"Contacted" vs "separated" aluminyls: Dynamic alkali metal effects in H_2 activation

Hellen Videa and Antonio J. Martínez-Martínez*

Laboratory of Supramolecular Organometallic and Main Group Chemistry
CIQSO-Center for Research in Sustainable Chemistry and Department of Chemistry
University of Huelva, Campus El Carmen, ES-21007 Huelva (Spain)
E-mail: antonio.martinez@ciqso.uhu.es

Website: https://uhu-ciqso.es/supramolecular-organometallic-chemistry-laboratory/
Twitter: @GroupMartinez

Keywords: *aluminium, aluminyl anion, caesium, potassium, dihydrogen activation.*

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 charge-separated and contacted species of the aluminyl anion* $[(BDI')Al^{I}]^{-}$ *(BDI' =* $H_2C{=}C(NAr){-}C(H){=}C(Me){-}NAr$*; Ar = 2,6-*$iPr_2C_6H_3$*) occurs in solution with* $[(L)M]^{+}$ *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 experimentally probed by NMR spectroscopy, including DOSY NMR, and X-ray crystallography, which provide intimate details of the ion-pairing reversibility and ionic separations. The lability in these aluminyls is important for their stability and reactivity with the non-polar* H_2*.*

Aluminyls have become avant-garde main group compounds featuring a new class of low-valent Al^{I} anions.[1] 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^{I} metal centre $[R_3Al^{I}]^{-}$ anchored to a flexible xanthene bis(amido) ligand, $[(NON^{Xant})Al^{I}]^{-}$ **I** (Figure 1A).[1a] Soon after that, two-coordinated aluminyl examples $[R_2Al^{I}]^{-}$ were also prepared.[2] These $[Al^{I}]^{-}$ anions are typically obtained by the two-electron reduction of neutral Al^{III}–halogen precursors with an excess of an alkali metal (M) or a suitable MC_8 reagent. Alternatively, they can also be accessed from Al^{II} or Al^{I} species.[2b-e, 3] Since the stabilisation of these highly reactive anions is succeeded by interaction with highly electropositive secondary metals,[4] examples involving aluminyls with different alkali metals have been reported.[3] The majority of the alkali metal aluminyls have a preference for aggregating as contacted species, either dimeric or monomeric ion pairs, through bimetallic M···Al interactions, and additionally, M···π(arene) contacts with ancillary aromatic groups. On the other hand, examples of alkali metal-separated aluminyls lacking these stabilising interactions are very scarce. So far, only four examples of charge-separated aluminyls systems are known (Figure 1A): the xanthene $[(NON^{Xantene})Al]^{-}$ **I**,[5] (alkyl)(amido) $[(CN^{Ad})Al]^{-}$ **II**,[2c, 6] bis(amido) $[(SiN^{Dipp})Al]^{-}$ **III**,[7] and $[(OSiN^{Dipp})Al]^{-}$ **VI** aluminyls.[3a, 8] These are exceptional examples of highly reactive "*naked*" $[Al^{I}]^{-}$ aluminyl anions.

Interestingly, charge-separated aluminyls exhibit divergent anionic reactivity with respect to their contacted derivatives. For example, the contacted dimeric pair $[(NON^{Xanthene})Al\cdots K]_2$ of **I**,[1a, 9] and also other dimeric aluminyls,[3c, 3d] selectively activate C–H bonds of arenes under thermal conditions. However, charge-separated aluminyls can be involved in more challenging transformations, *i.e.* the "*naked*" anion $[(NON^{Xanthene})Al]^{-}$ **I** reversibly cleaves a C–C bond of benzene at room temperature.[5]

