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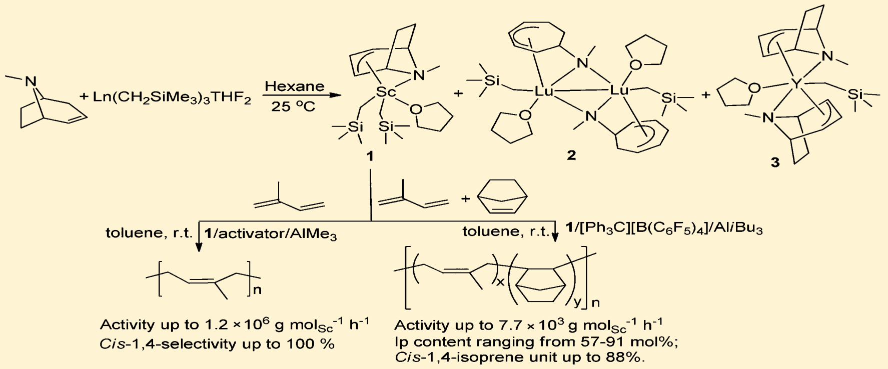
Cationic Tropidinyl Scandium Catalyst: A Perfectly Acceptable Substitute for Cationic Half-Sandwich Scandium Catalysts in *cis*-1,4-Polymerization of Isoprene and Copolymerization with Norbornene

Siqian Liu,[†] Gaixia Du,[†] Jianyun He,[†] Yingyun Long,[‡] Shaowen Zhang,*[,†] and Xiaofang Li*[,†]

[†]Key Laboratory of Cluster Science of Ministry of Education, Department of Chemistry, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing, 100081, China

[‡]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China

S *Supporting Information*



ABSTRACT: Different nonmetallocene rare earth metal alkyl complexes such as monotropidinyl (Trop) scandium dialkyl complex (Trop)Sc(CH_2SiMe_3)$_2$(THF) (**1**), ditropidinyl yttrium alkyl complex (Trop)$_2$Y(CH_2SiMe_3)(THF) (**3**) as well as binuclear lutetium alkyl complex bearing one tetradentate dianionic 6-*N*-methyl-1,4-cycloheptadienyl (NMCH) ligand [(NMCH)Lu(CH_2SiMe_3)(THF)]$_2$ (**2**) have been synthesized in high yields via one-pot acid−base reaction by using of the tris(trimethylsilylmethyl) rare earth metal complexes with the readily available natural product tropidine. The polymerization experiments indicate that the monotropidinyl scandium dialkyl complex **1** displays reactivity akin to that of the analogous monocyclopentadienyl scandium dialkyl complexes. In the presence of activator and a small amount of $AlMe_3$, complex **1** exhibits similar activities (up to 1.6×10^6 g $\mathrm{mol_{Sc}^{-1}\,h^{-1}}$) but higher *cis*-1,4-selectivities (up to 100%) than (C_5H_5)Sc(CH_2SiMe_3)$_2$(THF) (*cis*-1,4-selectivity as 95%) in the isoprene polymerization, yielding the pure *cis*-1,4-PIPs with moderate molecular weights (M_n = 0.5−11.2 × 10^4 g/mol) and bimodal molecular weight distributions (M_w/M_n = 1.48−6.07). Moreover, the complex **1**/[Ph_3C][B(C_6F_5)$_4$]/Al^iBu_3 ternary system also shows good comonomer incorporation ability in the copolymerization of isoprene and norbornene similar to the [C_5Me_4($SiMe_3$)]Sc(η^3-CH_2CHCH_2)$_2$/activator binary system, affording the random isoprene/norbornene copolymers with a wide range of isoprene contents around 57−91 mol % containing *cis*-1,4 configuration up to 88%.

INTRODUCTION

The development of high efficient and high regio-/stereo-selective homogeneous catalyst is a central theme in the field of metal catalyzed olefin polymerization.[1] *cis*-1,4-Polyisoprene (CPIP) is a major component of natural rubber and has drawn much attention from both academic and industrial researchers because of the limited supply of natural rubber and the increasing demands for synthetic rubber. So far, a large number of catalysts have been reported for the *cis*-1,4-polymerization of isoprene.[2] However, few cases of these catalysts display both high activity (>10^5 g CPIP $\mathrm{mol_{cat.}^{-1}\,h^{-1}}$) and high *cis*-1,4-selectivity (>99%).[2] Moreover, the development of high-quality elastomers via copolymerization of isoprene has grown in importance in consideration of the increasing demands for various high-performance synthetic rubber.[3] Nevertheless, the copolymerization of conjugated diene with monoolefin is usually rather difficult since these two classes of monomers show very different reactivity characteristics for a given catalyst.[4,5] To our knowledge, catalysts suitable for the incorporation of a cyclic olefin monomer in a polyisoprene remain scarce.[6] Yasuda and co-workers described the random copolymerization of isoprene with norbornene by a nickel-based catalyst, which yielded norbornene-rich (62−95 mol %) isoprene/norbornene copolymer with predominant

