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Polymerization Catalysts with Cyclopentadienyl Ligands Ring-Fused to Pyrrole and Thiophene Heterocycles

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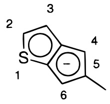
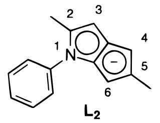
Ziegler−Natta metallocene catalysts for polypropylenes have been based entirely on substituted cyclopentadienyl (Cp), indenyl (Ind), and fluorenyl (Flu) ligands.[1] Notable progress has been made with single-site catalysts for ethylene polymers and copolymers with novel Ti half-metallocenes and late-metal catalysts without cyclopentadienyl ligands.[2] In contrast, there have been no reports of new types of ligands for stereoregular polypropylenes in recent years.

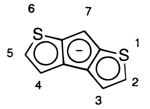
In this contribution we report our preliminary findings with catalysts for stereospecific propylene polymerizations bearing Cp rings with five-membered heterocyclic compounds fused to the cyclopentadienyl ligand. The heterocycles contribute 2 and 4 π-electrons to the Cp aromatic sextet in 5/5 and 5/5/5 ring systems, respectively. The new *ansa*-metallocenes contain the ligands 5-Me-cyclopenteno[*b*]thiophene (**L₁**), 2,5-dimethyl-1-phenyl-cyclopenteno[1.2-*b*]pyrrole (**L₂**), and cyclopenteno[1.2-*b*:4.3-*b*′]-dithiophene (**L₃**):



L₁



L₂



L₃

The heterocenes were selected for polypropylene catalysis on the premise that the novel 5/5 ring-fused structures and the range of group 15 and 16 elements would provide interesting tools for controlling polymer stereochemistry and molecular weights. In addition, the synthetic chemistry of substituted heterocycles has been intensely researched by the pharmaceutical industry[3] and the heterocene catalyst symmetries can be used to control the polymer tacticities.[4]

Ligands and Metallocenes. Ferrocenes with π-heterocyclic ligands **L₁** and 1,2,3-trimethylcyclopentenyl[1,2-*b*]pyrrole ligands decompose in solution.[5] In contrast, the group-4 heterocenes are stable and are both highly active and stereospecific for propylene polymerization in combination with methylalumoxane despite the fact that free Lewis bases often act as catalyst inhibitors.[1b]

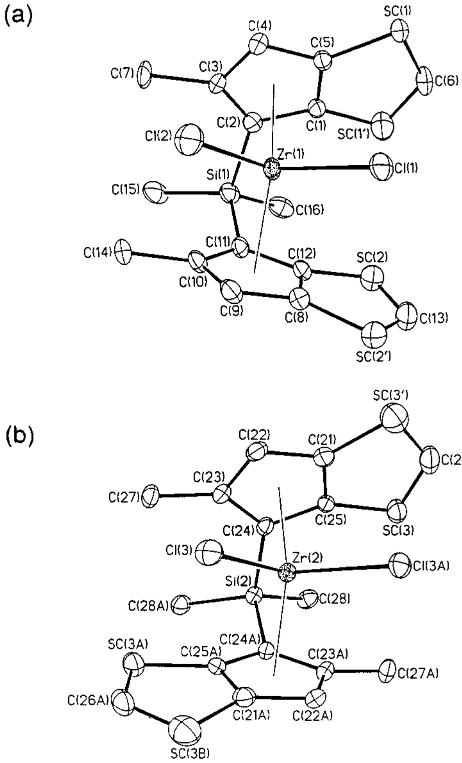


Figure 1. ORTEP diagrams of (a) *meso*-$Me_2Si(4,6\text{-}\mathbf{L_1})ZrCl_2$ and (b) *rac*-$Me_2Si(4,6\text{-}\mathbf{L_1})ZrCl_2$ showing the atom labeling scheme. Thermal ellipsoids shown at 30% probability and hydrogen atoms are omitted for clarity. Two of three independent molecules are shown.

