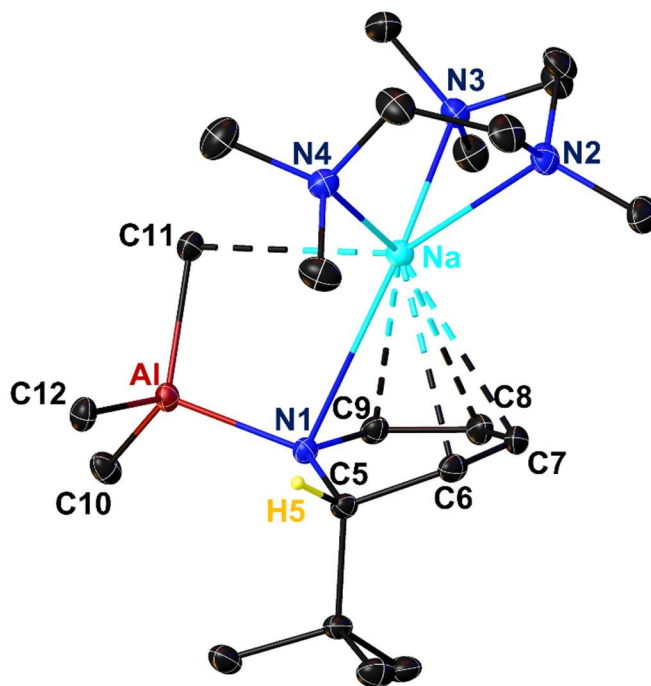


Figure 3 Molecular structure of one independent molecule of PMDETA·Na(μ -*t*BuDHP)AlMe₃ (**2**) with ellipsoids drawn at 30% probability and all hydrogen atoms (other than H5) removed for clarity

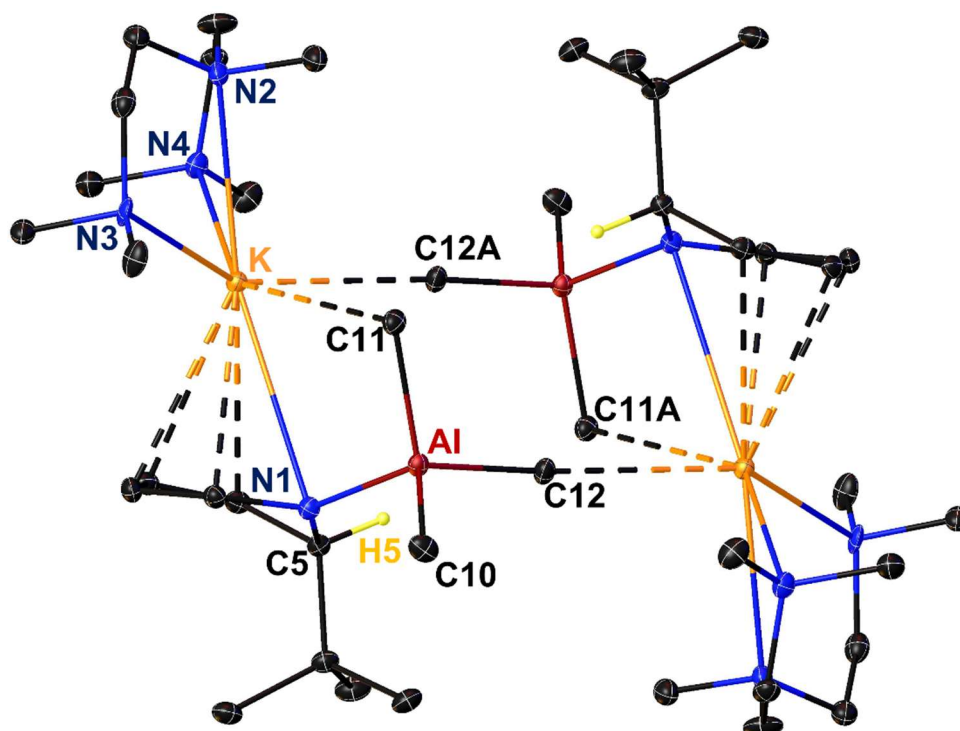


Figure 4 Molecular structure of one independent molecule of [PMDETA·K(μ -*t*BuDHP)AlMe₃]₂ (**3**) with ellipsoids drawn at 30% probability and all hydrogen atoms (other than H5) and disordered component of PMDETA removed for clarity. Symmetry operation to generate equivalent atoms labelled A: 1-x, 2-y, 1-z.