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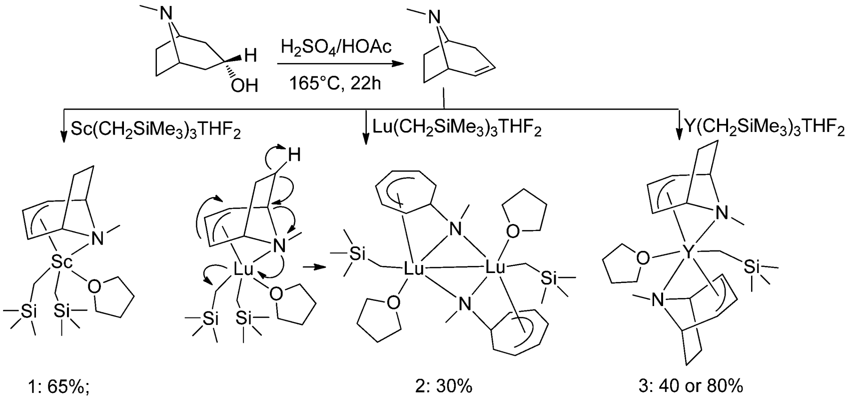
Scheme 1. Synthesis of Rare Earth Metal Alkyl Complexes 1−3 Derived from Tropidine



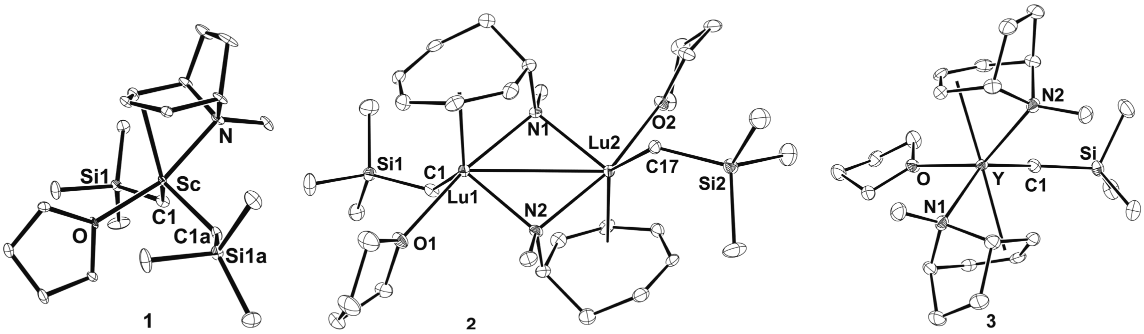


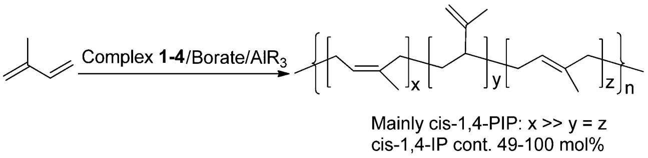
Figure 1. ORTEP drawings of **1**−**3** with 30% thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): (**1**) Sc−C(1) 2.264(5), Sc−N 2.263(5), Sc−O 2.200(4), Sc−allyl$_{Ct}$ 2.285, O−Sc−N 161.8(2), allyl$_{Ct}$−Sc−C1 123.5, Sc−C(1)−Si(1) 125.8(3), ∠allyl−THF 81.46; (**2**) Lu(1)−C(1) 2.351(5), Lu(1)−N(1) 2.312(4), Lu(1)−N(2) 2.310(4), Lu(1)−O(1) 2.377(3), Lu(1)−Cp$_{Ct1}$ 2.339, Lu(2)−C(17) 2.379(5), Lu(2)−N(2) 2.330(4), Lu(2)−N(1) 2.345(4), Lu(2)−O(2) 2.347(3), Lu(2)-Cp$_{Ct2}$ 2.522, N(1)−Lu(1)−O(1) 167.3(1), Cp$_{Ct1}$-Lu(1)−C(1) 120.2, Lu(1)−C(1)−Si(1) 127.7(3), N(2)−Lu(2)−O(2) 167.8(1), Cp$_{Ct2}$−Lu(2)−C(17) 113.1, Lu(2)−C(17)−Si(2) 131.3(3), ∠Cp(1)−THF(1) 64.10, ∠Cp(2)−THF(2) 58.56; (**3**) Y−C(1) 2.475(4), Y−N(1) 2.519(3), Y−N(2) 2.431(3), Y−O 2.406 (2), Y−allyl$_{Ct1}$ 2.480, Y−allyl$_{Ct2}$ 2.476, O−Y−N(1) 95.83(9), O−Y−N(2) 140.55(9), allyl$_{Ct1}$−Y−C(1) 89.1, allyl$_{Ct2}$−Y−C(1) 110.5, allyl$_{Ct1}$−Y−allyl$_{Ct2}$ 156.6, Y−C(1)−Si(1) 133.7(2), ∠allyl(1)1−THF 51.70, ∠allyl(2)−THF 21.90.

