# Rare earth metal bis(alkyl) complexes bearing amino phosphine ligands: Synthesis and catalytic activity toward ethylene polymerization

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## Abstract

Reactions of neutral amino phosphine compounds $HL^{1-3}$ with rare earth metal tris(alkyl)s, $Ln(CH_2SiMe_3)_3(THF)_2$, afforded a new family of organolanthanide complexes, the molecular structures of which are strongly dependent on the ligand framework. Alkane elimination reactions between 2-$(CH_3NH)$-$C_6H_4P(Ph)_2$ ($HL^1$) and $Lu(CH_2SiMe_3)_3(THF)_2$ at room temperature for 3 h generated mono(alkyl) complex $(L^1)_2Lu(CH_2SiMe_3)(THF)$ (**1**). Similarly, treatment of 2-$(C_6H_5CH_2NH)$-$C_6H_4P(Ph)_2$ ($HL^2$) with $Lu(CH_2SiMe_3)_3(THF)_2$ afforded $(L^2)_2Lu(CH_2SiMe_3)(THF)$ (**2**), selectively, which gradually deproportionated to a homoleptic complex $(L^2)_3Lu$ (**3**) at room temperature within a week. Strikingly, under the same condition, 2-$(2,6$-$Me_2C_6H_3NH)$-$C_6H_4P(Ph)_2$ ($HL^3$) swiftly reacted with $Ln(CH_2SiMe_3)_3(THF)_2$ at room temperature for 3 h to yield the corresponding lanthanide bis(alkyl) complexes $L^3Ln(CH_2SiMe_3)_2(THF)_n$ (**4a**: Ln = Y, $n = 2$; **4b**: Ln = Sc, $n = 1$; **4c**: Ln = Lu, $n = 1$; **4d**: Ln = Yb, $n = 1$; **4e**: Ln = Tm, $n = 1$) in high yields. All complexes have been well defined and the molecular structures of complexes **1**, **2**, **3** and **4b**–**e** were confirmed by X-ray diffraction analysis. The scandium bis(alkyl) complex activated by $AlEt_3$ and $[Ph_3C][B(C_6F_5)_4]$, was able to catalyze the polymerization of ethylene to afford linear polyethylene.
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## 1. Introduction

Rare earth metal alkyl complexes have gathered upsurge in research interest in the past decade, because they are highly active single component catalysts or crucial precursors of the cationic counterparts under the activation of MAO or borate toward olefin polymerizations [1] and highly regio- or stereoselective polymerizations of conjugated monomers [2] and polar monomers [3]. The ancillary ligands being attempted to stabilize rare earth metal alkyl species, up to date, have been dominated by cyclopentadie-

nyl environment and their derivatives [4]. Heteroatom compounds have attracted more and more attention recently due to their strong metal–ligand bonds and exceptional and tunable steric and electronic features required for compensating coordinative unsaturation of metal centers and catalytic activity toward polymerization. The majority of the proceeding studies involves chelating ligands such as bidentate amidinates [5], guanidinates [6], β-diketiminates [7], salicylaldiminates [8], etc. Whereas, formation of solvent or salt adduct, dimerization or ligand redistribution hinder the isolation of rare earth metal alkyl complexes especially bis(alkyl) complexes supported by such heteroatom compounds. Until recently, some N,N-bidentate ligands with exclusively "hard" donors, have been successfully introduced by Hessen's and Piers' groups, respectively,

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to stabilize bis(alkyl) complexes based on "hard" Lewis acidic rare earth metal centers [9]. The auxiliaries containing sterically demanding and "soft" phosphine electron donors, preferred to stabilize more acidic metal center, have been applied in transition metal chemistry. Fryzuk and co-workers have shown that zirconium complexes supported by multidentate amido phosphine ligands that contain –CH$_2$SiMe$_2$– back-bone are capable of nitrogen activation [10]. The o-phenylene-derivatives of amido-phosphine ligands reported by Liang [11] have been proved to be more robust in palladium complexes that are highly active to Heck reaction and Suzuki coupling, which was also introduced to support alkali metal complexes by Izod [12]. However, organolanthanide complexes bearing "soft" electronic donor of phosphine have remained less explored, as rare earth metal ions favor to coordinate to hard donors. Recently, rare earth metal halide or amido complexes supported by flexible bis(phosphineimino)methanids have been investigated by Roesky group [13]. Izod reported a rare earth metal iodide complex supported by donor-functionalized phosphide ligand, whereas, the sequential alkylation of metal iodide arouses deprotonation [14]. Up to date successfully isolated lanthanide dialkyl complexes are stabilized by P,N-multidentate ligands [15]. Our group also demonstrated that P,N-bidentate phosphino aldiminates are good candidates to stabilize bis(alkyl) species with six-membered-metallocycle coordination, and the isolated complexes are efficient initiators for the ring-opening polymerization of lactide [16]. Here we wish to report the synthesis of a series of lanthanide mono- or bis(alkyl) complexes bearing N-arylated or N-alkylated amino-phosphine auxiliaries, which combined with metal ion to generate rigid five-membered-metallocycle coordination. The polymerization of ethylene initiated by the scandium bis(alkyl) species in the presences of aluminum tris(alkyl)s and organoborate was also presented.

## 2. Results and discussion

### 2.1. Syntheses and characterization of complexes

#### 2.1.1. Synthesis and characterization of complexes 1–3

The reaction of Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ and an equivalent of neutral N-alkylated amino phosphine, (2-diphenylphosphinophenyl)-N-(methyl)aniline (HL$^1$) was carried out in toluene at room temperature and kept stirring for 3 h. Removal of volatiles gave pale yellow residue, which was dissolved by a mixture of toluene and hexane. Pale yellow solid was isolated from the above mixture after cooled at −30 °C for 24 h. However, it was not the expected bis(alkyl) product but a mono(alkyl) complex, [2-(CH$_3$N)-C$_6$H$_4$P(Ph)$_2$]$_2$LuCH$_2$SiMe$_3$(THF) (1). The $^1$H NMR and $^{13}$C NMR spectra were indicative for the formation of complex 1 according to the loss of the signal for amino proton of the ligand around δ 4.98 and the appearance of resonances of methylene protons of LuCH$_2$Si(CH$_3$)$_3$ that shifted downfield compared to that in Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Scheme 1).
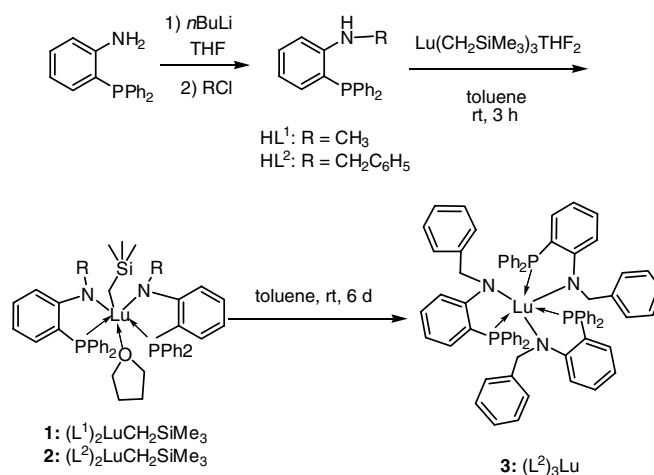


Scheme 1. Synthesis of complexes 1–3.

