Dalton
Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 2367

www.rsc.org/dalton

PAPER

Rare-earth metal bis(alkyl)s that bear a 2-pyridinemethanamine ligand: Dual catalysis of the polymerizations of both isoprene and ethylene†

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Received 6th October 2011, Accepted 14th November 2011
DOI: 10.1039/c1dt11890k

New pyridinemethanamido-ligated rare-earth metal bis(alkyl) complexes $[C_5H_4N\text{-}CH(Me)\text{-}NC_6H_3(^iPr)_2]Ln(CH_2SiMe_3)_2(THF)$ (Ln = Sc (**1**), Y (**2**), Lu (**3**)) have been prepared at 0 °C *via* a protonolysis reaction between rare-earth metal tris(alkyl)s and the corresponding 2-pyridinemethanamine ligand and fully characterized by NMR and X-ray diffraction analysis. Bis(alkyl) complexes **1–3** are analogous monomers of THF solvate, where the ligand bonds to the metal center in a $\kappa N{:}\kappa N$-bidentate mode. Complexes **1–3**, in combination with $[Ph_3C][B(C_6F_5)_4]$, showed a good activity towards isoprene polymerization to give polyisoprene with a main 3,4-selectivity (60%–66%); in particular the yttrium catalyst system, **2**/$[Ph_3C][B(C_6F_5)_4]$, displayed a living mode. By contrast, only the precatalyst **2** exhibited activity for isoprene polymerization in the presence of $[PhNMe_2H][B(C_6F_5)_4]$. The influence of alkylaluminium (AlR_3, R = Me, Et, ^iBu) and the metal center on the polymerization of isoprene was also studied, and it was found that addition of $AlMe_3$ to the catalyst systems could lead to a dramatic change in the microstructure of the polymer from 3,4-specific to 1,4-selective (89%–95%), but the ionic radius of the central metal had little influence on the selectivity. In addition, by using the **1**(Sc)/$[Ph_3C][B(C_6F_5)_4]$/10 Al^iBu_3, the polymerization of ethylene was also achieved with moderate activity (up to 3.2×10^5 g (PE) mol_{Sc}^{-1} h^{-1} bar^{-1}) and narrow polydispersity (M_w/M_n = 1.19–1.28); while the effect of temperature on the activity was discussed. Such dual catalysis for the polymerizations of both isoprene and ethylene is rare.

Introduction

One of the ongoing topics in macromolecular chemistry is to prepare polymers with designated properties through precisely controlling the microstructures of polymer chains. Thus, the polymerization of isoprene (a simple and cheap C5 monomer) has been one of the most important processes, which can generate *cis*-1,4, *trans*-1,4 or 3,4 regulated polyisoprene (PIP) to meet various applications.[1] To date a variety of catalyst systems have been reported for the polymerization of isoprene, among which those catalysts based on rare-earth metals have attracted special attention because of their high activity and selectivity.[2] For instance, *cis*-1,4-PIP, which is a major component of natural rubber and can act as one of the most important elastomers used for tires and other elastic materials, has been extensively reported by using Ziegler–Natta catalyst systems or cationic rare-earth metal catalytic systems;[3] while *trans*-1,4-PIP, which is produced naturally as gutta-percha and has been applied in the fabrication of golf ball and insulating materials,[4] can be synthesized by using some rare-earth catalyst systems, such as $[(C_5Me_5)Ln(AlMe_4)_2]$/organoborate, $Cp^*Ln(BH_4)_2(THF)_n/Mg(^nBu)_2$, and $Ln(allyl)_2Cl(MgCl_2)_2/AlR_3$.[5] Compared with the extensive number of reports on the 1,4-polymerization of isoprene, 3,4-selective polymerization of isoprene by rare-earth catalysts is less well explored,[6] especially in a living fashion,[6b,c,g] although 3,4-regulated PIP is an important component of high-performance rubbers such as those with wet-skid resistance or low-rolling resistance tread.[7]

On the other hand, polyethylene (PE), which is the largest volume synthetic polymer applied in every aspect of our daily lives, such as packaging materials, pipes, textiles, *etc*, has been extensively studied in both academic and industrial fields. Nevertheless, in contrast to the rare-earth catalyst systems for the polymerization of isoprene, catalyst systems for ethylene polymerization are mostly focused on transition metals or late-transition metals,[8] those based on rare-earth metals are less well explored.[9] So far, some Cp-based (or its derivatives) rare-earth metal complexes have exhibited excellent activities for the polymerization of ethylene;[10] while these non-Cp ligated rare-earth metal complexes, especially the N-type amino and imino ligand stabilized complexes, have also been reported to initiate the polymerization of ethylene with

