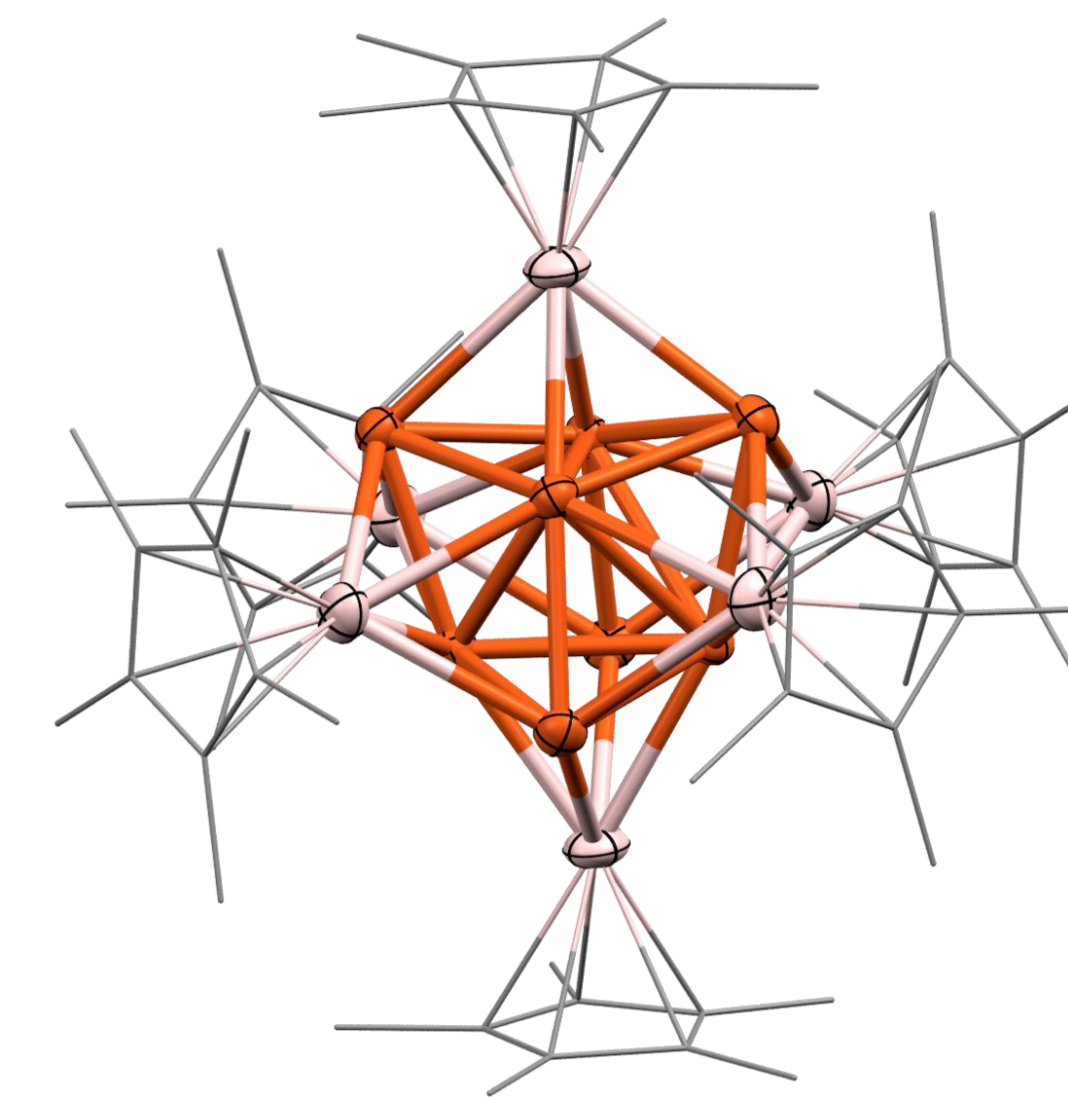


A closer look at the $[\text{Cu}_{7/8}\text{Al}_6](\text{Cp}^*)_6$ cluster family: Synthesis, characterization and reactivity

