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Manganese Catalysts with Scorpionate Ligands for Olefin Polymerization

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Summary: The catalyst systems composed of hydrotris(pyrazolyl)borate (Tp) manganese and coactivators showed good activity for ethylene polymerization and ethylene−α-olefin copolymerization. The activity of [MnCl(Tp)]/Al(i-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] for ethylene/1-butene copolymerizations goes up to 1.6×10^7 g mol(cat)$^{-1}$ h^{-1}, giving ethylene−1-butene copolymer with a narrow molecular weight distribution ($M_w/M_n = 1.8$) and a high melting point (120 °C). This system is also active toward propylene and gives isotactic polypropylene with a triad mm fraction of 0.905.

Since the discovery of group 4 metallocene single-site catalysts,[1] many efforts have been made for the survey of new transition metal complex catalysts.[2] In particular, Ni- or Pd-based non-metallocene catalysts were the most spectacular breakthroughs in this field.[3] Afterward, many transition metal complex catalysts based on vanadium,[4] chromium,[5] iron and cobalt,[6] and lanthanides[7] have been reported. However, less attention has been paid to group 7 metal catalysts.[8] Mn-based catalysts would be expected to have unique features different from both early and late transition metal catalysts. H. T. Ban and co-workers have reported Mn(acac)$_3$-, Cp$_2$Mn-, and Mn(salen)Cl-catalyzed ethylene polymerization when methylaluminoxane (MAO) was used as an activator.[8] In their report, they obtained linear polyethylene having a relatively narrow molecular weight distribution ($M_w/M_n = 2.8$). Among these catalysts, Cp$_2$Mn/MAO showed the highest activity of 6.3 kg mol(cat)$^{-1}$ h^{-1}, but this level is insufficient for practical use. In this report, we demonstrated three

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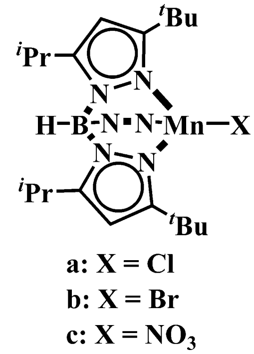

Figure 1. Scorpionate–manganese complexes.

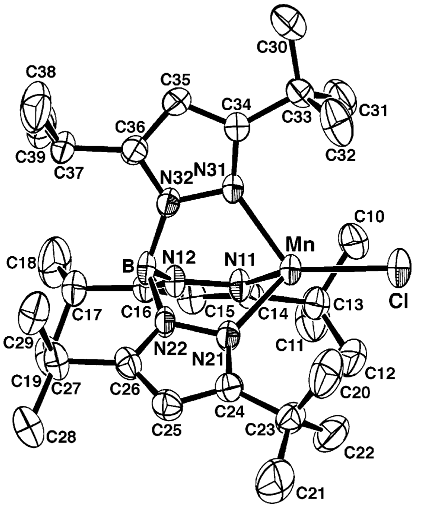

Figure 2. Molecular structure (50% probability ellipsoids) of complex **a**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn–Cl, 2.287(1), Mn–N11, 2.136(4), Mn–N21, 2.140(4), Mn–N31, 2.138(4), Cl–Mn–N11, 126.48(10), Cl–Mn–N21, 124.4(1), Cl–Mn–N31, 122.2(1).

types of novel Mn-based complex catalysts (**a**, **b**, **c**) having a sterically hindered tridentate pyrazolyl ligand, a so-called scorpionate ligand[9] (Figure 1).

The scorpionate–manganese complexes were prepared according to the literature method.[10] For example, complex **a** was synthesized in 53% yield as white crystals by the reaction of K(Tp$^{t\text{-Bu},i\text{-Pr}}$) with $MnCl_2\cdot 4H_2O$ (1:1.2 molar ratio) and by recrystallizing from a CH_3CN/CH_2Cl_2 mixed solvent.[11] The X-ray crystal structure of complex **a** is shown in Figure 2.[12] The polymerization reaction was carried out in toluene solution by using a 400 mL autoclave. Modified methylaluminoxane (MMAO)[13] (I) or Al(i-Bu)$_3$ (TIBA)/[Ph_3C][B(C_6F_5)$_4$] (TB) (II) was employed as an activator. The polymerization reaction stopped by adding methanol in the reactor. The polymer obtained was recovered by filtration and dried in vacuo. The results of ethylene homo-polymerization reactions with Mn(II) complexes (**a**–**c**) are summarized in Table 1. In all cases, their ethylene polymerization activity activated by TIBA/TB (II) is greater than that activated by MMAO (I). When activated by TIBA/TB (II), manganese complex **a** showed the highest catalytic activity of 920 kg mol(cat)$^{-1}$ h^{-1} for polymerization of ethylene at 60 °C under 2.0 MPa of ethylene pressure (entry 4). The polymers produced a unimodal molecular weight distribution ($M_w/M_n = 1.7–2.3$), indicating that the polymers were produced by a single-site active species. In these cases, Mn(II) chloro complex **a** shows the best catalytic activity in the case of TIBA/TB cocatalyst (II), and in the case of MMAO cocatalyst (I), Mn(II) nitrato complex **c** showed the same catalytic activity as **a**. Mn(II) bromo complex **b** was the least active with both cocatalysts. The results show that the coordinated anions (i.e., Cl^-, Br^-, and NO_3^-) have some influence on polymerization reactions.[14]

