

# Dynamic ion-pairing behaviour of “naked” aluminyls: Facile activation of H<sub>2</sub>

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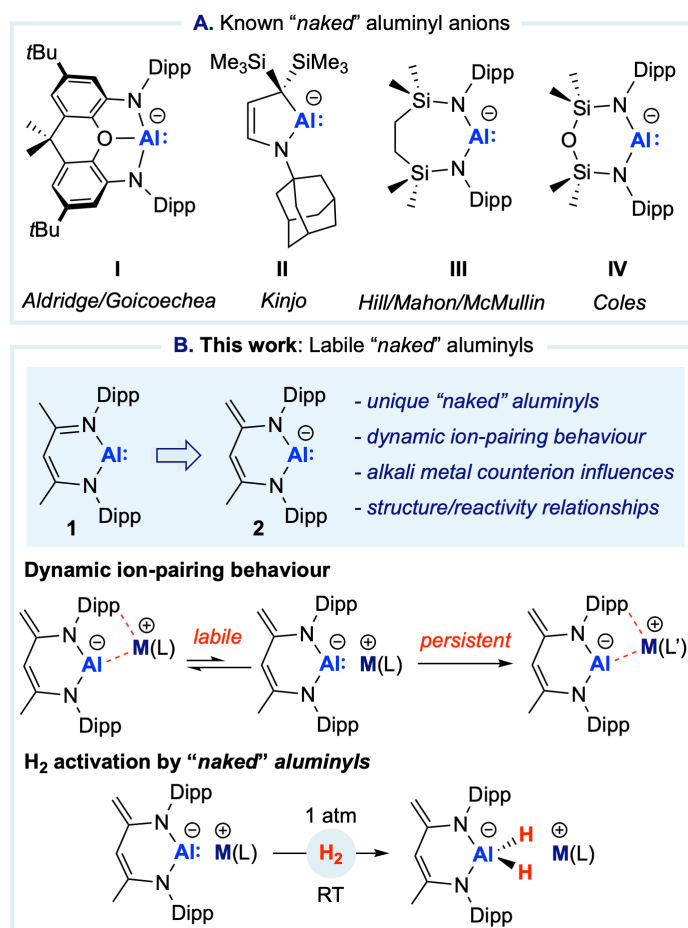
**Abstract:** This work discloses an unprecedented dynamic ion-pairing behaviour of “naked” aluminyl anions related to their stability and reactivity in solution. Rapid exchange between contacted and charge-separated species of the aluminyl anion  $[(BDI')Al]^-$  ( $BDI' = H_2C=C(NAr)-C(H)=C(Me)-NAr$ ;  $Ar = 2,6-iPr_2C_6H_3$ ) occurs in solution with  $[M(L)]^+$  counterions ( $M = Cs, K$ ). While the two-dimensional polyether 18-crown-6 (L) favours the formation of persistent contacted species, the three-dimensional 2.2.2-cryptand ligand allows facile exchange. These aluminyl processes are probed by NMR spectroscopy, including DOSY NMR, and X-ray crystallography, which provide intimate details of the ion-pairing equilibrium and ionic separations. The liabilities of these aluminyls are shown to be important in their stability and reactivity with the non-polar H<sub>2</sub>.

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Aluminyls have become avant-garde main group compounds featuring a new class of low-valent Al<sup>I</sup> anions.<sup>[1]</sup> These anionic species have brought about a paradigm shift in understanding unconventional Lewis basic/nucleophilic aluminium chemistry. The first class of an aluminyl, reported in 2018, comprised a three-coordinated anionic Al<sup>I</sup> metal centre  $[R_3Al]^-$  anchored to a flexible xanthene bis(amide) ligand,  $[(NON^{xant})Al]^-$  (**1**, Figure 1A).<sup>[2]</sup> Other two-coordinated examples  $[R_2Al]^-$  followed soon after that.<sup>[3]</sup> These  $[Al]^-$  anions are typically obtained by the two-electron reduction of neutral Al<sup>III</sup>-halogen precursors with an excess of an alkali metal (M) or suitable MC<sub>8</sub> reagent. Alternatively, they can also be prepared from Al<sup>II</sup> or Al<sup>I</sup> species.<sup>[3b-e, 4]</sup> Since the stabilisation of these highly reactive anions is succeeded by interaction with electropositive alkali metals,<sup>[5]</sup> examples with different alkali metals have been reported.<sup>[4]</sup> The majority of the aluminyls have a preference for aggregating as either contacted dimeric or monomeric pairs with alkali metals through bimetallic M...Al interactions, and additionally, M...π(arene) contacts with ancillary aluminyl ligands. On the other hand,

