J. Am. Chem. Soc. **1996,** *118,* 12453−12454

A Catalytic System for Ethylene Polymerization Based on Group III and Lanthanide Complexes of Tris(pyrazolyl)borate Ligands

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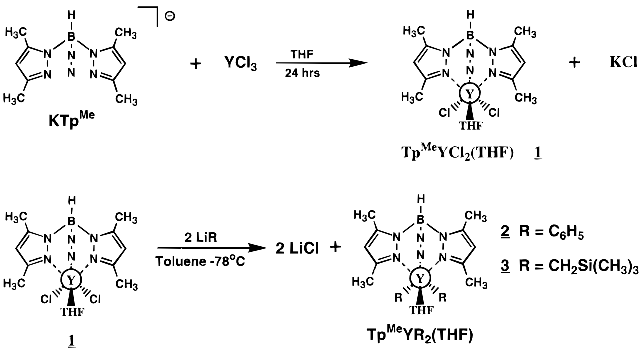
Received June 27, 1996

There has been recent interest in the use of soluble transition metal- and lanthanide-based catalysts for polymerization of ethylene and α-olefins.[1] For lanthanides, a variety of bis(substituted cyclopentadienyl) alkyl and hydride complexes of lanthanide metals have been shown to be active for olefin hydrogenation, oligomerization, isomerization, cyclization, methane transmetalation, and ethylene and butadiene polymerization.[2] Some lanthanide catalytic systems display advantages over analogous transition metal-based catalysts such as high stereoselectivity, activity over wide temperature ranges, simplicity of polymerization mechanisms, relative lack of decomposition reactions, and extremely high activity. However, their olefin polymerization efficiency is largely limited to sterically unhindered monomers because of the high degree of steric saturation required to stabilize alkyl and hydride complexes of these large and very reactive metals. Complexes of the general formula $CpLnR_2$ [$R = CH(SiMe_3)_2$, Me] were synthesized, but for these less sterically hindered complexes, any olefin polymerization activity reported was low.[3]

The tris(pyrazolyl)borate ligand is the focus of much research as a supporting ligand to control steric saturation and reactivity at a variety of metal centers.[4] It displays many advantages as a supporting ligand in lanthanide complexes over analogous cyclopentadienyl ligands due to the relative ease of tuning the blocking substituent groups on the 3-position of the pyrazole rings. Alteration of these substituents has been shown to effect large changes in the reactivities of metal complexes, because of the alteration of steric saturation and electronic character at the metal center. We report here the synthesis and characterization of tris(3,5-dimethyl-1-pyrazolyl)borohydride (Tp^{Me}) complexes of yttrium of the general formula [$Tp^{Me}YR_2(THF)_x$] [$R = C_6H_5$, CH_2SiMe_3]. We have found these complexes and similar ones of variously substituted Tp ligands, as well as analogous lanthanide complexes, to be active in the catalytic polymerization of ethylene to linear, extremely high molecular weight polymers. The variations in polymerization activity of polyethylene (PE) that are obtained from different members of this class of complexes show that synthetic tailoring allows control over the rate of polymerization reaction and the yield of the PE product.

Scheme 1



Reaction of anhydrous YCl_3 with 1 equiv of the KTp^{Me} in THF (Scheme 1) gives the monosubstituted $Tp^{Me}YCl_2(THF)$ **(1)** in 90−95% yield. The empirical formula was confirmed by ^1H NMR integration and chemical analysis. Reaction of $Tp^{Me}YCl_2(THF)$ with 2 equiv of the appropriate lithium reagent in toluene (Scheme 1) at −78 °C results in formation of $Tp^{Me}YR_2(THF)$ complexes ($R = C_6H_5$, CH_2SiMe_3), giving $Tp^{Me}YPh_2(THF)$ **(2)** and $Tp^{Me}Y(CH_2SiMe_3)_2(THF)$ **(3)**, which can be isolated in 70% yield by recrystallization from pentane. ^1H NMR and chemical analysis indicate the coordination of one THF molecule per metal in both complexes. Coordination of the phenyl and trimethylsilylmethyl groups directly to yttrium is established by ^1H and ^{13}C NMR: the ^1H spectrum of **3** shows a doublet for the methylene protons at $\delta = -0.637$ ppm ($J_{YH} = 2.95$ Hz), and ^{13}C spectra show doublets for the α-carbon resonances of **2** ($\delta = 187.7$ ppm, $J_{YC} = 50.9$ Hz) and **3** ($\delta = 32.1$ ppm, $J_{YC} = 36.1$ Hz). Both the dialkyl complexes **2** and **3** are monomeric in solution: ^{89}Y NMR of **2** and **3** show only one yttrium species is present. In the ^1H and ^{13}C NMR spectra of **2** and **3**, all of the pyrazole rings and alkyl ligands are equivalent and no coupling of the alkyls to more than one yttrium center is observed. In contrast, reaction of **1** with 2 equiv of *tert*-butyllithium does not give any isolable complex, although the reactivity of this mixture (see below) indicates that yttrium alkyl bonds are formed.