Switching to the bulky ligand HL$^2$, the major product isolated from the reaction was also mono(alkyl), [2-(C$_6$H$_5$CH$_2$N)-C$_6$H$_4$P(Ph)$_2$]$_2$LuCH$_2$SiMe$_3$(THF) (2). X-ray diffraction analysis defined that complex 2 was a monomer, adopting twisted tetragonal bipyramidal geometry with the alkyl carbon and phosphorous atoms axial and the THF oxygen and two nitrogen and a phosphorous atoms equatorial (Table 1, Fig. 1). The ligand coordinated to the lutetium ion in a bidentate mode. Complex 2 was unstable in solution at room temperature and slowly transferred to a homoleptic complex [2-(C$_6$H$_5$CH$_2$N)-C$_6$H$_4$P(Ph)$_2$]$_3$Lu (3) within a week due to ligand redistribution. In complex 3, all three ligands bonded to the metal ion with the chelated P and N atoms in bidentate modes and located around the central metal uniformly to generate trigonal bipyramidal geometry with the metal atom being the apex. No solvated THF was observed in the molecule (Fig. 2). The bond lengths of Lu–P (av. 2.953(4) Å for 2, av. 2.922(3) Å for 3), Lu–N (av. 2.230(14) Å for 2, av. 2.236(8) Å for 3) and Lu–C (2.326(18) Å) were comparable to those literature data [15,16], which did not need to discuss further (Tables 2 and 3).

#### 2.1.2. Synthesis and characterization of complexes 4a–e

We noted that the N-alkylated amino phosphines HL$^1$ and HL$^2$ could not support the highly unsaturated rare earth metal bis(alkyl) species because of their flexibility and deficit in spacial sterics. Thus, the rigid N-arylated compound 2-(2,6-Me$_2$C$_6$H$_3$NH)-C$_6$H$_4$P(Ph)$_2$ (HL$^3$) [11h] was chosen to react with 1 equiv of yttrium tris(alkyl)s, Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$, anticipated to generate the corresponding bis(alkyl) complex. The reaction performed smoothly at room temperature in toluene, leading to the isolation of the expected L$^3$Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (4a). It was evident from the $^1$H NMR spectrum that 4a was a monomer of bis(alkyl)s stabilized by mono-anionic L$^3$ fragment combined with two THF moieties. The resonances at δ −0.21 were assignable to the methylene protons of the 2 equiv metal alkyl species YCH$_2$SiMe$_3$, whilst those at δ

Table 1
Summary of crystallographic data for **2**, **3** and **4b–e**

| | 2 | 3 | 4b | 4c | 4d | 4e |
|---|---|---|---|---|---|---|
| Formula | $C_{58}H_{61}N_2OP_2SiLu$ | $C_{75}H_{63}N_3P_3Lu$ | $C_{44}H_{67}NOPSi_2Sc$ | $C_{44}H_{67}NOPSi_2Lu$ | $C_{44}H_{67}NOPSi_2Yb$ | $C_{38}H_{53}NOPSi_2Tm$ |
| Formula weight | 1067.09 | 1274.16 | 758.11 | 888.11 | 886.18 | 795.89 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 13.9822(13) | 15.0977(13) | 10.5599(9) | 10.5804(7) | 10.5672(6) | 10.5563(7) |
| $b$ (Å) | 23.079(2) | 16.4812(14) | 21.5029(18) | 21.7161(14) | 21.7677(13) | 21.7753(14) |
| $c$ (Å) | 17.5630(16) | 17.1770(15) | 19.5639(16) | 19.5813(13) | 19.6496(12) | 19.7009(13) |
| $\alpha$ (°) | 90 | 71.1310(10) | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 106.810(2) | 76.4280(10) | 94.478(2) | 94.9800(10) | 94.6670(10) | 94.5570(10) |
| $\gamma$ (°) | 90 | 88.057(2) | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 5425.3(9) | 3927.4(6) | 4428.8(6) | 4482.1(5) | 4504.9(5) | 4514.3(5) |
| $Z$ | 4 | 2 | 4 | 4 | 4 | 4 |
| $D_{calc}$ (g/cm$^3$) | 1.306 | 1.077 | 1.137 | 1.316 | 1.307 | 1.171 |
| $\mu$ (mm$^{-1}$) | 1.940 | 1.354 | 0.288 | 2.323 | 2.196 | 2.078 |
| $F(000)$ | 2184 | 1300 | 1640 | 1840 | 1836 | 1632 |
| Number of observed reflections | 10669 | 14853 | 8711 | 8789 | 8848 | 8864 |
| Number of parameters refined | 654 | 739 | 461 | 431 | 461 | 405 |
| Goodness-of-fit | 1.017 | 1.044 | 0.901 | 0.901 | 1.046 | 1.144 |
| $R_1$ | 0.1011 | 0.0646 | 0.0594 | 0.0384 | 0.0274 | 0.0529 |
| $wR_2$ | 0.2231 | 0.1375 | 0.1256 | 0.0821 | 0.0678 | 0.1835 |
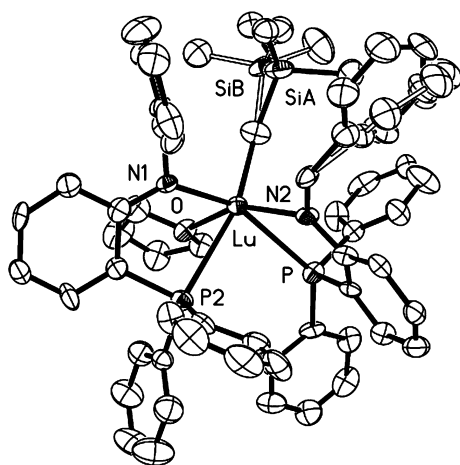


Fig. 1. X-ray structure of **2** with 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.
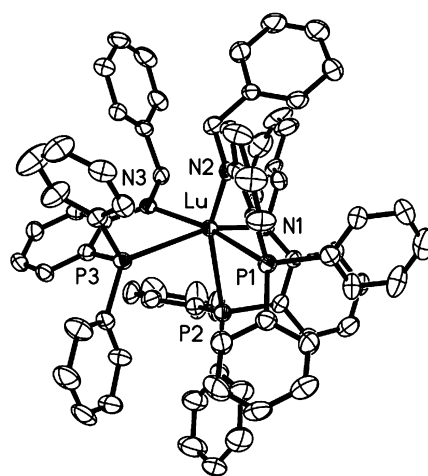


Fig. 2. X-ray structure of **3** with 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

1.37 and $\delta$ 3.72 were arising from the coordinated two THF molecules. Whereas, the repeated attempt to isolate single crystals of **4a** was failed. Monitoring the reaction by using NMR technique found that **4a** was unstable at room temperature. The signal of the methylene protons disappeared completely within 6 h, suggesting that **4a** transferred to unknown products.

