



Review

Carborane-based transition metal complexes and their catalytic applications for olefin polymerization: Current and future perspectives

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ABSTRACT

Polyhedral carborane clusters have been widely used as suitable ligands to coordinate with transition metals to construct various metal complexes. Most of the studies are on either dicarbollide anion ($[7-R^1-8-R^2-7,8-nido-C_2B_9]^{2-}$; $R^1, R^2 = H, \text{alkyl, aryl, etc.}$) or functionalized *closo*-carborane ($1-R^3-2-R^4-1,2-closo-C_2B_{10}H_{10}$; $R^1, R^2 = H$ or functional groups). Carborane-based ligands demonstrate varying coordinating models to form structurally unique metal complexes with interesting reactivity. This mini-review describes the syntheses and catalytic applications of the type complexes, specifically emphasizing their catalytic activity for olefin polymerization. Future perspectives in this area of research will also be discussed in this mini-review.

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1. Introduction

Closo-dicarbadoodecaborane, also called carborane is one of the most studied carbon-boron clusters. Structurally, carborane has three isomers, namely 1,2-(ortho-), 1,3-(meta-), and 1,10-(para-) carboranes based on the location of carbon atoms in the clusters [1].

The 1,3- and 1,10-carborane isomers can be produced by thermal rearrangement of 1,2-carborane at above 420 °C [1]. Comparing with 1,3- and 1,10-isomers, the 1,2-carborane are more reactive in deprotonation and decapitation reactions, and thus they can be conveniently functionalized and metalated [1]. Owing to their unique structures, carboranes have found multiple applications in boron neutron capture therapy [2] as a promising boron source, as well as for structure studies in crystallography [3], solid superacids [4] and catalysts for ethylene polymerizations as discussed here. Since the discovery of the first dicarbollide coordinated sandwich

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metal complex in 1965 [5], numerous compounds coordinated with this type ligands have been reported and reviewed [6–13]. Although the resulting metal complexes have shown increasing numbers of applications in catalysis, the palladium complexes, coordinated to carboranes-based phosphorus ligands, are active catalysts for C–C cross-coupling reactions [14] and a half-sandwich titanacarborane amide $[\sigma:\eta^1:\eta^5-(\text{OCH}_2)-(\text{Me}_2\text{NCH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NMe}_2)$ catalyzed trans amination of guanidines [15], this mini-review mainly discusses their application as catalyst in olefin polymerization.

2. Olefin polymerization catalyzed by carborane-based transition metal complexes

The π - and σ -carborane transitional metal complexes can be classified according to the coordination pattern of the metal center and carbon atoms within carborane clusters. Both the metal center and the functional groups attached to carborane cluster can be varied, and thus provide significantly different catalytic activity for olefin polymerization reactions.

2.1. The π -coordinating carborane transition metal complexes for ethylene polymerization

It has been repeatedly demonstrated that *closo*-1,2-carborane can be opened to form *nido*-carborane dianions namely $[\text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_9]^{2-}$ and $[\text{R}^1\text{R}^2\text{C}_2\text{B}_{10}\text{H}_{10}]^{2-}$ ($\text{R}^1, \text{R}^2 = \text{H}$ or functional groups) [6–13] (Fig. 1). The *nido*-dianions, which have 6 π electrons delocalized on the C_2B_3 , or C_2B_4 open faces, may coordinate with metal centers in an η^5 - or η^6 - fashion. The *nido*-dianions are electronically isolable with the cyclopentadienides which are commonly used to construct metallocene-based catalysts for olefin polymerization. Half-sandwiched metallocenes including bridged cyclopentadienyl and amido ligands, also known as constrained-geometry complexes (CGCs), have been reported to be excellent catalysts for ethylene polymerization reactions [16]. Following the discovery, various π -coordinated carborane-based CGCs have been reported (Fig. 2) [17–22]. In general, these type complexes were synthesized by a straightforward method. In this regard, the *closo*-carborane clusters were deprotonated and functionalized by nucleophilic reactions. The functionalized *closo*-carboranes could conduct cluster-opening reactions either by MOH ($\text{M} = \text{Na}, \text{K}$) or alkali metals (Na, K) to form *nido*-carborane anions. The carborane-based CGCs were prepared by metallization of the resulting *nido*-carboranes. For example, the reaction of 1,3-dichloro-1,1,3,3-tetramethyldisilazane with two equivalents of the lithium salt of a pre-prepared carboranyl anion, namely $[\text{closo-1-R-1,2-C}_2\text{B}_{10}\text{H}_{10}]^-$ ($\text{R} = \text{Me}, \text{Ph}$) led to the formation of the tetramethyldisilazane-bridged dicarborane precursors as shown in Scheme 1 [22]. After treating with excess sodium, the precursors were converted in situ

