

Synthesis and Reactivity of Tetranuclear Zinc Amidinate Complexes

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Very recently we reported on reactions of carbodiimides $C(NR)_2$ ($R = i\text{-Pr}$, Cy) with dimethylzinc at elevated temperatures, resulting in the formation of tetranuclear zinc amidinate complexes such as $\{C[C(NR)_2ZnMe]_4\}$ ($R = i\text{-Pr}$ **1a**, Cy **1b**) by an insertion/deprotonation mechanism.^[1] The $Zn\text{-Me}$ groups within these complexes were expected to be suitable for further substitution reactions, but reactions with H-acidic compounds failed to give the expected methane-elimination products, demonstrating that the $Zn\text{-Me}$ group is rather less reactive. In contrast, **1a** easily reacts with aluminum halides AlX_3 at moderate temperatures under methyl/halide exchange yielding the halide-substituted complexes $\{C[C(NR)_2ZnX]_4\}$ ($X = Cl$ **2**, Br **3**, I **4**), which are promising starting reagents for salt-elimination reactions. **2** reacts with $MeLi$, $n\text{-BuLi}$ and $EtMgBr$ almost quantitatively to the corresponding alkyl-substituted derivatives $\{C[C(NR)_2ZnR]_4\}$ ($R = Me$ **1a**, $n\text{-Bu}$ **5**, Et **6**).^[2]

Moreover, reactions of **2** with KH , $LiHBEt_3$ or CaH_2 yield the corresponding tetranuclear zinc hydride amidinate complex $\{C[C(NR)_2ZnH]_4\}$ **7** exhibiting four terminal $Zn\text{-H}$ bonds. Initial studies on reactions with phenylacetylene and acetylene showed an enhanced reactivity to give the hydrogen-elimination products $\{C[C(NR)_2ZnR]_4\}$ ($R = C\text{CPh}$ **8**, $C\text{CH}$ **9**), whereas the $Zn\text{-Me}$ complex **1a** failed to react even at elevated temperatures.^[3]

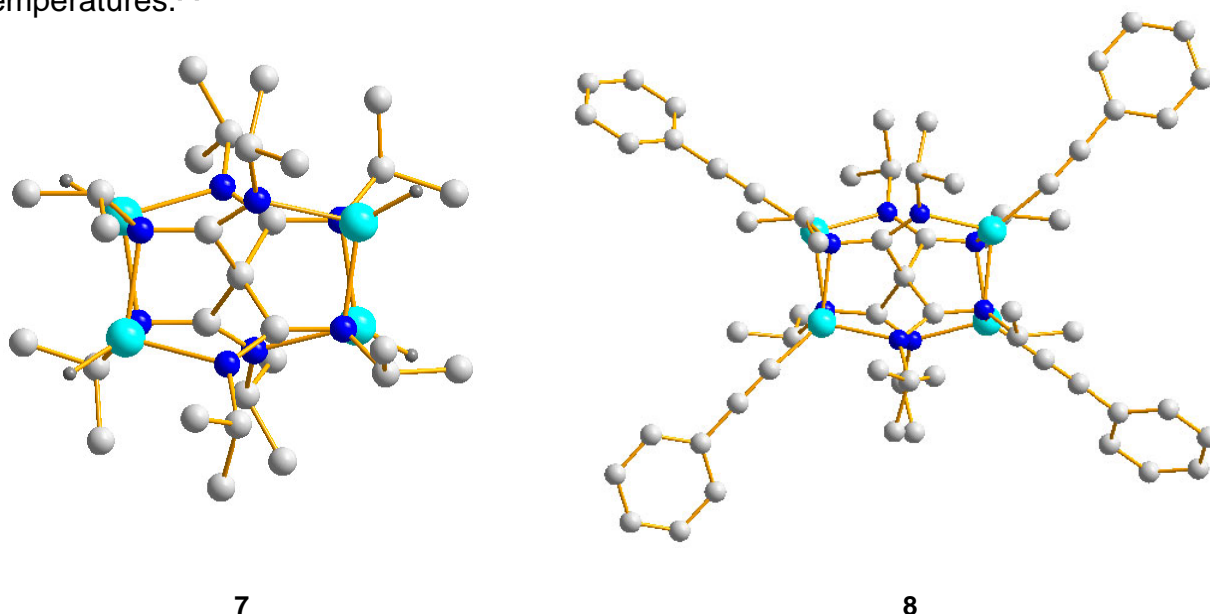


Figure 1. Crystal structures of complexes **7** and **8**. Hydrogen atoms are omitted for clarity.

References

- [1] M. Münch, M. Bolte, U. Flörke, S. Schulz, D. Gudat, *Angew. Chem.* **2008**, *120*, 1535-1537. S. Schmidt, S. Gondzik, S. Schulz, D. Bläser, R. Boese *Organometallics*. **2009**, *28*, 4371-4376.
[2] B. Gutschank, S. Schulz, U. Westphal, D. Bläser, R. Boese, *Organometallics* **2010**, *29*, 2093-2097.
[3] B. Gutschank, S. Schulz, D. Bläser, R. Boese, *in preparation*.