Fortunately, employing $Sc(CH_2SiMe_3)_3(THF)_2$, the similar reaction with HL$^3$ afforded the anticipated phosphide scandium bis(alkyl)s, $L^3Sc(CH_2SiMe_3)_2(THF)$ (**4b**), quantitatively. The yellow crystals of **4b** grew from a mixture of toluene/hexane at $-30$ °C in 24 h. In addition, treatments

of the corresponding lutetium, ytterbium and thulium tris(alkyl)s with HL$^3$, respectively, afforded the analogous complexes $L^3Ln(CH_2SiMe_3)_2(THF)$ (**4c**: Ln = Lu; **4d**: Ln = Yb; **4e**: Ln = Tm) (Scheme 2). The $^1H$ NMR spectra of **4b** and **4c** had similar pattern to that of **4a**. The methylene protons of $LuCH_2SiMe_3$ species displaying a signal at $\delta$ $-0.30$ downfield shifted compared to $\delta$ $-0.60$ in $Lu(CH_2SiMe_3)_3(THF)_2$. The resonance for methylene protons of $ScCH_2SiMe_3$ unit showed at much lower field $\delta$ 0.31, which overlapped with silylmethyl ($SiMe_3$) protons. It was noteworthy that **4b** or **4c** was bonded by one THF molecule different from **4a** with two THF coordination. Both **4b** and **4c**

Table 2
Selected bond lengths (Å) and angles (°) from **2**

| | |
|---|---|
| Lu–N(1) | 2.230(11) |
| Lu–N(2) | 2.219(13) |
| Lu–C(49) | 2.333(17) |
| Lu–O | 2.353(11) |
| Lu–P(1) | 2. 985(4) |
| Lu–P(2) | 2.917(4) |
| N(1)–Lu–C(49) | 104.4(6) |
| N(2)–Lu–C(49) | 103.9(6) |
| N(1)–Lu–P(1) | 67.5(3) |
| N(2)–Lu–P(2) | 67.2(3) |
| C(49)–Lu–P(1) | 99.7(5) |
| C(51)–Lu–P(2) | 163.5(5) |

Table 3
Selected bond lengths (Å) and angles (°) from **3**

| | |
|---|---|
| Lu(1)–N(2) | 2.220(8) |
| Lu(1)–N(3) | 2.243(8) |
| Lu(1)–N(1) | 2.246(8) |
| Lu(1)–P(2) | 2.906(3) |
| Lu(1)–P(3) | 2.921(3) |
| Lu(1)–P(1) | 2.940(3) |
| N(2)–Lu(1)–N(3) | 103.8(3) |
| N(2)–Lu(1)–N(1) | 107.2(3) |
| N(3)–Lu(1)–N(1) | 107.9(3) |
| N(2)–Lu(1)–P(2) | 68.0(2) |
| N(3)–Lu(1)–P(3) | 67.1(2) |
| N(1)–Lu(1)–P(1) | 67.2(2) |
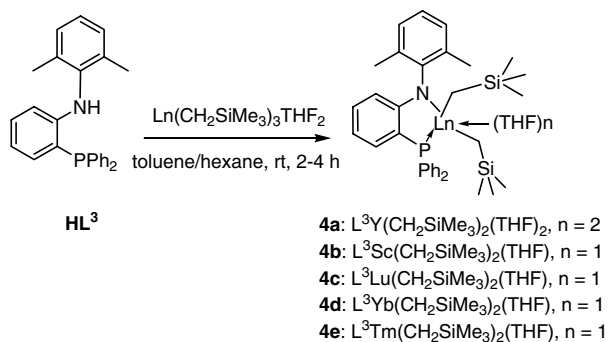


Scheme 2. Synthesis of complexes **4a**–**e**.

were stable without ligand redistribution in solution, which was probably attributed to the smaller ionic radii of Sc and Lu ions compared to that of Y ion. All complexes **4a**–**c** were $C_s$ symmetric in solution as the metal alkyl protons were equivalent. Complexes **4d** and **4e** did not give informative ^{1}H NMR spectra due to their paramagnetic nature.

X–ray diffraction analysis solved the overall molecular structures of complexes **4b**–**e** to be isomeric monomers. Each metal ion was chelated by N,P atoms of the phosphide ligand in bidentate mode, and a solvated THF molecule and two alkyl species locating in *cis*-positions, to generate distorted trigonal bipyramidal geometry around the metal center. The phosphorus donor and the THF molecule were

axial (av. P–Lu–O = 168.77°, Table 4) and the two alkyl carbon atoms and nitrogen atom of the ligand occupied the equatorial positions (Fig. 3, complex **4b**) [17]. The central metal ion sit out of the CCN plane with a distance of 0.207 Å for **4b**, 0.248 Å for **4c**, 0.251 Å for **4d** and 0.261 Å for **4e**, respectively, which were in contrast to complexes **2** and **3** where the Lu atom deviated from the CCN plane with much longer distance of 0.8387 Å for **2** and 0.9367 Å for **3**, which might be attributed to the crowded environment of metal centers. Interestingly, the rigid five-membered ring PC$_2$NLn was planar and almost perpendicular to the CCN plane with a dihedral angle 90.8° for **4b**, 91.6° for **4c**, 90.6° for **4d** and 91.6° for **4e**, respectively. Whereas in a closely related phosphine aldiminato complex [*o*-(PPh$_2$)C$_6$H$_4$CH$_2$NC$_6$H$_3$Me$_2$-2,6]Lu(CH$_2$SiMe$_3$)$_2$(THF) [16], the six-membered metallacycle NC(9)C$_2$PLn is much twisted due to the flexible feature of the ligand. The binding angle of amido phosphine ligand (P–Ln–N) was close to each other in complexes **4c**–**e** averaging 68.81°, but a larger angle was found in **4b** (72.12(7)°). This angle was comparable to those in complexes containing such rigid five-membered metallacycle, such as 67.46(3)° in complex **2**, 67.4(2)° in **3** and 65.83(7)° in (PNP$^{Ph}$)Lu(CH$_2$SiMe$_3$)$_2$ (THF) [15b], but smaller than 77.8(1)° in Sc(CH$_2$Si-Me$_3$)$_2$[N(SiMe$_2$CH$_2$PPri$_2$)$_2$] bearing flexible five-membered metallacycle [15a] and 78.53(7)° in L$^{2-Me}$Lu(CH$_2$SiMe$_3$)$_2$-(THF) containing six-membered metallacycle [16]. The C–Ln–C bond angles averaging 111.8° in complexes **4b**–**e** were slightly larger than 103.50(12)° [15b] found in the above mentioned complexes, which were comparable to those of C–Sc–C (113.5(2)°) [15a] and C–Y–C (119.5(2)°) in THF solvated amidinato yttrium bis(alkyl) complex [18], indicating the similar steric environment of the ligands. However, these bond angles were larger than those of C–Ln–C in the rare earth metal bis(alkyl) complexes supported by triazacyclononane (99.41(8)°) [19], triamino-amide (101.96(6)°) [20] and β-diketiminate (108.90(13)°) [21].

### 2.2. Catalysis on ethylene polymerization

Designing rare earth metal complexes possessing catalytic activity for ethylene polymerization has been an goal of organolanthanide chemists. *Ansa*-lanthanocene alkyls, linked and non-linked half-sandwich lanthanide hydrocarbyls [1,2g,h,k,9c,d], and the recent amidinato (non-metallocene) rare earth metal bis(alkyl)s [18,22] have been explored to exhibit high reactivity toward olefin polymerization.

