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Synthesis and Reactivity of Rare Earth Metal Alkyl Complexes Stabilized by Anilido Phosphinimine and Amino Phosphine Ligands

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Abstract: Anilido phosphinimino ancillary ligand H_2L^1 reacted with one equivalent of rare earth metal trialkyl $[Ln\{CH_2Si(CH_3)_3\}_3(thf)_2]$ (Ln = Y, Lu) to afford rare earth metal monoalkyl complexes $[L^1LnCH_2Si(CH_3)_3(THF)]$ (**1a**: Ln = Y; **1b**: Ln = Lu). In this process, deprotonation of H_2L^1 by one metal alkyl species was followed by intramolecular C–H activation of the phenyl group of the phosphine moiety to generate dianionic species L^1 with release of two equivalnts of tetramethylsilane. Ligand L^1 coordinates to Ln^{3+} ions in a rare C,N,N tridentate mode. Complex **1a** reacted readily with two equivalents of 2,6-diisopropylaniline to give the corresponding bis-amido complex $[(HL^1)LnY(NHC_6H_3iPr_2\text{-}2,6)_2]$ (**2**) selectively, that is, the C–H activation of the phenyl group is reversible. When **1a** was exposed to moisture, the hydrolyzed dimeric complex $[\{(HL^1)Y(OH)\}_2](OH)_2$ (**3**) was isolated. Treatment of $[Ln\{CH_2Si(CH_3)_3\}_3(thf)_2]$ with amino phosphine ligands $HL^{2\text{-}R}$ gave stable rare earth metal bis-alkyl complexes $[(L^{2\text{-}R})Ln\{CH_2Si(CH_3)_3\}_2(thf)]$ (**4a**: Ln = Y, R = Me; **4b**: Ln = Lu, R = Me; **4c**: Ln = Y, R = *i*Pr; **4d**: Ln = Y, R = *i*Pr) in high yields. No proton abstraction from the ligand was observed. Amination of **4a** and **4c** with 2,6-diisopropylaniline afforded the bis-amido counterparts $[(L^{2\text{-}R})Y(NHC_6H_3iPr_2\text{-}2,6)_2(thf)]$ (**5a**: R = Me; **5b**: R = *i*Pr). Complexes **1a**,**b** and **4a–d** initiated the ring-opening polymerization of D,L-lactide with high activity to give atactic polylactides.

Keywords: C–H activation · lanthanides · N ligands · N,P ligands · ring-opening polymerization

Introduction

Rare earth metal alkyl complexes, as single-component catalysts or key precursors of their cationic counterparts after activation by methylalumoxane or borates, which have shown tremendous catalytic activities towards olefin polymerization[1] and highly regio- or stereoselective polymerization of conjugated[2] and polar monomers,[3] are among the ultimate goals of organometallic chemists. Many ancillary ligands have been used in attempts to stabilize metal alkyls. To date, the rare earth metal alkyls have been dominated by cyclopentadienyl environments, including mono, bis, and ansa, auxiliaries.[4] Recently, heteroatom compounds such as bidentate amidinates,[5] guanidinates,[6] β-diketiminates,[7] and salicylaldiminates,[8] have been extensively explored as spectator ligands by virtue of their strong metal–ligand bonds and exceptional and tunable steric and electronic features required for compensating coordinative unsaturation of metal centers and for catalytic activity towards polymerization. However, rare earth metal monoalkyl and especially bis-alkyl complexes supported by such heteroatom compounds usually undergo salt addition, dimerization, or ligand redistribution[3c] due to the highly active character of the metal–carbon bonds and relatively less crowded steric environment of the molecules. Properly substituted amidinato, β-diketiminato, and anilido imido ligands have been successfully used by Hessen et al. and Piers et al. to stabilize rare earth metal bis-alkyl complexes which can be readily transformed into their cationic counterparts.[9] The recent surge of activity in the use of phosphinimine donors in organotransition metal chemistry[10] directed a new way for rare earth organometallic chemistry. Here we report on anilido phosphinimine and amino phosphine ligands as "softer" and less basic donors for supporting rare earth metal alkyl com-

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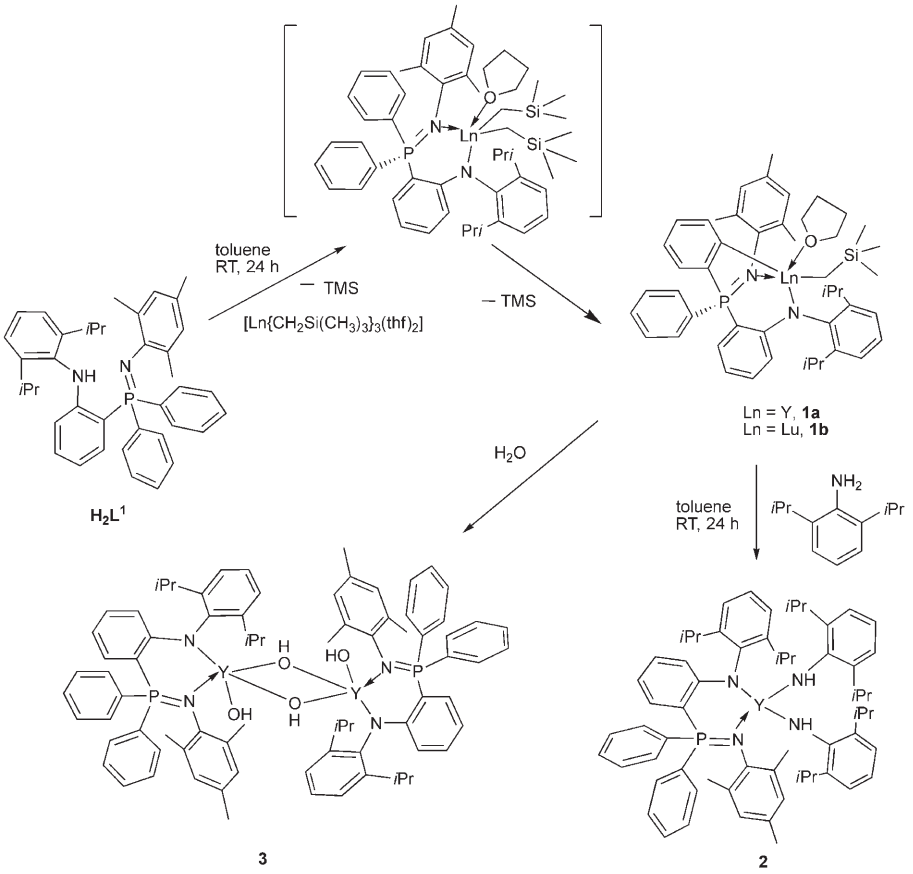
plexes. Although related ligands have been used to prepare lithium and aluminum complexes,[11] analogues based on rare earth metal, as far as we aware, have not appeared in the literature. In addition, the catalytic behavior of these metal alkyl complexes towards the polymerization of *rac*-lactide is discussed.

Results and Discussion

Synthesis of rare earth metal monoalkyl complexes 1a,b: Reaction between yttrium tris-alkyl $[Y\{CH_2Si(CH_3)_3\}_3(thf)_2]$ and one equivalent of neutral ligand H_2L^1 was swift in toluene at room temperature. After stirring for 24 h, volatile substances were removed under reduced pressure to leave a brownish residue, which was suspended in a small amount of hexane and cooled to −34 °C to give **1a** as a colorless crystalline solid over 12 h (Scheme 1). Crystals for X-ray analysis were isolated by recrystallization from benzene/hexane at room temperature over several days. In the ^{1}H NMR spectrum formation of **1a** is evidenced by the loss of the signal for the amino proton of the ligand around $\delta =$ 9.68 ppm and the changes in pattern and chemical shift of the resonances of methylene protons of $YCH_2Si(CH_3)_3$ compared to $[Y\{CH_2Si(CH_3)_3\}_3(thf)_2]$. To our surprise, the integrated intensities of the resonances of the methylene protons and the ligand indicated one alkyl moiety (bearing one negative charge) and one ligand (monoanionic) in **1a**, but it should contain two alkyl moieties and one ligand according to the reactant ratio and Y^{3+} oxidation state. In addition, the ^{13}C NMR spectrum displayed multiple resonances around $\delta = 200$ ppm (C coupled with Y) which arise from an *ipso*-carbon atom of a phenyl ring according to ^{1}H–^{13}C HMQC analysis. However, since no *ipso*-carbon atom of any phenyl ring of the ligand gives resonances below $\delta =$ 155 ppm,[11] this downfield shift could be attributed to a carbon atom of a phenyl ring that is directly bonded to the yttrium atom.[12] X-ray diffraction finally confirmed the molecular structure of **1a** (Figure 1). The anilido phosphinimino ligand protonates one yttrium alkyl moiety and then a C–H group of a phenyl ring of the phosphine moiety is activated to eliminate another molecule of TMS and form a dianionic species L^1 which coordinates to yttrium atom in a rare C,N,N tridentate fashion. The residual alkyl moiety and a THF molecule occupy the remaining *cis* positions opposite to the ligand. Thus, a twisted trigonal-bipyramidal geometry is formed around the central metal atom with atoms C40-(phenyl), C30(alkyl), and amino N1 in equatorial positions, while the O atom of THF and imino N2 have an axial arrangement. The aryl ring formed by C13–C18 together with atoms N1, Y, and P form a plane from which imino N2 atom deviates. The P-phenyl ring C25–C30 lies above the plane, and the P-phenyl ring of C19–C24 stands adjacent to it with a *trans* arrangement relative to the five-membered THF ring, the alkyl ligand, and the planar aniline moiety. The comparable Y–C30 and Y–C40 bond lengths of 2.435(5) and 2.418(5) Å, respectively, prove direct coordination of the phenyl carbon atom to yttrium. Lutetium complex **1b** was isolated by procedure similar to that for **1a**. Complex **1b** gives a similar ^{1}H NMR spectrum to **1a** except for a slightly difference in the chemical shifts of the methylene protons $LnCH_2Si(CH_3)_3$. Ligand H_2L^1 represents a new type of ligand containing a "soft" and "weakly" coordinating phosphorus atom, which was first introduced as an extension of the anilido imido ligand system by Piers et al. to prepare $(HL^1)AlMe_2$ and $(HL^1)AlH_2$ complexes.[11] Similarly, some aliphatic phosphinimine amido ligands were also successfully used by Stephan et al. to stabilize neutral and



Scheme 1. Synthesis and reactivity of complexes **1a**,**b**.

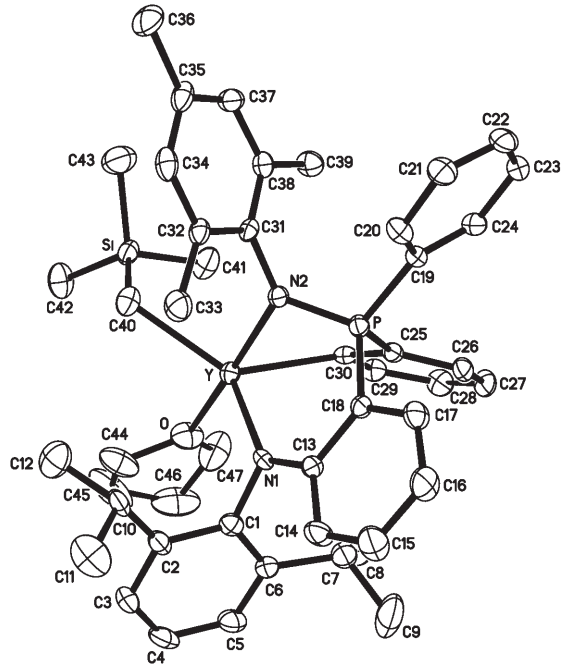


Figure 1. Molecular structure of complex **1a** with thermal ellipsoids with 50% probability (hydrogen atoms omitted for clarity).

cationic complexes of aluminum, palladium, and nickel.[10c,d] Complex **1a** is structurally different from the above-mentioned complexes, and the N1-Y-N2 bond angle of 82.45(14)° is much smaller than those in $(HL^1)AlMe_2$ (N1-Al-N2 99.07(12)°) and $(HL^1)AlH_2$ (N1-Al-N2 100.02(8)°).[11] Complex **1a** is extremely unsymmetric, and this results in obvious differences in the N1-Y-O (103.90(14)°) and N2-Y-O (172.93(14)°) bond angles. This is consistent with ^{1}H NMR data[12] (Table S1) showing that the methyl protons of isopropyl groups on the amino phenyl ring exhibit four discrete resonances as opposed to only one signal in free ligand H_2L^1. Recently, Fryzuk et al. reported a ruthenium amidophosphino complex that undergoes intermolecular C–H activation. The activated phenyl species originates from a neutral triphenylphosphine ligand and coordinates to the Ru atom as a monoanionic moiety.[13] Thus, the intramolecular C–H activation of the phenyl group of monoanionic phosphine species HL^1 forming dianionic species L to stabilize rare earth metal alkyl complexes like **1a**,**b** is unprecedented.

