A selective synthesis approach for aluminum-doped polycyclic aromatic hydrocarbons

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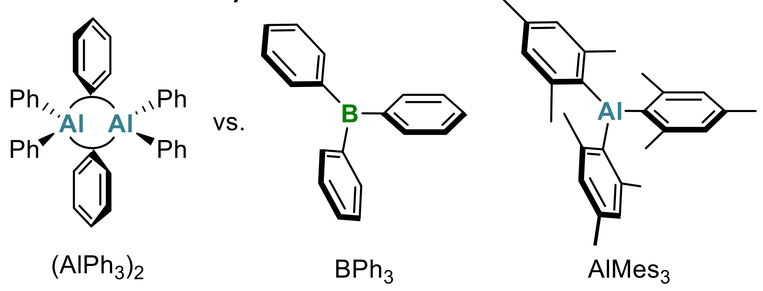
Introduction

ALUMINUM TRIORGANYLS[1–2]

- **Al**–**C** bond strongly polarized due to the low electronegativity of Al
- Stabilization by **Al**–**R**–**Al** 2e3c bonds if R is not too bulky

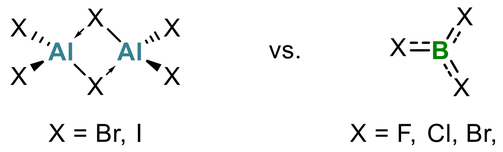


$(AlPh_3)_2$ BPh_3 $AlMes_3$

- Widely applied to organic synthesis and polymer chemistry

ALUMINUM TRIHALIDES[1,3]

- Lower tendency for π bond formation
- Stabilization by **Al–X–Al** halogen bridges



X = Br, I X = F, Cl, Br, I

- Use as Lewis acid catalyst (e.g. Friedel-Crafts alkylation and acylation) or as electrolytes in Al-based batteries

PREVIOUS APPROACHES[4–6]

- Mainly synthesized employing organolithium or organograignard reagents

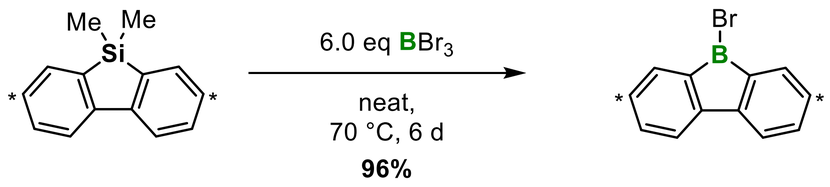
- Often require donor solvents
- Low selectivity and yields
- Lack of analytical data

TASK SETTING

- **Paving the way toward selective access routes to donor-free Al-doped PAHs.**
- **Exploring structure/property relationships of mixed aryl- and halogen-substituted alanes.**

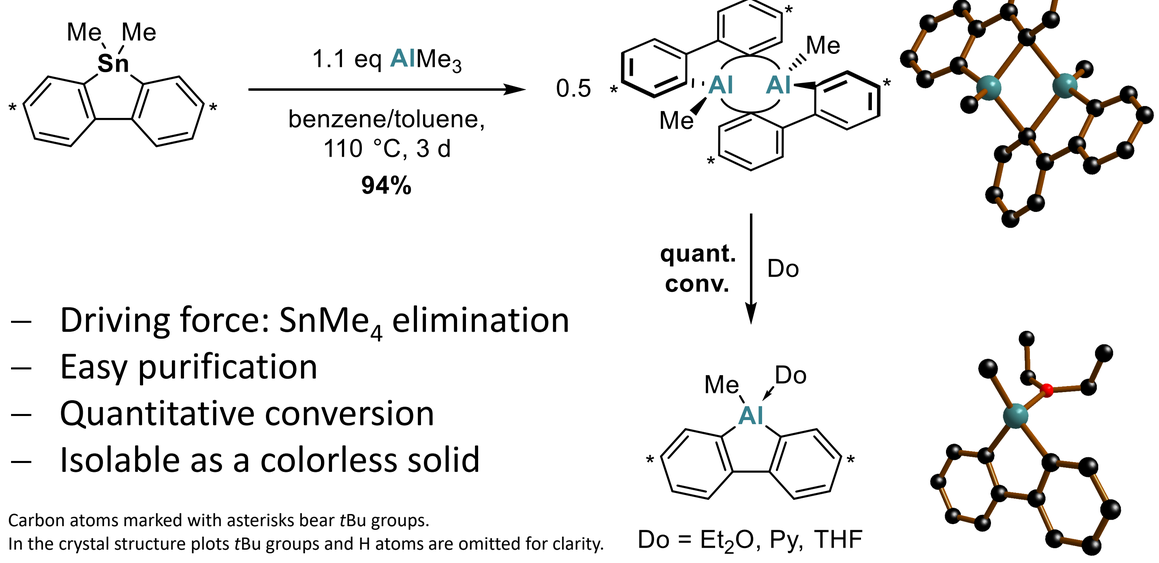
Synthesis and coalescence phenomenon of $(Me\text{-}AlFlu)_2$

