Synthesis of a low-valent Al$_4^+$ cluster cation salt

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Low-valent aluminium compounds are very reactive main-group species and have therefore been widely investigated. Since the isolation of a stable molecular Al(I) compound in 1991, [(AlCp$^*$)$_4$] (Cp$^* = $[C$_5$Me$_5$]$_-$), a variety of highly reactive neutral or anionic low-valent aluminium complexes have been developed. By contrast, their cationic counterparts have remained difficult to access. Here, we report the synthesis of [Al(AlCp$^*$)$_3$]$^+$(R$^-$ = C$_6$F$_5^-$) through a simple metathesis reaction between [(AlCp$^*$)$_4$] and Li[Al(OR)$_4$]. Unexpectedly, the [Al(AlCp$^*$)$_3$]$^+$ salt forms a dimer in the solid state and concentrated solutions. Addition of Lewis bases results in monomerization and coordination to the unique formal Al$^+$ atom, giving [(L)Al(AlCp$^*$)$_3$]$^+$ salts where L is hexaphenylcarbodiphosphorane (x = 1), tetramethylethlenediamine (x = 1) or 4-dimethylaminopyridine (x = 3). The Al–Al$_c^+$ bonds in the resulting [(L)Al(AlCp$^*$)$_3$]$^+$ cluster cations can be finely tuned between very strong (with no ligand L) to very weak and approaching isolated [Al(L)$_3$]$^+$ ions (when L is dimethylaminopyridine).

Results and discussion

Synthesis of [Al(AlCp$^*$)$_3$]$^+$(pf$^-$) 1. Numerous previous attempts to synthesize cationic, low-valent aluminium compounds via oxidative or reductive procedures have proven unsuccessful. Hence, [Al(AlCp$^*$)$_3$]$^+$ was chosen as an easily accessible starting material already in the correct oxidation state. Upon reaction of [(AlCp$^*$)$_4$] with Li[pf$^-$] in polar 1,2-difluorobenzene (1,2-DBF; relative permittivity $\varepsilon_{r,295K} = 13.8$), a colour change from yellow to red was observed instantly. The NMR spectra of the reaction mixture indicate the complete consumption of [(AlCp$^*$)$_4$], and crystallization of the reaction mixture yielded [Al(AlCp$^*$)$_3$]$^+$(pf$^-$) (1) as dark-purple crystals (Fig. 2). However, in initial experiments, precipitation of LiCp$^*$ was not observed and the product was contaminated with various, unidentifiable lithium-containing compounds as determined by means of Li NMR spectroscopy (Supplementary Fig. 6). After extraction of the crude product in much less-polar 1,3-difluorobenzene (1,3-DFB; $\varepsilon_{r,303K} = 5.0$), the by-products remained insoluble, and pure [Al(AlCp$^*$)$_3$]$^+$(pf$^-$) (1) could be crystallized in 33% yield as dark-purple crystals from the filtered extract (Fig. 2).

Characterization. Single-crystal X-ray diffraction analysis revealed a trigonal pyramidal geometry at the unique aluminium atom (Fig. 2). Average Al–Al bond lengths in known tetrahedral [(AlR)$_4$] complexes range from 2.602(2) Å ([(AlSi(SiMe$_3$)$_2$)$_4$] (ref. 48)) to 2.770(5) Å ([(Al)$_4$] (ref. 1)). In the molecular structure of 1, the average bond lengths between the AlCp$^*$ moieties and the unique aluminium atom are notably shortened to an average value of 2.546(2) Å (range 2.534(1)–2.575(2) Å). Moreover, the distances between the Al atoms of the AlCp$^*$ fragments are elongated to secondary bonds (range 2.534(1)–2.575(2) Å). The by-products remained insoluble, and pure [Al(AlCp$^*$)$_3$]$^+$(pf$^-$) (1) could be crystallized in 33% yield as dark-purple crystals from the filtered extract (Fig. 2).
fragments can be precluded, and complex 1 could be described as an aluminium cation Al\(^{+}\) accepting three strongly bound neutral AlCp\(^*\) ligands (vide infra). Intriguingly, single-crystal X-ray diffraction revealed the presence of two independent dimer structures of 1 in the unit cell (Fig. 2e). In one of those, a nearly ideal eclipsed conformation of the AlCp\(^*\) units in \([(\text{Cp}^*\text{Al})_3\text{Al}−\text{Al}](\text{AlCp}^*)_2]\) is present with an Al−Al distance of 2.838(2) Å.