examples of aluminyls lacking such bimetallic stabilising interactions with alkali metals are very scarce. So far, only four charge-separated aluminyl systems are known (Figure 1A): the xanthene  $[(\text{NON}^{\text{xanthene}})\text{Al}]^- \text{I}$ ,<sup>[6]</sup> (alkyl)(amido)  $[(\text{CN}^{\text{Ad}})\text{Al}]^- \text{II}$ ,<sup>[3c]</sup> bis(amido)  $[(\text{SiN}^{\text{Dipp}})\text{Al}]^- \text{III}$ ,<sup>[7]</sup> and  $[(\text{OSiN}^{\text{Dipp}})\text{Al}]^- \text{IV}$  aluminyl anions.<sup>[4a, 8]</sup> These are rare examples of highly reactive “naked”  $[\text{Al}]^-$  aluminyls.

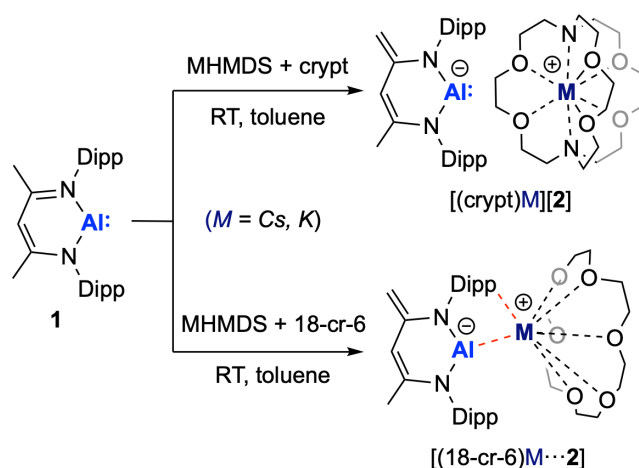
Aluminyls can exhibit different reactivity patterns depending on their solution aggregation state. For example, the contacted dimeric pair  $[(\text{NON}^{\text{xanthene}})\text{Al}\cdots\text{K}]_2$  of **I**,<sup>[2, 9]</sup> and also other dimeric aluminyls,<sup>[4c, 4d]</sup> thermally activate C–H bonds of aromatic substrates. However, charge-separated aluminyls can be involved in more challenging transformations, *i.e.* the anion  $[(\text{NON}^{\text{xanthene}})\text{Al}]^- \text{I}$  reversibly cleaves a non-polar C–C bond of benzene at room temperature.<sup>[6]</sup> It is then clear that the reactivity and stability of aluminyls are strongly influenced by their solution aggregation state and, therefore, the nature of the interactions with the alkali metal counterions. In this context, many efforts have been made to study the solution state of contacted aluminyl pairs;<sup>[1]</sup> by contrast, little is known about the solution behaviour of charge-separated aluminyls.



**Figure 1.** **A)** State-of-the-art “naked” aluminyls (cation =  $[(\text{crypt})\text{K}]^+$  for **I**;  $[(12\text{-cr-6})\text{K}]^+$  for **II**;  $[(\text{crypt})\text{K}]^+$  and  $[(18\text{-cr-6})_{1.5}\text{K}]^+$  for **III**;  $[(\text{tmeda})_2\text{Li}]^+$ ,  $[(\text{crypt})\text{Na}]^+$  and  $[(\text{crypt})\text{K}]^+$  for **IV**). **B)** This work: Labile “naked” aluminyls derived from **1**, dynamic pairing behaviour of the “naked” aluminyl **2**, and activation of  $\text{H}_2$  ( $\text{M} = \text{Cs}, \text{K}$ ;  $\text{L} = \text{crypt}, \text{L}' = 18\text{-cr-6}$ ,  $\text{Dipp} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ).