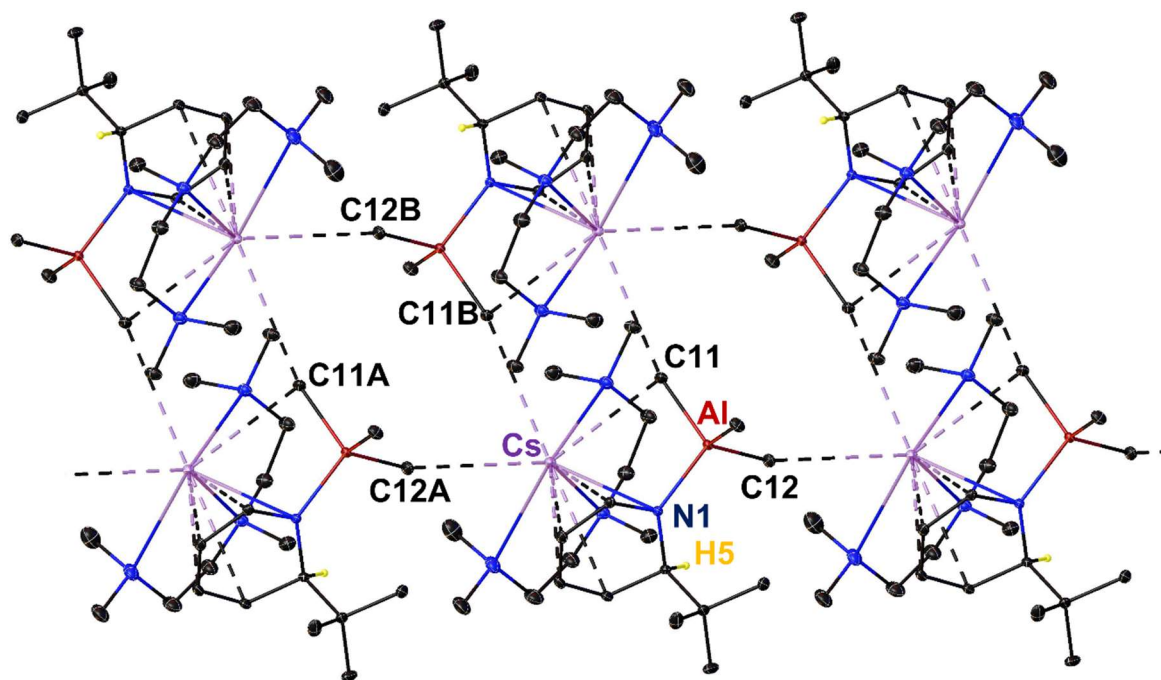


Figure 5 Section of polymeric structure of $[\text{PMDETA}\cdot\text{Cs}(\mu\text{-tBuDHP})\text{AlMe}_3]_\infty$ (**4**) with ellipsoids drawn at 30% probability and all hydrogen atoms (other than H5) removed for clarity. Symmetry operation to generate equivalent atoms labelled A: $-1+x, +y, +z$; B: $1-x, 1-y, 1-z$.

Table 1 Selected bond parameters of bimetallic complexes **1-4**

	1 (Li)	2 (Na) ^a	3 (K) ^a	4 (Cs)		
Interaction	Bond length (Å)					
Al1-N1	1.941(1)	1.929(3)	1.920(4)	1.929(2)	1.934(2)	1.930(2)
Al1-C10	1.998(1)	1.998(5)	1.999(5)	1.996(2)	1.996(2)	1.998(3)
Al1-C11	2.006(1)	2.007(4)	1.983(7)	2.007(2)	2.013(3)	2.010(3)
Al1-C12	1.989(1)	1.989(4)	2.004(4)	1.997(2)	1.996(2)	1.993(3)
AM1-N1	2.394(3)	2.895(4)	2.705(4)	3.282(2)	3.233(3)	3.583(2)
AM1-N2	2.111(3)	2.550(4)	2.520(4)	2.838(7)	2.940(2)	3.245(2)
AM1-N3	2.133(3)	2.494(3)	2.520(4)	2.896(23)	2.895(2)	3.346(3)
AM1-N4	-	2.529(4)	2.518(3)	3.022(5)	2.885(2)	3.215(3)
AM1-C9	2.373(3)	2.826(5)	2.734(5)	3.154(2)	3.117(2)	3.505(2)
AM1-C8	2.474(3)	2.904(5)	2.908(5)	3.161(2)	3.152(2)	3.552(3)
AM1-C7	2.424(2)	2.840(5)	2.947(6)	3.104(2)	3.127(2)	3.507(3)
AM1-C6	2.520(2)	2.969(4)	2.988(5)	3.294(2)	3.295(2)	3.648(3)
AM1-C11	3.261(3)	3.021(5)	3.102(6)	3.249(2)	3.222(2)	3.522(3)
C12-AM1A	-	-	-	3.131(2)	3.237(2)	3.676(3)
C11-AM1A	-	-	-	-	-	3.689(3)
AM-N1/AM-C7	0.988	1.012	0.918	1.057	1.034	1.022
AM-C8/AM-C6	0.982	0.978	0.973	0.960	0.957	0.974
Interaction	Bond angle (°)					
Al1-N1-AM1	106.61(7)	96.32(14)	98.47(14)	94.92(6)	96.00(7)	95.81(7)
Al1-C11-AM1	78.98(6)	90.82(16)	85.23(19)	94.38(8)	94.70(8)	96.15(12)