Amination of 1a to form yttrium bis-amido complex 2: Treatment of **1a** with 2,6-diisopropylaniline in toluene at room temperature afforded bis-amido complex $[(HL^1)Y(HNAr)_2]$ (**2**, $Ar = C_6H_3iPr_2$-2,6) as a pale yellow solid (Scheme 1). The ^{1}H NMR spectrum shows the absence of resonances of methylene protons in the upfield region and the appearance of signals arising from amino protons, that is, the alkyl moiety was aminated. The integrated intensity of resonances of the amino protons indicates two amino ligands in **2**, and its ^{13}C NMR spectrum showed that the signal around $\delta = 200$ ppm assigned to $Y-C_{phenyl}$ had disappeared. Thus, we conclude that the $Y-C_{phenyl}$ bond is cleaved by aniline to form $Y-N_{amino}$ species accompanied by recovery of the C–H-activated phenyl ring. Additionally, no matter whether the molar ratio of **1a** to aniline is 1:1 or 1:2, bis-amido complex **2** is the major product, and this suggests that the $Y-C_{phenyl}$ bond is weak. This assignment of the solution structure was supported by a single-crystal X-ray diffraction study confirming that **2** is unsolvated and crystallizes as two enantiomers. As shown in Figure 2, the yttrium

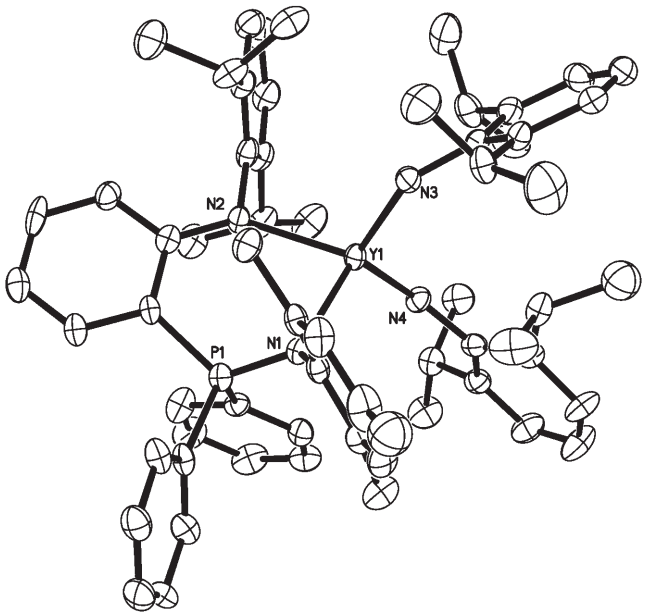


Figure 2. Molecular structure of complex **2** with thermal ellipsoids with 50% probability (hydrogen atoms omitted for clarity).

atom is coordinated by an *N*,*N*-bidentate monoanionic anilido phosphinimine ligand and two anilido moieties located in *cis* positions in the scarce four-coordinate tetrahedral geometry. Nitrogen atoms occupy the four apexes, while the Y atom sits in the center. Interestingly, the plane formed by N3Y1N4 is almost perpendicular to that formed by N1Y1N2. The N3-Y1-N4 bond angle of 119.41(16)° is larger than the C-Y-C bond angles in yttrium bis-alkyl complexes bearing β-diketiminato ligands (108.9(13)°)[14] and monocyclopentadienyl ligands (101.78(8)°),[2h] and much larger than O-Y-C(40) (87.78(17)°) in complex **1a**. This suggests more steric crowding of the anilido moiety compared to the alkyl group or THF molecule, which might be the reason why complex **2** is free from solvent.

Hydrolytic formation of complex 3: Isolation of the hydrolysis product of **1a** was an accident. When **1a** was recrystallized from benzene containing traces of water, we obtained crystals of **3** (Scheme 1) that were suitable for X-ray analysis. Stoichiometric reaction of **1a** with water, however, did not afford **3** in quantitative yield, and no metal alkyl could be recovered; instead, the ligand was usually regenerated, that is, the reaction was not controllable. Figure 3 displays

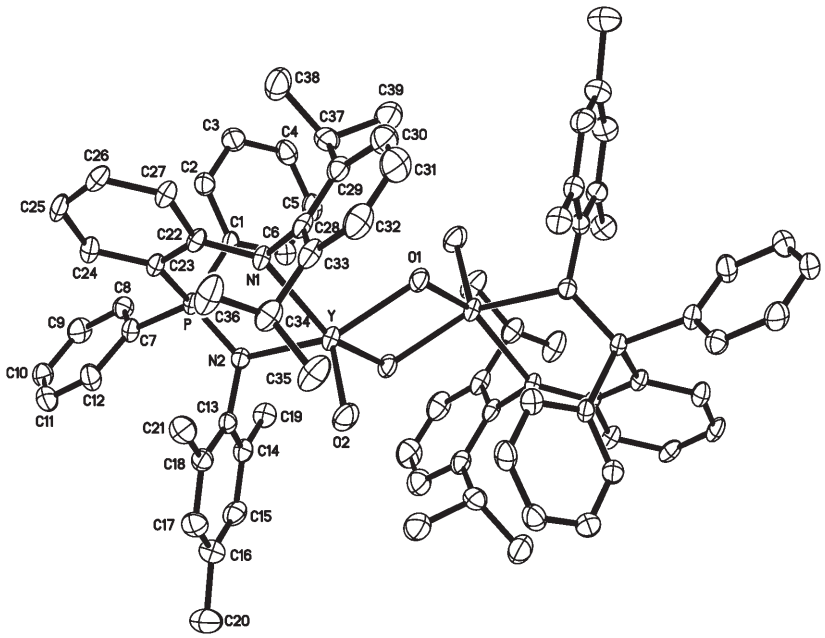
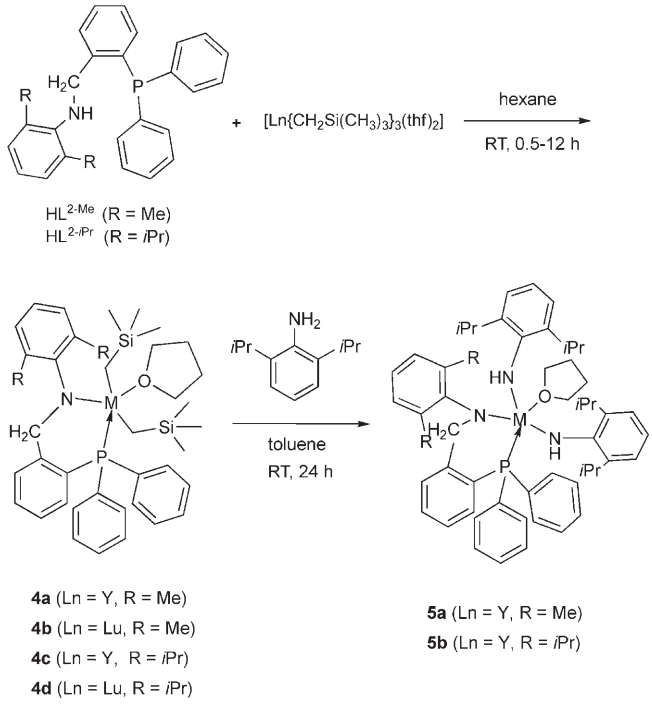


Figure 3. Molecular structure of complex **3** with thermal ellipsoids with 50% probability (hydrogen atoms omitted for clarity).

the molecular structure of **3**. Each yttrium atom is coordinated by an N,N bidentate ligand and a terminal hydroxy group to generate a unit, two of which are bridged by hydroxy groups to form dimeric complex **3** of C_s symmetry. The two N atoms and three O atoms form a pyramidal geometry around the central metal atom with the terminal O2 atom as the apex, while the Y atom protrudes from the base. All Y–N bonds, which range from 2.356(11) to 2.375(11) Å, are consistent with classical Ln–N bonding. The bridging Y–O bond lengths (Y–O(1) 2.215(10), Y–O1#1 (2.247(10) Å), are, as expected, longer than the terminal ones (Y–O2 2.054(11) Å).

Synthesis of rare earth bis-alkyl complexes 4a–d: The emergence of cationic alkyl complexes of Group 3 metals as key intermediates in homogeneous olefin polymerization[1d,2h] has promoted interest in synthesis of rare earth metal bis-alkyl precursors. Such precursors bearing non-cyclopentadienyl ligands appeared in the literature only recently,[8,9,15] and those supported by "soft" electronic donors such as phosphorus-containing ligands have not been reported, although the related diphosphanylamido ligands have been used by Roesky et al. to synthesize rare earth amido and chlorido complexes.[16] We found that amido phosphine ligands $HL^{2\text{-}R}$, derivatives of the reduction product of imino phosphines, are electronically and sterically appropriate to stabilize rare earth bis-alkyl species. Reaction between rare earth metal alkyls $[Ln\{CH_2Si(CH_3)_3\}_3(thf)_2]$ and $HL^{2\text{-}Me}$ proceeded smoothly at room temperature via metal alkyl abstraction to afford complexes **4a** (Ln = Y) and **4b** (Ln = Lu; Scheme 2). The ^{1}H NMR spectrum showed that the resonances of the methylene protons $LnCH_2Si(CH_3)_3$ shifted downfield to $\delta = -0.16$ ppm for **4a** and −0.33 for **4b** compared with $\delta = -0.60$ ppm in $[Ln\{CH_2Si(CH_3)_3\}_3(thf)_2]$. X-ray analysis established that the overall structures of **4a** and **4b** are analogous (Figure 4). Each metal atom bonds to the monoanionic N,P bidentate amido phosphine ligand, a THF molecule, and two alkyl moieties. The THF molecule is disordered. The spatial occupancy probability for each position is 50%. The ligands generate a trigonal-bipyramidal geometry around the central metal atom with N1, C28, and C32 axial and P and O equatorial. The C-Ln-C bond angles are 115.79(17)° in **4a** and 115.3(2)° in **4b**, and their similarity to the C-Y-C angle of 119.5(2)° in a THF-solvated amidinato yttrium bis-alkyl complex[9c] indicates similar steric environments of both ligands. However, these bond angles are larger than the C-Ln-C angles in rare earth metal bis-alkyl complexes supported by triazacyclononane (99.41(8)°),[15b] triamino amide (101.96(6)°)[15a] and β-diketiminate (108.90(13)°).[14] Treatment of $[Ln\{CH_2Si(CH_3)_3\}_3(thf)_2]$ with $HL^{2\text{-}iPr}$ in a similar procedure to that described above, albeit for longer time,



Scheme 2. Synthesis and reactivity of complexes **4a–d**.

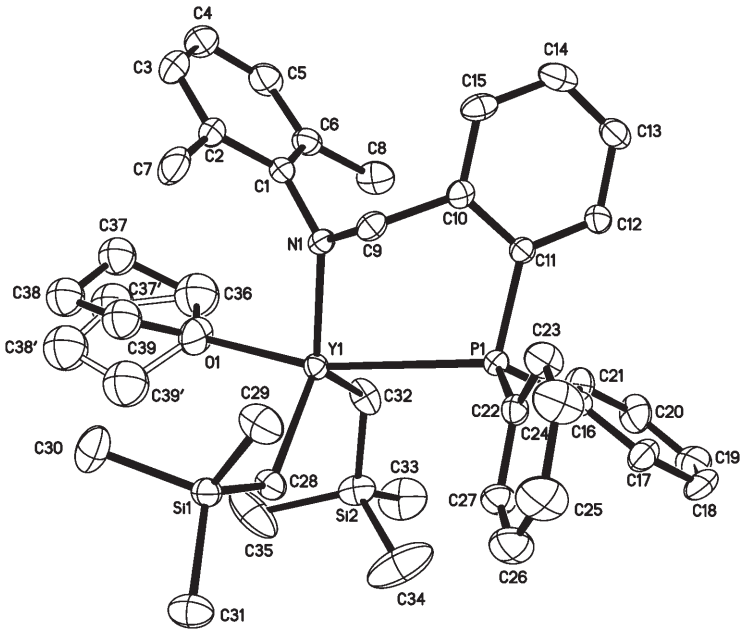


Figure 4. Molecular structure of complex **4a** with thermal ellipsoids with 50% probability (hydrogen atoms omitted for clarity).

afforded complexes **4c** (Ln = Y, Figure 5) and **4d** (Ln = Lu), respectively. The different substituents on the amino aryl ring and ionic radii of the central metal have little effect on

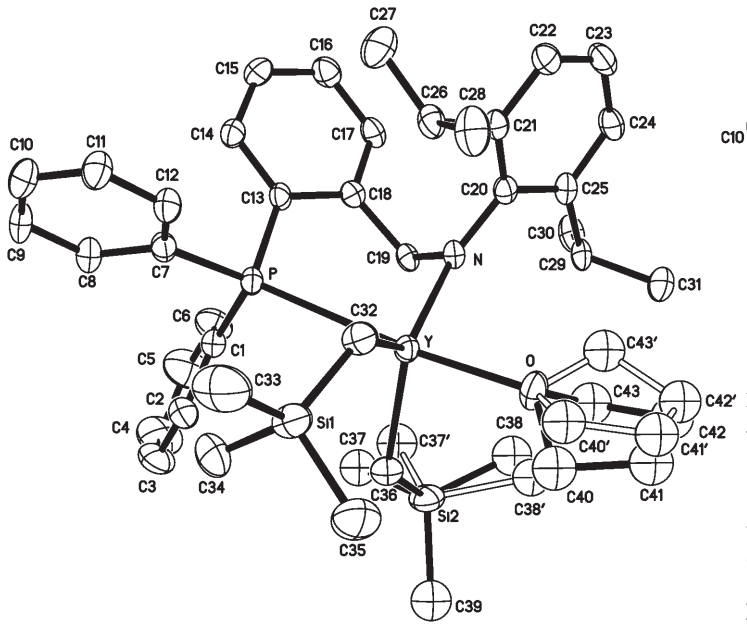


Figure 5. Molecular structure of complex **4c** with thermal ellipsoids with 50% probability (hydrogen atoms omitted for clarity).

the C-Ln-C bond angles in these four complexes (115.79(17)° in **4a**, 115.3(2)° in **4b**, 116.35(19)° in **4c** and 116.81(12)° in **4d**). However, a strong influence on the catalytic activity was observed (vide infra); moreover, the presence of the more sterically demanding isopropyl substituents instead of methyl groups on the amino aryl rings results in more twisted geometry of the complexes. Thus, C9 in **4c** and **4d** deviates from the plane formed by chelating atoms P1, Ln1, and N1 with torsion angles of 42.02 and 42.51°, respectively, which are much larger than those of 34.53° in **4a** and 34.04° in **4b**.

