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Metal-catalysed Polymerisation

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Copolymerization of ethylene with norbornene catalyzed by cationic rare earth metal fluorenyl functionalized N-heterocyclic carbene complexes[†]

Baoli Wang,^{*a,b*} Tao Tang,^{*a*} Yuesheng Li^{*a*} and Dongmei Cui*^{*a*}

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Rare earth metal bis(alkyl) complexes attached by fluorenyl modified N-heterocyclic carbene (NHC) (Flu-NHC)Ln(CH₂SiMe₃)₂ (Flu-NHC = (C₁₃H₈CH₂CH₂(NCHCCHN)C₆H₂Me₃-2,4,6); $Ln = Sc (2a); Y (2b); Ho (2c); Lu (2d)), (^{Bu}Flu-NHC)Ln(CH_2SiMe_3)_2 (^{Bu}Flu-NHC =$ $2,7-Bu_2C_{13}H_6CH_2CH_2(NCHCCHN)C_6H_2Me_3-2,4,6;$ Ln = Sc (1a); Lu (1d)) and attached by indenyl modified N-heterocyclic carbene (Ind-NHC) $Ln(CH_2SiMe_3)_2$ (Ind-NHC = $C_9H_6CH_2CH_2(NCHCCHN)C_6H_2Me_3-2,4,6$; Ln = Sc (3a); Lu (3d)), under the activation of AlⁱBu₃ and $[Ph_3C][B(C_6F_5)_4]$, showed varied catalytic activities toward homo- and copolymerization of ethylene and norbornene. Among which the scandium complexes, in spite of ligand type, exhibited medium to high catalytic activity for ethylene polymerization ($10^5 \text{ g mol}_{sc}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$), but all were almost inert to norbornene polymerization. Remarkably, higher activity was found for the copolymerization of ethylene and norbornene when using Sc based catalytic systems, which reached up to 5×10^6 g mol_{sc}^{-1} h⁻¹ atm⁻¹ with **2a**. The composition of the isolated copolymer was varying from random to alternating according to the feed ratio of the two monomers ($r_{\rm E} = 4.1, r_{\rm NB} = 0.013$). The molecular structure of complex 1d was characterized by X-ray analysis. The influences of structural factors of complexes and polymerization conditions on both the catalytic activity and the norbornene content in the copolymer were discussed.

Introduction

The copolymer (P(E-co-NB)) of ethylene (E) and norbornene (NB) has been extensively studied owing to its good process ability and other remarkable properties, such as a relatively high glass transition temperature (T_g) , excellent optical transparency and high refractive indices.¹ The properties of P(Eco-NB) are determined by its microstructure and NB content, which are primarily controlled by the catalyst structure and polymerization conditions. At present most catalysts for copolymerization of E with NB are confined to transition metals such as group 4 metallocene² and group 10 post-metallocene³ whereas little attention has been paid to rare earth metal counterparts.⁴ Only one kind of cationic rare earth metal halfsandwich species $Cp'Sc(CH_2SiMe_3)_2(THF)$ ($Cp' = C_5Me_4SiMe_3$,^{4a} $1,3-(SiMe_3)_2C_5H_3$,^{4a} C_5Me_5 ,^{4a} or $C_5Me_4SiMe_2(C_6F_5)^{4b}$) has been reported to copolymerize E and NB with high activity, although a number of cationic rare earth metal catalysts has been successfully employed in various homogeneous polymerizations of ethylene, styrene and 1,3-dienes etc.5 Obviously, extending the utilization of these catalysts for copolymerization, especially for that of E and NB, has remained as a fascinating and challenging subject.

In this subject, one essential step is to improve the catalytic activity and selectivity of rare earth metal complexes, which could be finely tuned by the type of the central metal ion as well as the steric bulkiness and electric effect of the ancillary moiety. Compared with some widely studied ligands, such as cyclopentadienyls (mono-Cp, bis-Cp, donor-functionalized Cp, etc.),⁶ β-diketiminates, anilido imines, benzamidinates and pyrrolyliminates etc.,⁷ deprotonated aza crowns and crown ethers,⁸ and phosphides,9 thermally stable N-heterocyclic carbene (NHC) compounds have emerged as versatile auxiliaries to stabilize and activate transition metal10 centers and intermediates in quite different key catalytic steps, whereas they have been less utilized in rare earth metals.^{11,12} A review about f-block N-heterocyclic carbene complexes has been released very recently,12 however, the reactivity of these complexes, especially catalysis on polymerization have been rarely investigated.^{13,14} We have previously reported the synthesis of indenyl and fluorenyl modified N-heterocyclic carbene supported rare earth metal bis(alkyl) complexes 2 and 3. Among which 2b, 2c or 2d activated by aluminum alkyls and $[Ph_3C][B(C_6F_5)_4]$ initiated the living polymerization of isoprene with high activity, high 3,4-selectivity and medium syndioselectivity.^{14a} However, the scandium analogue 2a is inert. Interestingly, opposite phenomenon has been discovered in this work that 2a had the highest catalytic activity for the copolymerization of E with NB in the present of aluminum alkyls and $[Ph_3C][B(C_6F_5)_4]$. Herein, we report the catalytic performances for the copolymerization of E and NB with these complexes and the newly synthesized 2,7-di-tert-butyl fluorenyl modified