N1-AM1-N2	124.43(12)	147.31(12)	147.74(12)	155.44(14)	160.75(5)	100.23(5)
N1-AM1-N3	145.01(12)	127.87(11)	126.80(12)	105.41(41)	111.11(6)	112.39(5)
N1-AM1-N4	-	110.20(12)	108.83(11)	137.34(10)	136.48(5)	113.59(6)
N2-AM1-N3	85.98(9)	74.90(11)	74.88(11)	62.22(48)	61.86(6)	54.49(6)
N2-AM1-N4	-	73.00(12)	74.04(11)	64.49(17)	62.44(6)	55.18(7)
N3-AM1-N4	-	112.44(12)	115.36(11)	113.38(40)	97.39(7)	99.49(7)
N1-AM1-C11	64.63(6)	63.03(11)	64.01(13)	58.38(5)	59.20(5)	53.55(6)
N1-Al1-C10	108.86(6)	108.44(17)	109.38(18)	109.44(9)	107.24(9)	106.92(11)
N1-Al1-C11	103.96(5)	103.61(18)	104.95(21)	108.05(8)	107.76(9)	108.67(11)
N1-Al1-C12	109.00(5)	110.25(17)	110.41(17)	109.24(8)	111.13(9)	110.76(11)
Al1-C12-AM1A	-	-	-	176.69(10)	174.41(11)	158.38(14)
Al1-C11-AM1B	-	-	-	-	-	155.59(13)
C6-C7-C8-C9	10.4(2)	11.9(7)	9.1(7)	11.9(3)	10.9(3)	10.8(4)

^a second set of values represents equivalent atoms in second independent molecule.

Lithium aluminate **1** and sodium aluminate **2** exist as monomers, clearly as a consequence of coordinative saturation at the alkali-metal provided by the DHP unit and their polydentate donor (TMEDA and PMDETA respectively) with an Al-Me...AM interaction completing the coordination sphere. For **3**, the steric bulk and tridentate coordination of PMDETA is insufficient to stabilize a monomer, with the complex rather dimerizing via an additional Al-Me...K intermolecular interaction on account of needing to fill the greater ionic radius of potassium. This oligomerizing interaction [3.132(2)Å] is actually shorter than the intramolecular Me...K interaction [3.249(2)Å] in one of the independent molecules but similar in the other [3.237(2)/3.222(2)Å respectively]. These values are close to that reported by *Goicoechea* and *Aldridge* in their potassium methyl aluminate dimer formed by the oxidative addition of the O-Me bond of anisole to a low-valent K/Al precursor and dimerises via a pair of Al-Me...K bridges [3.251(2)Å].^[13] This dimeric motif is also witnessed for **4** [intramolecular Me-Cs bond = 3.522(3)Å; intermolecular Me-Cs bond = 3.676(3)Å], but this additional interaction is insufficient to adequately protect the larger Cs cation and so an additional, slightly longer, Al-Me...Cs interaction [3.689(3)Å] facilitates the propagation of these dimeric units into an infinite polymer of dimers. These interactions are moderately longer than that seen in [(carbazoly)Cs·PMDETA]₂, which has an interaction between the metal and the Me group of the central N atom of PMDETA of [3.473(7)Å]^[14] or that seen in carbanionic MeCs [3.53Å] as determined by powder XRD.^[15]

Comparing the monomeric AM(*t*BuDHP)AlMe₃ units of **1-4**, there is very little variation in the metal ligand relationship beyond the extended alkali-metal ligand bonds as the ionic radius of the alkali-metal increases, with the alkali-metals preferring to bind to the π-system of the dihydropyridyl ring over a σ-bond to the anionic nitrogen heteroatom regardless of the extent of the hard/soft nature of the alkali-metal. The Me₃Al(*t*BuDHP) units display a narrow range of Al-C_{terminal} [1.989(4)-2.004(4) Å],