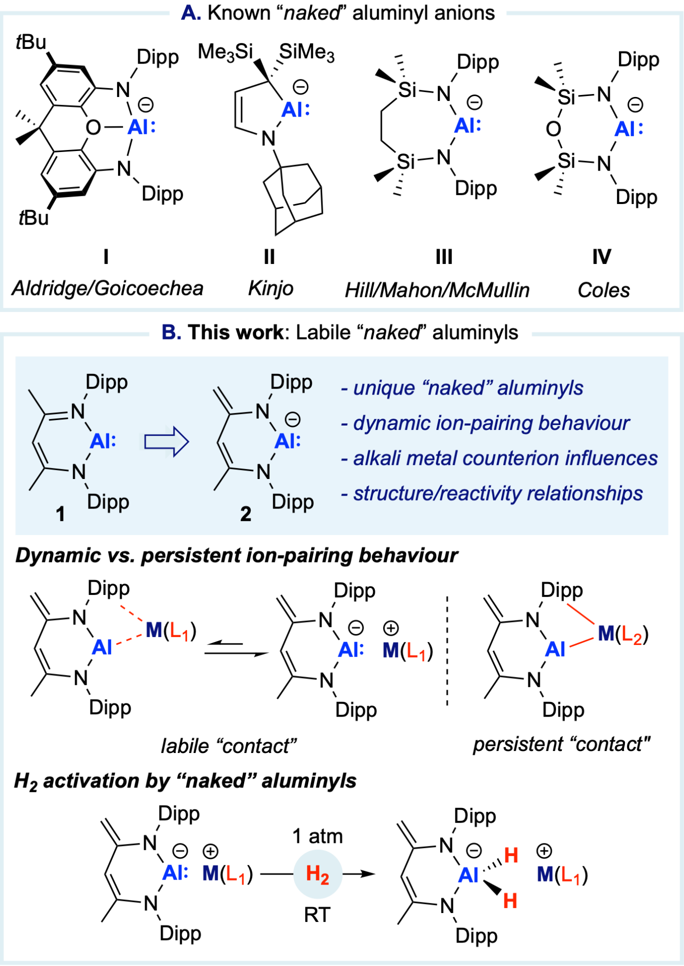
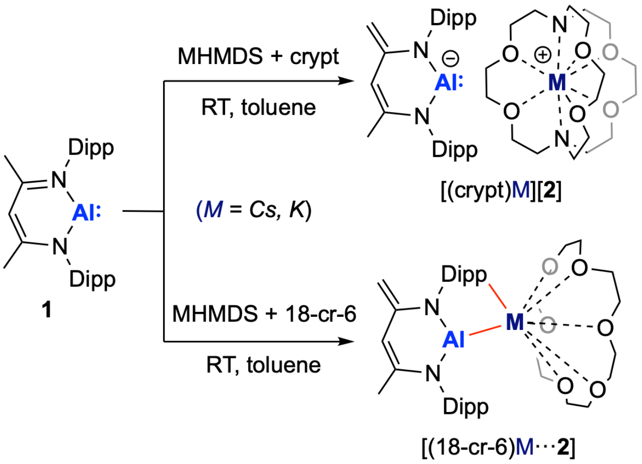


Figure 1. A) State-of-the-art "*naked*" aluminyls (cation = $[(crypt)K]^{+}$ for **I**; $[(12\text{-}cr\text{-}6)K]^{+}$ for **II**; $[(crypt)K]^{+}$ and $[(18\text{-}cr\text{-}6)_{1.5}K]^{+}$ for **III**; $[(tmeda)_2Li]^{+}$, $[(crypt)Na]^{+}$ and $[(crypt)K]^{+}$ for **IV**. **B**) This work: Labile "*naked*" aluminyls **2**, ion-pairing behaviour and activation of H_2 (M = Cs, K; L_1 = crypt, L_2 = 18-cr-6, Dipp = 2,6-$^{i}Pr_2C_6H_3$).

It is then clear that the stability and reactivity 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 alkali metal interactions and the solution state of contacted aluminyl pairs.[1b] By contrast, little is known about these interactions on charge-separated aluminyls in solution, often assumed to be marginal or absent.

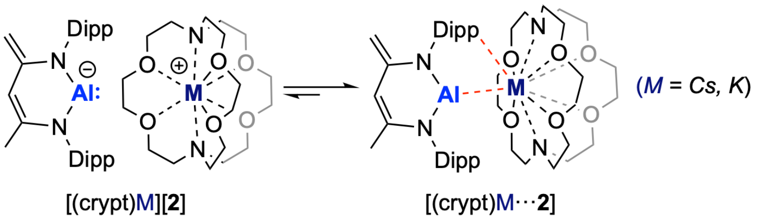
This contribution presents the first monomeric caesium and potassium (M) examples of the negatively charged aluminyl anion **2** derived from the well-known Roesky's monovalent aluminium compound (BDI)Al^{I} **1** (Figure 1B, BDI = *β*-diketiminate).[10] Furthermore, the "*naked*" aluminyl **2** exhibits 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 aluminyl pairs [(crypt)M···**2**]. Besides, the aluminyl anion **2** forms robust contacted aggregates with crown ether (18-cr-6) containing cations, [(18-cr-6)M···**2**], that are persistent in solution. We demonstrate differences in stability and reactivity with dihydrogen (H_2) related to the labile ion-pairing behaviour of the "*naked*" aluminyl **2** that strongly depends on the nature of the interactions with the alkali metal counterion.