Table 1. Polymerization of Ethylene Catalyzed by Scorpionate–Manganese Complexes with Cocatalysts[a]

entry	catalyst	cocatalyst[b]	activity[c]	M_w[d] × 10^{-3}	M_w/M_n[d]
1	**a**	I	10.5	64	1.9
2	**b**		0.1	62	1.9
3	**c**		6.0	61	1.8
4	**a**	II	920	96	2.3
5	**b**		70	59	1.9
6	**c**		70	90	2.1

[a] Conditions: toluene 200 mL, ethylene 2.0 MPa, polymerization time 60 min, temperature 60 °C. [b] (I) catalyst 10 μmol, MMAO-3A 10 mmol. (II) catalyst 10 μmol, TIBA 1.0 mmol, TB 20 μmol. [c] In kg mol(cat)$^{-1}$ h^{-1}. [d] Determined by GPC with polystyrene standards.

The catalyst system of **a**/TIBA/TB can copolymerize ethylene and an α-olefin such as 1-hexene. When the copolymerization of these was conducted under the same polymerization conditions as entry 6 in Table 1 except using 198 mL of toluene and 2 mL of 1-hexene instead of 200 mL of toluene, their catalytic activity was decreased dramatically with increased concentrations of 1-hexene (entries 6–10). As shown in Table 2, the melting points of these copolymers decreased as the amount of 1-hexene introduced increased. The results suggest, in the case of these catalyst systems, that the polymer forms in the dormant site from insertion of 1-hexene to the active species. On the other hand, in the case of ethylene–α-olefin copolymer made from group 4 metallocene with cocatalyst, Mülhaupt et al. reported that the molecular weight of the polymer generated decreased with increased concentrations of α-olefin.[15] In this case, the characteristic behavior for the scorpionate–manganese complex **a** is that the

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[11] **a**: yield 73%. Anal. Calcd for $C_{30}H_{52}N_6MnBCl$: C, 60.26; H, 8.76; N, 14.05. Found: C, 59.98; H, 8.67; N, 13.94. IR ν/cm^{-1} (KBr): 2574(νBH). **b**: yield 60%. Anal. Calcd for $C_{30}H_{52}N_6MnBBr\cdot 0.5H_2O$: C, 55.31; H, 8.20; N, 12.90. Found: C, 55.24; H, 8.00; N, 13.00. IR ν/cm^{-1} (KBr): 2576(νBH). **c**: yield 66%. Anal. Calcd for $C_{30}H_{52}N_7MnBO_3$: C, 57.70; H, 8.39; N, 15.70. Found: C, 57.69; H, 8.39; N, 15.57. IR ν/cm^{-1} (KBr): 2589(νBH).

[12] Crystal data for **a**: $C_{30}H_{52}N_6MnClB$, $M = 597.98$, monoclinic space group $P2_1/n$ (no. 14), $a = 9.715(3)$ Å, $b = 17.425(3)$ Å, $c = 20.357(3)$ Å, $\beta = 100.03(2)°$, $V = 3393(1)$ Å^3, $T = 296(2)$ K, $Z = 4$, μ(Mo Kα) = 4.95 cm^{-1}, $F(000) = 1284$, 6362 reflections measured, 5986 unique ($R_{int} = 0.020$), $R = 0.048$, $R_w = 0.051$ [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least squares on F. CCDC no. 234279. For further details, see the Supporting Information.

[13] MMAO is a modified methylaluminoxane activator containing 50% isobutyl groups.

[14] From preliminary EPR spectra of the reaction mixtures, the manganese species are considered to exist as Mn(II) ions in the polymerization reaction (see Figure S1). The coligands (Cl^-, Br^-, and NO_3^-) have some interactions in the reaction. However, detailed EPR experiments are needed to explain the reaction mechanism and the role of the coligands.

