Chiral, Non-C_2 Symmetric Zirconocene Complexes as Catalysts for Stereoregular α-Olefin Polymerization

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Major advances have been achieved in stereoregular α-olefin polymerization[1-4]/hydrooligomerization[5] using chiral "cationic"[6] group 4 metallocene catalysts. With few exceptions,[3,7] stereo-differentiating ancillary ligation (ring-bridged cyclopentadienyl, indenyl) has been arrayed in a C_2 symmetric fashion (**A**). The synthesis of such catalysts usually entails nontrivial separation of undesired meso isomers (**B**)[8] and subsequent derivatizations/separations[9] if individual antipodes are desired. The efficacy of complementary, diastereomeric ring-bridged C_1 symmetric "template" ligation (**C**) in enantioselective lanthanide-centered trans-

Scheme I.   Synthesis of Chiral Zirconium Complexes[a]

[a] (i) $ZrCl_4$/THF; (ii) pentane; (iii) MeLi·LiBr/toluene; (iv) pentane.

formations[10] raises conceptual questions of applicability to asymmetric group 4 chemistry. We communicate here the high efficiency of such ligation for Zr-centered stereoregular propylene polymerization[11] as well as some marked counterion effects.

Synthesis of chiral zirconocene complexes (Scheme I) begins with chelating ligands **1** (**a** = (−)-menthyl, **b** = (+)-neomenthyl) which can be readily prepared in multigram quantities.[10] Zirconation (i) proceeds in good (>60%) isolated yields with ~3:2 (R:S) diastereoselection for both auxilliaries. One recrystallization provides diastereomerically pure (R)-**2a**, while **2b** is obtained as 1:1 (R:S) mixed crystals.[12-14] Subsequent methylation proceeds in high (>85%) isolated yields and with retention of configuration. Recrystallization affords diastereomerically pure (R)-**3a** and (R:S)-**3b** crystals. The new complexes were characterized by standard analytical/spectroscopic techniques, and absolute configurations by X-ray diffraction and CD.[12,13]

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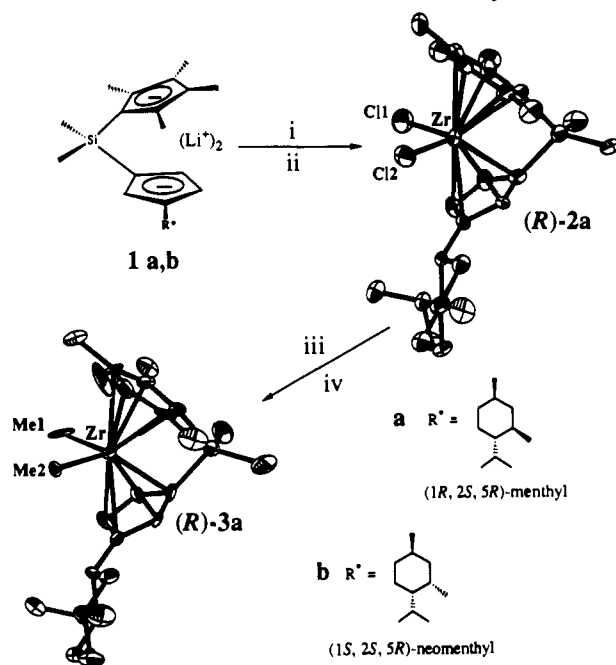
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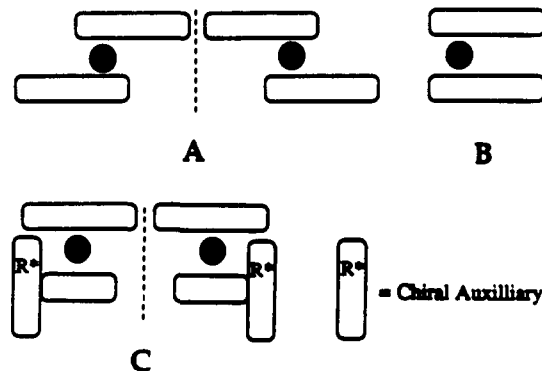
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Table I. Activity, Molecular Weight, and Isotacticity Data for the Polymerization of Propylene by Chiral Organozirconium Complexes

