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Rich C–H bond activations of yttrium alkyl complexes bearing phosphinimino-amine ligands

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ABSTRACT

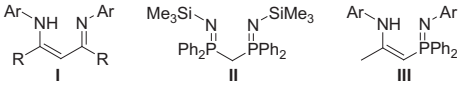
A series of phosphinimino-amine compounds (2,6–iPr$_2$–C$_6$H$_3$NH)C(Me)CHPPh$_2$(NAr) (Ar = 2,6–iPr$_2$–C$_6$H$_3$ (HL^1), 2,6–Et$_2$–C$_6$H$_3$ (HL^2), 2,6–Me$_2$–C$_6$H$_3$ (HL^3), C$_6$H$_5$ (HL^4), 3–CF$_3$–C$_6$H$_4$ (HL^5)) that existed in imine and amine forms were synthesized and fully characterized. Treatment of HL$^{1-5}$ with Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ afforded the corresponding yttrium mono- or bis(alkyl) complexes that depended significantly on the ancillary ligands. The reactions between HL$^{1-3}$ and Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ at room temperature generated mononuclear monoalkyl complexes **1**–**3** via deprotonation and C–H bond activation. However, when compounds HL^{4,5} were used, the dialkyl complexes **4** and **5** were isolated by deprotonation only. The molecular structures of complexes **1**–**4** were characterized with X-ray crystallography and discussed.

1. Introduction

During the past decades, many efforts have been made to develop novel ligands in order to prepare organolanthanide catalyst precursors with unique structure, reactivity, and enhance catalytic activity [1]. The use of β-diketiniminato ("nacnac") compound(I) as "hard" donor ligand has received much attention, because it is monoanionic, chelating ligand similar to cyclopentadienyl anion and its steric and electronic effects can be swiftly tuned via choosing appropriate starting agents [2–5]. To date many β-diketiniminato metal complexes have been reported and displayed plentiful and interesting chemistry, for instance, the β-diketiniminato rare-earth metal complexes are luminescent or catalytically active toward polymerizations of ϵ-caprolactone or lactide [4f,g,5c], methyl methacrylate [4b,g], ethylene [3c], isoprene [5g,h] and copolymerization of cyclohexene oxide and CO_2 [5e,f], etc. Recently research has directed to modify the "nacnac" framework by replacing two carbon atoms with phosphorus atoms to form bis(iminophosphorano)methandiide ligand, CH$_2$(PPh$_2$NSiMe$_3$)$_2$(II). Deprotonation of II could afford a monoanionic species CH(PPh$_2$NSiMe$_3$)$_2^-$ [6] or a dianionic species C(PPh$_2$NSiMe$_3$)$_2^{2-}$ [6o,7]. The monoanionic species is widely applied as an ancillary ligand in both divalent and trivalent rare-earth metal chloride, iodide, amide and alkyl complexes, which are homogenous catalysts for ϵ-carprolactone and methyl methacrylate polymerizations [6g], the intramolecular hydroamination/cyclization, the hydrosilylation and a sequential hydroamination/hydrosilylation reaction [6i,j,l]. The dianionic ligand is reported to stabilize yttrium and samarium to form carbene like complexes.

With similar consideration, by replacing only one imine-group of "nacnac" ligand with a phosphinimine fragment, a new type of phosphinimino-amine ligand (III) has been obtained. The coordination chemistry of III to Li, Pd, Ni and Al metals has been known only very recently [8], but that to the analogous rare-earth elements has remained unexplored yet. The introduction of a "large" and "soft" phosphorus donor is aimed to increase the steric bulk and lower the electron density of rare-earth metal center. Therefore, the rare-earth metal complexes bearing the phosphinimino-amine ligand are anticipated to have plentiful reactivity and excellent catalysis.

Herein, we report the synthesis of five phosphinimino-amine compounds and their reaction with Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ to form a series of new yttrium mono(alkyl) and dialkyl complexes as well as the C–H bond activation during the process. In addition the structural variation of the ligand that influences the C–H bond activation will also be discussed.



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2. Results and discussion

2.1. Synthesis and characterization of phosphinimino-amine ligands HL^{1-5}

The synthesis of ligands HL^{1-5} was described in Scheme 1. Compound **A** was synthesized from the condensation of the 2,6-diisopropylbenzenamine and acetone. Lithiation of **A** with *n*BuLi followed by treatment with $ClPPh_2$ gave compound **B** [8a]. Oxidation of **B** with the corresponding substituted arylazides formed compounds HL^{1-5} which were purified by recrystallization from a mixture of diethyl ether and hexane. All these compounds were isomers indicated by their ^1H, ^{13}C and ^{31}P NMR spectra. Compounds HL^{1-4} exist mainly in imine isomers whereas HL^5 exists in amine form. X-ray diffraction analysis of HL^1 had been reported previously [8b] and that of HL'^3 was shown in Fig. 1. The crystal structures show that HL^1 is an amine isomer whilst HL'^3 is an imine isomer.

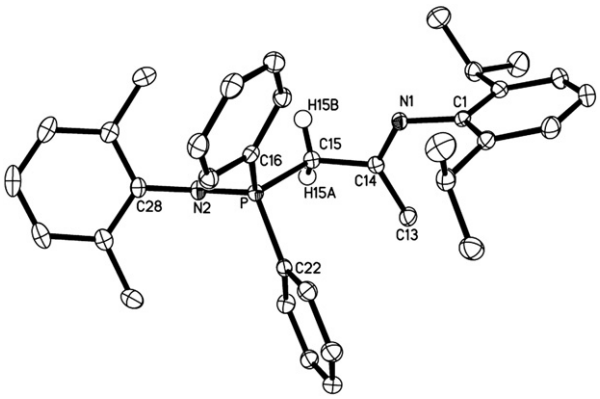


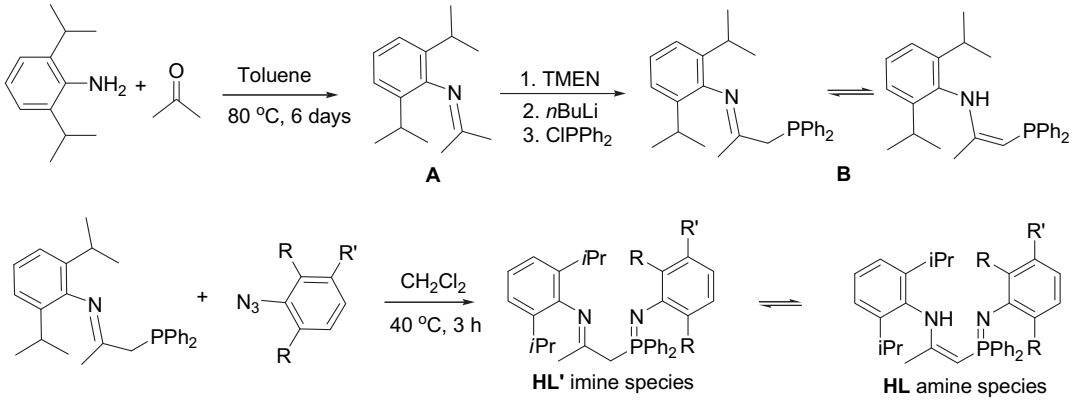
Fig. 1. Molecular structure of compound HL'^3. Thermal ellipsoids are set at 30% probability, and some hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P–N(2) 1.5616(18), P–C(16) 1.8053(19), P–C(15) 1.8170(19), N(1)–C(14) 1.272(2), C(14)–C(15) 1.517(3).

2.2. Synthesis and characterization of complexes ***1–5***

Rare-earth metal dialkyl complexes are highly active single-component catalysts or crucial precursors of the cationic counterparts after being activated by MAO or borates and have shown tremendous catalytic activities toward polymerizations of olefin [9], conjugated monomers [10], and polar monomers [11]. Therefore, exploration of new lanthanide dialkyl complexes has been a research concern. Unfortunately, preparation of rare-earth metal dialkyl complexes bearing monoanionic ligands has been hindered due to the highly active character of lanthanide alkyl species and the relatively less crowded environment of the metal center, which always result in ligand redistribution, dimerization of the molecule, and the formation of salt adduct [12].