Thus, these amido phosphine ligated rare earth metal bis(alkyl) complexes were investigated whether to have such performance. Complexes **4c**–**e** were inert even at the presences of both activators [Ph$_3$C][B(C$_6$F$_5$)$_4$] and AlEt$_3$ (Table 5, entries 1–3). Whereas strikingly, complex **4b** based on more Lewis acidic scandium ion was active at 20 °C and 1 bar of ethylene. The influences of the reaction conditions on the polymerization were investigated. At 40 °C, the catalytic activity of **4b** reached to 49 000 g/

Table 4
Selected bond lengths (Å) and angles (°) from **4b–e**

| | **4b** (Ln = Sc) | **4c** (Ln = Lu) | **4d** (Ln = Yb) | **4e** (Ln = Tm) |
|---|---|---|---|---|
| Ln–N | 2.131(3) | 2.236(3) | 2.239(2) | 2.243(6) |
| Ln–O | 2.175(2) | 2.268(3) | 2.295(2) | 2.301(5) |
| Ln–C(35) | 2.210(3) | 2.312(4) | 2.357(3) | 2.332(8) |
| Ln–C(31) | 2.240(3) | 2.359(4) | 2.328(3) | 2.362(8) |
| Ln–P | 2.8319(10) | 2.9289(11) | 2.9474(7) | 2.9597(19) |
| N–Ln–C(35) | 123.95(11) | 124.51(14) | 120.69(10) | 124.6(3) |
| N–Ln–C(31) | 120.84(11) | 119.97(14) | 124.47(10) | 120.1(3) |
| C(35)–Ln–C(31) | 112.55(13) | 112.08(16) | 111.31(11) | 111.4(3) |
| N–Ln–P | 72.12(7) | 69.26(9) | 68.87(6) | 68.29(16) |
| C(35)–Ln–P | 91.84(9) | 92.29(12) | 91.89(8) | 92.3(2) |
| C(31)–Ln–P | 91.13(9) | 91.60(11) | 92.37(8) | 91.8(2) |
| O–Lu–P | 169.89(7) | 168.03(8) | 168.31(6) | 168.84(15) |
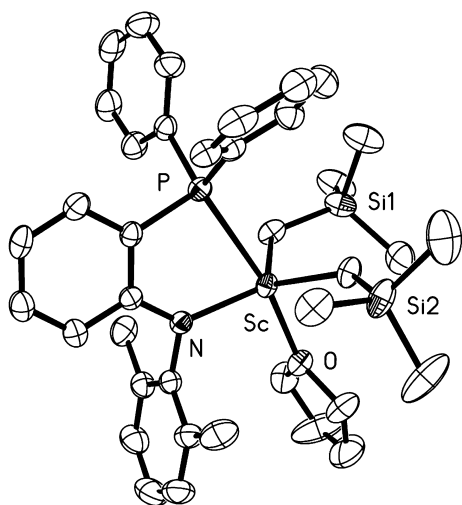


Fig. 3. X-ray structure of **4b** with 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

(mol Ln bar h), which was more than double of that (22 000 g/(mol Ln bar h)) at 20 °C. Meanwhile the molecular weight of the resultant polyethylene (PE) was also increased and the molecular weight distribution did not change obviously. Whereas, increasing the temperature to 50 °C, the molecular weight of PE lowered significantly and the molecular weight distribution became wider, although the activity dropped slightly. If the polymerization was performed at much higher temperature (60 °C), both catalytic activity and molecular weight of PE decreased greatly, which could be attributed to the decomposition of the complex and the rapid chain transfer reaction at high temperature (Table 5, entries 5–8). It was reasonable that prolonged reaction time would arouse high yield of PE. Almost no polymer could be isolated if the reaction time was shorter than 10 min, however, the catalytic activity decreased if polymerization carried out longer than 30 min (Table 5, entries 9–11).

Table 5
Polymerization of ethene under various conditions[a]

| Entry | Cat | Temperature (°C) | $t$ (min) | $t$ (min) (Al + Cat) | Yield (g) | Activity[d] ($\times 10^{-4}$) | $M_n^e$ ($\times 10^{-3}$) | $M_w$ ($\times 10^{-3}$) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **4c** | 20 | 30 | 5 | 0 | | | | |
| 2 | **4d** | 20 | 30 | 5 | 0 | | | | |
| 3 | **4e** | 20 | 30 | 5 | 0 | | | | |
| 4 | **4b** | 20 | 30 | 5 | 0.22 | 2.2 | 162.4 | 433.3 | 2.67 |
| 5 | **4b** | 30 | 30 | 5 | 0.37 | 3.7 | 225.8 | 560.6 | 2.48 |
| 6 | **4b** | 40 | 30 | 5 | 0.49 | 4.9 | 253.5 | 589.7 | 2.33 |
| 7 | **4b** | 50 | 30 | 10 | 0.41 | 4.1 | 89.7 | 535.5 | 5.97 |
| 8 | **4b** | 60 | 30 | 60 | 0.30 | 3.0 | 15.8 | 173.0 | 10.96 |
| 9 | **4b** | 40 | 10 | 5 | 0.03 | | | | |
| 10 | **4b** | 40 | 20 | 60 | 0.13 | 2.0 | 14.8 | 157.1 | 10.61 |
| 11 | **4b** | 40 | 30 | 60 | 0.18 | 1.8 | 20.5 | 199.8 | 9.73 |
| 12 | **4b** | 40 | 30 | 10 | 0.31 | 3.1 | 139.6 | 575.6 | 4.12 |
| 13[b] | **4b** | 50 | 30 | 5 | 1.10 | 4.4 | 138.2 | 592.2 | 4.29 |
| 14[c] | **4b** | 40 | 30 | 5 | 0.24 | 2.4 | 97.5 | 437.2 | 4.49 |

Conditions:
[a] Toluene 20 mL, catalyst: 20 μmol, AlEt$_3$: 100 μmol, [Ph$_3$C][B(C$_6$F$_5$)$_4$]: 20 μmol, 1 bar ethylene pressure unless otherwise noted.
[b] 5 bar ethylene pressure.
[c] AlEt$_3$: 50 μmol.
[d] g(PE)/(mol Ln bar h).
[e] Determined by GPC 220 type high-temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

Varying the ethylene pressure from 1 to 5 bar increased the yield of PE obviously whereas which seemed to have less influence on the activity (Table 5, entries 7 and 13). In contrast, AlEt$_3$-to-borate ratio affected the performance of **4b**. When the value was decreased from 5:1 to 2.5:1, the catalytic activity halved (Table 5, entries 6 and 14). To our surprise, an increase of the activation time of complex **4b** by AlEt$_3$ led to obvious drop in activity of **4b** and significantly broadened the molecular weight distribution (Table 5, entries 7–12). This suggested that at long activation time some unknown less active species were formed. It was also noteworthy when the reaction medium contained minimum amount of THF, the catalytic system **4b**/AlEt$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] lost its activity for ethylene polymerization completely. This might be explained that the strong electron donor THF intended to occupy the blank space of the cationic central metal ion to prohibit the coordination of non-polar ethylene monomer [18].

Based on the polymerization results, the mechanism of polymerization and the roles of the three components could be described as follow. When **4b** was treated with [Ph$_3$C][B(C$_6$F$_5$)$_4$], cationic species L$^3$Sc$^+$(CH$_2$SiMe$_3$)-(THF) were generated as shown in the $^1$H NMR spectrum according to the release of Ph$_3$CCH$_2$SiMe$_3$ [2h,k], which were the initiation species. However, the cationic units showed no activity at the absence of AlEt$_3$ in contrast to the previous reported systems [2h,k,22d]. This could be attributed to the coordination of THF molecule and too electron negative nature of the ligand, which inhibited the coordination and insertion of non-polar ethylene monomer. Thus, the addition of AlEt$_3$ activated the cationic units, which could be explained that AlEt$_3$ extruded the impurities in the system, abstracted the coordinated THF molecule and stabilized the cationic metal center [9c,d,23].

According to Mandelken's protocol and the reported result [24], all of the corresponding carbon resonances in high-temperature $^{13}$C NMR spectrum were assigned unambiguously, in which there were no signals for the branches, indicating linear microstructure of the isolated polyethylene.