This dimer dication \([\text{Al}_2(\text{Cp}^*)_6]^{2+}\), although two electrons in deficit, strongly resembles Schönherr’s neutral \([\text{Ga}_{12}\text{R}_6]\) cluster (R=\(\text{C(SiMe}_3)\)); ref. 13), which he defined as an ideal model for a 2e2c metal–metal bond. Yet, in the second unit, the Al\(_1\) pyramids are tilted against one another, resulting in a longer Al−Al distance of 3.005(2) Å. Related trans-bent structures are observed for main-group donor–acceptor dimers. With both geometries observed in the same crystal, the bonding modes between the two ‘naked’ aluminium atoms need to be energetically comparable.

Solid-state UV–visible spectroscopy revealed the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the dark-purple crystalline solid 1 including the dimer dication as 1.74–1.92 eV (645–725 nm), depending on the method of determination (Supplementary Figs. 17–20). Intriguingly, solutions of 1 in 1,2-DFB and 1,3-DFB show distinct colour changes from yellow to deep purple upon concentration or cooling of the reaction mixture. In the UV–visible spectrum of 1, the colour change is accompanied by the appearance of a broad UV–visible absorption band at wavelength \(\lambda = 564\) nm (Fig. 2f). The experimental spectrum of the purple solution is in line with the time-dependent density functional theory (DFT) computed spectrum of the dimer with the short Al−Al bond as observed in the molecular structure of 1 (calculated band position \(\lambda_{\text{calc.}} = 581\) nm, using the bp86 functional with d3bj dispersion correction and the def2-svp basis set (bp86-d3bj/def2-svp); Supplementary Fig. 62). By contrast, the computation of the UV–visible spectrum of the monomer does not include a band above 500 nm. Hence, an equilibrium between a purple \([\text{Al}_2(\text{Cp}^*)_6]^{2+}[\text{pf}]/2\) dimer and its corresponding yellow monomer is postulated, with the dimer being favoured at lower temperatures and higher concentrations.

Based on the results of the experimental data, an excess of the monomer at standard temperature and pressure conditions is suggested to yield an equilibrium constant for the dimerization in 1,2-DFB of \(K_{\text{dim.1,2-DFB}} = 0.1\) and thus a Gibbs free energy of \(\Delta G_{\text{1,2-DFB}}^0 = 6\) kJ mol\(^{-1}\). This hypothesis agrees with DFT calculations (bp86-d3bj/def2-svp), which suggest the dimerization in 1,2-DFB and 1,3-DFB solution to be exergonic at ambient temperatures (\(\Delta G_{\text{1,2-DFB}}^0 = -15\) kJ mol\(^{-1}\) and \(\Delta G_{\text{1,3-DFB}}^0 = -11\) kJ mol\(^{-1}\)). With enthalpy values \(\Delta H_{\text{1,2-DFB}} = 59\) kJ mol\(^{-1}\) and \(\Delta H_{\text{1,3-DFB}} = -55\) kJ mol\(^{-1}\), and entropy values \(\Delta S_{\text{1,2-DFB}} = 0.16\) kJ mol\(^{-1}\) K\(^{-1}\) and \(\Delta S_{\text{1,3-DFB}} = 0.16\) kJ mol\(^{-1}\) K\(^{-1}\) (at standard pressure conditions), the formation of the dimer \([\text{Al}_2(\text{Cp}^*)_6]^{2+}\) represents an enthalpy-driven process; higher temperatures induce an entropy-driven break-up into the monomers. In addition to the sharp resonance of the \([\text{pf}]/2\) anion at a shift of \(\delta = 34\) ppm (\(1^1\text{Al NMR})\), two distinct broad singlets are observed at \(\delta = -40\) ppm and \(-275\) ppm in 1,2-DFB solution of 1 at room temperature (Fig. 2c).