entry	cat.[b]	cocat.	[CoCat.][c]	T (°C)	[mon][d]	$M_n^{e,i}$	$M_w^{e,i}$	activity[f]	time (h)	yield (g)	% mmmm[g,i]
1	**2b**	MAO[a]	126	25	0.8	5 180	17 810	8.9×10^4	4.0	5.37	78
2	**2b**	MAO[a]	126	-5	2.4	8 160	20 390	3.2×10^4	2.0	2.73	82
3	**2b**	MAO[a]	126	-45	5.0	9 890	23 280	7.8×10^2	2.0	0.14	93
4	**2b**	MAO[a]	700	25	0.8	1 890	3 460	1.6×10^5	3.0	7.10	55
5	**2b**	MAO[a]	700	-5	2.4	12 360	25 890	1.3×10^4	2.0	1.10	75
6	**2b**	MAO[a]	700	-45	5.0	36 950	66 870	2.7×10^3	3.0	0.72	90
7	**3b**	MAO[a]	700	25	0.8	2 890	6 030	1.7×10^5	3.0	7.46	82
8	**3b**	$B(C_6F_5)_3$	0.7	25	0.8	1 500	2 400	4.5×10^4	3.0	1.94	83
9	**3b**	$Ph_3CB(C_6F_5)_4$	0.7	0	1.6	37 800	90 900	1.9×10^5	0.5	2.73	95
10	**3b**	$HNR_3B(C_6F_5)_4$	0.7	0	1.6	17 700	63 300	1.3×10^5	0.5	1.93	91
11	**2a**	MAO[a]	700	25	0.8	1 740	2 170	5.4×10^4	3.0	2.32	35
12	**2a**	MAO[a]	700	-5	2.4	6 570	9 940	2.0×10^4	3.0	2.60	70
13	**2a**	MAO[a]	700	-45	5.0	8 810	14 230	2.5×10^3	3.0	0.67	90
14	**3a**	MAO[a]	700	25	0.8	2 850	13 510	4.6×10^4	3.0	2.00	35
15	**3a**	$B(C_6F_5)_3$	0.7	25	0.8	190[h]	–	5.4×10^4	3.0	2.34	–
16	**3a**	$B(C_6F_5)_3$	0.7	0	1.6	250[h]	–	5.4×10^4	3.0	4.70	–
17	**3a**	$Ph_3CB(C_6F_5)_4$	0.7	0	1.6	15 100	31 200	1.6×10^4	0.5	0.23	64

[a] Methylalumoxane, solvent removed from a 20 wt % solution in toluene (Schering) at 25 °C/10^{-6} Torr. [b] [Catalyst] = 0.7 mM in toluene. [c] [Cocatalyst], mM in toluene. [d] [Monomer], M in toluene. [e] By GPC, relative to polystyrene standards (reproducibility between runs >15%). [f] Grams total polymer/mol Zr (mol L^{-1} propylene) h (reproducibility between runs >15%). [g] From pentad analysis in 5/1 v/v 1,2,4-trichlorobenzene/DMSO-d_6 130 °C; delay = 6 s, 45° PW (reproducibility between runs >3% for large mmmm values). [h] From end-group analysis. [i] Pentane-insoluble fraction.

Cationic catalysts were generated by standard methodologies:[1-3,6c,h] **2** + methylalumoxane (MAO); **3** + MAO, $B(C_6F_5)_3$, $Ph_3C^+B(C_6F_5)_4^-$, or $HN(^nBu)_3^+B(C_6F_5)_4^-$. Propylene polymerizations were carried out under rigorously anhydrous/anaerobic vacuum line conditions,[6h] and reactions were quenched after measured time intervals with acidified methanol prior to polymer collection, washing with pentane, and drying. Polymer microstructure was characterized by $^1H/^{13}C$ NMR using standard pentad analysis for tacticity assay.[1a,15] Microstructures were consistent with 1,2 insertions, while the presence of vinylic and *n*-propyl end groups indicates chain transfer exclusively via β-H elimination.[16] Several interesting trends are evident in the propylene polymerization data (Table I). First, isotacticities can be very high, rivaling or exceeding those of many C_2 catalysts,[1] with stereoregulation increasing and activity falling with lowering

temperature. Equally striking is the marked dependence of catalyst activity, stereodifferentiation, and polymer molecular weight on the identity and concentration of the cocatalyst. Thus, for **2b** + MAO, increasing Al:Zr ratios result in increased activities and molecular weights but decreased stereoregularity (entries **1–7**). Under similar conditions, $B(C_6F_5)_3$-cocatalyzed polymerizations proceed with similar activity and stereoregulation but with significantly lower molecular weights (entries **8, 15, 16**). Cocatalysts introducing the $B(C_6F_5)_4^-$ counterion exhibit high, comparable activities and stereoregularities, yielding the highest molecular weights for a given precatalyst and temperature (entries **9, 10, 17**). It appears that the presence of an exogeneous amine base (entry **9** vs **10**) significantly depresses the molecular weight of the polymer produced. We suggest that many of these cocatalyst effects are a consequence of the demonstrated tight,[6a,b,h] sterically demanding, and differing ion pairing between the various anions and chiral cationic reaction centers. This previously unemphasized factor may, in fact, be accentuated by the unsymmetrical disposition of the present ancillary ligation.