## 3. Conclusion

A series of amido phosphine supported organolanthanide complexes have been prepared by treatment of rare earth metal tris(alkyl)s with the neutral amido phosphine compounds via alkane elimination. The N-alkylated amido phosphine ligand bonded to the central metal to generate a twisted flexible five-membered metallocycle to stabilize rare earth metal mono(alkyl) species. Whereas, the N-arylated amido phosphine ligand formed a rigid five-membered metallocyclic coordination, which was able to support rare earth metal bis(alkyl) units. Moreover, the resultant bis(alkyl) complex based on more Lewis acidic scandium ion, upon activation with equimolar [Ph$_3$C][B(C$_6$F$_5$)$_4$] in

the presence of 5 equiv aluminum triethyls, was active toward ethylene polymerization with modest activity at room temperature under normal pressure to give linear polyethylene.

## 4. Experimental

### 4.1. 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 an MBRAUN glovebox. All solvents were purified from 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, $^{13}$C NMR spectra were recorded on a Bruker AV400 or AV600 (FT, 400 MHz for $^1$H; 100 MHz for $^{13}$C or FT, 600 MHz for $^1$H; 150 MHz for $^{13}$C) spectrometer. NMR assignments were confirmed by the $^1$H–$^1$H COSY and $^1$H–$^{13}$C HMQC experiments when necessary. The NMR spectra of the polyethylene were recorded on a Varian Unity 400 MHz spectrometer with o-dichlorobenzene as the solvent at 120 °C. IR spectra were recorded on VERTEX 70 FT-IR or IFS66V/S FTIR. The molecular weight and the polydispersitiy of the polymer samples were determined at 150 °C by a PLGPC 220 type high-temperature chromatograph equipped with three PLgel 10 µm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). (2-Diphenylphosphino) aniline and (2-diphenylphosphinophenyl)-N-(methyl) aniline (HL$^1$) were prepared according to the literature [25]. N-(2-Diphenylphosphinophenyl)-2,6-dimethylaniline was prepared according to the literature [11h].

### 4.2. 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 −86 °C on a Bruker SMART APEX diffractometer with a CCDC area detector, using graphite monochromated Mo K radiation ($\lambda = 0.71073$ 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 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.

## 4.3. Syntheses of complexes

### 4.3.1. Syntheses of (2-diphenylphosphinophenyl)-N-(benzyl) aniline (HL$^2$)

At $-78$ °C under stirring, a THF solution (40 mL) of the compound (2-diphenylphosphino)aniline (2.77 g, 10.00 mmol) was added $n$BuLi dropwise (6.56 mL, 10.00 mmol) and reacted for 1h, then, benzyl chloride (1.21 mL, 10.00 mmol) was syringed into the system. After maintained for 2 h at $-78$ °C, the reaction mixture was warmed to room temperature gradually and kept stirring overnight. Volatiles were removed off under reduced pressure and degassed water (10 mL) was added. The resultant mixture was extracted with deoxygenated dichloromethane ($20 \times 3$ mL). The organic phase was separated, dried over degassed MgSO$_4$, and filtered. Removal of dichloromethane afforded residue, which was recrystallized from CH$_2$Cl$_2$/CH$_3$CH$_2$OH at $-30$ °C for several days to give white solid of HL$^2$ (3.32 g, 90%). $^1$H NMR (400 MHz, DMSO-$d^6$, 25 °C): $\delta$ 4.35 (d, $J_{H-H} = 6$ Hz, 2H, CH$_2$), 5.74 (m, 1H, NH), 6.51–6.54 (m, 2H, $o$-PC$_6$H$_4$N, $p$-NC$_6$H$_4$P), 6.62–6.65 (m, 1H, $o$-NC$_6$H$_4$P), 7.01–7.19 (m, 4H, $o,p$-CH$_2$C$_6$H$_5$, $p$-PC$_6$H$_4$N), 7.21–7.28 (m, 6H, $m$-CH$_2$C$_6$H$_5$, $o$-P(C$_6$H$_5$)$_2$), 7.40–7.42 (m, 6H, $m$, $p$-P(C$_6$H$_5$)$_2$). $^{13}$C NMR (100 MHz, DMSO-$d^6$, 25 °C): $\delta$ 46.46 (s, 1C, CH$_2$), 110.53 (s, 1C, $p$-NC$_6$H$_4$P), 116.59 (s, 1C, $p$-NC$_6$H$_4$P), 118.25 (d, 1C, $^1J_{C-P} = 9$ Hz, ipso-PC$_6$H$_4$N), 126.55 (s, 1C, $p$-CH$_2$C$_6$H$_5$), 126.68 (s, 2C, $o$-CH$_2$C$_6$H$_5$), 128.19 (s, 2C, $m$-CH$_2$C$_6$H$_5$), 128.66 (d, $^3J_{C-P} = 6$ Hz, 4C, $m$-P(C$_6$H$_5$)$_2$), 128.85 (s, 2C, $p$-P(C$_6$H$_5$)$_2$), 130.34 (s, 1C, $p$-PC$_6$H$_4$N), 133.24 (d, $^2J_{C-P} = 19$ Hz, 4C, $o$-P(C$_6$H$_5$)$_2$), 133.65 (s, 1C, $o$-PC$_6$H$_4$N), 135.32 (d, $^1J_{C-P} = 9$ Hz, 2C,), 139.66 (s, 1C, ipso-CH$_2$C$_6$H$_5$), 150.42 (d, 1C, ipso-NC$_6$H$_4$P). IR (KBr pellets): $v$ 3396(m), 3045(m), 3028(m), 2861(m), 1961(w), 1897(w), 1824(w), 1771(w), 1581(s), 1567(s), 1497(s), 1475(s), 1433(s), 1357(m), 1321(s), 1298(s), 1289(s), 1254(m), 1232(w), 1177(m), 1165(m), 1131(w), 1089(m), 1069(m), 1042(w), 1025(m), 999(w), 913(w), 840(m), 807(m), 797(m), 745(s), 697(s). Anal. Calc. for C$_{25}$H$_{22}$NP: C, 81.72; H, 6.04; N, 3.81. Found: C, 81.68; H, 6.10; N, 3.79%.

### 4.3.2. Synthesis of [2-(CH$_3$N)-C$_6$H$_4$P(Ph)$_2$]$_2$Lu(CH$_2$SiMe$_3$)(THF) (1)

To a hexane solution (2.0 mL) of Lu(CH$_2$SiMe$_3$)$_3$THF$_2$ (0.175 g, 0.301 mmol), 1 equiv of HL$^1$ (0.087 g, 0.301 mmol in 4 mL toluene) was dropwise added at room temperature and reacted for 3 h. After concentrated, the solution was added small amount of hexane and then cooled to $-30$ °C. Pale yellow solid was isolated overnight, which was washed with hexane (1 mL) carefully to remove off impurities and dried in vacuum to afford pale yellow powders of 1 in 63% yield (0.086 g). $^1$H NMR (400 MHz, C$_6$D$_6$, 25 °C): $\delta$ $-0.45$ (s, 2H, CH$_2$SiMe$_3$), 0.38 (s, 9H, SiMe$_3$), 1.09 (br, 4H, THF), 3.19 (br, 6H, ArMe), 3.74 (br, 4H, THF), 6.58 (t, $J_{H-H} = 7.2$ Hz, 2H, $p$-NC$_6$H$_4$P), 6.65 (br, 2H, $o$-NC$_6$H$_4$P), 7.02–7.24 (m, 18H, $o$-PC$_6$H$_4$N,