Comparison with the DFT-computed NMR shifts (\(\delta_{\text{calc.}}\)) as well as those of known AlCp\(^*\) clusters’ (\(\delta_{\text{exp.}}\)) shows that the resonance at \(\delta = -40\) ppm (\(\delta_{\text{calc.}} = -44\) ppm) belongs to the aluminium atoms of the AlCp\(^*\) moieties, and the \(-275\) ppm signal to the unique aluminium atom (calculated NMR chemical shifts for the monomer \([\text{Al}_2(\text{Cp}^*)_6]^{2+}\), \(\delta_{\text{calc.}} = -329\) ppm and the dimer \(\delta_{\text{calc.}} = -300\) ppm). Similarly high-field shifted \(2^1\text{Al NMR resonances have been observed only for the large metalloid clusters \([\text{Al}_8(\text{Cp}^*)_6\text{Al}_3]^{2+}\) (\(\delta = -272\) ppm)\) and \([\text{SiAl}_2(\text{Cp}^*)_6]^{2+}\) (\(\delta = -273\) ppm)\). While no decomposition of solid 1 stored in a glove box at room temperature was observed after months, the concentrated, violet solution of 1 in 1,3-DFB (125 mg ml\(^{-1}\)) turns yellow at room temperature after 12 h accompanied by the formation of metallic aluminium. In the \(2^1\text{Al NMR spectrum of the decomposition products, the resonance of literature-known \([\text{Al}_3(\text{Cp}^*)_6]^{2+}\) \(\delta_{\text{calc.}} = -114\) ppm (\(2^1\text{Al NMR; Supplementary Fig. 24})\). Moreover, the broad singlet at \(\delta = -79\) ppm indicates the formation of \([\text{Al}_2(\text{Cp}^*)_6]^{2+}\). Hence, 1 disproportionates into solution into elementary Al(0) and \([\text{Al}_3(\text{Cp}^*)_6]^{2+}[\text{pf}]/2\) with \([\text{Al}_2(\text{Cp}^*)_6]^{2+}\) as a by-product (Fig. 3a). Notably, less concentrated solutions of 1 (50 mg ml\(^{-1}\)) took five days before a fading of the purple solution to yellow accompanied with formation of elemental aluminium was completed. In addition, \([\text{Al}_2(\text{Cp}^*)_6]^{2+}\) was absent in the \(2^1\text{Al NMR spectrum of the decomposition products (Supplementary Fig. 26)\). Rather, crystallization of the solution yielded yellow crystals of \([([\text{C}_6\text{F}_5\text{Al}]\text{Al}_2(\text{Cp}^*)_6)\text{Al}(\text{Cp}^*)_2]^{2+}[\text{pf}]/2\) (2).

Salt 2 is a further example of the higher, and very different, reactivity of aluminium compared to that of its heavier homologues gallium and indium. The pentagonal bipyramidal inverse-sandwich cations of type \([\text{M}_n(\text{Cp}^*)_m]^{2+}\) (WCA) – when \(M = \text{Ga, WCA} = [\text{BAr}_n]^{-} (= [\text{B}(C_6\text{H}_11)(\text{CF}_3)_4])}\); ref. 56; when \(M = \text{In}, \text{WCA} = [\text{B}(\text{CF}_3)_n]^{-}\); ref. 55) are readily accessible. By contrast, the formation of the respective Al complex could not be achieved to date. Rather, compound 2 can be regarded as an inverse-sandwich complex, in which the lone pairs at the reactive low-valent aluminium atoms are masked by reformation of the tetrameric cluster. Overall, the dimer dication is sensitive towards disproportionation into Al(0) and
Fig. 2 | Synthesis and characterization of [Al(AlCp*)3]+[pf]− (1). a, Synthesis of 1 via a simple metathesis reaction. b, Molecular structure of an [Al(AlCp*)3]+ unit. Al atoms shown in blue; hydrogen atoms and [pf]− anion omitted for clarity. Thermal displacement of the ellipsoids was set at 50% probability. c, The 27Al NMR spectrum (78 MHz, 1,2-DFB, 300 K) of 1 showing the extraordinarily high-field shifted resonance of formal Al⁺ in [Al(AlCp*)3]+ at δ = −276 ppm and the down-field shift of the signal of the AlCp* units at δ = −41 ppm. The decomposition product [Al(III)(Cp*)2]+=−276 ppm and the down-field shift of the signal of the AlCp* units at δ = −14 ppm. d, Broad signal at δ = −66 ppm originates from the NMR probe head. d, Dark-pink crystals of 1, e, Molecular structures of the dimeric [AlCp*)(Cp*)2] units with a short (top) and a long (bottom) Al−Al distance. Units displayed as a side view (left) and view along the Al−Al bond (right). Hydrogen atoms and [pf]− anions omitted for clarity. Thermal displacement of the ellipsoids was set at 50% probability, f, UV-visible spectra of a solution of 1 in 1,2-DFB (c=19 mg ml⁻¹) measured at room temperature (yellow) and at −40 °C (purple; insets show the solution colours) showing the dimerization at lower temperatures.