Treating the monovalent compound (BDI)Al^{I} **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 *β*-diketiminate ligand in toluene at room temperature. This methodology[11] allowed direct access to charge-separated species of the aluminyl anion **2**, particularly the separated ion pairs [(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 species [(18-cr-6)M···**2**] (M = Cs and K, Scheme 1). While contacted aluminyls [(18-cr-6)M···**2**] are soluble in toluene, the separated species [(crypt)M][**2**] needed the more polar fluorobenzene. We have attempted the preparation of lighter separated sodium and lithium pairs of **2** using NaHMDS or LiHMDS and crypt; however, rapid decomposition of the aluminyl systems was observed. The increased stability for the heavier alkali metal charge-separated aluminyls [(crypt)M][**2**] (M = Cs ~ K > Na ~ Li) contrasts with the recently contacted dimeric pairs $[M\cdots\mathbf{2}]_2$ (decreasing from Li to Cs).[3d] This different alkali metal stabilising effect emphasises the importance of the aggregation state and the diverse M···Al and M···π(ancillary-arene) interactions that are established for a given aluminyl ligand set (Lewis donor/ancillary groups). In addition, we have not observed C–H, C–C or C–F activations with toluene, benzene or fluorobenzene, in contrast to other reported reactivities for related contacted aluminyls[2b, 9, 3c, 3d] or monovalent aluminium systems.[12]



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

As for all the other reported aluminyls to date, these anions are ^{27}Al NMR silent.[13] ^{1}H NMR data in aromatic solvents (toluene and fluorobenzene) mirror the asymmetry of the aluminyl skeleton of **2** with two sets of Dipp resonances (Dipp = 2,6-$^{i}Pr_2C_6H_3$). The new methylene backbone CH_2 resonates as two characteristic doublets with comparable chemical shifts for [(crypt)M][**2**] and [(18-cr-6)M···**2**] aluminyls (range δ 3.36-3.69 and 2.60-2.84, $J \sim 2$ Hz). ^{133}Cs NMR spectroscopic analyses reveal a broad resonance for [(crypt)Cs][**2**] that is at a lower field chemical shift of δ 191.5 compared to δ 19.6 in [(18-cr-6)Cs···**2**]. The $\delta(^{133}\mathrm{Cs})$ reflects a prominent Cs···Al interaction between the negatively charged aluminyl **2** and Cs in the contacted ion pair [(18-cr-6)Cs···**2**] compared to the separated aluminyl [(crypt)Cs][**2**]. Diffusion-Ordered NMR Spectroscopy (DOSY) provided insightful data about the solution state of these aluminyls. The contacted caesium and potassium ion pair aluminyls [(18-cr-6)M···**2**] diffuse as single species with diffusion coefficient *D* values of 4.04 and 4.31 ($\times 10^{-10}$ m^2/s), respectively, agreeing with MW values of these contacted ion pairs persisting in toluene solution.[14] However, the aluminyl **2** exhibits an unusual hydrodynamic solution behaviour when in the form of charge-separated species [(crypt)M][**2**]. Each charge-separated aluminyl diffuses as two species in fluorobenzene solution with *D* values of 4.91/5.19 and 5.07/4.62 ($\times 10^{-10}$ m^2/s) for the (crypt)M$^+$/aluminyl counterparts in [(crypt)Cs][**2**] and [(crypt)K][**2**], respectively. Interestingly, the measured *D* values relate to MW of aggregation states that are intermediate between charge-separated and contacted monomeric pairs. These data denote an ongoing separated-contacted aluminyl equilibrium between monomers [(crypt)M][**2**] ⇄ [(crypt)M···**2**] that is slightly shifted towards the contacted pairs for the caesium and potassium congeners (Scheme 2).[14] We observed average chemical shifts in the ^{1}H VT NMR data (temperature range 248-298 K) for both systems, suggesting that this is a fast dynamic process in the NMR time scale.[14] In this context, while most of the reported charge-separated aluminyls retain their unconnected ionic structures in solution,[5, 2c, 8, 7] only the lighter lithium-separated derivative [Li(tmeda)$_2$][(OSiN$^{\mathrm{Dipp}}$)Al]] seemed to co-exist with contacted species through discoordination of a tmeda ligand.[3a] Nevertheless, it is an intriguing behaviour involving charge-separated aluminyl anions of **2** without losing a ligand. It provides proof of the dynamic solution nature of "*naked*" aluminyl anions with their counterions through labile contacted monomeric species that influence their stability and reactivity (*vide infra*).