Thus, ligand HL^1 with the bulky isopropyl group was treated firstly with 1.1 equiv of $Y(CH_2SiMe_3)_3(THF)_2$ at room temperature for 0.5 h, anticipating to synthesize the corresponding dialkyl complex. Noteworthy was that an equilibrium exists between amine structure and imine structure. As the reaction went on, the amine isomer of HL^1 was consumed through deprotonation by $Y(CH_2SiMe_3)_3(THF)_2$ and then the imine isomer gradually transferred into the amine isomer during the reaction. The colorless crystals were obtained from the mixture of hexane and THF at −30 °C for several days. To our surprise, the integral of the resonances of CH_2SiMe_3 group and the ligand showed only one alkyl moiety (bearing one negative charge) and one ligand (monoanionic) in the ^1H NMR spectroscopy (C_6D_6), but complex **1** should contain two alkyl moieties and one ligand according to the reactant ratio of the starting materials and Y^{3+} oxidation state. The phenomenon was similar to scandium alkyl complex stabilized by "nacnac" ligand [3b,k]. Therefore a suspicion that one C–H bond of the *i*Pr-methyl group was activated crept into our mind. Sure enough, the solid structure determined by X-ray diffraction proved our suspicion (Fig. 2). The intramolecular C–H bond activation occurred at one *i*Pr-methyl of the amine aryl. The ^1H NMR and ^1H–^1H COSY spectra showed that two methylene groups attached to the yttrium atom, Y–CH_2SiMe_3 and Y–CH_2CHCH_3, appeared as two independent AB spin systems in the upfield regions, indicating the diastereotopic CH_2 protons. The methylene protons of Y–CH_2SiMe_3 group featured at −0.20 and 0.16 ppm, while the Y–CH_2CHCH_3 resonances exhibited at 0.02 and 0.57 ppm.

The intramolecular C–H bond activation of mono(alkyl) complex **1** might be attributed to the excessively steric hindrance of HL^1. Thus, the less bulky HL^2 with ethyl groups of phosphinimino moiety was treated with $Y(CH_2SiMe_3)_3(THF)_2$ in order to isolate dialkyl complex. However, the ^1H NMR spectrum of the resulting complex **2** indicated the resonances of one CH_2SiMe_3 group and one ligand L^2, suggesting the presence of the C–H bond activation.



R' = H:
R = *i*Pr, HL'^1: HL^1 = 83:17; R = Et, HL'^2: HL^2 = 64:36;
R = Me, HL'^3: HL^3 = 93:7; R = H, HL'^4 : HL^4 = 83:17.
R = H, R' = CF_3, HL'^5: HL^5 = 42:58.

Scheme 1. Synthesis of ligands HL^{1-5}.

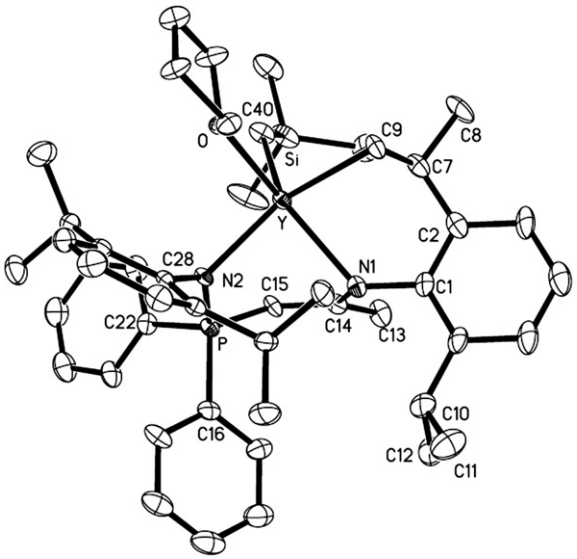


Fig. 2. Molecular structure of complex **1**. Thermal ellipsoids are set at 30% probability, and hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): O–Y 2.401(3), Y–N(2) 2.353(3), Y–C(9) 2.377(4), Y–N(1) 2.399(4), Y–C(40) 2.421 (5); N(2)–Y–C(9) 137.08(14), N(2)–Y–N(1) 86.28(12), C(9)–Y–N(1) 79.03(14), N(2)–Y–O 83.94(11), C(9)–Y–O 84.36(13), N(1)–Y–O 143.22(11), N(2)–Y–C(40) 120.53(15), C(9)–Y–C(40) 100.59(17), N(1)–Y–C(40) 125.10(15), O–Y–C(40) 90.00(14).

This was further confirmed by X-ray diffraction analysis as illustrated in Fig. 3, which showed that a C–H bond of the PPh_2 moiety was activated by Y–CH_2SiMe_3 species. In the ^{1}H NMR spectrum, doublets of doublets around 7.63 ppm ($^3J_{Y-H}$ = 10.8 Hz, $^3J_{H-H}$ = 8 Hz) could be assigned to *o*-YC_6H_4P. And a singlet in the upfield (−0.38 ppm) was attributed to the protons of CH_2SiMe_3. A quartet at δ = 198.31 ppm in the ^{13}C NMR spectrum should be assigned to *ipso*-YC_6H_4P, typical for the aromatic carbon bonding to yttrium ion [13].

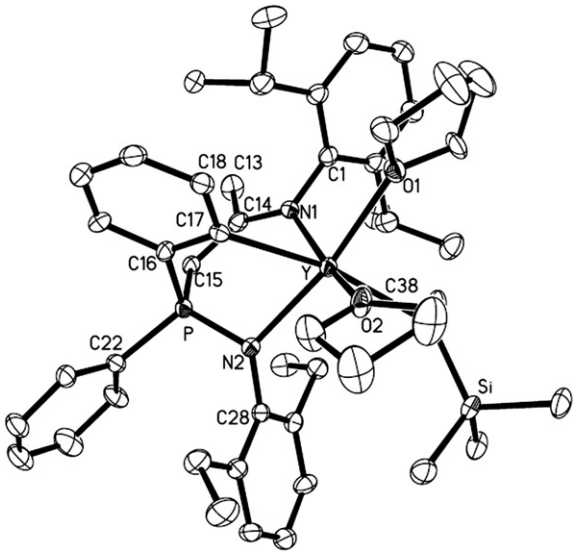


Fig. 3. Molecular structure of complex **2**. Thermal ellipsoids are set at 30% probability, and hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Y–N(2) 2.319(3), Y–O(1) 2.425(3), Y–O(2) 2.444(3), Y–C(38) 2.445(4), Y–N(1) 2.446(3), Y–C(17) 2.502(4); N(2)–Y–O(1) 69.15(11), N(2)–Y–O(2) 101.69(10), O(1)–Y–O(2) 76.42(10), N(2)–Y–C(38) 100.23(13), O(1)–Y–C(38) 90.19(13), O(2)–Y–C(38) 82.96(13), N(2)–Y–N(1) 85.78(11), O(1)–Y–N(1) 93.80(10), O(2)–Y–N(1) 165.06(11), C(38)–Y–N(1) 108.67(13), N(2)–Y–C(17) 74.82(12), O(1)–Y–C(17) 94.34(12), O(2)–Y–C(17) 80.81(11), C(38)–Y–C(17) 161.61(13), N(1)–Y–C(17) 88.83(12).

