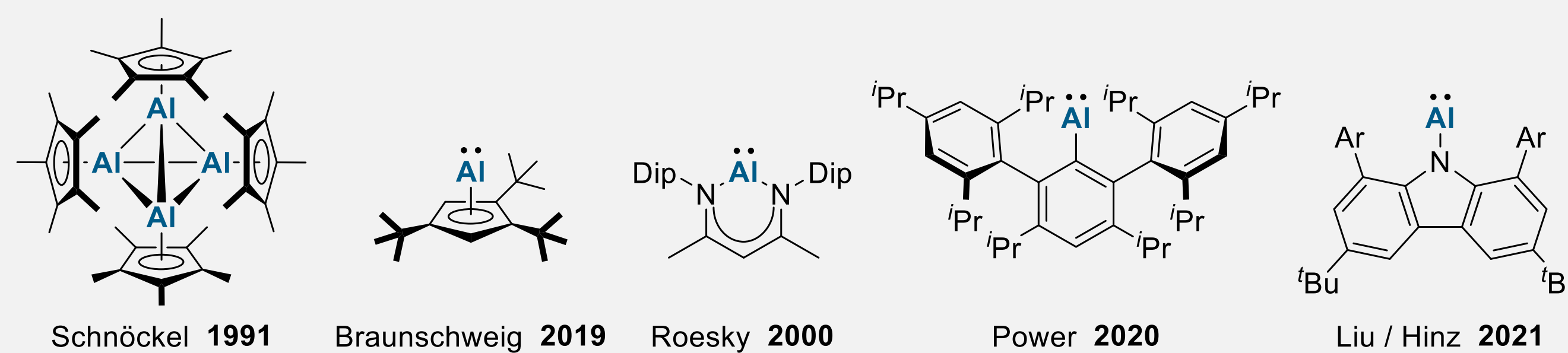


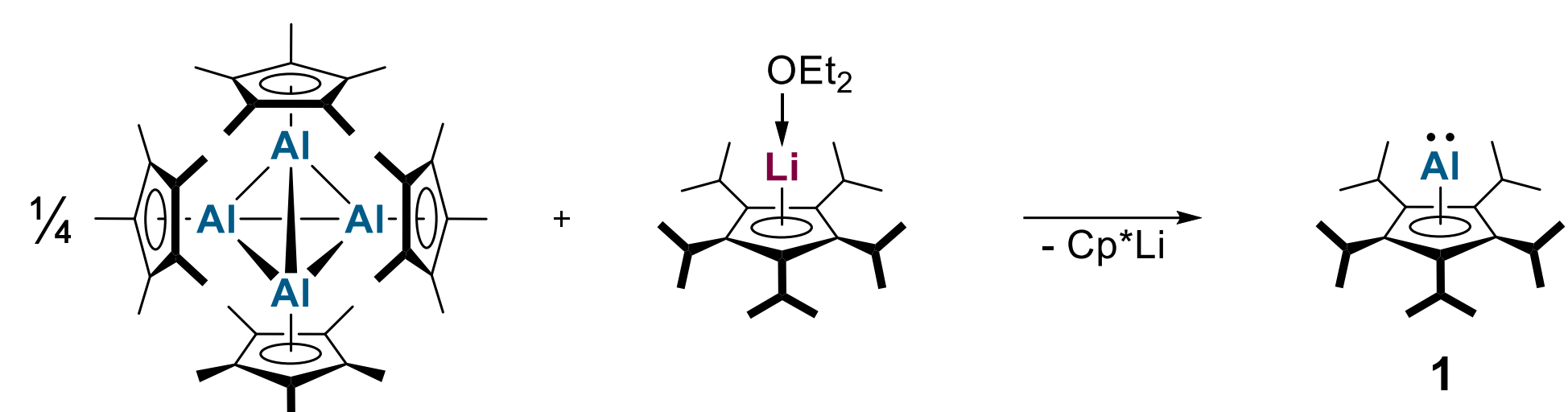


INTRODUCTION

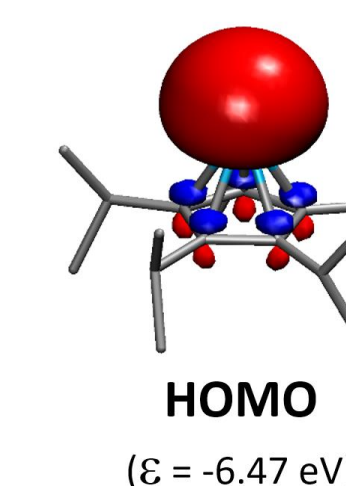
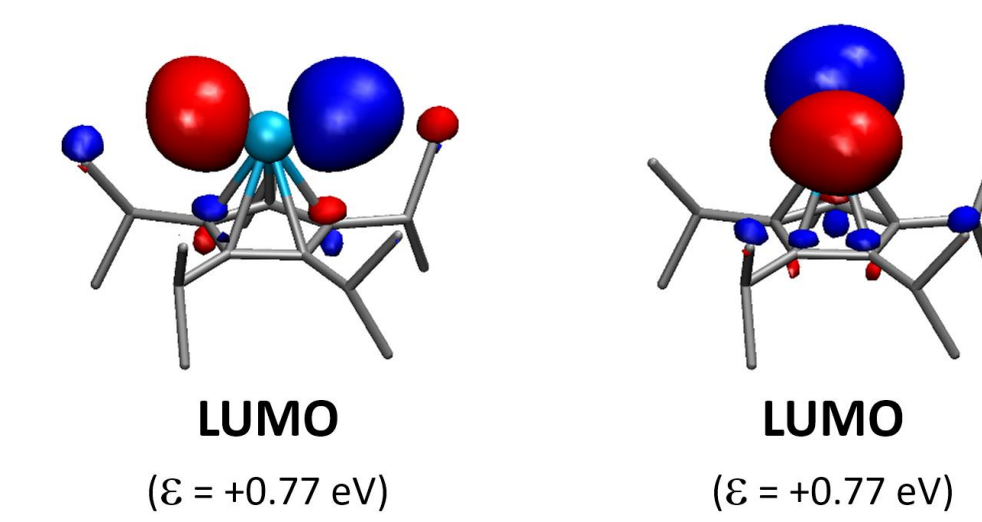
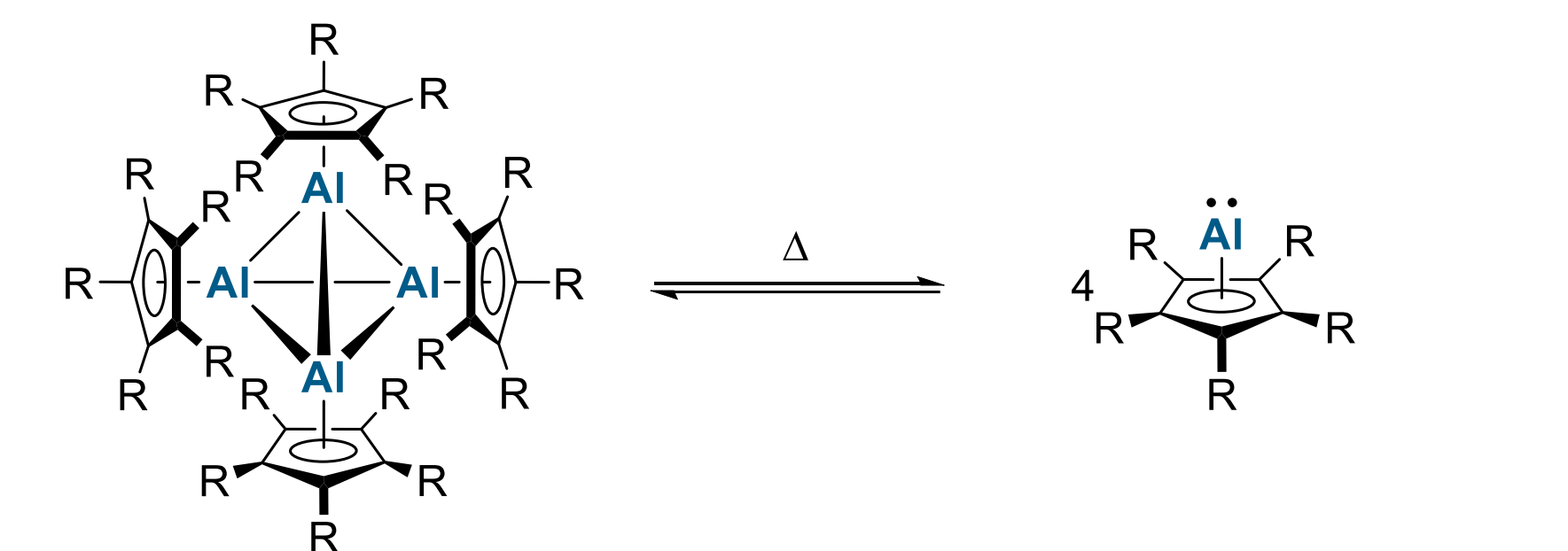
The isolation of mono-substituted aluminum compounds with the aluminum atom in the oxidation state +I – so called aluminyls – is challenging and typically requires bulky substituents for kinetic stabilization and/or donor-type ligands to compensate the inherent electron deficiency.^[1] In 1991, Schnöckel reported the isolation and structural characterization of (pentamethylcyclopentadienyl)aluminum(I), highlighting the ability of cyclopentadienyl ligands to stabilize an aluminum(I) center.^[2] However, this compound does not exhibit the general formula “R–Al”, but exists in tetrameric form in the solid-state and in solution at room temperature, although Schnöckel demonstrated in a follow-up work that monomeric cyclopentadienyl aluminyls can be obtained at room temperature, with more bulky substitution patterns on the Cp moiety.^[3] The first isolation of a monomeric cyclopentadienyl aluminylene was achieved by Braunschweig only recently, complementing some other aluminyls reported by Roesky, Power, Liu and Hinz in recent years.^[4]