Amination of 4a,c to form bis-amido complexes 5a,b: Bis-alkyl complexes **4a**,**c** are highly reactive to 2,6-dimethylaniline to afford the corresponding bis-amido complexes **5a**,**b** selectively, analogous to formation of **2** by amination of a metal alkyl moiety in **1a**. In the ^{1}H NMR spectra of **5a**,**b**, the resonances attributed to metal alkyl cannot be observed, and NH signals appear, while the remainders of the spectra are similar to those of precursors **4a**,**c**. X-ray diffraction revealed the solid-state structure of **5a** to be a THF-solvated monomer (Figure 6). The N,P bidentate ligand coordinates

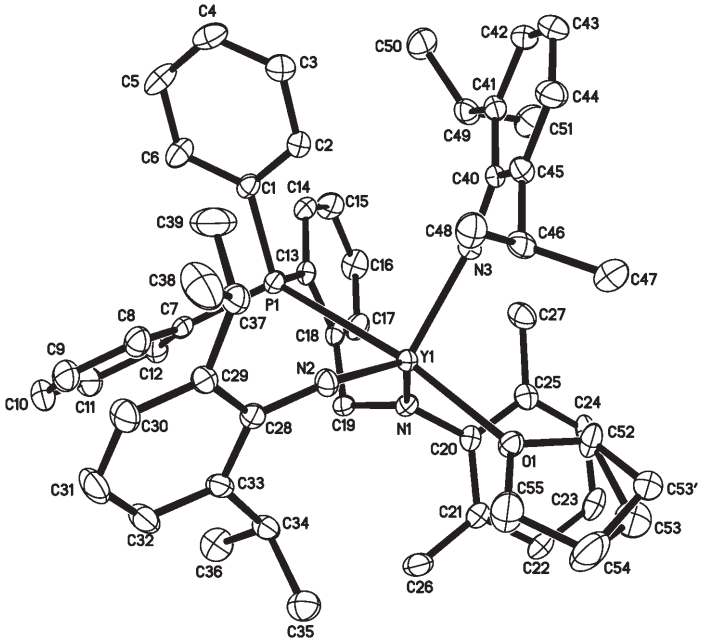


Figure 6. Molecular structure of complex **5a** with thermal ellipsoids with 50% probability (hydrogen atoms omitted for clarity).

to the Y atom in a "chair" shape with the phenyl ring C13–C18 forming the "back". The chelating atoms N1, Y1 together with C19 and P1 form the "seat" with C19 deviating 20.86° from the plane P1Y1N1 which unevenly divides the bond angle formed by the amino ligands and the Y atom. The geometry of the central metal atom is five-coordinate trigonal-bipyramidal with a distortion value of $\tau = 0.61$.[17] The Y–N bond lengths, which range from 2.215(3) to 2.232 Å, are comparable to those in **2** and are reasonable for rare earth metal–nitrogen bonds. Coordination of the THF molecule increases the steric crowding of complex **5a**, so that the N2-Y1-N3 bond angle of 103.04(9)° is much

smaller than the N3-Y-N4 bond angle of 119.41(16)° in unsolvated complex **2**.

Catalytic activity towards polymerization of lactide: Biodegradable polymers have long been considered as an alternative to polyolefins, among which linear aliphatic polyesters are particularly attractive and widely used. Polylactide (PLA) is the most promising linear aliphatic polyester, as its monomer is a derivative of natural products and its degradation products are nontoxic CO_2 and H_2O. Numerous aluminum,[18] magnesium,[19] and zinc[20] complexes have been reported to catalyze ring-opening polymerization (ROP) of lactide (LA). Some lanthanide oxo,[21] halogen,[22] and amido[23] complexes containing Ln–O, Ln–Cl, and Ln–N initiators, respectively, are also active catalysts.[24] We investigated our new of lanthanide alkyl complexes in the ROP of D,L-LA. As shown in Table 1, complex **1a** is highly active in

Table 1. Polymerization of D,L-lactide with various complexes.[a]

Entry	Complex	Yield	$M_{calcd}\times10^{-4}$[b]	$M_n\times10^{-4}$[c]	PDI
1	**1a**	95.5	2.75	2.60	1.83
2	**1b**	trace	n.d[d]	n.d	n.d
3	**4a**	99.7	2.87	1.87	1.92
4	**4b**	93.5	2.69	1.83	1.75
5	**4c**	50.1	1.44	0.93	1.50
6	**4d**	60.2	1.73	1.45	1.75

[a] Conditions: 25 °C, 8 min, THF, [LA] = 0.5 mol L^{-1}, [LA]/[Ln] = 200. [b] Calculated by ([LA]/[Ln]) × 144.14 × X (X = conversion).[c] Determined by GPC against polystyrene standard. [d] n.d = not determined.

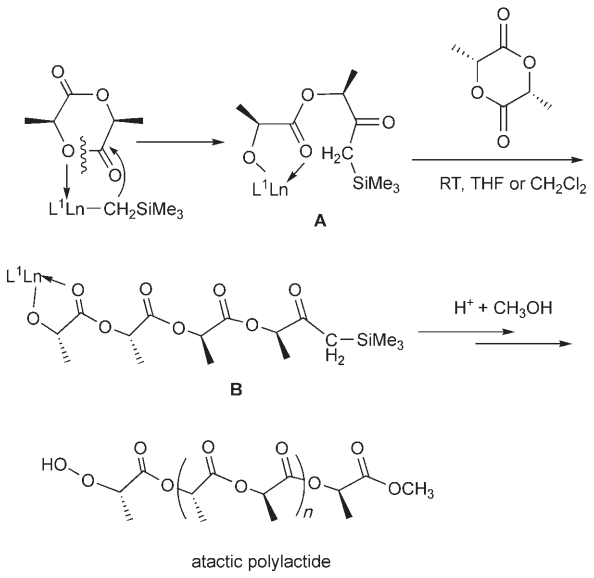
ROP of lactide and reaches 95.5% conversion in 8 min at room temperature. Contrarily, the lutetium counterpart **1b** shows poor activity, and almost no polymer could be isolated in such a short time (Table 1, entries 1, 2). This is consistent with many previous reports that the smaller the ionic radius of the central metal ion, the lower the catalytic activity. In contrast, such an effect of the nature of the metal was negligible when bis-alkyl complexes were used. Both yttrium and lutetium complexes **4a** and **4b** exhibited similar catalytic behaviors, comparable to that of **1a** (Table 1, entries 1, 3, 4) due to the highly active character of the alkyl ligands. However, increasing the steric crowding of substituents on the amino aryl rings by replacing methyl by isopropyl dramatically decreased activity for both yttrium (**4c**) and lutetium (**4d**) complexes, that is, the spatial environment of the ligand also plays important role (Table 1, entries 5, 6). To further investigate the characteristics of the polymerization, the reactions were performed at different monomer-to-initiator ratios in different solvents. Representative data are listed in Table 2. With **1a** as catalyst, polymerizations carried out in CH_2Cl_2 are controllable. The molecular weight of the resultant polymer increases with increasing monomer-to-initiator ratio and fits well with the theoretic value. In THF the molecular weight of the isolated polymer is lower than the calculated value at high ratio (Table 2, entries 1, 2). In contrast, the polymerization initiated by using complex **4a** is more controllable in THF. Increasing monomer-to-initiator

Table 2. Polymerization of D,L-lactide by complexes with different monomer/catalyst ratios and solvents.[a]

Entry	Complex	[LA]/[Ln]	solvent	$M_{calcd}\times10^{-4}$[b]	$M_n\times10^{-4}$[c]	PDI
1	**1a**	300	THF	4.32	4.17	1.48
2	**1a**	500	THF	7.20	5.62	1.53
3	**1a**	300	CH_2Cl_2	4.32	4.77	1.47
4	**1a**	500	CH_2Cl_2	7.20	7.00	1.61
5	**4a**	300	THF	2.16	2.81	1.50
6	**4a**	500	THF	3.60	4.29	1.51
7	**4a**	800	THF	5.86	6.20	1.49
8	**4a**	500	CH_2Cl_2	3.60	5.03	1.32
9	**4a**	800	CH_2Cl_2	5.86	5.51	1.38

[a] Conditions: 25 °C, 2 h, yield: 100%, [LA] = 1.0 mol L^{-1}. [b] Calculated by ([LA]/[Ln]) × 144.14 × X for **1a** and by ([LA]/(2[Ln])) × 144.14 × X (X = conversion) for **4a**. [c] Determined by GPC against polystyrene standard.

ratio results in nearly linear increase of molecular weight of the resultant polymer, while the molecular weight distribution remains constant. Note that all of the measured values are close to the theoretical ones, that is, both alkyl species in **4a** participate in initiation. However, when CH_2Cl_2 was used as solvent, the results were ambiguous. The molecular weight does not correlate well with monomer-to-initiator ratio, although a high yield of polymer can always be isolated and the molecular weight distribution does not change much (Table 2, entries 8, 9). The ^1H NMR spectrum of the oligomer shows signals at 4.35, 2.70, and 1.47 for the HOC(CH$_3$)C(O)– end group.[23d,25] The resonance around δ = 3.75 ppm is assignable to an –OCOCH$_3$ end group, which may be derived from exchange reaction between the terminator CH$_3$OH and the true end group Me$_3$SiCH$_2$CO–, which is difficult to assign. Thus, the mechanism of the polymerization can be explained as in Scheme 3. The acyl oxygen atom O_{acyl} of the monomer D-LA or L-LA first coordinates to the lanthanide ion, and this is followed by nucleophilic



Scheme 3. Probable mechanism for the polymerization of lactide.

attack of metal alkyl carbon atom on the carbonyl carbon atom $C_{carbonyl}$, which induces cleavage of the acyl–oxygen bond to form lanthanide alkoxyl species with carbonyl end group **A**. Further insertion of LA into **A** gives five-membered ring intermediate **B**.[26] Addition of terminator (solution of methanol in $CHCl_3$) to **B** affords polylactide with hydroxyl and methoxyl end groups. When a monoalkyl complex such as **1a** is used as initiator, only the metal alkyl moiety initiates ROP of LA. The Ln–C_{phenyl} species in **1a** takes part in the amination reaction but can not initiate the ROP of LA, as the molecular weight of the resultant PLA is close to the calculated value based on one active site in each complex. When bis-alkyl complexes are used as catalysts, both metal alkyl species act as initiators to give PLAs with molecular weights consistent with the calculated values based on two active sites per complex. The resultant polylactides are atactic, as indicated by the methine region of the homonuclear decoupled ^{1}H NMR spectrum, due to the less sterically crowded environment in the monoalkyl complex and the presence of more than one reactive site in the bis-alkyl complex.

Conclusion

Anilido phosphinimine ligands react with rare earth metal alkyls by protolysis followed by intramolecular C–H activation of the ligand to afford rare earth metal monoalkyl complexes supported by a dianionic C,N,N tridentate ligand. Amido phosphines react with rare earth metal alkyls to give a series of rare earth metal bis-alkyl complexes stabilized N,P bidentate ligands in high yields under mild conditions. These alkyl complexes readily undergo amination with aniline to form the corresponding amino counterparts. All the complexes are well characterized as having novel structures, which, as far as we aware, have not appeared in the literature. Moreover, we demonstrated that these complexes with metal–carbon bonds are highly active initiators for the ROP of LA to give atactic polylactides.

Experimental Section

General conditions: All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an M. Braun glovebox. Solvents were purified by an M. Braun SPS system. Starting materials for the synthesis of complexes **1**–**5** were purchased from Aldrich or Fluka and distilled before use.

Instruments and measurements: Organometallic samples for NMR spectroscopic measurements were prepared in a glove box by using NMR tubes sealed with paraffin film. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H–^{1}H (COSY) and ^{1}H–^{13}C (HMQC) experiments when necessary. The molecular weights and molecular weight distributions of the polymers were measured on a GPC Waters 410. Crystals for X-ray analysis were obtained as described in the experimental section. The crystals were manipulated in the glove box. Data were collected at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystal class and unit cell parameters were determined with the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. IR spectra were obtained on a Bruker Vertex 70 FTIR spectrometer. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry.

