Donor-free Al-doped PAHs: molecular structures and reactivity

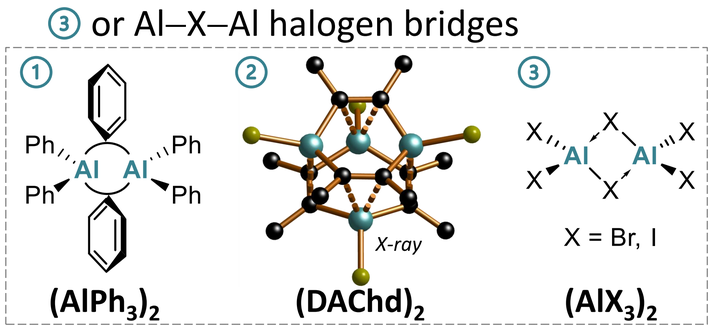
Paula Louise Lückert, Jannik Gilmer, Alexander Virovets, Hans-Wolfram Lerner, Matthias Wagner*

Institute of Inorganic and Analytical Chemistry, Goethe-University Frankfurt am Main, Max-von-Laue Str. 7, 60438 Frankfurt am Main, Germany

Introduction

AlX_3 & AlR_3[1,2]

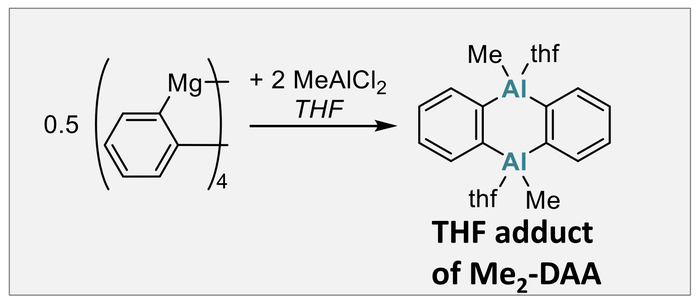
- High bond polarization (Al–C > B–C)
- Coordination numbers > 4 are possible
- In donor-free solvents stabilized by
  ① Al–R–Al 2e3c bonds,
  ② Al···π(Ar) complexes,
  ③ or Al–X–Al halogen bridges



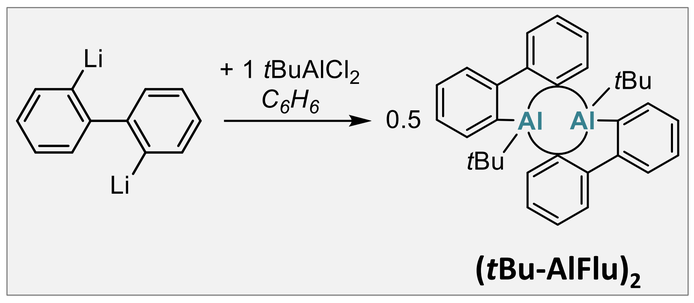
$(AlPh_3)_2$ $(DAChd)_2$ $(AlX_3)_2$

PREVIOUS APPROACHES[3,4]

- Mainly synthesized using organolithium or organomagnesium reagents



THF adduct of Me_2-DAA



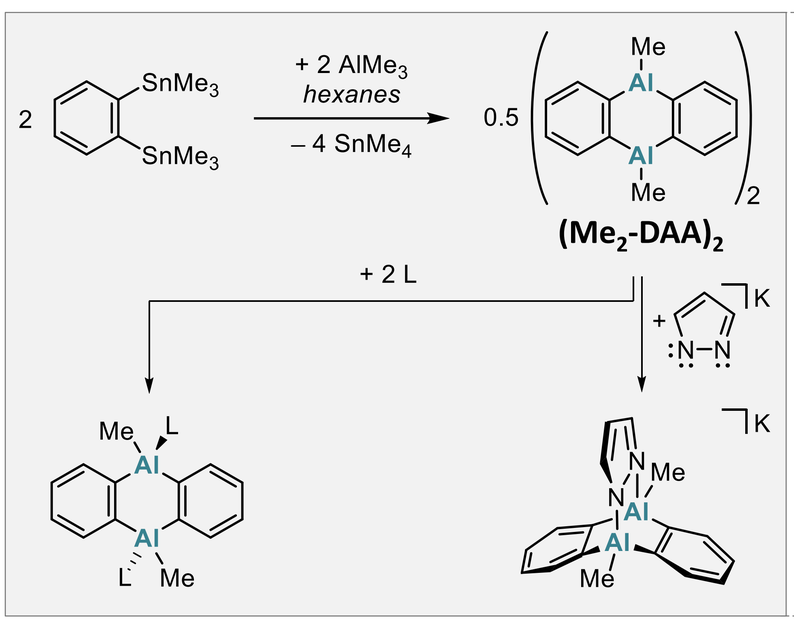
$(t$Bu-AlFlu$)_2$

- Often requires donor solvents that diminish reactivity (removal not possible afterwards)
- Late-stage derivatization is not feasible

