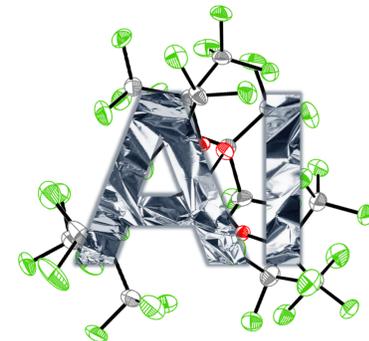


From an Al₄-Cluster to Al⁺ Complexes: Lessons on Metalloid Clustering

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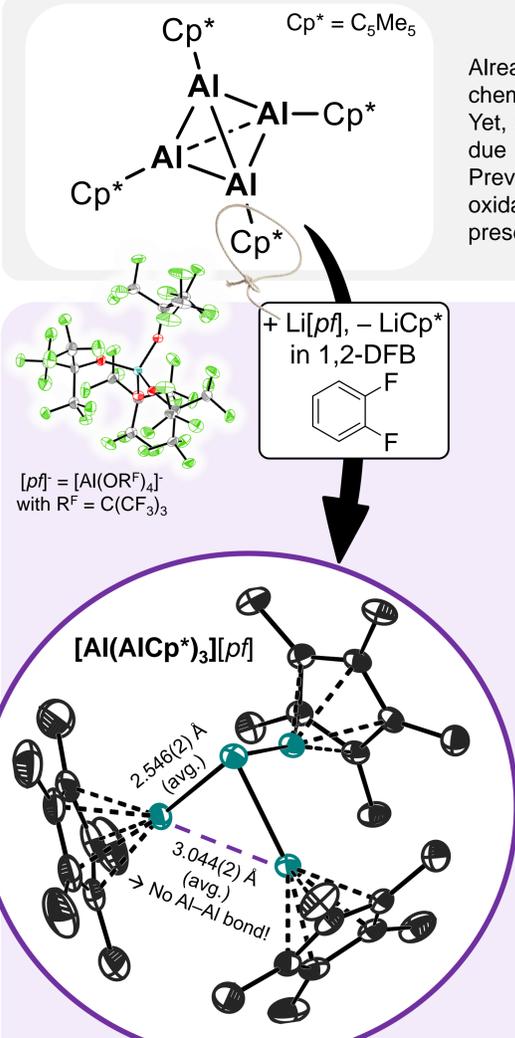


Introduction

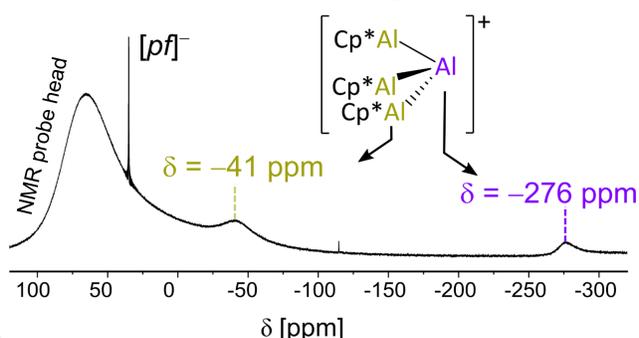
Already in 1991, the synthesis of the first low-valent aluminum complex [(AlCp^{*})₄] was reported by Schnöckel (left).[1] Since then, the low-valent Al chemistry has flourished and expanded to anionic Al(I) complexes and multi-bonded systems, showing high activity in small molecule activation.[2] Yet, an accessible cationic, low-valent aluminum compound is hitherto unknown. Low-valent main-group metal-cations are interesting synthetic goals due to the stabilization of the lower oxidation states by the cationic charge, making them promising candidates for reversible redox-chemistry. Previous attempts aiming for the isolation of a low-valent Al cation focused on the oxidation of aluminum metal with a large variety of newly developed oxidant salts.[3] However, successful oxidation could only be observed upon addition of hard ligands (e.g. MeCN) and yielded Al(III) cations. Here, we present the synthesis of the complex salt [Al(AlCp^{*})₃][Al(OR^F)₄] (R^F = C(CF₃)₃) starting from [(AlCp^{*})₄].[4]

