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Highly substituted zirconium and hafnium cyclopentadienyl bifunctional β-diketiminate complexes – Synthesis, structure, and catalytic activity towards ethylene polymerization

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ABSTRACT

A series of tetramethyl-(Cp′) and pentamethylcyclopentadienyl (Cp*) metal complexes (η^5-C_5Me_4R)$ZrCl_2L^{CO}$ (R = H(**1**), Me(**2**)) and (η^5-C_5Me_4R)$HfCl_2L^{CO}$ (R = H(**3**), Me(**4**)) where L^{CO} is a bifunctional β-diketiminate ligand [2-(MeO)–C_6H_4)]NC(Me)CHC(Me)N[2-(MeO)–C_6H_4)] (L^{CO}) were prepared from corresponding tetramethyl- and (pentamethylcyclopentadienyl)metal trichlorides and the lithium precursor LiL^{CO}. All complexes were characterized by their melting point, elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy. In addition their solid-state structures were determined by X-ray diffraction techniques. In all cases, a pseudo-tetragonal pyramidal coordination environment of the metal centre with cyclopentadienyl ligand on the top and nearly isobidentately bonded nitrogen atoms of the chelating L^{CO} ligand in an open η^5-fashion was observed. The oxygen atoms positioned at the diketiminate periphery remained uncoordinated to transition metal in the solid phase as well as in solution.

Besides the desired compounds, two hafnium complexes bearing either 2-methoxyaniline or 2-methoxyanilide ligands were isolated and structurally characterized as minor decomposition and dismutation products of **3** and **4**, respectively.

Complexes containing the β-diketiminate ligand as well as its precursors were tested for catalytic activity in the polymerization of ethylene using different activators (MAO, MMAO and $Al^iBu_3/(Ph_3C)^+$ $[B(C_6F_5)_4]^-$). Among the new complexes, the best activity as high as 340 kg_{PE} $(mol_M hbar)^{-1}$ was achieved with **1**/$Al^iBu_3/(Ph_3C)^+$ $[B(C_6F_5)_4]^-$ system.

In attempts to clarify the activation process of group 4 metal-based precatalysts, the synthesis and NMR studies of the aluminium β-diketiminate complex $Al(^iBu)_2L^{CO}$ were also carried out.

Introduction

The first reference of β-diketiminates in classical coordination chemistry studies fall into the mid to late 1960s, when conjugated monoanionic β-bifunctional ligands were reported to be used for the preparation of nickel(II) complexes containing benzyl or aryl groups [1].

A major development was achieved in the mid-1990s, with the recognition that β-diketiminates could play a useful role as spectator ligands, as for example cyclopentadienyl ones, by virtue of their strong, usually isobidentate, metal-ligand bonds and exceptionally tuneable steric properties due to a possible variation of the substituent R^1 on the nitrogen atoms. Particularly in group 4 chemistry, the increased interest in β-diketiminate ligands was driven also by attempts to replace the widely used cyclopentadienyl ligands.

In 1994, Lappert reported syntheses and crystal structures of $[LiL]_2$, $[SnL(Cl)Me_2]$ where L = N(R)C(Ph)C(H)C(Ph)NR, R = $SiMe_3$, $[SnL'(Cl)Me_2]$ where L′ = N(H)C(Ph)C(H)C(Ph)NH and $[ZrL''Cl_3]$ where L″ = N(R)C(Ph)C(H)C(^{t}Bu)NR, R = $SiMe_3$, and showed the last zirconium complex to be an effective catalyst for the polymerization of ethylene and propylene [2]. In 1998, the dichlorido and

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dialkyl titanium(III) and vanadium(III) paramagnetic compounds $LTiCl_2$ and $LVCl_2$, L = $[\{N(R)C(Me)\}_2C(H)]^-$ where R = 2,6-(i-Pr)$_2C_6H_3$ were published [3].

In 1998 Collins and co-workers published the synthesis of monocyclopentadienyl *β*-diketiminato complexes of zirconium (A in Chart 1) from monosubstituted *β*-diketiminato chloro precursors by reaction with LiCp. The corresponding methyl derivatives were prepared by further treatment of the dichloro complex with methyllithium [4].

In addition, the preparation of unsymmetrical *N*,*N*′-β-diketiminato complexes of Ti(III), Ti(IV), Zr(IV), and Hf(IV), which contained two different aryl groups connected to nitrogen atoms, an extraordinary bulky substituent Tbt = 2,4,6- $[(Me_3Si)_2CH]_3C_6H_2$ and a moderate bulky substituent Mes = 2,4,6-$Me_3C_6H_2$ was established and some half sandwich complexes of Ti(IV) and Zr(IV) containing this ligand were prepared (B in Chart 1). The reaction of one equivalent of Li $[N(R^1)C(Me)C(H)C(Me)NR^2]$ (R^1 = Mes, R^2 = Tbt) in benzene with one equivalent of $(\eta^5\text{-}C_5H_5)TiCl_3$, $(\eta^5\text{-}C_5Me_5)TiCl_3$ and $(\eta^5\text{-}C_5H_5)ZrCl_3$ provided the corresponding half sandwich complexes [5].

β-Diketiminato-Titanium(III) complexes containing $(\eta^5\text{-}C_5H_5)$ and $(\eta^5\text{-}C_5Me_4H)$ ligands (C in Chart 1) were prepared and reduced with Na/K in order to study nitrogen fixation and stabilization of the formed Ti(II) species [6].