[Al(III)(Cp*)3]+, and the rate of decomposition strongly depends on the concentration of the dimer in the solution.

Lewis base adducts. Addition of the Lewis bases tetramethylethylendiamine (tmeda), hexaphenylcarbodiphosphorane (C(PPh3)2), cdp or dimethylaminopyridine (dmap) to solutions of 1 in 1,2-DFB allowed for the isolation of salts of the respective cluster cations [(L)Al(AlCp*)3]+ (Fig. 4a). Here, the complexes [(tmeda)Al(AlCp*)3]+[pf]− (3) and [(cdp)Al(AlCp*)3]+[pf]− (4) were isolated as yellow and orange crystals in 71% and 55% yields, respectively. Moreover, [(dmap)Al(AlCp*)3]+[pf]− (5) was isolated as crystalline, orange powder (44%). The addition of the ligands resulted in a coordination at the unique aluminium atom (Fig. 4b).

Following the recently reported cyclic alkyl amino carbene (cAAC)22 and N-heterocyclic carbene (NHC)33 complexes of low-valent aluminium, complex [(cdp)Al(AlCp*)3]+[pf]− 4 represents the first example of a carbene ligand-coordinated to a low-valent aluminium atom. In 4, the Al−C(PPh3) bond length of 2.041(2) Å is similar to that in known trivalent cdp−Al(III)Br3 (1.969(3) Å)33 and cdp−Al(III)Me3 (2.096(2) Å)24 complexes and close to the regular covalent and terminal Al(III)−C bonds as in AlCMe3 (Al−Cterm, 1.993(10) Å, Al−Ctermm, 1.958(11) Å)33. The Al1−AlCp* bonds of [(tmeda)Al(AlCp*)3]+[pf]− 3 and [(cdp)Al(AlCp*)3]+[pf]− 4 are non-symmetric and notably elongated compared to 1+. With Al1−AlCp* bond lengths ranging from 2.628(1) Å to 2.727(1) Å in 3+ and from 2.754(1) Å to 2.801(1) Å in 4+, they correspond to distances in known [(AlL)3] complexes (Supplementary Table 1). Moreover, the AlCp*−AlCp* distances shrink to an average of 2.787 Å for 3+ and 2.773 Å for 4+.

Hence, the covalent bonding between the AlCp* atoms is concentrated in the complexes. Notably, the Al−Al bond length-change upon complexation is even more pronounced in the complex [(dmap)Al(AlCp*)3]+[pf]− 5. Here, the average Al1−AlCp* bond length of 2.802(1) Å is even larger than the average AlCp*−AlCp* bond length of 2.670(1) Å. Hence, with coordination of dmap as a strong donor ligand, an inversion of the relative Al−Al bonds in the non-symmetric Al4 complexes compared to 1+ could be achieved, and apparently 5+ is already very close to an isolated [:Al(III)3]+ complex ion. These structural changes of the cationic Al4 clusters are also reflected in the 27Al NMR spectra.

For 3+ and 4+, the resonances of the aluminium atoms of the AlCp* moieties are shifted high-field compared to 1, that is, shifted to δexp = −65 ppm (δcalc = −66 ppm) and to δexp = −59 ppm (δcalc = −59 ppm), respectively. However, only for the tmeda complex, an NMR signal of the unique Al atom can be observed at δexp = 48 ppm (δcalc = 9 ppm). Upon dissolution of 5 in 1,2-DFB, the orange solution shows an NMR signal at δexp = −83 ppm, fitting to the calculated value of δcalc = −86 ppm. Yet, already after a few minutes, a 27Al NMR resonance at δ = −79 ppm, indicative of the formation of free ([AlCp*]3)+, was observed. After two weeks at room temperature, the colour of the solution changed to yellow and only the 27Al NMR resonance of ([AlCp*]3)+ was detected.
Hence, the thermodynamics for the break-up of the tetrameric clusters in a monomeric Al species of type \([\text{Al}(\text{L})]^+\) (\(\text{L} = \text{tmeda}, \text{cdp}, (\text{dmap})_3\)) and an \([\text{AlCp}^*]^3\) trimer were investigated by DFT calculations. Here, the dmap complex \(5^+\) was computed to be more prone to a decomposition compared to \(4^+\) and \(5^+\) (\(\Delta G_{\text{1,2-DFB}}^0 = 237 \text{ kJ mol}^{-1}\); \(\Delta G_{\text{1,2-DFB}}^0 = 245 \text{ kJ mol}^{-1}\); \(\Delta G_{\text{1,2-DFB}}^0 = 229 \text{ kJ mol}^{-1}\)). Hence, \(5\) is unstable at room temperature in solution and decomposes into \([\text{AlCp}^*]^3\) and potentially a cationic aluminium complex, which could not be identified on the basis of the NMR spectroscopic analysis or be isolated, yet.