Al-C_{bridging} [1.983(7)-2.013(3) Å] and Al-N [1.920(4)-1.941(1) Å] bond distances regardless of alkali-metal identity. These Al-N distances are longer than those seen in *Nikonov's* recent series of neutral Al-DHP complexes [1.815(5)-1.839(2) Å]^[16] on account of having four anionic ligands rather than three, and are more in line with the related AM(*t*BuDHP)Al(TMP)*i*Bu₂ complexes [1.937(2)-1.986(2) Å] which have a similar arrangement.^[8] The Al-DHP relationship also differs from that in AM(*t*BuDHP)AlMe₃ on account of the poorer bridging ability of the Me group (*vide infra*) in comparison to the bridging TMP groups. In the AM(*t*BuDHP)Al(TMP)*i*Bu₂ family of complexes, the bridging TMP group pulls the Al atom into a tighter ring resulting in the C_γ-N_{DHP}-Al angle (which we use as a proxy to determine the movement of the Al atom away from the general plane of the DHP ring; note the rings are not perfectly planar due to the quaternization of the α-carbon atom although the conjugated double bonds of the ring provide a considerable degree of planarity with C_α-C_β-C_γ-C_β dihedral angles all lying close to 10°) being constricted to the range 138.7(1)-149.3(1)°, whereas in complexes **1-4** the Al lies closer to the DHP ring plane in the range 155.6(1)-162.9(2)° due to the weaker bridging ability of the Me group in comparison.

The AM-N_{DHP} distances are longer than the dative AM-N_{donor} distances in each complex **1-4**, suggesting that there is little interaction between the alkali-metal and the formally amido (DHP) anion. The position of the alkali-metal barely changes across the series **1-4**, as demonstrated by the AM-N/AM-C_γ and AM-C_β/AM-C_{β'} ratios which lie in a tight range (0.918-1.057) and demonstrate the central location of the alkali-metal above the C₅N ring in all cases. Collectively, this evidence promotes the designation of these complexes as pseudo-solvent-separated ion pairs, that is that the four anionic centres bind exclusively to the Al with the alkali-metal forming a cationic moiety solvated exclusively by neutral ligands in the form of Lewis donating polydentate amines, the DHP π surface and agostic or anagostic^[17] type interactions with Al-bound Me groups, with effectively no direct interactions with an anionic centre present.

Interestingly, while complexes **1**, **2** and **4** could be obtained from cooling down a room temperature reaction between the alkali-metal DHP and AlMe₃, anomalously complex **3** had to be carried out and maintained at low temperature. The room temperature reaction of K(*t*BuDHP) with AlMe₃ in the presence of PMDETA preferentially yielded the homoleptic complex [K·(PMDETA)₂]⁺ [AlMe₄]⁻ (**3a**) presumably as a result of a disproportionation process which would also generate K(*t*BuDHP)₂AlMe₂.^[18] Complex **3a** has been reported previously from the related reaction of equimolar quantities of AlMe₃ and KO*t*Bu in a hexane/toluene mixture to which was added PMDETA.^[18] Here, we changed the Lewis donor to TMEDA finding that it did not alter the outcome of the room temperature reaction, with crystalline [K·(TMEDA)₂]⁺ [AlMe₄]⁻ being obtained instead. Adding interest to this reaction, from the solutions we were able to crystallise two different polymorphs (**3b** and **3b'**, figure

6) having similar unit cells. The first structure is a discrete monomeric structure with a four-coordinate distorted tetrahedral Al centre and a six-coordinate pseudo-octahedral potassium cation formed via two bidentate *N,N'*-TMEDA donor ligands and also two of the methyl components of the adjacent bidentate $[AlMe_4]^-$ unit, which can formally be considered as lying cisoid to one another. The second polymorph exhibits a polymeric structure where the two TMEDA molecules lie in a crystallographically imposed equatorial plane (across an inversion centre) and the $[AlMe_4]^-$ unit has switched from a bidentate chelating-type anion to a monodentate bridging ligand between two cationic $[K \cdot (TMEDA)_2]^+$ moieties.