^aState Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, 130022, China. E-mail: dmcui@ciac.jl.cn; Fax: +86 431-8526-2773

^bGraduate School of the Chinese Academy of Sciences, Beijing, 100039, China

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N-heterocyclic carbene ligated rare earth metal bis(alkyl) complexes (**1a** and **1d**) in the presence of Al'Bu₃ and $[Ph_3C][B(C_6F_5)_4]$. The influences of the molecular structures of the catalysts and polymerization conditions on the catalytic activity and composition of the polymer will be presented.

Results and discussion

Preparation of complexes

Preparation of complexes 2 and 3 was in accordance with the literature.¹⁴ Complex 1 was synthesized as described as follows: ethylene bridged 2,7-di-tert-butyl-fluorenyl N-heterocyclic carbene ("BuFluH-NHC) was obtained by treatment of 2,7di-tert-butyl fluorenyl modified imidazolium bromide (2,7- $^{t}Bu_{2}C_{13}H_{7}CH_{2}CH_{2}(NCHCHCHN)C_{6}H_{2}Me_{3}-2,4,6)Br$ (($^{tBu}FluH$ -NHC-H)Br) with 1 equiv. LiCH2SiMe3. 'BuFluH-NHC reacted with rare earth metal tris(alkyl)s (Ln(CH₂SiMe₃)₃(THF)₂) to afford the constrained geometry configuration (CGC) type rare earth metal bis(alkyl) complexes ('BuFlu-NHC)Ln(CH2SiMe3)2 (Ln = Sc (1a); Lu (1d)) via alkane elimination (Scheme 1). Complexes 1a and 1d are analogous THF-free monomers. The ¹H NMR spectra of complexes 1a and 1d display AB spin systems at the upfield (*i.e.* high frequency) region (δ –1.4 ppm to δ –2.2 ppm) that are assigned to the diastereotopic methylene protons of the metal alkyl species (LnCH₂SiMe₃). The resonances at the very low field region in ¹³C NMR spectra around δ 187.68 and 199.08 ppm arise from the Ln-Cylidene, suggesting that the coordination of the carbene moiety to the central metal ion is robust and is maintained in solution. This further confirmed a rigid and chiral metal center. The molecular structure of 1d in the solid state was confirmed by X-ray diffraction analysis (Fig. 1). The CGC 'Bu Flu-NHC ligand coordinates to Lu ion in a η^5/κ^1 mode via the five-membered ring and the ylidene carbon, adopting a tetrahedron geometry around the central Lu ion with the centroid of the five-membered cyclopentadienyl (Cp) ring as the apex. The two alkyl ligands locate in cis-positions with one endo and the other exo against the imidazolyl ring, paralleling to the N-aryl ring. The bond distances of Lu(1)– C_{ring} , Lu(1)– C_{cent} and Lu(1)–plane_{Cp} in 1d (2.677 Å (av.), 2.382 Å, 2.379 Å), in 2d (2.654 Å (av.), 2.357 Å, 2.357 Å) and in 3d (2.636 Å (av.), 2.344 Å, 2.342 Å) have a descending trend, consistent with the steric bulkiness of the ligands. Complex 1d bearing the most sterically bulky ligand had the longest bond lengths.