L₁[6] and **L₃**[7] were prepared according to literature procedures. **L₂** was obtained from 1-phenyl-2-methlpyrrole following the methods for 1,2-dimethyl-1-azapentalene.[8] The metallocenes were prepared by using standard synthetic procedures for Cp, Ind, and Flu analogues.[9] $Me_2Si(4,6\text{-}\mathbf{L_1})_2ZrCl_2$ (Figure 1), $Me_2Si(4\text{-}\mathbf{L_2})_2ZrCl_2$, and $Me_2Si(4\text{-}\mathbf{L_2})(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)ZrCl_2$ were obtained as a 1:1 mixture of *meso* and *rac* stereoisomers which were polymerization tested together. The six $Me_2Si(4,6\text{-}\mathbf{L_1})_2ZrCl_2$ isomers cocrystallized together resulting in sulfur−carbon compositional disorder which was refined as sulfur atoms with 0.69 occupancy and labeled SC.[10]

Polymerizations. 2-D representations of the new metallocenes are displayed in Figure 2. Polymerization data obtained in liquid propylene with complexes **1**−**5** are compared with their Ind[11] and Flu[9,12,13] structural analogues in Table 1.

The C_2, C_1, and C_s symmetrical heterocenes were prepared to determine the generality of *Ewen's* symmetry rules.[1a,14] The

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(10) For $Me_2Si(L_1)_2ZrCl_2$ ($C_{18}H_{18}Cl_2S_2Zr$): monoclinic, $C2/c$; a = 31.6018(9) Å, b = 20.7340(6) Å, c = 11.6986(3) Å, β = 98.4343(7)°, V = 7582.4(6) Å^3, Z = 16, T = 198(2) K, D_{calc} = 1.712 g cm^{-3}, $R(F)$ = 6.02% for 4563 observed independent reflections ($4° \le 2\theta \le 52°$). The asymmetric unit consists of one molecule of approximate C_s symmetry and two essentially identical half-molecules of crystallographic C_2 symmetry.

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Table 1. Bulk Propylene Polymerization Results[a]

entry	metallocene	activity, (kg/(mmol cat.h))	MW[b] (10^3 g/mol)	mp (°C)	pentad[c] (%)
		polymerization temperature = 50 °C[d]			
1	Me$_2$C(3-*t*-Bu-1-Cp)(7-**L$_3$**)ZrCl$_2$	13	91	130	84
2[12]	Me$_2$C(3-*t*-Bu-1-Cp)(9-Flu)ZrCl$_2$	13	91	125	80
3	Me$_2$C(1-Cp)(7-**L$_3$**)ZrCl$_2$	14	98	110	74
4[13]	Me$_2$C(1-Cp)(9-Flu)ZrCl$_2$	89	133	140	82
5[c]	Me$_2$Si(4-**L$_2$**)(2-Me-4-Ph-1-Ind)ZrCl$_2$	550	997	161	97
		polymerization temperature = 70 °C[e]			
6	Me$_2$Si(4,6-**L$_1$**)$_2$ZrCl$_2$	97	113	125	80
7[11]	Me$_2$Si(2-Me-1-Ind)$_2$ZrCl$_2$	99	195	145	88
8	Me$_2$Si(4-**L$_2$**)$_2$ZrCl$_2$	560	198	155	96
9	Me$_2$Si(4-**L$_2$**)(2-Me-4-Ph-1-Ind)ZrCl$_2$	865	709	156	–
10[11]	Me$_2$Si(2-Me-4-Ph-1-Ind)$_2$ZrCl$_2$	755	1287[f]	156	95

[a] The low catalyst concentrations used in bulk polymer tests make *meso/rac* bimolecular catalyst inhibition unlikely. [b] Entries 1–4 are M_v and entires 5–10 are M_w. [c] *mmmm* and *rrrr* pentads are from ^{13}C NMR of as-polymerized samples. *mmmm* for entry 6 was calculated with the 2-site enantiomeric model.[13b] The *meso* isomers were inactive for entries 5 and 8. [d] 1 L autoclave. 0.2–2 mg of catalyst, 5 mL 10 wt % MAO, 1 h. The higher s-PP DSC mpt. [e] 4 L stainless steel autoclaves, 0.16–1.0 mg of catalyst, 10 mL of 10 wt % MAO, 1 h. [f] The M_w = 760 000 for Me$_2$Si(2-Me-4-Ph-1-Ind)$_2$ZrCl$_2$[11] could not be reproduced.