1,4-isoprene microstructure.[6a] Very recently, Hou and coworkers reported the incorporation of norbornene (33−88 mol %) into 3,4-rich polyisoprene (3,4-selectivity up to 70%) by a $[C_5Me_4(SiMe_3)]Sc(\eta^3\text{-}CH_2CHCH_2)_2$/activator binary system.[6b] To date, the *cis*-1,4-selective copolymerization of isoprene with norbornene has not been reported previously, as far as we are aware. The search for more efficient and selective catalyst for the regio-/stereoselective polymerization of isoprene and copolymerization with norbornene is therefore of significant importance and interest.

Recently, cationic rare earth metal alkyl catalyst has attracted considerable attention as a potentially novel olefin polymerization catalyst.[7] Among these catalysts, cationic half-sandwich scandium alkyl catalysts ($[R'ScR(THF)_n]^+$; R′ = Cp, Ind, Flu; n = 0, 1) generated by the half-sandwich scandium dialkyl complex bearing one cyclopentadienyl (Cp) ligand or one cyclopentadienyl derivative such as indenyl (Ind) or fluorenyl (Flu) ligand ($R'ScR_2(THF)_n$; R′ = Cp, Ind, Flu; n = 0, 1) are unique because they not only exhibit extremely high activity and regio-/stereoselectivity in olefin polymerization but also demonstrate extensive ability to incorporate comonomer in copolymerization of various olefins.[8,9] Even though many nonmetallocene cationic rare earth metal alkyl catalysts have been reported before and after and show high regio-/stereoselectivities in olefin homopolymerization,[10] few of them could promote the copolymerization of olefins. Therefore, the exploration of nonmetallocene ligands that are isoelectronic with cyclopentadienyl ligand but might confer copolymerization capability on the derived metal complexes still remains a challenge.

The anionic bicyclic tropidinyl ligand, easily derived from the natural product tropidine, usually coordinates with metal center through the bridging nitrogen atom as well as the three allylic carbon atoms with $2\sigma/4\pi$-electron donor sites and thus is regarded as an analogue to the cyclopentadienyl ligand.[11] Since the first tropidinyl titanium complex was reported by Bergman in 1997,[12] some tropidinyl complexes based on Zr, Mn, and Ru had been subsequently synthesized.[13] Activated by MAO, most of these complexes showed high activities in the ethylene polymerization.[13] In comparison, such tropidinyl complex based on rare earth metal has not been reported previously. Its catalytic potential for the olefin polymerization has remained unexplored to date. Herein, we report the synthesis and structural characterization of nonmetallocene rare earth metal alkyl complexes **1**−**3** derived from the tropidine. In the presence of activator and AlR_3, the tropidinyl scandium dialkyl complex **1** serves as perfectly acceptable substitute for the known half-sandwich scandium dialkyl complexes in the *cis*-1,4-polymerization of isoprene and copolymerization with norbornene.

Table 1. Isoprene Polymerization by the Cationic Rare Earth Metal Alkyl Species Generated by Complexes 1−4[a]