SYNTHESIS AND STRUCTURE



(Pentaisopropylcyclopentadienyl)aluminylene (⁵CpAl) **1** was synthesized by treatment of the pentamethylcyclopentadienyl aluminum(I) tetramer^[2] {Cp*Al}₄ with (pentaisopropylcyclopentadienyl)lithium diethyletherate (⁵Cp*Li-OEt₂). **1** was fully characterized by multinuclear NMR spectroscopy in solution and in the solid-state, and its structure was determined by single crystal X-ray diffraction.



Kohn-Sham molecular frontier orbital contours of **1** (M06-2X/def2-TZVP//M06-2X/def2-SVP; isodensity = 0.05 a.u.)

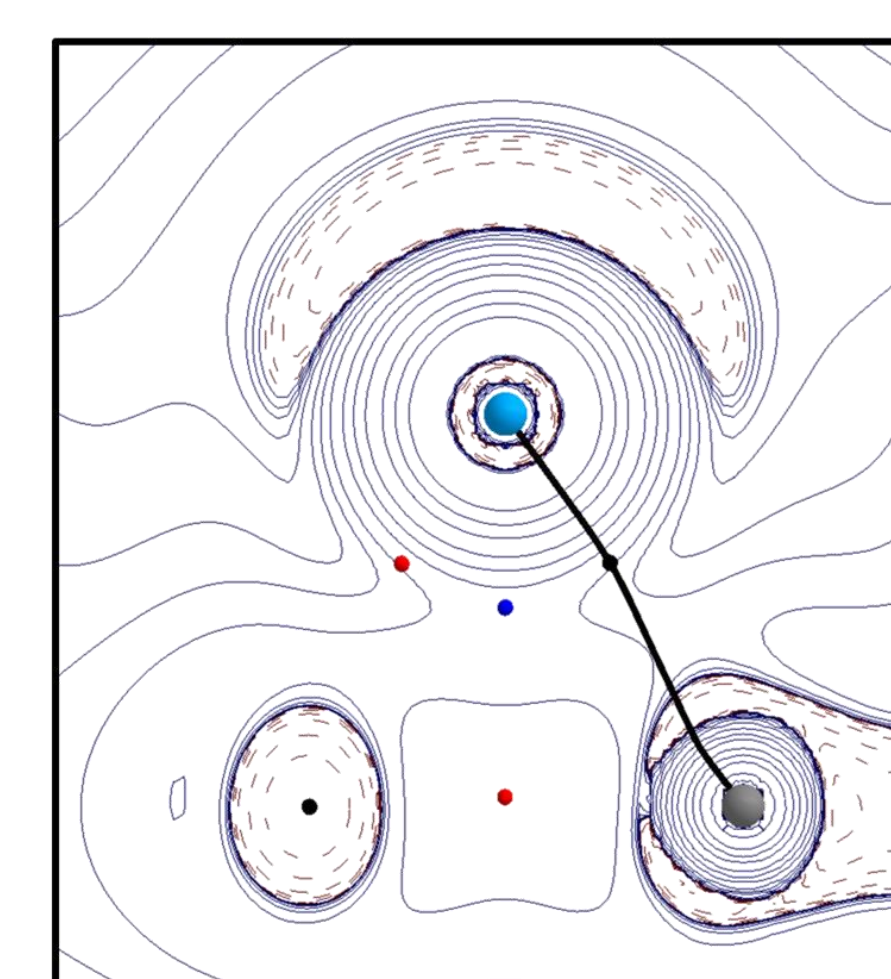
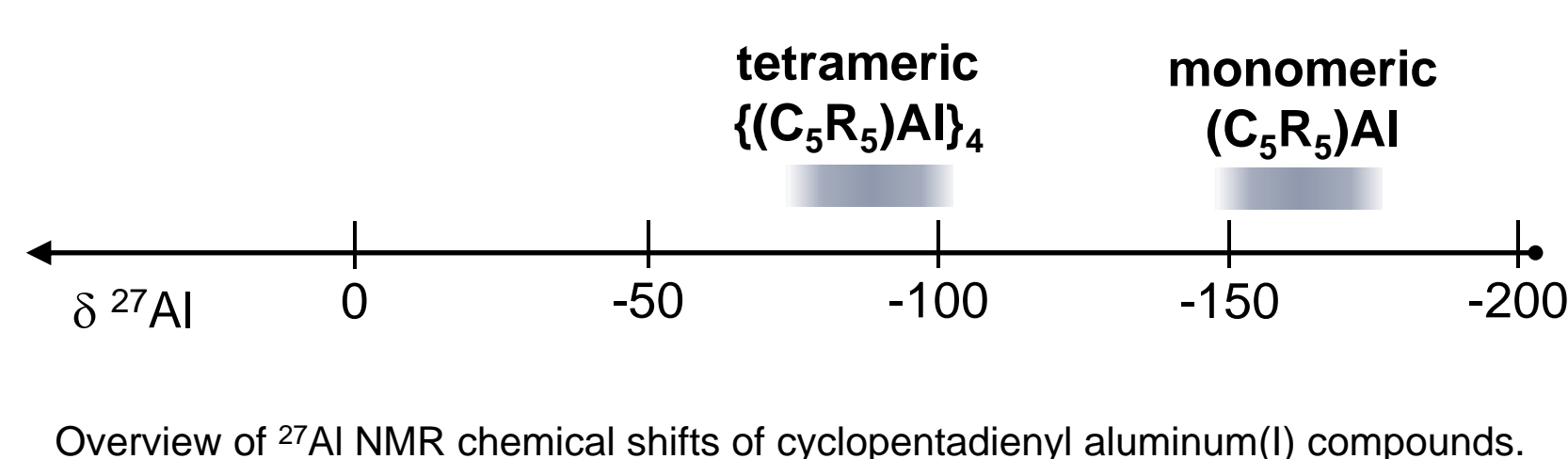
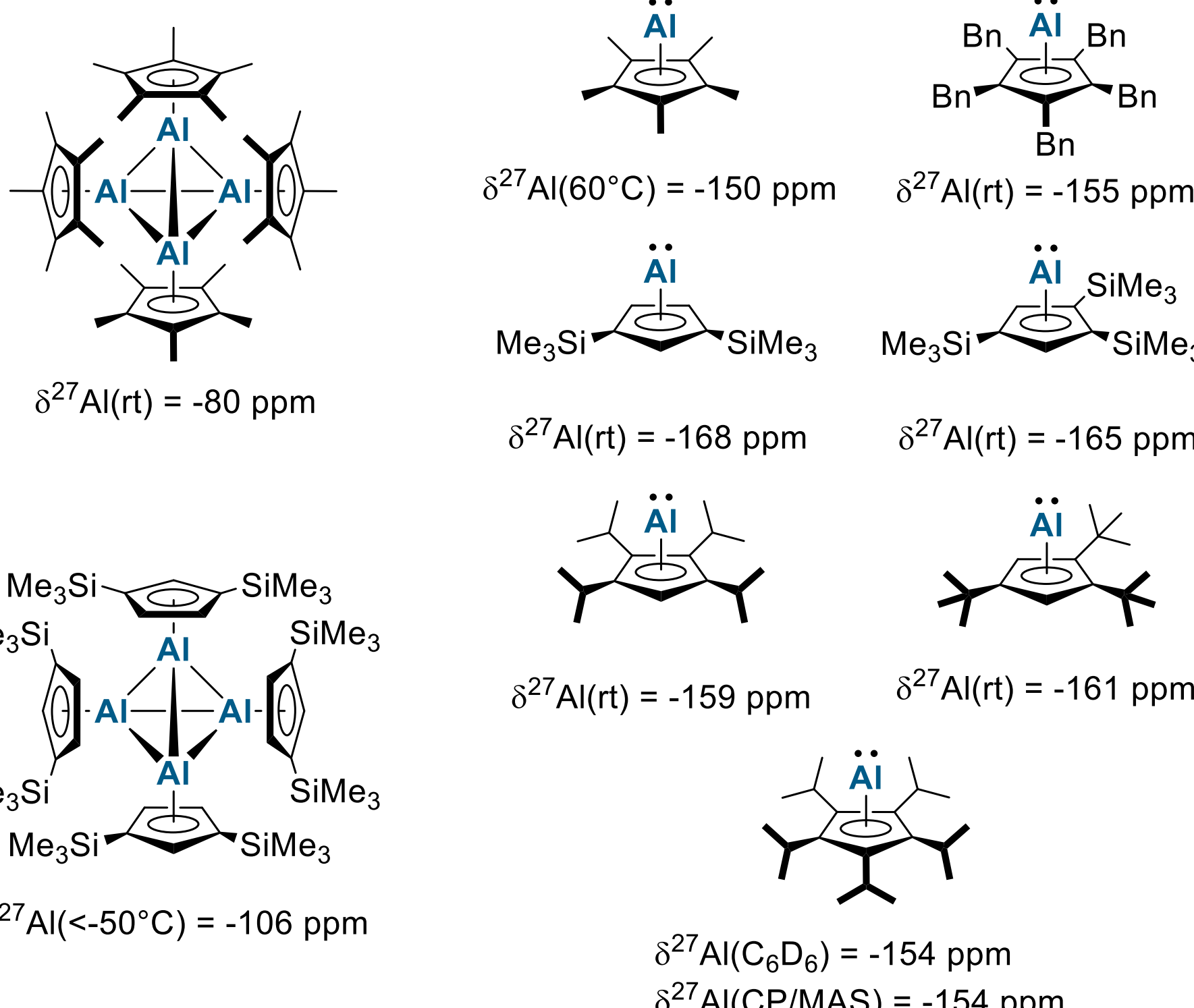
The Kohn-Sham molecular orbitals of **1** consist of a lone pair at the aluminum atom (HOMO) and two degenerated 3p orbitals (LUMO), which is the typical situation for aluminyls.