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† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR of complexes **1–3**. CCDC reference number 837822. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11890k

medium to high activities (10^4–10^6 g (PE) mol^{-1} h^{-1} bar^{-1}).[11] However, despite the development of those rare-earth catalysts for the polymerization of either isoprene or ethylene, one catalyst, which is able to concurrently promote the polymerization of both isoprene and ethylene, still remains scarce and challenging,[10d,e,11j,k] because these two monomers show completely different reactivity for a given catalyst, and in some cases conjugated dienes can act as poisons for the catalysts designed for ethylene polymerization.[12] Carpentier[10d] and Maron[11k] reported an allyl *ansa*-neodymocene catalyst and a borohydrido half-lanthanidocene complex for the both polymerizations of *trans*-1,4 selective isoprene and ethylene, respectively; while Hou[10e] also presented Cp-based scandium bis(alkyl)s for the polymerizations of both living 3,4-selective isoprene and ethylene. In contrast, only one non-Cp aminopyridinate-stabilized lanthanide complex was described by Kempe for the polymerizations of both non-living 3,4-selective isoprene and ethylene.[11j] However, one non-Cp lanthanide catalyst for the polymerizations of both living 3,4-selective isoprene and ethylene has been not reported to date.

In the past two decades, there has been tremendous research progress in non-Cp lanthanide chemistry.[13] Within this development, we are always interested in the N-type donor ligands, among which the pyridinemethanamino-type N,N-bidentate ligands are important. Since the first pyridinemethanamido-ligated hafnium catalyst was explored for the chain shuttling polymerization of olefins,[14] the pyridinemethanamido-type ligands have received a lot of attention and have been developed for Ti, Zr, Hf, Pd and Ni based catalysts for olefin polymerizations due to their rich variation and potential for the control of olefin catalysis, which clearly emphasizes the general applicability of the ligand class (Chart 1).[15] However, it is well known that, in the pyridinemethanamido-ligated metal alkyl or hydrido complexes, when the 6-position of pyridine has a substituent R^3 group (such as R^3 = phenyl, 1-naphthyl), a C–H activation reaction always takes place on the R^3 group *via* alkane elimination. For example, a family of yttrium mono(alkyl) complexes has been synthesized *via* C–H activation.[16]

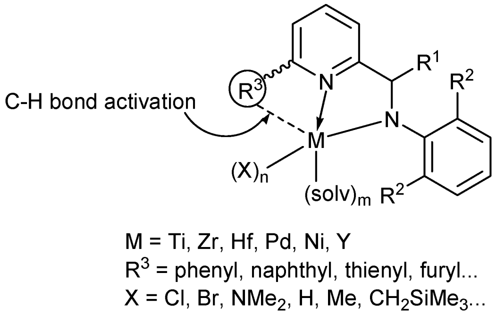


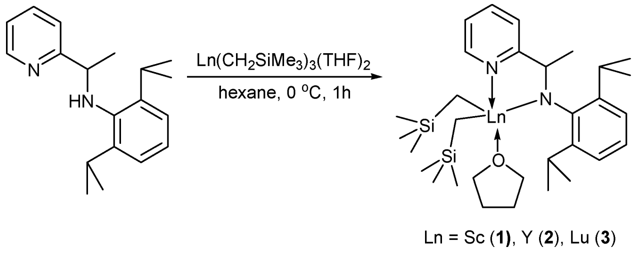
Chart 1 Related complexes based on pyridinemethanamido-type ligands.

In this contribution, on the basis of a strategy of preparing new rare-earth bis(alkyl) catalysts for the polymerizations of both isoprene and ethylene, we selected the simple and available compound 2,6-diisopropyl-*N*-(1-(pyridin-2-yl)ethyl)aniline, C_5H_4N-CH(Me)-$NHC_6H_3(^iPr)_2$, as a suitable pyridinemethanamido-type ligand. Treatment of the ligand with $Ln(CH_2SiMe_3)_3(THF)_2$ successfully yielded the desired 2-pyridinemethanamido rare-earth metal bis(alkyl) complexes *via* alkane elimination, where the C–H activation was avoided. Under the activation of different cocatalysts, all these rare-earth metal bis(alkyl) complexes displayed varied catalytic performances towards the polymerization of isoprene, while the scandium bis(alkyl)s also showed moderate activity for the polymerization of ethylene. In addition, the factors that influence the catalytic activity and the specific regularity of the resultant polymers will also be discussed.