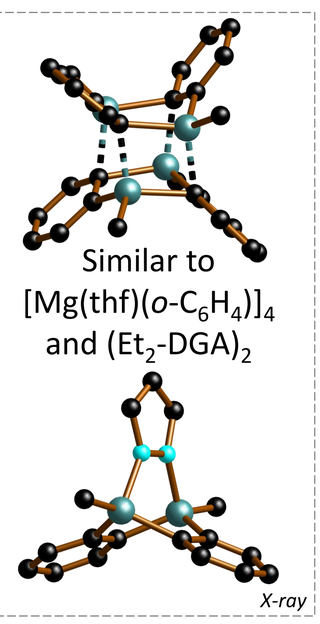
TARGET: Selective access to donor-free Al-doped PAHs to study structure-property relationships.

Synthesis of Al-doped PAHs

9,10-DIHYDRO-9,10-DIALUMINAANTHRACENE (DAA)[5]



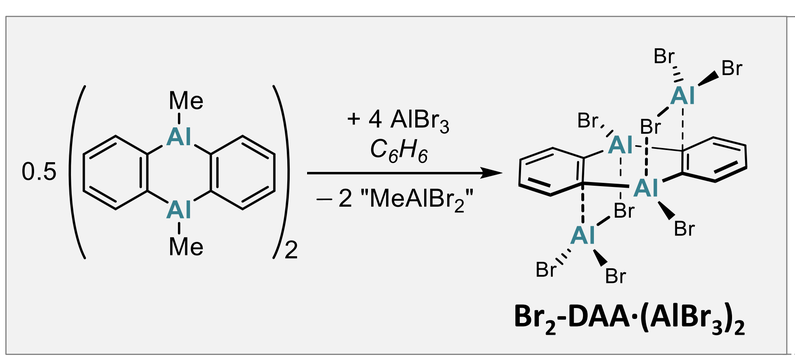
$(Me_2$-DAA$)_2$



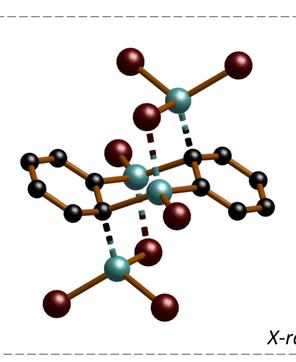
Similar to $[Mg(thf)(o\text{-}C_6H_4)]_4$ and $(Et_2$-DGA$)_2$