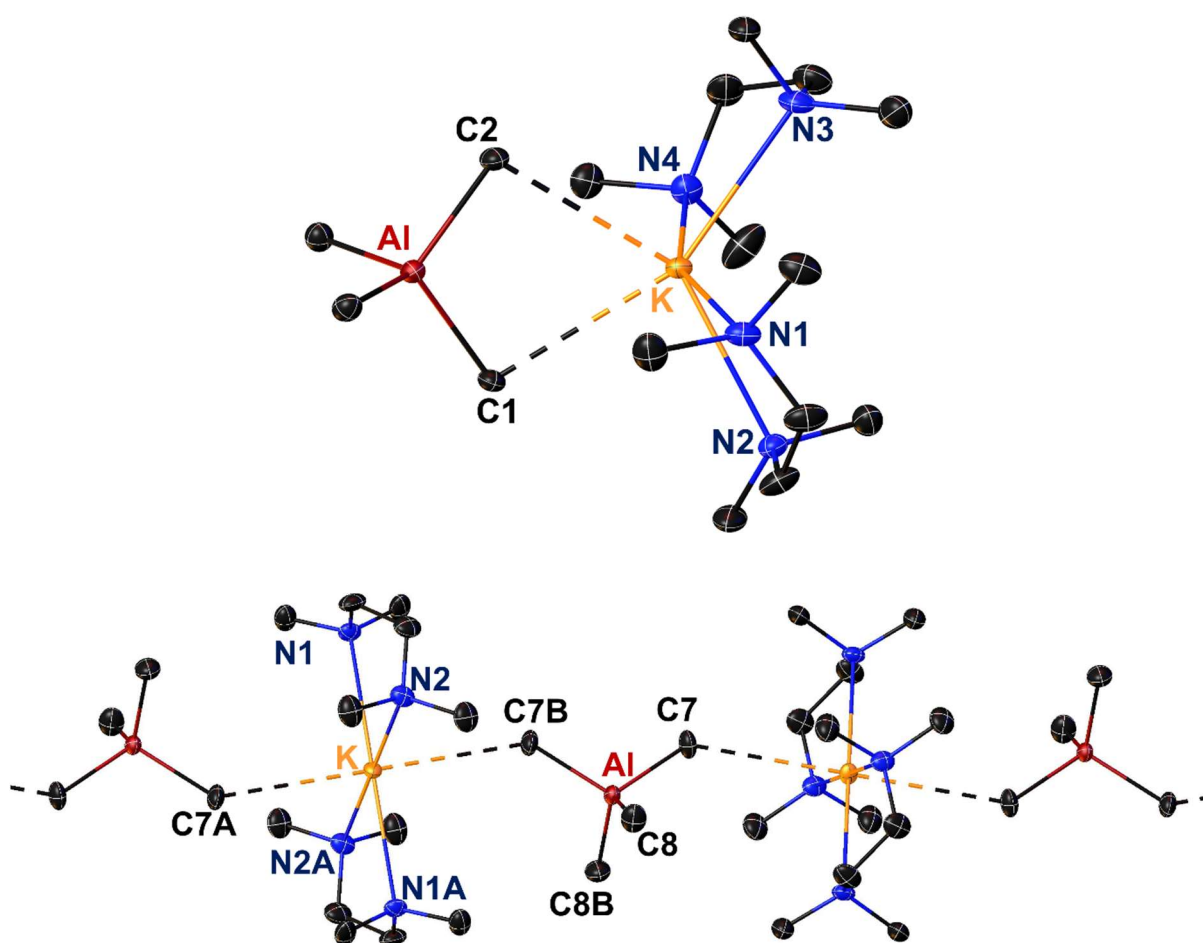


Figure 6 Molecular structure of $[K \cdot (TMEDA)_2]^+ [AlMe_4]^-$ (**3b**, top) and part of polymeric structure of $\{[K \cdot (TMEDA)_2]^+ [AlMe_4]^- \}_\infty$ (**3b'**, bottom) with ellipsoids drawn at 30% probability and all hydrogen atoms and disordered TMEDA components removed for clarity. Symmetry operations to generate equivalent atoms labelled 'A': $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; 'B': $-x, y, -z + \frac{1}{2}$. Selected bond parameters for **3b**: Al1-C1, 2.020(5); Al1-C2, 2.004(5); Al1-C3, 1.997(5); Al1-C4, 1.998(5); K1-C1, 3.038(4); K1-C2, 3.052(4); K1-N1, 2.867(4); K1-N2, 2.842(4); K1-N3, 2.884(4); K1-N4, 2.826(4); K1-C1-Al1, 89.8(2); K1-C2-Al1, 89.7(2); C1-Al1-C2, 113.4(2); C1-Al1-C3, 106.4(2); C1-Al1-C4, 109.0(2); C2-Al1-C3, 107.5(2); C2-Al1-C4, 106.5(2); C3-Al1-C4, 114.2(2); N1-K1-N2, 64.3(1); N1-K1-N3, 119.4(1); N1-K1-N4, 109.8(1); N2-K1-N3, 100.1(1); N2-K1-N4, 159.7(1); N3-K1-N4, 64.8(1); C1-K1-N1, 84.2(1); C1-K1-N2, 100.1(1); C1-K1-N3, 154.1(1); C1-K1-N4, 98.5(2); C2-K1-N1, 145.7(1); C2-K1-N2, 101.1(1); C2-K1-N3, 93.1(1); C2-K1-N4, 93.2(1). Selected bond parameters for **3b'**: K1-N1, 2.861(2); K1-N2, 2.825(2); K1-C7,

3.378(2); Al1-C7, 1.996(2), Al1-C8, 1.994(3); Al1-C7-K1, 135.9(1); C7-Al1-C8, 107.5(1); C7-Al1-C7B, 112.6(2); C8-Al1-C8B, 115.1(2); C7-Al1-C8B, 107.1(1); N1-K1-N2, 64.75(6); N1-K1-N1A, 180; N1-K1-N2A, 115.25(6); C7-K1-C7A, 180.0; C7-K1-N1, 88.39(7); C7-K1-N2, 86.32(7); C7-K1-N1A, 91.61(7); C7-K1-N2A, 93.68(7).