Results and discussion

Synthesis and characterization of rare-earth metal bis(alkyl) complexes 1–3

It is well known that the preparation of rare-earth metal bis(alkyl) complexes usually encounters problems of salt addition, dimerization, ligand scrambling, and unpredictable C–H activation, due to the highly active character of the metal–carbon bonds and relatively less crowded steric environment of the molecules.[17] Treating 1 equiv. of 2-pyridinemethanamine ligand C_5H_4N-CH(Me)-$NHC_6H_3(^iPr)_2$ with rare-earth tris(alkyl)s $Ln(CH_2SiMe_3)_3(THF)_2$ at room temperature, only a mixture of both the bis(alkyl) complex and the mono(alkyl) complex was isolated. Fortunately, the acid–base reaction between $Ln(CH_2SiMe_3)_3(THF)_2$ and 1 equiv. [(C_5H_4N-CH(Me)-$NHC_6H_3(^iPr)_2$] in hexane at lower temperature, 0 °C, selectively afforded the corresponding pyridinemethanamido-ligated rare-earth bis(alkyl) complexes [C_5H_4N-CH(Me)-$NC_6H_3(^iPr)_2$]$Ln(CH_2SiMe_3)_2$(THF) (Ln = Sc (**1**), Y (**2**), Lu (**3**)) in 54%–62% yields (Scheme 1). The ^1H NMR spectra of **1–3** clearly confirmed the absence of the N-*H* proton and the presence of two alkyls; while interestingly the two methylene protons arising from the CH_2SiMe_3 alkyl groups gave completely different signals. For example, the scandium complex **1** exhibits four broad singlets at –0.30, –0.13, 0.03, 0.12 ppm for the CH_2SiMe_3 groups; in contrast, the yttrium complex **2** displays four doublets at –0.54, –0.43, –0.27, –0.21 ppm with the same coupling constant $^2J_{Y-H}$ = 12.0 Hz; while the AB spin systems at –0.73, –0.63, –0.48, –0.37 ppm ($^2J_{H-H}$ = 11.4 Hz) are observed for the diastereotopic methylene protons in the lutetium complex **3**. The existence of two alkyls was also reflected by ^{13}C NMR spectra, in which the complexes **1** and **3** give two singlets at 33.63, 35.93 ppm and at 37.36, 40.10 ppm, respectively; but the yttrium complex **2** exhibits two doublets at 31.32, 33.23 ppm (J_{Y-C} = 37.5 Hz). Furthermore, the doublet signals of the H proton on the 6-position of the pyridine ring are also found at 9.08, 9.02, 8.98 ppm, respectively, which confirm the absence of a C–H activation reaction. X-ray diffraction analysis further revealed that complexes **1–3** were analogous monomers with a coordinating THF molecule (Fig. 1).[18] The 2-pyridinemethanamido ligand in



Scheme 1 Synthesis of rare-earth metal bis(alkyl) complexes **1–3**.

1 bonds to the scandium center in a κN:κN-bidentate binding mode with reasonable Sc–N distances (Sc(1)–N(1) 2.292(2) Å and Sc(1)–N(2) 2.085(2) Å); while the five-membered ring (Sc1, N1, C5, C6, N2) almost constitutes a perfect planar geometry. The two alkyl ligands are located in the two sides of the plane. The bond angle of C(20)–Sc(1)–C(24) (108.44(12)°) also falls within the normal range observed in other lanthanide bis(alkyl) complexes.[19]

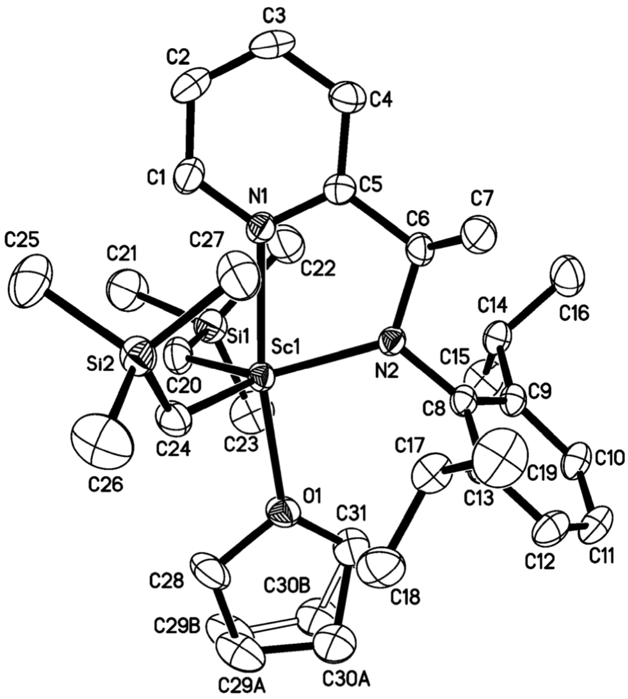


Fig. 1 X-ray structures of complex **1** with 35% probability of thermal ellipsoids. Hydrogen atoms and solvents are omitted for clarity. Selected bond distances (Å) and angles (deg): Sc(1)–N(1) 2.292(2), Sc(1)–N(2) 2.085(2), Sc(1)–C(20) 2.259(3), Sc(1)–C(24) 2.242(3), Sc(1)–O(1) 2.2100(19); N(1)–Sc(1)–N(2) 73.65(8), C(20)–Sc(1)–C(24) 108.44(12), C(20)–Sc(1)–N(2) 130.43(11), C(24)–Sc(1)–N(2) 119.54(11).