Reaction of **1** with 2 equiv of methyllithium produces a $Tp^{Me}-Y$ methyl complex, observed in the ^1H NMR by the appearance two doublets ($\delta = -0.87, -0.97$ ppm, $J_{YH} = 2.0$ Hz). The methyl complex is much more thermally unstable than the complexes of the larger R groups and decomposes quickly even at low temperatures. The appearance of the methyl protons as doublets confirms their coupling to a single yttrium, suggestive of, though not conclusive for, a monomeric structure.[5] Similarly, reaction of **3** with 8 atm of H_2 at 0 °C for 24 h in toluene generates a $Tp^{Me}-Y$ hydride complex that is also very thermally unstable, but which can be isolated by recrystallization from pentane at −40 °C. IR spectroscopy of this complex shows a broad, strong absorption centered at 1344 cm^{-1}, which is characteristic of the M−H−M stretch of bridging hydrides in lanthanide complexes.[6a] Use of D_2 in the analogous reaction produces the corresponding metal deuteride, with the M−H−M

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S0002-7863(96)02169-5 CCC: $12.00

Table 1. Ethylene Polymerization Data from $Tp^{Me}YCl_2(THF) + 2RLi$[a]

catalyst	N_t[b]	t (h)	M_w	M_w/M_n
$R = CH_3$[c]	29.5	6		
$R = C_6H_5$ **(2)**	1096	6	1.0×10^5	2.50
$R = C_6H_5$ **(2)**	1688	18	1.2×10^6	4.14
$R = C(CH_3)_3$	1932	6		
$R = CH_2Si(CH_3)_3$ **(3)**	15.1	6		
(3) $+ H_2$[d]	3000	2	1.9×10^6	15.86

[a] All polymerizations run at 120 psi of ethylene with 0.19 mmol of **1** at 25 °C in 150 mL of toluene unless otherwise noted. [b] Overall turnover numbers calculated as (moles of PE/moles of Y). [c] All alkyllithium reagents are allowed to react with **1** overnight at −35 °C before polymerization. [d] Polymerization run at 1000 psi in 10 mL of toluene with 0.03 g of the isolated hydride complex.

stretching band at 1344 cm^{-1} absent in the IR spectrum. ^1H NMR of the hydride complex shows complete loss of the trimethylsilylmethyl ligand and suggests an aggregated structure: resonances arising from two inequivalent pyrazoles and from coordinated THF are observed, as well as a quartet at $\delta = 7.46$ ppm ($J_{YH} = 16.25$ Hz), indicative of direct Y−H bonding. An identical quartet is also observed in the ^2D NMR of the deuteride complex. A trimeric solution structure is therefore suggested for this Tp^{Me}−Y hydride. A trimeric complex $[(Cp)_2ErH]_3^+$ containing a triply bridging hydride has been crystallographically characterized,[6b] and a trimeric structure with equivalent bridging methyl groups is indicated for $[CpYMe_2]_3$ in which the ^1H NMR resonances of the methyl groups also appear as a quartet.[3a]

All of the Tp^{Me}−Y alkyl and hydride complexes were found to be catalysts for the polymerization of ethylene,[7] yielding linear PE with M_w (by GPC)[8] in some cases exceeding 2×10^6 Da (see Table 1). In all cases, including the complexes containing the large phenyl and trimethylsilylmethyl ligands, polymerization occurred even though THF remained coordinated to the initial yttrium complexes. The catalytic system produced by a mixture of $Tp^{Me}YCl_2(THF)$ and 2 equiv of *tert*-butyllithium proved to be the most active (Table 1), giving the highest N_t and yield of polymer. Polymerization with sterically large alkyl or aryl groups at the active sites in the presence of coordinating solvent and with two potential polymerization sites per metal center is a feature that is unusual in early transition metal and lanthanide metallocene catalysts. This activity in the presence of conditions that hinder olefin polymerizations in metallocene complexes indicates that greater steric unsaturation and consequent higher reactivity is obtained by use of a single Tp^{Me} supporting ligand compared to bis(cyclopentadienyl) systems.

Another advantage of this new polymerization system over metallocene-based catalysts is its versatility, arising from the easy variation of the steric and electronic characteristics of the Tp ligand by substitution of the 3-position of the pyrazole rings. Yttrium dialkyl complexes of tris(1-pyrazolyl)borohydride (Tp) and tris(3-phenyl-1-pyrazolyl)borohydride (Tp^{Ph}) are also active ethylene polymerization catalysts, as are analogous $Tp^RLn(alkyl)_n(THF)_x$ complexes ($Ln = La^{3+}, Nd^{3+}, Sm^{2+}$). In this class of Tp-substituted catalysts, variations in the blocking Tp substituents and the sizes of the metal centers cause significant changes in the extent of the polymerization reactions. The large number of possible variations in this catalyst system allows for more specifically designed catalysts, possibly selective for the optimized polymerization of a desired monomer or the production of copolymers.