Matthias Huber*

Introduction

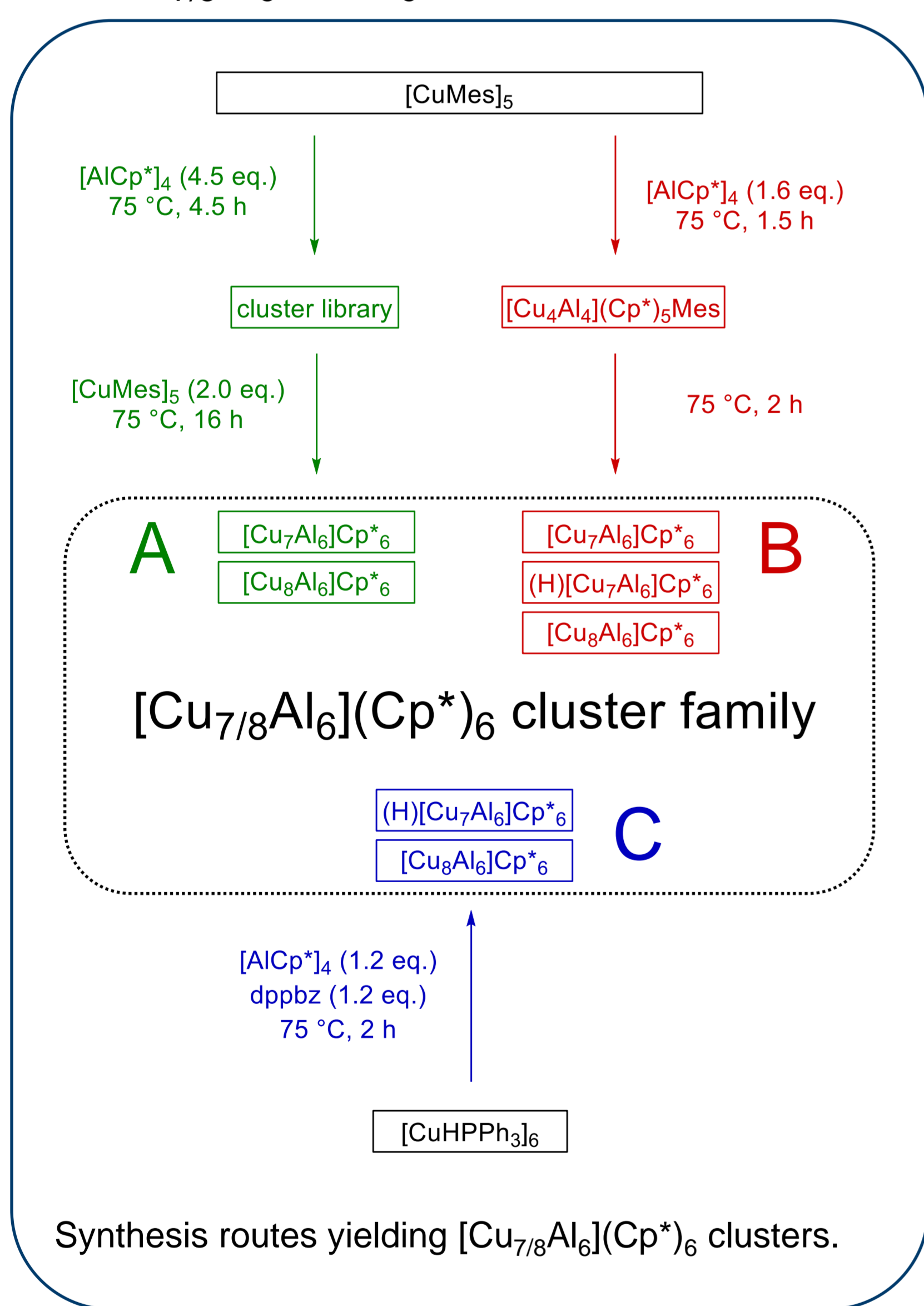
Due to their variable electronic and geometric properties molecular clusters can be seen as models for active sites of solid catalysts.^[1] The clusters (for example the M_{55} superatom $[\text{Cu}_{43}\text{Al}_{12}](\text{Cp}^*)_{12}$) often show structural and electronic analogies to the corresponding solid-state phases but their synthesis is usually intricate, and the mechanisms of cluster growth are rarely understood.^[2] In the scope of this work, identity, synthesis and reactivity of Cu/Al clusters belonging to the $[\text{Cu}_{7/8}\text{Al}_6](\text{Cp}^*)_6$ family were further elucidated. These clusters are known to be accessible from $[\text{AlCp}^*]_4$ and either $[\text{CuMes}]_5$ or $[\text{CuHPPH}_3]_6$, their exact identity, however, has not been resolved so far. Therefore, high resolution LIFDI-MS was applied to identify and rationalize differences between the synthetic routes. Reactivity of mixtures of different cluster species in solution was probed by means of *in situ* LIFDI-MS.