										structures[d]					
entry	cat.	A[b]	AlR_3	[Al/Ln]	[IP/Ln]	*t*/h	*T*/°C	*Y*/%	*A*[c]	C-1,4	T-1,4	3,4	M_n[e]/10^3	M_w/M_n[e]	T_g[f]/°C
1	**1**	A	–	–	200	6	25	38	0.9	58	26	17	112	2.50	−55
2	**1**	A	Al^iBu_3	2	200	6	25	100	2.3	85	0	15	7	1.48	−53
3	**1**	B	Al^iBu_3	2	200	6	25	62	1.4	85	0	15	6	3.63	–
4	**1**	C	Al^iBu_3	2	200	9	25	14	0.2	88	0	12	49	3.79	−59
5	**1**	A	$AlMe_3$	2	200	0.3	25	100	40.8	99	0	1	9	4.06	−61
6	**1**	A	$AlMe_3$	5	200	0.3	25	100	40.8	99	0	1	10	4.13	−61
7	**1**	A	$AlMe_3$	15	200	0.3	25	100	40.8	99	0	1	9	5.55	−61
8	**1**	B	$AlMe_3$	2	200	0.5	25	70	19.1	93	0	7	6	5.58	−61
9	**1**	C	$AlMe_3$	2	200	24	25	12	0.1	78	19	3	13	4.62	−62
10	**1**	A	$AlMe_3$	2	600	0.3	25	100	122.4	99	0	1	10	6.07	−59
11	**1**	A	$AlMe_3$	2	1200	0.3	25	100	244.8	99	0	1	11	5.04	−56
12	**1**	A	$AlMe_3$	2	2400	0.3	25	100	189.6	99	0	1	9	6.03	−58
13	**1**	A	$AlMe_3$	2	3600	0.3	25	89	870.5	99	0	1	11	5.41	−58
14	**1**	A	$AlMe_3$	2	4800	0.3	25	80	1568.7	98	0	2	15	4.96	−57
15	**1**	A	$AlMe_3$	2	200	24	−30	100	0.6	100	0	<1	13	5.24	−64
16	**1**	A	$AlMe_3$	2	200	24	−15	100	0.6	>99	0	<1	12	5.96	−63
17	**1**	A	$AlMe_3$	2	200	24	0	100	0.6	>99	0	<1	12	3.65	−62
18	**1**	A	$AlMe_3$	2	200	0.2	50	100	68.4	98	0	2	8	5.09	−61
19	**1**	A	$AlMe_3$	2	200	0.08	70	100	119.0	96	0	4	7	4.72	−61
20	**1**	A	$AlMe_3$	2	200	0.03	90	100	408.0	92	0	7	6	3.65	−61
21	**3**	A	–	–	200	3	25	–	–	–	–	–	–	–	–
22	**3**	A	Al^iBu_3	2	200	3	25	100	4.5	75	0	25	36	2.91	−47
23	**3**	B	Al^iBu_3	2	200	3	25	100	4.5	77	0	23	34	2.78	−50
24	**3**	C	Al^iBu_3	2	200	8	25	13	0.2	93	0	7	5	2.89	−60
25	**3**	A	$AlMe_3$	2	200	3	25	100	4.5	51	39	10	10	4.94	−59
26	**3**	B	$AlMe_3$	2	200	3	25	100	4.5	49	38	13	18	4.69	−55
27	**3**	C	$AlMe_3$	2	200	72	25	–	–	–	–	–	–	–	–
28	**4**[g]	A	–	–	600	0.08	25	100	489.6	95	0	5	120	2.39	−57

[a] Conditions: 25 μmol of Ln complex, 25 μmol of activator, and 5 mL of toluene. [b] Activator: A = $[Ph_3C][B(C_6F_5)_4]$, B = $[PhNHMe_2][B(C_6F_5)_4]$, and C = $B(C_6F_5)_3$. [c] Activity: kg of PIP mol_{Sc}^{-1} h^{-1}. [d] Determined by ^1H, ^{13}C NMR spectra. [e] Determined by GPC in THF at 40 °C against polystyrene standard. [f] Measured by DSC. [g] $(C_5H_5)Sc(CH_2SiMe_3)_2(THF)$ as catalyst precursor.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes 1−3. Tropidine could be readily prepared by dehydration of tropine under strongly acidic conditions according the literature (Scheme 1).[11a] The acid−base reactions between rare earth metal trialkyl complexes $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Lu, and Y) and tropidine in hexane at 25 °C afforded rare earth metal alkyl complexes **1**−**3** with different structures depending on ionic radius of metal center (Scheme 1, Figure 1). If the smallest scandium cation was used as metal center, the monotropidinyl (Trop) scandium dialkyl complex $(Trop)Sc(CH_2SiMe_3)_2(THF)$ (**1**) was obtained ca. 65% yield. With the further increasing ionic radius of metal center, such monotropidinyl lutetium dialkyl complex was unstable. Instead, a relatively more stable binuclear lutetium alkyl complex bearing one tetradentate dianionic 6-*N*-methyl-1,4-cycloheptadienyl (NMCH) ligand $[(NMCH)Lu(CH_2SiMe_3)(THF)]_2$ (**2**, yield: 30%) was finally obtained probably through the alkyl departure of one trimethylsilylmethyl group in the dialkyl complex from metal which resulted in opening this tropidinyl ring and generating an nitrogen anion. Such ring-opening reaction is first observed in the organometallic complex bearing the same tropidinyl ligand. For the largest yttrium cation, the ditropidinyl yttrium alkyl complex $(Trop)_2Y(CH_2SiMe_3)(THF)$ (**3**, yield: 40 or 80%) was prepared either 1 equiv or 2 equiv of $Y(CH_2SiMe_3)_3(THF)_2$ was added in the reaction.

Complexes **1** and **3** were soluble in common organic solvents such as THF, toluene, and hexane, and gave well resolved NMR spectra in C_6D_6. ^1H NMR spectra of the tropidinyl complexes **1** and **3** showed two multipeaks for the central and terminal allylic protons between 3.84−5.64 ppm, clearly indicating the presence of the allyl ligand. The signals at high field assigned for the methylene protons of the $Ln-CH_2SiMe_3$ groups were found for **1** at −0.11 ppm (s, 4H) and for **3** at −0.57 ppm (s, 2H), respectively. Furthermore, only one singlet for the methylene protons of the Ln-alkyl groups indicates that the two alkyls in the complex **1** is fluxional in the solution state, which can be rotation freely similar to the non or less substituted monocyclopentadienyl scandium dialkyl complex $(C_5H_{5-n}R_n)Sc(CH_2SiMe_3)_2(THF)$ (n = 1−2).[5b] Unlike the half-sandwich scandium dialkyl complexes $(C_5H_{5-n}R_n)Sc(CH_2SiMe_3)_2(THF)$ (n = 1−5) only with one THF,[5b,7c] two