While both structures contain similar Al-C and K-N bond distances in the anionic and cationic moieties respectively, there is a clear distinction in their K-C bond distances. In the contacted ion pair **3b**, this distance is noticeably shorter at 3.038(4)/3.052(4) Å; whereas for the polymeric complex **3b'** the transoid-disposed Me groups are 3.378(2) Å away from potassium. The polymer does contain an almost perfectly octahedral K centre other than the enforced bite angles of the TMEDA ligands in the exactly planar equatorial plane [64.75(6)°]. However, the presence of three chelating ligands around K in **3b** (2 x TMEDA, 1 x Me₄Al) enforces considerable deviation from octahedral geometry as demonstrated by the formally transoid ligands deviating considerably from 180° [C1-K1-N3, 154.1(1)°; C2-K1-N1, 145.7(1)°; N2-K1-N4, 159.7(1)°].

Table 2 Selected NMR spectroscopic data of DHP complexes **1**, **2** and **4** recorded in C₆D₆

	1 (Li)	2 (Na)	4 (Cs)
Position	¹ H/ ¹³ C Chemical shift (ppm)		
C _α	3.81/61.0	4.00/60.9	3.92/62.2
C _β	4.72/106.6	4.67/103.3	4.59/104.0
C _γ	5.80/124.8	6.03/125.1	5.79/126.9
C _{β'}	4.79/97.1	4.67/92.5	4.68/93.7
C _{α'}	7.01/144.3	7.18/146.0	6.97/147.6
C _q	-/41.3	-/41.2	-/41.5
Me _(tBu)	1.21/25.5	1.30/25.2	1.32/25.6
Me _(Al)	-0.33/n.r.	-0.31/n.r.	-0.33/n.r.

n.r. = not resolved

Satisfactory NMR spectra of complex **3** could not be obtained as solid samples of this complex prepared at low temperature (*vide supra*) quickly degraded upon isolation, presumably via the disproportionation process which results in the formation of homoleptic **3a**. However, satisfactory NMR spectroscopic analyses were obtained for the other bimetallic aluminate complexes. Given the similarities in the solid-state structures described, it is perhaps unsurprising that the three heteroleptic complexes **1**, **2** and **4** display essentially similar ¹H and ¹³C NMR spectra in C₆D₆. The key resonances are summarized in table 2. All equivalent environments show similar shifts independent of alkali-metal identity, with the range for each ring CH and methyl environment less than 0.25 ppm in the ¹H spectra.

The chemical shifts for the ring hydrogens demonstrate the lack of aromaticity within the ring with a clear conjugated double bond system present. These chemical shifts are similar to those of the related bimetallic complexes $AM(\mu\text{-}t\text{BuDMP})(\mu\text{-TMP})Al\text{iBu}_2$ (also recorded in C_6D_6 : for example, C_{α} , 3.81-4.00 ppm for **1**, **2**, **4**; 3.76-3.85 ppm in TMP complexes)^[8] and are noticeably shifted downfield compared with the homo alkali-metallic starting materials (C_{α} 3.20-3.31 ppm),^[8, 10] albeit such complexes are recorded in THF solution due to their insolubility in benzene and so solvent effects cannot be discounted. However, both the homometallic family and bimetallic TMP-based family of complexes mentioned show a clear trend in the shielding/deshielding of resonances as the size of the alkali-metal is increased; this is not the case in the three complexes reported herein, with the middle (sodium) complex showing the most shielded resonance for C_{α} , C_{γ} and $C_{\alpha'}$ (4.00, 6.03, 7.18 ppm respectively), although the different Lewis donor (PMDETA, compared to TMEDA for Li) may also be a contributing factor for such an anomaly. In all cases, the ^{13}C NMR resonance of the methyl groups bound to aluminium and the ^{27}Al resonance itself could not be discerned, presumably due to the asymmetry at the quadrupolar Al centre causing considerable broadening.

Experimental

General Experimental: All reactions and manipulations were conducted in a protective argon atmosphere using either standard Schlenk techniques or an MBraun glove box fitted with an in-built gas purification and recirculation unit. Solvents were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. $t\text{BuLi}$ and AlMe_3 (1.7 M in hexanes and 2.0 M in hexanes respectively) were obtained from a commercial source and used as received. TMEDA and PMDETA were obtained from a commercial source, distilled and stored over 4 Å molecular sieves prior to use. $M(t\text{BuDHP})$ $M = \text{Li},^{[9a]} \text{Na}, \text{K},^{[10]} \text{Rb}, \text{Cs}^{[8]}$ were prepared by literature methods. ^1H , ^7Li and ^{13}C NMR spectra were recorded on a Bruker AV400 MHz spectrometer operating at 400.03, 155.47 and 100.58 MHz, respectively.