These results show that chiral, non-C_2 symmetric group **4** metallocene centers are competent for the efficient isospecific polymerization of propylene and, by inference, other cognate asymmetric transformations. It is also evident that strong ion-pairing effects offer additional means to manipulate polymer stereoregularity and molecular weight.

Supplementary Material Available: Synthetic, spectroscopic, and analytical data; X-ray experimental details including tables of positional and anisotropic displacement parameters, and tables of bond lengths and angles (29 pages); listing of observed and calculated structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

(13) (R)-Me$_2$SiCp''[(−)menthylCp]ZrCl$_2$ (**2a**). ^{1}H NMR (C$_6$D$_6$): δ 6.78 (t, 1 H), 5.55 (t, 1 H), 5.38 (t, 1 H), 3.19 (t of d, 1 H), 2.52 (m, 1 H), 2.19 (m, 1 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 1.82 (s, 3 H), 1.79 (s, 3 H), 1.71 (m, 2 H), 1.50 (br m, 2 H), 1.05 (d, 3 H), 1.01 (d, 3 H), 0.95 (d, 3 H), 0.85 (m, 1 H), 0.45 (s, 6 H). CD (pentane), λ$_{max}$ ([θ]): 372 (−7089), 308 (−14 515), 274 (+10 886) nm. Anal. Calcd for C$_{26}$H$_{41}$Cl$_2$SiZr: C, 57.53; H, 7.43. Found: C, 57.84; H, 7.58. (R/S)-Me$_2$SiCp[(+)neomenthylCp]ZrCl$_2$ (**2b**). ^{1}H NMR (CDCl$_3$): δ 6.99 (t, 1 H), 6.81 (t, 1 H), 5.65 (t, 1 H), 5.64 (t, 1 H), 5.42 (t, 1 H), 5.38 (t, 1 H), 3.61 (m, 1 H), 3.29 (m, 1 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 1.99 (s, 3 H), 1.95 (s, 3 H), 1.89 (s, 3 H), 1.40–1.10 (m, 3 H), 1.04 (d, 3 H), 0.90 (d, 3 H), 0.88 (d, 3 H), 0.86 (d, 3 H), 0.85 (d, 3 H), 0.84 (s, 3 H), 0.83 (s, 3 H), 0.81 (d, 3 H). Anal. Calcd for C$_{26}$H$_{40}$Cl$_2$SiZr: C, 57.53; H, 7.43. Found: C, 57.23; H, 7.17. (R)-Me$_2$SiCp''[(−)menthylCp]ZrMe$_2$ (**3a**). ^{1}H NMR (C$_6$D$_6$): δ 6.71 (t, 1 H), 5.51 (t, 1 H), 5.32 (t, 1 H), 2.78 (t of d, 1 H), 2.29 (m, 1 H), 1.98 (s, 3 H), 1.93 (s, 3 H), 1.75 (s, 3 H), 1.73 (s, 3 H), 1.47 (br m, 2 H), 1.25–1.08 (m, 3 H), 0.96–0.88 (3d, 9 H), 0.44 (s, 3 H), 0.37 (s, 3 H), −0.18 (s, 3 H), −0.27 (s, 3 H). CD (pentane), λ$_{max}$ ([θ]): 351 (+1857), 288 (−10 036) nm. Anal. Calcd for C$_{28}$H$_{46}$SiZr: C, 67.00; H, 9.24. Found: C, 67.08; H, 9.21. (R/S)-Me$_2$SiCp''[(+)neomenthylCp]ZrMe$_2$ (**3b**). ^{1}H NMR (toluene-d_8): δ 6.92 (t, 1 H), 6.78 (t, 1 H), 5.45 (t, 1 H), 5.39 (t, 1 H), 5.37 (t, 1 H), 5.24 (t, 1 H), 3.55–3.45 (br m, 2 H), 1.98 (s, 3 H), 1.95 (s, 9 H), 1.91 (s, 3 H), 1.70 (s, 3 H), 1.69 (s, 3 H), 1.68 (s, 6 H), 1.40–1.19 (m, 3 H), 1.10 (d, 3 H), 1.02 (d, 3 H), 0.98 (d, 3 H), 0.93 (d, 3 H), 0.90 (d, 3 H), 0.73 (d, 3 H), 0.42 (s, 3 H), 0.40 (s, 6 H), 0.37 (s, 3 H), −0.33 (s, 3 H), −0.35 (s, 3 H), −0.38 (s, 3 H), −0.40 (s, 3 H). Anal. Calcd for C$_{28}$H$_{46}$SiZr: C, 67.00; H, 9.24. Found: C, 67.00; H, 9.29.

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