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Synthesis and characterization of methyl-phenyl-substituted cyclopentadienyl zirconium complexes

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Abstract

The trisubstituted methyl-phenyl-silyl-cyclopentadienes [Me-Ph-C_5H_3($SiMe_2$X)] (X = Me, Cl, NH*t*-Bu) and [(Me-Ph-C_5H_3)$_2$$SiMe_2$] and the lithium salts Li_2[Me-Ph-C_5H_2($SiMe_2$N*t*-Bu)] and Li_2[(Me-Ph-C_5H_2)$_2$$SiMe_2$] have been isolated by conventional methods and characterized by NMR spectroscopy. Desilylation of [Me-Ph-C_5H_3($SiMe_3$)] with $ZrCl_4(SMe_2)_2$ gave the monocyclopentadienyl complex [Zr(η^5-1-Ph-3-Me-C_5H_3)Cl_3]. The *ansa*-metallocene [Zr{(η^5-2-Me-4-Ph-C_5H_2)$SiMe_2$(η^5-2-Ph-4-Me-C_5H_2)}Cl_2] was obtained from the mixture of isomers formed by transmetallation of Li_2[(Me-Ph-C_5H_2)$_2$$SiMe_2$] to $ZrCl_4$ and characterized as the *meso*-diastereomer by X-ray diffraction methods. Similar transmetallation of Li_2[Me-Ph-C_5H_2($SiMe_2$N*t*-Bu)] gave the silyl-η-amido complex [Zr{η^5-2-Me-4-Ph-C_5H_2($SiMe_2$-η-N*t*-Bu)}Cl_2] that was further alkylated to give [Zr{η^5-2-Me-4-Ph-C_5H_2($SiMe_2$-η-N*t*-Bu)}R_2] (R = Me, CH_2Ph) and used as a catalyst precursor, activated with MAO, for ethene and propene polymerization. All of the new compounds were characterized by elemental analysis and NMR spectroscopy.

Keywords: Cyclopentadienyl; Zirconium; Metallocenes; Silyl-amido; Polymerization

1. Introduction

Group 4 transition metal cyclopentadienyl-type complexes have received special and intense research interest through their applications as olefin polymerization catalysts. The electronic and steric effects of different substituents in the cyclopentadienyl ring give rise to significant changes in the reactivity and catalytic activity of their metal complexes in ethene and propene polymerization [1]. The control of the polyolefin stereochemistry and the stereoselectivity in propene polymerization induced by C_2-symmetric *ansa*-metallocenes are well established [2]. Similarly, styrene polymerisation has driven much of the chemistry of the mono-cyclopentadienyl and -indenyl group 4 metal compounds with many studies reporting [3] the effect of different substituents on the activity, tacticity and molecular weight of the resulting polystyrene. The CGC-catalysts based on η^5-cyclopentadienyl-silyl-η-amido group 4 metal compounds [4,5] are receiving increasing interest, initially reported with a tetramethyl substituted ring containing a silyl-η-*t*-butylamido group [6,7] and more recently extended to studying aspects of stereospecific copolymerization [8] and the effect of different substituents at the amido-N [9] and the bridging group [10].

Although some stereochemical mechanistic studies on different transition metal complexes with the 1-phenyl-3-methyl-cyclopentadienyl ligand had been reported previously [11,12], this ligand was used [13] to prepare the first group 4 *ansa*-metallocenes with tetramethylethylene and dimethylsilyl bridges. Similar disubstituted tetrahydroindenyl compounds have been reported [14] more

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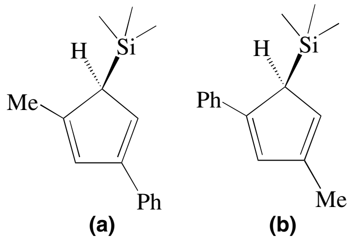
recently. However, few studies have been focused on the regioselectivity of reactions made to introduce a third substituent on any of the three possible positions of the 1-Ph-3-Me-cyclopentadiene or on the electronic and steric effects of the methyl and phenyl substituents and their relative location on the reactivity of the resulting metal complexes. In line with our interest in studying the steric and electronic effects of bulky ligands on the reactivity of their metallocene and cylopentadienylsilyl-η-amido group 4 metal complexes, we have reported [15] the use of the disubstituted Me-Ph-cyclopentadienyl ligand to prepare non-bridged and tetramethyldisiloxane-bridged group 4 metallocene complexes. We report herein the results observed when different silyl groups [$SiMe_3$, $SiMe_2Cl$, $SiMe_2(NHt\text{-}Bu)$ and $SiMe_2(Me\text{-}Ph\text{-}C_5H_3)$] are introduced into the 1-Ph-3-MeC_5H_4 ring and the structural consequences when the corresponding cyclopentadienyl ligand is used to prepare monocyclopentadienyl, *ansa*-dicyclopentadienyl and *ansa*-cyclopentadienyl-silyl-η-amido zirconium complexes.