Complex 1a: Ligand H_2L^1 (0.20 g, 0.35 mmol), which was synthesized according to the literature procedures,[11], in toluene (2 mL) was gradually added to a solution of $[Y\{CH_2Si(CH_3)_3\}_3(thf)_2]$ (0.17 g, 0.35 mmol) in toluene (3 mL). The reaction mixture was stirred for 24 h at room temperature. After removal of volatile substances, the residue was dissolved in hexane (1.5 mL) and then cooled to −34 °C to afford of **1a** as an orange crystalline solid (0.17 g, 56 %), which was recrystallized from benzene/hexane to afford colorless single crystals for X-ray analysis after several days. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = -0.68$ (m, 2H; CH_2Si(CH$_3$)$_3$), 0.23 (s, 9H; CH$_2$Si(CH_3)$_3$), 0.70 (d, ^3J(H,H) = 6.8 Hz, 3H; NC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 0.76 (d, ^3J(H,H) = 6.8 Hz, 3H; NC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 1.29 (br, 4H; THF), 1.45 (d, ^3J(H,H) = 6.8 Hz, 3H; NC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 1.60 (d, ^3J(H,H) = 6.8 Hz, 3H; NC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 1.98 (m, 1H; NC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 2.16 (s, 3H; *o*-NC$_6$H$_2$(CH_3)$_3$), 2.21 (s, 3H; *o*-NC$_6$H$_2$(CH_3)$_3$), 2.76 (s, 3H; *p*-NC$_6$H$_2$(CH_3)$_3$), 3.54 (br, 4H; THF), 4.11 (m, 1H; NC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 6.24 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,P) = 6.0 Hz, 1H; *o*-YC$_6H_4$P), 6.50 (td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 2.8 Hz, 1H; *m*-PC$_6H_4$Y), 6.64 (s, 1H; *m*-NC$_6H_2$Me$_3$), 6.92 (td, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.8 Hz, 2H; *m*-PC$_6H_5$), 6.97 (s, 1H; *m*-NC$_6H_2$Me$_3$), 7.00 (t, ^3J(H,H) = 7.0 Hz, 1H; *p*-PC$_6H_5$), 7.03 (t, ^3J(H,H) = 7.2 Hz, 1H; *p*-PC$_6H_4$Y), 7.16 (dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H; *m*-NC$_6H_3i$Pr$_2$), 7.22 (t, ^3J(H,H) = 7.2 Hz, 1H; *p*-NC$_6H_3i$Pr$_2$), 7.26 (m, 1H; *m*-PC$_6H_4$N), 7.36 (dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H; *m*-NC$_6H_3i$Pr$_2$), 7.45 (t, ^3J(H,H) = 7.2 Hz, 1H; *p*-PC$_6H_4$N), 7.47 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.6 Hz, 1H; *o*-PC$_6H_4$Y), 7.64 (d, ^3J(H,H) = 7.2, 1H; *o*-PC$_6H_4$N), 7.69 (d, ^3J(H,H) = 7.2 Hz, 1H; *o*-PC$_6H_5$), 7.71 (d, ^3J(H,H) = 7.2 Hz, 1H; *o*-PC$_6H_5$), 8.21 ppm (d, ^3J(H,H) = 7.1 Hz, 1H; *o*-NC$_6H_4$P); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 4.69 (s, 3C, CH$_2$Si(CH_3)$_3$), 20.41 (s, 1C, *p*-NC$_6$H$_2$(CH_3)$_3$), 21.29, 21.71 (s, 2C, *o*-NC$_6$H$_2$(CH_3)$_3$), 24.88, 25.13 (s, 2C, NC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 25.62 (s, 1C, NC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 25.80 (s, 2C, THF), 27.25, 27.83 (s, 2C, NC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 30.11 (s, 1C, CH$_2$SiMe$_3$), 30.46 (s, 1C, NC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$) 69.70 (s, 2C, THF), 113.55 (d, ^3J(C,P) = 13 Hz, 1C, *m*-PC$_6$H$_4$Y), 114.52, 115.48 (s, 2C, *o*-NC$_6$H$_3i$Pr$_2$), 117.36 (d, ^3J(C,P) = 8 Hz, 1C, *o*-YC$_6$H$_2$P), 124.93 (s, 1C, *p*-NC$_6$H$_3i$Pr$_2$), 125.63, 125.77 (s, 1C, *o*-PC$_6$H$_4$Y, 1C, *p*-PC$_6$H$_4$N), 126.28, 126.38 (s, 2C, *m*-NC$_6$H$_3i$Pr$_2$), 128.00 (overlap, 1C, *m*-PC$_6$H$_4$N), 129.00, 129.26, 129.57 (s, 1C, *m*-NC$_6$H$_2$Me$_3$, 1C, *p*-PC$_6$H$_5$, 1C, *p*-PC$_6$H$_4$Y), 131.65, 132.01, 132.29, 132.64 (s, 2C, *m*-PC$_6$H$_5$, 1C, *m*-NC$_6$H$_2$Me$_3$, 1C, *o*-PC$_6$H$_4$N), 133.62 (s, 1C, *p*-NC$_6$H$_2$Me$_3$), 134.58, 134.66 (s, 2C, *o*-PC$_6$H$_5$), 135.31 (d, ^3J(C,P) = 6 Hz, 1C, *o*-NC$_6$H$_2$Me$_3$), 135.69 (d, ^3J(C,P) = 6 Hz, 1C, *o*-NC$_6$H$_2$Me$_3$), 137.16 (s, 1C, *o*-NC$_6$H$_4$P), 137.40 (s, 1C, *ipso*-PC$_6$H$_4$N), 143.33 (s, 1C, *ipso*-NC$_6$H$_4$P), 145.02 (d, ^1J(C,P) = 9 Hz, 1C, *ipso*-PC$_6$H$_4$Y), 148.21 (s, 1C, *ipso*-NC$_6$H$_3i$Pr$_2$), 150.39 (s, 1C, *ipso*-NC$_6$H$_2$Me$_3$), 160.49 (d, ^1J(C,P) = 5 Hz, 1C, *ipso*-PC$_6$H$_5$), 200.24 ppm (dd, ^1J(C,Y) = 50 Hz, ^2J(C,P) = 36 Hz, 1C, *ipso*-YC$_6$H$_4$P); IR (KBr): $\tilde{\nu}$ = 3061 (w), 2959 (s), 2868 (m), 1588 (m), 1569 (m), 1477 (m), 1443 (s), 1378 (m), 1331 (w), 1249 (m), 1163 (w), 1108 (m), 1069 (w), 1045 (w), 1028 (w), 938 (w), 858 (s), 797 (w), 749 (m), 697 (m), 638 (w), 586 (w), 534 cm^{-1} (m); elemental analysis calcd (%) for C$_{47}$H$_{60}$N$_2$OPSiY: C 69.10, H 7.40, N 3.43; found: C 68.76, H 8.17, N 3.15.

Complex 1b: Following a procedure similar to that described for the synthesis of **1a**, H_2L^1 (0.23 g, 0.41 mmol) in toluene (2 mL) was treated with $[Lu\{CH_2Si(CH_3)_3\}_3(thf_2)]$ (0.24 g, 0.40 mmol in toluene (3 mL) at room temperature with stirring for 24 h. Removal of volatile substances gave a light brownish residue to which was added hexane to afford after 2 d at −34 °C **1b** as an orangish crystalline solid (0.17 g, 56 %). Crystals for X-ray analysis were isolated by recrystallization from benzene/hexane at room temperature over several days. ^{1}H NMR (400 MHz, [D$_6$]benzene,

25 °C): $\delta = -0.78$, -0.87 (AB, $^2J(H,H) = 12$ Hz, 2H; $CH_2Si(CH_3)_3$), 0.22 (s, 9H; $CH_2Si(CH_3)_3$), 0.72 (d, $^3J(H,H) = 6.8$ Hz, 3H; $NC_6H_3(CH(CH_3)_2)_2$), 0.74 (d, $^3J(H,H) = 6.8$ Hz, 3H; $NC_6H_3(CH(CH_3)_2)_2$), 1.35 (br, 4H; THF), 1.45 (d, $^3J(H,H) = 6.8$ Hz, 3H; $NC_6H_3(CH(CH_3)_2)_2$), 1.60 (d, $^3J(H,H) = 6.8$ Hz, 3H; $NC_6H_3(CH(CH_3)_2)_2$), 2.01 (m, 1H; $NC_6H_3(CH(CH_3)_2)_2$), 2.13 (s, 3H; *o*-$NC_6H_2(CH_3)_3$), 2.21 (s, 3H; *o*-$NC_6H_2(CH_3)_3$), 2.75 (s, 3H; *p*-$NC_6H_2(CH_3)_3$), 3.58 (br, 4H; THF), 4.18 (m, 1H; $NC_6H_3(CH(CH_3)_2)_2$), 6.28 (dd, $^3J(H,H) = 8.0$ Hz, $^4J(H,P) = 6.0$ Hz, 1H; *o*-LuC_6H_4P), 6.49 (td, $^3J(H,H) = 7.2$ Hz, $^4J(H,H) = 2.8$ Hz, 1H; *m*-PC_6H_4Lu), 6.64 (s, 1H; *m*-$NC_6H_2Me_3$), 6.92 (td, $^3J(H,H) = 8.0$ Hz, $^4J(H,H) = 2.8$ Hz, 2H; *m*-PC_6H_5), 6.97 (s, 1H; *m*-$NC_6H_2Me_3$), 7.02 (t, $^3J(H,H) = 7.0$ Hz, 1H; *p*-PC_6H_5), 7.04 (t, $^3J(H,H) = 7.2$ Hz, 1H; *p*-PC_6H_4Lu), 7.16 (dd, $^3J(H,H) = 7.2$ Hz, $^4J(H,H) = 1.6$ Hz, 1H; *m*-$NC_6H_3iPr_2$), 7.25 (t, $^3J(H,H) = 7.2$ Hz, 1H; *p*-$NC_6H_3iPr_2$), 7.26 (m, 1H; *m*-PC_6H_4N), 7.36 (dd, $^3J(H,H) = 7.2$ Hz, $^4J(H,H) = 1.6$ Hz, 1H; *m*-$NC_6H_3iPr_2$), 7.45 (dd, $^3J(H,H) = 8.0$ Hz, $^4J(H,H) = 1.6$ Hz, 1H; *o*-PC_6H_4Lu), 7.47 (t, $^3J(H,H) = 7.2$ Hz, 1H; *p*-PC_6H_4N), 7.69–7.75 (m, 1H; *o*-PC_6H_4N, 2H; *o*-PC_6H_5), 8.28 ppm (d, $^3J(H,H) = 7.1$ Hz, 1H; *o*-NC_6H_4P); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = 5.39$ (s, 3C, $CH_2Si(CH_3)_3$), 20.40 (s, 1C, *p*-$NC_6H_2(CH_3)_3$), 21.27, 21.76 (s, 2C, *o*-$NC_6H_2(CH_3)_3$), 24.74, 25.05 (s, 2C, $NC_6H_3(CH(CH_3)_2)_2$), 25.68 (br., 1C, $NC_6H_3(CH(CH_3)_2)_2$, 2C, THF), 27.28, 27.83 (s, 2C, $NC_6H_3(CH(CH_3)_2)_2$), 29.82 (s, 1C, CH_2SiMe_3), 32.41 (s, 1C, $NC_6H_3(CH(CH_3)_2)_2$) 70.22 (s, 2C, THF), 113.74 (d, $^3J(C,P) = 13$ Hz, 1C, *m*-PC_6H_4Lu), 114.52, 115.48 (s, 2C, *o*-$NC_6H_3iPr_2$), 118.32 (d, $^3J(C,P) = 9$ Hz, 1C, *o*-LuC_6H_4P), 124.84 (s, 1C, *p*-$NC_6H_3iPr_2$), 125.74, 125.88 (s, 1C, *o*-PC_6H_4Lu, 1C, *p*-PC_6H_4N), 126.16, 126.31 (s, 2C, *m*-$NC_6H_3iPr_2$), 128.00 (overlap, 1C, *m*-PC_6H_4N), 128.96, 129.24, 129.49 (s, 1C, *m*-$NC_6H_2Me_3$, 1C, *p*-PC_6H_5, 1C, *p*-PC_6H_2Lu), 132.15, 132.34, 132.43, 132.52 (s, 2C, *m*-PC_6H_5, 1C, *m*-$NC_6H_2Me_3$, 1C, *o*-PC_6H_4N), 133.82 (s, 1C, *p*-$NC_6H_2Me_3$), 134.65, 134.73 (s, 2C, *o*-PC_6H_5), 135.57 (d, $^3J(C,P) = 6$ Hz, 1C, *o*-$NC_6H_2Me_3$), 135.78 (d, $^3J(C,P) = 6$ Hz, 1C, *o*-$NC_6H_2Me_3$), 137.97 (s, 1C, *o*-NC_6H_4P), 138.20 (s, 1C, *ipso*-PC_6H_4N), 144.36 (s, 1C, *ipso*-NC_6H_4P), 145.27 (d, $^1J(C,P) = 8$ Hz, 1C, *ipso*-PC_6H_4Lu), 148.29 (s, 1C, *ipso*-$NC_6H_3iPr_2$), 149.70 (s, 1C, *ipso*-$NC_6H_2Me_3$), 160.43 (d, $^1J(C,P) = 5$ Hz, 1C, *ipso*-PC_6H_5), 208.89 ppm (d, $^2J(C,P) = 35$ Hz, 1C, *ipso*-LuC_6H_4P); IR (KBr): $\tilde{\nu} = 3055$ (w), 2960 (s), 2866 (m), 1584 (s), 1538 (w), 1455 (s), 1431 (s), 1361 (m), 1309 (s), 1249 (m), 1159 (m), 1108 (s), 1067 (w), 1040 (m), 982 (s), 949 (w), 858 (s), 796 (m), 748 (s), 696 (s), 592 (m), 544 cm^{-1} (m); elemental analysis calcd (%) for $C_{47}H_{60}N_2OPSiLu$: C 62.51, H 6.70, N 3.10; found: C 61.95, H 7.19, N 3.15.