Catalysis of the polymerization of isoprene

We first explored the isoprene polymerization catalyzed by **1–3** precursors in toluene under different conditions, these results are summarized in Table 1. Upon activation with $[Ph_3C][B(C_6F_5)_4]$ only, complexes **1–3** showed a medium to high activity towards isoprene polymerization to give PIP with a main 3,4-selectivity (60%–66%) (Table 1, runs 1 and 6–9 and 17). It is noteworthy that the performance of **2**/$[Ph_3C][B(C_6F_5)_4]$ in isoprene polymerization was studied in detail, which converted 500 equiv. of isoprene into PIP in 30 min (Table 1, run 6). The resultant PIP had moderate 3,4-regularity (66%) and narrow molecular weight distribution (M_w/M_n = 1.04). When the monomer loading was doubled and quadrupled, the molecular weight of the obtained PIP was almost doubled and quadrupled and the narrow molecular weight distribution remained unchanged (M_w/M_n = 1.03–1.04), indicating a living fashion (Table 1, runs 7 and 8). The living mode could be further confirmed by adding another 500 equiv. of isoprene to a completely converted isoprene (500 equiv.) polymerization system, a total of 100% conversion was achieved to give PIP with doubled molecular weight (Table 1, run 9). To the best of our knowledge, the 3,4-selective living polymerization of isoprene remains scarce to date.[6b,c,g] By contrast, in combination with $[PhNMe_2H][B(C_6F_5)_4]$, only the ytttrium complex **2** showed activity towards isoprene polymerization to give a main 3,4-selective PIP (Table 1, run 10). The possible mechanism for the formation of 3,4-PIP has been described by Hou and coworkers.[3g,10e]

It has been reported that the alkylaluminium (AlR_3) could influence the catalytic performances and the microstructures of the isolated polymers in the polymerization of conjugated dienes.[3g–i,11j] Herein, AlR_3 was also added to the catalyst system to see whether the alkylaluminium compounds have any influence on the polymerization of isoprene. Under the activation of $[Ph_3C][B(C_6F_5)_4]$, the addition of $AlEt_3$ or Al^iBu_3 had little effect on the microstructures of the obtained PIP (Table 1, runs 2, 12, 13, 20, and 21). In the presence of $[PhNMe_2H][B(C_6F_5)_4]$, however, upon the addition of 10 equiv. $AlEt_3$ or Al^iBu_3, complexes **1** and **3** exhibited a complete change for the polymerization of isoprene from inertness (Table 1, runs 4 and 18) to high activity (Table 1, runs 5, 23, and 24). All obtained PIP had main 3,4-selectivity (61%–63%), as well. To our surprise, in the presence of either $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$, addition of 10 equiv. $AlMe_3$ to the catalyst systems of complexes **2** and **3** changed the selectivity of the polymerization dramatically from main 3,4-specific (64%–66%) to 1,4-selective (89%–95%) (Table 1, runs 11, 14, 19 and 22), although the polymerization activity decreased. This unusual effect of $AlMe_3$ on the polymerization of isoprene was also observed in the amidinate-ligated and aminopyridinate-stabilized rare-earth catalyst systems,[3g,11j] while a possible mechanism has also been proposed by Hou and coworkers to explain the dramatic switch of the regioselectivity.[3g]

We further focused on the influence of the central metal on the selectivity. Under the same polymerization conditions, with increasing ionic radius of the central metal (Sc < Lu < Y), we observed that the 3,4-selectivity of PIP almost remained unchanged, suggesting that the microstructure of the polymer does not depend on the metal size, which is a significant contrast to those results reported previously.[3g,6d] On the basis of this fact, because the **1**(Sc)/$[Ph_3C][B(C_6F_5)_4]$/$10Al^iBu_3$ catalyst system showed the highest activity for isoprene polymerization (Table 1, run 2), the polymerization was further carried out at low temperature (−20 °C); a higher 3,4-selectivity (80%) was expectedly achieved with a good activity (Table 1, run 3).

Catalysis of the polymerization of ethylene

It has recently been demonstrated that the pyridinemethanamido-ligated Hf or Ni catalysts showed an excellent polymerization behavior for ethylene. Therefore these 2-pyridinemethanamido rare-earth metal bis(alkyl) complexes **1–3** were anticipated to polymerize the ethylene with a good activity, although rare-earth metal catalysts usually showed no or low activity for the ethylene polymerization. Upon activation with an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ and 10 equiv. Al^iBu_3, the yttrium and lutetium bis(alkyl) complexes **2–3**, unfortunately, displayed no activity towards the polymerization of ethylene. In contrast, under the conditions of 1 bar ethylene atmosphere and room temperature (20 °C), the scandium complex **1** showed a moderate activity (1.4×10^5 g (PE) mol_{Sc}^{-1} h^{-1} bar^{-1}) to afford PE with low molecular weight

Table 1 Isoprene polymerization using **1–3** as precursors under various conditions[a]