Fig. 1 X-Ray structure of 1d with 30% probability of thermal ellipsoids. Hydrogen atoms and the other equivalent molecule containing Lu(2) are omitted for clarity. Selected bond distances (Å) and angles (°) in Lu(1) molecule: Lu(1)-C_{ring} 2.677 (av.), Lu(1)-C_{cent} 2.382, Lu(1)-plane_{Cp} 2.379, Lu(1)-C(1) 2.653(4), Lu(1)-C(6) 2.696(4), Lu(1)-C(7) 2.719(4), Lu(1)-C(12) 2.697(4), Lu(1)-C(13) 2.618(4), Lu(1)-C(24) 2.482(4), Lu(1)-C(36)2.317(4), Lu(1)–C(37) 2.293(4); C(36)–Lu(1)–C(37) 106.43(16), C(36)-Lu(1)-C(24)109.65(14), C(37)-Lu(1)-C(24)103.38(15), Lu(1)-C(24)-N(2) 132.4(3). Corresponding bond distances (Å) and angles (°) in Lu(2) independent molecule: Lu(2)-C_{ring} 2.668 (av.), Lu(2)-C_{cent} 2.373, Lu(2)-plane_{Cp} 2.372, Lu(2)-C(44) 2.690(4), Lu(2)-C(49) 2.660(4), Lu(2)-C(50) 2.666(4), Lu(2)-C(55) 2.674(4), Lu(2)-C(56) 2.652(4), Lu(2)-C(67) 2.493(4), Lu(2)-C(79) 2.315(4), Lu(2)-C(80) 2.308(4); C(79)-Lu(2)-C(80) 104.56(17), C(79)-Lu(2)-C(67) 112.49(15), C(80)-Lu(2)-C(67) 104.21(14), Lu(2)-C(67)-N(4) 131.0(3).

Copolymerization of ethylene with norbornene

Complexes 1, 2 or 3 (Scheme 1 and Chart 1) activated with $[Ph_3C][B(C_6F_5)_4]$ to generate cationic units showed very low activity for the homo- and copolymerization of ethylene (E) or norbornene (NB). This might be ascribed to the impurities in the polymerization solution or the unstable nature of these cationic units that decomposed into none active species. Further *in situ* generated ternary catalyst systems composed of the complexes and Al'Bu₃ and $[Ph_3C][B(C_6F_5)_4]$ showed moderate activity for the homopolymerization of E (10⁵ g mol_{Se}⁻¹ h⁻¹ atm⁻¹) and very low activity for that of NB under the same experimental conditions. Surprisingly, this ternary system could exhibit high



Scheme 1 Synthesis of 2,7-di-tert-fluorenyl N-heterocyclic carbene (^{18u}Flu-NHC) ligated rare earth metal bis(alkyl) complexes 1a and 1d.



Chart 1 Molecular structures of fluorenyl and indenyl *N*-heterocyclic carbene (Flu-NHC and Ind-NHC) ligated rare earth metal bis(alkyl) complexes **2a–2d**, **3a** and **3d**.

catalytic activity for the copolymerization of E and NB, depending significantly on the structural factors of the catalyst precursors and polymerization conditions. The Y, Ho and Lu based complexes showed low activity in spite of ligand types and organoborate applied, whilst all scandium complexes were highly active. This was ascribed mainly to the Lewis acidic nature of Sc3+. The indenyl-modified NHC attached complex 3a (ScInd) exhibited a lower activity (0.28×10^6 g mol_{sc}⁻¹ h⁻¹ atm⁻¹), as the strong electron donating nature of indenyl fragment reduced the Lewis acidity of the central Sc³⁺. Whilst complex 2a (Sc^{Flu}), bearing the fluorenyl-modified NHC, displayed the highest activity $2.37 \times$ 10⁶ g mol_{sc}⁻¹ h⁻¹ atm⁻¹ under the same conditions owing to the relatively weak electron donating ability of the fluorenyl group.¹⁵ This could be further confirmed by the catalytic performance of 1a (ScrBuFlu) stabilized by tert-butyl fluorenyl modified NHC, which showed moderate activity 1.25×10^6 g mol_{sc}⁻¹ h⁻¹ atm⁻¹ compared with 2a, because tert-butyl groups were electrondonating and their spacial sterics blocked E or NB insertion into the copolymer chain. It was noteworthy that when using the Brønsted base [PhMe₂NH][B(C₆F₅)₄] or borane B(C₆F₅)₃ instead of $[Ph_3C][B(C_6F_5)_4]$, the resultant ternary system still showed similar high activity (4×10^5 g mol_{sc}⁻¹ h⁻¹ atm⁻¹), different from the previous systems composed of $B(C_6F_5)_3$ that are inactive.^{4a,4b}

On the basis of its excellent performance, the catalytic system $2a/Al^{i}Bu_{3}/[Ph_{3}C][B(C_{6}F_{5})_{4}]$ was chosen to examine the influence of the polymerization conditions. Keeping the other factors constant, the copolymerization was carried out under various temperatures. The results showed that both higher and lower temperatures were not preferred and 40 °C was optimised. Meanwhile the NB content of copolymer also decreased with temperature from 37.3% (40 °C) to 33.7% (50 °C) in spite of the increasing NB-to-E ratio.¹⁶ The reason was complicated, as temperature affected not only the concentration of ethylene in the reaction medium (toluene) but also the reactivity ratios of the two monomers. The Fineman-Ross17 plot for the copolymerization of E with NB performed at 40 °C is depicted in Fig. 2. A plot of F(f-1)/f as ordinate and (F^2/f) as abscissa is a straight line whose slope is $r_{\rm E}$ and whose intercept is minus $r_{\rm NB}$ (F = [E]/[NB]in feed, f = [E]/[NB] in copolymer). The monomer reactivity ratios were calculated to be $r_{\rm E} = 4.1$ and $r_{\rm NB} = 0.013$, respectively, indicating a much higher activity for homopolymerization of ethylene as compared to that of norbornene. Thus, at a higher temperature, although the content of ethylene in reaction medium