Complex 2: 2,6-Diisopropylaniline (0.04 g, 0.25 mmol) in toluene (1 mL) was added to a solution of complex **1a** (0.11 g, 0.13 mmol) in toluene (4 mL). The reaction mixture was stirred for 24 h at room temperature. After removal of the volatile substances, the residue was dissolved in hexane (1 mL) and then cooled to -34 °C to afford complex **2** as a yellow solid in 60% yield. Crystals for X-ray analysis was isolated by recrystallization from benzene/hexane at room temperature. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.14$ (d, $^3J(H,H) = 6.4$ Hz, 12H; $NHC_6H_3(CH(CH_3)_2)_2$), 1.18 (d, $^3J(H,H) = 6.8$ Hz, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 1.27 (d, $^3J(H,H) = 6.4$ Hz, 12H; $NHC_6H_3(CH(CH_3)_2)_2$), 1.37 (d, $^3J(H,H) = 6.8$ Hz, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 2.22 (s, 3H; *p*-$NC_6H_2(CH_3)_3$), 2.35 (s, 6H; *o*-$NC_6H_2(CH_3)_3$), 2.77 (m, 4H; $NHC_6H_3(CH(CH_3)_2)_2$), 3.36 (m, 2H; $NC_6H_3(CH(CH_3)_2)_2$), 6.29 (td, $^3J(H,H) = 7.8$ Hz, $^4J(H,H) = 2.4$ Hz, 1H; *m*-PC_6H_4N), 6.35 (dd, $^3J(H,H) = 6.8$ Hz, $^4J(H,H) = 1.6$ Hz, 1H; *o*-NC_6H_4P), 6.78 (s, 2H; *m*-$NC_6H_2Me_3$), 6.86 (dd, $^3J(H,H) = 8.0$ Hz, $^4J(H,H) = 1.6$ Hz, 1H; *o*-PC_6H_4N), 6.90 (t, $^3J(H,H) = 7.6$ Hz, 2H; *p*-$NHC_6H_3iPr_2$), 7.01 (m, 1H; *p*-$P(C_6H_5)_2$, 4H; *m*-$P(C_6H_5)_2$), 7.12 (m, 1H; *p*-PC_6H_4N, 1H; *p*-$P(C_6H_5)_2$) 7.15 (d, $^3J(H,H) = 7.6$ Hz, 4H; *m*-$NHC_6H_3iPr_2$), 7.34 (m, 3H; *m*,*p*-$NC_6H_3iPr_2$), 7.47 (d, $^3J(H,H) = 7.6$ Hz, 2H; *o*-$P(C_6H_5)_2$), 7.51 ppm (d, $^3J(H,H) = 7.6$ Hz, 2H; *o*-$P(C_6H_5)_2$); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = 21.25$, 21.43 (s, 3C, *o*,*p*-$NC_6H_2(CH_3)_3$), 24.39 (s, 4C, $NC_6H_3(CH(CH_3)_2)_2$), 24.65 (s, 8C, $NHC_6H_3(CH(CH_3)_2)_2$), 27.45 (s, 1C, $NC_6H_3(CH(CH_3)_2)_2$), 29.56 (s, 1C, $NC_6H_3(CH(CH_3)_2)_2$), 30.36 (s, 4C, $NHC_6H_3(CH(CH_3)_2)_2$), 106.85 (s, 1C, *o*-$NC_6H_3iPr_2$), 107.90 (s, 1C, *o*-$NC_6H_3iPr_2$), 113.76 (s, 1C, *p*-$NHC_6H_3iPr_2$), 113.90 (s, 1C, *p*-$NHC_6H_3iPr_2$), 116.69 (s, 1C, *m*-PC_6H_4N, 1C, *o*-NC_6H_4P), 119.20 (s, 1C, *o*-$NC_6H_2Me_3$), 119.40 (s, 1C, *o*-$NC_6H_2Me_3$), 123.34 (s, 4C, *o*-$NHC_6H_3iPr_2$), 128.26 (s, 1C, *p*-PC_6H_4N), 129.00 (s, 4C, *m*-$NHC_6H_3iPr_2$), 129.11 (s, 2C, *m*-$P(C_6H_5)_2$), 129.77 (s, 1C, *p*-$P(C_6H_5)_2$), 131.01 (s, 2C, *m*-$NC_6H_2Me_3$), 133.28 (s, 1C, *p*-$P(C_6H_5)_2$), 134.28 (s, 2C, *m*-$P(C_6H_5)_2$), 134.53 (s, 2C, *o*-$P(C_6H_5)_2$), 134.62 (s, 2C, *o*-$P(C_6H_5)_2$), 135.57 (d, $^2J(C,P) = 13$ Hz, 1C, *o*-PC_6H_4N), 136.64 (d, $^1J(C,P) = 5$ Hz, 1C, *ipso*-PC_6H_4N), 140.55 (s, 1C, *ipso*-$NC_6H_3iPr_2$), 140.69 (s, 1C, *ipso*-$NC_6H_2Me_3$), 151.85 (s, 2C, *ipso*-$P(C_6H_5)_2$), 161.75 ppm (s, 1C, *ipso*-NC_6H_4P); IR (KBr): $\tilde{\nu} = 3062$ (w), 2962 (s), 2869 (m), 1620 (m), 1588 (m), 1571 (m), 1508 (m), 1477 (s), 1439 (s), 1383 (w), 1362 (m), 1332 (m), 1312 (m), 1266 (m), 1164 (w), 1109 (m), 1068 (w), 1057 (w), 1045 (w), 1027 (w), 934 (w), 797 (m), 746 (s), 713 (s), 696 (s), 585 (w), 563 (w), 533 cm^{-1} (s); elemental analysis calcd (%) for $C_{63}H_{78}N_4PY$: C 74.83, H 7.77, N 5.54; found: C 74.40, H 8.71, N 4.71.

Ligand HL$^{2\text{-Me}}$ (*o*-(PPh_2)$C_6H_4CH_2NHC_6H_3(Me)_2$-2,6): Imino phosphine ligand *o*-(PPh_2)$C_6H_4C{=}NC_6H_3Me_2$-2,6 was prepared by a modified literature procedure.[27] *o*-(Diphenylphosphino)benzaldehyde[28] (1.66 g, 5.73 mmol) was treated with 2,6-dimethylaniline (1.0 mL, 8.60 mmol) in MeOH/CH_2Cl_2 (3/1, 60 mL) under N_2 at room temperature. After stirring for 48 h, the solution was concentrated to about 10 mL and cooled to -20 °C to give *o*-(PPh_2)$C_6H_4C{=}NC_6H_3Me_2$-2,6 as a light yellow microcrystalline solid over 24 h. The solids were collected by filtration and washed with cold methanol. The methanol filtrate was concentrated and cooled at -20 °C to give a second crop of $HL^{2\text{-Me}}$ with total yield of 77% (1.73 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.88$ (s, 6H; $NC_6H_3(CH_3)_2$), 6.92 (t, $^3J(H,H) = 6.0$ Hz, 1H; *p*-NC_6H_3Me), 7.00 (d, $^3J(H,H) = 6.0$ Hz, 1H; *o*-CHC_6H_4P), 7.25 (d, $^3J(H,H) = 6.0$ Hz, 2H; *m*-$NC_6H_3Me_2$), 7.31 (m, 4H; *o*-$P(C_6H_5)_2$), 7.34–7.42 (m, 4H; *m*-$P(C_6H_5)_2$, 2H; *p*-$P(C_6H_5)_2$, 1H; *m*-PC_6H_4N), 7.51 (t, $^3J(H,H) = 7.5$ Hz, 1H; *p*-PC_6H_4), 8.32 (m, 1H; *o*-PC_6H_4N), 8.93 ppm (d, $^3J(H,H) = 6.0$ Hz, 1H; N=C*H*). Reduction of the imino phosphine with $LiAlH_4$ afforded $HL^{2\text{-Me}}$: Imino phosphine *o*-(PPh_2)-$C_6H_4C{=}NC_6H_3(Me)_2$-2,6 (1.99 g, 4 mmol) and $LiAlH_4$ (0.34 g, 9 mmol) were added to diethyl ether (30 mL) under N_2. After stirring for 48 h at room temperature, the solution was quenched with aqueous 10% NH_4Cl (5 mL). The supernatant ether layer was decanted and dried over anhydrous magnesium sulfate. Filtering off the solids followed by concentrating the solution to about 4 mL and cooling to -20 °C overnight gave colorless microcrystalline $HL^{2\text{-Me}}$, which was collected by filtration and dried in vacuum (1.34 g, 85%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): $\delta = 2.12$ (s, 6H; $NHC_6H_3(CH_3)_2$), 4.17 (br, 1H; N*H*CH_2, 2H; NHC*H*$_2$), 6.71 (t, $^3J(H,H) = 10.5$ Hz, 1H; *p*-$NHC_6H_3Me_2$), 6.77 (m, 1H; *o*-$CH_2C_6H_4P$), 6.89 (d, $^3J(H,H) = 7.2$ Hz, 2H; *m*-$NHC_6H_3Me_2$), 7.15–7.28 (m, 4H; *o*-$P(C_6H_5)_2$, 1H; *p*-PC_6H_4N), 7.36–7.45 (m, 4H; *m*-$P(C_6H_5)_2$, 2H; *p*-$P(C_6H_5)_2$, 1H; *m*-PC_6H_4N), 7.70 ppm (m, 1H; *o*-PC_6H_4N); ^{13}C NMR (75 Hz, [D$_6$]DMSO, 25 °C): $\delta = 19.07$ (s, 2C, $NHC_6H_3(CH_3)_2$), 50.60 (d, $^3J(C,P) = 25.0$ Hz, 1C, $NHCH_2$), 122.24 (s, 1C, *p*-$NHC_6H_3Me_2$), 128.99 (s, 1C, *o*-$CH_2C_6H_4P$), 128.05 (s, 1C, *p*-PC_6H_4N), 129.23 (d, $^2J(C,P) = 4.5$ Hz, 1C, *o*-PC_6H_4N), 129.35 (s, 2C, *m*-$NHC_6H_3Me_2$), 129.70 (d, $^3J(C,P) = 6.7$ Hz, 4C, *m*-$P(C_6H_5)_2$), 129.90 (s, 2C, *p*-$P(C_6H_5)_2$), 130.23 (s, 2C, *o*-$NHC_6H_3Me_2$), 133.40 (s, 1C, *m*-PC_6H_4N), 134.25 (d, $^1J(C,P) = 18.0$ Hz, 2C, *ipso*-$P(C_6H_5)_2$), 135.28 (d, $^1J(C,P) = 13.5$ Hz, 1C, *ipso*-PC_6H_4N), 136.70 (d, $^2J(C,P) = 12.5$ Hz, 4C, *o*-$P(C_6H_5)_2$), 145.45 (d, $^2J(C,P) = 23.0$ Hz, 1C, *ipso*-$CH_2C_6H_4P$), 146.79 ppm (s, 1C, *ipso*-$NHC_6H_3Me_2$).

Ligand HL$^{2\text{-iPr}}$ (*o*-(PPh_2)$C_6H_4CH_2NHC_6H_3iPr_2$-2,6): Imino phosphine *o*-(PPh_2)$C_6H_4C{=}NC_6H_3iPr_2$-2,6 was synthesized by the above-described method. *o*-(Diphenylphosphino)benzaldehyde (2.05 g, 7.07 mmol) and 2,6-diisopropylaniline (2 mL, 10.60 mmol) were dissolved in MeOH/CH_2Cl_2 (3/1, 60 mL) under N_2. The reaction mixture was stirred at room temperature for 48 h, and then concentrated to about 10 mL and cooled to -20 °C for 24 h. Light yellow microcrystals of imino phosphine *o*-(PPh_2)-$C_6H_4C{=}NC_6H_3iPr_2$-2,6 deposited on the bottom of the flask, were collected by filtration, and washed with cold methanol. The methanol filtrate was concentrated and cooled at -20 °C to give a second crop of imino phosphine *o*-(PPh_2)$C_6H_4C{=}NC_6H_3iPr_2$-2,6 with a total yield of 82% (2.76 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.01$ (s, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 1.03 (s, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 2.77 (m, 2H; $NC_6H_3(CH(CH_3)_2)_2$), 6.96 (m, 1H; *o*-$CH_2C_6H_4P$), 7.06–7.13 (m, 2H; *m*-$NC_6H_3iPr_2$, 1H; *p*-$NC_6H_3iPr_2$), 7.21–7.28 (m, 4H; *o*-$P(C_6H_5)_2$), 7.31–7.37 (m, 4H; *m*-$P(C_6H_5)_2$, 2H; *p*-$P(C_6H_5)_2$), 7.41 (t, $^3J(H,H) = 7.2$ Hz, 1H; *m*-PC_6H_4N), 7.53 (t, $^3J(H,H) = 7.2$ Hz, 1H; *p*-PC_6H_4N), 8.33 (m, 1H; *o*-

PC_6H_4N), 9.60 ppm (d, ^4J(H,P) = 5.4 Hz, 1H; C*H*=N). Reduction of the imino phosphine with $LiAlH_4$: Imino phosphine *o*-$(PPh_2)C_6H_4C$=$NC_6H_3iPr_2$-2,6) (2.76 g, 6.15 mmol) and $LiAlH_4$ (0.58 g, 15.37 mmol) were dissolved in diethyl ether (40 mL) under N_2. After stirring for 48 h at room temperature, the solution was quenched with aqueous 10% NH_4Cl (5 mL). The ether layer was separated and dried over anhydrous magnesium sulfate. The clear solution was separated from the drying agent, concentrated to about 4 mL, and then kept at −20 °C overnight. Colorless microcrystals were isolated and dried in vacuum to afford $HL^{2\text{-}iPr}$ (2.65 g, 84%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.05 (s, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 1.07 (s, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 3.25 (m, 2H; $NC_6H_3(CH(CH_3)_2)_2$), 3.84 (br, 1H; N*H*CH_2), 4.08 (s, 2H; NHCH_2), 6.78 (m, 1H; *o*-$CH_2C_6H_4$P), 6.98–7.03 (m, 2H; *m*-$NC_6H_3iPr_2$, 1H; *p*-$NC_6H_3iPr_2$), 7.16–7.20 (m, 4H; *o*-P$(C_6H_5)_2$), 7.25 (t, ^3J(H,H) = 7.2 Hz, 1H; *m*-PC_6H_4N), 7.30–7.38 (m, 4H; *m*-P$(C_6H_5)_2$, 2H; *p*-P$(C_6H_5)_2$), 7.40 (t, ^3J(H,H) = 7.2 Hz, 1H; *p*-PC_6H_4N), 7.73 ppm (m, 1H; *o*-PC_6H_4N); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 25.08 (s, 4C, $NHC_6H_3(CH(CH_3)_2)_2$), 27.73 (s, 2C, $NHC_6H_3(CH(CH_3)_2)_2$), 54.39 (d, ^3J(C,P) = 23.0 Hz, 1C, CH_2NH), 124.10 (s, 2C, *m*-$NHC_6H_3iPr_2$), 124.66 (s, 1C, *p*-$NHC_6H_3iPr_2$), 128.17 (s, 1C, *p*-PC_6H_4N), 128.5 (overlap, 1C, *m*-PC_6H_4N), 129.04 (d, ^2J(C,P) = 4.2 Hz, 1C, *o*-PC_6H_4N), 129.70 (d, ^3J(C,P) = 9.0 Hz, 4C, *m*-P$(C_6H_5)_2$), 129.89 (s, 2C, *p*-P$(C_6H_5)_2$), 133.48 (s, 1C, *o*-$CH_2C_6H_4$P), 134.19 (d, ^1J(C,P) = 19.0 Hz, 2C, *ipso*-P$(C_6H_5)_2$), 135.31 (d, ^1J(C,P) = 14.0 Hz, 1C, *ipso*-PC_6H_4N), 136.66 (d, ^2J(C,P) = 12.5 Hz, 4C, *o*-P$(C_6H_5)_2$), 143.67 (s, 2C, *o*-$NHC_6H_3iPr_2$), 143.81 (s, 1C, *ipso*-$NHC_6H_3iPr_2$P), 144.90 ppm (d, ^2J(C,P) = 23.0 Hz, 1C, *ipso*-$CH_2C_6H_4$).