Bond distances in **1** in [pm]:

	⁵ CpAl	{Cp*Al} ₄
Al1-Cp ^{cent}	196.7(6)	199.8(2) to 203.2(3)
Al1-C ^{Cp}	226.9(7) to 235.7(8)	229(1) to 237(1)

Molecular structure of **1** in the crystal (displacement ellipsoids at 30% probability level, H atoms omitted) and overview of selected bond lengths.

The molecular structure of **1** shows well-separated monomeric (pentaisopropylcyclopentadienyl)aluminum moieties with an η⁵ coordination of the ⁵Cp ligand towards aluminum, resulting in a pentagonal pyramidal structure, or rather a nido cluster.

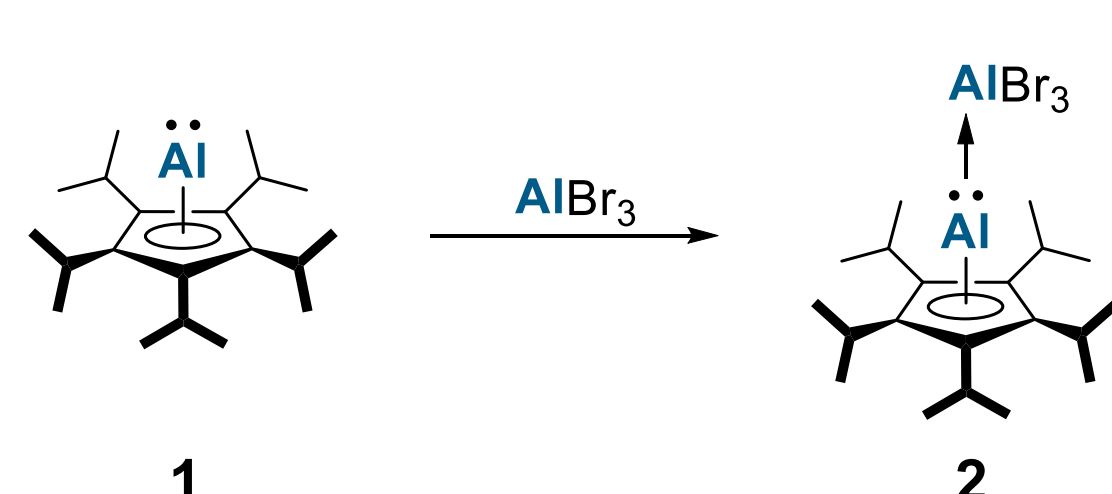


The Natural Population Analysis (NPA) and Atoms in Molecules (AIM) show that the aluminum atom is positively charged.

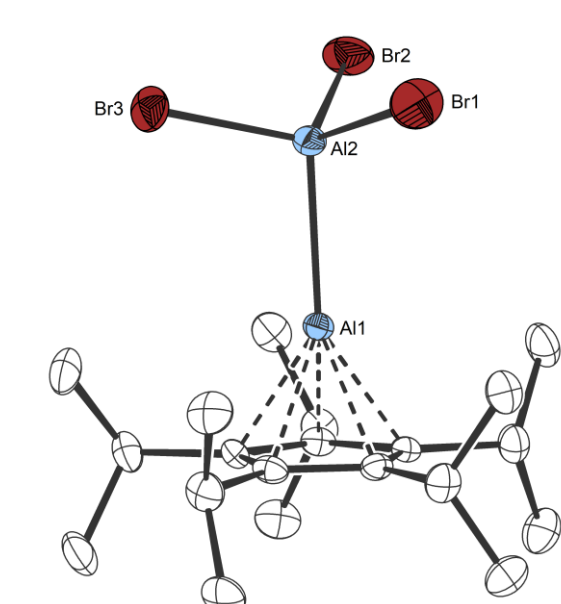
Q(Al)_{NPA} = +0.70
Q(Al)_{AIM} = +0.81

Laplacian distribution of the electron density V²ρ(r) of **1**.