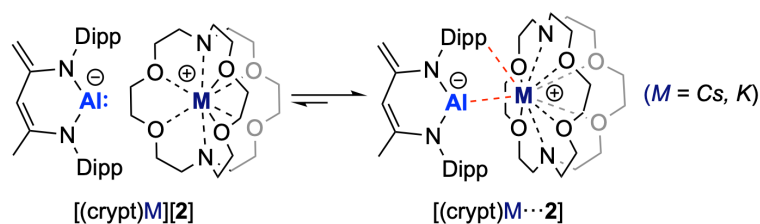
This contribution presents the first monomeric caesium and potassium (M) examples of the negatively charged alumanyl anion **2** derived from the well-known Roesky's monovalent aluminium compound (BDI)Al<sup>I</sup> **1** (Figure 1B, BDI =  $\beta$ -diketiminato).<sup>[10]</sup> The “*naked*” alumanyl **2** exhibits an unusual dynamic ion-pairing behaviour in solution with 2.2.2-cryptand (crypt) caesium and potassium counterions, characterised by the fast exchange between charge-separated [(crypt)M][**2**] and contacted alumanyl pairs [(crypt)M $\cdots$ **2**]. Besides, the alumanyl anion **2** forms robust contacted aggregates with crown ether (18-cr-6) containing cations, [(18-cr-6)M $\cdots$ **2**], that are persistent in solution. We demonstrate differences in stability and reactivity with dihydrogen (H<sub>2</sub>) related to the labile behaviour of the “*naked*” alumanyl **2** that strongly depends on the nature of the alkali metal counterion.

Treating the monovalent compound (BDI)Al<sup>I</sup> **1** with either CsHMDS or KHMDS (HMDS = bis(trimethylsilyl)amide) in the presence of the encapsulating crypt ligand resulted in clean deprotonation of one methyl from the backbone of the  $\beta$ -diketiminato ligand in toluene at room temperature. This methodology allowed direct access to charge-separated species of the alumanyl anion **2**, particularly the separated ion pairs (SIP) [(crypt)M][**2**] (M = Cs and K, Scheme 1). Switching to the less bulky crown ether, 18-cr-6, deprotonation under the same conditions resulted in the contacted monomeric pair (CMP) species [(18-cr-6)M $\cdots$ **2**] (M = Cs and K, Scheme 1). While contacted alumanyls [(18-cr-6)M $\cdots$ **2**] are soluble in toluene, the separated species [(crypt)M][**2**] needed the more polar fluorobenzene. We attempted the preparation of lighter separated sodium and lithium pairs of **2** using NaHMDS or LiHMDS and crypt; however, rapid decomposition of the alumanyl systems was observed. The observed increased stability for the heavier alkali metal charge-separated alumanyls [(crypt)M][**2**] (M = Cs  $\sim$  K > Na  $\sim$  Li) contrasts with that recently reported for the contacted dimeric pairs (CDP) [M $\cdots$ **2**]<sub>2</sub> (decreasing from Li to Cs).<sup>[4d]</sup> This different alkali metal stabilising effect emphasises the importance of the aggregation state and the diverse M $\cdots$ Al and M $\cdots$  $\pi$ (ancillary-arene) interactions that are established for given alumanyl ligand set (Lewis donor/ancillary groups). In addition, we did not observe C–H, C–C or C–F activations with toluene, benzene or fluorobenzene, in contrast to the reactivities reported for related contacted alumanyls<sup>[3b, 9, 4c, 4d]</sup> or monovalent aluminium systems.<sup>[11]</sup>



**Scheme 1.** Synthesis of charge-separated [(crypt)M][**2**] and contacted alumanyls [(18-cr-6)M $\cdots$ **2**] (M = Cs, K).

