

(Amido)- and (Chlorido)titanium and -zirconium Complexes Coordinated by ansa-Bis(amidinate) Ligands with a Rigid o-Phenylene Linker

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Abstract

© 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim Bis(amido)-Ti IV and -Zr IV complexes stabilized by the bis(amidinate) ligands $\{C_6H_4-1,2-[NC(tBu)N(2,6-R_2C_6H_3)]_2\}M(NMe_2)_2$ [$M = Zr^{IV}$, $R = Me$ (3), $R = iPr$ (4); $M = Ti^{IV}$, $R = Me$ (5), $R = iPr$ (6)] and $\{C_6H_4-1,2-[NC(tBu)N(2,6-Me_2C_6H_3)]_2\}Zr(NMe_2)_3H(3 \cdot HNMe_2)$ were prepared in fairly good yields by treating a (bis)amidine ligand $C_6H_4-1,2-[NC(tBu)N(2,6-R_2C_6H_3)H]_2$ [$R = Me$ (1), iPr (2)] with an equimolar amount of the metal precursor $M(NMe_2)_4$ ($M = Zr^{IV}$, Ti^{IV}). The salt metathesis reactions between equimolar amounts of the sodium amidinates $C_6H_4-1,2-[NC(tBu)N(2,6-R_2C_6H_3)]_2Na_2$ and $ZrCl_4(thf)_2$ were also scrutinized to synthesize the corresponding Zr IV bis(amidinate) dichlorides $\{C_6H_4-1,2-[NC(tBu)N(2,6-R_2C_6H_3)]_2\}ZrCl_2$ [$R = Me$ (7), iPr (8)]. The coordination mode of the ligand to the M IV ions was strongly affected by the steric hindrance of the amidinate ligand (Me- vs. iPr -substituted aniline moieties) as well as by the nature of the ancillary groups bound to the metal center (NMe_2 vs. Cl). The bis(amido) ligand with the 2,6- $Me_2C_6H_3$ substituents at the amidinate nitrogen atoms coordinates to the zirconium ion in a tetradentate fashion both in solution and in the solid state (3 and $3 \cdot HNMe_2$). The compounds containing the bulkier 2,6- $iPr_2C_6H_3$ units prefer a tridentate coordination mode (4). With the smaller Ti IV ion, the bis(amidinate) ligands from this series are tridentate in the solid state (5 and 6), whereas they reversibly switch their denticity from tridentate to tetradentate (κ_3 vs. κ_4) in solution depending on the temperature. The Zr IV complex 4, featuring the bulkier bis(amidinate) ligand 2, shows a behavior similar to that of its Ti IV analogue, that is, a tridentate ligand coordination in the solid state and a temperature-induced denticity change in solution. The standard thermodynamic parameters for the κ_3/κ_4 interconversions of the two model compounds 4 and 5 in $[D_8]toluene$ solution were determined from the respective linear van't Hoff plots. Finally, the Zr IV bis(chloride) complexes 7 and 8 invariably show a tetracoordinate mode for their bis(amidinate) ligands (1 and 2) in solution and in the solid state.

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Keywords

Coordination modes, N ligands, Titanium, Zirconium

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