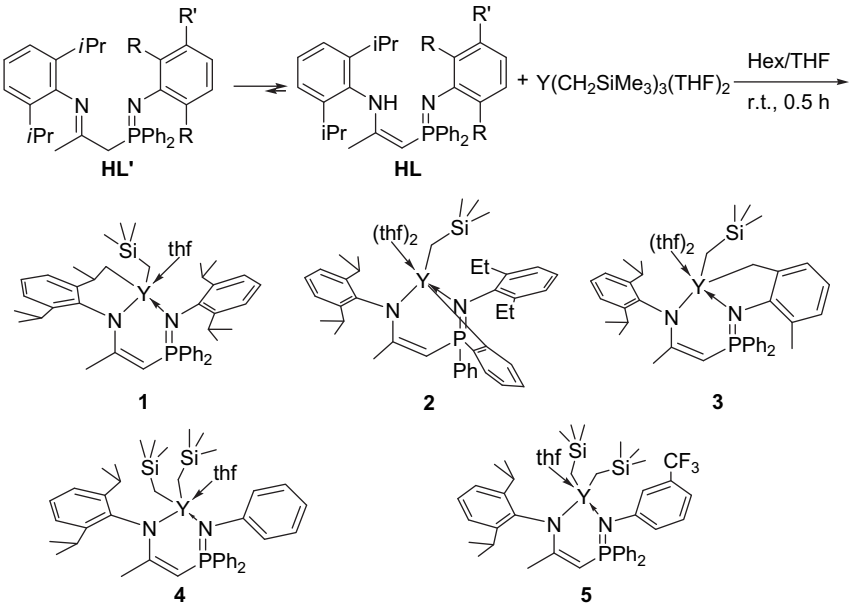
Switching to the ligand HL^3 bearing methyl groups, the dialkyl complex was not obtained because of the unpredictable intramolecular C–H bond activation of one methyl group of phosphinimino fragment leading to form the monoalkyl complex **3**. The similar reaction had been documented for yttrium monoalkyl complex supported by amidopyridinate ligand [13c,14]. The NMR data revealed that methylene protons of Y–CH_2SiMe_3 and Y–CH_{2Aryl} displayed two AB spin systems: δ 0.12/−0.25 for Y–CH_2SiMe_3, δ 0.17/0.66 for Y–CH_{2Aryl}. Further splitting of the AB spin systems into doublets due to coupling with the Y atom (I = 1/2) was observed as shown in Scheme 2.

To our delight, the yttrium dialkyl complexes were obtained finally when no substituting groups were at the *ortho* position of the N-aryl. Treatment of $HL^{4,5}$ with $Y(CH_2SiMe_3)_3(THF)_2$ afforded the corresponding yttrium dialkyl complexes (**4** and **5**). The hydrogen atoms of the ligand and alkyl groups appeared in ^{1}H NMR spectrum of **4** with the integral ratio of 1:2. A singlet at −0.33 ppm was assigned to the two equivalent methylene protons of alkyls owing to their fluxional nature within the NMR timescale. For complex **5**, an electron withdrawing group CF_3 was introduced at the *meta* position of phenyl in order to investigate the electronic effect to the structure. No obvious effect to the structure was observed because ^{1}H NMR spectrum has very similar topology to **4**. In addition, yttrium dialkyl complex **4** exhibited a certain thermodynamic stability. When the reaction of HL^4 with $Y(CH_2SiMe_3)_3(THF)_2$ was performed in toluene at 50 °C for 1 h or at room temperature for 24 h, the same yttrium dialkyl complex **4** was obtained. The C–H bond activation reaction did not happen, unlike that of rare-earth metal (Sc, Y) β-diketiniminato complexes which cationic counterparts tended to be less robust and decompose via C–H activation of one *ortho*-group of the N-aryl units when the reaction temperature was raised or at a prolonged reaction time [3b].

2.3. X-ray crystal structures

ORTEP diagrams of compounds **1**–**4** showing the structures from various perspectives are given in Figs. 2–5.

In complex **1** (or **2**, or **3**), the phosphinimino-amine ligand is deprotonated by one Y–alkyl group and then one C–H bond of ligand is activated to eliminate another Y–alkyl group to form a dianionic species $(L)^{2-}$ which coordinates to yttrium ion in the C,N,N tridentate mode. The five-coordinate yttrium center in **1** has a twisted trigonal-bipyramidal geometry with N(2) and C(9) occupying the apical sites (N(2)–Y–C(9) 137.08(14)°) and N(1), O and C(40) as the base. The close contacts of Y···C(14) and Y···C(15) (2.765(7) Å, 2.784(11) Å) increase the coordination ability of ligand L^1 to the central metal. The bond lengths of N(2)=P and C(14)=C (15) in complex **1** are longer whilst the N(1)–C(14) and C(15)–P lengths are shortened as compared with those in ligand HL^1. The space-filling drawings of the molecular structures of **1** and **2** clearly display that there is an overcrowded environment around the Y^{3+} ion in **1** as compared with **2**. Noteworthy is that two bulky isopropyl groups of the phosphinimino fragment in **1** limit the rotation of the phenyl of PPh_2. In **2**, however, the smaller ethyl groups could not prevent the phenyl of PPh_2 from approaching the metal center, leading to C–H bond activation of a phenyl ring of the phosphine moiety. Both **2** and **3** adopt distorted octahedron geometry. However, the X-ray data of complex **3** are not good enough, so the solid structure character isn't discussed. The solid structure of dialkyl complex **4** has the same distorted trigonal-bipyramid geometry with complex **1**. The five-coordinate yttrium center is generated by a *N,N,*-bidentate ligand, a THF molecule and two alkyl groups arranging in *trans*-positions. The distance between Y and C (15) (2.84(9) Å) is close suggesting a weak interaction between



Scheme 2. Synthesis of complexes **1**–**5**.

them. The ligand L^4 coordinates to the central metal ion to generate a six-membered metallacycle that is twisted into a boat conformation. The Y–CH_2Si distances and Y–CH_2–Si angles of complexes **1**, **2** and **4** fall in the range of the values previously reported for related yttrium alkyl complexes (2.404–2.476 Å and 129.1–145.4°) [15]. The bite angles of N(2)–Y–N(1) (86.28° (1), 85.78° (2), 86.59 (9)° (4)) are almost as large as that found in yttrium complex bearing β-diketiniminato (86.13(9)°) [3i].

3. Conclusion

The replacement of an imine-carbon of "nacnac" with a PPh_2 fragment apparently increases the steric congestion of the resultant phosphinimino-amine ligands. Consequently, when treated those ligands with yttrium trisalkyl complexes, the C–H bond activations take place at different sites of ancillary ligands. Although at present we are unable to rationalize definitely those C–H bond activations within complexes **1**–**3**, it is undoubtedly that the activation

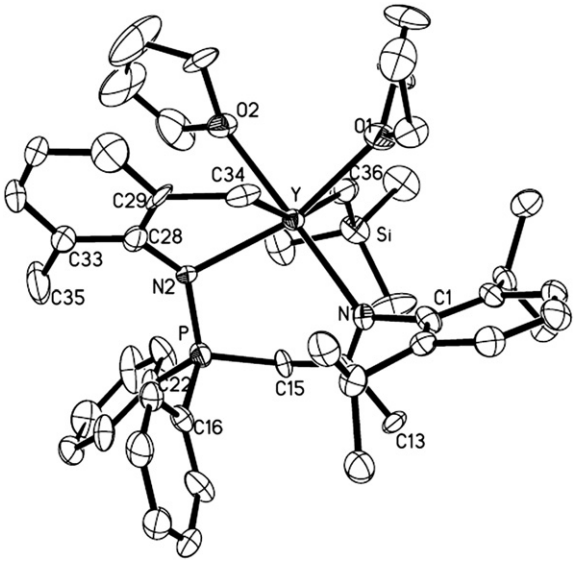


Fig. 4. Molecular structure of complex **3**. Thermal ellipsoids are set at 30% probability, and hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Y–N(2) 2.328(14), Y–O(2) 2.377(13), Y–O(1) 2.410(14), Y–N(1) 2.430(14), Y–C(36) 2.51(2), Y–C(34) 2.522(19); N(2)–Y–O(2) 81.6(5), N(2)–Y–O(1) 149.8(5), O(2)–Y–O(1) 87.3(5), N(2)–Y–N(1) 96.3(5), O(2)–Y–N(1) 171.5(5), O(1)–Y–N(1) 90.5(5), N(2)–Y–C(36) 126.0(7), O(2)–Y–C(36) 83.1(6), O(1)–Y–C(36) 80.0(7), N(1)–Y–C(36) 104.6(6), N(2)–Y–C(34) 69.0(6), O(2)–Y–C(34) 81.2(5), O(1)–Y–C(34) 81.5(6), N(1)–Y–C(34) 90.4(5), C(36)–Y–C(34) 156.1(7).