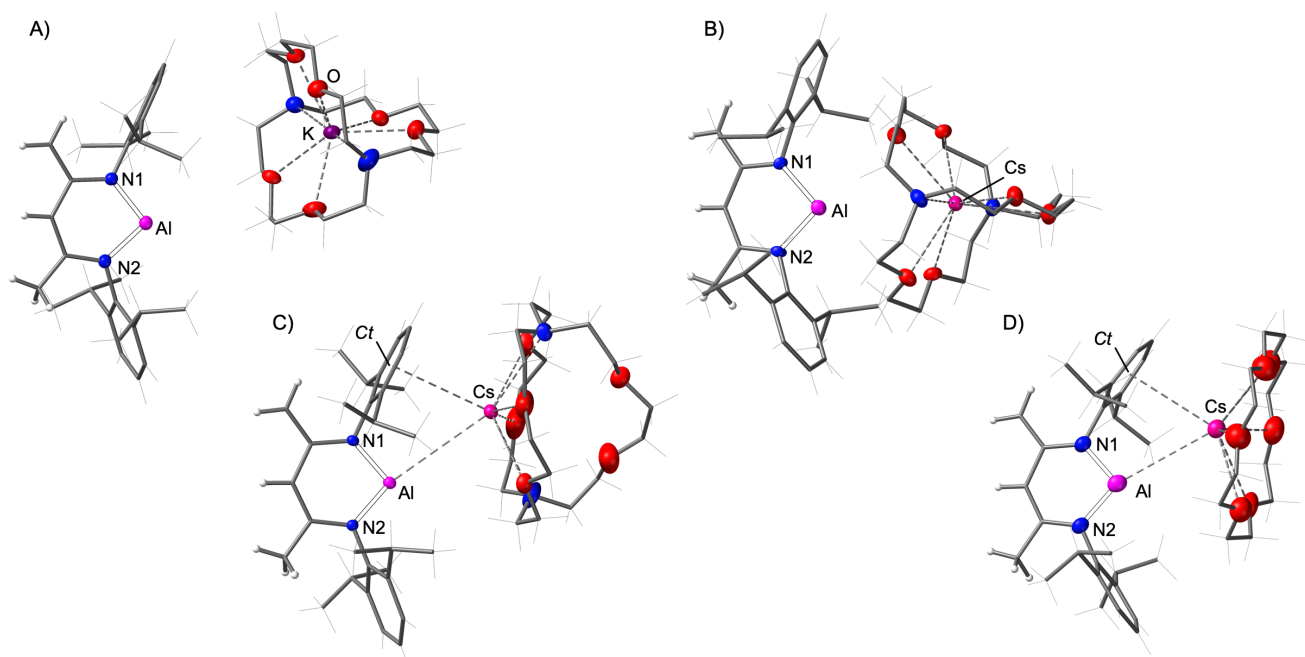
As for all other aluminyls reported to date, these aluminyls are  $^{27}\text{Al}$  NMR silent.<sup>[12]</sup>  $^1\text{H}$  NMR data in aromatic solvents (toluene and fluorobenzene) mirrors the asymmetry of the aluminyl **2** skeleton with two distinct sets of Dipp resonances (Dipp = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ ). The new methylene backbone  $\text{CH}_2$  resonates as two characteristic doublets with comparable chemical shifts for  $[(\text{crypt})\text{M}][\mathbf{2}]$  and  $[(18\text{-cr-6})\text{M}\cdots\mathbf{2}]$  aluminyls (range  $\delta$  3.36-3.69 and 2.60-2.84,  $J \sim 2$  Hz).  $^{133}\text{Cs}$  NMR spectroscopic analyses reveal a broad resonance for  $[(\text{crypt})\text{Cs}][\mathbf{2}]$  that is at a lower field chemical shift of  $\delta$  191.5 compared to  $\delta$  19.6 in  $[(18\text{-cr-6})\text{Cs}\cdots\mathbf{2}]$ . The  $\delta(^{133}\text{Cs})$  reflects a prominent  $\text{Cs}\cdots\text{Al}$  interaction between the negatively charged aluminyl **2** and Cs in the contacted ion pair  $[(18\text{-cr-6})\text{Cs}\cdots\mathbf{2}]$  compared to the separated aluminyl  $[(\text{crypt})\text{Cs}][\mathbf{2}]$ . Diffusion-Ordered NMR Spectroscopy (DOSY) provided insightful data about the solution state of these aluminyls. The contacted ion pair aluminyls  $[(18\text{-cr-6})\text{M}\cdots\mathbf{2}]$  diffuse as single species with diffusion coefficient  $D$  and MW values agreeing with a contacted ion pair persistent in toluene solution.<sup>[13]</sup> However, the aluminyl **2** exhibits an unusual dynamic solution behaviour when in the form of charge-separated species  $[(\text{crypt})\text{M}][\mathbf{2}]$ . Each charge-separated aluminyl diffuse as two species in fluorobenzene solution with  $D$  values of 4.91/5.19 and 5.07/4.62 ( $\times 10^{-10}$   $\text{m}^2/\text{s}$ ) for the  $(\text{crypt})\text{M}^+$ /aluminyl counterparts in  $[(\text{crypt})\text{Cs}][\mathbf{2}]$  and  $[(\text{crypt})\text{K}][\mathbf{2}]$ , respectively. Interestingly, the measured  $D$  values average to MW of aggregation states that are intermediate between charge-separated (SIP) and contacted monomeric pairs (CMP). These data denote an ongoing SIP-CMP ion-pairing equilibrium between monomers  $[(\text{crypt})\text{M}][\mathbf{2}] \rightleftharpoons [(\text{crypt})\text{M}\cdots\mathbf{2}]$  that is slightly shifted towards the contacted pairs in both (Scheme 2).<sup>[13]</sup>  $^1\text{H}$  VT NMR studies suggested this is a fast dynamic process in the NMR time scale, and we observed average chemical shifts in the temperature range of 243-298K for both systems. In this context, most of the reported dimeric aluminyls retain their contacted or separated structures in solution.<sup>[2, 8, 4c]</sup> Only a monomer-dimer equilibrium has recently been observed in benzene solution involving contacted species.<sup>[4d]</sup> Nevertheless, this is an intriguing and unprecedented solution behaviour involving charge-separated aluminyl anions. It shows the labile nature of “naked” aluminyl anions with their counterions through monomeric species in solution for the first time, influencing their stability and reactivity (*vide infra*).