**Computational analysis.** To investigate the bonding situation of \(1\)—as a monomer and a dimer—and of the cationic clusters \(3^–5\), supporting DFT calculations were performed. Apparently, the dimerization represents a first example for the ambiphilic reactivity of the unique aluminium atom in \(1\). In the monomeric
Fig. 5 | Bonding analysis of the metalloid clusters. a, Kohn–Sham orbitals (isovalue 0.05) for \( ^1 \) (computed at pbe0-d3bj/def2-tzvpp/bp86-d3bj/def2-svp-level of DFT). b, Display of electron donation from AlCp* lone pairs into \( p_x/p_y \) orbitals at Al* as the major orbital interaction in \( ^1 \) shown in plots of deformation densities \( \Delta \rho_{\text{Orb}}/\Delta \rho_{\text{Orb}} \) (isovalue 0.001; pairwise orbital interaction between Al* (S, \([\text{Ne}]3s^23p^6\) with S = singlet electron configuration) and (AlCp*) (S fragments) associated with major contributing energy terms \( \Delta E_{\text{Orb}}/\Delta E_{\text{Orb}(2)} \) (values in kilocalories per mole). Furthermore, underlying fragment orbital \( \Delta \rho_{\text{Orb}}/\Delta \rho_{\text{Orb}} \) plots are shown (LUMO/LUMO +1 of Al* and HOMO/HOMO-1 of (AlCp*), fragment; isovalue 0.05). The rest of the \( \Delta \rho_{\text{Orb}} \) plots are in Supplementary Fig. 84. Charge flows from yellow to purple. Computed at bp86-d3bj/tz2p/bp86-d3bj/def2-svp-level of DFT. c, Display of σ-bonding interactions between [Al(AlCp*)] \(^+\) units in \([\text{Al}_2(\text{AlCp*})_6]^{2+}\) in the form of plots of deformation densities \( \Delta \rho_{\text{Orb}}/\Delta \rho_{\text{Orb}} \) (isovalue 0.001; pairwise orbital interaction of [Al(AlCp*)] \(^+\) (S fragments in the dimer [Al(AlCp*)] \(^+\)) associated with major contributing energy terms \( \Delta E_{\text{Orb}}/\Delta E_{\text{Orb}(2)} \) (values in kilocalories per mole). The rest of the \( \Delta \rho_{\text{Orb}} \) plots are in Supplementary Fig. 66. Charge flows from yellow to purple. Computed at bp86-d3bj/tz2p/bp86-d3bj/def2-svp level of DFT. d, Display of delocalization of the lone pair at dmap-coordinated Al* into (AlCp*), fragment as major orbital interaction in \( ^5 \) shown in plot of deformation densities \( \Delta \rho_{\text{Orb}}/\Delta \rho_{\text{Orb}} \) (isovalue 0.001; pairwise orbital interaction between (dmap),Al* (S, \([\text{Ne}]3s^23p^6\)) and (AlCp*), fragments) associated with the major contributing energy term \( \Delta E_{\text{Orb}}/\Delta E_{\text{Orb}(2)} \) (values in kilocalories per mole). Furthermore, underlying fragment orbital \( \Delta \rho_{\text{Orb}}/\Delta \rho_{\text{Orb}} \) plot are shown (HOMO of (dmap),Al* fragment and LUMO of (AlCp*), fragment; isovalue 0.05). The rest of the \( \Delta \rho_{\text{Orb}} \) plots are in Supplementary Fig. 90. Charge flows from yellow to purple. Computed at bp86-d3bj/tz2p/bp86-d3bj/def2-svp level of DFT.