Run	Cat.	Borate[b]	$\mathrm{AlR_3}$	t/min	Conv. (%)	$M_n{}^c \times 10^{-4}$	$M_w/M_n{}^c$	1,4[d] (%)	3,4[d] (%)
1	**1**	A	—	5	100	5.5	1.56	40	60
2	**1**	A	$\mathrm{Al^iBu_3}$	2	100	8.9	1.10	37	63
3[e]	**1**	A	$\mathrm{Al^iBu_3}$	10	87	40.1	1.63	20	80
4	**1**	B	—	20	trace	—	—	—	—
5	**1**	B	$\mathrm{Al^iBu_3}$	20	100	8.5	1.50	38	62
6[f]	**2**	A	—	30	100	2.9	1.04	34	66
7	**2**	A	—	60	100	6.6	1.03	35	65
8[g]	**2**	A	—	90	100	13.5	1.04	35	65
9[h]	**2**	A	—	60	100	6.7	1.05	34	66
10	**2**	B	—	60	100	2.2	1.56	36	64
11	**2**	A	$\mathrm{AlMe_3}$	180	100	15.7	2.20	95	5
12	**2**	A	$\mathrm{AlEt_3}$	90	100	3.8	1.54	50	50
13	**2**	A	$\mathrm{Al^iBu_3}$	60	100	4.7	1.32	36	64
14	**2**	B	$\mathrm{AlMe_3}$	180	24	10.6	1.82	89	11
15	**2**	B	$\mathrm{AlEt_3}$	180	100	4.7	1.26	35	65
16	**2**	B	$\mathrm{Al^iBu_3}$	60	100	2.3	1.56	37	63
17	**3**	A	—	60	92	9.7	1.36	36	64
18	**3**	B	—	60	trace	—	—	—	—
19	**3**	A	$\mathrm{AlMe_3}$	90	49	15.8	1.97	93	7
20	**3**	A	$\mathrm{AlEt_3}$	90	100	5.7	1.40	40	60
21	**3**	A	$\mathrm{Al^iBu_3}$	60	100	5.3	1.71	36	64
22	**3**	B	$\mathrm{AlMe_3}$	180	18	6.6	1.59	90	10
23	**3**	B	$\mathrm{AlEt_3}$	180	100	5.4	1.29	39	61
24	**3**	B	$\mathrm{Al^iBu_3}$	60	100	2.7	1.78	37	63

[a] Polymerization conditions: 20 °C; toluene (5.0 ml); Ln (10 µmol); Borate (10 µmol); $[\mathrm{AlR_3}]/[\mathrm{Ln}] = 10$; $[\mathrm{IP}]/[\mathrm{Ln}] = 1000$. [b] A = $[\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]$; B = $[\mathrm{PhNMe_2H}][\mathrm{B(C_6F_5)_4}]$. [c] Measured by GPC in THF at 40 °C calibrated with standard polystyrene samples. [d] Determined by ^{1}H NMR spectroscopy in $\mathrm{CDCl_3}$. [e] $T_p = -20$ °C. [f] $[\mathrm{IP}]/[\mathrm{Ln}] = 500$. [g] $[\mathrm{IP}]/[\mathrm{Ln}] = 2000$. [h] After polymerization of 5 mmol of isoprene for 30 min, another 5 mmol of isoprene were added and the reaction mixture was stirred for another 30 min.

Table 2 Ethylene polymerization with **1**(Sc)/$[\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]/\mathrm{Al^iBu_3}$[a]

Run	T_p (°C)	Yield (g)	Activity[b]	$M_n{}^c \times 10^{-3}$	$M_w/M_n{}^c$	$T_m{}^d$ (°C)
1	20	0.12	1.4	1.2	1.28	107
2	40	0.17	2.0	1.7	1.25	112
3	60	0.27	3.2	2.6	1.19	119

[a] Polymerization conditions: toluene (40.0 mL), Sc (10 µmol), $[\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]$ (10 µmol), $[\mathrm{Al^iBu_3}]/[\mathrm{Sc}] = 10$, ethylene pressure (1.0 bar), 5 min. [b] Given in 10^5 g of PE $\mathrm{mol_{Sc}}^{-1}$ h^{-1} bar^{-1}. [c] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard. [d] Determined by DSC.

($M_n = 1200$) and narrow molecular weight distribution ($M_w/M_n = 1.28$) (Table 2, run 1). Furthermore, we studied the influence of temperature on the activity. With the increase of temperature from 20 °C to 60 °C, the polymerization activity increased from 1.4×10^5 g (PE) $\mathrm{mol_{Sc}}^{-1}$ h^{-1} bar^{-1} to 3.2×10^5 g (PE) $\mathrm{mol_{Sc}}^{-1}$ h^{-1} bar^{-1}; while the molecular weight also increased from $M_n = 1200$ to $M_n = 2600$, but the molecular weight distribution still remained narrow ($M_w/M_n = 1.19$–1.28) (Table 2, runs 2 and 3). In the DSC curve, we also found that all three PEs exhibited a melting point (T_m) peak at 107 °C, 112 °C, and 119 °C, respectively.