Fig. 2 Fineman–Ross plot for copolymerization of ethylene and norbornene with $2a/Al'Bu_3/[Ph_3C][B(C_6F_5)_4]$ at 40 °C (F = [E]/[NB] in feed, f = [E]/[NB] in copolymer, E = ethylene, NB = norbornene).

was reduced, the incorporation rate into copolymer increased due to the higher $r_{\rm E}$ value, whereas in contrast, the incorporation of norbornene could not be improved so obviously due to the much lower reactivity ratio $r_{\rm NB}$, as a result an away from alternating microstructure of the copolymer was obtained.

The content of NB in the copolymer could be adjusted by fixing NB feed amount but changing the volume of toluene (that means changing the feed amount of E) (Table 1, entries 6-8). Fig. 3 showed the typical ¹³C NMR spectra of the resultant P(E-co-NB)s, the assignment of which was according to the literatures.¹⁸ The common feature seen from these spectra is that the NB repeat unit is discrete, indicating that there is no NB homopolymerization sequence. This was in agreement with the lower $r_{\rm NB}$ according to Fineman–Ross plot. With the reducing of toluene volume meaning that NB-to-E ratio increased, the chance of incorporating NB into copolymer became higher, when the volume was low enough, the almost alternating arrangement of E and NB was achieved (Table 1, entries 6 and 7; Fig. 3). The ¹³C NMR spectrum of the P(E-alt-NB) (entry 7) showed the typical eight singles around δ 45.80, 45.20, 40.01, 39.52, 31.00, 28.72, 28.33 and 28.06 ppm, respectively. It was not surprised that with the increase of the feed value of NB-to-E, the polymerization became sluggish, which could be explained that the coordinated NB resided longer at the catalyst center before insertion compared with E.¹⁹ Solvent-fractionation experiments revealed negligible quantities of homopolymer impurities (The alternating P(E-co-NB)s were soluble in toluene, whereas homopolyethylene and homopolynorbornene were insoluble).

The NB content of resultant P(E-co-NB) indeed showed significant influence on T_g value of the copolymer, which increased from 26.8 to 46.3% resulting in an obvious change of T_g from 56.8 to 117.3 °C. The NB content and T_g value had perfect linear correlation as shown in Fig. 4 ($T_g = 2.66$ (NB%) – 11.3).^{19c}

Conclusion

We have demonstrated that a ternary catalyst system composed of rare earth metal bis(alkyl) complexes bearing CGC-type functional NHC ancillaries and aluminum alkyls and organoborates, presented various activity for the copolymerization of ethylene

Table 1 Copolymerization of ethylene with norbornene by 1a, 2a or $3a/Al^{i}Bu_{3}/[Ph_{3}C][B(C_{6}F_{5})_{4}]^{a}$

			3	+	1a, 2a or 3a / Al ⁱ Bu₃ / [Ph₃C]](B(C₅F₅)₄] x toluene, 25 °C ~ 50 °C x							
Entry	Sc	NB-feed mmol	V_{tol}/mL	[E]/mol L ⁻¹	[NB]/[E]	T∕°C	<i>t</i> /min	Activity ^b	NB cont. ^c (mol%)	$M_{\rm n}{}^{\rm d}\!\!\times\!\!10^{\rm -4}$	$M_{ m w}/M_{ m n}{}^d$	$T_{g}^{e}/^{\circ}C$
1	1a	50	100	0.108	4.63	40	5	1.25	30.1	3.98	1.83	60.4
2	2a	50	100	0.108	4.63	40	5	2.37	37.1	7.12	1.75	83.4
3	3a	50	100	0.108	4.63	40	5	0.28	37.1	0.89	1.53	86.3
4	2a	50	100	0.133	3.76	25	5	0.058	n.d. ^f	n.d.	n.d.	n.d.
5	2a	50	100	0.095	5.26	50	5	0.27	33.7	1.57	2.09	79.0
6	2a	50	20	0.108	23.15	40	5	0.43	46.3	1.20	1.96	117.3
7	2a	50	50	0.108	9.26	40	5	1.61	44.5	2.47	1.60	104.9
8	2a	50	200	0.108	2.31	40	5	2.02	26.8	6.13	1.70	56.8
9	2a	100	100	0.108	9.26	40	5	1.86	43.5	5.06	1.79	100.9
10	2a	50	100	0.108	4.63	40	2	5.08	37.4	3.12	1.39	87.0

