Ancillary Ligand Effect on Single-Site Styrene Polymerization: Isospecificity of Group 4 Metal Bis(phenolate) Catalysts

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One of the major achievements of metallocene catalysis is the in-depth understanding of the molecular mechanism and the origin of stereoselectivity in α-olefin polymerization catalysis.[1] Whereas a remarkable level of stereocontrol during propylene polymerization has become possible through the rational design of the metallocene structure,[2] there have so far been no general methods to influence the stereoselectivity during the polymerization of the vinylaromatic commodity monomer styrene.[3] While syndiotactic polystyrene, discovered by Ishihara et al. at Idemitsu,[4] is produced by trivalent mono(cyclopentadienyl)titanium catalysts,[5] isotactic polystyrene, known for almost half a century, is best produced by heterogeneous Ziegler−Natta catalysis.[6−8] We wish to report here a family of structurally well-characterized nonmetallocene group 4 metal catalyst precursors[9,10] that are capable of efficiently polymerizing styrene isospecifically.

Following the observation that titanium complexes with a 2,2′-sulfur-bridged bis(phenolato) ligand of the type [Ti{(OC$_6$H$_2$-^{t}Bu-6-Me-4)$_2$S}X$_2$] are active in syndiospecific styrene polymerization[11] and the report on isospecific 1-hexene oligomerization by a diamine-bis(phenolato) zirconium catalyst,[9a] we set out to prepare two new bis(phenols), (HOC$_6$H$_2$-^{t}Bu$_2$-4,6)$_2${S(CH$_2$)$_n$S} **1a** ($n = 2$) and **1b** ($n = 3$), with a 1,ω-dithiaalkanediyl bridge, by nucleophilic substitution of the corresponding 1,ω-dibromoalkane by 3,5-di-*tert*-butyl-2-hydroxybenzenethiol.[12] Reaction of **1a** with titanium tetrachloride or titanium tetra(isopropoxide) in toluene cleanly afforded the corresponding complexes **2a** and **3a** in quantitative yield (Scheme 1). **1b** analogously gave the titanium complexes **2b** and **3b**.

According to NMR spectra, the 1,4-dithiabutane-linked derivative **2a** differs from the 1,5-dithiapentane-linked bis(phenolato) complex **2b** by its configuration. All NMR spectroscopic data of the complexes **2a** and **3a** indicate molecular C_2-symmetry, which is evident from the symmetry-related phenolate rings and the presence of an AB spin pattern for the CH$_2$ units in the bridge. Zirconium and hafnium dibenzyl complexes **4a** and **5a**, obtained by the reaction of **1a** with zirconium and hafnium tetrabenzyl, show an additional AB pattern for the CH$_2$ groups due to the two *cis*-benzyl ligands. The temperature invariance of the NMR spectra furthermore suggests configurational stability in solution.

Crystallographic structure determination of **5a** (Figure 1) confirms that this complex adopts a C_2-symmetrical configuration with *cis*-arranged benzyl (C−Hf−C 94.3(1)°) and thioether groups (Hf−S1 2.9222(9), Hf−S2 2.8260(8) Å). The two sulfur atoms of the link, which shows a gauche conformation with a dihedral angle
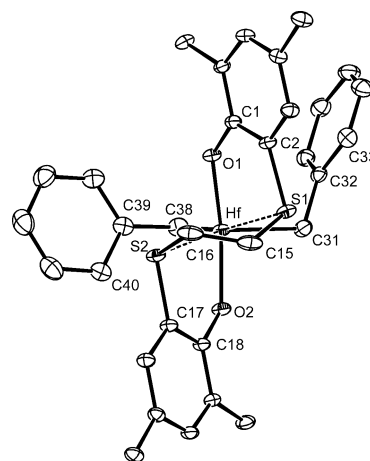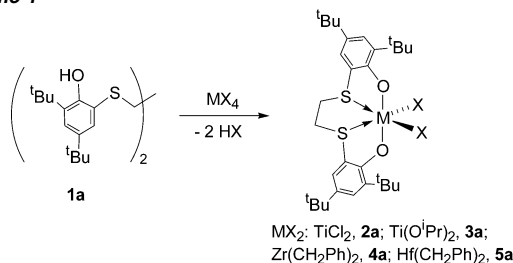

Figure 1. Molecular structure of **5a**. Methyl groups of the *tert*-butyl groups have been omitted. See the Supporting Information for details of the structure.

Scheme 1

MX$_2$: TiCl$_2$, **2a**; Ti(O^{i}Pr)$_2$, **3a**;
Zr(CH$_2$Ph)$_2$, **4a**; Hf(CH$_2$Ph)$_2$, **5a**

SCCS of 58.1(3)°, evidently enforce the *trans*-coordination of the two bulky phenolato ligand moieties. Notably, the two benzyl groups adopt different conformations, one displaying a dihapto coordination (Hf−C38−C39 96.2(2)° versus Hf−C31−C32 113.6-(2)°), indicating a fairly open reaction site at the 10-electron metal center.