$m$-P(C$_6$H$_5$)$_2$, $m$-NC$_6$H$_4$P, $p$-PC$_6$H$_5$), 7.43–7.47 (m, 8H, $o$-P(C$_6$H$_5$)$_2$). $^{13}$C NMR (100 MHz, C$_6$D$_6$, 25 °C): $\delta$ 4.93 (s, 3C, SiMe$_3$), 25.58 (s, 2C, THF), 33.33 (s, 1C, CH$_2$SiMe$_3$), 36.64 (s, 1C, NCH$_3$), 71.90 (s, 2C, THF), 111.91 (s, 2C, $o$-NC$_6$H$_4$P), 114.86 (s, 2C, $p$-NC$_6$H$_4$P), 129.05 (br, 8C, $m$-P(C$_6$H$_5$)$_2$), 129.51 (s, 4C, $p$-P(C$_6$H$_5$)$_2$), 134.06 (br, 8C, $o$-P(C$_6$H$_5$)$_2$), 135.50 (br, 4C, ipso-P(C$_6$H$_5$)$_2$), 136.17 (s, 2C, $o$-PC$_6$H$_4$N), 165.60 (d, $^2J_{C-P} = 23$ Hz, 2C, ipso-NC$_6$H$_4$P). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 161.90 MHz) $\delta$ $-4.27$. IR (KBr pellets): $v$ 3689(w), 3380(w), 3054(s), 2950(s), 2891(s), 2856(s), 2784(s), 1963(w), 1896(w), 1817(w), 1775(w), 1588(s), 1459(s), 1437(s), 1414(s), 1312(s), 1300(s), 1247(m), 1168(w), 1126(m), 1094(w), 1069(w), 1037(m), 1027(m), 998(w), 914(w), 857(s), 746(s), 723(s), 694(s) cm$^{-1}$. Anal. Calc. for C$_{46}$H$_{53}$N$_2$OP$_2$SiLu (914.93): C, 60.39; H, 5.84; N, 3.06. Found: C, 59.95; H, 5.74; N, 2.88%.

### 4.3.3. Synthesis of [2-(C$_6$H$_5$CH$_2$N)-C$_6$H$_4$P(Ph)$_2$]$_2$LuCH$_2$SiMe$_3$(THF) (2)

To a hexane solution (2.0 mL) of Lu(CH$_2$SiMe$_3$)$_3$THF$_2$ (0.175 g, 0.301 mmol), 1 equiv of HL$^2$ (0.128 g, 0.301 mmol in 4 mL toluene) was dropwise added at room temperature. The mixture was stirred for 3 h, then concentrated and added 3 mL hexane. The mixture was cooled to $-30$ °C and kept overnight to afford pale yellow solid, which was washed with small amount of hexane to remove off impurities and then dried in vacuum to give complex 2 in 75% yield (0.120 g). The crystal grew from a solution of toluene/hexane (1:3 vol/vol) at $-30$ °C within a couple of days. $^1$H NMR (400 MHz, C$_6$D$_6$, 25 °C): $\delta$ $-0.55$ (s, 2H, CH$_2$SiMe$_3$), 0.24 (s, 9H, SiMe$_3$), 1.24 (br, 8H, THF), 3.81(br, 8H, THF), 5.10 (br, 2H, CH$_2$C$_6$H$_5$), 6.51 (t, 4H, $o,p$-NC$_6$H$_4$P), 6.99 (t, $J_{H-H} = 8$ Hz, 2H, $m$-NC$_6$H$_4$P), 7.13–7.32(m, 32H, P(C$_6$H$_5$)$_2$, CH$_2$C$_6$H$_5$, $o,m$-PC$_6$H$_4$N), 7.43 (br, 8H, $o$-P(C$_6$H$_5$)$_2$). $^{13}$C NMR (100 MHz, C$_6$D$_6$, 25 °C): $\delta$ 4.88 (s, 9C, SiMe$_3$), 25.86 (s, 2C, THF), 37.76 (s, 1C, CH$_2$SiMe$_3$), 48.04 (s, 2C, CH$_2$Ph), 71.36 (s, 2C, THF), 114.69 (s, 2C, $o$-NC$_6$H$_4$P), 115.46 (s, 2C, $p$-NC$_6$H$_4$P), 126.40 (s, 4C, $p$-CH$_2$C$_6$H$_5$), 128.01 (s, 4C, $o$-CH$_2$C$_6$H$_5$), 129.26 (d, $^3J_{C-P} = 7$ Hz, 8C, $m$-P(C$_6$H$_5$)$_2$), 129.82 (s, 4C, $p$-P(C$_6$H$_5$)$_2$), 133.50 (s, 2C, $p$-PC$_6$H$_4$N), 134.29 (d, $^2J_{C-P} = 12$ Hz, 8C, $o$-P(C$_6$H$_5$)$_2$), 135.48 (s, 4C, $o$-CH$_2$C$_6$H), 142.08 (s, 2C, ipso-CH$_2$C$_6$H$_5$), 163.86 (s, 2C, ipso-NC$_6$H$_4$P). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 161.90 MHz) $\delta$ $-0.94$. IR (KBr pellets): $v$ 3395(w), 3054(m), 2999(w), 2947(m), 2889(w), 2817(w), 2794(w), 1959(w), 1895(w), 1811(w), 1771(w), 1576(s), 1544(m), 1493(s), 1479(m), 1457(s), 1434(s), 1353(m), 1313(s), 1290(s), 1269(s), 1249(m), 1236(m), 1165(s), 1134(m), 1093(m), 1069(w), 1039(s), 1026(s), 1000(w), 884(s), 852(s), 818(s), 747(s), 731(s), 696(s) cm$^{-1}$. Anal. Calc. for C$_{58}$H$_{61}$N$_2$OP$_2$SiLu (1067.09): C, 65.28; H, 5.76; N, 2.63. Found: C, 64.87; H, 5.33; N, 2.18%.

### 4.3.4. Synthesis of [2-(C$_6$H$_5$CH$_2$N)-C$_6$H$_4$P(Ph)$_2$]$_3$Lu (3)

To a hexane solution (2.0 mL) of Lu(CH$_2$SiMe$_3$)$_3$THF$_2$ (0.175 g, 0.301 mmol), 1 equiv of HL$^2$ (0.128 g, 0.301 mmol

in 4 mL toluene) was dropwise added at room temperature. The mixture was then stirred for 24 h. Removal of the volatiles gave a deep red solid, which was dissolved with 2 mL toluene and kept at room temperature for 5 days to give colorless crystalline complex **3** (0.087 g, 68%). IR (KBr pellets): $\nu$ 3388(w), 3054(w), 3028(w), 2863(w), 1955(w), 1586(s), 1572(s), 1501(s), 1478(w), 1446(s), 1434(s), 1360 (w), 1316(m), 1288(m), 1164(m), 1137(w), 1092{w), 1070(w), 1041(w), 1027(m), 999(w), 901(w), 845(w), 816 (w), 745(s), 696(s) cm$^{-1}$. Anal. Calc. for $C_{75}H_{63}N_3P_3Lu$ (1274.21): C, 70.69; H, 4.98; N, 3.30. Found: C, 70.11; H, 4.31; N, 2.91%.