^{*a*} Conditions: Sc (10 µmol), $[Ph_3C][B(C_6F_5)_4]$ (10 µmol), $Al^{j}Bu_3$ (200 µmol), $p_{ethylene} = 1$ atm. ^{*b*} 10⁶ g of copolymer g mols_c⁻¹ h⁻¹ atm⁻¹. ^{*c*} NB content determined by ¹³C NMR spectroscopy in C₂D₄Cl₂. ^{*d*} Determined by means of gel permeation chromatography (GPC) against polystyrene standards. ^{*e*} Determined by differential scanning calorimetry (DSC). ^{*f*} n.d. = not determined.



Fig. 3 ¹³C NMR spectra of P(E-co-NB)s with $2a/Al'Bu_3/[Ph_3C][B(C_6F_5)_4]$ (Table 1, entries 2 and 6–8).

with norbornene. The catalytic activity is significantly dependent on the type of the central metal ion and the electronics and sterics of the ancillary moiety. The more Lewis acidic scandium complex **2a** bearing the less electron-donating and sterically bulky Flu-NHC ligand, shows the highest activity as compared to its analogues containing Ind-NHC or ^{(Bu}Flu-NHC ligand. The microstructures of the copolymers vary from random to alternating adjusted by the NB-to-E feed ratio during the course of polymerization, in which the NB units exist only as isolated fragments owing to its very low reactivity ratio calculated according to Fineman–Ross method. This is a rare example to utilize a rare earth metal catalytic system for the copolymerization of ethylene with norbornene.

Experimental

General considerations

All manipulations were performed under a dried and oxygenfree argon atmosphere using standard high vacuum Schlenk techniques or in a glove box.

Materials

All solvents were purified from MBRAUN SPS system. Indene (98%), fluorene (98%), AlⁱBu₃ (1.0 M in hexane) and LiCH₂SiMe₃ solution (1.0 M in pentane) were purchased from Aldrich. Polymerization grade ethylene was donated by the China



Fig. 4 Dependence of glass transition temperature (T_g) upon NB content in copolymers (Table 1, entries 2 and 5–10).

Petroleum & Chemical Corporation. Norbornene (99%, Alfa) was purified by stirring it over potassium at 80 °C for 48 h and distilled before use. Bromoethylidene, mesitylamine, glyoxal, para-formaldehyde, *etc.*, were bought from the National Medicine Company (China), and were used without further purification. The rare earth metal bis(alkyl) complexes (**2a**, **2b**, **2c**, **2d**, **3a** and **3d**),¹⁴ [Ph₃C][B(C₆F₅)₄],^{20a} [PhMe₂NH] [B(C₆F₅)₄],^{20b} 2,7-di-*tert*-fluorene²¹ and 1-(mesityl)imidazole²² were prepared according to the literature.

Ligands and complexes analyses

¹H and ¹³C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ¹H; 100 MHz for ¹³C) or a Bruker AV300 (FT, 300 MHz for ¹H; 75 MHz for ¹³C). NMR assignments were confirmed by the ¹H–¹H COSY, ¹H–¹³C HMQC and ¹H–¹³C HMBC experiments when necessary. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). For the organometallics the carbon analyses are a bit low probably owing to carbide formation. Crystallographic data were collected at –86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector (MoK α , $\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The structures were solved by using SHELXTL program.

Ethylene/norbornene copolymerization procedure

In the glove box, a Schlenk bottle containing a magnetic stirring bar was charged with a toluene solution of norbornene and alkyl aluminum. The reactor was equipped with an ampoule bottle filled with 2 mL toluene solution of the rare earth metal complexes, alkyl aluminum and borate. The reactor was taken out of the glove box, connected to the Schlenk line, and set in the thermostated oil bath. The solution was degassed and then saturated with ethylene for 15 min under vigorous stirring. The solution of catalyst system was quickly transferred to the polymerization bottle to initiate the polymerization. The polymerization was terminated by addition of acidified ethanol. The reaction mixture was slowly poured into 300 mL ethanol. The precipitated polymer was filtered and washed with mass ethanol, and then dried under vacuum at 60 °C for several hours.