Insertion polymerization, similar to the well-documented polymerization of olefins by other lanthanide catalysts,[2a−e,3a] is indicated as the operative mechanism of the $Tp^{Me}YR_2$ catalysts. In low molecular weight polymer obtained from $Tp^{Me}Y(CH_2SiMe_3)_2(THF)$ as the catalyst, trimethylsilylmethyl endgroups are observed by IR.[9] For $Tp^{Me}Y(Ph)_2(THF)$, CMPAS ^{13}C NMR show completely linear PE. In all cases, IR spectra of the PE indicate linear polymers, while thermal analysis yielding T_m of 142.3 °C (first melt) demonstrates very high linearity. Use of larger alkyls in $Tp^{Me}YR_2$ catalysts (with the exception of R = *tert*-butyl[10]) or use of Tp^{Ph} catalysts results in smaller quantities of polymer, showing that steric bulk at the metal center affects the extent of polymerization. These data all suggest an insertion mechanism.

Dissociation of coordinated THF from the metal center appears to be a controlling factor in the initiation of these polymerizations. Dissociation of THF from the yttrium dialkyls significantly affects the steric saturation at the metal center, as seen in ^1H NMR spectra of the dialkyl complexes. For **3**, dissociation of THF is not rapid in benzene-d_6, as demonstrated by the line broadening of the 3-methyl and methylene protons, caused by steric saturation at the metal center which creates a rigid environment around the alkyl sites. This line broadening is not seen in the spectrum done in THF-d_8, since rapid exchange relieves the steric saturation. In the polymerization reaction mixtures, open sites for coordination of ethylene are probably provided by loss of THF, slowing initiation of polymerization in complexes where solvent remains coordinated,[1b−d,2a,b,e] No polymerization occur in THF solution, due to successful competition for open sites by THF over ethylene.

Typical molecular weights (M_w) of the polyethylene obtained from various catalysts range from 1.0×10^5 to $>2.0 \times 10^6$ Da,[8] with polydispersities ranging from 2.5 to 4.1 (except for the Tp^{Me}-Y hydride where the large number of catalytic sites leads to a highly polydisperse product). Overall catalytic activity is fairly low, as is common in catalytic systems with Lewis bases coordinated to the metal centers,[1b−d,2a,b,e] with N_t (mole of PE/mole of yttrium) = 1200−3000. However, in the linear PE of M_w over two million, the degree of polymerization is approximately 67 000; the specific catalytic sites that produced this polymer must therefore have turnover numbers much greater than the overall. This discrepancy suggests that although some catalytic sites are highly active in the polymerization, polymerization is not initiated at all the potential catalytic sites.

These first examples of olefin polymerization catalysts containing the tris(pyrazolyl)borate supporting group demonstrates the potential of this class of ligands for controlling the activity and enhancing the stability of catalytic systems. The advantageous characteristics of Tp ligands, as discussed above, combined with the inherently highly electrophilic nature of lanthanides, may allow for the design of single-source, well-defined olefin polymerization catalysts that do not require the use of Lewis acid cocatalysts such as methyl aluminoxanes.

Acknowledgment. We thank A. Benesi and J. Pawlow for their assistance in obtaining NMR and DSC data. P.A.B. is a Camille and Henry Dreyfus Teacher−Scholar Award (1992−1997), a Sloan Fellow (1994−1996), and the recipient of a DuPont Young Professor Award (1994−1997).

Supporting Information Available: Spectroscopic and analytical data for compounds **1**−**3** (1 page). See any current masthead page for ordering and Internet access instructions.

JA962169B

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(7) The alkyl or hydride complexes (either the pure isolated products or generated in situ) under inert atmosphere were exposed to 120 psi of ethylene in toluene at room temperature for between 2 and 18 h. PE is also produced within minutes by bubbling ethylene at 1 atm through a toluene solution of the yttrium hydride complex.

(8) Polyethylene samples were analyzed in trichlorobenzene at 145 °C; molecular weights are reported against polystyrene standards. Samples of $M_w > 2 \times 10^6$ daltons did not fully dissolve, and the molecular weight reported reflects the soluble portion of the sample only.

(9) Partial IR (KBr) cm^{-1} 1247 (w), 862 (w), 834 (w) [$-SiMe_3$].

(10) The high catalytic activity of the *tert*-butyl group in this system is theorized to arise from the inability of more than one such large alkyl to coordinate to the relatively congested yttrium, resulting in a vacant coordination site.