X-ray

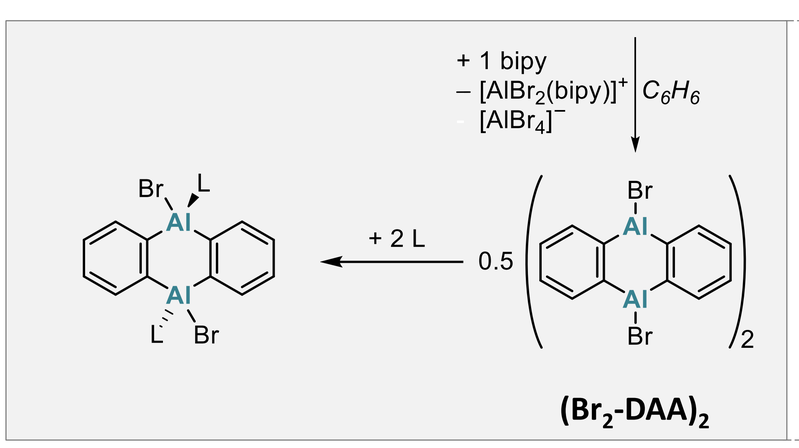
X-ray



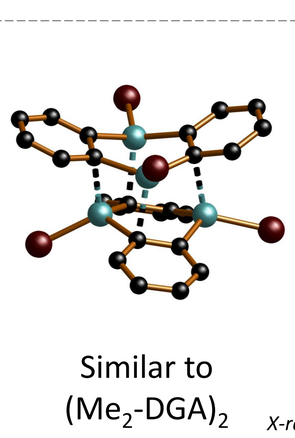
Br_2-DAA·$(AlBr_3)_2$



X-ray



$(Br_2$-DAA$)_2$



Similar to $(Me_2$-DGA$)_2$

X-ray

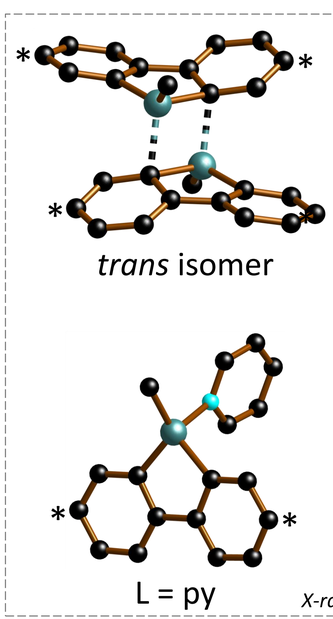
AlMe

AlBr·AlBr$_3$

AlBr

AlR

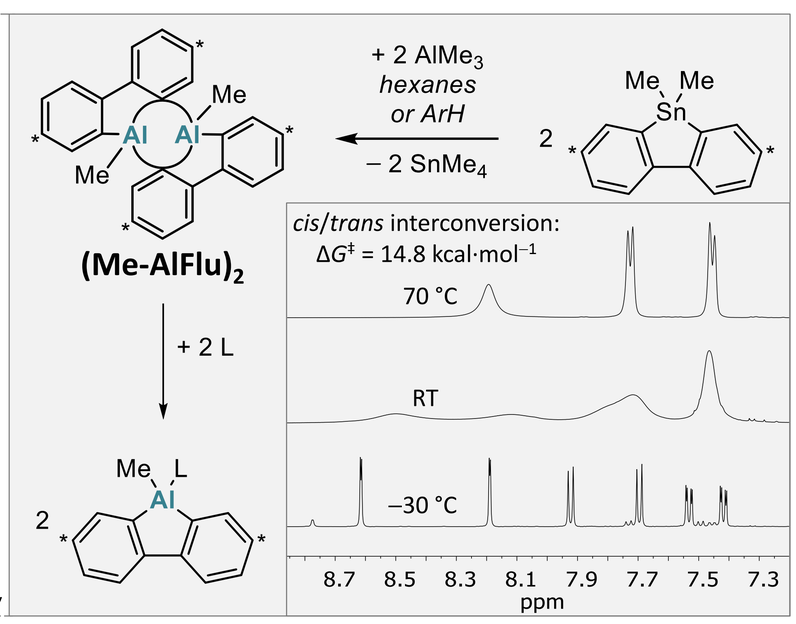
9-ALUMINAFLUORENE (AlFlu)[6]