Conclusions

We have demonstrated that by introduction of a simple N,N-bidentate ligand, $\mathrm{C_5H_4N\text{-}CH(Me)\text{-}NHC_6H_3(^iPr)_2}$, new pyridinemethanamido-ligated rare-earth metal bis(alkyl) complexes have been successfully synthesized and fully characterized, in which the C–H activation reaction is avoided. Upon activation with $[\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]$, all complexes show a good activity towards isoprene polymerization to give PIP with a main 3,4-microstructure, especially the yttrium catalyst system which exhibits a living fashion. Addition of alkylaluminium has various effects on the isoprene polymerization depending on the nature of alkylaluminium. In particular, the incorporation of $\mathrm{AlMe_3}$ can dramatically change the microstructure of the polymer from 3,4-specific to 1,4-selective. By contrast, the ionic radius of the central metal has little influence on the selectivity. Moreover, the scandium precursor, in combination with $[\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]$ and $\mathrm{Al^iBu_3}$, also shows a moderate activity for the polymerization of ethylene, and the polymerization activity increases with increasing temperature. Such a dual catalyst for the polymerizations of both isoprene and ethylene is rare. Study on the copolymerization of isoprene and ethylene is in progress.

Experimental

General methods

All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a MBraun glovebox. All solvents were purified with a MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV600 (FT, 600 MHz for ^{1}H; 150 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC experiments when necessary. Elemental analyses were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). Isoprene was dried over $\mathrm{CaH_2}$ under stirring for 48 h and distilled under vacuum before use. The 2-pyridinemethanamine ligand 2,6-diisopropyl-*N*-(1-(pyridin-2-yl)ethyl)aniline, C_5H_4N-CH(Me)-$NHC_6H_3(^iPr)_2$, was prepared by following the known procedure.[15g] $Ln(CH_2SiMe_3)_3(THF)_2$[20] was prepared according to the literature. $[Ph_3C][B(C_6F_5)_4]$ and $[PhNMe_2H][B(C_6F_5)_4]$ were synthesized following the literature procedures.[21] The microstructure (1,4- and 3,4-) of polyisoprene was determined by ^1H NMR spectra. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polyisoprene were measured by a TOSOH HLC-8220 GPC. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polyethylene were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220 type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C. 1,2,4-trichlorobenzene (TCB), containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol (BHT) was employed as the solvent at a flow rate of 1.0 mL min^{-1}. The calibration was made by polystyrene standard Easi Cal PS-1 (PL Ltd). T_m of polyethylene was measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 10 °C min^{-1} (temperature range: 25~300 °C).

X-ray crystallographic studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

Synthesis of complex $[(C_5H_4N\text{-}CH(Me)\text{-}NC_6H_3(^iPr)_2]Sc(CH_2SiMe_3)_2(THF)$ (1)

Under a nitrogen atmosphere, to a hexane solution (10 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.451 g, 1.0 mmol), 1 equiv. of ligand (0.282 g, 1.0 mmol) was added slowly at 0 °C. The mixture was stirred for 1 h to afford a clear yellow solution. Evaporation of the solvent left complex **1** as a yellow crystalline solid (0.357 g, 62.3%). Recrystallization from hexane gave single crystals suitable for X-ray analysis. ^1H NMR (600 MHz, C_6D_6, 25 °C): δ −0.30 (br s, 1H, $ScCH_2SiMe_3$), −0.13 (br s, 1H, $ScCH_2SiMe_3$), −0.03 (br s, 1H, $ScCH_2SiMe_3$), 0.12 (br s, 1H, $ScCH_2SiMe_3$), 0.25 (s, 9H, CH_2SiMe_3), 0.30 (s, 9H, CH_2SiMe_3), 1.24 (br s, 4H, THF), 1.32–1.41 (m, 15H, $NCHCH_3$ and $CH(CH_3)_2$), 3.46 (br s, 2H, THF), 3.53–3.60 (sept, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $CH(CH_3)_2$), 3.78 (br s, 2H, THF), 4.15–4.21 (sept, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $CH(CH_3)_2$), 4.88–4.92 (quart, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $NCHCH_3$), 6.78 (t, $^3J_{H\text{–}H}$ = 12.8 Hz, 1H, pyridyl-*H*), 6.86 (d, $^3J_{H\text{–}H}$ = 8.0 Hz, 1H, pyridyl-*H*), 7.07 (t, $^3J_{H\text{–}H}$ = 15.4 Hz, 1H, pyridyl-*H*), 7.20–7.21 (m, 2H, Ar*H*), 7.28–7.29 (m, 1H, Ar*H*), 9.08 ppm (d, $^3J_{H\text{–}H}$ = 5.4 Hz, 1H, pyridyl-*H*). ^{13}C NMR (150 MHz, C_6D_6, 25 °C): δ 4.58 (s, 6C, CH_2SiMe_3), 25.40 (s, 2C, THF), 24.58, 25.76, 25.94, 26.11, 27.20 (s, 5C, $CH(CH_3)_2$ and $NCHCH_3$), 27.57, 27.98 (s, 2C, $CH(CH_3)_2$), 33.63, 35.93 (br s, 2C, $ScCH_2SiMe_3$), 66.86 (s, 1C, $NCHCH_3$), 71.52 (s, 2C, THF), 121.76, 122.93, 124.32, 124.43, 124.95 (s, 5C, Ar-*C* and Pyridyl-*C*), 138.25 (s, 1C, Pyridyl-*C*), 146.62, 147.56 (s, 2C, Ar-*C*), 148.31 (s, 1C, Pyridyl-*C*), 149.80 (s, 1C, Ar-*C*), 170.03 (s, 1C, Pyridyl-*C*). Anal. Calcd for $C_{31}H_{55}ON_2Si_2Sc$ (%): C, 64.99; H, 9.68; N, 4.89. Found: C, 65.23; H, 9.51; N, 4.75.