Si/B EXCHANGE REACTION FOR THE SYNTHESIS OF BORAFLUORENES[7]



- Si/Al exchange reaction not possible
- Synthesis of the more reactive stannafluorene precursor necessary

Sn/Al EXCHANGE REACTION FOR THE SYNTHESIS OF ALUMINAFLUORENES

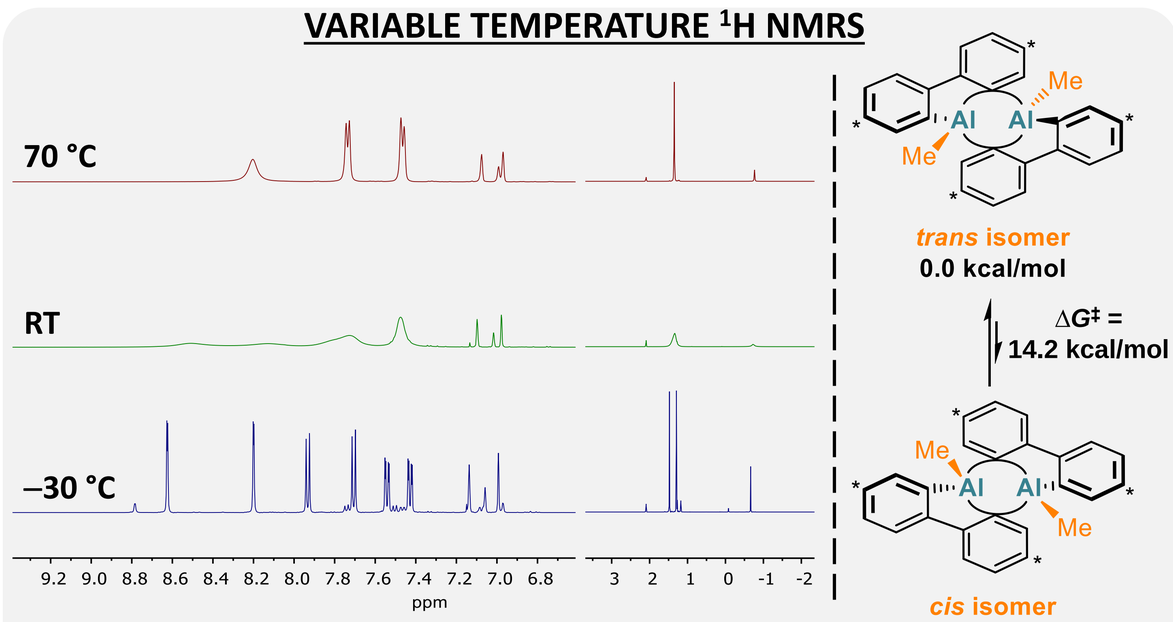


Do = Et_2O, Py, THF

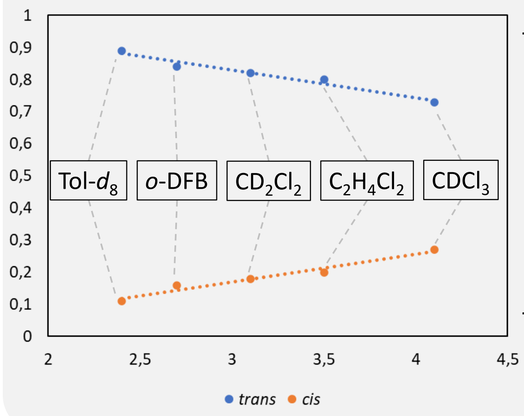
- Driving force: $SnMe_4$ elimination
- Easy purification
- Quantitative conversion
- Isolable as a colorless solid

Carbon atoms marked with asterisks bear *t*Bu groups.
In the crystal structure plots *t*Bu groups and H atoms are omitted for clarity.