Complex 4a: Ligand $HL^{2\text{-}Me}$ (0.29 g, 0.75 mmol) was gradually added to a solution of $[Y\{CH_2Si(CH_3)_3\}_3(thf)_2]$ (0.37 g, 0.76 mmol) in hexane (4 mL). The reaction mixture was stirred for 30 min at room temperature and then cooled to −34 °C to afford single crystals of **4a** (0.27 g, 50.0%) over two days. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): δ = −0.16 (s, 4H; CH_2Si$(CH_3)_3$), 0.34 (s, 18H; $CH_2Si(CH_3)_3$), 1.19 (br, 4H; THF), 2.40 (s, 6H; *o*-$NC_6H_3(CH_3)_2$), 3.72 (br, 4H; THF), 4.81 (s, 2H; NC$H_2C_6H_4$P), 6.75 (m, 1H; *o*-PC_6H_4N), 6.89 (m, 1H; *m*-PC_6H_4N, 1H; *o*-$CH_2C_6H_4N$), 6.92 (t, ^3J(H,H) = 7.2 Hz, 1H; *p*-$NC_6H_3Me_2$), 7.11 (m, 1H; *p*-PC_6H_4N), 7.13 (d, ^3J(H,H) = 7.2 Hz, 2H; *m*-$NC_6H_3Me_2$), 7.15–7.25 (m, 4H; *o*-P$(C_6H_5)_2$, 2H; *p*-P$(C_6H_5)_2$), 7.71 ppm (t, ^3J(H,H) = 8 Hz, 4H; *m*-P$(C_6H_5)_2$); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 4.92 (s, 6C, $CH_2Si(CH_3)_3$), 21.16 (s, 2C, $NC_6H_3(CH_3)_2$), 25.30 (s, 2C, THF), 36.50 (d, ^1J(C,Y) = 29.0 Hz, 2C, $CH_2Si(CH_3)_3$), 51.47 (d, ^3J(C,P) = 15.0 Hz, 1C, N$CH_2C_6H_4$P), 70.92 (s, 2C, THF), 121.59 (s, 1C, *p*-$NC_6H_3Me_2$), 127.60 (s, 2C, *m*-PC_6H_4N), 129.37 (s, 2C, *p*-P$(C_6H_5)_2$), 129.59 (d, ^2J(C,P) = 7.5 Hz, 4C, *o*-P$(C_6H_5)_2$), 130.26 (s, 1C, *p*-PC_6H_4N), 130.45 (s, 1C, *o*-$CH_2C_6H_4$P), 130.60 (s, 2C, *m*-$NC_6H_3Me_2$), 131.36 (d, ^1J(C,P) = 14.0 Hz, 1C, *ipso*-PC_6H_4N), 132.93 (d, ^1J(C,P) = 10.5 Hz, 2C, *ipso*-P$(C_6H_5)_2$), 134.15 (s, 1C, *o*-PC_6H_4N), 134.80 (s, 4C, *m*-P$(C_6H_5)_2$), 134.94 (s, 2C, *o*-$NC_6H_3Me_2$), 149.26 (d, ^2J(C,P) = 18 Hz, 1C, *ipso*-$CH_2C_6H_4$P), 153.33 ppm (s, 1C, *ipso*-$NC_6H_3Me_2$); IR (KBr): $\tilde{\nu}$ = 3054 (m), 2948 (s), 2893 (m), 1962 (w), 1822 (w), 1772 (w), 1544 (s), 1474 (s), 1435 (s), 1374 (s), 1250 (s), 1216 (w), 1193 (m), 1160 (w), 1097 (m), 1069 (w), 1027 (m), 980 (w), 913 (w), 858 (vs), 746 (vs), 697 (vs), 636 (w), 609 (w), 545 (m), 504 cm^{-1} (m); elemental analysis calcd (%) for $C_{39}H_{55}NOPSi_2Y$: C 64.18, H 7.59, N 1.92; found: C 63.99, H 7.42, N 1.65.

Complex 4b: Following the same procedure described for complex **4a**, ligand $HL^{2\text{-}Me}$ (0.25 g, 0.63 mmol) was gradually added to a solution of $[Lu\{CH_2Si(CH_3)_3\}_3(thf)_2]$ (0.37 g, 0.63 mmol) in hexane (4 mL). The reaction mixture was stirred for 2.5 h at room temperature. Removal of the volatile substances gave a residue to which toluene and hexane were added and kept at −34 °C for two days to afford crystals of **4b** (0.34 g, 60.0%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): δ = −0.33 (s, 4H; CH_2Si$(CH_3)_3$), 0.32 (s, 18H; $CH_2Si(CH_3)_3$), 1.16 (m, 4H; THF), 2.40 (s, 6H; $NC_6H_3(CH_3)_2$), 3.72 (m, 4H; THF), 4.69 (s, 2H; NC$H_2C_6H_4$P), 6.72 (m, 1H; *o*-PC_6H_4N), 6.90 (t, ^3J(H,H) = 6.8 Hz, 1H; *m*-PC_6H_4N), 6.92 (d, ^3J(H,H) = 7.2 Hz, 1H; *o*-$CH_2C_6H_4$P), 6.93 (t, ^3J(H,H) = 7.2 Hz, 1H; *p*-$NC_6H_3Me_2$), 7.12 (td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H; *p*-PC_6H_4N), 7.16 (d, ^3J(H,H) = 7.2 Hz, 2H; *m*-$NC_6H_3Me_2$), 7.18 (d, ^3J(H,H) = 7.2 Hz, 2H; *o*-P$(C_6H_5)_2$), 7.21 (t, ^3J(H,H) = 7.2 Hz, 2H; *o*-P$(C_6H_5)_2$), 7.25 (td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 2H; *p*-P$(C_6H_5)_2$), 7.74 (t, ^3J(H,H) = 8 Hz, 4H; *m*-P$(C_6H_5)_2$) ppm; ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 5.04 (s, 6C, $CH_2Si(CH_3)_3$), 20.93 (s, 2C, $NC_6H_3(CH_3)_2$), 25.27 (s, 2C, THF), 43.74 (d, ^1J(C,Lu) = 8.4 Hz, 2C, $CH_2Si(CH_3)_3$), 51.69 (d, ^3J(C,P) = 14.5 Hz, 1C, CH_2N), 71.26 (s, 2C, THF), 121.82 (s, 1C, *o*-$NC_6H_3Me_2$), 127.54, 127.57 (s, 1C, *p*-$NC_6H_3Me_2$, 1C, *o*-PC_6H_4N), 129.26 (s, 2C, *p*-P$(C_6H_5)_2$), 129.39 (s, 1C, *m*-PC_6H_4N), 129.53 (d, ^2J(C,P) = 8 Hz, 4C, *o*-P$(C_6H_5)_2$), 130.29 (s, 1C, *o*-$CH_2C_6H_4$P), 130.52 (s, 1C, *p*-PC_6H_4N), 130.57 (s, 2C, *m*-$NC_6H_3Me_2$), 131.53 (d, ^1J(C,P) = 15.5 Hz, 1C, *ipso*-PC_6H_4N), 132.99 (d, ^1J(C,P) = 15 Hz, 2C, *ipso*-P$(C_6H_5)_2$), 134.86 (d, ^3J(C,P) = 5 Hz, 4C, *m*-P$(C_6H_5)_2$), 134.97 (s, 2C, *o*-$NC_6H_3Me_2$), 149.69 (d, ^2J(C,P) = 18.5 Hz, 1C, *ipso*-$CH_2C_6H_4$P), 154.56 ppm (s, 1C, *ipso*-$NC_6H_3Me_2$); IR (KBr): $\tilde{\nu}$ = 3053 (s), 2947 (s), 2851 (s), 1961 (w), 1820 (w), 1768 (w), 1641 (w), 1587 (w), 1474 (s), 1433 (s), 1376 (w), 1343 (w), 1307 (w), 1255 (m), 1215 (m), 1193 (m), 1161 (w), 1096 (m), 1068 (m), 1026 (m), 999 (w), 913 (w), 849 (m), 745 (s), 697 (s), 598 (w), 558 (w), 544 (w), 504 cm^{-1} (m); elemental analysis calcd (%) for $C_{39}H_{55}NOPSi_2Lu$: C 57.41, H 6.79, N 1.72; found: C 57.10, H 5.79, N 2.51.

Complex 4c: Following the procedure described for complex **4a**, ligand $HL^{2\text{-}iPr}$ (0.25 g, 0.55 mmol) was gradually added to a solution of $[Y\{CH_2Si(CH_3)_3\}_3(thf)_2]$ (0.27 g, 0.55 mmol) in hexane (4 mL). The reaction mixture was stirred for 12 h at room temperature. Toluene and hexane were added to the concentrated reaction mixture, which was kept at −34 °C for 2 d to afford single crystals of complex **4c** (0.27 g, 50.0%), which were good enough for X-ray analysis. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): δ = −0.16 (s, 4H; CH_2Si$(CH_3)_3$), 0.33 (s, 18H; $CH_2Si(CH_3)_3$), 1.12 (d, ^3J(H,H) = 6.8 Hz, 6H; $NC_6H_3(CH(CH_3)_2)$, 1.23 (br, 4H; THF), 1.28 (m, 1H; $NC_6H_3(CH(CH_3)_2)_2$), 1.41 (d, ^3J(H,H) = 6.8 Hz, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 3.76 (m, 1H; $NC_6H_3(CH(CH_3)_2)_2$), 3.79 (br, 4H; THF), 4.88 (s, 2H; -NC$H_2C_6H_4$P), 6.77 (m, 1H; *o*-PC_6H_4N), 6.82 (t, ^3J(H,H) = 8 Hz, 1H; *m*-PC_6H_4N), 6.86 (t, ^3J(H,H) = 7.2 Hz, 1H; *p*-$NC_6H_3iPr_2$), 7.09 (td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.2 Hz, 1H; *p*-PC_6H_4N), 7.16–7.20 (m, 1H; *o*-$CH_2C_6H_4$P, 2H; *m*-$NC_6H_3iPr_2$, 2H; *p*-P$(C_6H_5)_2$), 7.24 (dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 4H; *o*-P$(C_6H_5)_2$), 7.73 ppm (t, ^3J(H,H) = 8.0 Hz, 4H; *m*-P$(C_6H_5)_2$); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 4.84 (s, 6C, $CH_2Si(CH_3)_3$), 25.33 (s, 2C, THF), 25.50, 26.69 (s, 2C, $NC_6H_3(CH(CH_3)_2)_2$), 28.73 (s, 4C, $NC_6H_3(CH(CH_3)_2)_2$), 35.48 (d, ^1J(C,Y) = 38 Hz, 2C, $CH_2Si(CH_3)_3$), 53.63 (d, ^3J(C,P) = 15.5 Hz, 1C, -N$CH_2C_6H_4$P), 70.97 (s, 2C, THF), 123.34 (s, 1C, *p*-PC_6H_4N), 124.43 (s, 2C, *p*-$NC_6H_3iPr_2$), 127.90 (d, ^3J(C,P) = 3.8 Hz, 1C, *m*-PC_6H_4N), 129.56 (d, ^3J(C,P) = 7.0 Hz, 4C, *m*-P$(C_6H_5)_2$), 130.01 (d, ^2J(C,P) = 7.0 Hz, 1C, *o*-PC_6H_4N), 130.37 (s, 2C, *p*-P$(C_6H_5)_2$), 130.61 (s, 2C, *m*-$NC_6H_3iPr_2$ 131.59 (d, ^1J(C,P) = 15.0 Hz, 2C, *ipso*-PC_6H_4N), 132.88 (d, ^1J(C,P) = 15.0 Hz, 2C, *ipso*-P$(C_6H_5)_2$), 134.73 (d, ^2J(C,P) = 13.5 Hz, 4C, *o*-P$(C_6H_5)_2$), 135.34 (s, 1C, *o*-$CH_2C_6H_4$P), 145.73 (s, 2C, *o*-$NC_6H_3iPr_2$), 148.64 (d, ^2J(C,P) = 19.5 Hz, 1C, *ipso*-$CH_2C_6H_4$P), 150.12 ppm (s, 1C, *ipso*-$NC_6H_3iPr_2$); IR (KBr): $\tilde{\nu}$ = 3054 (m), 2961 (s), 2866 (m), 1963 (w), 1818 (w), 1632 (w), 1586 (m), 1566 (w), 1462 (s), 1434 (s), 1383 (m), 1363 (m), 1337 (w), 1309 (w), 1247 (m), 1189 (m), 1160 (w), 1126 (w), 1094 (m), 1054 (m), 1027 (m), 999 (w), 966 (w), 948 (w), 929 (w), 857 (m), 829 (m), 801 (m), 745 (s), 697 (s), 609 (w), 578 (w), 532 (w), 504 cm^{-1} (m); elemental analysis calcd (%)for $C_{43}H_{63}NOPSi_2Y$: C 65.71, H 8.08, N 1.78; found: C 65.37, H 8.03, N 1.89.

