

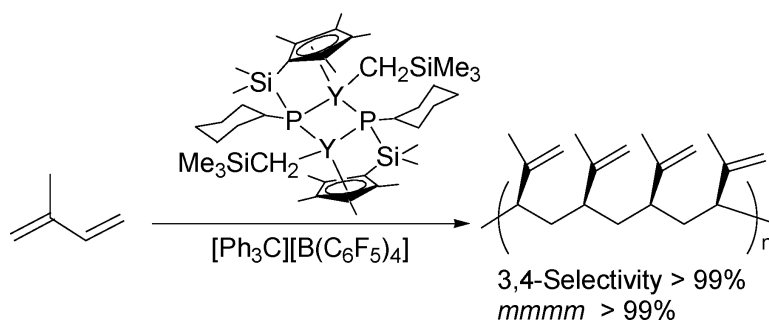
Communication

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J. Am. Chem. Soc., **2005**, 127 (42), 14562-14563 • DOI: 10.1021/ja055397r • Publication Date (Web): 30 September 2005

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Unprecedented Isospecific 3,4-Polymerization of Isoprene by Cationic Rare Earth Metal Alkyl Species Resulting from a Binuclear Precursor

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Cationic alkyl complexes of group 4 metals have been the subject of intensive investigations over the past two decades because of their crucial importance in catalytic olefin polymerization.¹ In contrast, cationic alkyl species of rare earth (group 3 and lanthanide) metals are much less developed.^{2,3} However, recent studies have shown that cationic rare earth metal alkyls are highly efficient olefin polymerization catalysts³ and can show unique activities that differ from those of group 4 metals.^{3a,b,e} Treatment of a neutral di- or trialkyl precursor with an equimolar amount of a borate compound proved to be a convenient route to generate a cationic trivalent rare earth metal alkyl species. Due to the lack of appropriate precursors, the cationic rare earth metal alkyls reported so far were limited solely to mononuclear species, while a binuclear cationic rare earth metal alkyl species remained unknown to date.⁵

During our investigations on new organo rare earth metal catalysts,⁴ we have synthesized several silylene-linked cyclopentadienyl–phosphido rare earth metal alkyl complexes, such as **1** and **2** (Chart 1).⁶ These complexes adopt a relatively robust binuclear structure through the phosphido bridges, in which each of the two metal centers bears a terminal alkyl ligand. In view of the novel activity observed recently for the cationic alkyl species generated from the mononuclear rare earth metal dialkyl complexes, such as **3** and **4** in olefin polymerization,^{3a,b,e} we became interested in the olefin polymerization behavior of the cationic alkyl species generated from the binuclear complexes **1** and **2**. In this Communication, we report that such binuclear cationic alkyl species can show unprecedented regio- and stereoselectivity in the polymerization of isoprene, which afford isotactic 3,4-polyisoprene with extremely high regio- and stereoselectivity (3,4-selectivity: 100%, *mmmm* > 99%). As far as we are aware, this is the first example of isospecific 3,4-polymerization of isoprene. Previously, various metal catalysts or initiators have been reported for the polymerization of isoprene, but most of them yielded predominantly 1,4-polyisoprene and none were reported to show isospecific 3,4-selectivity.^{7,8}

The binuclear Y and Lu dialkyl complexes **1** and **2** were easily obtained in 60–70% isolated yields by reaction of Me₂Si(C₅Me₄H)-(PHCy) (Cy = cyclohexyl) with an equimolar amount of Ln(CH₂-SiMe₃)₃(THF)₂ in hexane.⁶ ¹H NMR monitoring of the reaction of **1** with an equimolar amount of [Ph₃C][B(C₆F₅)₄] (**A**) in C₆D₆ or C₆D₅Cl showed instant disappearance of the signals for the neutral complex **1** and appearance of new signals assignable to Ph₃CCH₂-SiMe₃. However, the possible resulting cationic Y alkyl species could not be assigned because of the complexity of the spectrum. Nevertheless, addition of 600 equiv of isoprene to a mixture of **1** and **A** in C₆H₅Cl led to rapid polymerization of isoprene, which yielded regiospecifically 3,4-polyisoprene (99%) with isotactic-rich stereo microstructures (*mm* ≈ 80%, *mmmm* ≈ 30%) and a relatively narrow molecular weight distribution (*M_w/M_n* = 1.8) (Table 1, run 5). This is in sharp contrast with the reaction of either the neutral

