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Stereospecific Octahedral Group 4 Bis(phenolate) Ether Complexes for Olefin Polymerization

Elizabeth T. Kiesewetter, Sören Randoll, Madalyn Radlauer, and Robert M. Waymouth*

Department of Chemistry, Stanford University, Stanford, California 94305-5080

Received January 23, 2010; E-mail: waymouth@stanford.edu

Homogeneous catalysts have played a central role in illuminating the mechanistic details of stereospecific olefin polymerization,[1−3] but the stereospecificity of even the most highly optimized catalysts[1,4−6] is inferior to that of heterogeneous catalysts,[7] particularly at the elevated temperatures typical of most commercial processes.

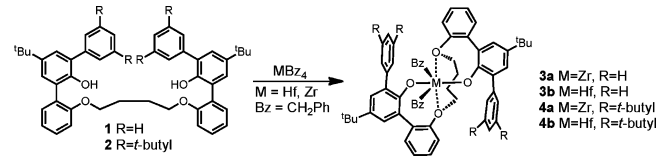
Recently, a new family of octahedral bis(phenolate) ether complexes has been reported in patents by SYMYX to yield high molecular weight polymers at high temperatures.[8] The stereospecificity of the C_2-symmetric bisphenolate ether catalysts can be tuned by changing the steric bulk of the aryl group to yield a wide variety of polypropylenes, from highly isotactic crystalline polymers to amorphous or semicrystalline lower tacticity polypropylenes.[8] The SYMYX patent suggests that stereoblock polypropylenes can be made with this class of catalysts, but it was not obvious from the examples provided which coordination geometries generated these microstructures.[8]

We initially targeted the less stereospecific complexes (**3a,b**, R = H, Scheme 1) to study the stereosequence distribution by ^{13}C NMR and to assess the degree to which these catalysts yield stereoblock polypropylenes.[9,10] Herein we report the synthesis of two bis(phenolate) ether ligands **1** and **2** and stereospecific propylene polymerization with both Zr and Hf complexes. Ligands **1** and **2** were prepared utilizing Pd catalyzed cross-coupling chemistry in a sequence modified from that previously reported (see Supporting Information).[8] Complexes **3a** and **3b** were prepared in toluene by reaction of the ligand **1** with tetrabenzylzirconium ($ZrBz_4$) and tetrabenzylhafnium ($HfBz_4$) respectively (Scheme 1). Crystallization of complexes **3a, b** from a 1:1 mixture of toluene/pentane gave crystals suitable for X-ray analysis. The two compounds are isostructural with similar bond lengths and angles. The bond lengths of the Hf complex are slightly shorter, but the maximum deviation is only 0.062 Å for the M(1)−O(4) distance (Figure 1, Supporting Information).[9]

When activated by methylaluminoxane (MAO) in toluene solution at 80 psig propylene at 80 °C, the Hf complex **3b** (4 μM) generates 10 g of high molecular weight polypropylene (M_n = 130 000 g/mol) within 30 min, corresponding to a productivity of 52 kg PP (mmol Hf)$^{-1}$ h^{-1} (Table 1). Under the same conditions, the Zr complex **3a** yields approximately 4 g of polymer (20 kg PP (mmol Zr)$^{-1}$ h^{-1}). These activities and molecular weights are comparable to those obtained with the pyridylamido catalysts (114 kg PP (mmol Hf)$^{-1}$ h^{-1} at 90 °C, 100 psig),[11] but notably, the molecular weight distributions are narrower (M_w/M_n = 2.09) than those obtained for the pyridylamido complexes, which exhibit multisite behavior.[12]

The nature of the transition metal has a surprising influence on the tacticity. The stereospecificity of the Hf complex **3b** is greater than that of the Zr complex **3a** as evidenced by the larger fraction of isotactic pentads in the polymer produced by **3b** ([mmmm] = 0.65) than that produced by **3a** ([mmmm]) = 0.32, Table 1). The Zr complex **3a** is also less regioselective and exhibited a higher fraction of 2,1-regioerrors in the polypropylenes (entries 3,4 vs 1,2, Table 1). This difference in stereospecificity between a Zr complex and its isostructural Hf analogue is unusual.[9,13]

Scheme 1. Synthesis of Group IV Bisphenolate Ether Complexes



Others have observed subtle differences in the stereospecificity of octahedral Zr and Hf complexes ([mmmm] = 0.970 (Hf) vs 0.904 (Zr)).[14] More significant differences were observed with conformationally dynamic 2-arylindene catalysts where the higher stereospecificities of the Zr complexes relative to their Hf analogues was attributed to similar conformational dynamics but different rates of propagation.[9,10]

To test whether the lower stereospecificity of the Zr complexes relative to the Hf complexes might be due conformational dynamics,[15] we carried out variable temperature NMR studies on both the Hf complex **3b** and the Zr complex **3a**. Over a temperature range of 30−90 °C, the ^{1}H NMR spectra remained consistent with a C_2-symmetric geometry over the entire temperature range. In addition, analysis of the stereosequence distribution of the polypropylenes derived from both **3a** and **3b** gave no evidence for a stereoblock microstructure and were consistent with enantiomorphic site control statistics, evidencing a 2:2:1 ratio of the [mmmr]/[mmrr]/[mrrm] stereosequences.[1,3]