In contrast, at room temperature, **2b** shows a pattern of broad signals due to fluxional behavior. The crystallographic analysis shows that it adopts a C_1-symmetric structure in which one sulfur atom is disposed trans to the chloro and another trans to the oxygen atom, resulting in *cis*-coordinated phenolato groups.

Upon activation with methylaluminoxane (MAO), the complexes **2a**−**5a** were found to be active for isospecific styrene polymerization, whereas **2b** and **3b** exhibit low activity for syndiospecific polymerization toward styrene. The polymerization results are summarized in Table 1.

The 1,5-dithiapentane-bridged complexes **2b** and **3b** are 1 order of magnitude less active than the 1,4-dithiabutane-bridged deriva-

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Table 1. Styrene Polymerization with Bis(phenolato) Complexes Activated by Methylaluminoxane

run	catalyst	yield (g)	activity[a]	T_m (°C)	$M_n \times 10^{-4}$	M_w/M_n
1[b]	**2a**	15.50	1543	223	265.4	2.0
2[b]	**3a**	11.90	571	223	171.8	1.8
3[c]	**2a**	2.00	70	217	34.5	1.7
4[d]	**3a**	1.30	24	227	95.8	1.8
5[d]	**4a**	1.20	22	218	16.3	1.9
6[c]	**5a**	0.50	9	220	4.0	1.9
7[c,e]	**5a**	0.17	3	208	1.0	2.1
8[c,f]	**5a**	0.03	0.6	225	4.2	3.0
9[b]	**2b**	1.30	52	260	0.7	43.5[g]
10[d]	**2b**	0.16	3	264	n.d.	n.d.
11[d]	**3b**	0.15	3	267	n.d.	n.d.

[a] g(polymer)/(mmol catalyst)·[styrene mol/L]·h. [b] Polymerization conditions: 1.00×10^{-4} mol of complex; [Al]:[M] = 1500; 3.5 mol/L styrene in toluene at 40 °C. [c] Polymerization conditions: 1.25×10^{-5} mol of complex; [Al]:[M] = 500; 5 mL of styrene in 15 mL of toluene at 50 °C. [d] In 5 mL of toluene. [e] At 25 °C. [f] At 0 °C. [g] Bimodal.

tives **2a** and **3a**. Melting temperatures, data from WAXS analysis, and NMR spectroscopy unambiguously show that the polystyrenes produced in runs 1−8 have an isotactic microstructure, whereas the polystyrenes produced in runs 9−11 have a syndiotactic microstructure.[13] GPC analysis of the isotactic polymers shows polydispersity indices of about 2, as predicted for single-site catalysts.

When polymerization by **2a** was performed in the presence of ^{13}C-enriched $Al(CH_3)_3$, the isolated polymer contained a labeled methyl group due to $CH(Ph)CH_2{}^{13}CH_3$; this suggests that the active species formed from the dichloro complex contains a methyl group at the titanium center as a result of methyl exchange between aluminum and titanium. Moreover, the chemical shift of δ 11.8 ppm in the ^{13}C NMR spectrum of this material indicates that the first insertion into the Ti−$^{13}CH_3$ bond of the active species must have occurred in a 2,1- or secondary fashion.[14] The absence of any detectable head-to-head sequence in the spectrum suggests that the polymerization is highly regiospecific in either the initiation step or the propagation step.

Remarkably, the 1,4-dithiabutane-bridged complexes of zirconium and hafnium **4a** and **5a** also polymerize styrene isospecifically, albeit with lower activity. This finding indicates that the C_2-symmetric ligand sphere is crucial for the isospecific polymerization. On the other hand, the low activity of the 1,5-dithiapentane-bridged titanium complexes **2b** and **3b** suggests that the catalytic species is a product of decomposition of the catalyst precursor under the polymerization conditions, as is commonly accepted for syndiospecific styrene polymerization.[5d]

In conclusion, we have introduced a new class of easily accessible group 4 complexes that are structurally well-characterized single-site catalyst precursors for isospecific styrene polymerization. We are currently studying the ligand parameters responsible for the activity as well as stereoselectivity of these *ansa*-metallocene mimics[1,15] and are exploring the applicability of this new catalyst family to a wide range of monomers.

Supporting Information Available: Experimental procedures for the preparation of bis(phenols) **1a** and **1b**, complexes **2a**−**5a**, **2b**, and **3b**; polymerization procedure; polymer analysis data; crystallographic data, atomic coordinates, and bond lengths and angles for **2b** and **5a** (PDF and TXT). This material is available free of charge via the Internet at http://pubs.acs.org.

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