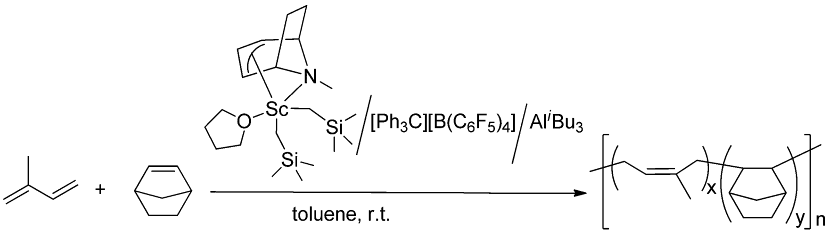
THF molecules which showed signals around 1.22 and 3.55 ppm were found in the ^{1}H NMR spectra of these two complexes, implying the smaller steric hindrance of the tropidinyl ligand than that of the cyclopentadienyl ligand.

Single crystals of complexes **1**−**3** suitable for an X-ray determination were grown from a concentrated hexane solution at −30 °C. The ORTEP diagrams and selected bond lengths and angles of these complexes are shown in Figure 1. Unlike all of the half-sandwich rare earth metal dialkyl complexes only containing one cyclopentadienyl ligand, X-ray diffraction studies reveal that the tropidinyl rare earth metal alkyl complexes **1** and **3** have completely different structures similar to group 4 tropidinyl complexes (Figure 1 and Supporting Information). Like (Trop)$TiCl_3$, the small scandium complex **1** consists of one tropidinyl ligand, two trimethylsilylmethyl groups, and one THF molecule. The tropidinyl ligand binds to the metal center via a dative bond through the nitrogen atom and a covalent bond through the anionic allyl moiety. The *N*-methyl bond in the tropidinyl ligand bisects the $Me_3SiH_2C{-}Sc{-}CH_2SiMe_3$ plane and points to the same direction as the vector from the central scandium to the THF molecule in **1**, which was also seen in the structure of (Trop)$TiCl_3$.[12,13] By comparison, the large yttrium center forces two tropidinyl ligands with different orientation respect to one methylsilylmethyl ligand to lie closer to the metal center relative to **1**, resulting in a higher isomerization barrier as zirconium ditropidinyl complex $(Trop)_2ZrCl_2$.[12,13] For the moderate lutetium center, the monotropidinyl dialkyl complex is not stable, however, there is not enough space around the metal center to form the ditropidinyl alkyl complex. Finally, a binuclear lutetium complex **2** is obtained in which each of the metal centers is bonded with one tetradentate dianionic 6-*N*-methyl-1,4-cycloheptadienyl unit with $2\sigma/6\pi$-electron donor containing cyclopentadienyl segment, one trimethylsilylmethyl group, and one THF molecule. Because of the ionic radius of the metal center in a trend of Sc (0.89 Å) < Lu (1.00 Å)) < Y (1.04 Å), the bond distances of the chelating Ln−N(1), Ln−N(2), and Ln−O(1) as well as Ln−C(1) bond increase in order of **1** < **2** < **3**. The Ln−allyl/Cp_{Ct} bond distances also increase in order of **1** < **2** < **3**, which are somewhat longer than those reported for the corresponding half-sandwich rare earth metal dialkyl complexes.[5b,7c] The geometry of the N−Sc−O (161.8(2)°), N−Lu−O (average 167.5(1)°), and $allyl_{Ct1}$−Y−$allyl_{Ct2}$ (156.6°) is nearly linear. The Ln−C(1) −Si(1) angle is 125.8(3)° in **1**, 127.7(3)° in **2**, and 133.7(2)° in **3**. The allyl/Cp_{Ct}−Ln−C(1) angle in the complexes decreases from **1** (123.5°), **2** (120.2, 113.1°) to **3** (89.1, 110.5°). Among **1**−**3**, differences in the orientation of the THF and CH_2SiMe_3 ligands were observed, possibly as a result of the ionic radius influence of the metal center. In **1** and **2**, the THF ring plane is oriented almost vertically toward the Trop ring plane (angle as 81.46 for **1**, 64.10, 58.56 for **2**, respectively), and the CH_2SiMe_3 groups adopts a pallel supine configuration, which was also observed in the structure of the nonsubstituted or less substituted cyclopentadienyl scandium complex $(C_5H_{5\text{-}n}R_n)Sc(CH_2SiMe_3)_2(THF)$ ($n = 1{-}2$).[5b,7c] When the steric hindrance around the metal center becomes bigger due to the existence of the two tropidinyl ligands in **3**, the orientations of the THF ligand (angle as 51.70° for Trop 1 and 21.9° for Trop 2, respectively) and the CH_2SiMe_3 group are changed to nearly parallel to the tropidinyl ring similar to the more substituted cyclopentadienyl scandium alkyl complexes $(C_5H_{5\text{-}n}R_n)Sc(CH_2SiMe_3)_2(THF)$ ($n = 4{-}5$).[5b,7c] These results clearly indicate that the steric hindrance of the tropidinyl ligand is smaller than that of the cyclopentadienyl ligand.

cis-1,4-Polymerization of Isoprene by Cationic Rare Earth Metal Species Generated by Complexes 1 and 3.