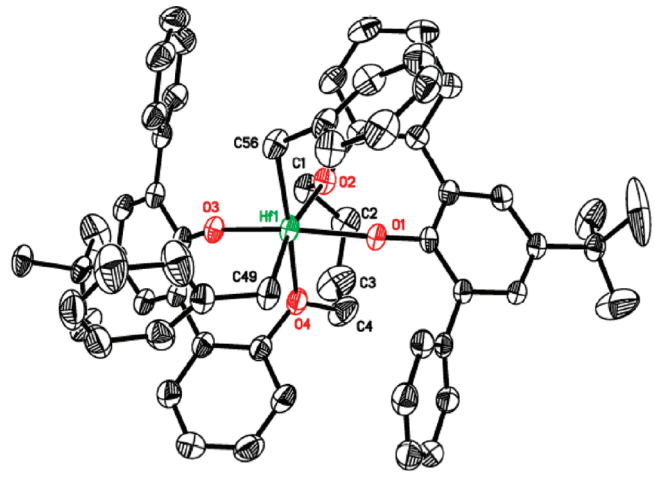


Figure 1. X-ray crystal structure of Hf bis(ether phenolate) complex **3b**.

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Table 1. Propylene Polymerization Using Group IV Bisphenolate Ether Complexes **3a** and **3b**

run[a]	cat.	metal	T (°C)	propylene (Psig)	yield (g)	activity[b]	M_n[c] (g/mol)	PDI[c] (M_n/M_w)	[mmmm][d]	regioerrors[d] (%)	$T_m(\Delta H)$ (°C, J/g)
1[e]	**3b**	Hf	80	80	10.4	52	129 800	2.09	0.68	0.8	95(44)
2[f]	**3b**	Hf	80	80	11.04	55	179 500	2.16	0.64	0.6	n.d.
3[e]	**3a**	Zr	80	80	3.99	20	214 000	3.43	0.32	2.2	none
4[f]	**3a**	Zr	80	80	2.20	11	384 900	2.08	0.35	1.8	none
5[e]	**3a**	Zr	35	80	1.26	6.0	161 000	3.51	0.35	n.d.[g]	none
6[e]	**3a**	Zr	80	30	0.11	0.56	19 100	2.28	0.35	n.d.[g]	none
7[e]	**4b**	Hf	80	80	0.95	4.7	359 500	2.06	0.98	0.3	160(90)
8[e]	**4a**	Zr	80	80	0.42	2.1	167 100	2.19	0.92	0.8	152(71)
9[e,h]	**4b**	Hf	50	50	0.72	9.8	612 000	2.62	0.99	0.2	165(82)

[a] Conditions: activated with 110 mg of mMAO; solvent =100 mL of toluene; [cat.] = 4×10^{-6} M; [Al]/[M] = 5000; Time = 30 min. [b] kg PP/(mmol·h). [c] Determined by gel permeation chromatography (GPC). [d] Determined by ^{13}C NMR. [e] Metal complex generated in situ by mixing 1 equiv of ligand with MBz_4. [f] Metal complex isolated and purified prior to polymerization. [g] n.d. = not determined. [h] Activated with 127 mg of mMAO; solvent = 50 mL of toluene; [cat.] = 8×10^{-6} M; [Al]/[M] = 5000; Time = 10 min.

The stereospecificity of **3a** showed little sensitivity to both changes in monomer concentration and temperature (entries 3,5,6, Table 1) which implies that conformational dynamics are not responsible for the different polymer microstructures observed between **3a** and **3b** under these polymerization conditions.[10]

The ligand also has a significant influence on the stereospecificity.[8] The *tert*-butyl substituted complexes **4a** (Zr) and **4b** (Hf) afford highly isotactic polypropylenes with [mmmm] = 92% and 98% respectively. The polypropylene prepared with complex **4a** has a T_m = 152 °C while that derived from complex **4b** exhibits a melting point of T_m = 160 °C. Under slightly different conditions (50 °C, 50 psig, entry 9), the Hf complex **4b** yields a high molecular weight, isotactic polypropylene with a melting point of 165 °C, comparable to that of commercial samples.[7] Thus, while the productivities of the complexes **4a** and **4b** are lower than those of **3a, 3b** and the most highly active single site catalysts,[1,4,5] the ability to generate high molecular weight, high melting polypropylenes at elevated temperatures illustrates the potential of this family of single-site polymerization catalysts.

In summary, chiral bis(phenolate) group 4 complexes are active catalyst precursors which generate high molecular weight, highly isotactic polypropylenes at elevated temperatures (50−80 °C). Despite similar coordination geometries in the solid state, the Hf complexes are more stereo- and regioselective than the Zr congeners. To the extent that nonbonded steric interactions are responsible for stereodifferentiation and the structure of the neutral precursors are predictive of active-site geometries, these results suggest that the factors influencing the stereodifferentiation of olefin insertion are extraordinarily subtle. The higher tacticity of the polypropylenes generated with the Hf complex **3b** and Zr complex **3a** constitutes a significant difference in microstructure, but at 80 °C, the energetic difference in the relative transition state energies is estimated to be only 0.7 kcal/mol, illustrating the formidable challenges of predicting, *a priori*, the structural features that lead to high stereospecificity.

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Supporting Information Available: Synthetic procedures for **1**, **2**, **3a**, and **3b**; polymerization procedures; variable temperature NMR studies; crystallographic details for **3a** and **3b** and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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