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

Single crystal X-ray diffraction data[15] disclose both [(crypt)K][**2**][14] and [(crypt)Cs)][**2**] (Figure 2A) as separated ion pairs. Moreover, the contacted ion pair [(crypt)Cs···**2**], which co-exists in equilibrium with [(crypt)Cs)][**2**] by DOSY NMR studies, was successfully trapped and crystallographically characterised (Figure 2B). The nearest K metal is far from forming an interaction with Al (distance > 7 Å) in the solid-state structure of [(crypt)K][**2**].[14] However, this interionic separation is noticeable short for [(crypt)Cs][**2**] with a Cs to Al distance of 5.36 Å ($\sum_{cov}$ = 3.24 and 3.65 Å, for K/Al and Cs/Al,[16] respectively), denoting an increase in the Coulomb interaction between these counterions (Figure 2A). As a result, the aluminyl **2** squeezes in through an open face of the [(crypt)Cs]$^{+}$ cation and approaches towards the Cs atom. Therefore, [(crypt)Cs][**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 2B), 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).[3c, 3d] In addition, the molecular structure of [(crypt)Cs···**2**] shows (crypt)Cs···π(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).[3c, 3d] This abstraction of Cs from the crypt ligand and the formation of Cs···anion interactions have also been observed to be key in other multiply-charged negative ions,[17] allowing charge-disproportionation processes between counterions.[18] Dissolving a small sample of crystals of [(crypt)Cs][**2**] resulted in the same NMR data (^{1}H, ^{133}Cs and DOSY) as using a mixture of crystals of [(crypt)Cs][**2**] and [(crypt)Cs···**2**]. This observation provides further support to the fact that these species reach equilibrium rapidly in solution according to [(crypt)Cs][**2**] ⇄ [(crypt)Cs···**2**].

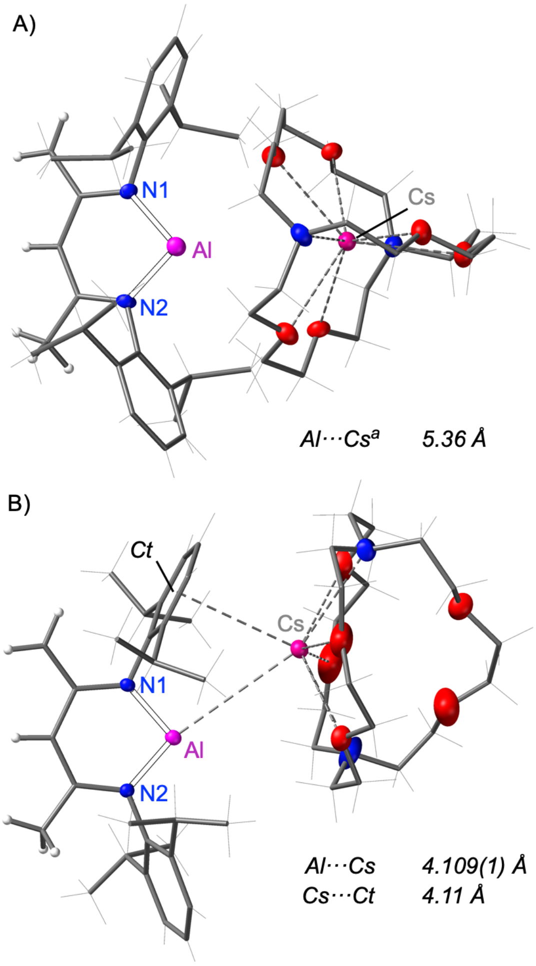


Figure 2. Molecular structures of **A**) [(crypt)Cs][**2**] and B) [(crypt)Cs···**2**]. All hydrogen atoms except those at the backbone of the aluminyl anion **2** are omitted for clarity. Heteroatoms are shown with thermal ellipsoids at a 35% probability. *Ct* = centroid. ^{a} Average interatomic distance between two molecules from the asymmetric unit.