Molecular structure of $[\text{Cu}_8\text{Al}_6](\text{Cp}^*)_6$, a closed shell cluster with Cu_8 core surrounded by six AlCp^* moieties.

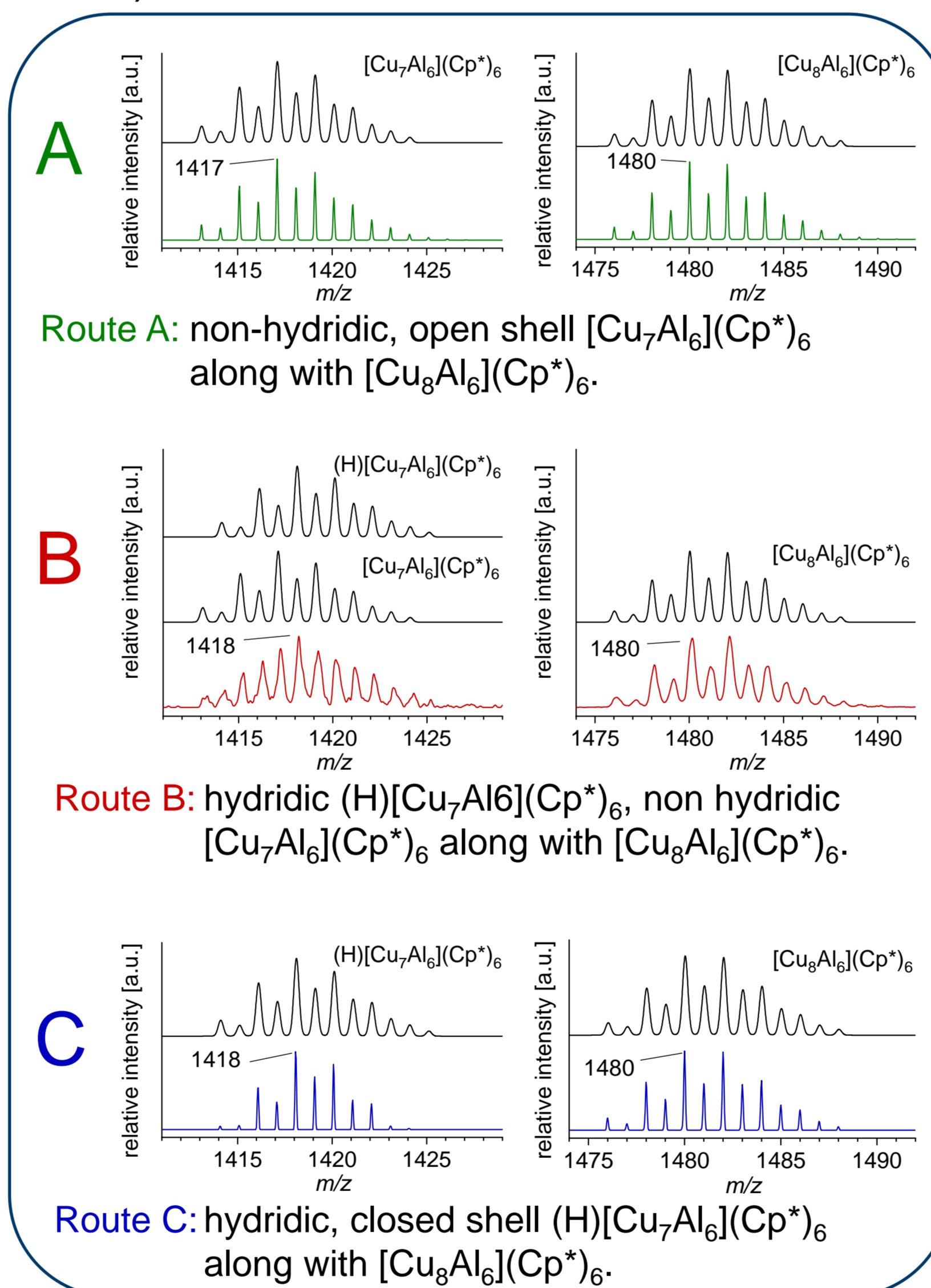
Synthesis of $M_{13/14}$ clusters

$[\text{AlCp}^*]_4$ is reacted with either $[\text{CuMes}]_5$ or $[\text{CuHPPH}_3]_6$ to yield different clusters of the $[\text{Cu}_{7/8}\text{Al}_6](\text{Cp}^*)_6$ family.



