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(η^5-Pentamethylcyclopentadienyl)tin(II) Tetrakis(pentafluorophenyl)borate: A New Cocatalyst for the Polymerization of α-Olefins

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*Summary: The organotin compound (η^5-pentamethylcyclopentadienyl)tin tetrakis(pentafluorophenyl)borate (**1**) has been synthesized from a reaction between (pentamethylcyclopentadienyl)tin chloride and lithium tetrakis(pentafluorophenyl)borate. This cation proved to be an effective Ziegler−Natta α-olefin cocatalyst. Activities for ethylene polymerizations using dimethylzirconocene and **1** were 7.3×10^5 g of PE/(mol of $\mathbf{1}\cdot[C_2H_4]\cdot h$) at 20 °C and 1.2×10^6 g of PE/(mol of $\mathbf{1}\cdot[C_2H_4]\cdot h$) at 70 °C. This system was also effective for the polymerization of propylene. Activities using rac-ethylenebis(indenyl)-dimethylzirconium with the tin cation were 3.0×10^5 g of PP/(mol of $\mathbf{1}\cdot[C_3H_6]\cdot h$). Activities increased markedly when using zirconocene dichlorides/tri(i-butyl)aluminum/**1**. Activities for ethylene polymerization using zirconocene dichloride/tri(i-butyl)aluminum/**1** at 20 °C were 7.0×10^6 g of PE/(mol of $\mathbf{1}\cdot[C_2H_4]\cdot h$). Activities for the polymerization of propylene using rac-ethylenebis-(indenyl)zirconium dichloride/tri(i-butyl)aluminum/**1** at 20 °C were 5.4×10^6 g of PP/(mol of $\mathbf{1}\cdot[C_3H_6]\cdot h$).*

Research on homogeneous Ziegler (single-site) catalysis began with titanocene dichloride activated by AlR_2Cl cocatalyst.[1] This catalyst system exhibits low ethylene polymerization activity,[2] probably because of the low concentration of ionic catalytic species[3] and rapid reduction of Ti,[1a,b,2] and does not polymerize propylene. Many subsequent studies established the cationic d^0 complexes of the type Cp_2M^+R (M = group 4 element) as the catalytically active species.[4] They are generally synthesized by the reactions of metallocene dialkyls with salts of Ag^+ or Cp_2Fe^+,[4b] weakly acidic ammonium salts,[4d,e] triphenylcarbenium salts,[5] and Lewis acids.[5d,6] Recent studies suggest that many of the properties of such catalysts are intimately connected with the nature of the relatively strong cation−anion pairing.[7]

We report here the synthesis of (η^5-pentamethylcyclopentadienyl)tin(II)[8] tetrakis(pentafluorophenyl)borate (**1**) and an investigation of the polymerization behavior of single-site zirconocene catalyst systems with this new cocatalyst.

All operations were performed using standard Schlenk techniques under an argon atmosphere. The cocatalyst **1** was prepared by adding $LiB(C_6F_5)_4$[9] (4.27 g, 6.22 mmol) in CH_2Cl_2 (20 mL) to a solution of Cp*SnCl (**2**)[10] (1.80 g, 6.22 mmol) in CH_2Cl_2 (50 mL) at room temperature and stirring overnight. The LiCl was removed by filtration through a Celite plug, giving an intense red solution. Removal of the solvent followed by extraction with $CHCl_3$ to remove insoluble impurities and elimination of chloroform gave crude **1** (4.44 g, 77% yield). Recrystallization from CH_2Cl_2/hexane gave elementally pure **1** (3.89 g, 67% yield): ^1H NMR ($CDCl_3$) δ 2.25 (s, 15H); ^{11}B NMR ($CDCl_3$) δ −16.49 (s, B); ^{13}C NMR ($CDCl_3$) δ 148.12 (d, *o*-C_6F_5), 137.26 (d, *p*-C_6F_5), 136.66 (d, *m*-C_6F_5), 122.97 (s, C_5Me_5), 9.07 (s, C_5Me_5); ^{19}F NMR ($CDCl_3$) δ −132.41 (d, *o*-F), −162.43 (t, *p*-F), −166.31 (t, *m*-F); ^{119}Sn NMR ($CDCl_3$) δ −2219 (s, Sn). Anal. Found (calcd): C, 43.73 (43.77); H, 1.88 (1.62); F, 41.2 (40.7). The catalyst precursors Cp_2ZrMe_2 (**3**),[11] *rac*-$Et(Ind)_2ZrMe_2$ (**4**),[12] and *rac*-$Et(Ind)_2ZrCl_2$ (**5**)[13] were

