

Berichte aus der Chemie

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**Neutral and Cationic Zirconium Alkyl
and Hydride Complexes Supported
by a Macrocycle Based on Cyclen**

Synthesis, Characterization and Reactivity

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Cationic alkyl and cationic hydride complexes of zirconium are of particular interest as they play an important role as the active species in olefin polymerization and hydrogenation. The main objective of this work was to study the accessibility of cationic alkyl and hydride complexes of zirconium stabilized with macrocyclic ligands based on cyclen, their characterization, both in solid state and in solution, as well as their reactivity towards small molecules (e.g. CO).

This work describes the preparation, isolation, and characterization of new cationic alkyl and hydride compounds of zirconium. Detailed analysis of the coordination chemistry of these complexes in solution and in the solid state established the basis for understanding structure-reactivity-relationships, like C–H bond activation of heterocycles (e.g. THF) and Fischer-Tropsch reactions.

In chapter B.1, the synthesis and characterization of new neutral group 4 alkyl complexes stabilized with a mono- and a dianionic macrocyclic ligand based on cyclen are presented ($[\text{Zr}(\text{Me}_3\text{TACD})(\text{CH}_2\text{SiMe}_3)_3]$ and $[\text{Zr}(\text{Me}_2\text{TACD})(\text{CH}_2\text{SiMe}_3)_2]$).

Chapter B.2 reports on the synthesis, characterization and reactivity of the corresponding cationic zirconium alkyl complexes with alkylation reagents, alcohols and amines.

Chapter B.3 addresses the unusual C–H bond activation of heterocycles (e.g. THF and pyridine) by the cationic dialkyl complexes $[\text{Zr}(\text{Me}_3\text{TACD})(\text{CH}_2\text{SiMe}_3)_2][\text{A}]$ in the presence of phenylsilane. Kinetic and mechanistic investigations suggest a multistep reaction mechanism while a cationic alkyl silyl complex is formed, which activates the C–H bond of THF in the *ortho*-position and give the thermally stable complexes $[\text{Zr}(\text{Me}_3\text{TACD})(\text{CH}_2\text{SiMe}_3)(\text{C}_4\text{H}_7\text{O})][\text{A}]$.

Chapter B.4 deals with the synthesis, characterization and reactivity of cationic zirconium hydride complexes. The reaction of $[\{\text{Zr}(\text{Me}_3\text{TACD})(\mu\text{-H})_2\}_2][\text{A}]_2$ and carbon monoxide give ethylene through an oxymethylene and an enolate intermediate while two different propenolate species were also observed but do not release propene.

Chapter B.5 introduces a new ligand class (*meta*-cyclophanes) suitable for early main group as well as early transition metals. The synthesis and characterization of a cationic zirconium complex $[\text{Zr}(\text{Me}_3\text{TAMC}_2)(\text{CH}_2\text{C}_6\text{H}_5)_2][\text{A}]$ and a dicationic dimeric lutetium hydride complex $[\text{Lu}(\text{Me}_3\text{TAMC}_2)(\text{THF})(\mu\text{-H})_2][\text{A}]_2$ are presented.