X-ray Diffraction: Crystallographic data for all complexes except **3b'** were collected on an Oxford Diffraction instrument using Mo- K_{α} or Cu- K_{α} radiation ($\lambda = 0.71073$ or 1.54184 Å respectively) at 100K (Cu) or 153K (Mo). Structures were solved using OLEX2, while refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method by the Gauss-Newton algorithm using OLEX2.^[19] All non-hydrogen atoms were refined using anisotropic displacement parameters. Selected crystallographic and refinement details can be found in table S1. For **3b'** data were collected on a Bruker SMART instrument using Mo- K_{α} radiation at 160K. The structure was solved and refined with programs of the SHELX family.^[20]

The TMEDA ligands of structures **1** and **3b** were modelled as disordered over two sites, a similar treatment was used for the PMDETA ligands of structure **3**. In all cases suitable restraints and constraints were applied to bond lengths and to displacement parameters of the disordered units to ensure that both geometry and displacement behaviour approximated to normal behaviour.

Data measured for structures **2** and **3** was treated as twinned and refinement was against hklf 5 formatted reflection files. For structure **2** the twin law used corresponded to a 180 degree rotation about 100 and the twin ratio refined to 0.3274(13). For structure **3** the twin law used again corresponded to a 180 degree rotation about 100 and the twin ratio refined to 0.2471(6).

Synthesis of (TMEDA)Li(tBuDHP)AlMe₃ (**1**)

Li(tBuDHP) (0.140 g, 1 mmol) was dissolved in hexane (5 mL). AlMe₃ (0.51 mL, 1 mmol) was added dropwise via a syringe which resulted in the formation of a cream-coloured suspension. A few drops of TMEDA were added via a syringe and a change from a light brown suspension to an orange solution was observed. The solution was left to stand at -26 °C for 72 h. Colourless crystals, identified as **1**, were isolated. Yield: 0.190 g, 0.57 mmol, 57%.

¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 7.01 (1H, d, ³J_{H-H} = 6.35 Hz, H_α), 5.80 (1H, dq, ³J_{H-H} = 5.36 Hz, H_γ), 4.79 (1H, dt, ³J_{H-H} = 5.27 Hz, H_{β'}), 4.72 (1H, dd, ³J_{H-H} = 5.71 Hz, H_β), 3.81 (1H, d, 2.29, ³J_{H-H} = 5.62 Hz, H_α), 1.68 (12H, s, TMEDA Me), 1.50 (4H, s, TMEDA CH₂), 1.20 (9H, s, tBu), -0.33 ppm (9H, s, AlMe₃).

¹³C NMR (100.6 MHz, C₆D₆, 300 K): δ 144.3 (C_{α'}), 124.8 (C_γ), 106.6 (C_β), 97.1 (C_{β'}), 61.0 (C_α), 56.1 (TMEDA CH₂), 45.6 (TMEDA Me), 41.3 (tBu quaternary), 25.5 ppm (tBu Me).

⁷Li NMR (155.5 MHz, C₆D₆, 300 K): δ -1.53 ppm.

Synthesis of (PMDETA)Na(tBuDHP)AlMe₃ (**2**)

Na(tBuDHP) (0.159 g, 1 mmol) was suspended in hexane (10 mL). AlMe₃ (0.51 mL, 1 mmol) was added dropwise via a syringe which resulted in a cream suspension. PMDETA (2 mL) was added which resulted in a change from a cream suspension to a pale brown solution. The solution was left to stand at -26 °C for 72 h. Colourless crystals, identified as **2**, were isolated. Yield: 0.150 g, 0.37 mmol, 37%.

¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 7.18 (1H, d, ³J_{H-H} = 6.07 Hz, H_α), 6.03 (1H, dq, ³J_{H-H} = 5.55 Hz, H_γ), 4.67 (2H, m, H_β + H_{β'}), 4.00 (1H, d, ³J_{H-H} = 5.69 Hz, H_α), 1.87 (12H, s, PMDETA Me x 4), 1.74 (3H, s, PMDETA Me x 1), 1.66 (8H, s, PMDETA CH₂ x 4), 1.30 (9H, s, tBu), -0.31 ppm (9H, s, AlMe₃).

^{13}C NMR (100.6 MHz, C_6D_6 , 300 K): δ 146.0 ($\text{C}_{\alpha'}$), 125.1 (C_{γ}), 103.3 (C_{β}), 92.5 ($\text{C}_{\beta'}$), 60.9 (C_a), 56.4 (PMDETA CH_2), 53.7 (PMDETA CH_2), 44.8 (PMDETA Me x 4), 43.0 (PMDETA Me x 1), 41.2 (*t*Bu quaternary), 25.2 ppm (*t*Bu Me).