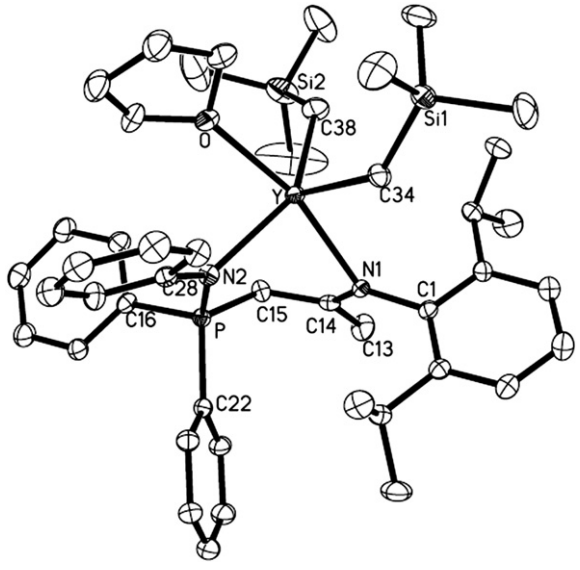


Fig. 5. Molecular structure of complex **4**. Thermal ellipsoids are set at 30% probability, and hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Y–N(2) 2.371(3), Y–O 2.376(2), Y–N(1) 2.392(3), Y–C(34) 2.407(3), Y–C(38) 2.417 (3); N(2)–Y–O 78.78(9), N(2)–Y–N(1) 86.59(9), O–Y–N(1) 165.36(8), N(2)–Y–C(34) 112.33(10), O–Y–C(34) 97.22(11), N(1)–Y–C(34) 87.79(10), N(2)–Y–C(38) 139.87(12), O–Y–C(38) 85.33(11), N(1)–Y–C(38) 106.58(11), C(34)–Y–C(38) 106.04(13).

position roughly correlates with the steric bulkiness of aryl substituents of phosphinimino moiety. Therefore the dialkyl complexes could be successfully synthesized when the steric congestion of ligand is less. All complexes alone could polymerize lactide, ϵ-caprolactone and methyl methacrylate and the polymerization of conjugated dienes is under investigation.

4. Experimental

4.1. General methods

All reactions were carried out under a dry and an oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glove box. All solvents were purified from an MBraun SPS system. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer and a Bruker AV300 (FT, 300 MHz for ^{1}H; 75 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. ^{31}P NMR spectra were referenced to an external standard of H_3PO_4 (0.0 ppm) in C_6D_6 and were recorded on a Bruker AV400 spectrometer. Elemental analyses were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC).

X-ray crystallographic studies: Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glove box. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo K_α 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 SHELXTL program. For the crystallographic data and the refinement of complexes **1**–**4** and ligand L^3, see Table 1.

4.2. Synthesis of ligands HL$^{1-5}$

The synthesis of HL^1 was according to the literature by Stephan et al. [8a]. The syntheses of HL$^{2-5}$ were carried out by a similar procedure for the synthesis of HL^1, but the corresponding azides (2,6–R_2–C_6H_3)N_3 (HL^2 R = Et, HL^3 R = Me, HL^4 R = H), and (3–CF_3–C_6H_3)N_3 (HL^5) were used in place of (2,6–*i*Pr_2–C_6H_3)N_3. The yields of these ligands were in moderation (HL^2 66.2%, HL^3 69.7%, HL^4 75.3% and HL^5 78.5%).

4.2.1. The characterization of ligand HL^2

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.86 (m, 4H, *o*-PPh_2), 7.18 (br, 3H, C_6H_3*i*Pr_2), 7.14 (br, 3H, $C_6H_3Et_2$), 7.08 (br, 6H, *m,p*-PPh_2), 3.80 (d, $^2J_{P-H}$ = 14 Hz, 2H, PCH_2), 2.92 (m, 4H, CH_2Me), 2.71 (sept, $^3J_{H-H}$ = 7 Hz, 2H, $C_6H_3(CHMe_2)_2$), 1.60 (s, 3H, $NCCH_3$),1.32 (t, $^3J_{H-H}$ = 7.5 Hz, 6H, $C_6H_3(CH_2CH_3)_2$), 1.15 (m, 12H, $C_6H_3(CH(CH_3)_2)_2$) ppm. ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 165.77 (d, $^2J_{P-C}$ = 6.0 Hz, 1C, NC), 161.48 (s, 1C, *ipso*-C_6H_3*i*Pr_2), 147.88 (s, 1C, *o*-C_6H_3*i*Pr_2), 145.9 (d, $^2J_{P-C}$ = 8.0 Hz, 1C, *ipso*-$C_6H_3Et_2$), 138.87 (d, J_{P-C} = 7.2 Hz, 1C, *ipso*-PPh_2), 137.99 (d, $^3J_{P-C}$ = 6.0 Hz, 1C, *ipso*-PPh_2), 136.68 (s, 1C, *o*-C_6H_3*i*Pr_2), 135.23 (s, 1C, *o*-$C_6H_3Et_2$), 133.90 (s, 1C, *o*-$C_6H_3Et_2$), 131.76 (m, 5C, *o,p*-PPh_2), 128.94 (d, $^2J_{P-C}$ = 11.8 Hz, 4C, *m*-PPh_2), 125.88 (s, 1C, *p*-C_6H_3*i*Pr_2), 124.03 (s, 2C, *m*-C_6H_3*i*Pr_2), 123.40 (s, 2C, *m*-$C_6H_3Et_2$), 119.21 (s, 1C, *p*-$C_6H_3Et_2$), 45.81 (d, J_{P-C} = 60.7 Hz, 1C, PCH_2), 28.15 (s, 2C, $C_6H_3(CHMe_2)_2$), 26.83 (s, 1C, $NCCH_3$), 24.14 (s, 2C, $C_6H_3(CH_2Me)_2$), 23.68 (s, 4C, $C_6H_3(CH(CH_3)_2)_2$), 14.91 (s, 2C, $C_6H_3(CH_2CH_3)_2$) ppm. ^{31}P NMR (400 MHz, C_6D_6, 25 °C): δ −3.92, −15.19 ppm. Anal. Calcd for $C_{37}H_{45}N_2P$ (548.74): C, 80.98; H, 8.27; N, 5.11. Found: C, 81.33; H, 8.56; N, 4.93%.