Synthesis of complex $[(C_5H_4N\text{-}CH(Me)\text{-}NC_6H_3(^iPr)_2]Y(CH_2SiMe_3)_2(THF)$ (2)

Following a similar procedure described for the preparation of **1**, complex **2** was isolated from the acid–base reaction of $Y(CH_2SiMe_3)_3(THF)_2$ (0.495 g, 1.0 mmol) with 1 equiv. of ligand (0.282 g, 1.0 mmol) in a 54.3% yield (0.335 g). ^1H NMR (600 MHz, C_6D_6, 25 °C): δ −0.54 (d, $^2J_{Y\text{–}H}$ = 12.0 Hz, 1H, YCH_2SiMe_3), −0.43 (d, $^2J_{Y\text{–}H}$ = 12.0 Hz, 1H, YCH_2SiMe_3), −0.27 (d, $^2J_{Y\text{–}H}$ = 12.0 Hz, 1H, YCH_2SiMe_3), −0.21 (d, $^2J_{Y\text{–}H}$ = 12.0 Hz, 1H, YCH_2SiMe_3), 0.31 (s, 9H, CH_2SiMe_3), 0.41 (s, 9H, CH_2SiMe_3), 1.22 (br s, 4H, THF), 1.33–1.42 (m, 15H, $NCHCH_3$ and $CH(CH_3)_2$), 3.48 (br s, 4H, THF), 3.58–3.65 (sept, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $CH(CH_3)_2$), 4.25–4.32 (sept, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $CH(CH_3)_2$), 4.90–4.94 (quart, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $NCHCH_3$), 6.74 (t, $^3J_{H\text{–}H}$ = 12.0 Hz, 1H, pyridyl-*H*), 6.87 (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, pyridyl-*H*), 7.04 (t, $^3J_{H\text{–}H}$ = 12.0 Hz, 1H, pyridyl-*H*), 7.17 (t, $^3J_{H\text{–}H}$ = 18.0 Hz, 1H, Ar*H*), 7.22 (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, Ar*H*), 7.27 (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, Ar*H*), 9.02 ppm (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, pyridyl-*H*). ^{13}C NMR (150 MHz, C_6D_6, 25 °C): δ 4.93 (s, 3C, CH_2SiMe_3), 5.02 (s, 3C, CH_2SiMe_3), 25.35 (s, 2C, THF), 25.21, 25.69, 26.44, 26.80, 26.87 (s, 5C, $CH(CH_3)_2$ and $NCHCH_3$), 27.56, 28.05 (s, 2C, $CH(CH_3)_2$), 31.32 (d, $J_{Y\text{–}C}$ = 37.5 Hz, 1C, YCH_2SiMe_3), 33.23 (d, $J_{Y\text{–}C}$ = 37.5 Hz, 1C, YCH_2SiMe_3), 67.55 (s, 1C, $NCHCH_3$), 70.52 (s, 2C, THF), 121.79, 123.19, 123.91, 124.33, 125.02 (s, 5C, Ar-*C* and Pyridyl-*C*), 138.29 (s, 1C, Pyridyl-*C*), 148.13, 143.19 (s, 2C, Ar-*C*), 148.37 (s, 1C, Pyridyl-*C*), 148.59 (s, 1C, Ar-*C*), 171.35 (s, 1C, Pyridyl-*C*). Anal. Calcd for $C_{31}H_{55}ON_2Si_2Y$ (%): C, 60.36; H, 8.99; N, 4.54. Found: C, 60.64; H, 9.01; N, 4.45.