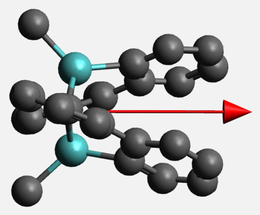
VARIABLE TEMPERATURE ^{1}H NMRS



INFLUENCING THE ISOMER RATIO



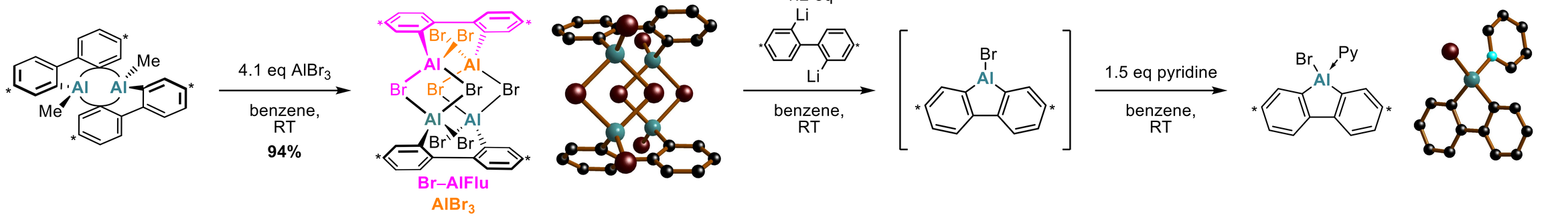
- Due to the dipole moment of the *cis* isomer, its relative quantity increases with the polarity of the solvent.
- The largest amount of *cis* is observed in $CDCl_3$ (≈ 30%).



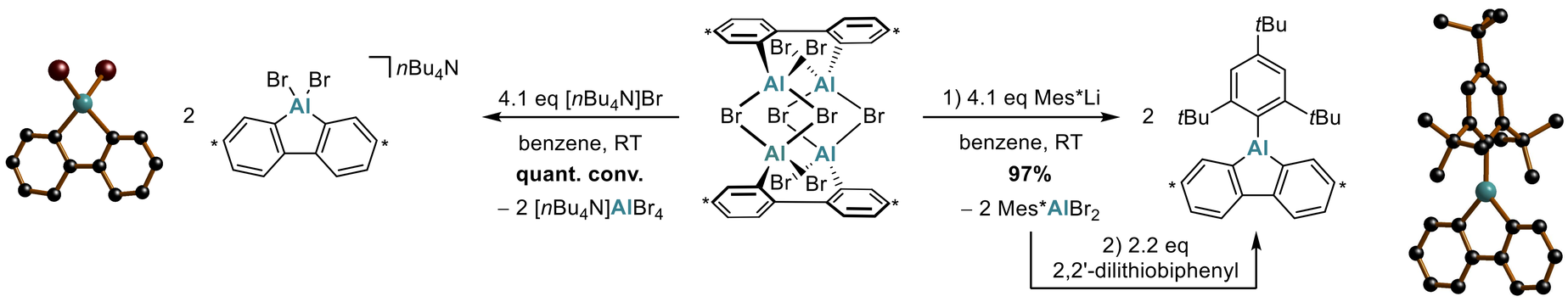
Dipole moment of *cis* Me-AlFlu

SMD(C_6H_6)/ωB97XD/def2-QZVP//
SMD(C_6H_6)/ωB97XD/6-31+G**

Synthesis route to halogenated aluminafluorenes



Further derivatizations of dimeric Br–AlFlu · $AlBr_3$



A monomeric and donor-free Al-doped PAH!

- The $AlBr_3$ adduct shows the same reactivity as a 2,2'-biphenylylene-substituted alumole.
- Reactivity studies of Br_2–$AlFlu^-$ and Mes*–AlFlu (esp. reduction) are undergoing.

References:
[1] *Lehrbuch der Anorganischen Chemie*, Walter De Gruyter, Berlin **2007**.
[2] *J. Organomet. Chem.* **1974**, *72*, 157–162.
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[7] *Angew. Chem. Int. Ed.* **2012**, *51*, 12514–12518.