**Scheme 2.** Dynamic ion-pairing behaviour of the aluminyl anion **2** switching between charge-separated  $[(\text{crypt})\text{M}][\mathbf{2}]$  and monomeric contacted pair  $[(\text{crypt})\text{M}\cdots\mathbf{2}]$  species ( $M = \text{Cs}, \text{K}$ ).

Single crystal X-ray diffraction data<sup>[14]</sup> disclose both  $[(\text{crypt})\text{Cs}][\mathbf{2}]$  and  $[(\text{crypt})\text{K}][\mathbf{2}]$  as separated ion pairs (Figure 2A-B). Moreover, the contacted ion pair  $[(\text{crypt})\text{Cs}\cdots\mathbf{2}]$ , suggested to co-exist with  $[(\text{crypt})\text{Cs}][\mathbf{2}]$  in solution by DOSY NMR studies, was successfully trapped and crystallographically characterised (Figure 2C). The nearest K metal is far from forming an interaction with Al (distance  $> 7$  Å) in the solid-state structure of

[(crypt)K][**2**] (see Figure 2A). However, this interionic separation is noticeably shorter for [(crypt)Cs][**2**] with a Cs to Al distance of  $\sim 5.20$  Å ( $\sum_{cov} = 3.24$  and  $3.65$  Å, for K/Al and Cs/Al,<sup>[15]</sup> respectively), denoting an increase in the Coulomb interaction between these counterions. As a result, the aluminyl **2** squeezes in through an open face of the [(crypt)Cs]<sup>+</sup> cation and approaches towards the Cs atom (Figure 2B). Therefore, [Cs(crypt)][**2**] should be considered a charge-separated aluminyl anion with an additional long-range stabilising electrostatic attractive interaction. This effect is maximised in the structure of the contacted pair [(crypt)Cs⋯**2**] (Figure 2C), where **2** has forced the Cs out from the cryptand cage, enhancing the formation of a Cs⋯Al contact (distance of  $4.109(1)$  Å). The Cs⋯Al distance is comparable to the longest Cs⋯Al contacts found in related caesium dimeric contacted aluminyls (range  $3.813(1)$ - $4.034(9)$  Å).<sup>[4c, 4d]</sup> In addition, the molecular structure of [(crypt)Cs⋯**2**] shows (crypt)Cs⋯ $\pi$ (arene) contacts with one ancillary Dipp group (Cs⋯Ct distance of  $4.11$  Å), slightly longer than in the dimers mentioned above (range  $3.247(1)$ - $3.930(3)$  Å).<sup>[4c, 4d]</sup> This abstraction of Cs from the crypt ligand and the formation of Cs⋯anion interactions has also been observed to be key in other multiply-charged negative ions<sup>[16]</sup> and allowing charge-disproportionation processes between counterions.<sup>[17]</sup> Dissolving isolated crystals of [Cs(crypt)][**2**] resulted with the same NMR data (<sup>1</sup>H, <sup>133</sup>Cs and DOSY) than using a mixture of crystals of [Cs(crypt)][**2**] and [(crypt)Cs⋯**2**]. This provides further support for these species rapidly equilibrating in solution according to [Cs(crypt)][**2**]  $\rightleftharpoons$  [(crypt)Cs⋯**2**].