[Al(AlCp*)] \(^+\) unit, the 3s \(^2\)-like lone-pair orbital at the formally cationic aluminium atom resides as HOMO–2 (that is, the third highest occupied molecular orbital) at an energy of –8.55 eV (Fig. 5a). The HOMO and HOMO–1 (–8.50 eV) are energetically very close, are degenerate and present an interaction of the lone-pair orbitals of the AlCp* moieties with the 3p \( x \) and 3p \( y \) orbitals at the unique Al atom (Supplementary Fig. 92).

The LUMO (–4.32 eV) of \( ^1 \) has strong 3p \( x \) character, whereas LUMO+1 and LUMO+2 are dominated by the 3p \( x \) and 3p \( y \) orbitals of the unique Al\(^+\) atom. Upon dimerization to the dication [Al(AlCp*)] \(^{2+}\), interactions of the HOMO–2 with the LUMO of the two cations result in a weak σ-bonding interaction as indicated by the small calculated Al\(^+\)–Al\(^+\) Wiberg bond index of 0.64 as well as by low values for electron density \( \rho(r) = 0.25 \text{ electrons Å}^{-3} \) and its ellipticity \( \epsilon = 0.01 \) at the Al\(^+\)–Al\(^+\) bond critical point from quantum theory of atoms in molecules analysis (QTAIM analysis; Supplementary Fig. 62).

This result is further supported by an energy decomposition analysis combined with natural orbitals for chemical valence (EDA-NOCV; Fig. 5c) as promoted by Frenking and coworkers in recent years\(^5\). The plots of the deformation density values \( \Delta \rho_{\text{Orb}} \) in Fig. 5c (associated with contributing energy terms \( \Delta E_{\text{Orb}}/\Delta E_{\text{Orb}(2)} \) represent the major orbital interaction energy \( E_{\text{Orb}} \) terms (69% of \( E_{\text{Orb}} \)) and display a charge flow from the HOMO–2 to the LUMO of the fragments (Fig. 5a). Here, \( \Delta \rho_{\text{Orb}} \) shows the predominant σ-bond between the unique Al\(^+\) atoms, whereas \( \Delta \rho_{\text{Orb}} \) displays a minor σ\(^*\)-bonding component. Yet, the anti-bonding character of the latter is diminished by admixture of the LUMO (\( p_z \) at Al\(^+\), resulting in a strengthening of the interaction in the respective Al\(^+\) clusters (more detail is in Supplementary Section 3.2). Although the Al\(^+\)–Al\(^+\) bonding interaction between the [Al(AlCp*)] \(^+\) fragments is very labile, it is sufficient to overcome the Coulomb repulsion between the cationic fragments. Furthermore, the dimerization demonstrates the amphiphilicity of the low-valent aluminium cation.

To analyse the acceptor properties of the Al cation, the monomeric Al\(^+\) clusters \( ^1 \) and \( ^3 \) were investigated via EDA-NOCV calculations. In \( ^1 \), the majority of the total orbital interaction energy between the Al\(^+\) and (AlCp*), fragment in \( ^1 \) stems from donation of electron density from the lone-pair orbitals of the AlCp* units into
electron donation from the (AlCp*)₃ unit into the 3q₁ or 5₂%; Fig. 5d). The Lewis basic AlCp* units. In comparison to the QTAIM analysis of the same sequence (Supplementary Figs. 86–91). In summary, we report the synthesis of a cationic, low-valent aluminum(I) compound ([Al(n-C₅H₄)₂Me]₃). Angew. Chem. Int. Ed. 30, 564–565 (1991).

Hence and in agreement with our deduction from the structure and chemistry, monomeric 1⁺ is best described as a cationic aluminum atom, which is coordinated by three strongly electron-donating AlCp* substituents. This assignment agrees with the absence of bond critical points between the AlCp*⁻⁻⁻ atoms in the QTAIM analysis of 1⁺ (Supplementary Fig. 78). Yet, the situation changes upon complexation of the unique aluminum atom. Here, the orbital interaction terms associated with the delocalization of the lone pair of the [(L),Al⁺] moiety ([L] = (tmeda), (cdp), (dmap)]) decrease in the same sequence (Supplementary Figs. 86–91). In 5⁺, the energy term of the delocalization of the lone-pair orbital at (dmap)Al⁺ into the (AlCp*)₃ fragment, even becomes the dominant contribution to the total orbital interaction energies (ΔEorb= = –61.02 kcal mol⁻¹ or 52%; Fig. 5d). The π-bonding interactions combine to ΔEorb= = –37.90 kcal mol⁻¹ (32%; Supplementary Fig. 90). Consequently, the role of the AlCp* units can be altered decisively upon complexation of the unique Al atom in 1⁺. Whereas the AlCp* units mainly act as Lewis bases in 1⁺, the AlCp* units become increasingly Lewis acidic in the isolated clusters and finally lead to the observed shortening and inversion of the Al–Al bond lengths in the molecular structure of 5⁺.