An Accessible Low-Valent Al Cation

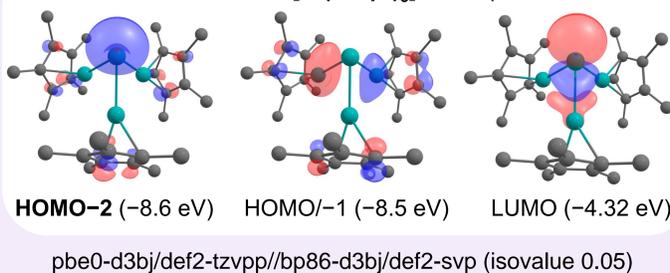
The complex salt [Al(AlCp^{*})₃][pf] was synthesized on a gram-scale in a simple metathesis procedure. The molecular structure of the cation displays a unique Al⁺ atom coordinated by three AlCp^{*} units. Indicating an ambiphilic reactivity, dimerization to [Al₂(AlCp^{*})₆]²⁺ dications is observed in solid state and solution.



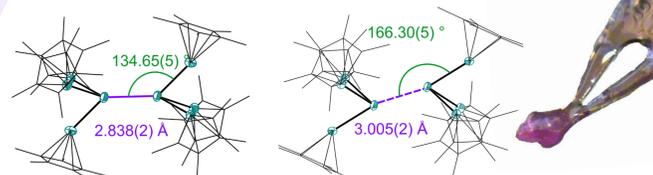
²⁷Al NMR spectrum: exceptional high-field ²⁷Al NMR shift



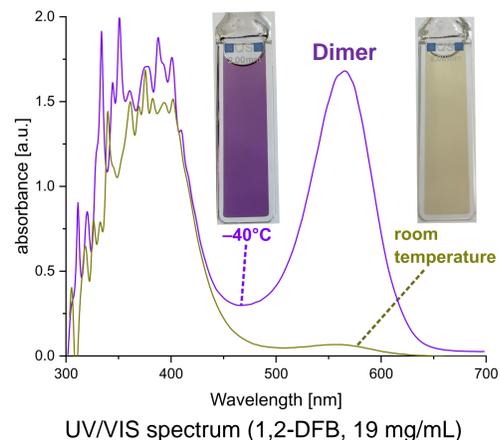
Frontier orbitals of [Al(AlCp^{*})₃]⁺: lone-pair at Al⁺



Elusive [Al₂(AlCp^{*})₆]²⁺ dimers in solid state...



...and in 1,2-DFB-solution at high conc. and/or low temp.



... Re-Clustering upon Addition of Lewis Bases

Addition of Lewis bases results in reformation of the tetrahedral Al₄⁺ clusters. While the bond lengths can be fine-tuned depending on the donor-strength of the Lewis bases, a bond-length inversion is observed in the (dmap)₃-substituted cluster which readily decomposes in solution and potentially acts as synthon for an elusive [(dmap)₃Al]⁺.