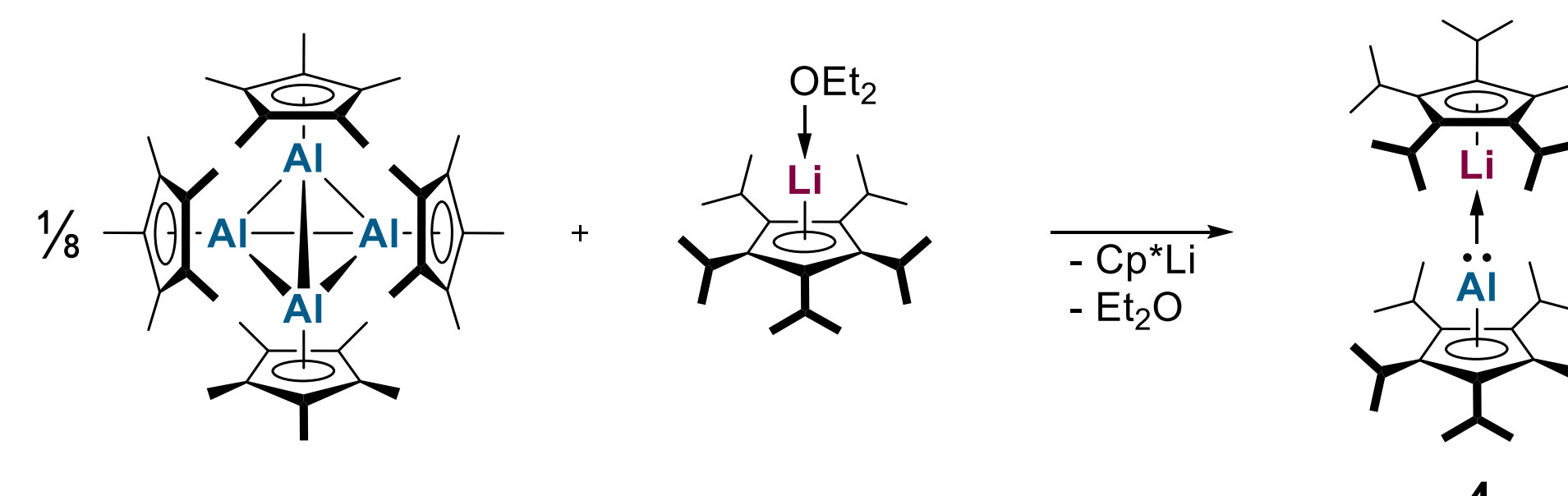
METAL COMPLEXES



Treatment of **1** with AlBr₃ at room temperature in toluene gives adduct **2** with a Al1–Al2 bond length of 255.5(1) pm, which is similar to that found in Braunschweig's (trifert-butylcyclopentadienyl) aluminylene aluminum tribromide complex (255.4(1)).^[4a]



Molecular structure of **2** in the crystal (displacement ellipsoids at 50% probability level, H atoms omitted).



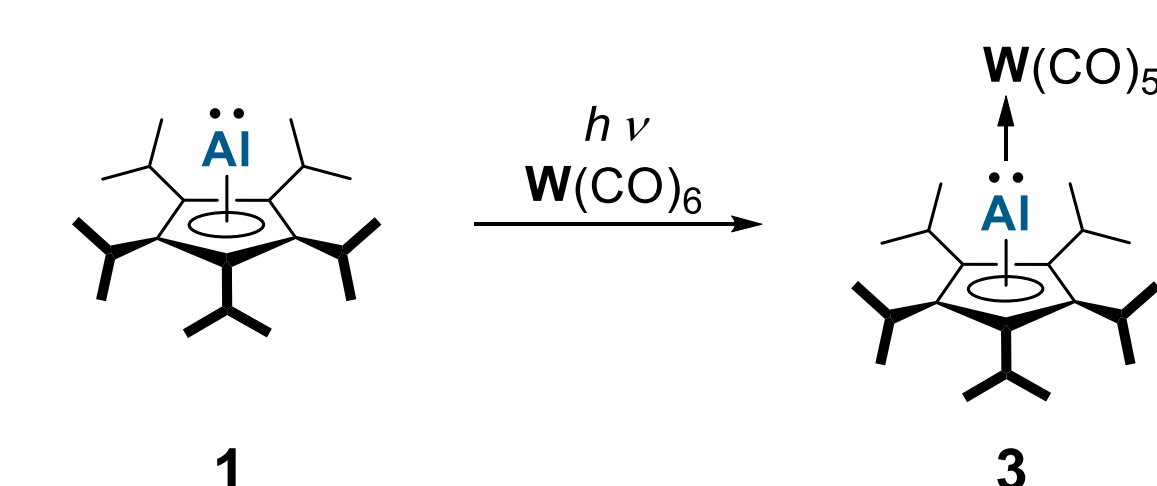
Reaction of (pentamethylcyclopentadienyl)aluminum(I) tetramer with 8 equivalents of ⁵CpLi-OEt₂ results in the formation of dimetalloocene **4**.