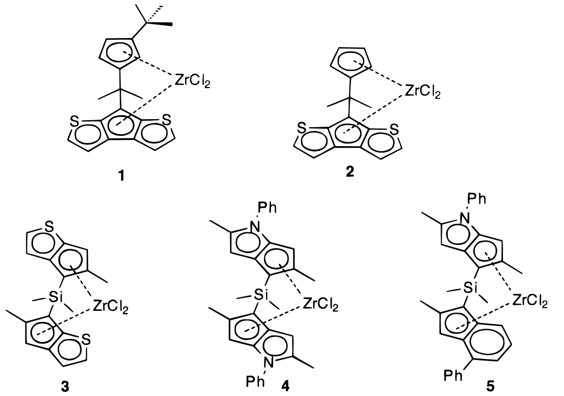

Figure 2. 2-D representations of the five heterocenes that were prepared and tested as polymerization catalysts: (**1**) Me$_2$C(3-*t*-Bu-1-Cp)(**L$_3$**)ZrCl$_2$, (**2**) Me$_2$C(Cp)(**L$_3$**)ZrCl$_2$, (**3**) Me$_2$Si(4,6-**L$_1$**)$_2$ZrCl$_2$, (**4**) Me$_2$Si(4-**L$_2$**)$_2$ZrCl$_2$; and (**5**) Me$_2$Si(4-**L$_2$**)(2-Me-4-Ph-1-Ind)ZrCl$_2$.

cationic monoalkyl catalyst Me$_2$C(3-*t*-Bu-1-Cp)(7-**L$_3$**)Zr(Pl)$^+$ (Pl = polymer chain)[1] produced i-PP at about the same rate as the Me$_2$C(3-*t*-Bu-1-Cp)(9-Flu)Zr(Pl)$^+$ analogue and with the same M_w but with a higher stereospecificity (Table 1, entries 1, 2). However, the stereospecificity of Me$_2$C(3-*t*-Bu-1-Cp)(9-Flu)Zr(Pl)$^+$ at 50 °C increased from *mrrm* = 3.7% in bulk to *mrrm* = 2.5% at [C$_3$H$_6$] = 0.9 M in toluene, as predicted,[12b] while for Me$_2$C(3-*t*-Bu-1-Cp)(7-**L$_3$**)Zr(Pl)$^+$ *mrrm* = 3% at both these conditions. These observations are in accord with the back-skip reaction of the chain from the more crowded side of Me$_2$C(3-*t*-Bu-1-Cp)(7-**L$_3$**)Zr(Pl)$^+$ being faster relative to insertion than for Me$_2$C(3-*t*-Bu-1-Cp)(9-Flu)Zr(Pl)$^+$ and with the latter catalyst therefore being marginally more stereospecific than the former with the chain residing on its less crowded side. Similarly, C_s symmetric Me$_2$C(Cp)(7-**L$_3$**)Zr(Pl)$^+$ afforded s-PP (*rmmr* = 1.8% and *rrmr* = 8.1%) at a slower rate than Me$_2$C(Cp)(9-Flu)Zr(Pl)$^+$ (*rmmr* = 1.6% and *rrmr* = 2.3%) (Table 1, entries 3 and 4). The equivalent number of *rmmr* site-control errors,[13] the higher number of back-skip errors, [13] and the relative activities of the catalysts are consistent with a higher $R_{\text{back-skip}}/R_{\text{insertion}}$ ratio for the heterocene.

The C_2-symmetric heterocenes are equally as active as their indenyl analogues (Table 1, entries 5–10). The three *rac-Me*$_2$-Si(4,6-**L$_1$**)$_2$Zr(Pl)$^+$ isomers (entry 6) produce i-PP with M_w/M_n = 2.1, which is characteristic of a single-site catalyst.[15] The 20 °C lower i-PP melting point than the 2-methylindene analogue (entry 7) is advantageous because indenyl based catalysts do not produced high M_w i-PP with melting points *below* 145 °C.[16] C$_2$-heterocenes produce I-PP with M_w higher than for the prototype Et(Ind)$_2$ZrCl$_2$[1a,9] but lower than for their structural analogues (Table 1). The activities (**4** > **3**) and the ordering of M_w (**3** > **4**) follow the indenyl trends (entries 6, 8 *versus* entries 7, 10). The 5/5 *versus* 5/6 ring ligand effects on M_w are additive (entries 8–10). **L$_2$** (entry 8) led to polypropylenes with the same melting point produced by one of the better indenyl derivatives (entry 10), high molecular weights (entries 5, 8, 9), and to materials closely akin to those made with conventional heterogeneous catalysts having *mmmm* > 95%.

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Supporting Information Available: Synthetic procedures, ^{1}H and ^{13}C NMR and mass spectra for the ligands and metallocenes, polymerization procedures, and listings of experimental procedures and crystal data and structure refinement, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and generated atomic coordinates for hydrogen atoms (24 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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