Synthesis of complex $[(C_5H_4N\text{-}CH(Me)\text{-}NC_6H_3(^iPr)_2]Lu(CH_2SiMe_3)_2(THF)$ (3)

Following a similar procedure described for the preparation of **1**, complex **3** was isolated from the acid–base reaction of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.581 g, 1.0 mmol) with 1 equiv. of ligand (0.282 g, 1.0 mmol) in a 60.1% yield (0.423 g). ^1H NMR (600 MHz, C_6D_6, 25 °C): δ −0.73, −0.63 (AB, $^2J_{H\text{–}H}$ = 11.4 Hz, 2H, $LuCH_2SiMe_3$), −0.48, −0.37 (AB, $^2J_{H\text{–}H}$ = 11.4 Hz, 2H, $LuCH_2SiMe_3$), 0.29 (s, 9H, CH_2SiMe_3), 0.39 (s, 9H, CH_2SiMe_3), 1.20 (br s, 4H, THF), 1.34–1.43 (m, 15H, $NCHCH_3$ and $CH(CH_3)_2$), 3.32 (br s, 2H, THF), 3.57 (br s, 2H, THF), 3.59–3.66 (sept, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $CH(CH_3)_2$), 4.26–4.33 (sept, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $CH(CH_3)_2$), 4.96–4.99 (quart, $^3J_{H\text{–}H}$ = 6.6 Hz, 1H, $NCHCH_3$), 6.74 (t, $^3J_{H\text{–}H}$ = 12.0 Hz, 1H, Pyridyl-*H*), 6.86 (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, Pyridyl-*H*), 7.04 (t, $^3J_{H\text{–}H}$ = 18.0 Hz, 1H, Pyridyl-*H*), 7.18 (t, $^3J_{H\text{–}H}$ = 12.0 Hz, 1H, Ar*H*), 7.23 (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, Ar*H*), 7.29 (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, Ar*H*), 8.98 ppm (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, Pyridyl-*H*). ^{13}C NMR (150 MHz, C_6D_6, 25 °C): δ 5.01 (s, 3C, $CH_2Si\mathit{Me}_3$), 5.14 (s, 3C, $CH_2Si\mathit{Me}_3$), 25.37 (br s, 2C, THF), 25.50, 25.83, 26.22, 26.60, 26.99 (s, 5C, $CH(\mathit{C}H_3)_2$ and $NCH\mathit{C}H_3$), 27.51, 27.98 (s, 2C, $\mathit{C}H(CH_3)_2$), 37.36, 40.10 (s, 2C, $Lu\mathit{C}H_2SiMe_3$), 67.67 (s, 1C, $N\mathit{C}HCH_3$), 70.76 (s, 2C, THF), 121.86, 123.31, 123.82, 124.31, 124.96 (s, 5C, Ar-*C* and Pyridyl-*C*), 138.29 (s, 1C, Pyridyl-*C*), 147.70, 147.97 (s, 2C, Ar-*C*), 148.17 (s, 1C, Pyridyl-*C*), 150.22 (s, 1C, Ar-*C*), 171.32 (s, 1C, Pyridyl-*C*). Anal. Calcd for $C_{31}H_{55}ON_2Si_2Lu$ (%): C, 52.97; H, 7.89; N, 3.99. Found: C, 53.31; H, 7.71; N, 4.05.

Isoprene polymerization

A detailed polymerization procedure is described as follows (run 2, Table 1). Under a nitrogen atmosphere and room temperature, a toluene solution (2 mL) of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 µmol) was added to a toluene solution (3 mL) of complex **1** (5.7 mg, 10 µmol) in a 25 mL flask. Then 10 equiv. of Al^iBu_3 (0.1 mL, 100 µmol, 1.0 M in toluene) were added under stirring after a few minutes. Upon the addition of 1000 equiv. of isoprene (1 mL, 0.01 mol), polymerization was initiated and carried out for 2 min. The reaction mixture was poured into a large quantity of methanol and then dried under vacuum at ambient temperature to a constant weight (0.68 g, 100%).

Ethylene polymerization

A detailed polymerization procedure is described as a typical example (run 3, Table 2). In a glovebox, a toluene solution (40 mL) of complex **1** (5.7 mg, 10 µmol) was charged into a two-necked flask with a magnetic stir bar. The flask was taken outside of the glove box and set in a water bath, and connected to a well-purged Schlenk ethylene line with a mercury-sealed stopper by use of a three-way cock. Ethylene (1.0 bar) was introduced into the system and was saturated in the solution at 60 °C by stirring for 5 min. The toluene solution of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 µmol) and Al^iBu_3 (0.1 mL, 100 µmol, 1.0 M in toluene) was then added through a syringe under vigorous stirring. The mixture was stirred under constant ethylene pressure (1.0 bar) for 5 min. After that, methanol (2 mL) was added to terminate the reaction, and the reaction mixture was added to acidified methanol (20 mL concentrated HCl in 500 mL of ethanol). Polyethylene was obtained by filtration, washed with methanol, and dried at 40 °C for 24 h in vacuum.

Acknowledgements

This work was partly supported by The National Natural Science Foundation of China for project Nos. 20934006, 51073148, and 51021003. The Ministry of Science and Technology of China for projects Nos. 2009AA03Z501 and 2011DF50650.

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