Complex 4d: Following the same procedure described for complex **4c**, ligand $HL^{2\text{-}iPr}$ (0.32 g, 0.71 mmol) was gradually added to a solution of $[Lu\{CH_2Si(CH_3)_3\}_3(thf)_2]$ (0.41 g, 0.71 mmol) in hexane (4 mL). The reaction mixture was stirred for 12 h at room temperature. The reaction mixture was concentrated and kept at −34 °C for two days to afford single crystals of complex **4d** (0.34 g, 60.0%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): δ = −0.35 (s, 4H; CH_2Si$(CH_3)_3$), 0.29 (s, 18H; $CH_2Si(CH_3)_3$), 1.11 (d, ^3J(H,H) = 6.8 Hz, 6H; $NC_6H_3(CH(CH_3)_2)$, 1.23 (m, 4H; THF), 1.26 (m, 1H; $NC_6H_3(CH(CH_3)_2)_2$), 1.41 (d, ^3J(H,H) = 6.8 Hz, 6H; $NC_6H_3(CH(CH_3)_2)$, 3.78 (m, 1H; $NC_6H_3(CH(CH_3)_2)_2$), 3.81 (m, 4H; THF), 4.75 (s, 2H; CH_2N), 6.77 (m, 1H; *o*-PC_6H_4N), 6.82 (d, ^3J(H,H) = 7.2 Hz, 1H; *m*-PC_6H_4N), 6.87 (t, ^3J(H,H) = 7.2 Hz,1H; *p*-$NC_6H_3iPr_2$), 7.06 (td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.2 Hz, 1H; *p*-PC_6H_4N), 7.15 (m, 1H; *o*-$CH_2C_6H_4$P), 7.18 (m, 2H; *m*-$NC_6H_3iPr_2$), 7.24 (d, ^3J(H,H) = 7.2 Hz, 4H; *o*-P$(C_6H_5)_2$), 7.26 (t, ^3J(H,H) = 7.2 Hz, 2H; *p*-P$(C_6H_5)_2$), 7.71 ppm (t, ^3J(H,H) = 8.0 Hz, 4H; *m*-P$(C_6H_5)_2$); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 4.95 (s, 6C, $CH_2Si(CH_3)_3$), 25.26 (s, 2C, THF), 25.67, 26.61 (s, 2C, $NC_6H_3(CH$-

$(CH_3)_2)_2$), 28.58 (s, 4C, $NC_6H_3(CH(CH_3)_2)_2$), 42.39 (d, ^1J(C,Lu) = 8.4 Hz, 2C, CH_2SiMe_3), 53.63 (d, ^3J(C,P) = 15.0 Hz, 1C, $NCH_2C_6H_4P$), 71.28 (s, 2C, THF), 123.33 (s, 1C, *p*-PC_6H_4N), 124.43 (s, 1C, *p*-$NC_6H_3iPr_2$), 127.88 (d, ^3J(C,P) = 2.6 Hz, 1C, *m*-PC_6H_4N), 129.46 (d, ^3J(C,P) = 7.8 Hz, 4C, *m*-$P(C_6H_5)_2$), 129.76 (d, ^2J(C,P) = 7.0 Hz, 1C, *o*-PC_6H_4N), 130.38 (s, 2C, *p*-$P(C_6H_5)_2$), 130.53 (s, 2C, *m*-$NC_6H_3iPr_2$), 131.93 (d, ^1J(C, P) = 15.5 Hz, 2C, *ipso*-PC_6H_4N), 132.97 (d, ^1J(C,P) = 15 Hz, 2C, *ipso*-$P(C_6H_5)_2$), 134.72 (d, ^2J(C,P) = 13.5 Hz, 4C, *o*-$P(C_6H_5)_2$), 135.44 (s, 1C, *o*-$CH_2C_6H_4P$), 146.00 (s, 2C, *o*-$NC_6H_3iPr_2$), 148.98 (d, ^2J(C,P) = 19.0 Hz, 1C, *ipso*-$CH_2C_6H_4P$), 151.36 ppm (s, 1C, *ipso*-$NC_6H_3iPr_2$); IR (KBr): $\tilde{\nu}$ = 3054 (m), 2961 (s), 2866 (m), 1968 (w), 1929 (w), 1819 (w), 1633 (w), 1586 (m), 1568 (w), 1478 (m), 1461 (s), 1435 (s), 1384 (m), 1363 (m), 1341 (w), 1308 (w), 1246 (m), 1188 (m), 1160 (w), 1126 (w), 1094 (m), 1053 (m), 1027 (m), 999 (w), 966 (w), 949 (w), 928 (w), 858 (w), 829 (m), 801 (m), 749 (s), 698 (s), 608 (w), 579 (w), 532 (w), 502 cm^{-1} (m); elemental analysis calcd (%) for $C_{43}H_{63}NOPSi_2Lu$: C 59.22, H 7.28, N 1.61; found: C 59.19, H 6.60, N 2.19.

Complex 5a: 2,6-Diisopropylaniline (0.04 g, 0.25 mmol) in toluene (1 mL) was added to a solution of complex **4a** (0.09 g, 0.12 mmol) in toluene (4 mL). The reaction mixture was stirred for 12 h at room temperature. Removal of the volatile substances afforded an oily residue, which was dissolved in hexane (1 mL) and then cooled to −34 °C to generate crystals of complex **5a**. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): δ = 1.09 (br, 4H; THF), 1.38 (s, 12H; $NHC_6H_3(CH(CH_3)_2)_2$), 1.40 (s, 12H; $NHC_6H_3(CH(CH_3)_2)_2$), 2.33 (s, 6H; $NC_6H_3(CH_3)_2$), 3.36 (m, 4H; $NHC_6H_3(CH(CH_3)_2)_2$), 3.62 (br, 4H; THF), 4.72 (br, 2H; $NHC_6H_3(CH(CH_3)_2)_2$), 5.11 (s, 2H; CH_2N), 6.76 (m, 1H; *p*-$NC_6H_3Me_2$), 6.94–7.01 (m, 2H; *m*-$NC_6H_3Me_2$, 4H; *o*-$P(C_6H_5)_2$, 2H; *p*-$P(C_6H_5)_2$, 1H; *o*-PC_6H_4N, 1H; *p*-PC_6H_4N), 7.03 (t, ^3J(H,H) = 7.2 Hz, 2H; *p*-$NHC_6H_3iPr_2$), 7.20 (m, 1H; *o*-$CH_2C_6H_4P$), 7.23 (d, ^3J(H,H) = 7.2 Hz, 2H; *m*-$NHC_6H_3iPr_2$), 7.26 (d, ^3J(H,H) = 7.2 Hz, 2H; *m*-$NHC_6H_3iPr_2$), 7.30 (t, ^3J(H,H) = 6.8 Hz, 1H; *m*-PC_6H_4N), 7.60 ppm (t, ^3J(H,H) = 7.2 Hz, 4H; *m*-$P(C_6H_5)_2$); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 20.52 (s, 2C, $NC_6H_3(CH_3)_2$), 24.51 (s, 8C, $NHC_6H_3(CH(CH_3)_2)_2$), 25.51 (s, 2C, THF), 30.36 (s, 4C, $NHC_6H_3(CH(CH_3)_2)_2$), 57.56 (d, ^3J(C,P) = 14 Hz, 1C, $NCH_2C_6H_4P$), 72.12 (s, 2C, THF), 116.11 (s, 2C, *p*-$NHC_6H_3iPr_2$), 123.30 (s, 1C, *p*-$NC_6H_3Me_2$), 123.60 (s, 4C, *m*-$NHC_6H_3iPr_2$), 127.50 (d, ^2J(C,P) = 2.8 Hz, 1C, *o*-PC_6H_4N), 129.36 (s, 2C, *p*-$P(C_6H_5)_2$), 129.51 (d, ^2J(C,P) = 8.2 Hz, 4C, *o*-$P(C_6H_5)_2$), 129.90 (d, ^3J(C,P) = 6.8 Hz, 1C, *m*-PC_6H_4N), 130.38 (s, 2C, *m*-$NC_6H_3Me_2$), 130.53 (s, 1C, *p*-PC_6H_4N), 132.16 (d, ^3J(C,P) = 7 Hz, 4C, *m*-$P(C_6H_5)_2$), 134.00 (s, 1C, *o*-$CH_2C_6H_4P$), 134.38 (s, 1C, *ipso*-PC_6H_4N), 134.74 (d, ^1J(C,N) = 19.5 Hz, 2C, *ipso*-$NHC_6H_3iPr_2$), 135.26 (d, ^1J(C,P) = 15 Hz, 2C, *ipso*-$P(C_6H_5)_2$), 137.00 (s, 4C, *o*-$NHC_6H_3iPr_2$), 149.57 (d, ^2J(C,P) = 17.5 Hz, 1C, *ipso*-$CH_2C_6H_4P$), 152.59 (s, 1C, *ipso*-$NC_6H_3Me_2$), 154.04 ppm (s, 2C, *o*-$NC_6H_3Me_2$); IR (KBr): $\tilde{\nu}$ = 3055 (m), 2961 (s), 2869 (m), 1620 (m), 1589 (m), 1461 (s), 1436 (s), 1383 (m), 1362 (m), 1306 (w), 1263 (m), 1192 (m), 1156 (w), 1118 (w), 1097 (m), 1044 (m), 1027 (w), 914 (w), 883 (m), 843 (m), 822 (w), 788 (w), 744 (s), 697 (s), 615 (w), 546 (m), 504 cm^{-1} (m); elemental analysis calcd (%) for $C_{55}H_{69}N_3OPY$: C 72.75, H 7.66, N 4.63; found: C 72.22, H 8.54, N 5.06.

Complex 5b: 2,6-Diisopropylaniline (0.04 g, 0.25 mmol) in toluene (1 mL) was added to a solution of complex **4c** (0.10 g, 0.12 mmol) in toluene (4 mL). The reaction mixture was stirred for 12 h at room temperature. Removal of the volatile substances afforded an oily residue, which was dissolved in hexane (1 mL) and then cooled to −34 °C to give solid complex **5b**. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): δ = 1.28 (br, 4H; THF), 1.32 (d, ^3J(H,H) = 6.8 Hz, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 1.34 (d, ^3J(H,H) = 8 Hz, 12H; $NHC_6H_3(CH(CH_3)_2)_2$), 1.45 (d, ^3J(H,H) = 6.8 Hz, 6H; $NC_6H_3(CH(CH_3)_2)_2$), 1.55 (d, ^3J(H,H) = 8 Hz, 12H; $NHC_6H_3(CH(CH_3)_2)_2$), 2.83 (m, 1H; $NC_6H_3(CH(CH_3)_2)_2$), 3.32 (m, 2H; $NHC_6H_3(CH(CH_3)_2)_2$), 3.34 (s, 1H; CH_2N), 3.63 (m, 2H; $NHC_6H_3(CH(CH_3)_2)_2$), 3.68 (m, 1H; $NC_6H_3(CH(CH_3)_2)_2$), 4.82 (s, 1H; CH_2N), 3.94 (br, 4H; THF), 4.61 (s, 1H; $NHC_6H_3(CH(CH_3)_2)_2$), 4.63 (s, 1H; $NHC_6H_3(CH(CH_3)_2)_2$), 7.03 (t, ^3J(H,H) = 7.6 Hz, 1H; *p*-$NHC_6H_3iPr_2$), 7.07 (t, ^3J(H,H) = 7.6 Hz, 1H; *p*-$NHC_6H_3iPr_2$), 7.13 (t, ^3J(H,H) = 7.6 Hz, 1H; *m*-PC_6H_4N), 7.19–7.23 (m, 4H; *o*-$P(C_6H_5)_2$, 2H; *p*-$P(C_6H_5)_2$, 1H; *p*-$NC_6H_3iPr_2$, 1H; *o*-PC_6H_4N), 7.29 (d, ^3J(H,H) = 7.6 Hz, 2H; *m*-$NHC_6H_3iPr_2$, 1H; *m*-$NC_6H_3iPr_2$), 7.33 (m, 1H; *p*-PC_6H_4N), 7.35 (d, ^3J(H,H) = 7.6 Hz, 2H; *m*-$NHC_6H_3iPr_2$, 1H; *m*-$NC_6H_3iPr_2$), 7.51 (m, 4H; *m*-$P(C_6H_5)_2$), 7.84 ppm (m, 1H; *o*-$CH_2C_6H_4P$); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 23.03, 24.08, 24.97 (s, 8C, $NHC_6H_3(CH(CH_3)_2)_2$, 4C, $NC_6H_3(CH(CH_3)_2)_2$), 25.77 (s, 2C, THF), 28.45, 28.61, 30.69 (s, 4C, $NC_6H_3(CH(CH_3)_2)_2$, 2C, $NHC_6H_3(CH(CH_3)_2)_2$), 55.25 (d, ^3J(C,P) = 23 Hz, 1C, $NCH_2C_6H_4P$), 72.62 (s, 2C, THF), 115.83 (s, 2C, *p*-$NHC_6H_3iPr_2$), 119.40 (s, 1C, *p*-$NC_6H_3iPr_2$), 123.55, 124.42 (s, 4C, *m*-$NHC_6H_3iPr_2$), 125.13 (s, 2C, *m*-$NC_6H_3iPr_2$), 128.99 (s, 2C, *p*-PC_6H_4N), 129.39 (d, ^3J(C,P) = 7 Hz, 4C, *m*-$P(C_6H_5)_2$), 129.72 (d, ^2J(C,P) = 6 Hz, 1C, *ipso*-PC_6H_4N), 129.96 (s, 2C, *p*-$P(C_6H_5)_2$), 132.77, 133.21 (s, 1C, *o*-PC_6H_4N, 1C, *m*-PC_6H_4N), 134.48 (s, 1C, *o*-$CH_2C_6H_4P$), 134.60, 134.80 (s, 4C, *o*-$NHC_6H_3iPr_2$,), 136.56 (d, ^1J(C,P) = 14 Hz, 2C, *ipso*-$P(C_6H_5)_2$), 137.66 (d, ^2J(C,P) = 10 Hz, 4C, *o*-$P(C_6H_5)_2$), 143.84 (s, 2C, *ipso*-$NHC_6H_3iPr_2$), 143.90 (s, 2C, *o*-$NC_6H_3iPr_2$), 145.61 (d, ^2J(C,P) = 24 Hz, 1C, *ipso*-$CH_2C_6H_4P$), 152.61 ppm (s, 1C, *ipso*-$NC_6H_3iPr_2$); IR (KBr): $\tilde{\nu}$ = 3056 (m), 2962 (s), 2868 (m), 1621 (m), 1586 (w), 1460 (s), 1436 (s), 1384 (m), 1363 (m), 1308 (w), 1265 (m), 1189 (m), 1145 (w), 1119 (w), 1094 (m), 1047 (m), 1027 (w), 999 (w), 965 (w), 927 (m), 885 (w), 829 (m), 800(m), 747 (s), 698 (s), 608 (w), 581 (w), 547 (w), 533 (w), 502 cm^{-1} (m); elemental analysis (%) calcd for $C_{59}H_{77}N_3OPY$: C 73.50, H 8.05, N 4.36; found: C 73.10, H 8.41, N 4.36.