Synthesis of [(PMDETA)K(*t*BuDHP)AlMe₃]₂ (**3**)

K(*t*BuDHP) (0.0875 g, 0.5 mmol) was suspended in hexane (10 mL) and cooled to 0°C. AlMe₃ (0.25 mL, 0.5 mmol) was added dropwise via a syringe which resulted in a cream suspension. The ice bath was removed and PMDETA (2 mL) was then added which resulted in a change from a cream suspension to a clear solution. The solution was left to stand at -26 °C for 72 h. A small crop of colourless crystals, identified as **3**, were isolated.

Synthesis of [K·(TMEDA)₂]⁺ [AlMe₄]⁻ (**3b/3b'**)

K(*t*BuDHP) (0.0875 g, 0.5 mmol) was suspended in hexane (7.5 mL). AlMe₃ (0.25 mL, 0.5 mmol) was added dropwise via a syringe which resulted in a cream suspension. Excess TMEDA (approx. 4 mL) was added followed by THF (approx. 2 mL) which gave an oily solution. After being left to stand at -26 °C overnight X-ray quality crystals subsequently identified as **3b** were obtained.

^1H NMR (400.1 MHz, NC_5D_5 , 300 K): δ 2.42 (8H, s, TMEDA CH_2), 2.22 (24H, s, TMEDA Me), -0.05 ppm (12H, sextet, $^2J_{\text{H-Al}} = 6.2\text{Hz}$, AlMe₄).

^{13}C NMR (100.6 MHz, NC_5D_5 , 300 K): 58.6 (TMEDA CH_2), 46.3 (TMEDA Me), -2.8 ppm (AlMe₄).

Synthesis of [(PMDETA)Cs(*t*BuDHP)AlMe₃]_∞ (**4**)

Cs(*t*BuDHP) (0.100 g, 0.37 mmol) was suspended in hexane (10 mL). AlMe₃ (0.18 mL, 0.37 mmol) was added dropwise via syringe. After addition of a few drops of PMDETA, a sharp change from a green suspension to a colourless solution was observed. The solution was left to stand at -26 °C for 72 h. Colourless crystals, identified as **4** were isolated. Yield: 0.139 g, 0.35 mmol, 71%.

^1H NMR (400.1 MHz, C_6D_6 , 300 K): δ 6.97 (1H, d, $^3J_{\text{H-H}} = 6.40\text{ Hz}$, $\text{H}_{\alpha'}$), 5.79 (1H, dq, $^3J_{\text{H-H}} = 5.39\text{ Hz}$, H_{γ}), 4.68 (1H, t, $^3J_{\text{H-H}} = 5.81\text{ Hz}$, $\text{H}_{\beta'}$), 4.58 (1H, q, $^3J_{\text{H-H}} = 5.61\text{ Hz}$, H_{β}), 3.92 (1H, d, $^3J_{\text{H-H}} = 5.45\text{ Hz}$, H_{α}), 2.21 (4H, t, $^3J_{\text{H-H}} = 5.44\text{ Hz}$, PMDETA CH_2), 2.14 (4H, t, $^3J_{\text{H-H}} = 5.88\text{ Hz}$, PMDETA CH_2), 1.97 (12H, s, PMDETA Me x 4), 1.96 (3H, s, PMDETA Me x 1), 1.32 (9H, s, *t*Bu), -0.33 ppm (9H, s, AlMe₃).

^{13}C NMR (100.6 MHz, C_6D_6 , 300 K): δ 147.6 ($\text{C}_{\alpha'}$), 126.9 (C_{γ}), 104.0 (C_{β}), 93.7 ($\text{C}_{\beta'}$), 62.2 (C_a), 57.4 (PMDETA CH_2), 56.1 (PMDETA CH_2), 45.2 (PMDETA Me x 4), 41.2 (PMDETA Me x 1), 41.5 (*t*Bu quaternary), 25.6 ppm (*t*Bu Me).

Conclusions

A surprising diversity of crystal structures has been found on adding trimethylaluminium to 1-alkali-metal-2-*tert*butyldihydropyridines in the presence of the popular polydentate amine donor ligands PMDETA or TMEDA. These co-complexation reactions afforded monomers, a dimer and a polymer, with aggregation increasing in the order Li,Na < K < Cs. Intriguingly, the dimeric potassium aluminate structure undergoes disproportionation resulting in the aluminate $[K\cdot(TMEDA)_2]^+ [AlMe_4]^-$, which exists as two distinct aggregated structures in the crystalline state. Future work will focus on exploring the reactivity of these $[donor\cdot AM(\mu\text{-}tBuDHP)AlMe_3]_n$ aluminate complexes, especially given their diversity of structures and the fact they can be interpreted as either amide or hydride sources.

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Keywords

Alkali-metals • Aluminate • Bimetallic • Dihydropyridyl • Structure

Data Availability Statement

The data that supports the findings of this study are available from the University of Strathclyde KnowledgeBase at <https://doi.org/10.15129/57108930-b54f-4d48-8cea-f8ec35eb6718>

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