Polymer characterization

 13 C NMR spectra for the copolymers were obtained using C₂D₂Cl₄ as a solvent on a Bruker AV400 (FT, 400 MHz for ¹H; 100 MHz for ¹³C) working at 100 °C. Hexamethyldisiloxane was used as internal reference. The NB contents in the P(E-co-NB) were calculated from the ¹³C NMR spectra by using eqn (1).^{18c}

mol NB% =
$$\frac{1}{3} \frac{I_{C_1/C_4} + I_{C_2/C_3} + 2I_{C_7}}{I_{CH_2}} \times 100$$
 (1)

Where I_{C_2/C_4} is the integral of signals between 39.5 and 40.1 ppm, I_{C_2/C_3} is the integral of signals between 45.0 and 46.0 ppm, I_{C_7} is the integral of signals between 30.5 and 31.0 ppm and I_{CH_2} is the integral of signals between 27.0 and 29.0 ppm. ($\delta_{C_2D_2Cl_4} = 72.11$ ppm, chemical shifts referred to hexamethyldisiloxane)

The number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the copolymer samples 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_g of copolymers were measured through differential scanning calorimetry (DSC) analyses, which were carried out on a Q 100 DSC from TA Instruments under nitrogen atmosphere. The instrument was calibrated for temperature and enthalpy using pure indium (m.p. = 156.6 °C) and sapphire before experiment. Measurements during the first heating from 25 °C to 250 °C and then the first cooling from 250 °C to 25 °C as well as the second heating from 25 °C to 250 °C at 10 °C min⁻¹ were performed.

Synthesis of 9-(2-bromoethyl)-2,7-di-tert-butyl-9H-fluorene

The synthesis was based on the method reported in the literature.²³ At -40 °C, 22.4 mL (1.60 mol L⁻¹, hexane) n-butyl lithium was added dropwise to the THF solution (50 mL) of 2,7-ditert-fluorenyl (10.000 g, 35.926 mmol) and warmed to room temperature slowly and kept stirring overnight. The THF-hexane solution of 2,7-di-tert-fluorenyl lithium was cooled to -40 °C, which was added dropwise to the THF solution (100 mL) of bromoethylidene (33.736 g, 179.578 mmol) over 2 h and warmed to room temperature slowly and reacted for more than 12 h. The solution was treated with a saturated aqueous solution of NH₄Cl and washed several times with water. The organic phase was separated and dried over MgSO4. Removal of the solvent and recrystallization from n-pentane yielded a beige solid (10.025, 72.4%). The ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 1.44 (s, 18 H, $C(CH_3)_3$, 2.52–2.57 (m, 2 H, CH_2CH_2), 3.43 (t, ${}^{3}J_{H-H} = 7.2$ Hz, 2 H, CH₂CH₂), 4.16 (t, ${}^{3}J_{H-H} = 5.8$ Hz, 1 H, fluorene), 7.46, 7.67 (AB, ${}^{3}J_{H-H} = 8.0$ Hz, 4 H, fluorene), 7.58 (s, 2 H, fluorene). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 30.87 (s, 1 C, CH₂CH₂), 31.62 (s, 6 C, C(CH₃)₃), 34.86 (s, 2 C, C(CH₃)₃), 36.94 (s, 1 C, CH₂CH₂), 46.40 (s, 1 C, fluorene), 119.25, 121.05, 124.43 (s, 6 C, fluorene), 138.42, 145.82, 149.95 (s, 6 C, ipso-fluorene) Anal. calcd for C₂₃H₂₉Br (%): C 71.68, H 7.58. Found: C 71.20, H 7.15.