4.2.2. The characterization of ligand HL^3

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.85 (m, 4H, *o*-PPh_2), 7.22 (m, 6H, *m,p*-PPh_2), 7.07 (m, 5H, *m*-C_6H_3*i*Pr_2 and *m,p*-$C_6H_3Me_2$), 6.93 (t, $^3J_{H-H}$ = 7.0 Hz, 1H, *p*-$C_6H_3Me_2$), 3.77 (d, $^2J_{P-H}$ = 14 Hz, 2H, PCH_2), 2.78 (m, 2H, $C_6H_3(CHMe_2)_2$), 2.51 (s, 6H, $C_6H_3(CH_3)_2$), 1.62 (s, 3H, $NCCH_3$), 1.16 (q, $^3J_{H-H}$ = 7.0 Hz, 12H, $C_6H_3(CH(CH_3)_2)_2$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 165.30 (d, $^2J_{P-C}$ = 6.0 Hz, 1C, NC), 161.27 (s, 1C, *ipso*-C_6H_3*i*Pr_2), 147.50 (s, 1C, *o*-C_6H_3*i*Pr_2), 146.92 (s, 1C, *ipso*-$C_6H_3Me_2$), 145.53 (s, 1C, *ipso*-PPh_2), 136.32 (s, 1C, *ipso*-PPh_2), 135.12 (s, 1C, *o*-C_6H_3*i*Pr_2), 133.79 (s, 1C, *o*-$C_6H_3Me_2$), 131.92 (d, $^3J_{P-C}$ = 8.6 Hz, 1C, *o*-$C_6H_3Me_2$), 131.29 (m, 5C, *o,p*-PPh_2), 128.61 (d, $^2J_{P-C}$ = 11.8 Hz, 4C, *m*-PPh_2), 128.00 (s, 1C, *p*-C_6H_3*i*Pr_2), 123.63 (s, 2C, *m*-C_6H_3*i*Pr_2), 123.40 (s, 2C, *m*-$C_6H_3Me_2$), 119.21 (s, 1C, *p*-$C_6H_3Me_2$), 45.62 (d, J_{P-C} = 60.0 Hz, 1C, PCH_2), 27.73 (s, 2C, $C_6H_3(CHMe_2)_2$), 24.75 (s, 1C, $NCCH_3$), 23.69 (s, 2C, $C_6H_3(CH(CH_3)_2)_2$), 23.31 (s, 2C, $C_6H_3(CH(CH_3)_2)_2$), 21.75 (s, 2C, $C_6H_3(CH_3)_2$) ppm. ^{31}P NMR (400 MHz, C_6D_6, 25 °C): δ −3.55, −15.48 ppm. Anal. Calcd for $C_{35}H_{41}N_2P$ (520.69): C, 80.73; H, 7.94; N, 5.38. Found: C, 80.99; H, 8.28; N, 5.11%.

Table 1
Main crystallographic data and structure refinement details for **1**–**4** and L^3.

	1	**2**	**3**	**4**	**L^3**
formula	$C_{47}H_{63}N_2OPSiY$	$C_{49}H_{71}N_2O_2PSiY$	$C_{51}H_{74}N_2O_3PSiY$	$C_{48}H_{68}N_2OPSi_2Y$	$C_{35}H_{41}N_2P$
Fw	819.96	868.05	911.09	865.10	520.67
cryst syst	Triclinic	Triclinic	Orthorhombic	Triclinic	Triclinic
space group	$P-1$	$P-1$	$P2(1)/c$	$P-1$	$P-1$
a (Å)	11.7930(7)	11.0918(10)	10.2842(8)	12.3153(10)	10.2869(6)
b (Å)	11.8481(7)	11.2455(10)	12.1122(10)	13.0153(10)	11.4033(7)
c (Å)	18.1030(11)	20.5159(18)	40.067(3)	16.6571(12)	13.6805(9)
α (°)	101.3400(10)	90.2010(10)	90	85.4490(10)	77.8380(10)
β (°)	91.2740(10)	101.402(2)	90.003(2)	82.2290(10)	74.2630(10)
γ (°)	113.5310(10)	109.5580(10)	90	66.8760(10)	71.6080(10)
V (Å^3)	2259.5(2)	2357.0(4)	4990.9(7)	2431.9(3)	1451.92(16)
Z	2	2	4	2	2
D_{calcd} (g/cm^3)	1.205	1.223	1.213	1.181	1.191
$2\theta_{max}$, °	52.04	52.12	51.42	52.18	52.28
μ (cm^{-1})	13.87	13.35	12.65	13.16	1.21
F(000)	870	926	1944	920	560
no. of obsd reflns	8787	9075	9479	9510	5702
no. of params refnd	489	515	496	507	350
GOF	1.001	1.009	1.223	1.019	1.049
R_1	0.1128	0.1057	0.2279	0.0742	0.0697
wR_2	0.1503	0.1372	0.5003	0.1340	0.1391

4.2.3. The characterization of ligand HL[4]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.92 (m, 4H, *o*-PPh_2), 7.52 (br, 6H, *m,p*-PPh_2), 7.46 (br, 5H, *o,m,p*-C_6H_5), 7.05 (br, 2H, *m*-C_6H_3iPr$_2$), 6.68 (t, $^3J_{H-H}$ = 7.0 Hz, 1H, *p*-C_6H_3iPr$_2$), 3.97 (d, $^2J_{P-H}$ = 14 Hz, 2H, PCH_2), 2.31 (m, 2H, $C_6H_3(CHMe_2)_2$), 1.76 (s, 3H, NCCH_3), 0.96 (br, 12H, $C_6H_3(CH_3)_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 165.11 (d, $^2J_{P-C}$ = 6.0 Hz, 1C, N*C*), 161.18 (s, 1C, *ipso*-C_6H_3iPr$_2$), 147.43 (s, 1C, *o*-C_6H_3iPr$_2$), 145.42 (s, 1C, *ipso*-C_6H_5), 145.47 (s, 1C, *ipso*-PPh_2), 136.27 (s, 1C, *ipso*-PPh_2), 134.86 (s, 1C, *o*-C_6H_3iPr$_2$), 131.81 (m, 5C, *o,p*-PPh_2), 130.92 (d, $^2J_{P-C}$ = 11.8 Hz, 4C, *m*-PPh_2), 128.95 (s, 1C, *p*-C_6H_3iPr$_2$), 128.51 (s, 2C, *m*-C_6H_3iPr$_2$), 123.35 (s, 2C, *o*-C_6H_5), 123.11 (s, 2C, *p*-C_6H_5), 116.87 (s, 1C, *m*-C_6H_5), 41.47 (d, J_{P-C} = 60.7 Hz, 1C, PCH_2), 28.27 (s, 2C, $C_6H_3(CHMe_2)_2$), 27.68 (s, 1C, NCCH_3), 24.51 (s, 2C, $C_6H_3(CH(CH_3)_2)_2$), 23.47 (s, 2C, $C_6H_3(CH(CH_3)_2)_2$) ppm. ^{31}P NMR (400 MHz, C_6D_6, 25 °C): δ 2.51, −3.12 ppm. Anal. Calcd for $C_{33}H_{37}N_2P$ (492.63): C, 80.46; H, 7.57; N, 5.69. Found: C, 80.86; H, 7.92; N, 5.41%.

4.2.4. The characterization of ligand HL[5]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.79 (s, 1H, N*H*), 7.93 (m, 4H, *o*-PPh_2), 7.47 (m, 4H, *m,p*-C_6H_3iPr$_2$, *o*-$C_6H_4CF_3$), 7.19 (m, 2H, *p*-PPh_2), 7.07 (m, 5H, *m*-PPh_2, *p*-$C_6H_4CF_3$), 6.88 (m, 1H, *m*-$C_6H_4CF_3$), 4.49 (d, $^2J_{P-H}$ = 21 Hz, 1H, PC*H*), 2.81 (m, $^3J_{H-H}$ = 6.9 Hz, 2H, $C_6H_3(CH(CH_3)_2)_2$), 1.70 (s, 3H, NCCH_3), 1.07 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $C_6H_3(CH(CH_3)_2)_2$), 0.78 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $C_6H_3(CH(CH_3)_2)_2$) ppm. ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 164.36 (d, $^2J_{P-C}$ = 6.0 Hz, 1C, N*C*), 160.95 (s, 1C, *ipso*-C_6H_3iPr$_2$), 151.57 (s, 1C, *o*-C_6H_3iPr$_2$), 150.69 (s, 1C, *ipso*-C_6H_5), 146.27 (s, 1C, *ipso*-PPh_2), 144.32 (s, 1C, *ipso*-PPh_2), 135.25 (s, 1C, *o*-C_6H_3iPr$_2$), 133.32 (s, 1C, *ispo*-CF_3−C_6H_4), 132.85 (s, 1C, *C*F_3), 131.01 (m, 4C, *o*-PPh_2), 130.49 (m, 2C, *p*-PPh_2), 127.87 (d, $^2J_{P-C}$ = 11.5 Hz, 4C, *m*-PPh_2), 124.48 (s, 1C, *p*-C_6H_3iPr$_2$), 122.62 (s, 2C, *m*-C_6H_3iPr$_2$), 122.24 (s, 1C, *o*-$NC_6H_4CF_3$), 119.13 (s, 1C, *m*-$NC_6H_4CF_3$), 118.24 (s, 1C, *o*-$NC_6H_4CF_3$), 112.59 (s, 1C, *p*-$NC_6H_4CF_3$), 71.62 (d, J_{P-C} = 108 Hz, 1C, PCH_2), 27.81 (s, 2C, $C_6H_3(CHMe_2)_2$), 26.66 (s, 1C, NCCH_3), 23.13 (s, 2C, $C_6H_3(CH(CH_3)_2)_2$), 21.59 (s, 2C, $C_6H_3(CH(CH_3)_2)_2$) ppm. ^{31}P NMR (400 MHz, C_6D_6, 25 °C): δ 24.50, 20.41 ppm. Anal. Calcd for $C_{34}H_{36}F_3N_2P$ (560.63): C, 72.84; H, 6.47; N, 5.00. Found: C, 73.24; H, 6.89; N, 4.67%.