**Figure 2.** Molecular structures of **A**) [(crypt)K][**2**], **B**) [(crypt)Cs][**2**], **C**) [(crypt)Cs⋯**2**] and **D**) [(18-cr-6)Cs⋯**2**]. All hydrogen atoms except those at the backbone of the aluminyl anion **2** and minor disordered components are omitted for clarity. Heteroatoms are shown with thermal ellipsoids at a 35% probability. Ct = centroid.

The aluminyl [(18-cr-6)Cs⋯**2**] crystallised the retention of its solution contacted pair aggregation state (Figure 2D). Akin to [(crypt)Cs⋯**2**], the Cs metal is interacting with both the ancillary Dipp arene and the Al metal centre, allowing an asymmetric molecular array. The crystal structure of [(18-cr-6)Cs⋯**2**] has a Cs⋯Al distance ( $\sim 3.71$

Å) that is close to the sum of the covalent radii ( $\sum_{cov} = 3.65$  Å for Cs-Al),<sup>[15]</sup> and a Cs $\cdots\pi$ (arene) contact of  $\sim 3.62$  Å.<sup>[18]</sup> These metrics indicate a more robust interaction of the negatively charged aluminyll **2** with the less bulky [(18-cr-6)Cs]<sup>+</sup> to [(crypt)Cs]<sup>+</sup>, reminiscent of the retention of the contacted ion pair [(18-cr-6)M $\cdots$ **2**] aggregation state and the lability of [(crypt)M $\cdots$ **2**] in solution (*vide supra*).

The dimeric aluminylls [(NON<sup>Xanthene</sup>)Al $\cdots$ K]<sub>2</sub> and [(OSiN<sup>Dipp</sup>)Al $\cdots$ M]<sub>2</sub> can react with the non-polar dihydrogen (H<sub>2</sub>), forming bimetallic dihydride Al<sup>III</sup> species, [(NON<sup>Xanthene</sup>)Al(H)<sub>2</sub>(K)]<sub>2</sub> (2 bar, 5 days, room temperature) or [(OSiN<sup>Dipp</sup>)Al(H)<sub>2</sub>M]<sub>2</sub> (1.5 bar, 100°C;  $t_{1/2} = 1.5$  (Li), 6 (Na), 12 (K) days;  $t_{1/2} \sim 50\%$  conversion).<sup>[2, 8]</sup> However, the activation of H<sub>2</sub> by monomeric aluminylls involving charge-separated species has not been explored experimentally yet.<sup>[19]</sup> To address this query and better understand the reactivity of the distinct monomeric aggregates of the metal anion **2**, we have monitored their reactivity with H<sub>2</sub> gas by *in-situ* <sup>1</sup>H NMR spectroscopy. We found that the contacted aluminylls [(18-cr-6)M $\cdots$ **2**] do not react with H<sub>2</sub> gas (1.5 bar) at room temperature.<sup>[13]</sup> Instead, we recovered unchanged [(18-cr-6)M $\cdots$ **2**] aluminylls. This result compares with a persistent Cs $\cdots$ Al interaction of **2** with [(18-cr-6)M]<sup>+</sup> cations shutting down the reactivity of the aluminyll **2**. Interestingly, the anion **2** exhibit distinct reactivity with [(crypt)M]<sup>+</sup> counterions. While the labile potassium [(crypt)K]<sup>+</sup> congener of **2** quickly degrades with H<sub>2</sub> (1.5 bar, room temperature), the aluminyll **2** cleanly activates H<sub>2</sub> gas when aggregated with [(crypt)Cs]<sup>+</sup> ions, forming the corresponding the hydride derivative [(crypt)Cs][**2**(H)<sub>2</sub>] (60%, 24 h) under the same reaction conditions in fluorobenzene.<sup>[20]</sup> The higher stability of caesium vs potassium cryptand-derivatives of **2** is reminiscent of the excellent predisposition of the softer [(crypt)Cs]<sup>+</sup> cation to engage in distinctive stabilising Cs $\cdots$ Al interionic interactions with **2**, in contrast to [(crypt)K]<sup>+</sup>; thus, their distinct contacted pair [(crypt)Cs][**2**] structures (Figure 2A vs 2B). Akin to [(18-cr-6)M $\cdots$ **2**], **2** would not react with H<sub>2</sub> when forming the contacted pairs [(crypt)M $\cdots$ **2**]. Still, [(crypt)M $\cdots$ **2**] will act as a reservoir of reactive charge-separated aluminyll anions **2** through labile Cs $\cdots$ Al/Cs $\cdots\pi$ (arene) interactions and, at the same time, provide some enhancement in stability to the aluminyll **2**.

