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Olefin Polymerization Catalyst Derived by Activation of a Neutral Monoalkyl Titanium Complex with an Aminopyrrole Ligand Using Triisobutylaluminum and Trityl Borate

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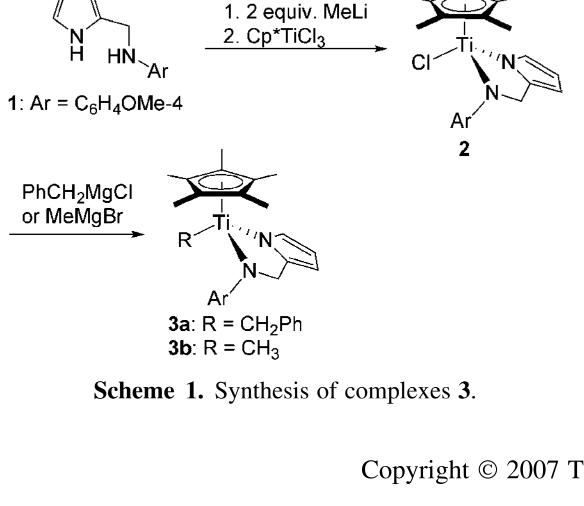
A neutral monocyclopentadienyl titanium monobenzyl complex **3a** bearing an aminopyrrole ligand can be activated by treating with $Al(^iBu)_3$ and $[Ph_3C][B(C_6F_5)_4]$ to became a catalyst for olefin polymerization via the methine proton abstraction of $Al(^iBu)_3$ by $[Ph_3C][B(C_6F_5)_4]$.

In the last two decades, the development of homogeneous olefin polymerization catalysts has been remarkable.[1] The catalytically active species with appropriate supporting ligands such as cyclopentadienyl anions and nitrogen-based chelating anions are cationic monoalkyl complexes, and the propagation process involves consecutive monomer insertion into an electrophilic metal—alkyl bond. Methylaluminoxane (MAO) has been utilized as a unique cocatalyst for generating cationic monoalkyl species, functioning in both the methylation of dihalide precatalysts and the abstraction of one of two methyl groups bound to the metal. Moreover, cocatalysts such as $B(C_6F_5)_3$, $[Ph_3C]$-$[B(C_6F_5)_4]$, and $[NR_3H][B(C_6F_5)_4]$ abstract one of two alkyl groups bound to the metal center to form the corresponding cationic monoalkyl species that can initiate olefin polymerization.[1c] Although neutral monoalkyl complexes of group 3,[2] group 4,[3] and group 10 metals[4] can function as polymerization catalysts without any cocatalysts, in some cases a cocatalyst improves catalytic activity of neutral monoalkyl complexes.[5–8] The mechanism, however, is not known. Herein, we report a new activation route of a neutral monobenzyl titanium complex **3a** bearing an aminopyrrole ligand using $Al(^iBu)_3$ and $[Ph_3C][B(C_6F_5)_4]$ as cocatalysts and its catalytic performance for homopolymerizations of ethylene and 1-hexene.

Scheme 1 shows a synthetic route of monoalkyl titanium complexes **3a** and **3b**: the reaction of Cp^*TiCl_3 with the dilithium salt of **1** in ether quantitatively afforded a monochloride complex **2**, which was treated with $PhCH_2MgCl$ and MeMgBr to give the corresponding monobenzyl complex **3a** and monomethyl complex **3b**. The benzyl complex **3a** was thermally stable enough to be isolated, while the methyl derivative **3b** decomposed during the isolation. The monomeric three-legged piano-stool structure of the complexes **2** and **3** was identified by spectroscopy as well as a single-crystal X-ray analysis for **2**.[9] Notable spectral data of **3a** is that a benzyl moiety bound to the titanium center adopts η^1-coordination mode as judged from the $^1J_{CH}$ value (125.8 Hz) of the methylene carbon and the chemical shift (149.9 ppm) of ipso-carbon of the phenyl group, which is comparable to the previously reported value for the η^1-coordination benzyl group.



Scheme 1. Synthesis of complexes **3**.

The monochloride complex **2** and the monobenzyl complex **3a** were tested as catalyst precursors for ethylene polymerization under various conditions, and the results are summarized in Table 1. The monobenzyl complex **3a** showed no activity in the absence of any cocatalysts; however, **3a** upon activated by $[Ph_3C][B(C_6F_5)]$ (1 equiv.) and $Al(^iBu)_3$ (100 equiv.) had the highest activity for ethylene polymerization (Entry 6), and its activity was higher than that of **2** under the same condition (Entry 1). Both additives are key components to activate the neutral complex **3a** because two catalyst systems, **3a**/$Al(^iBu)_3$ (Entry 11) and **3a**/$[Ph_3C][B(C_6F_5)_4]$ (Entry 12), had no activity. The special role of $Al(^iBu)_3$ in the activation of **3a** was further supported by following experimental evidences: (i) when $AlMe_3$ was used instead of $Al(^iBu)_3$, the catalytic activity of complexes **2** and **3a** in the presence of $[Ph_3C][B(C_6F_5)_4]$ was severely suppressed (Entries 2 and 7); (ii) the catalyst system of **3a**/MMAO, which contains $Al(^iBu)_3$, had higher activity than the catalyst **3a**/MAO (Entries 8 and 10).