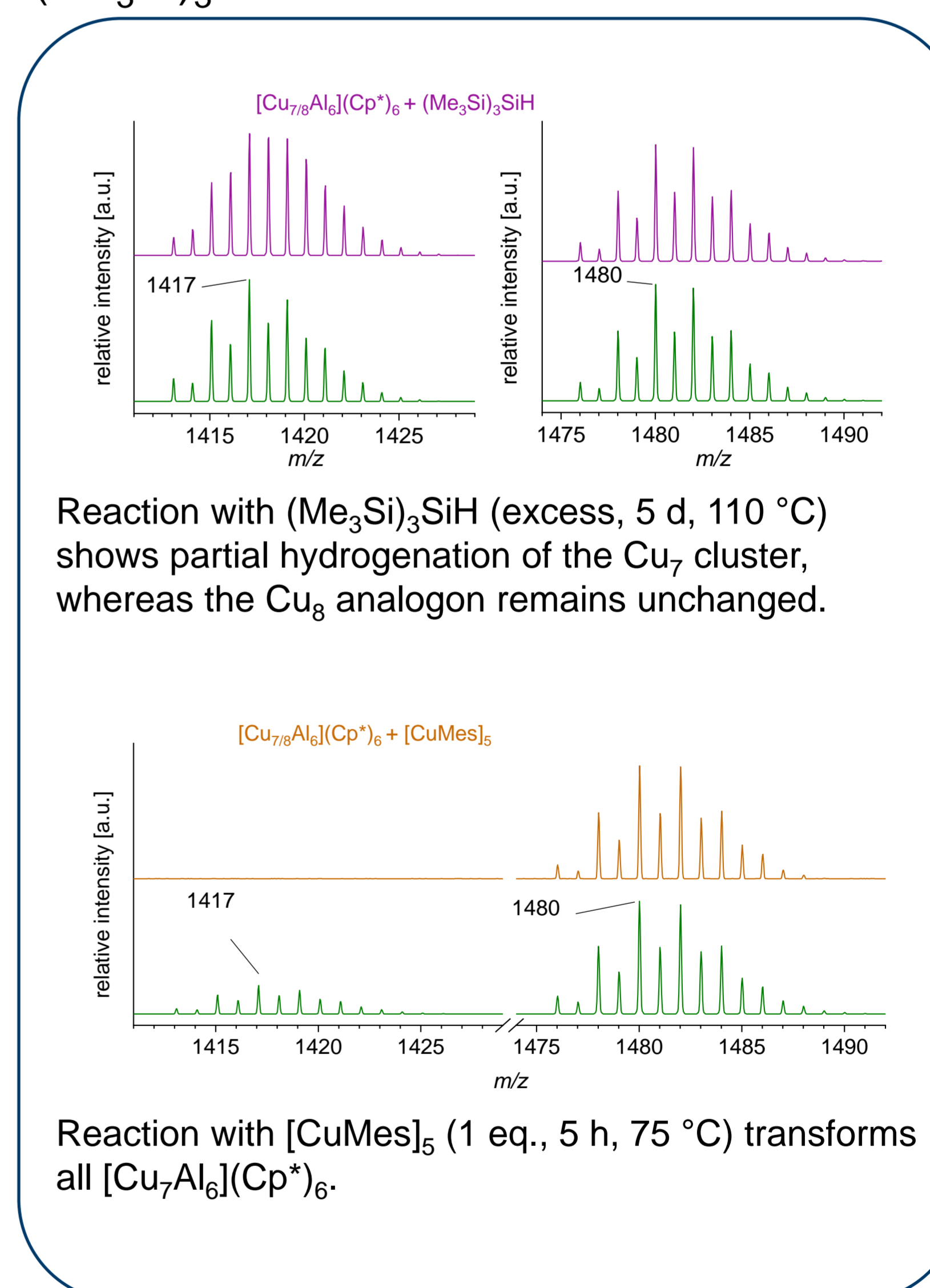
Identification of the reaction products

LIFDI-MS allows the identification of the reaction products (calculated spectra in black):



Reactivity of the clusters

Reactivity of the mixture of $[\text{Cu}_7\text{Al}_6](\text{Cp}^*)_6$ and $[\text{Cu}_8\text{Al}_6](\text{Cp}^*)_6$ from route A was probed by addition of $[\text{CuMes}]_5$ and $(\text{Me}_3\text{Si})_3\text{SiH}$.



Conclusion

The synthesis route C, using the phosphine precursor $[\text{CuPPh}_3]_6$, was proven to yield the hydridic (H) $[\text{Cu}_7\text{Al}_6](\text{Cp}^*)_6$ along with $[\text{Cu}_8\text{Al}_6](\text{Cp}^*)_6$. In contrast, a mixture of the non-hydridic clusters $[\text{Cu}_{7/8}\text{Al}_6](\text{Cp}^*)_6$ was selectively obtained from the reaction of $[\text{CuMes}]_5$ with $[\text{AlCp}^*]_4$ (route A). This shows that two different species with Cu_7Al_6 core exist, namely the closed-shell hydride, as well as the open shell radical. The hypothesis of a higher reactivity of the latter compared to the diamagnetic $[\text{Cu}_8\text{Al}_6](\text{Cp}^*)_6$ was verified by reactions with $(\text{Me}_3\text{Si})_3\text{SiH}$ and $[\text{CuMes}]_5$. In addition, thermal decomposition of the medium size Cu/Al cluster $[\text{Cu}_4\text{Al}_4](\text{Cp}^*)_5\text{Mes}$ (route B) turned out to result in a mixture of $[\text{Cu}_7\text{Al}_6](\text{Cp}^*)_6$, (H) $[\text{Cu}_7\text{Al}_6](\text{Cp}^*)_6$ and $[\text{Cu}_8\text{Al}_6](\text{Cp}^*)_6$ among others.

* Chair of Inorganic and Metal-Organic Chemistry (Prof. Roland A. Fischer)

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