Synthesis of 2,7-di-*tert*-fluorenyl imidazolium bromide (^{rBu}FluH-NHC-H)Br

The synthesis was similar with the method reported in the literature.14,24 Treatment of 9-(2-bromoethyl)-2,7-di-tert-butyl-9Hfluorene (5.000 g, 12.974 mmol) with 1-(mesityl)imidazole (2.416 g, 12.974 mmol) in 1,4-dioxane (80 mL) under refluxing for 5 d gave sticky oils after removal of volatiles. The sticky oils were dissolved in CH₂Cl₂ and precipitated with ether. The resulting viscous products were passed through a silica-gel column with acetyl acetate as eluent to wash off the movable parts. The silica gel column was washed with methanol to collect the non-movable part. Driving of methanol gave the white power anticipated compound (^{rBu}FluH-NHC-H)Br (5.985 g, 80.7%). The ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 1.37 (s, 18 H, C(CH₃)₃), 2.00 (s, 6 H, C₆H₂Me₃), 2.31 (s, 3 H, C₆H₂Me₃), 2.89–2.96 (m, 2 H, CH₂CH₂), 4.23 (t, ${}^{3}J_{H-H} = 5.1$ Hz, 1 H, fluorene), 4.43 (t, ${}^{3}J_{H-H} = 6.9$ Hz, 2 H, CH₂CH₂), 6.60 (s, 1 H, NCH), 6.84 (s, 1 H, NCH), 6.96 (s, 2 H, C₆ H_2 Me₃), 7.43, 7.65 (AB, ${}^{3}J_{H-H} = 6.9$ Hz, 4 H, fluorene), 7.59 (s, 2 H, fluorene), 10.44 (s, 1 H, imidazolium-H). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 17.58 (s, 2 C, C₆H₂Me₃), 20.87 (s, 1 C, $C_6H_2Me_3$, 31.51 (s, 6 C, C(CH₃)₃), 33.81 (s, 1 C, CH₂CH₂), 34.83 (s, 2 C, C(CH₃)₃), 45.03 (s, 1 C, fluorene), 47.47 (s, 1 C, CH₂CH₂), 119.27 (s, 2 C, fluorene), 121.40 (s, 2 C, fluorene), 122.66 (s, 2 C, NCH), 124.79 (s, 2 C, fluorene), 129.65 (s, 2 C, $C_6H_2Me_3$), 130.40 (s, 1 C, $ipso-C_6H_2Me_3$), 133.88 (s, 2 C, $ipso-C_6H_2Me_3$), 137.95 (s, 1 C, Cylidene), 138.31 (s, 2 C, ipso-fluorene), 141.03 (s, 1 C, ipso-C₆H₂Me₃), 145.08 (s, 2 C, ipso-fluorene), 150.41 (s, 2 C, ipso-fluorene). Anal. calcd for C₃₅H₄₃BrN₂ (%): C 73.54, H 7.58, N 4.90. Found: C 72.97, H 7.27, N 4.34.

Synthesis of complex (^{rBu}Flu-NHC)Sc(CH₂SiMe₃)₂ (1a)

(^{tBu}FluH-NHC-H)Br (0.209 g, 0.366 mmol) and LiCH₂SiMe₃ (0.035 g, 0.366 mmol) and 10 mL toluene were added to a flask. After reacting for 1 h under vigorous stirring, the reaction mixture was added to a toluene solution (10 mL) of Sc(CH₂SiMe₃)₃(THF)₂ (0.165 g, 0.366 mmol). The mixture remained stirring for another 12 h at 30 °C until turned to clear solution. Concentration, filtration and cooling at -30 °C afforded yellow solid **1a** (0.149 g, 57.4%). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ –1.44, –1.40 (AB, ${}^{2}J_{H-H} = 10.5 \text{ Hz}, 4 \text{ H}, \text{ Sc-C}H_{2}\text{SiMe}_{3}), 0.21 \text{ (s, } 18 \text{ H}, \text{ Sc-C}H_{2}\text{Si}Me_{3}),$ 1.57 (s, 18 H, C(CH₃)₃), 1.90 (s, 6 H, C₆H₂Me₃), 2.18 (s, 3 H, $C_6H_2Me_3$), 3.09 (t, ${}^{3}J_{H-H} = 5.1$ Hz, 2 H, CH_2CH_2), 3.87 (t, ${}^{3}J_{H-H} =$ 5.1 Hz, 2 H, CH₂CH₂), 5.91 (d, ${}^{3}J_{H-H} = 1.5$ Hz, 1 H, NCH), 6.13 $(d, {}^{3}J_{H-H} = 1.5 \text{ Hz}, 1 \text{ H}, \text{NC}H), 6.74 (s, 2 \text{ H}, C_{6}H_{2}\text{Me}_{3}), 7.38 (d,$ ${}^{3}J_{H-H} = 8.4$ Hz, 2 H, fluorene), 7.40 (s, 2 H, fluorene), 8.43 (d, ${}^{3}J_{H-H} = 8.4$ Hz, 2 H, fluorene). ${}^{13}C$ NMR (75 MHz, C₆D₆, 25 °C): δ 4.93 (s, 6 C, Sc-CH₂SiMe₃), 19.39 (s, 2 C, C₆H₂Me₃), 21.40 (s, 1 C, C₆H₂Me₃), 27.44 (s, 1 C, CH₂CH₂), 32.31 (s, 6 C, C(CH₃)₃), 35.73 (s, 2 C, C(CH₃)₃), 49.64 (br, 2 C, Sc-CH₂SiMe₃), 52.33 (s, 1 C, CH₂CH₂), 93.89 (s, 1 C, *ipso*-fluorene), 113.93 (s, 2 C, fluorene), 117.75 (s, 2 C, ipso-fluorene), 119.50 (s, 2 C, fluorene), 121.69 (s, 1 C, NCH), 122.18 (s, 1 C, NCH), 125.13 (s, 2 C, fluorene), 129.75 (s, 2 C, C₆H₂Me₃), 133.16 (s, 2 C, *ipso*-fluorene), 135.63 (s, 2 C, *ipso-C*₆H₂Me₃), 136.76 (s, 1 C, *ipso-C*₆H₂Me₃), 139.97 (s, 1 C, *ipso-C*₆H₂Me₃), 147.84 (s, 2 C, *pso-*fluorene), 187.68 ppm (br, 1 C, Sc- C_{vlidene}); Anal. calcd for C₄₃H₆₃ScN₂Si₂ (%): C 72.83, H 8.96, N 3.95. Found: C 72.17, H 8.33, N 3.21.