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Table 1. Ethylene Polymerization while Varying Zr:Sn Ratio[a]

[**3**] (mM)	[**1**] (mM)	yield of PE (g)	activity[b]	M_w[c]
3.0	3.0	0.52	2.8×10^5	
3.0	2.0	0.89	7.2×10^5	
3.0	1.0	0.44	7.1×10^5	1.1×10^5
3.0	0.50	0.23	7.4×10^5	
0	3.0	0	0	

[a] Solvent = 50 mL of toluene + 1 mL chlorobenzene, $P(C_2H_4)$ = 15 psi. Polymerizations were run for 2 min. T_p = 20 °C. [b] Activity = g of PE/(mol of **1**·$[C_2H_4]$·h). [c] M_w by viscometry in decalin at 135 °C.

Table 2. Comparison of 1 and 7 as Cocatalysts for the Polymerization of Ethylene[a]

run no.[d]	catalyst precursor	cocatalyst	yield of PE (g)	activity[b]	M_w[c]
1	**6**	**1**/TIBA	0.88	9.5×10^6	5.0×10^5
2	**6**	**7**/TIBA	1.76	1.9×10^7	4.7×10^5
3	**3**	**1**	0.39	4.2×10^5	2.0×10^5
4	**3**	**7**	1.15	1.2×10^6	1.3×10^5

[a] Solvent = 50 mL of toluene + 1 mL of chlorobenzene, $P(C_2H_4)$ = 15 psi. Polymerizations were run for 30 min. T_p = 20 °C. [b] Activity = g of PE/(mol of **1**·$[C_2H_4]$·h). [c] M_w by viscometry in decalin at 135 °C. [d] In runs 1 and 2, [**6**] = [**1**] = [**7**] = 10 μM and [TIBA] = 200 μM. In runs 2 and 3, [**3**] = 1 mM and [**1**] = [**7**] = 100 μM.

prepared according to literature procedures. Tri(*i*-butyl)aluminum (TIBA) and Cp_2ZrCl_2 (**6**) were purchased from Aldrich and used without further purification. $Ph_3C^+B(C_6F_5)_4^-$ (**7**) was also prepared according to the literature.[5a]

Initial studies concentrated on finding the ideal conditions for polymerization with these systems by varying the ratio of **3**:**1**.[14] Ratios of 1:1 to 6:1 were used, and the results are summarized in Table 1. In this system, **3** is also acting as a scavenger. Thus, when a 1:1 ratio is used, an excess of **1** is present and the activity is apparently low. At 1.5:1 ratios or below, activities are almost constant. If polymerization of ethylene is attempted in the absence of **3**, no polymer is formed, indicating that **1** is not the catalytically active species.

A direct comparison of **1** versus **7** as the cocatalyst was carried out (Table 2). Ethylene polymerization for 30 min showed activities with **7** were higher under identical conditions ((1.2 × 10^6 g of PE/(mol of **7**·$[C_2H_4]$·h) compared to 4.2 × 10^5 g of PE/(mol of **1**·$[C_2H_4]$·h)).

Ethylene polymerization was also performed from −20 to +70 °C (Table 3). The **1**/**3** catalyst system shows a modest but definite increase in ethylene polymerization activity as T_p increases. With this system, polymerizations at temperatures of 0 °C and below show a substantial drop in polymerization activity.

Table 3. Variable-Temperature Ethylene Polymerization[a]

temperature (°C)	time (min)	yield of PE (g)	activity[b]	T_m (°C)	M_w[c]
70	2	0.36	1.2×10^6	129	4.9×10^4
50	2	0.36	9.1×10^5	129	5.1×10^4
20	2	0.46	8.6×10^5	132	1.2×10^5
0	10	0.18	5.8×10^4	133	4.1×10^5
−20	10	0.19	5.4×10^4	132	7.3×10^5

[a] Solvent = 50 mL of toluene + 1 mL of chlorobenzene, $P(C_2H_4)$ = 15 psi. [**3**] = 3.0 mM, [**1**] = 0.87 mM. [b] Activity = g of PE/(mol of **1**·$[C_2H_4]$·h). [c] M_w by viscometry in decalin at 135 °C.