4.3. Synthesis and characterization of complexes **1**–**5**

Complexes **1**–**5** were obtained by the same synthetic method. The reaction procedure was representatively described for **1**. To a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.54 g, 1.1 mmol) in hexane ligand HL[1] (0.49 g, 1 mmol) in THF was added at ambient temperature. The light yellow mixture was stirred for 0.5 h. The solution was concentrated under vacuum and then was kept several days at −30 °C. Complexes **1**–**5** were isolated as microcrystalline solids. The yields of **1**–**5** were respectively 53.6%, 62.8%, 70.4%, 68.3% and 67.1%.

4.3.1. The characterization of complex **1** $L^1Y(CH_2SiMe_3)(THF)$

^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.83 (br, 2H, *o*-PPh_2), 7.52 (br, 2H, *o*-PPh_2 and 1H, *p*-PPh_2), 7.28 (br, 2H, *m*-PPh_2 and 1H, *p*-PPh_2), 7.16 (br, 2H, *m*-PPh_2), 7.07 (br, 6H, *m,p*-C_6H_3iPr$_2$), 3.72 (s, 2H, THF), 3.53 (br, 1H, PC*H* and 1H, $C_6H_3(CH(CH_3)_2)_2$), 3.48 (s, 4H, THF), 3.32 (sept, $^3J_{H-H}$ = 6.8 Hz, 1H, $C_6H_3(CH(CH_3)_2)_2$), 3.12 (br, 2H, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 2.01 (s, 6H, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$ and NCCH_3), 1.37 (d, $^3J_{H-H}$ = 6.4 Hz, 3H, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 1.20 (br, 3H, $C_6H_3(CH(CH_3)_2)_2$ and 4H, THF), 1.14 (d, $^3J_{H-H}$ = 6.8 Hz, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 1.00 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, $C_6H_3(CH(CH_3)_2)_2$), 0.69 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, $C_6H_3(CH(CH_3)_2)_2$), 0.63 (s, 9H, $Si(CH_3)_3$), 0.48 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, $C_6H_3(CH(CH_3)_2)_2$), 0.57, 0.02 (ABX, $^2J_{H-H}$ = 11.0 Hz, 2H, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 0.16, −0.20 (ABX, $^2J_{H-H}$ = 10.4 Hz, 2H, CH_2SiMe_3) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 172.42 (s, 1C, N*C*), 148.22 (s, 1C, *ipso*-$C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 146.28 (d, $^2J_{P-C}$ = 6.1 Hz, 1C, *ipso*-$C_6H_3(CH(CH_3)_2)_2$), 145.22 (d, J_{P-C} = 7.3 Hz, 1C, *ipso*-PPh_2), 142.59 (d, J_{P-C} = 9.1 Hz, 1C, *ipso*-PPh_2), 139.66 (s, 2C, *o*-$C_6H_3(CH(CH_3)_2)_2$), 139.03 (s, 1C, *o*-$C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 138.10 (s, 1C, *o*-$C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 133.18 (br, 4C, *o*-$PPh_2$), 131.85 (d, 2C, *m*-$PPh_2$), 128.74 (overlap with C_6D_6, 2C, *m*-PPh_2), 124.92, 124.75, 124.54, 124.20 (q, 6C, *m,p*-Ar), 123.25 (s, 1C, *p*-PPh_2), 122.75 (s, 1C, *p*-PPh_2), 71.06 (s, 2C, THF), 54.90, 53.67 (d, $^2J_{P-C}$ = 123.3 Hz, 1C, NC(Me)*C*HP), 49.58 (d, J_{Y-C} = 39.2 Hz, 1C, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 36.47 (s, 1C, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 29.74 (d, J_{Y-C} = 42.1 Hz, 1C, YCH_2Si), 29.13 (s, 1C, $C_6H_3(CH(CH_3)_2)_2$), 28.90 (s, 1C, $C_6H_3(CH(CH_3)_2)_2$), 28.05 (s, 1C, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 27.87, 27.74 (d, 2C, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$ and $C_6H_3(CH(CH_3)_2)_2$), 25.81 (s, 1C, $C_6H_3(CH(CH_3)_2)_2$), 25.63 (s, 2C, $C_6H_3(CH(CH_3)CH_2Y)(CH(CH_3)_2)$), 25.53 (s, 1C, NC$CH_3$), 25.37 (s, 2C, THF), 24.03 (s, 1C, $C_6H_3(CH(CH_3)_2)_2$), 23.67 (s, 1C, $C_6H_3(CH(CH_3)_2)_2$), 5.35 (s, 3C, Si$(CH_3)_3$) ppm. ^{31}P NMR (400 MHz, C_6D_6, 25 °C): δ 8.80 ppm. Anal. Calcd for $C_{47}H_{66}N_2OPSiY$ (823.21): C, 68.59; H, 8.08; N, 3.40. Found: C, 68.87; H, 8.21; N, 3.23%.