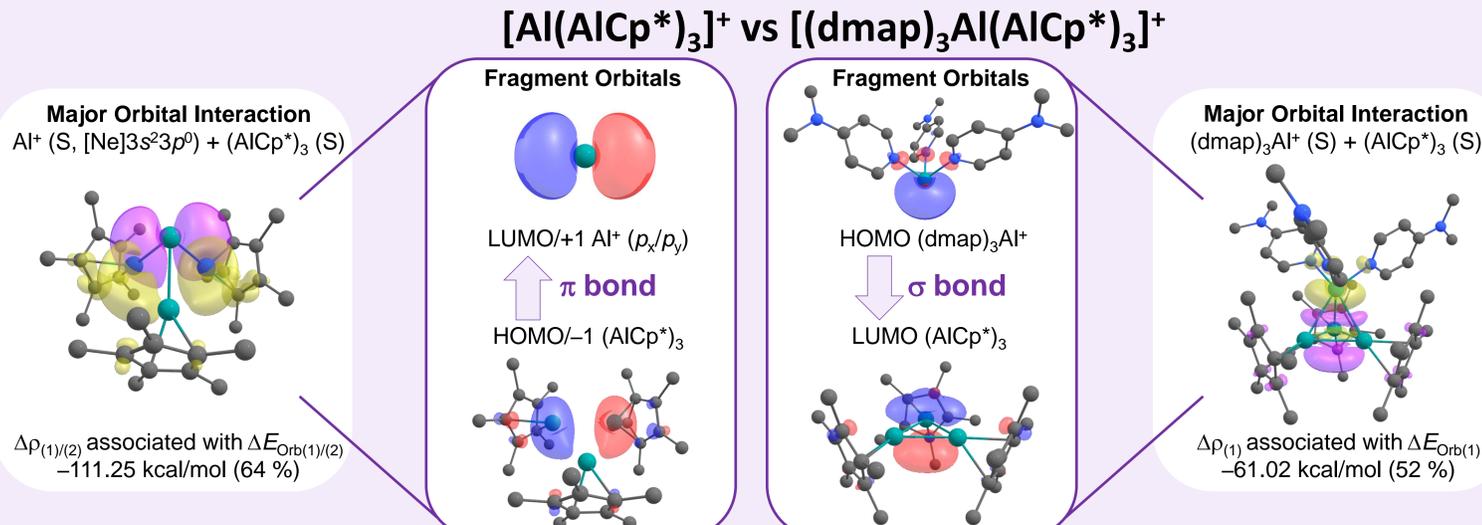
Table 1: ²⁷Al NMR shifts and selected bond lengths for the cationic, low-valent Al-clusters

Compound	δ(²⁷ Al) Al _{Cp*} [ppm]	δ(²⁷ Al) Al ⁺ [ppm]	d(Al ⁺ -Al _{Cp*}) _{av.} [Å]	d(Al _{Cp*} -Al _{Cp*}) _{av.} [Å]
[Al(AlCp [*]) ₃][pf]	-41.0	-274.3	2.546(2)	3.044(2)
[(tmeda)Al(AlCp [*]) ₃][pf]	-64.8	47.6	2.695(1)	2.782(1)
[(cdp)Al(AlCp [*]) ₃][pf]	-59.2	invisible	2.662(1)	2.773(1)
[(AlCp [*]) ₄]	-80.7	-	-	2.769(5)[3]
[(dmap) ₃ Al(AlCp [*]) ₃][pf]	-83.3	invisible	2.802(1)	2.670(1)

EDA-NOCV

Energy Decomposition Analysis coupled with Natural Orbitals of Chemical Valence (EDA-NOCV) breaks the bonding between two fragments down into the contributing interaction energies. Δρ_{(1)/(2)} plots display the difference of electron density upon bond formation (charge flows from yellow to purple).

In [Al(AlCp^{*})₃]⁺, the major orbital interaction is the donation of electron density from the AlCp^{*} units into empty p-orbitals at Al⁺. The bonding situation changes in the dmap-substituted cluster, where the major orbital interaction represents the delocalisation of the Al⁺ lone-pair into the (AlCp^{*})₃ fragment.



bp86-d3bj/def2-tzvp/bp86-d3bj/def2-svp (isovalue 0.002 for Δρ, 0.05 for FMOs)

Literature: [1] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem. Int. Ed.* **1991**, 30, 564-565.

[2] a) K. Hobson, C. J. Carmalt, C. Bakewell, *Chem. Sci.* **2020**, 11, 6942-6956. b) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2021**, 60, 1702-1713.

[3] P. Dabringhaus, A. Barthélemy, I. Krossing, *Z. Anorg. Allg. Chem.* **2021**, 18, 1660-1673.

[4] P. Dabringhaus, J. Willrett, I. Krossing, *Nat. Chem.* **2022**, DOI: 10.1038/s41557-022-01000-4.

See the Paper:

