

Controlled isospecific polymerization of α -olefins by dichloro zirconium complexes bearing an [OSSO]-type bis(phenolate) ligand

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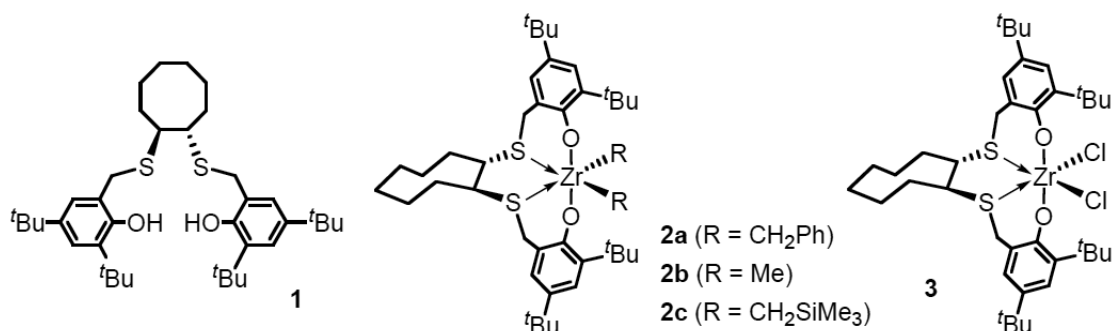
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[OSSO]-type bis(phenolates), in which the two phenoxide frameworks are linked to two donor sulfur atoms in the *ortho*- or benzyl-positions, have been of great interest as dianionic ancillary tetradentate ligands for Group 4 metal centers.^[1] Recently, we reported the development of a new [OSSO]-type bis(phenolate) ligand **1** based on a *trans*-1,2-cyclooctanediyl platform and syntheses of a variety of dialkyl zirconium complexes **2**.^[2,3] Upon activation with $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$, dibenzyl zirconium complex **2a** achieved highly active ($> 2500 \text{ g mmol}^{-1} \text{ h}^{-1}$) and completely isospecific polymerization of 1-hexene.^[2] We present here the catalytic behavior of dichloro zirconium complex **3** as a pre-catalyst in the polymerization of α -olefins.

Dichloro zirconium complex **3** was prepared by the reaction of the dilithium salt of ligand **1** with $ZrCl_4$ at -78°C in 73% yield as colorless crystals. The complex **3** activated by dMAO (dried methylalminoxane) showed an extremely high activity ($> 18,000 \text{ g mmol}^{-1} \text{ h}^{-1}$) toward polymerization of 1-hexene and provided highly isotactic poly(1-hexene) with a narrow polydispersity ($M_w = 40,000 \text{ g mol}^{-1}$, $PDI = 1.9$). Moreover, the polymerization of 4-methyl-1-pentene (4-MP) catalyzed by the **3**/dMAO system in toluene at $25\text{--}70^\circ\text{C}$ produced excellently isotactic poly(4-MP)s ($M_w = 10,400\text{--}17,500 \text{ g mol}^{-1}$, $PDI = 1.9\text{--}2.2$) with good activities ($160\text{--}500 \text{ g mmol}^{-1} \text{ h}^{-1}$). We also describe the catalytic ability for the cyclopolymerization of 1,5-hexadiene with the **3**/dMAO system.



References

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