### 4.3.5. Synthesis of [2-(2,6-Me₂C₆H₃N)-C₆H₄P(Ph)₂]Y(CH₂SiMe₃)₂ (THF)₂ (4a)

In a NMR sample tube, a solution of Y(CH₂Si-Me₃)₃THF₂ (0.02 g, 0.04 mmol) in $C_6D_6$ (0.6 mL) was added equimolar HL³ (0.015 g, 0.04 mmol). The obtained solution was transferred to a NMR sample tube and the reaction was monitored by ¹H NMR technique at different reaction time. The molar ratio of complexes was calculated on the relative integral intensity to TMS. After 20 min, HL³ was completely consumed and after 6 h, the signal of C*H₂*SiMe₃ and CH₂Si*Me₃* nearly disappeared. ¹H NMR (400 MHz, $C_6D_6$, 25 °C): $\delta$ −0.21 (s, 4H, C*H₂*SiMe₃), 0.08 (s, SiMe₄), 0.30 (s, 18H, SiMe₃), 1.37 (s, 16H, THF), 2.29 (s, 6H, Ar*Me*), 3.73 (s, 16H, THF), 6.01 (d, $J_{H-H}$ = 7.2 Hz, 1H, o-NC₆H₄P), 6.54 (t, $J_{H-H}$ = 7.2 Hz, 1H, p-NC₆H₄P), 6.94 (t, $J_{H-H}$ = 7.2 Hz, 1H, p-NC₆H₃), 7.04–7.07 (dt, 3H, m-NC₆H₃Me₂, p-PC₆H₄N), 7.15 (tt, $J_{H-H}$ = 7.2 Hz, 2H, p-P(C₆H₅)₂), 7.20–7.24 (m, 5H, o-PC₆H₄N, m-P(C₆H₅)₂), 7.79–7.83 (dd, 4H, o-P-(C₆H₅)₂). ¹³C NMR (100 MHz, $C_6D_6$, 25 °C): $\delta$ 0.34 (s, SiMe₄), 4.77,4.97 (s, Si*Me₃*), 19.61 (s, 2C, Ar*Me*), 25.60 (s, 8C, THF), 34.06 (d, $J_{Y-C}$ = 35.3 Hz, Y(C*H₂*SiMe₃)₃), 40.54 (d, 2C, $J_{Y-C}$ = 29.1 Hz, C*H₂*SiMe₃), 70.14 (s, 8C, THF), 112.95 (s, 1C, o-NC₆H₄P), 116.04 (s, 1C, p-NC₆H₄P), 125.19 (s, 1C, p-NC₆H₃Me₂), 129.19 (d, $^3J_{C-P}$ = 7.8 Hz, 4C, m-P(C₆H₅)₂), 129.71 (s, 2C, m-NC₆H₃Me₂), 129.95 (s, 2C, p-P(C₆H₅)₂), 133.59 (s, 1C, p-PC₆H₄N), 133.31 (d, $^2J_{C-P}$ = 13.7 Hz, 4C, o-P(C₆H₅)₂), 134.11 (s, 2C, ipso-P(C₆H₅)₂), 136.58 (s, 1C, o-PC₆H₄N), 138.64 (s, 2C, ipso-Me₂C₆H₃), 145.35 (s, 1C, ipso-NC₆H₃Me₂), 161.73 (s, 1C, ipso-NC₆H₄P). ³¹P{¹H} NMR ($C_6D_6$, 161.90 MHz) $\delta$ −12.99. IR (KBr pellets): $\nu$ 3361(m), 3050(m), 2951(m), 1959(w), 1584(s), 1566(s), 1485(s), 1434(s), 1378(w), 1303(s), 1284(w), 1247(m), 1205(w), 1183(w), 1160(m), 1125(w), 1095(m), 1066(w), 1026(m), 999(w), 918(w), 861(s), 748(s), 695(s) cm$^{-1}$. Anal. Calc. for $C_{48}H_{75}NO_2PSi_2Y$ (873.06): C, 66.03; H, 8.66; N, 1.60. Found: C, 65.56; H, 8.43; N, 1.54%.

### 4.3.6. Synthesis of [2-(2,6-Me₂C₆H₃N)-C₆H₄P(Ph)₂]Sc(CH₂SiMe₃)₂ (THF) (4b)

To a hexane solution (2.0 mL) of Sc(CH₂SiMe₃)₃THF₂ (0.180 g, 0.400 mmol), equivalent HL³ (0.152 g, 0.400 mmol) in 4 mL toluene was dropwise added at room

temperature. The mixture was then stirred for 4 h. Removal of the volatiles gave a yellow residue which was added toluene and hexane and kept at −30 °C for 1 day to afford crystals of complex **4b** in 89% yield (0.270 g). ¹H NMR (400 MHz, $C_6D_6$, 25 °C): $\delta$ 0.45–0.31 (22H, C*H₂*SiMe₃). 1.23 (br, 4H, THF), 2.33 (s, 6H, Ar*Me*), 3.56 (br, 4H, THF), 6.05 (t, $J_{H-H}$ = 6 Hz, 1H, o-NC₆H₄P), 6.60 (t, $J_{H-H}$ = 7.6, 1H, p-NC₆H₄P), 7.09 (t, $J_{H-H}$ = 6.8 Hz, 1H, p-NC₆H₃Me₂), 7.06–7.11 (dt, 3H, m-NC₆H₃Me₂, p-PC₆H₄N), 7.17 (tt, 2H, p-P(C₆H₅)₂), 7.24–7.31 (m, 4H, m-PC₆H₅, o-PC₆H₄N), 7.91–7.95 (dd, $J_{H-H}$ = 8.4 Hz, 4H, o-PC₆H₅). ¹³C NMR (100 MHz, $C_6D_6$, 25 °C): $\delta$ 4.52 (s, 6C, Si*Me₃*),19.78 (s, 2C, Ar*Me*), 25.40 (s, 4C, THF), 46.62 (s, 2C, C*H₂*SiMe₃), 71.87 (s, 4C, THF), 112.88 (s, $^3J_{C-P}$ = 6 Hz, 1C, o-NC₆H₄P), 116.97 (s, 1C, p-NC₆H₄P), 125.14 (s, 1C, p-NC₆H₃Me₂), 129.26 (s, $^3J_{C-P}$ = 7 Hz, 4C, m-P(C₆H₅)₂), 129.52 (s, 2C, o-NC₆H₃Me₂), 130.08 (s, 2C, p-P(C₆H₅)₂), 133.87 (s, 1C, p-PC₆H₄N), 134.43 (d, $^2J_{P-C}$ = 12 Hz, 4C, o-P(C₆H₅)₂), 134.74 (d, $^1J_{C-P}$ = 18 Hz, 2C, ipso-P(C₆H₅)₂), 136.92 (s, 1C, o-PC₆H₄N), 137.90 (s, 2C, m-NC₆H₃Me₂), 147.85 (s, 1C, ipso-NC₆H₃Me₂), 161.87 (d, $^1J_{C-P}$ = 26 Hz, 1C, ipso-NC₆H₄P). ³¹P{¹H} NMR ($C_6D_6$, 161.90 MHz) $\delta$ −14.91. IR (KBr pellets): $\nu$ 3363(m), 3052(m), 2953(m), 1955(w), 1584(s), 1569(s), 1489(s), 1435(s), 1377(w), 1302(s), 1281(w), 1248(m), 1207(w), 1181(w), 1160(m), 1125(w), 1094(m), 1068(w), 1027(m), 999(w), 917(w), 861(s), 746(s), 697(s) cm$^{-1}$. Anal. Calc. for $C_{44}H_{67}NOPSi_2Sc$ (758.11): C, 69.71; H, 8.91; N, 1.85. Found: C, 69.24; H, 8.77; N, 1.72%.