For comparison, we have also reacted the neutral monovalent (BDI)Al<sup>I</sup> **1** compound with H<sub>2</sub> gas under the same reaction conditions. We found that **1** adds H<sub>2</sub> (1.5 bar, room temperature) to give a reaction mixture of the aluminohydrides (BDI)Al(H)<sub>2</sub> **3** (35%) and [(BDI)(H)Al]<sub>2</sub> **4** (50%), and unreacted **1** (15%) after 48 h.<sup>[13]</sup> While **3** formally results from adding H<sub>2</sub> to **1**, the dimer **4** is formed as the main product by the oxidative addition of an Al–H bond from **3** to **1**, as previously shown.<sup>[21]</sup> In contrast, we have not observed a similar Al–H addition to the anionic **2**. Therefore, the charge-separated aluminyll **2**, in labile interaction with [(crypt)Cs]<sup>+</sup> counterions, exhibits higher selectivity, stability and reactivity towards H<sub>2</sub> than its neutral congener **1** and any other known aluminyll systems. These results emphasise the important consequences of understanding monomer formation and solution behaviour on the stability and reactivity of aluminylls.

In conclusion, we have prepared unique examples of monomeric caesium and potassium derivatives of the “naked” alumanyl anion **2**. We demonstrate the dynamic nature of the alumanyl **2** in solution, easily switching between charge-separated and contacted pairs with cryptand-encapsulated caesium and potassium cations [(crypt)M]<sup>+</sup>. The charge-separated alumanyl **2** activates H<sub>2</sub> to form the corresponding dihydroaluminate **2**(H)<sub>2</sub> when stabilised with labile [(crypt)Cs]<sup>+</sup> cations. In contrast, **2** is unstable with [(crypt)K]<sup>+</sup> ions, denoting the pivotal role of the caesium counterions in stabilising highly reactive “naked” alumanyls with H<sub>2</sub>. The formation of persistent monomeric contacted pairs of **2** with [(18-cr-6)M]<sup>+</sup> cations inhibit reactivity with H<sub>2</sub>. These observations about the lability of “naked” alumanyls represent a significant advance in understanding their solution behaviour and stability that may provide a source of further anionic reactivities.

**Electronic Supplementary Information (ESI):** Experimental procedures and characterisation data for all new compounds, including crystallographic data in CIF format (CCDC deposition numbers: 2205103, 2205104, 2205105, 2205106, 2205107 and 2205559).

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## References

- [1] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2021**, *60*, 1702-1713; *Angew. Chem.* **2021**, *133*, 1726-1737.
- [2] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature* **2018**, *557*, 92-95.
- [3] a) R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles, *Angew. Chem. Int. Ed.* **2019**, *58*, 1489-1493; *Angew. Chem.* **2019**, *131*, 1503-1507; b) S. Grams, J. Eyslein, J. Langer, C. Färber, S. Harder, *Angew. Chem. Int. Ed.* **2020**, *59*, 15982-15986; *Angew. Chem.* **2020**, *132*, 16116-16120; c) K. Koshino, R. Kinjo, *J. Am. Chem. Soc.* **2020**, *142*, 9057-9062; d) S. Kurumada, S. Takamori, M. Yamashita, *Nat. Chem.* **2020**, *12*, 36-39; e) R. J. Schwamm, M. P. Coles, M. S. Hill, M. F. Mahon, C. L. McMullin, N. A. Rajabi, A. S. S. Wilson, *Angew. Chem. Int. Ed.* **2020**, *59*, 3928-3932; *Angew. Chem.* **2020**, *132*, 3956-3960.
- [4] a) M. J. Evans, M. D. Anker, M. G. Gardiner, C. L. McMullin, M. P. Coles, *Inorg. Chem.* **2021**, *60*, 18423-18431; b) M. M. D. Roy, J. Hicks, P. Vasko, A. Heilmann, A.-M. Baston, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2021**, *60*, 22301-22306; *Angew. Chem.* **2021**, *133*, 22475-22480; c) 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; d) S. Grams, J. Mai, J. Langer, S. Harder, *Dalton Trans.* **2022**, *51*, 12476-12483.
- [5] T. X. Gentner, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2021**, *60*, 9247-9262; *Angew. Chem.* **2021**, *133*, 9331-9348.
- [6] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *J. Am. Chem. Soc.* **2019**, *141*, 11000-11003.