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Table 2. Polymerization of Ethylene and 1-Hexene Catalyzed by a/TIBA/TB

entry	[1-hexene] (mL)	activity[b]	M_w[c] ($\times 10^{-3}$)	M_w/M_n[c]	T_m (deg)	1-hexene content[d]
7	2	6700	58	1.8	132.8	0.23
8	10	3130	61	1.7	127.7	0.61
9	30	2090	62	1.7	116.4	1.60
10	50	720	57	1.9	113.7	2.55

[a] Conditions: ethylene 2.0 MPa, polymerization time 60 min, temperature 60 °C; **a** 1.0 μmol, TIBA 1.0 mmol, TB 3.0 μmol. Solvent: toluene + 1-hexene = 200 mL. [b] In kg mol(cat)$^{-1}$ h^{-1}. [c] Determined by GPC with polystyrene standards. [d] mol %, determined by ^{13}C NMR spectroscopy.

molecular weights of polymers produced from **a**/TIBA/TB do not change as a function of the concentration of 1-hexene. When ethylene and 1-butene were copolymerized with the catalyst system **a**/TIBA/TB under an ethylene pressure of 2.0 MPa at 60 °C,[16] the catalytic activity was maintained at 16 000 kg mol(cat)$^{-1}$ h^{-1} to give copolymer having a narrow molecular weight distribution (1-butene content = 2.3 mol %, $M_w = 1.1 \times 10^5$, $M_w/M_n = 1.8$). Such an activity level competes with that of the general metallocene catalyst systems.[2b,17] Therefore, the scorpionate–manganese complex catalysts possess good activity for polymerization reactions, the first example for this class of compounds.

It is worth noting that the **a**/TIBA/TB system also catalyzed isospecific propylene polymerization. Propylene bulk polymerization at 60 °C for 60 min proceeded at an activity of 40 kg mol(cat)$^{-1}$ h^{-1}, to give polymer having an mmmm pentad of 0.81 ($M_w = 52 \times 10^3$, $M_w/M_n = 2.6$, $T_m = 137.4$ °C).[18] The relatively narrow molecular weight distribution of the polymer suggests that the isospecific polymerization proceeds at a single active species. The ^{13}C NMR spectrum reveals that the isotactic polymer contains isotactic sequences spanned by isolated rr triads, indicating that isospecific propagation is governed by an enantiomorphic site control mechanism (Figure 3).[19] In the ^{13}C NMR spectrum, besides signals attributed to carbons in the head-to-tail sequences, many small signals assigned to regioirregular propylene sequence were observed (see Figure S2). Similar stereoirregularity as well as isotacticity was detected in the isotactic polypropylenes prepared with C_2-symmetrical ansa-zirconocene/MAO[20] or TIBA/TB/inorganic solid systems.[21] It is still unclear whether the active species are C_{3v}-symmetrical manganese species[22] or aluminum species.[21] In the former case, this is the first report regarding isospecific polymerization with a transition metal catalyst with a C_{3v}-symmetrical structure. Further studies concerning the structure of the actual active species and the origin of isospecific propylene polymerization are currently in progress.

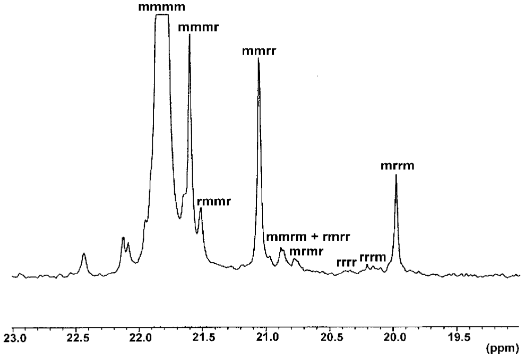

Figure 3. ^{13}C NMR spectrum of polypropylene obtained with Al(i-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] as an activator.

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Supporting Information Available: Detailed reaction conditions of polymerization reactions, text and tables (Table S1–S5) giving a full description of the X-ray crystal structure determination, preliminary EPR spectra of the reaction (Figure S1), and ^{13}C NMR spectra of polypropylene obtained by Al(i-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] as an activator (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] A 400 mL stainless steel autoclave. Conditions: toluene 180 mL, 1-butene 10 g, ethylene 2.0 MPa, temperature 60 °C, polymerization time 60 min, **a** 1 μmol, TIBA 0.25 mmol, TB 3 μmol.

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[18] A 100 mL stainless steel autoclave. Conditions: liquid propylene 40 g, temperature 60 °C, polymerization time 60 min, **a** 10 μmol, TIBA 1.25 mmol, TB 20 μmol.

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