In line with Lappert's primary investigations of the catalytic activity of the mentioned *β*-diketiminato zirconium complex, Collins et al. recently reported that mixed cyclopentadienyl(*β*-diketiminato) zirconium dichlorides (A in Chart 1) upon activation with dried MAO behave as single-site catalysts for the polymerization of ethylene, and high catalytic activity [300 kg_{PE} $(mol_{Zr}hbar)^{-1}$] was observed for the particular complex (Cp)(PhNC(Me)CHC(Me)NPh)$ZrCl_2$ [7]. In addition, the authors demonstrated that introduction of an electron-withdrawing group into the *N*-aryl moiety increases the performance of this catalyst by *ca.* one order of magnitude and, furthermore, replacement of MAO in the (Cp) (PhNC(Me)CHC(Me)NPh)$ZrMe_2$/MAO system by a cationic borate activator $(Ph_3C)^+$ $[B(C_6F_5)_4]^-$ improves the catalyst efficiency about five times.

In 2005 Andrés incorporated a *β*-diketiminato ligand to carbosilane dendrimers and reported the preparation of titanium and zirconium cyclopentadienyl(*β*-diketiminato) complexes [8]. The complexes were used as catalysts for ethylene polymerization and an increased activity in comparison with non-dendritic analogues was observed, according to results published by Collins [4].

Systematic investigation of zirconium complexes derived from the combination of cyclopentadienyl ring and a modified *β*-diketiminato framework carrying additional functionalites (CN group, Lewis acid adducts of the nitrile group with $B(C_6F_5)_3$) on the ligand backbone (D and E in Chart 1) was performed by Erker et al. [9] Evaluation of effects of these functionalities on the ligand behaviour afforded valuable findings concerning changes in the electron density on the metal, structural alterations around the metal center and efficiency of catalysts for ethylene polymerization. The enhanced activity of the complexes bearing Lewis base on the *β*-diketiminato ligand compared to the unmodified counterparts was interpreted by reduction of the electron density at the zirconium center by inductive effects, thus making the metal center more electrophilic.

More recently, Hamaki and co-workers reported ethylene and ethylene/1-hexene polymerizations catalysed by various *β*-diketiminato and 1-aza-1,3-butadienyl-imido group 4 metal complexes having two different extremely bulky substituents on the N-terminals in the presence of several cocatalysts. They found high copolymerization activities for complexes bearing *β*-diketiminato and cyclopentadienyl (Cp or Cp*) ligands when a binary cocatalyst $Al^iBu_3/[PhNHMe_2]^+$ $[B(C_6F_5)_4]^-$ was used as an activator [5b].

Related alkyl monocyclopentadienyl-zirconium and -hafnium acetamidinates were used by Sita and co-workers as models for study of steric and electronic factors in living polymerization of *α*-olefins [10].

The bifunctional *β*-diketiminate ligand [2-(MeO)$-C_6H_4$)] NC(Me)CHC(Me)N[2-(MeO)$-C_6H_4$)] (L^{CO}) containing OMe groups in *ortho* positions of phenyl substituents as potentially extra coordinating groups was first introduced in 2003 when the lithium complex $[L^{CO}Li]_2$was reported [11].

The same ligand system was also used for the preparation of trinuclear zinc alkoxide $L^{CO}ZnO(\mu\text{-}Bn)\}_2ZnO(\mu\text{-}Bn)_2]$ and homoleptic zinc complexes $L^{CO}{}_2Zn$ ($R^1 = R^2 = C_6H_4{-}OMe\text{-}2$) [12].

Along with the mentioned *d*-block metal complexes decorated by bifunctional *β*-diketiminate ligands, also *f*-block metal complexes such as $L^{CO}Ln\ [CH_2(SiMe_3)]_2$ [13] and $L^{CO}Ln[N(SiMe_3)_2]_2$ have been published including investigations of their catalytic activity in hydroamination and polymerization processes [14]. The use of the same ligand for stabilization of low valent *p*-block elements — group 14 — was established by us very recently [15]. And finally, the preparation of boron complex $L^{CO}BF_2$ was also reported [16].

In line with our previous studies describing group 4 metal complexes combining η^5-cyclopentadienyl and *C*, *N*- chelating ligands [17] or attached pendant *N*-donor groups [18] we decided to utilize functionalized *β*-diketiminate ligands as well. Taking into account that heavier group 4 metal complexes belong to the most important olefin polymerization catalysts [19] and the fact that the combination of various spectator ligands proved to be successful for these purposes recently, we would like to contribute to this area

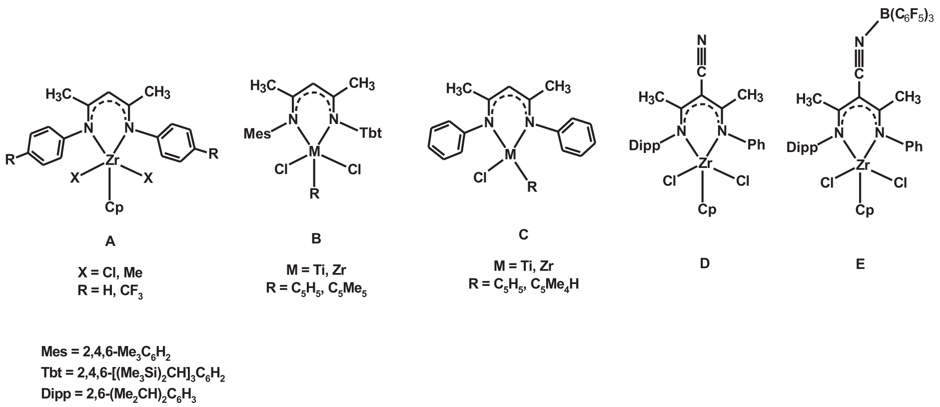

Chart 1. Known cyclopentadienyl *β*-diketiminate complexes of group 4 metals.