- [7] R. J. Schwamm, M. S. Hill, H.-Y. Liu, M. F. Mahon, C. L. McMullin, N. A. Rajabi, *Chem. Eur. J.* **2021**, *27*, 14971-14980.
- [8] M. J. Evans, M. D. Anker, C. L. McMullin, S. E. Neale, M. P. Coles, *Angew. Chem. Int. Ed.* **2021**, *60*, 22289-22292; *Angew. Chem.* **2021**, *133*, 22463-22466.
- [9] J. Hicks, P. Vasko, A. Heilmann, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2020**, *59*, 20376-20380; *Angew. Chem.* **2020**, *132*, 20556-20560.
- [10] C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem. Int. Ed.* **2000**, *39*, 4274-4276; *Angew. Chem.* **2020**, *112*, 4444-4446.
- [11] a) T. Chu, Y. Boyko, I. Korobkov, G. I. Nikonov, *Organometallics* **2015**, *34*, 5363-5365; b) M. R. Crimmin, M. J. Butler, A. J. P. White, *Chem. Commun.* **2015**, *51*, 15994-15996; c) O. Kysliak, H. Görls, R. Kretschmer, *Chem. Commun.* **2020**, *56*, 7865-7868.
- [12] Observing an alumanyl resonance in the  $^{27}\text{Al}$  NMR has been difficult for all known alumanyl systems, and no resonances have been reported yet.
- [13] See Electronic Supporting Information for complete experimental data.
- [14] CCDC deposition numbers with the supplementary crystallographic data for this paper: 2205103 for [(crypt)K][**2**], 2205104 for [(crypt)Cs][**2**], 2205105 for [(crypt)Cs]·**2**, 2205106 for [(18-cr-6)Cs]·**2**, 2205559 for [(crypt)K][**2**(H)**2**] and 2205107 for [(crypt)Cs][**2**(H)**2**]. The joint Cambridge Crystallographic Data Centre and FIZ Karlsruhe provides these data free of charge.
- [15] B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832-2838.
- [16] D. I. Nazarov, M. G. Andronov, A. V. Kuzmin, S. S. Khasanov, E. I. Yudanov, A. F. Shestakov, A. Otsuka, H. Yamochi, H. Kitagawa, D. V. Konarev, *Dalton Trans.* **2021**, *50*, 15620-15632.
- [17] D. V. Konarev, A. V. Kuzmin, S. S. Khasanov, A. F. Shestakov, D. I. Nazarov, A. Otsuka, H. Yamochi, H. Kitagawa, R. N. Lyubovskaya, *Eur. J. Inorg. Chem.* **2020**, *2020*, 2615-2623.
- [18] Averaged distances are given between the disordered components in the molecular structure of [(18-cr-6)Cs]·**1**. See Electronic Supporting Information for complete experimental data.
- [19] N. Villegas-Escobar, A. Toro-Labbé, H. F. Schaefer Iii, *Chem. Eur. J.* **2021**, *27*, 17369-17378.
- [20] The dihydride aluminate compounds [(crypt)K][**2**(H)**2**] and [(crypt)Cs][**2**(H)**2**] were prepared and fully characterised, including NMR and IR (Al–H stretchings at 1685 and 1739  $\text{cm}^{-1}$ ) spectroscopies, and their molecular structures were studied crystallographically. See Electronic Supporting Information for full experimental details.
- [21] T. Chu, I. Korobkov, G. I. Nikonov, *J. Am. Chem. Soc.* **2014**, *136*, 9195-9202.