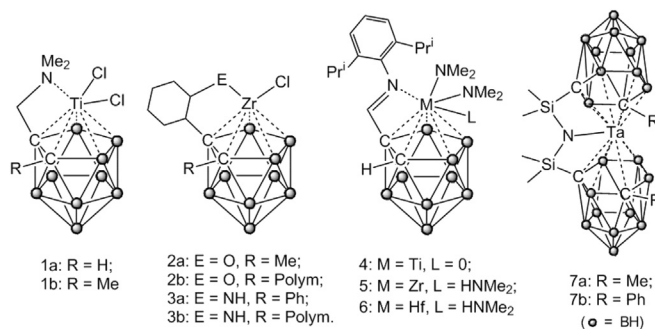
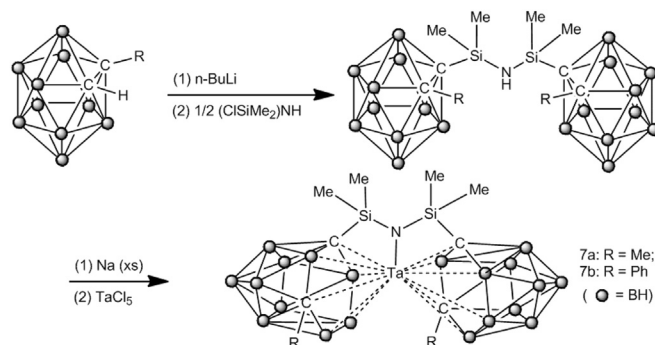


Fig. 2. π -Bonded carborane-based CGCs catalysts for ethylene polymerization.

to their constrained- geometry ligands. The ligands were metalated with TaCl_5 to form catalysts **7a** and **7b** [22].

Versatile reaction conditions including co-catalyst, solvent, temperature, time, and ethylene pressure have been employed in a number of laboratories to examine the π -coordinating carborane-based transition metal complexes. Although it is impossible to strictly compare their catalytic activity with different reaction conditions, the inherent advantages, particularly for the metals in same group of complexes, can be estimated. Table 1 summarizes the literature results obtained from the studied catalysts indicating the following trends and conclusions: (1) metal center in the CGC play key role in the ethylene polymerization. In general, they follow an activity trend of $\text{Zr} > \text{Ti} > \text{Hf}$, see catalysts **4–6**. Metals with high oxidation states such as Ta(V), provide better catalyst activity in forming polyethylene with relatively higher Mw and narrow PDI, as shown for catalysts **7a** and **7b**. However, the typical CGC catalyst generally shows medium to low activity compared with existing metallocene or Dow–CGC complexes as shown in Table 1. (2) Substituent groups attached to a carbon atom in the carborane cage also modify the catalytic activity. A trend of $\text{Me} > \text{H} > \text{Ph} > \text{Polymer}$ was observed for catalysts **1a, 1b, 2a, 2b, 3a, 3b, 7a** and **7b**. (3) Application of suitable co-catalyst and initiator together improves the activity. Addition of initiator $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ results in higher activities of catalysts **1a** and **1b** under elevated ethylene pressure. (4) In cooperation with other conditions, higher ethylene pressure benefits the reaction. Interestingly, we found that morphologically different polyethylenes (PEs), one fibrous and the other powdery, could be produced from one-pot polymerization reaction with **7a** and co-catalyst MAO. The PEs products show dramatically different images in SEM analysis (Fig. 3). Micro-scale rods comprising nano-scale particles are found in fibrous PE SEM images, which are not seen in the powdery PE. The morphologically different PEs also show different T_m (based on DSC analysis) of 135°C and 127°C for fibrous polyethylene and powdery polyethylene, respectively.



Scheme 1. Synthesis of catalyst **7a** and **7b**.

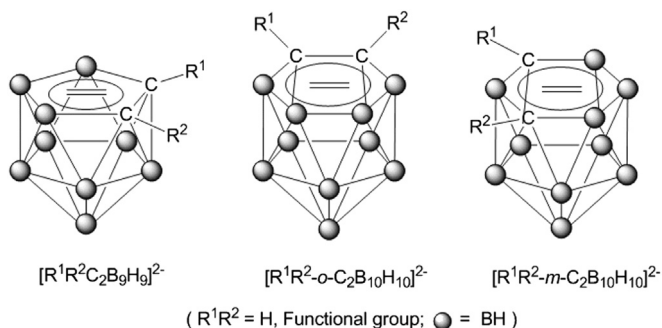


Fig. 1. *Nido*-carborane-based ligands.

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