The cationic tropidinyl rare earth metal species in situ generated by the complex **1** or **3**, 1 equiv of activator, with or without excess of AlR_3 were active for the polymerization of isoprene, with the activity and selectivity being significantly dependent on the ionic radius and the steric hindrance around the metal center to yield the homopolyisoprene materials with different microstructures and compositions. Some representative results are summarized in Table 1. The neutral complexes **1**−**3** alone were inactive, suggesting that the generation of a cationic metal alkyl species is essential for the present polymerization. Activated by $[Ph_3C][B(C_6F_5)_4]$, the complex **1** showed low activity (0.9×10^3 g mol_{Sc}^{-1} h^{-1}) and regio-/stereoselectivity (1,4-selectivity = 83%, *cis*-1,4-selectivity = 58%) in the isoprene polymerization, producing polyisoprene with a mixture of 1,4-*cis*/*trans*- and 3,4 microstructures (Table 1, entry 1). In contrast, the combination of **1**, activator (such as $[Ph_3C][B(C_6F_5)_4]$ (**A**), $[PhNHMe_2][B(C_6F_5)_4]$ (**B**), and $B(C_6F_5)_3$ (**C**)) and Al^iBu_3 exhibited moderate activities (up to 2.3×10^3 g mol_{Sc}^{-1} h^{-1}) and high *cis*-1,4-selectivities for the isoprene polymerization to prepare polyisoprenes with main *cis*-1,4-microstructures (*cis*-1,4-selectivity >85%) (Table 1, entries 2−4). It is noteworthy that the high activity (up to 4.1×10^4 g mol_{Sc}^{-1} h^{-1}) and almost complete *cis*-1,4-selectivity (>99%) were observed in the isoprene polymerization catalyzed by the complex **1**/activator/$AlMe_3$ ternary systems (Table 1, entries 5−9). Such catalytic performance has also been obtained for the nonsubstituted $(C_5H_5)Sc(CH_2SiMe_3)_2(THF)$ (**4**)/activator binary system (*cis*-1,4-selectivity up to 95%) (Table 1, entry 28).[5b] Moreover, only 18 min was needed to completely convert 4800 equiv of monomer (activity up to 1.6×10^6 g mol_{Sc}^{-1} h^{-1}), producing moderate molecular weight CPIPs (*cis*-1,4-selectivity >99%, Mn > 10301 g mol^{-1}) with bimodal molecular weight distributions ($M_w/M_n = 4.96{-}6.07$) (Table 1, entries 10−14). If the isoprene polymerizations by the **1**/$[Ph_3C][B(C_6F_5)_4]$/$AlMe_3$ system were carried out at lower temperatures, further high *cis*-1,4-selectivities (≈ 100%) were observed as shown by the ^{1}H and ^{13}C NMR analyses (Figure 1 and See Supporting Information) (Table 1, entries 15−17). When the temperature increased from 50 to 90 °C, the activities increased from 0.7 to 4.1×10^5 g mol^{-1} h^{-1} while the *cis*-1,4-selectivities decreased from 98 mol % to 92 mol % (Table 1, entries 18−20). In contrast, the cationic yttrium species generated by the more hindered ditropidinyl complex **3** showed low activities and low *cis*-1,4-selectivites under the similar conditions (Table 1, entries 21−28). The yttrium complex **3**/activator/Al^iBu_3 ternary systems displayed similar activities to the complex **3**/activator/$AlMe_3$ ternary systems (ca. 4.5×10^3 g mol_Y^{-1} h^{-1}) (Table 1, entries 21−27). However, the structures of the resulting PIPs by these two systems are very different. Similar to the **1**/activator/Al^iBu_3 ternary system, the **3**/activator/Al^iBu_3 ternary system also gave the *cis*-1,4-rich polyisoprenes (*cis*-1,4-selectivity = 75−93%) (Table 1, entries 22−24). By comparison, the catalytic performance of the **3**/activator/$AlMe_3$ ternary system is very different from the **1**/activator/$AlMe_3$ ternary system (Table 1, entries 25−27). The resulting polyisoprenes had mixed 1,4-*cis*/*trans*- and 3,4 microstructures similar to that obtained by the **1**/activator binary system (Table1, entry 1). As an activator, the trityl and anilinium borate activators **A** and **B** exhibited similar influences

Table 2. Copolymerization of Isoprene and Norbornene by Complex 1/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ Ternary System[a]



