

Synthesis and Characterization of Novel Organozinc Compounds

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Amidines (LH) and amidinates (L-) ($L = RC(NR')_2^-$) have been widely investigated in main group, transition, and lanthanide metal chemistry, due to their flexible steric and electronic properties, which can be tuned to some extent by variation of the organic substituents (R, R'). Moreover, their flexibility to coordinate as monodentate (η^1), chelating (η^2) or bridging monodentate (μ - η^1 - η^1) four-electron donor render these complexes very promising for technical applications in catalysis and material sciences.^[1] We became only recently interested in zinc amidinate complexes and investigated reactions of dialkylzinc complexes and carbodiimides. $C(Ni-Pr)_2$ was found to react with $ZnEt_2$ with formation of $[EtC(Ni-Pr)_2ZnEt]_2$, whereas the reaction with $ZnMe_2$ yielded polynuclear zinc amidinate complexes such as $\{C[C(Ni-Pr)_2ZnMe]_4\}$ rather than the expected monoamidinate complex $LZnMe$ (L=amidinate).^[2]

Herein, we report on the synthesis and single-crystal X-Ray structures of novel amidinate complexes such as $[t-BuC(NDipp)_2]ZnMe$ **1**, which was synthesized by a methane elimination reaction between $t-BuC(NHDipp)(NDipp)$ and $ZnMe_2$. Unexpectedly, the amidinate ligand in **1** was found to coordinate in a η^1 -N, η^3 -arene mode, which is rather unusual for this type of ligand. The corresponding iodine-substituted amidinate zinc complex **2**, which was synthesized by methyl exchange reaction of **1** with iodine, in contrast shows the expected N,N'-chelating binding mode. **1** was also found to react with *t*-butyl pyridine with formation of adduct **3**, in which the amidinate group also adopts a N,N'-chelating binding mode.^[3]

In addition, we expanded our studies on the reaction of $ZnMe_2$ with carbodiimides to reactions with heterocumulenes such as isocyanates $RNCO$ and report on first results obtained from the reaction between $ZnMe_2$ and $RNCO$ (R = *t*-Bu **4**, *i*-Pr **5**).^[4]

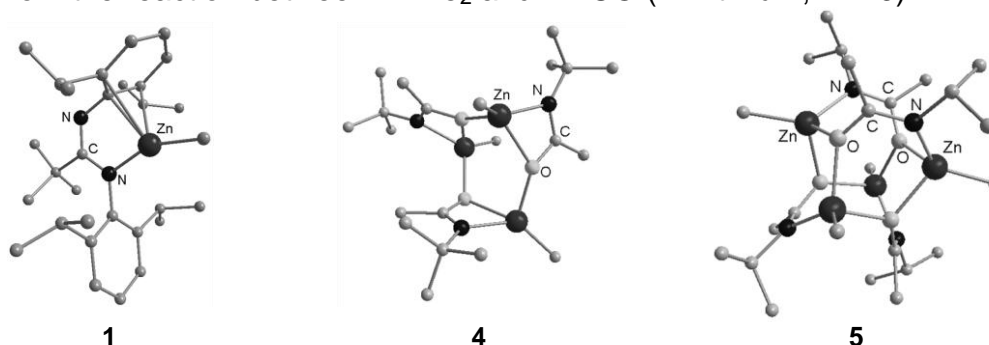


Figure 1. Single-crystal X-Ray structures of complexes **1**, **4** and **5**. Hydrogen atoms are omitted for clarity.

References:

- [1] See the following and references cited therein: M. L. Cole, *J. Chem. Soc., Chem. Commun.* **2007**, 1579; F. T. Edelman, *Adv. Organomet. Chem.* **2008**, 57, 183; F. T. Edelman, *Chem. Soc. Rev.* **2009**, 38, 2253. [2] S. Schulz, M. Münch, U. Flörke, *Z. Anorg. Allg. Chem.* **2008**, 634, 2221; M. Münch, U. Flörke, M. Bolte, S. Schulz, D. Gudat, *Angew. Chem.* **2008**, 120, 1535; *Angew. Chem. Int. Ed.* **2008**, 47, 1512. [3] S. Schmidt, S. Schulz, U. Westphal, D. Bläser, R. Boese, *Organometallics*, submitted. [4] S. Schmidt, S. Schulz, in preparation.