2. Results and discussion

2.1. Mono- and di-cyclopentadienyl complexes

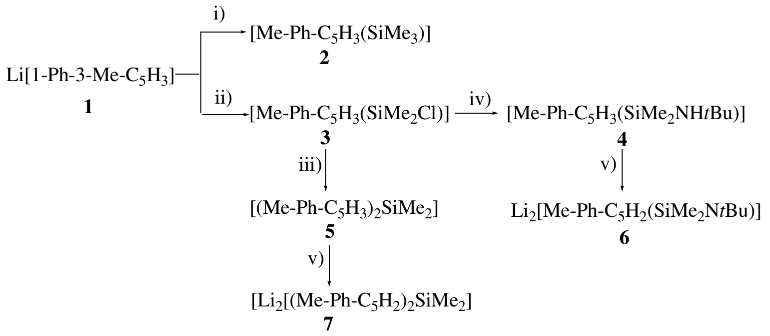
The lithium salt of the disubstituted 1-phenyl-3-methyl-cyclopentadiene Li[1-Ph-3-Me-C_5H_3] (**1**) has been prepared and reacted in situ [13] with dichlorodimethylsilane to prepare the dimethylsilyl-bis (2-methyl-4-phenyl-cyclopentadiene), which was further deprotonated and used for the subsequent formation of the corresponding dimethylsilyl-bridged metallocenes. With the aim of isolating the CG-type silyl-η-amido complexes of this disubstituted methyl-phenyl-cyclopentadienyl ligand, it was convenient to isolate all of the intermediate cyclopentadienes and their lithium salts involved in that procedure (see Scheme 1).

The lithium salt **1** was obtained in high yield by deprotonation of [1-Ph-3-Me-C_5H_4] with Li*n*-Bu as a white solid, which was characterized by elemental analysis and ^1H NMR spectroscopy (see Section 4). Reaction of **1** with 1.1 equiv (10% excess) of chlorotrimethylsilane and dichlorodimethylsilane in THF gave the trisubstituted silyl derivatives [Me-Ph-$C_5H_3(SiMe_3)$] (**2**) and [Me-Ph-$C_5H_3(SiMe_2Cl)$] (**3**), respectively. Further reaction of **3** with 2 equiv of *t*-BuNH_2 in THF gave the aminosilylcyclopentadiene [Me-Ph-$C_5H_3(SiMe_2NHt\text{-}Bu)$] (**4**), whereas reaction of **3** with 1 equiv of the lithium salt **1** in diethyl ether gave the dimethylsilyl-di(cyclopentadiene) [$(Me\text{-}Ph\text{-}C_5H_3)_2SiMe_2$] (**5**) in 80% yield. Compounds **2**–**4** were isolated as yellow liquids and were characterized by ^1H NMR spectroscopy and elemental analysis (**2** and **4**). The ^1H NMR spectra show that compounds **2** and **4** contain a mixture of two isomers whereas **3** is one unique isomer. In agreement with the data discussed below for their metal complexes, the ^1H NMR spectra are consistent with **2** and **4** being mixtures in 3:1 and 5:1 molar ratios, respectively, of the two isomers (**a**) and (**b**) represented in Scheme 2, in which the silyl substituent is always bound to C(sp^3) and located in an α position with respect to Me (**a**) and Ph (**b**), whereas the third possible isomer with the silyl group between both Me and Ph groups was absent. In contrast, the more electrophilic –$SiMe_2Cl$ selectively gave the isomer **3**(**a**) as the unique reaction product.



Scheme 2.

On the basis of these data, formation of three isomers would be expected for the dicyclopentadiene **5** resulting from the different combinations of these two isomeric configurations. However, compound **5** appeared as a mixture of isomers which could not be identified in the ^1H NMR spectrum, which shows very broad signals.



i) $SiClMe_3$; ii) $SiCl_2Me_2$; iii) **1**; iv) 2 NH_2tBu; v) 2 BuLi

Scheme 1.