								IP structure[c]					
entry	cat.	IP/mmol	NB/mmol	[IP/NB]	*t*/h	A[b]	IP cont[c]/mol %	C-1,4	T-1,4	3,4	M_n[d]/10^3	M_w/M_n[d]	T_g[e]/°C
1	**1**	–	2.5	–	2	0.1	–	–	–	–	–	–	–
2	**1**	5	2.5	2/1	2	6.7	91	83	0	17	12	2.91	−50
3	**1**	5	5	1/1	2	7.7	85	85	0	15	4	2.29	−48
4	**1**	5	10	1/2	2	7.1	84	85	0	15	12	2.45	−44
5	**1**	5	15	1/3	2	7.4	83	87	0	13	4	4.20	−48
6	**1**	5	25	1/5	3	2.4	74	88	0	12	3	3.61	–
7	**1**	5	50	1/10	3	3.7	64	87	0	13	4	3.51	–
8	**1**	5	75	1/15	3	4.4	65	87	0	13	4	3.37	–
9	**1**	5	100	1/20	3	1.9	57	87	0	13	4	1.77	–
10[f]	**5**	5	5	1/1	0.25	48	86	15	15	70	15	1.29	9
11[f]	**5**	5	50	1/10	0.25	5.6	33	14	15	71	9	1.59	66

[a]Conditions: 21 μmol of Sc, 21 μmol of activator, 42 μmol of Al^iBu_3, 25 mL of toluene, 25 °C. [b]kg of copolymer mol_{Sc}^{-1} h^{-1}. [c]Determined by ^1H and ^{13}C NMR. [d]Determined by high temperature GPC in 1,2,4-trichlorobenzene at 140 °C. [e]Measured by DSC. [f]$[C_5Me_4(SiMe_3)]Sc(\eta^3\text{-}CH_2CHCH_2)_2$ as catalyst precursor.

on the polymerization activity, while the neutral borane compound **C** showed lower activity (Table 1, entries 2–4, 7–9, and 22–27).

The resulting poly(isoprene)s all showed good solubility in THF and $CHCl_3$. The ^1H NMR spectra of the PIPs obtained by the complex **1**/activator/$AlMe_3$ system in $CDCl_3$ indicated almost complete 1,4-microstructures and the ^{13}C NMR spectra showed diagnostic signals for a pure *cis*-1,4 configuration (δ = 23.4, 26.4, 32.2, 125.0, and 135.2 ppm) (*cis*-1,4-PIP selectivity >99%) (see Supporting Information). GPC curves revealed that these PIPs had moderate molecular weights in the range of 5000–112000 g/mol and the bimodal molecular weight distributions (M_w/M_n = 1.48–6.07), suggesting that more than one active species may be generated in the complex **1**/activator/$AlMe_3$ system. Moreover, the molecular weights of the PIPs generated from **1**/activator/$AlMe_3$ ternary system were much lower than those observed for the $(C_5H_5)Sc(CH_2SiMe_3)_2(THF)$ (**4**)/activator binary system, indicating that chain transfer was more facile for the Trop-bearing complex. Glass transition temperature in the range of −47 to −64 °C were observed in the curves of the resulting *cis*-1,4-rich PIPs characterized by differential scanning calorimetry (DSC). These results indicate that at least to some degree the tropidinyl ligand enhances the regio-/stereoselectivity of the scandium metal centers in the isoprene polymerization relative to the half-sandwich scandium dialkyl precursors.

Copolymerization of Isoprene and Norbornene by Complex 1/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ Ternary System. To compare the copolymerization behavior of the tropidinyl scandium catalyst relative to the half-sandwich scandium catalysts, the copolymerizations of isoprene with norbornene were carried out by feeding varying amounts of norbornene under a certain amount of isoprene (5 mmol) in toluene at 25 °C in the presence of the tropidinyl scandium dialkyl complex **1**, $[Ph_3C][B(C_6F_5)_4]$, and Al^iBu_3, affording isoprene/norbornene random copolymers with isoprene content ranging from 57 to 91 mol % adopting *cis*-1,4-configuration up to 88%. These copolymerization experimental results implied that replacement of the cyclopentadienyl ligand with a tropidinyl ligand results in the formation of a completely different regio-/stereoselective catalyst system. Representative results are shown in Table 2.

