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Review

Constrained geometry complexes—Synthesis and applications

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Abstract

Transition metal complexes bearing linked cyclopentadienyl amido ligands, regularly referred to as constrained geometry complexes (CGCs), have found wide interest both in academia and industry since their first description in 1990. Particularly, Group 4 CGCs were applied as catalyst precursors for the polymerisation of α-olefins, often yielding polymers with unique microstructure and material properties. Moreover, the potential of CGCs to mediate transformations other than polymerisation reactions is increasingly acknowledged. The present review aims to give a comprehensive survey about the chemistry of CGCs and covers reports in the open literature between 1990 and spring 2005.

Keywords: Constrained geometry complexes; Cyclopentadienyl amido ligands; α-Olefins

1. Introduction

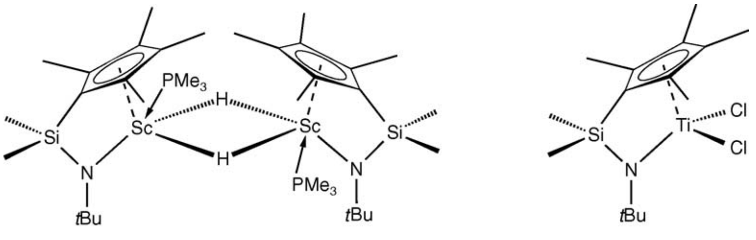
The amount of the classic polyolefins (polyethylene, PE, polypropylene, PP, and polystyrene, PS) currently produced world-wide is well above 130 × 10^6 tonnes per year, thus making up some 60% of the entire production of plastics [1]. Polyolefins (besides low-density polyethylene from the ICI high pressure radical process) are afforded by transition metal catalysts originating from the discovery of Ziegler [2,3] and Natta [4–6] that ethylene and propylene polymerise in the presence of $TiCl_4$ and Et_2AlCl even at low pressure or the discovery of the catalytic activity for olefin polymerisation of chromium oxides (Phillips-type catalysts) by Hogan and Banks [7,8]. A major shortcoming of these early systems was the heterogeneous nature of the catalysts, which prevented a thorough characterisation of the active sites and left many questions concerning the mechanisms involved in polymer growth [9,10].

Stimulated by related developments in other fields of catalysis, homogeneous organometallic compounds were introduced as suitable model systems for a deeper investigation of the polymerisation process at transition metal centres. Metallocenes were particularly attractive for mechanistic studies of Ziegler–Natta type systems, since they exhibit simple coordination geometries, only one type of active site and easily polymerise ethylene when activated by alkylaluminiums [9,11–15]. With the discovery by Kaminsky and co-workers of methylaluminoxane (MAO) as a highly effective activator [16,17], polymerisation rates and yields have been increased to an industrially useful level. These developments combined with the attractive product properties, e.g. well defined structure, little branching and very narrow molar mass distribution, initiated extensive efforts in industry and academia to expand further the capabilities of the system. Besides attempts to alter polymerisation characteristics and product properties by simple variation of the substituents on the cyclopentadienyl ring, more sophisticated alterations were introduced [18]. Since the 1980s, work by Ewen, Brintzinger et al. in particular showed how the controlled, stereoselective polymerisation of propylene and other α-olefins may be achieved by employing catalysts of suitable symmetry and geometry [9,19–23].

More recently, a new family of active polymerisation catalysts was developed by formally exchanging one cyclopentadienyl ring by an amido moiety; these are often referred to as constrained geometry complexes (CGCs), given the chelate bite angle imposed by the cyclopentadienyl and amido donors. Dianionic, bifunctional chelating ligands of this type have been first employed by Bercaw and co-workers for the preparation of Sc(III) complexes, such as **1** (Fig. 1) [24,25]. Only a short time later, reports appeared on the preparation of related Group 4 complexes, such as **2** (Fig. 1) [26] and their exceptional characteristics in ethylene polymerisation and copolymerisation of ethylene and higher α-olefins [27,28].

The superiority of the CGCs for copolymerisation of ethylene and α-olefins when compared to metallocenes and metallocenophanes is generally ascribed to (i) a less crowded coordination sphere, (ii) a smaller $Cp_{centroid}$–M–N bite angle (by 25–30° compared to $\angle Cp_{centroid}$–M–$Cp_{centroid}$ in metallocenes and metallocenophanes) and (iii) a decreased tendency of the bulk polymer chain to undergo chain transfer reactions. The latter, as well as the high activity of such CGCs, most probably result from a more Lewis-acidic transition metal centre (according to the "neutral ligand formalism", an amido moiety can donate, at most, three electrons to the transition metal and thereby two electrons less than a cyclopentadienyl group) [24,25,29]. Another advantage is the higher thermal stability of alkyl and dialkyl CGCs when compared to related metallocenes [30,31] that allows higher polymerisation temperatures.

Since the early 1990s, the chemistry of CGCs experienced a rapid advancement, particularly because catalytic systems based on such compounds gave access to a wide array of polymers with



1 **2**

Fig. 1. First reported scandium and titanium CGCs.