4.3.2. The characterization of complex **2** $L^2Y(CH_2SiMe_3)(THF)_2$

^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.45 (d, $^3J_{H-H}$ = 6.8 Hz, 1H, *o*-PC_6H_4Y), 8.11 (m, 2H, *m*-C_6H_3iPr$_2$), 7.92 (dd, $^3J_{Y-H}$ = 8 Hz, $^3J_{H-H}$ = 10.8 Hz, 1H, *o*-YC_6H_4P), 7.69 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, *m*-PC_6H_4Y), 7.56 (br, 1H, *m*-YC_6H_4P, 2H, *o*-PC_6H_5, 2H, *m*-$C_6H_3Et_2$), 7.50 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, *m*-PC_6H_5), 7.41 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, *p*-PC_6H_5), 7.32 (br, 1H, *m*-PC_6H_5, 1H, *p*-$C_6H_3Et_2$), 7.27 (overlap with C_6D_6, 1H, *p*-C_6H_3iPr$_2$), 5.08 (d, $^2J_{P-H}$ = 23.6 Hz, 1H, PC*H*), 4.24 (sept, $^3J_{H-H}$ = 6.8 Hz, 1H, ArC*H*Me$_2$), 4.05 (m, 1H, ArCH_2Me), 3.87 (s, 8H, THF), 3.70 (m, 1H, ArCH_2Me), 3.50 (m, 1H, ArCH_2Me), 2.83 (m, 1H, ArCH_2Me), 2.46 (sept, $^3J_{H-H}$ = 6.8 Hz, 1H, ArC*H*Me$_2$) 2.08 (s, 3H, NCCH_3), 1.98 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, $ArCH_2CH_3$), 1.84 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, $ArCH(CH_3)_2$), 1.74 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, $ArCH(CH_3)_2$), 1.70 (s, 8H, THF), 1.47 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, $ArCH_2CH_3$), 1.20 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, $ArCH(CH_3)_2$), 1.08 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, $ArCH(CH_3)_2$), 0.48 (s, 9H, $Si(CH_3)_3$), −0.38 (s, 2H, CH_2SiMe_3) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 198.31 (q, $^2J_{P-C}$ = 36.0 Hz, J_{Y-C} = 36.0 Hz, 1C, *ipso*-YC_6H_4P), 168.30 (s, 1C, N*C*), 148.44 (s, 1C, *ipso*-C_6H_3iPr$_2$), 147.43 (d, $^3J_{P-C}$ = 9 Hz, 1C, *ipso*-$C_6H_3Et_2$), 145.99 (s, 1C, *o*-C_6H_3iPr$_2$), 144.51 (s, 1C, *o*-C_6H_3iPr$_2$), 140.78 (d, J_{P-C} = 5.7 Hz, 1C, *ipso*-PC_6H_5), 140.06 (d, J_{P-C} = 5.0 Hz, 1C, *ipso*-PC_6H_4Y), 139.88 (s, 1C, *o*-$C_6H_3Et_2$), 138.72 (s, 1C, *o*-$C_6H_3Et_2$), 136.19 (d, $^3J_{P-C}$ = 23.2 Hz, 1C, *o*-PC_6H_4Y), 133.45 (d, 2C, *o*-C_6H_3iPr$_2$), 131.91 (s, 1C, *o*-YC_6H_4P), 128.25 (overlap with C_6D_6, 1C, *p*-C_6H_3iPr$_2$), 127.89 (s, 1C, *m*-PC_6H_4Y), 126.08 (s, 1C, *p*-PC_6H_5), 125.78, 125.64, 125.51, 125.47 (m, 2C, *o*-PC_6H_5, 2C, *m*-$C_6H_3Et_2$), 125.02 (s, 1C, *m*-YC_6H_4P), 124.48 (s, 1C, *m*-PC_6H_5), 123.33 (br, 1C, *m*-PC_6H_5, 1C, *p*-$C_6H_3Et_2$), 77.94 (d, J_{P-C} = 107 Hz, 1C, *C*HP), 69.14 (s, 4C, THF), 32.38 (d, J_{Y-C} = 36.0 Hz, 1C, YCH_2Si), 29.03 (s, 1C, $C_6H_3(CHMe_2)_2$), 28.23 (s, 1C, $C_6H_3(CHMe_2)_2$), 26.33 (br, 1C, $C_6H_3(CH_2Me)_2$), 25.96 (s, 2C, $C_6H_3(CH(CH_3)_2)_2$), 25.52 (br, 1C, $C_6H_3(CH_2Me)$), 25.11 (s, 1C, $C_6H_3(CH(CH_3)_2)_2$), 24.89 (s, 1C, $C_6H_3(CH(CH_3)_2)_2$), 24.66 (s, 1C, NCCH_3), 16.02 (s, 1C, $C_6H_3(CH_2CH_3)_2$), 14.49 (s, 1C, $C_6H_3(CH_2CH_3)_2$), 4.70 (s, 3C, $CH_2Si(CH_3)_3$) ppm. ^{31}P NMR (400 MHz, C_6D_6, 25 °C): δ 6.68 ppm. Anal. Calcd for $C_{49}H_{70}N_2O_2PSiY$ (866.42): C, 67.88; H, 8.14; N, 3.23. Found: C, 68.21; H, 8.32; N, 3.01%.

4.3.3. The characterization of complex **3** $L^3Y(CH_2SiMe_3)(THF)_2$

^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.75 (m, 2H, *o*-PPh_2), 7.54 (m, 2H, *o*-PPh_2), 7.49 (s, 1H, *m*-C_6H_3iPr$_2$), 7.28 (overlap with C_6D_6, 2H, *m,p*-C_6H_3iPr$_2$), 7.21 (br, 2H, *m*-$C_6H_3(CH_2Y)Me$), 7.12 (br, 4H, *m,p*-PPh_2 and *p*-$C_6H_3(CH_2Y)Me$), 7.05 (br, 3H, *m,p*-PPh_2), 3.72 (d, $^2J_{P-H}$ = 16.0 Hz, 1H, PC*H*), 3.64 (br, 8H, THF), 3.12 (m, 1H, C*H*Me$_2$),

2.71(m, 1H, C*H*Me$_2$), 2.05 (d, $^3J_{H-H}$ = 6.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.99 (s, 3H, NCC*H*$_3$), 1,67 (s, 3H, C$_6$H$_3$(CH$_2$Y)(C*H*$_3$)), 1.32 (br, 8H, THF), 1.17 (br, 3H, CH(C*H*$_3$)$_2$), 0.79 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 0.68 (s, 9H, Si(C*H*$_3$)$_3$), 0.63 (br, 3H, CH(C*H*$_3$)$_2$), 0.66, 0.17 (ABX, $^2J_{H-H}$ = 10.8 Hz, J_{Y-H} = 2.4 Hz, 2H, C$_6$H$_3$(C*H*$_2$Y)(CH$_3$)), 0.12, −0.25 (ABX, $^2J_{H-H}$ = 10.8 Hz, J_{Y-H} = 2.4 Hz, 2H, YC*H*$_2$SiMe$_3$) ppm. ^{13}C {^{1}H} NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 172.39 (s, 1C, N*C*), 147.28 (d, J_{P-C} = 10.4 Hz, 1C, *ipso*-PPh$_2$), 145.22 (s, 1C, *ipso*-*C*$_6$H$_3$*i*Pr$_2$), 144.50 (d, J_{P-C} = 7.0 Hz, 1C, *ipso*-PPh$_2$), 139.83 (s, 1C, *o*-*C*$_6$H$_3$*i*Pr$_2$), 139.57 (s, 1C, *o*-*C*$_6$H$_3$*i*Pr$_2$), 135.32 (d, $^2J_{P-C}$ = 8.3 Hz, 1C, *ipso*-*C*$_6$H$_3$Me$_2$), 134.14 (s, 1C, *o*-*C*$_6$H$_3$Me(CH$_2$Y)), 133.33 (s, 1C, *o*-*C*$_6$H$_3$(CH$_2$Y)Me), 132.52 (s, 2C, *o*-PPh$_2$), 132.42 (s, 2C, *o*-PPh$_2$), 131.80 (s, 2C, *p*-PPh$_2$), 131.68 (s, 4C, *m*-PPh$_2$), 130.17 (s, 1C, *p*-*C*$_6$H$_3$Me$_2$), 126.13 (s, 1C, *p*-*C*$_6$H$_3$*i*Pr$_2$), 124.74 (s, 2C, *m*-*C*$_6$H$_3$Me$_2$), 123.35 (s, 1C, *m*-*C*$_6$H$_3$*i*Pr$_2$), 122.61 (s, 1C, *m*-*C*$_6$H$_3$*i*Pr$_2$), 69.78 (br, 4C, THF), 53.06 (d, $^2J_{P-C}$ = 122.9, 1C, NC(Me) *C*HP), 52.07 (d, J_{Y-C} = 39.3 Hz, 1C, C$_6$H$_3$(*C*H$_2$Y)Me), 36.88 (s, 1C, *C*HMe$_2$), 29.16 (s, 1C, *C*H$_2$SiMe$_3$), 27.99 (s, 1C, *C*HMe$_2$), 27.61 (s, 2C, *C*HMe$_2$), 25.42 (br, 8C, CH(*C*H$_3$)$_2$ and THF), 24.68 (s, 2C, CH(*C*H$_3$)$_2$), 24.15 (d, $^3J_{P-C}$ = 10.5 Hz, 1C, NCCH$_3$), 22.20 (s, 1C, C$_6$H$_3$(CH$_3$)(CH$_2$Y)), 5.32 (s, 3C, Si(*C*H$_3$)$_3$) ppm. ^{31}P NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 5.88 ppm. Anal. Calcd for C$_{47}$H$_{66}$N$_2$O$_2$PSiY (838.91): C, 67.28; H, 7.93; N, 3.34. Found: C, 67.66; H, 8.11; N, 3.18%.