Chart 1. Bi- and Mononuclear Rare Earth Metal Dialkyl Complexes

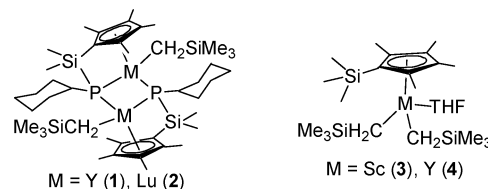
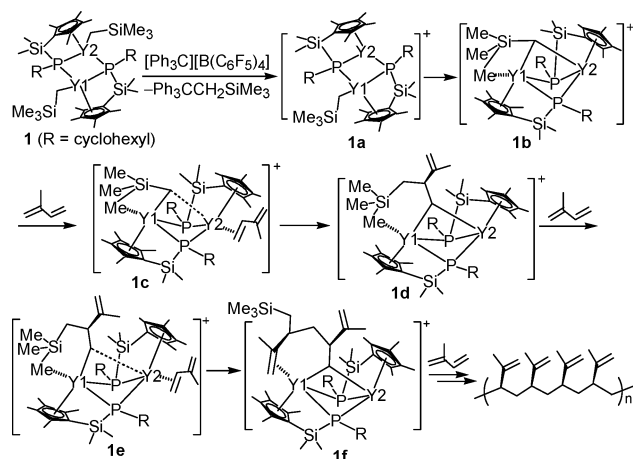


Table 1. Polymerization of Isoprene under Various Conditions^a

run	cat.	<i>T_p</i> (°C)	<i>t</i> (h)	yield (%)	<i>M_n^b</i> (×10 ⁵)	<i>M_w/M_n^b</i>	microstructure (%) ^c			<i>T_g/T_m^d</i> (°C)
							3,4	<i>mm</i>	<i>mmmm</i>	
1	1	25	2	0						
2	A	25	2	80	0.3	7.9	<5 ^e			n.d. ^f
3	B	25	2	0						
4	C	25	2	0						
5	1+A	25	2	92	1.0	1.8	99	80	30	42/–
6	1+A	–10	16	41	4.3; 0.3	1.6; 1.4	100	96	80	28/148
7	1+A	–20	48	50	3.2; 0.3	1.7; 1.4	100	100	>99	30/154
8	1+A	25	2	100	1.2	1.3	99	80	30	41/–
9	1+A	–10	16	60	3.7	1.6	100	96	80	31/138
10	1+A	–20	48	87	5.0	1.6	100	100	>99	33/162
11 ^g	1+A	25	2	65	0.8	1.6	99	25		38/–
12	1+B	25	2	85	1.4	1.3	99	40		n.d.
13	1+C	25	2	63	1.1	1.4	99	38		n.d.
14	2+A	25	2	17	1.3	1.6	89			n.d.
15	4+A	25	2	100	0.9	1.06	66 ^h			n.d.

^a Conditions: C₆H₅Cl, 10 mL; neutral complex, 2.5 × 10^{–5} mol; [isoprene]₀/[complex]₀ = 600, [complex]₀/[activator]₀ = 1:1, unless otherwise noted. **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhMe₂NH][B(C₆F₅)₄], **C** = B(C₆F₅)₃. In runs 5–7, isoprene was added to a mixture of **1** and **A**. In runs 8–15, an activator **A**, **B**, or **C** was added to a mixture of a neutral complex and isoprene. ^b Determined by GPC against polystyrene standard. ^c Determined by ¹H and ¹³C NMR. ^d Determined by DSC. ^e The *trans*-1,4 unit is a major component. ^f n.d. = not determined. ^g Toluene was used as a solvent. ^h The 1,4-unit: 34%.

dialkyl complex **1** or the borate compound **A** with isoprene. In the case of **1**, no reaction was observed under the similar conditions (Table 1, run 1), while the borate **A** alone caused cationic isoprene polymerization and yielded a polymer with 1,4-rich microstructures and a very broad molecular weight distribution (*M_w/M_n* = 7.9) (Table 1, run 2). When the polymerization was carried out at low temperatures by use of a combination of **1** and **A** as a catalyst, further high regio- and stereoselectivity (3,4-selectivity 100%, *mmmm* up to 99%) were achieved (Table 1, runs 6 and 7). Unfortunately, however, the GPC curves of the polymers obtained at low temperatures became bimodal. These results suggest that the cationic alkyl species generated in the reaction of **1** with **A** is unstable and could decompose or change to other species.⁹ To trap and utilize more efficiently the cationic alkyl species prior to its