These results are supported by the computed QTAIM charges at the unique Al atoms. For 1⁺, the QTAIM charge at the unique Al atom of +0.58 reflects the charge delocalization onto the strongly Lewis basic AlCp* units. In comparison to the QTAIM analysis of ([AlCp*]⁺ 1) qph= = –0.84, qph= = +0.84), the negative partial charges at the Cp* substituents decrease in 1⁺ (qph= = –0.65, qph= = +0.79). Nevertheless, a substantial positive charge remains at the unique Al atom. Although for 3⁺ and 4⁺ only a marginal increase of the QTAIM charges to 0.63 and 0.68 compared to 1⁺ is calculated, the dmap-ligated Al atom in 5⁺ bears a highly positive charge of qAl= = 1.17 and can be denoted as a cationic, low-valent aluminum atom. Consequently, 5⁺ may act as a source of a cationic, monomeric Al⁺ and will be studied in future research.

Conclusion

In summary, we report the synthesis of a cationic, low-valent aluminum compound [Al(AlCp*)]⁺[p̅]⁻ (1) accessible on the gram scale via a simple metathesis route. Indicating an ambiphilic reactivity, crystallographic as well as UV–visible spectrometric and computational studies reveal the dimeric structure [Al(AlCp*)]⁺(p̅)⁻ of 1 in the solid state as well as in solution at high concentration and low temperature. At lower concentrations and higher temperatures, the monomeric structure prevails. Addition of Lewis bases to solutions of 1 uses the monomeric cation as acceptor and allows for the synthesis of cluster cations of type [(L)₃Al(AlCp*)]⁺[p̅]⁻ ([L] = (tmeda), (cdp), (dmap)). Their solid-state structures, the NMR shifts and computational studies demonstrate that the dominating bonding interactions can be fine-tuned and even inverted by the donor strength of the added ligands, as maximized in the highly non-symmetric dmap-substituted cluster. Consequently, this salt may potentially be used as a synthon for an [Al(L)]⁺ salt, which due to its cationic nature potentially may be able to conduct reversible oxidative addition and reductive elimination chemistry with small molecules.

Online content

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Methods

General methods and instrumentation. All manipulations of air- and/or water-sensitive compounds were performed under an inert argon atmosphere using standard Schlenk or glove box techniques. All glassware used in reactions was stored overnight in a desiccator flushed with purified Ar and thoroughly flame dried prior to usage. Cp(H (Sigma-Aldrich), potassium hexamethylsalazide (Sigma-Aldrich, >95%), dmap (Sigma-Aldrich, >98%) and tmda (Sigma-Aldrich, >99%) were used as received. Li[ref. (ref. 1)], cdp (ref. (ref. 2) and [Al(OC4F9)4] (ref. 2) were prepared using procedures known in the literature. The 1,3-DFB- and 1,2-DFB (Fluorochem) were refluxed over CaH2, fractionally distilled and stored over activated 3 Å molecular sieves. The n-pentane was collected from the solvent-purification system and used as received. NMR samples were prepared inside an inert atmosphere glove box in NMR tubes equipped with a gas-tight J. Young valve. The H, Li, O, C, F, 19F, and 31P NMR spectra were acquired either on a Bruker Biospin Avance II 400 MHz WB or a Bruker Avance III HD 300 MHz spectrometer. The H and 13C NMR spectra are reported relative to the internal tetramethylsilane and referenced to residual solvent resonances. Underlined atoms represent the atoms/groups causing the respective NMR signal. A small s corresponds to singlet, a centered multiplet. Data analysis was performed using Bruker TOPSPIN 3.5 software. The broad resonance at δ = 70 ppm observed in 21Al NMR spectra corresponds to a background from Al nuclei in the probe head. The mass-spectrometric experiments were performed with a Thermo-Fischer LTQ XL linear ion-trap mass spectrometer equipped with an electrospray-ionization source (Capillary temperature Tcap = 100°C; source voltage, 3.75 kV; tube lens voltage, 95 V). Mass spectra were obtained by electrospray ionization from a millicomol solution in 1,2-DFB. In the CID (charged induced dissociation) experiments, helium served as the collision gas. The supplied collision energy was adjusted by varying the normalized collision energy between 0 and 0.15. Data processing was done with the Bruker OPUS 7.5 software package and, if not stated otherwise, a baseline correction with three iterations was performed. Fourier transform infrared spectra (FTIR) were recorded within a glove box with a Bruker ALPHA equipped with QuickSnap Ecoc-ATR (attenuated total reflection) module and ZnSe crystal. The spectra were measured at room temperature in the range of 4,000–300 cm⁻¹ with 64 scans and a resolution of 2 cm⁻¹. The data were processed with the Bruker OPUS 7.5 software package and, if not stated otherwise, a baseline correction with five iterations was performed. Further transform Raman spectra were recorded with a VERTEX 70 with Bruker RAM II Modul (1,064 nm exciting line of a Nd–YAG laser) and liquid-nitrogen-cooled Ge detector. The 13C NMR (75.48 MHz, 1,2-DFB, 298 K) data were as follows: δ = 15.9 ppm (s, [AlOC4F9]3–). The FTIR (ZnSe-ATR) data were as follows: wave-number range 2,920–2,860 (vw), 1,800 (s), 1,455 (w), 1,418 (vw), 1,390 (s), 1,352 (s), 1,298 (s), 1,275 (s), 1,241 (m), 1,161 (s), 1,161 (w), 971 (s), 831 (w), 798 (w), 756 (w), 726 (vs), 585 (w), 560 (w) cm⁻¹. The Raman data were as follows (1,000 scans): δ = 2,927 (vw), 1,420 (s), 1,393 (w), 593 (w), 473 (w), 396 (w), 307 (vs), 283 (w), 210 (w), 183 (vs), 160 (m), 83 (s) cm⁻¹.