Bond distances in **4** in [pm]:

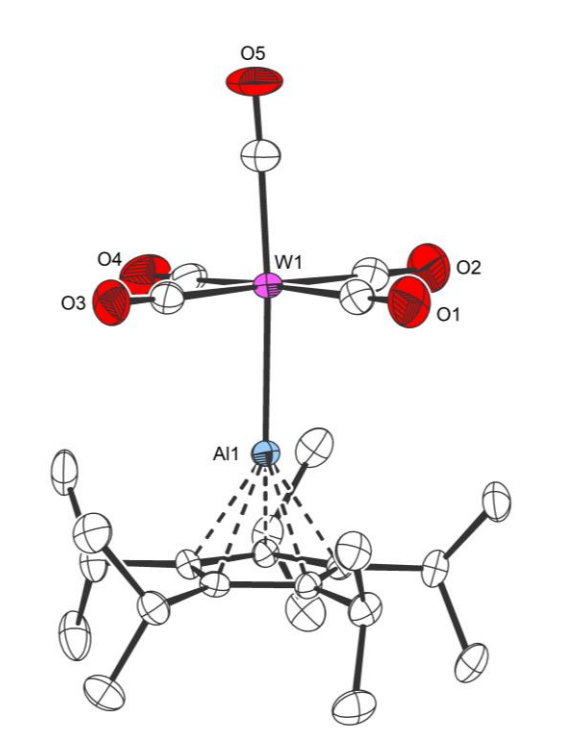
	⁵ CpAl→Li ⁵ Cp
Al1–Li1	258.1(6)
Al1–Cp ^{cent}	191.0(2); 191.7(2)
Li1–Cp ^{cent}	172(1) to 173(1)
Al1–C ^{Cp}	225.1(9) to 228(1)

Dimetalloocene **4** is the first main-group and heterobimetallic dimetalloocene with an Al1–Li1 bond of 258.1(6) pm.

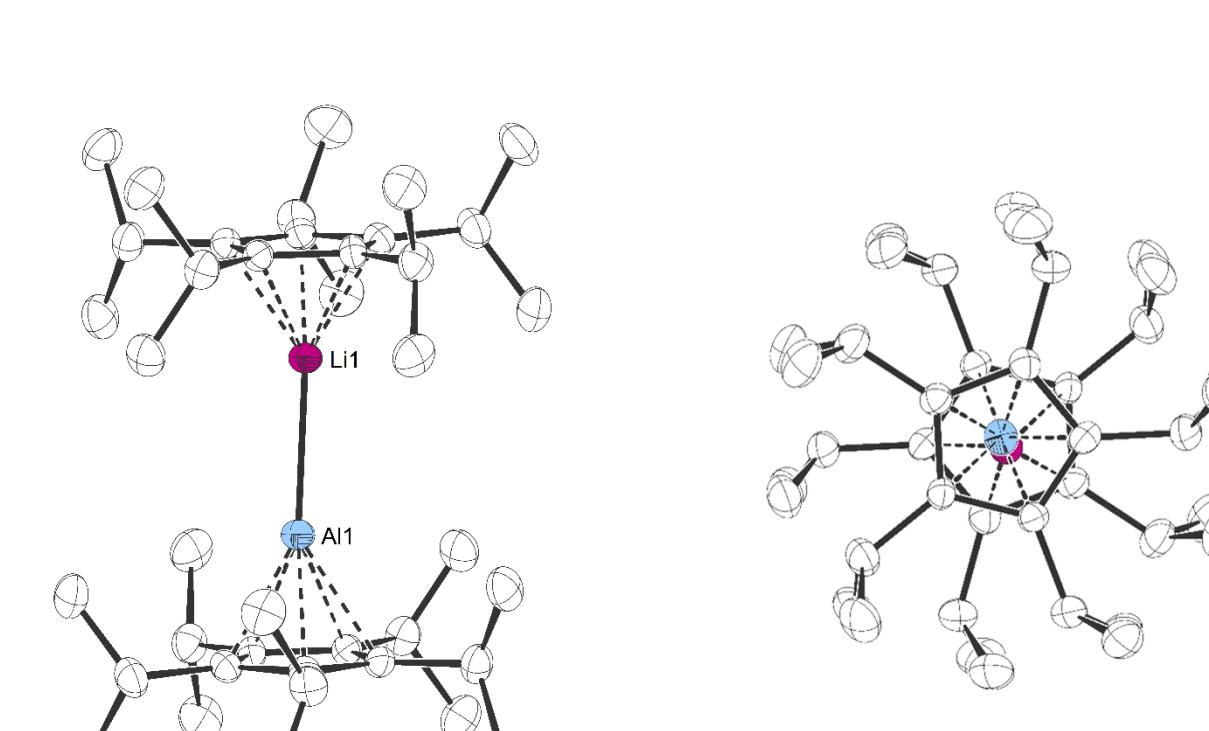
The orbital interaction is dominated by the donation of the lone pair of the aluminum atom of the ⁵CpAl fragment into the formally vacant orbital of the lithium atom of the ⁵CpLi fragment. The dispersion interactions between the ⁵Cp ligands are the key factor to stabilizing the Al–Li bonding interaction in **4**.