The aluminyl [(18-cr-6)Cs···**2**] crystallised with retention of its solution contacted pair aggregation state (Figure 3). 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 (3.71 Å) that is close to the sum of the covalent radii ($\sum_{cov}$ = 3.65 Å for Cs-Al),[16] and a Cs···π(arene) contact of 3.62 Å.[19] These metrics indicate a more robust interaction of the negatively charged aluminyl **2** with the less bulky [(18-cr-6)Cs]$^{+}$ compared to [(crypt)Cs]$^{+}$ and are reminiscent of the persistent nature of the contacted pair [(18-cr-6)M···**2**] and the lability of [(crypt)M···**2**] in solution.

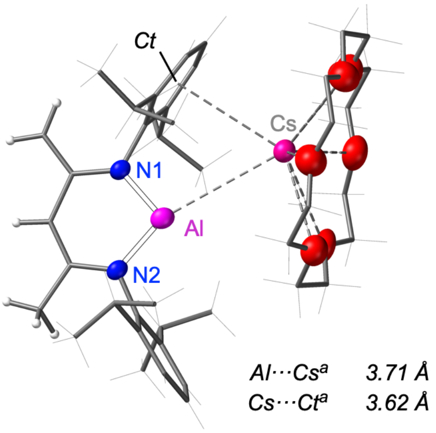


Figure 3. Molecular structure of [(18-cr-6)Cs···**2**]. All hydrogen atoms except those at the backbone of the aluminyl anion **2** and minor disordered components are omitted for clarity. Heteroatoms are shown with thermal ellipsoids at a 35% probability. ^{a} Average distances for two cationic units from the asymmetric unit.

Contacted aluminyls, in particular, the dimeric species [(NON^{Xanthene})Al···K]$_2$ and [(OSiN^{Dipp})Al···M]$_2$, can react with the non-polar dihydrogen (H_2), forming bimetallic dihydride Al^{III} species, [(NON^{Xanthene})Al(H)$_2$(K)]$_2$ (2 bar, 5 days, room temperature) or [(OSiN^{Dipp})Al(H)$_2$M]$_2$ (1.5 bar, 100°C; $t_{1/2}$ = 1.5 (Li), 6 (Na), 12 (K) days; $t_{1/2}$ ~ 50% conversion).[1a, 8] However, the activation of H_2 by monomeric aluminyls involving charge-separated species has not been explored experimentally yet.[20] To address this query and better understanding of the reactivity of the distinct monomeric aggregates of the metal anion **2** (*separated vs contacted*), we have monitored their reactivity with H_2 gas by *in-situ* ^{1}H NMR spectroscopy. We have found that the contacted aluminyls [(18-cr-6)M···**2**] do not react with H_2 gas (1.5 bar, room temperature).[14] Instead, unchanged [(18-cr-6)M···**2**] aluminyls were recovered. This result compares with a persistent Cs···Al interaction of **2** with [(18-cr-6)M]$^+$ cations shutting down the reactivity of the aluminyl **2**. Interestingly, the anion **2** exhibits distinct reactivity with [(crypt)M]$^+$ counterions. While the labile potassium [(crypt)K]$^+$ salt of **2** quickly degrades with H_2 (1.5 bar, room temperature), the aluminyl **2** cleanly activates H_2 gas when aggregated with [(crypt)Cs]$^+$ ions, forming the corresponding dihydroaluminate [(crypt)Cs][**2**(H)$_2$] (60%, 16 h) under the same reaction conditions in fluorobenzene.[21] The higher stability of caesium vs potassium cryptand-derivatives of **2** is reminiscent of the excellent predisposition of the softer [(crypt)Cs]$^+$ cation to engage in distinctive stabilising Cs···Al interionic interactions with **2**, in contrast to [(crypt)K]$^+$, as seen in their distinct molecular structures. Akin to [(18-cr-6)M···**2**], **2** would not react with H_2 when forming the contacted pairs [(crypt)M···**2**], but when free as a charge-separated aluminyl **2**. Still, the contacted species [(crypt)M···**2**] would act as a reservoir of reactive charge-separated aluminyl anions **2** through labile Cs···Al/Cs···π(arene) interactions and, at the same time, provide some enhancement in stability to the aluminyl **2**.