### 4.3.7. Synthesis of [2-(2,6-Me₂C₆H₃N)-C₆H₄P(Ph)₂]Lu(CH₂SiMe₃)₂ (THF) (4c)

To a hexane solution (2.0 mL) of Lu(CH₂SiMe₃)₃THF₂ (0.235 g, 0.405 mmol), equivalent HL³ (0.153 g, 0.405 mmol) in 4 mL toluene was dropwise added at room temperature. The mixture was then stirred for 4 h. Removal of the volatiles gave a yellow residue which was added toluene and hexane and kept at −30 °C for 1 day to afford crystals of complex **4c** in 72% yield (0.259 g). ¹H NMR (600 MHz, $C_6D_6$, 25 °C): $\delta$ −0.34 (br, 4H, C*H₂*SiMe₃), 0.31 (s, 18H, SiMe₃), 1.14 (s, 4H, THF), 2.34 (s, 6H, Ar*Me*), 3.38 (s, 4H, THF), 6.06 (d, $J_{H-H}$ = 7.2 Hz, 1H, o-NC₆H₄P), 6.55 (t, $J_{H-H}$ = 7.2 Hz, 1H, p-NC₆H₄P), 6.96 (t, $J_{H-H}$ = 7.2 Hz, 1H, p-NC₆H₃), 7.08 (dt, $J_{H-H}$ = 7.2 Hz, 3H, m-NC₆H₃Me₂, p-PC₆H₄N), 7.16 (tt, $J_{H-H}$ = 7.2 Hz, 2H, p-P(C₆H₅)₂), 7.21 (t, 1H, o-PC₆H₄N), 7.22–7.25 (m, 4H, m-P(C₆H₅)₂), 7.87 (dd, $J_{H-H}$ = 8.4 Hz, 4H, o-P(C₆H₅)₂). ¹³C NMR (150 MHz, $C_6D_6$, 25 °C): $\delta$ 4.55 (s, 6C, Si*Me₃*),19.20 (s, 2C, Ar*Me*), 24.86 (s, 4C, THF), 46.73 (d, 2C, $J_{Lu-C}$ = 10.5 Hz, C*H₂*SiMe₃), 70.75 (s, 4C, THF), 113.12 (s, $^3J_{C-P}$ = 6 Hz, 1C, o-NC₆H₄P), 115.81 (s,$^3J_{C-P}$ = 4.5 Hz, 1C, p-NC₆H₄P), 124.58 (s, 1C, p-NC₆H₃Me₂), 128.29 (s, 1C, ipso-PC₆H₄N), 128.83 (d, $^3J_{C-P}$ = 7.5 Hz, 4C, m-P(C₆H₅)₂), 129.17 (s, 2C, m-NC₆H₃Me₂), 129.67 (s, 2C, p-P(C₆H₅)₂), 133.48 (s, 1C, p-PC₆H₄N), 133.98 (d, $^2J_{C-P}$ = 13.5 Hz, 4C, o-P(C₆H₅)₂),

134.11 (s, 2C, *ipso*-P(C$_6$H$_5$)$_2$), 136.45 (s, 1C, *o*-PC$_6$H$_4$N), 137.87 (s, 2C, *ipso*-Me$_2$C$_6$H$_3$), 146.30 (s, 1C, *ipso*-NC$_6$H$_3$Me$_2$), 162.31 (d, $^1J_{C-P} = 24.2$ Hz, 1C, *ipso*-NC$_6$H$_4$P). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 161.90 MHz) $\delta$ −7.99. IR (KBr pellets): $\nu$ 3363(m), 3053(m), 2954(s), 2872(w), 1584(s), 1489(s), 1435(s), 1377(w), 1300(s), 1272(w), 1248(s), 1208(w), 1184(w), 1160(w), 1122(w), 1094(m), 1068(w), 1037(m), 1000(w), 860(s), 768(w), 746(s), 696(s) cm$^{-1}$. Anal. Calc. for C$_{44}$H$_{67}$NOPSi$_2$Lu (888.12): C, 59.50; H, 7.60; N, 1.58. Found: C, 58.89; H, 7.34; N, 1.45%.

### 4.3.8. Synthesis of [2-(2,6-Me$_2$C$_6$H$_3$N)-C$_6$H$_4$P(Ph)$_2$]Yb(CH$_2$SiMe$_3$)$_2$(THF) (4d)

To a hexane solution (2.0 mL) of Yb(CH$_2$SiMe$_3$)$_3$THF$_2$ (0.232 g, 0.400 mmol), equivalent HL$^3$ (0.153 g, 0.400 mmol) in 4 mL toluene was dropwise added at room temperature. The mixture was then stirred for 4 h. Removal of the volatiles gave a deep red residue which was added toluene and hexane and kept at −30 °C for 2 days to afford crystals of complex **4d** in 86% yield (0.304 g). IR (KBr pellets): $\nu$ 3361(w), 3053(m), 2950(s), 2857(s), 1906(w),1580(s), 1544(m), 1533(w), 1481(w), 1458(s), 1429(s), 1377(m), 1295(s), 1270(s), 1249(w), 1236(m), 1186(s), 1160(m), 1130(s), 1092(m), 1068(m), 1037(s), 1010(s), 876(w), 853(s), 766(w), 750(s), 712(w), 695(s) cm$^{-1}$. Anal. Calc. for C$_{44}$H$_{67}$NOPSi$_2$Yb (886.39): C, 59.63; H, 7.62; N, 1.58. Found: C, 58.11; H, 7.56; N, 1.49%.

### 4.3.9. Synthesis of [2-(2,6-Me$_2$C$_6$H$_3$N)-C$_6$H$_4$P(Ph)$_2$]Tm(CH$_2$SiMe$_3$)$_2$(THF) (4e)

To a hexane solution (2.0 mL) of Tm(CH$_2$SiMe$_3$)$_3$THF$_2$ (0.230 g, 0.400 mmol), equivalent HL$^3$ (0.153 g, 0.400 mmol) in 4 mL toluene was dropwise added at room temperature. The mixture was then stirred for 4 h. Removal of the volatiles gave a deep red residue which was added toluene and hexane and kept at −30 °C for 2 days to afford crystals of complex **4e** in 51% yield (0.162 g). IR (KBr pellets): $\nu$ 3382(m), 3052(m), 2921(s), 2852(m), 1585(s), 1569(m), 1489(s), 1435(s), 1377(w), 1301(s), 1248(w), 1207(w), 1182(w), 1160(m), 1125(w), 1093(m), 1069(w), 1027(m), 999(w), 854(m), 745(s), 696(s) cm$^{-1}$. Anal. Calc. for C$_{38}$H$_{53}$NOPSi$_2$Tm (795.89): C, 57.34; H, 6.71; N, 1.76. Found: C, 56.13; H, 6.44; N, 1.46%.

### 4.4. Ethylene polymerization

In a glovebox, [PN]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_n$ 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 atm) was introduced into the system and was saturated in the solution by stirring for 2 min. A hexane solution (0.25 M) of AlEt$_3$ and a toluene solution of [Ph$_3$C][B(C$_6$F$_5$)$_4$] was then added through a syringe under vigorous stirring. The polymerization was quenched by

addition of ethanol (100 mL). The polymer product was collected by filtration, washed with ethanol, and then dried *in vacuo* at 60 °C to a constant weight.

### Appendix A. Supplementary material

CCDC 635731, 622504, 627390, 614088, 628755 and 607919 contain the supplementary crystallographic data for **2**, **3**, **4b**, **4c**, **4d** and **4e**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.022.

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