In the absence of isoprene, the complex **1**/**A**/Al^iBu_3 ternary catalytic system only afforded trace amount of polynorbornene (Table 2, entry 1). In the copolymerization of isoprene and norbornene, the complex **1**/**A**/Al^iBu_3 ternary catalytic system exhibited lower activities (<7.7 × 10^3 g of copolymer mol_{Sc}^{-1} h^{-1}) than the half-sandwich scandium dialkyl complex $[C_5Me_4(SiMe_3)]Sc(\eta^3\text{-}CH_2CHCH_2)_2$ (**5**)/**A** binary catalytic system (4.8 × 10^4 g of copolymer mol_{Sc}^{-1} h^{-1}) (Table 2).[6b] However, the resulting isoprene/norbornene copolymers exhibited very different microstructures and compositions from those obtained by the **5**/**A** binary catalytic system. The ^{13}C NMR spectra showed that the isoprene units in these copolymers have main *cis*-1,4-configuration (up to 88 mol %) whereas most of the isoprene units in those obtained by the **5**/**A** binary catalytic system adopt 3,4-configuration (See Supporting Information). Furthermore, isoprene incorporation in the present copolymerization reactions was easily controlled simply by changing the isoprene/norbornene feed ratio to give the corresponding random copolymers with a wide range of isoprene content (91–57 mol %; Table 2, entries 5–9). In contrast, other ternary systems such as the **1**/activator/$AlMe_3$, the **3**/activator/$AlMe_3$ or Al^iBu_3 could not promote whether the norbornene polymerization or the copolymerization of isoprene with norbornene. This is the first nonmetallocene rare earth metal catalyst which could promote the copolymerization of olefin, as far as we are aware. These results also testify the cationic tropidinyl scandium catalyst showed similar or better performances than the cationic cyclopentadienyl scandium catalyst in the *cis*-1,4-polymerization of isoprene and copolymerization with norbornene process.

Quantum Chemistry Calculation. We performed quantum chemistry calculation on the structures and molecular orbitals for the tropidinyl, 6-*N*-methyl-1,4-cycloheptadienyl, and cylcopentadienyl ligands. The optimized geometries of these ligands are close to those in the crystal structures, indicating the quantum chemistry calculation is reasonable for these ligands. Since the symmetry and energy of the highest occupied molecular orbital (HOMO) of each molecule plays an important role in chemical reactions, we showed the energy and illustration of the HOMOs of these ligands (see Supporting Information). It is clear that the HOMOs of the cyclopentadienyl ligand are 2-fold degenerate bonding orbitals with the lowest energy level of −1.078 eV among the three, which ensure the cyclopentadienyl ligand to form strong coordination bond with the rare earth metal cation. In contrast, the HOMOs of the 6-*N*-methyl-1,4-cycloheptadienyl ligand and tropidinyl are both nonbonding orbitals with the higher energy levels of −0.324 and 0.338 eV, respectively, implying that the coordination bonds between these ligands and the rare earth metal cation are weaker than the Cp−M bond. Moreover, the high energy HOMO is easier to be oxidized, which makes the tropidinyl and 6-*N*-methyl-1,4-cycloheptadienyl ligands less stable than the cyclopentadienyl ligand. These observations partly explain the different structures and catalytic performances in olefin polymerization between the tropidinyl rare earth metal complexes and the known half-sandwich scandium dialkyl complexes.

CONCLUSIONS

In summary, a series of nonmetallocene rare earth metal alkyl complexes **1**−**3** with the completely different structures have been easily synthesized in high yields via one-pot acid−base reaction by using of the tris(trimethylsilylmethyl) rare earth metal complexes with the readily available natural product tropidine. Polymerization results indicate that the cationic tropidinyl scandium catalyst is a suitable substitute for the known cationic half-sandwich scandium catalyst in the *cis*-1,4-polymerization of isoprene and copolymerization with norbornene. The tropidinyl scandium dialkyl complex **1**/activator/AlMe$_3$ ternary systems exhibit high activity and almost complete *cis*-1,4-selectivity better than the (C$_5$H$_5$)Sc(CH$_2$SiMe$_3$)$_2$(THF)/activator binary system in the isoprene polymerization, affording the moderate molecular weight CPIP with bimodal molecular weight distribution. Moreover, in comparison with the [C$_5$Me$_4$(SiMe$_3$)]Sc(η^3-CH$_2$CHCH$_2$)$_2$/activator binary system, the complex **1**/activator/Al^{i}Bu$_3$ could also promote the regio-/stereoselective copolymerization of isoprene with norbornene to produce the novel isoprene/norbornene copolymers with isoprene content ranging from 91 to 57 mol % adopting *cis*-1,4-configuration up to 88% under the similar conditions. These quantum chemistry calculation results demonstrated that the coordination bonds between the tropidinyl ligands and the scandium cation was weaker than the Cp−Sc bond, which resulted in the less hindered metal center in the tropidinyl scandium dialkyl catalyst than that in the half-sandwich scandium dialkyl complex. Further studies will be required to add substituents to the tropidinyl ligand to investigate and improve the selectivity and/or activity of this catalyst system.

ASSOCIATED CONTENT

Supporting Information

Experimental procedure and figures showing XRD, GPC, DSC, and NMR (^{1}H and ^{13}C) spectra of representative polymer products, tables of crystallographic data, and .cif files and PLATON reports. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*(X.L.) E-mail: xfli@bit.edu.cn.
*(S.Z.) E-mail: swzhang@bit.edu.cn.

Notes

The authors declare no competing financial interest.

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