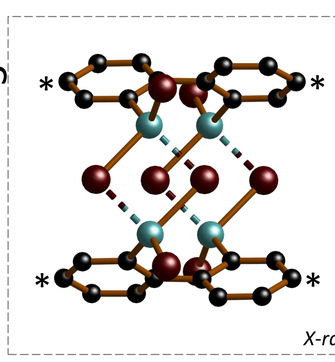
trans isomer

L = py

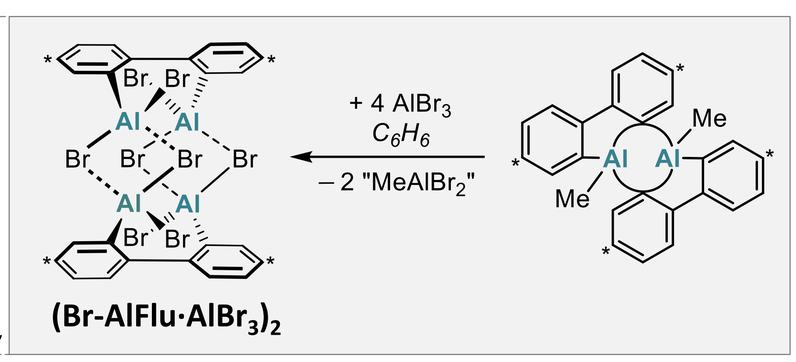
X-ray



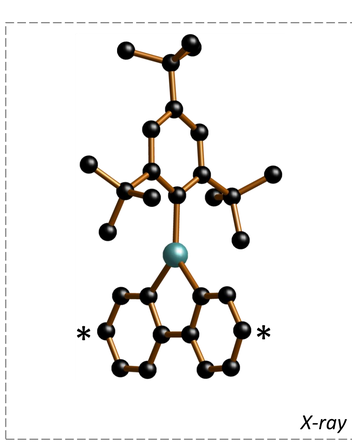
$(Me$-AlFlu$)_2$



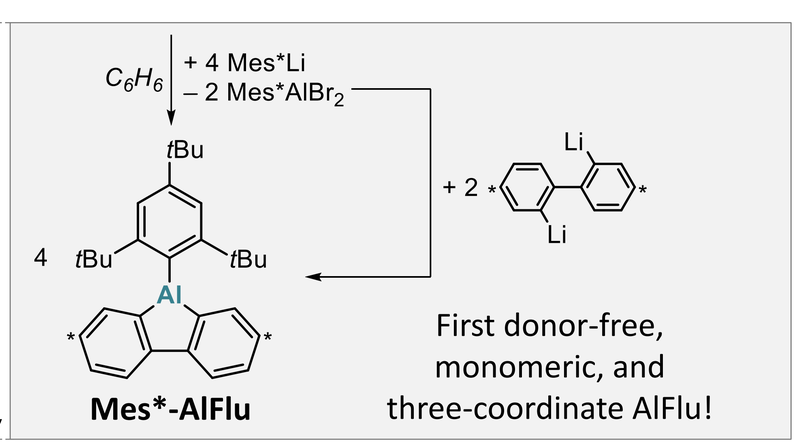
X-ray



(Br-AlFlu·$AlBr_3)_2$



X-ray

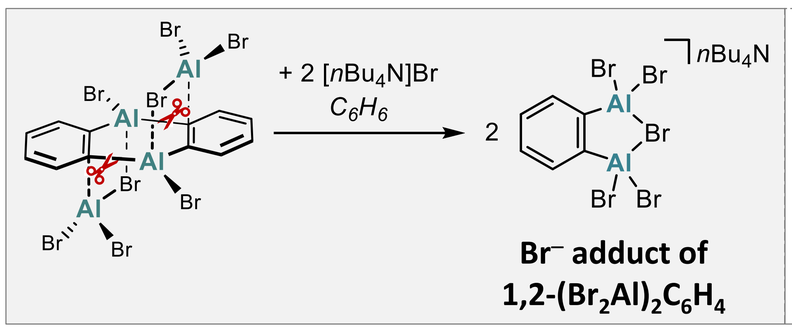


Mes*-AlFlu

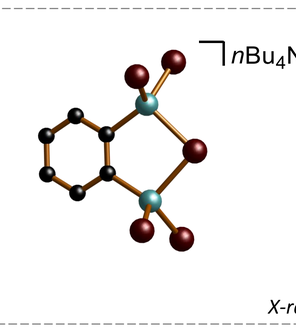
First donor-free, monomeric, and three-coordinate AlFlu!

DONOR-FREE ✓ **UPSCALABLE ✓** **EASY PURIFICATION ✓** **LATE-STAGE DERIVATIZATION ✓**

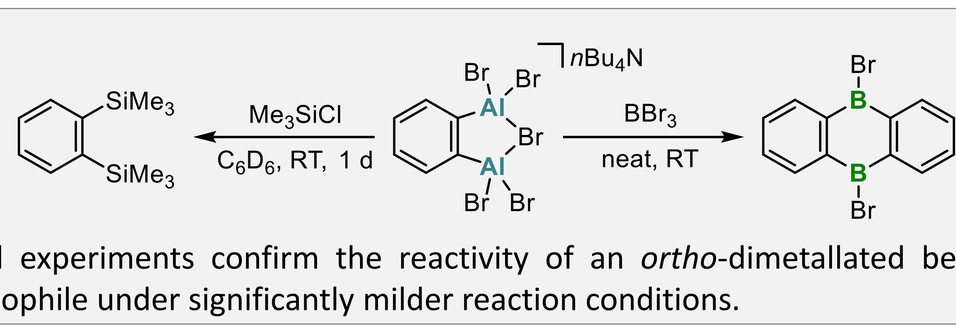
Synthesis and reactivity of a synthetic equivalent of the 1,2-dideprotonated benzene nucleophile



Br^- adduct of $1,2\text{-}(Br_2Al)_2C_6H_4$



X-ray



Initial experiments confirm the reactivity of an *ortho*-dimetallated benzene nucleophile under significantly milder reaction conditions.

REFERENCES:

[1] Holleman & Wiberg, *Lehrbuch der Anorganischen Chemie*, De Gruyter, Berlin **2007**.
[2] H. Schnöckel *et al.* in *Angew. Chem. Int. Ed.* **1986**, *25*, 921–922.
[3] F. Bickelhaupt *et al*. in *Organometallics* **1999**, *18*, 1706–1709.
[4] H. Braunschweig *et al*. in *Dalton Trans.* **2021**, *50*, 10400–10404.
[5] P. L. Lückert & M. Wagner *et al*. in *Chem. Sci.*, 10.1039/D4SC06940D.
[6] P. L. Lückert & M. Wagner *et al*. in *Dalton Trans.*, 10.1039/D4DT03148B.

Carbon atoms marked with asterisks carry *t*Bu groups. | *X-ray*: *t*Bu groups and H atoms are omitted for clarity.

FREUNDE DER UNIVERSITÄT

GDCh Gesellschaft Deutscher Chemiker

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