Synthesis of [(tmda)Al(OC4F9)3]2[PF6] (4). The [Al(OC4F9)3]2[PF6] (17 mg, 0.02 mmol, 1 equiv.) was suspended in 1,2-DFB (0.1 mL). The solution of 1 was added to the suspension of cdp at room temperature to yield an orange solution. Subsequently, n-pentane was diffused onto the solution at −30°C. The title compound (25 mg, 17 mol%) was isolated as yellow powder.

Synthesis of [(dpdf)(Al(OC4F9)3)3][PF6] (5). The [Al(OC4F9)3]2[PF6] (10 mg, 0.05 mmol, 1 equiv.) was dispersed in 1,2-DFB (1 mL) and dried under reduced pressure. The obtained orange powder was washed with toluene (3 mL) and dried under vacuo. The title compound (28 mg, 15 mol%) was isolated as yellow powder. 27Al NMR (78.22 MHz, 1,2-DFB, 298 K) data were as follows: δ = 75.5 ppm (s, [AlOC4F9]3–). The 13C NMR (78.22 MHz, 1,2-DFB, 298 K) data were as follows: δ = 55.0 ppm (s, [AlOC4F9]3–). The FTIR (ZnSe-ATR) data were as follows: wave-number range 2,920–2,860 (vw), 1,800 (s), 1,455 (w), 1,418 (vw), 1,390 (s), 1,352 (s), 1,298 (s), 1,275 (s), 1,241 (m), 1,161 (s), 1,161 (w), 971 (s), 831 (w), 798 (w), 756 (w), 726 (vs), 585 (w), 560 (w) cm⁻¹. The Raman data were as follows (1,000 scans): δ = 2,927 (vw), 1,420 (s), 1,393 (w), 593 (w), 473 (w), 396 (w), 307 (vs), 283 (w), 210 (w), 183 (vs), 160 (m), 83 (s) cm⁻¹.

The full experimental details and characterization of the new compounds can be found in the Supplementary Information.
Data availability
X-ray crystallographic data are available free of charge from the Cambridge Crystallographic Data Centre (CCDC) under the reference numbers 2123471 (1), 2124880 (2), 2123536 (3), 2123485 (4) and 2123538 (5) via https://www.ccdc.cam.ac.uk/structures/. All other data supporting the findings are contained in the main text or the Supplementary Information. Source data are provided with this paper.

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Author contributions
P.D. and J.W. planned and carried out all experiments and analysed the data. P.D. carried out the single-crystal X-ray diffraction measurements and the mass spectrometry measurements and conducted the computational investigations. P.D. and I.K. wrote the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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