Scheme 1. A Possible Polymerization Mechanism

decomposition, the polymerization reaction was then carried out by addition of the activator **A** to a mixture of the neutral dialkyl **1** and isoprene, so that the resulting cationic metal alkyl species could have a chance to react immediately with isoprene, although this might risk undesired isoprene polymerization caused by **A**. By use of this improved experimental procedure, a significant increase in catalytic activity was achieved without loss of the selectivity, and more remarkably, the bimodal problem observed above was also solved successfully (Table 1, runs 8–10 versus 5–7). No polymerization caused by **A** was observed, suggesting that the reaction of **A** (or a reaction intermediate of **A** and isoprene) with **1** to give an active cationic Y alkyl species is extremely fast and should be much faster than its reaction with isoprene. Thus, when the polymerization was carried out at $-20\text{ }^\circ\text{C}$ by addition of **A** to a mixture of **1** (1 molar equiv) and isoprene (600 equiv) in $\text{C}_6\text{H}_5\text{Cl}$, a polyisoprene polymer with almost perfect isotactic 3,4-microstructure (3,4-selectivity 100%, *mmmm* > 99%), high molecular weight ($M_n = 5 \times 10^5$), and unimodal narrow molecular weight distribution ($M_w/M_n = 1.6$) was obtained (Table 1, run 10). No evidence for other structures was observed in ^1H and ^{13}C NMR. At low temperatures, an increase in molecular weight of the resulting polymers was also observed, possibly as a result of decrease in chain transfer. The isotactic 3,4-polyisoprene obtained is a new polymer, which is crystalline, as shown by XRD, and has a melting point at $162\text{ }^\circ\text{C}$ (DSC).

Since the true active species in the present catalyst system is extremely unstable, it is very difficult to obtain experimentally a piece of information about its structure and its interaction with isoprene. A theoretical study was therefore carried out, which shed some light on the mechanistic aspects of the polymerization process. A possible mechanism based on DFT calculation is shown in Scheme 1. The reaction of the dialkyl complex **1** with an equimolar amount of **A** should yield straightforwardly the corresponding binuclear monocationic monoalkyl species, such as **1a**. A DFT calculation suggested that the remaining alkyl group, CH_2SiMe_3 , in **1a** prefers bridging the two metal centers, Y1 and Y2, via the methylene carbon and yielding simultaneously an agostic interaction with Y1 via a Me group, thus leading to **1b**.¹⁰ These new interactions make **1b** 6.90 kcal/mol more stable than **1a**. Because of the agostic interaction between Y1 and the SiMe_3 group, the coordination of an incoming isoprene molecule could occur selectively at Y2 in a 4,3-fashion to afford **1c**, which after 4,3-insertion of isoprene would afford **1d**. The newly inserted isoprene unit in **1d** could also bridge the two metal centers via its methylene end, while the agostic interaction between Y1 and the SiMe_3 group remains. Hence, the coordination and insertion of the second

isoprene molecule would follow the same way at the Y2 center. After the insertion of the second isoprene, the interaction between Y1 and the SiMe_3 group could be replaced by that between Y1 and a $\text{C}=\text{C}$ double bond in the side chain (**1f**). Therefore, the coordination and insertion of the following isoprene monomers could take place always at the Y2 metal center in the same fashion, and thus afford isotactic 3,4-polyisoprene selectively.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078224, “Reaction Control of Dynamic Complexes”) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Computational resources were provided by RIKEN Advanced Center for Computing and Communication. Dr. Tardif is gratefully acknowledged for assistance in the synthesis of **1** and **2**.

Supporting Information Available: Detailed experimental procedures, GPC, NMR, DSC, and powder XRD data of selected polymers, and computations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) The decomposition product of the initially formed cationic active species might be active for isoprene polymerization, but its lifetime at room temperature might be very short, and further decomposition to give an inactive species could take place very rapidly. At low temperatures, however, it might survive for a longer time to initiate isoprene polymerization.
- (10) Attempts to confirm the alkyl bridge by ^{13}C NMR analysis of the in situ generated cationic Y alkyl species at low temperatures was not successful because of the poor solubility and instability of the organometallic species.

JA055397R