We have also compared the reactivity of the alkali metal-free monovalent (BDI)Al^{I} **1** compound with H_2 gas under the same reaction conditions. **1** adds H_2 (1.5 bar, room temperature) to give a reaction mixture where the neutral dihydro aluminate (BDI)Al(H)$_2$[22] **3** is formed in only 35% yield after 48 hours.[14] Therefore, the charge-separated aluminyl **2,** in labile interaction with [(crypt)Cs]$^+$ counterions, enhances the aluminyl system's stability and increases reactivity towards H_2 compared to other aluminyl systems and its neutral congener **1.** These results emphasise the important consequences of understanding the formation of monomers and their solution behaviour on the stability and reactivity of aluminyls.

In conclusion, we present the preparation of singular examples of monomeric caesium and potassium derivatives of the "*naked*" aluminyl anion **2**. We demonstrate the dynamic nature of the aluminyl **2** in solution, easily switching between charge-separated and contacted pairs with cryptand-encapsulated caesium and potassium cations [(crypt)M]$^+$. The charge-separated aluminyl **2** activates H_2 to form the corresponding dihydroaluminate **2**$(H)_2$ when stabilised with labile [(crypt)Cs]$^+$ cations. In contrast, **2** is unstable with [(crypt)K]$^+$ ions in the presence of H_2, denoting the pivotal role of the caesium counterions in stabilising highly reactive "*naked*" aluminyls. The formation of persistent monomeric contacted pairs of **2** with [(18-cr-6)M]$^+$ cations inhibits reactivity with H_2. These observations about the ion-pairing lability of "*naked*" aluminyls represent a significant advance in understanding their solution behaviour and stability, which may provide a source of new anionic reactivities. Further research is ongoing in our group to exploit these unconventional labile monomeric aluminyls in bond activation chemistry and catalysis.

Supplementary Information (SI): 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).

Acknowledgements: We are grateful to the Spanish Ministry of Science and Innovation, FEDER and the Andalusian Government for financial support of this work (grants numbers EUR2020-112189, PID2019-108292RA-I00 and P20-00373), and the University of Huelva (grant number UHU-202043). AJMM is thankful to the AEI Research State Agency for a *Ramón y Cajal* Research Contract (RYC-2017-21783), and HV also acknowledges for co-financing a predoctoral research contract.

References

[1] a) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature* **2018**, *557*, 92-95; b) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2021**, *60*, 1702-1713; *Angew. Chem.* **2021**, *133*, 1726-1737.

[2] 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. Eyselein, 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.

[3] 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.

[4] T. X. Gentner, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2021**, *60*, 9247-9262; *Angew. Chem.* **2021**, *133*, 9331-9348.

[5] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *J. Am. Chem. Soc.* **2019**, *141*, 11000-11003.

[6] C. Yan, R. Kinjo, *Angew. Chem. Int. Ed.* **2022**, e202211800 doi: *10.1002/anie.202211800*; *Angew. Chem.* **2020**, doi: *10.1002/ange.202211800*.

[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] Attempts to deprotonate **2** with organoalkali metal reagents of the type MCH$(SiMe_3)_2$ (M = K, Cs) failed, resulting in intractable reaction mixtures. However, deprotonation of **2** with KCH$(SiMe_3)_2$ in the absence of donor ligands cleanly affords the dimeric species [K···**2**]$_2$, see: S. Grams, J. Eyselein, J. Langer, C. Färber, S. Harder, *Angew. Chem. Int. Ed.* **2020**, *59*, 15982-15986; *Angew. Chem.* **2020**, *132*, 16116-16120.

[12] 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.

[13] Observing an aluminyl resonance in the ^{27}Al NMR has been difficult for all known aluminyl systems, and no resonances have been reported yet.

[14] See Supporting Information for complete experimental data.

[15] 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 provide these data free of charge.

[16] B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832-2838.

[17] D. I. Nazarov, M. G. Andronov, A. V. Kuzmin, S. S. Khasanov, E. I. Yudanova, A. F. Shestakov, A. Otsuka, H. Yamochi, H. Kitagawa, D. V. Konarev, *Dalton Trans.* **2021**, *50*, 15620-15632.

[18] 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.

[19] Average distances are given between the disordered components in the molecular structure of [(18-cr-6)Cs···**1**]. See Supporting Information for complete experimental data.

[20] N. Villegas-Escobar, A. Toro-Labbé, H. F. Schaefer III, *Chem. Eur. J.* **2021**, *27*, 17369-17378.

[21] 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 cm^{-1}) spectroscopies, and their molecular structures were studied crystallographically. See Supporting Information for full experimental details.

[22] T. Chu, I. Korobkov, G. I. Nikonov, *J. Am. Chem. Soc.* **2014**, *136*, 9195-9202.