Synthesis of complex ('BuFlu-NHC)Lu(CH₂SiMe₃)₂ (1d)

Following the procedure described above, treatment of ("Bu FluH-NHC-H)Br (0.209 g, 0.366 mmol) with LiCH₂SiMe₃ (0.035 g, 0.366 mmol) and Lu(CH₂SiMe₃)₃(THF)₂ (0.213 g, 0.366 mmol) in 20 mL toluene generated yellow single crystals 1d in a 61.5% yield (0.189 g). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ -2.17, -2.11 $(AB, {}^{2}J_{H-H} = 10.8 \text{ Hz}, 4 \text{ H}, Lu-CH_{2}SiMe_{3}), 0.23 \text{ (s, 18 H, Lu-}$ CH₂SiMe₃), 1.59 (s, 18 H, C(CH₃)₃), 1.88 (s, 6 H, C₆H₂Me₃), 2.19 (s, 3 H, $C_6H_2Me_3$), 3.14 (t, ${}^{3}J_{H-H} = 5.2$ Hz, 2 H, CH_2CH_2), 3.91 (t, ${}^{3}J_{H-H} = 5.2 \text{ Hz}, 2 \text{ H}, \text{CH}_{2}\text{CH}_{2}$), 5.92 (d, ${}^{3}J_{H-H} = 1.6 \text{ Hz}, 1 \text{ H}, \text{NCH}$), 6.14 (d, ${}^{3}J_{H-H} = 1.6$ Hz, 1 H, NCH), 6.75 (s, 2 H, C₆H₂Me₃), 7.38 (d, ${}^{3}J_{H-H} = 8.8$ Hz, 2 H, fluorene), 7.43 (s, 2 H, fluorene), 8.38 (d, ${}^{3}J_{\text{H-H}} = 8.8 \text{ Hz}, 2 \text{ H}, \text{fluorene}$). ${}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{C}_{6}\text{D}_{6}, 25 \,^{\circ}\text{C})$: δ 5.32 (s, 6 C, Lu-CH₂SiMe₃), 19.15 (s, 2 C, C₆H₂Me₃), 21.39 (s, 1 C, C₆H₂Me₃), 27.62 (s, 1 C, CH₂CH₂), 32.20 (s, 6 C, C(CH₃)₃), 35.73 (s, 2 C, C(CH₃)₃), 47.70 (s, 2 C, Lu-CH₂SiMe₃), 52.77 (s, 1 C, CH₂CH₂), 91.17 (s, 1 C, ipso-fluorene), 112.88 (s, 2 C, fluorene), 116.34 (s, 2 C, ipso-fluorene), 118.84 (s, 2 C, fluorene), 120.98 (s, 1 C, NCH), 122.11 (s, 1 C, NCH), 124.44 (s, 2 C, fluorene), 129.94 (s, 2 C, C₆H₂Me₃), 133.70 (s, 2 C, ipso-fluorene), 135.49 (s, $2 C, ipso-C_6H_2Me_3$, 136.20 (s, 1 C, ipso-C_6H_2Me_3), 140.24 (s, 1 C, *ipso-C*₆H₂Me₃), 148.20 (s, 2 C, *ipso-*fluorene), 199.08 ppm (s, 1 C, Lu-C_{vlidene}); Anal. calcd for C₄₃H₆₃LuN₂Si₂ (%): C 61.55, H 7.57, N 3.34. Found: C 60.42, H 7.51, N 3.23.

Crystal data for 1d

 $C_{43}H_{63}LuN_2Si_2$, M = 839.10, monoclinic, space group $P2_1/c$, a = 11.2455(6), b = 23.7372(12), c = 33.4091(17) Å, $\beta = 92.5170(10)^\circ$, V = 8909.5(8) Å³, Z = 8, $\rho_{calcd} = 1.251$ g cm⁻³, μ (MoKa) = 2.298 mm⁻¹, T = 187(2) K, $\lambda = 0.71073$ Å, 49.863 reflections measured, and 17.559 reflections with $I > 2\sigma(I)$. $R_{int} = 0.0445$, final $R_1 = 0.0374$ (observed data), $wR_2 = 0.0852$ (all data).

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