Reaction of **1** with W(CO)₆ in thf under UV irradiation (365nm) yields the corresponding tungsten pentacarbonyl complex **3**.



Molecular structure of **3** in the crystal (displacement ellipsoids at 50% probability level, H atoms omitted).

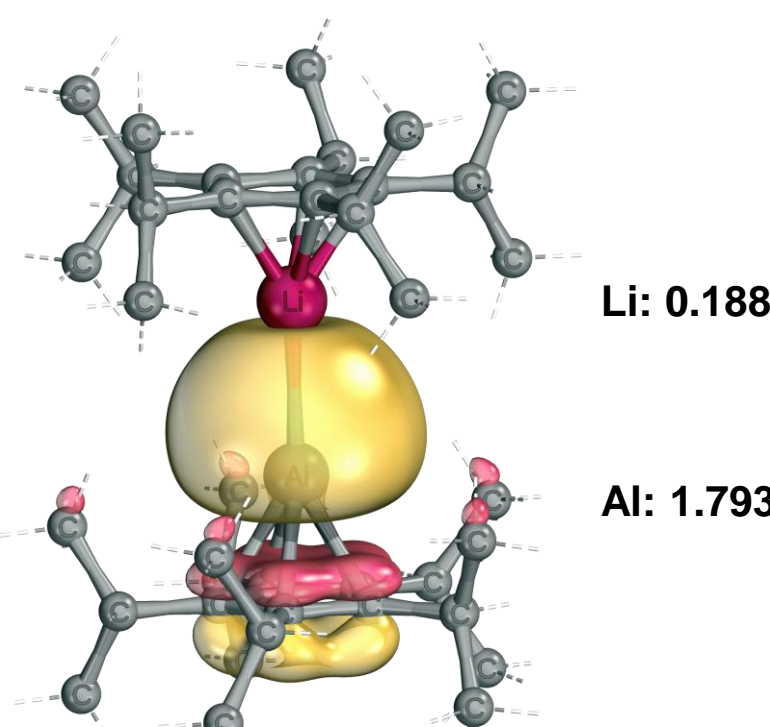


Molecular structure of **4** in the crystal (displacement ellipsoids at 50% probability level, H atoms omitted).

Bond distances in **2** and **3** in [pm]:

	⁵ CpAl→AlBr ₃	⁵ CpAl→W(CO) ₅
Al1–[M]	255.5(1) ([M] = AlBr ₃)	258.5(6) ([M] = W(CO) ₅)
Al1–Cp ^{cent}	178.3(9)	183.5(6)
C ^{Cp} –C ^{Cp}	142.9(4) to 143.9(4)	142.8(1) to 143.6(9)
M–CO ^{cis}	-	202.2(3) to 204.5(3)
M–CO ^{trans}	-	199.7(3)
C–O ^{cis}	-	113.7(3) to 115.0(3)
C–O ^{trans}	-	114.4(4)

In both complexes, **2** and **3**, the Al1–Cp^{cent} distance decreases in comparison to **1**, due to the electron deficiency at the aluminum(I) center, the electron-withdrawal power of the coordinated metal fragment respectively, and the corresponding compensation by the ⁵Cp ligand.



Left: Intrinsic Bond Orbitals (IBO: M06-2X/def2-SVP); center: Molecular Orbital diagram for the Al–Li bond in dimetalloocene **4**; right: dispersion interaction density (DID) plot (LMP2/cc-pVTZ(C,H,Al)&cc-pCVTZ(Li)).

REFERENCES:

- X. Zhang, Y. Mei, L. L. Liu *Chem. Eur. J.* **2022**, *28*, e202202102.
- C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 564.
- H. Sitzmann, M. F. Lappert, C. Dohmeier, C. Üffing, H. Schnöckel *J. Organomet. Chem.* **1998**, *561*, 203.
- a) A. Hofmann, T. Tröster, T. Kupfer, H. Braunschweig *Chem. Sci.* **2019**, *10*, 3421; b) C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu *Angew. Chem. Int. Ed.* **2000**, *39*, 4274; c) J. D. Queen, A. Lehmann, J. C. Fetting, H. M. Tuononen, P. P. Power *J. Am. Chem. Soc.* **2020**, *142*, 49, 20554; d) X. Zhang, Y. Mei, L. L. Liu *Chem. Eur. J.* **2022**, *28*, e202202102; e) A. Hinz, M. P. Müller *Chem. Commun.* **2021**, *57*, 12532.

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