Table 4. Polymerization of Propylene Using 5/TIBA/1[a]

temperature (°C)	yield of PP (g)	activity[b]	T_m (°C)	M_w[c]	[*mmmm*] pentad[d]
70	2.16	1.5×10^7	101	1.7×10^5	54%
20	4.47	5.4×10^6	140	3.7×10^5	
0	1.49	1.4×10^6	148	6.3×10^5	
−20	0.77	5.3×10^5	152	5.8×10^5	93%

[a] Solvent = 50 mL of toluene + 1 mL of chlorobenzene, $P(C_3H_6)$ = 15 psi. [**5**] = [**1**] = 50 μM, [TIBA] = 10 mM. Polymerizations were run for 30 min. [b] Activity = g of PP/(mol of **1**·$[C_2H_4]$·h). [c] M_w by viscometry in decalin at 135 °C. [d] [*mmmm*] pentads by ^{13}C NMR spectroscopy in 1,2,4-trichlorobenzene at 100 °C.

Propylene polymerization was also catalyzed by **1**/**4**. Using the following conditions, [**4**] = 3 mM; [**1**] = 1 mM; T_p = 20 °C; and polymerization time = 30 min, 4.95 g of polypropylene was obtained, which corresponds to an activity of 3.0 × 10^5 g of PP/(mol of **1**·$[C_3H_6]$·h). The polymer had a M_w of 3.0 × 10^5 and a melting point of 133 °C. This system is less active than using **7** as the cocatalyst, where activities of 8.5 × 10^6 g of PP/(mol of **7**·$[C_3H_6]$·h) were obtained under similar conditions.[5a] Although activities were lower, stereoselectivity was still very high. Analysis of the methyl pentad distributions of the polymer by ^{13}C NMR spectroscopy in 1,2,4-trichlorobenzene at 100 °C showed 85% [*mmmm*] pentads.

Activities were greatly increased when zirconocene dichlorides/TIBA/**1** catalyst systems were used.[14,16] In this case, TIBA alkylates the zirconocene dichloride and acts as a scavenger in the reactor. Polymerization of ethylene using **6**/TIBA/**1** for 5 min gave 0.54 g of polyethylene which corresponds to an activity of 7.0 × 10^6 g of PE/(mol of **1**·$[C_2H_4]$·h), almost a 10-fold increase in activity over the **3**/**1** catalyst system. Polymerizations for 30 min gave similar activities, but again, activities using **1** as the cocatalyst were lower than when using **7** (9.5 × 10^6 g of PE/(mol of **1**·$[C_2H_4]$·h) versus 1.9 × 10^7 g of PE/(mol of **7**·$[C_2H_4]$·h)) (Table 2).

Polymerization of propylene using **5**/TIBA/**1** for 30 min gave 4.47 g of polypropylene, which corresponds to an activity of 5.4 × 10^6 g of PP/(mol of **1**·$[C_3H_6]$·h) (Table 4) which is almost 20 times more active than the **1**/**4** system. Again, as seen in variable-temperature ethylene polymerizations, an increase in activity is observed as polymerization temperature increases. Stereoselectivity of the polymerization catalyst is still high, producing PP with 93% [*mmmm*] pentads and a melting point of 152 °C at a polymerization temperature of −20 °C. If

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(14) Polymerizations were carried out in a 250 mL crown-capped glass pressure reactor containing 50 mL of toluene and were equilibrated with monomer at 15 psi. Known concentrations of **3**, **4**, **5**, **6**, and TIBA were made in toluene. Solutions of the cocatalysts **1** and **7** were prepared in chlorobenzene, due to the very low solubility of **1** in toluene. One milliliter portions of **3**, **4**, **5**, or **6** and **1** or **7** were added to the reactor in that order to form the active polymerization catalyst in situ. If TIBA was used, this was introduced to the reactor first. The polymerization was quenched with a methanol/2% HCl solution, and the polymer was worked up as detailed elsewhere.[15]

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zirconium is absent during the polymerization (i.e., just **1** and TIBA are present in the polymerization vessel), no polymer is formed, indicating that TIBA does not react with **1** to form an active polymerization catalyst. The reason for the marked increase may be two-fold. The excess TIBA is probably acting as a superior scavenger compared to **3** or **4**. Also, coordination of the tin lone pair to the Lewis-acidic aluminum present in large excess may occur instead of coordination to the zirconium species. Coordination of the tin lone pair to aluminum has been observed in similar organotin(II) compounds.[17]

An investigation of the mechanism of these processes as well as further polymerization studies are underway. Also, extensions to related organotin cocatalyst systems are under current study.

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