4.3.4. The characterization of complex **4** *L^{4}Y(CH$_2$SiMe$_3$)$_2$(THF)*

^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 7.63 (m, 4H, *o*-PPh$_2$), 7.13 (br, 3H, *m,p*-C$_6$*H*$_5$), 7.02 (br, 2H, *p*-PPh$_2$, 4H, *m*-PPh$_2$, 2H, *m*-C$_6$*H*$_3$*i*Pr$_2$, 2H, *o*-C$_6$*H*$_5$), 6.74 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, *p*-C$_6$*H*$_3$*i*Pr$_2$), 3.70 (br, 6H, THF), 3.22 (br, 2H, C$_6$H$_3$(*C*H(CH$_3$)$_2$)$_2$), 2.88 (dd, $^2J_{P-H}$ = 8.8 Hz, 1H, C*H*P), 1.76 (s, 3H, NCC*H*$_3$), 1.48 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, C$_6$H$_3$(CH(C*H*$_3$)$_2$)$_2$), 1.19 (br, 6H, THF), 0.86 (br, 6H, C$_6$H$_3$(CH(C*H*$_3$)$_2$)$_2$), 0.33 (s, 18H, Si (C*H*$_3$)$_3$), −0.33 (s, 4H, YC*H*$_2$Si) ppm. ^{13}C {^{1}H} NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 179.27 (s, 1C, N*C*), 150.07 (d, $^2J_{P-C}$ = 6 Hz, 1C, *ipso*-*C*$_6$H$_5$), 145.92 (s, 1C, *ipso*-*C*$_6$H$_3$*i*Pr$_2$), 141.81 (s, 2C, *o*-*C*$_6$H$_3$*i*Pr$_2$), 136.08 (d, J_{P-C} = 88.0 Hz, 2C, *ipso*-PPh$_2$), 133.00 (d, $^2J_{P-C}$ = 9.7 Hz, 4C, *o*-PPh$_2$), 131.93 (s, 2C, *m*-*C*$_6$H$_3$*i*Pr$_2$), 129.96 (s, 2C, *p*-PPh$_2$), 129.08 (d, $^3J_{P-C}$ = 11.5 Hz, 4C, *m*-PPh$_2$), 126.07 (s, 1C, *p*-*C*$_6$H$_5$), 124.44 (s, 2C, *m*-*C*$_6$H$_5$), 123.60 (d, $^2J_{P-C}$ = 12 Hz, 2C, *m*-*C*$_6$H$_5$), 121.92 (s, 1C, *p*-*C*$_6$H$_3$*i*Pr$_2$), 69.85 (s, 2C, THF), 45.63 (d, J_{P-C} = 121.8 Hz, 1C, P*C*H), 33.92 (d, J_{Y-C} = 38.7 Hz, Y*C*H$_2$Si), 29.10 (s, 2C, C$_6$H$_3$(*C*H(CH$_3$)$_2$)$_2$), 26.44 (d, $^3J_{P-C}$ = 7.4 Hz, 1C, NCCH$_3$), 25.69 (s, 2C, THF), 25.55 (s, 2C, C$_6$H$_3$(CH(*C*H$_3$)$_2$)$_2$), 25.04 (s, 2C, C$_6$H$_3$(CH(*C*H$_3$)$_2$)$_2$), 5.24 (s, 6C, CH$_2$Si (*C*H$_3$)$_3$) ppm. ^{31}P NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 11.54 ppm. Anal. Calcd for C$_{47}$H$_{70}$N$_2$OPSi$_2$Y (827.05): C, 65.40; H, 8.17; N, 3.25. Found: C, 65.98; H, 8.25; N, 3.01%.

4.3.5. The characterization of complex **5** *L^{5}Y(CH$_2$SiMe$_3$)$_2$(THF)*

^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 7.70 (m, 4H, *o*-PPh$_2$), 7.35 (br, 1H, *o*-C$_6$*H*$_4$CF$_3$), 7.23 (br, 1H, *o*-C$_6$*H*$_4$(CF$_3$)), 7.12 (br, 3H, *m,p*-C$_6$*H*$_3$*i*Pr$_2$), 6.98 (m, 8H, *m,p*-C$_6$*H*$_4$CF$_3$, *m,p*-PPh$_2$), 3.72 (br, 4H, THF), 3.14 (m, 2H, C$_6$H$_3$(*C*H(CH$_3$)$_2$)$_2$), 2.85 (dd, $^2J_{P-H}$ = 9.6 Hz, 1H, PC*H*), 1.72 (s, 3H, NCC*H*$_3$), 1.46 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, C$_6$H$_3$(CH(C*H*$_3$)$_2$)$_2$), 1.03 (br, 4H, THF), 0.84 (d, $^3J_{H-H}$ = 5.6 Hz, 6H, C$_6$H$_3$(CH(C*H*$_3$)$_2$)$_2$), 0.31 (s, 18H, Si(C*H*$_3$)$_3$), −0.33 (s, 4H, C*H*$_2$SiMe$_3$) ppm. ^{13}C {^{1}H} NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 179.18 (s, 1C, N*C*), 168.92 (s, 1C, *ipso*-CF$_3$*C*$_6$H$_4$), 150.54 (d, $^2J_{P-C}$ = 4.6 Hz, 1C, *ipso*-*C*$_6$H$_4$CF$_3$), 146.06 (s, 1C, *ipso*-*C*$_6$H$_3$*i*Pr$_2$), 144.99 (s, 1C, *C*F$_3$C$_6$H$_4$), 141.12 (s, 2C, *o*-*C*$_6$H$_3$*i*Pr$_2$), 134.64 (d, J_{P-C} = 87.5 Hz, 2C, *ipso*-PPh$_2$), 132.33 (d, J_{P-C} = 10 Hz, 4C, *o*-PPh$_2$), 131.82 (s, 2C, *p*-PPh$_2$), 130.02 (s, 2C, *m*-*C*$_6$H$_3$*i*Pr$_2$), 128.77 (d, $^3J_{P-C}$ = 11.5 Hz, 4C, *m*-PPh$_2$), 127.22 (d, $^3J_{P-C}$ = 13.2 Hz, 1C, *o*-*C*$_6$H$_4$CF$_3$),125.78 (s, 1C, *p*-*C*$_6$H$_4$CF$_3$), 124.03 (s, 1C, *p*-*C*$_6$H$_3$*i*Pr$_2$), 118.72 (d, $^3J_{P-C}$ = 10.4 Hz, 1C, *o*-CF$_3$*C*$_6$H$_4$), 117.61 (s, 1C, *m*-*C*$_6$H$_4$CF$_3$), 69.80 (2C, THF), 43.79 (d, J_{P-C} = 120.0 Hz, 1C, P*C*H), 34.26 (d, J_{Y-C} = 40 Hz, 2C, Y*C*H$_2$), 28.62 (s, 2C, C$_6$H$_3$(*C*H(CH$_3$)$_2$)$_2$), 25.86 (d, $^3J_{P-C}$ = 6.7 Hz, 1C, NCCH$_3$), 25.07 (br, 2C, THF, 2C, C$_6$H$_3$(CH(*C*H$_3$)$_2$)$_2$), 24.50 (s, 2C, C$_6$H$_3$(CH(*C*H$_3$)$_2$)$_2$), 4.71 (s, 6C, Si(*C*H$_3$)$_3$) ppm. ^{31}P NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 35.04 ppm. Anal. Calcd for C$_{46}$H$_{65}$F$_3$N$_2$OPSi$_2$Y (895.01): C, 61.73; H, 7.32; N, 3.13. Found: C, 62.13; H, 7.46; N, 3.01%.

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Appendix A. Supplementary material

CCDC Nos. 774857, 774854, 774856, 774858 and 774855 contain the supplementary crystallographic data for compounds **1**, **2**, **3**, **4** and L^3, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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