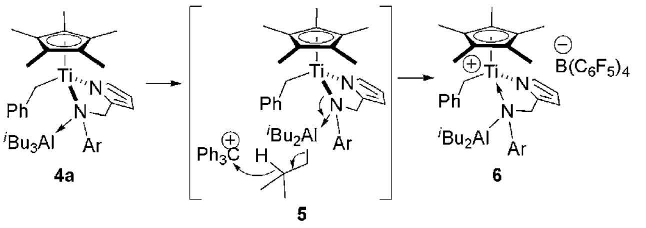
We also found that the catalyst system of complex **3a** with 1 equivalent each of $Al(^iBu)_3$ and $[Ph_3C][B(C_6F_5)_4]$ in C_6H_5Cl polymerized 1-hexene with moderate activity (34 kg-polymer/mol-cat·h). The molecular weight distribution ($M_n = 5300$, $M_w/M_n = 2.3$) of poly(1-hexene) was narrow enough as a single site catalyst, though the polymer was atactic. When the complex **3a** was treated by $[Ph_3C][B(C_6F_5)_4]$ without $Al(^iBu)_3$, no poly(1-hexene) was obtained.

To further elucidate the function of the combined cocatalyst system $Al(^iBu)_3$ and $[Ph_3C][B(C_6F_5)_4]$ for activating the precatalyst **3a**, we first attempted to detect species in situ generated by the reaction of **3a** with one equivalent each of $Al(^iBu)_3$ and $[Ph_3C][B(C_6F_5)]$ without monomer in C_6D_5Br at −30 °C. Any identifiable species was not detected because the oily catalytically active species was very unstable in the absence of the monomer; however, we detected proton signals due to triphenylmethane and isobutene but no benzyl abstraction product, 1,1,1,2-tetraphenylethane, suggesting that the trityl cation selectively abstracted one methine proton of isobutyl group bound to

Table 1. Ethylene polymerization by the monochloride complex **2** and the monobenzyl complex **3a**[a]

Entry	Cat.	Cocatalyst	Time /min	Activity[b]	M_w[c] (10^5)
1	**2**	$[Ph_3C][B(C_6F_5)_4]/Al(^iBu)_3$	5	48	1.6
2	**2**	$[Ph_3C][B(C_6F_5)_4]/AlMe_3$	30	<1	—
3	**2**	MMAO	10	19	
4	**2**	$AlMe_3$	60	trace	—
5	**2**	$Al(^iBu)_3$	60	trace	—
6	**3a**	$[Ph_3C][B(C_6F_5)_4]/Al(^iBu)_3$	5	327	2.5
7	**3a**	$[Ph_3C][B(C_6F_5)_4]/AlMe_3$	15	trace	—
8	**3a**	MMAO	5	111	—[d]
9	**3a**	dMMAO	5	135	—[d]
10	**3a**	MAO	5	60	0.6
11	**3a**	$[Ph_3C][B(C_6F_5)_4]$	30	0	—
12	**3a**	$Al(^iBu)_3$	30	<1	—
13	**3a**	$Al(C_6F_5)_3$	30	0	—

[a]Reaction conditions: complex 4.5 µmol, ethylene pressure 1 atom, [cat.] = 0.5 mM in touene, temperature = 25 °C, $[Ph_3C][B(C_6F_5)_4]$ = 4.5 µmol, $Al(C_6F_5)_3$ = 4.5 µmol, AlR_3 100 equiv., MMAO 1000 equiv. [b]kg-PE/mol-cat·h. [c]Determined by GPC. [d]Not determined because of high molecular weight.



Scheme 2.

aluminum.[10] On the other hand, the reaction of **3a** with $AlMe_3$ and $[Ph_3C][B(C_6F_5)_4]$ immediately resulted in insoluble oil along with the formation of 1,1,1,2-tetraphenylethane, a product of benzyl abstraction by trityl cation. Addition of $Al(^iBu)_3$ to complex **3a** in C_6D_6 resulted in the quantitative formation of an aluminum adduct **4a**, in which $Al(^iBu)_3$ coordinated to the amino nitrogen atom of the metallacycle of **3a** and the addition of 1 equivalent of THF to the aluminum adduct **4a** regenerated **3a** along with a THF adduct of $Al(^iBu)_3$. These experimental results suggest the formation of a cationic monoalkyl species **6** through a possible intermediate **5** with the abstraction of proton at the coordinated $Al(^iBu)_3$ of **4a** (Scheme 2). It is likely that such a unique activation process is involved in catalytic systems of group 4 metal complexes bearing imine-based ligands upon activation by $Al(^iBu)_3$ and $[Ph_3C][B(C_6F_5)_4]$, because of the detection of the imine reduction products.[11–14]

In conclusion, we demonstrated a new route to generate catalytically active species by treating the neutral monobenzyl titanium complex **3a** bearing an aminopyrrole ligand with $[Ph_3C][B(C_6F_5)_4]$ and $Al(^iBu)_3$ as cocatalysts. Our finding extends the flexibility in design of precatalysts for olefin polymerization and has the potential to improve catalytic performance.

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