Crystal data of 1a: The unit cell of **1a** was found to contain half a molecule of benzene. $C_{47}H_{60}N_2OPSiY{\cdot}0.5C_6H_6$, M_r = 855.99,triclinic, space group $P\bar{1}$, a = 10.264(1), b = 10.630(1), c = 22.492(3) Å, α = 94.669(2), β = 92.970(2), γ = 107.154(2)°, V = 2329.8(5) Å^3, Z = 2, ρ_{calcd} = 1.220 g cm^{-3}, μ(Mo$_{K\alpha}$) = 1.348 mm^{-1}, 13547 reflections measured, and 8994 reflections with $I_o > 2\sigma(I_o)$. Final $R1$ = 0.0729, $wR2$ = 0.1218 (all data).

Crystal data of 2: The unit cell of complex **2** was found to contain one molecule of benzene. $C_{63}H_{78}N_4PY{\cdot}C_6H_6$, M_r = 1087.27, orthorhombic, space group $Pna2_1$, a = 21.6717(9), b = 13.0374(5), c = 42.9617(18) Å, V = 12138.5(9) Å^3, Z = 8, ρ_{calcd} = 1.190 g cm^{-3}, μ(Mo$_{K\alpha}$) = 1.030 mm^{-1}, 90207 reflections measured, and 23832 reflections with $I_o > 2\sigma(I_o)$. Final $R1$ = 0.0621, $wR2$ = 0.148 (all data).

Crystal data of 3: The unit cell of complex **3** contains some disordered molecules of benzene. $C_{50.40}H_{53}N_2O_2PY$, M_r = 839.03, triclinic, space group $P\bar{1}$, a = 11.7407(8), b = 15.0546(10), c = 15.8911(10) Å, α = 116.925(1), β = 93.044(1), γ = 102.804(1)°, V = 2403.7(3) Å^3, Z = 2, ρ_{calcd} = 1.159 g cm^{-3}, μ(Mo$_{K\alpha}$) = 1.284 mm^{-1}, 12166 reflections measured, and 9039 reflections with $I_o > 2\sigma(I_o)$. Final $R1$ = 0.0839, $wR2$ = 0.2548 (all data).

Crystal data of 4a: $C_{39}H_{55}NOPSi_2Y$, M_r = 729.90, triclinic, space group $P\bar{1}$, a = 12.425(1), b = 12.464(1), c = 13.628(1) Å, α = 101.812(2), β = 93.393(2), γ = 93.170(2)°, V = 2057.1(3) Å^3, Z = 2, ρ_{calcd} = 1.178 g cm^{-3}, μ(Mo$_{K\alpha}$) = 1.542 mm^{-1}, 11220 reflections measured, and 7518 reflections with $I_o > 2\sigma(I_o)$. Final $R1$ = 0.0622, $wR2$ = 0.166 (all data).

Crystal data of 4c: $C_{43}H_{63}NOPSi_2Y$, M_r = 785.00, monoclinic, space group $C2/c$, a = 31.149(2), b = 17.326(9), c = 22.541(1) Å, α = 90, β = 121.6890(10), γ = 90°, V = 10351.6(10) Å^3, Z = 8, ρ_{calcd} = 1.007 g cm^{-3}, μ(Mo$_{K\alpha}$) = 1.23 mm^{-1}, 29529 reflections measured, and 10170 reflections with $I_o > 2\sigma(I_o)$. Final $R1$ = 0.0746, $wR2$ = 0.2396 (all data).

Crystal data of 5a: The unit cell of complex **5a** was found to contain one and a half molecules of toluene. $C_{65.50}H_{78.50}N_3OPY$, M_r = 1043.69, triclinic, space group $P\bar{1}$, a = 11.1416(8), b = 14.375(1), c = 18.712(2) Å, α = 76.138(1), β = 88.896(1), γ = 86.297(1)°, V = 2904.8(4) Å^3, Z = 2, ρ_{calcd} = 1.193 g cm^{-3}, μ(Mo$_{K\alpha}$) = 1.074 mm^{-1}, 16528 reflections measured, and 10833 reflections with $I_o > 2\sigma(I_o)$. Final $R1$ = 0.0542, $wR2$ = 0.1391 (all data).

CCDC-603441 (**1a**), CCDC-611321 (**1b**), CCDC-606628 (**2**), CCDC-299006 (**3**), CCDC-299007 (**4a**), CCDC-607114 (**4b**), CCDC-606626 (**4c**), CCDC-607115 (**4d**), and CCDC-606627 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] Reviews: a) Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1–22; b) J. Gromada, J. F. Carpentier, A. Mortreux, *Coord. Chem. Rev.* **2004**, *248*, 397–410; c) J. Y. Hyeon, J. Gottfriendsen, F. T. Edelmann, *Coord. Chem. Rev.* **2005**, *249*, 2787–2844; d) P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404–2433, and references therein.

[2] a) Y. Zhang, Z. Hou, Y. Wakatsuki, *Macromolecules* **1998**, *31*, 8650–8652; b) S. Kaita, Z. Hou, Y. Wakatsuki, *Macromolecules* **1999**, *32*, 9078–9079; c) Z. Hou, Y. Zhang, H. Tezuka, P. Xie, O. Tardif, T. A. Koizumi, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **2000**, *122*, 10533–10542; d) K. C. Hultzsch, P. Voth, K. Beckerle, T. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228–243; e) Z. Hou, S. Kaita, Y. Wakatsuki, *Macromolecules* **2001**, *34*, 1539–1541; f) Z. Hou, S. Kaita, Y. Wakatsuki, *Pure Appl. Chem.* **2001**, *73*, 291–294; g) Y. Luo, Y. Yao, Q. Shen, *Macromolecules* **2002**, *35*, 8670–8671; h) Y. Luo, J. Baldamus, Z. Hou, *J. Am. Chem. Soc.* **2004**, *126*, 13910–13911; i) E. Kirillov, C. W. Lehmann, A. Razavi, J. F. Carpentier, *J. Am. Chem. Soc.* **2004**, *126*, 12240–12241; j) X. Li, Z. Hou, *Macromolecules* **2005**, *38*, 6767–6769; k) X. Li, J. Baldamus, Z. Hou, *Angew. Chem.* **2005**, *117*, 984–987; *Angew. Chem. Int. Ed.* **2005**, *44*, 962–965; l) L. Zhang, Y. Luo, Z. Hou, *J. Am. Chem. Soc.* **2005**, *127*, 14562–14563.

[3] a) H. Yasuda, H. Yamamoto, K. Yokota, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 4908–4910; b) E. Ihara, M. Morimoto, H. Yasuda, *Macromolecules* **1995**, *28*, 7886–7892; c) H. Yasuda, K. Yamamoto, W. E. Piers, D. J. H. Emslie, *Coord. Chem. Rev.* **2002**, *233–234*, 131–155; d) O. D. Cabaret, B. M. Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176; e) D. Cui, M. Nishiura, Z. Hou, *Macromolecules*, **2005**, *38*, 4089–4095.

[4] a) G. Jeske, E. Laurel, P. Schock, P. N. Swepston, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110; b) W. Roll, H.-H. Brintzinger, B. Rieger, R. Zolk, *Angew. Chem.* **1990**, *102*, 339–341; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 279–280; c) H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–986, and references therein. d) S. Arndt, J. Okuda, *Chem. Rev.* **2002**, *102*, 1953–1976, and references therein. e) O. Tardif, M. Nishiura, Z. Hou, *Tetrahedron* **2003**, *59*, 10525–10593.

[5] a) E. A. Bijpost, R. Duchateau, J. H. Teuben, *J. Mol. Catal. B J. Mol. Catal. A* **1995**, *95*, 121–128; b) R. Duchateau, C. T. van Wee, J. H. Teuben, *Organometallics* **1996**, *15*, 2291–2302; c) K. B. Aubrecht, K. Chang, M. A. Hillmyer, W. B. Tolman, *J. Polym. Sci. Part A*## **2001**, *39*, 284–293.

[6] a) R. Duchateau, C. T. van Wee, A. Meetsma, J. H. Teuben, *J. Am. Chem. Soc.* **1993**, *115*, 4931–4932; b) P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91–141; c) G. R. Giesbrecht, G. D. Whitener, J. Arnold, *J. Chem. Soc. Dalton Trans.* **2001**, *6*, 923–927; d) Z. Lu, G. P. A. Yap, D. S. Richeson, *Organometallics* **2001**, *20*, 706–712.

[7] P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood, W. Clegg, *Organometallics* **2001**, *20*, 2533–2544.

[8] D. J. H. Emslie, W. E. Piers, R. McDonald, *J. Chem. Soc. Dalton Trans.* **2002**, 293–294.

[9] a) P. G. Hayes, W. E. Piers, R. McDonald, *J. Am. Chem. Soc.* **2002**, *124*, 2132–2133; b) P. G. Hayes, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2003**, *125*, 5622–5623; c) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J. H. Teuben, *Chem. Commun.* **2003**, 522–523; d) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, *J. Am. Chem. Soc.* **2004**, *126*, 9182–9183; e) P. G. Hayes, W. E. Piers, M. Parvez, *Organometallics* **2005**, *24*, 1173–1183.

[10] a) D. W. Stephan; J. C. Stewart, F. Guerin, R. E. Spence, W. Xu, D. G. Harrison, *Organometallics* **1999**, *18*, 1116–1118; b) R. G. Cavell, R. P. Kamalesh Babu, K. Aparna, *J. Organomet. Chem.* **2001**, *617–618*, 158–169; c) J. D. Masuda, P. Wei, D. W. Stephen, *Dalton Trans.* **2003**, 3500–3505; d) J. D. Masuda, D. M. Walsh, P. Wei, D. W. Stephan, *Organometallics* **2004**, *23*, 1819–1824.

[11] G. C. Welch, W. E. Piers, M. Parvez, R. McDonald, *Organometallics* **2004**, *23*, 1811–1818.

[12] For the ^{1}H NMR spectrum, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HMQC, and a table of chemical shifts of protons in the aliphatic region of **1a**, see Supporting Information. The multiple resonances are attributed to the coupling of carbon with the yttrium atom, which indicates direct linkage between them.

[13] a) The C–H activation of benzene was first reported by C. C. Cummins, C. P. Schaller, G. D. Van Duyne, P. T. Wolczanski, A. W. E. Chan, R. Hoffman, *J. Am. Chem. Soc.* **1991**, *113*, 2985–2994; b) M. D. Fryzuk, M. P. J. Petrella, B. O. Patrick, *Organometallics* **2005**, *24*, 5440–5454.

[14] P. G. Hayes, G. C. Welch, D. J. H. Emslie, C. L. Noack, W. E. Piers, M. Parvez, *Organometallics* **2003**, *22*, 1577–1579.

[15] a) S. Bambirra, S. J. Boot, D. van Leusen, A. Meetsman, B. Hessen, *Organometallics* **2004**, *23*, 1891–1898; b) C. G. J. Tazelaar, S. Bambirra, D. van Leusen, A. Meetsman, B. Hessen, J. H. Teuben, *Organometallics* **2004**, *23*, 936–939; c) C. S. Tredget, F. Bonnet, A. R. Cowley, P. Mountford, *Chem. Commun.* **2005**, 3301–3303; d) J. Scott, S. Gambarotta, I. Korobkov, Q. Knijnenburg, B. de Bruin, P. H. M. Budzelaar, *J. Am. Chem. Soc.* **2005**, *127*, 17204–17206.

[16] a) T. G. Wetzel, S. Dehnen, P. W. Roesky, *Angew. Chem.* **1999**, *111*, 1155–1158; *Angew. Chem. Int. Ed.* **1999**, *38*, 1086–1088; b) M. T. Gamer, S. Dehnen, P. W. Roesky, *Organometallics* **2001**, *20*, 4230–4236; c) M. T. Gamer, P. W. Roesky, *Organometallics* **2004**, *23*, 5540–5544; d) P. W. Roesky, M. T. Gamer, N. Marinos, *Chem. Eur. J.* **2004**, *10*, 3537–3542; e) M. Rastatter, A. Zulys, P. W. Roesky, *Chem. Commun.* **2006**, 874–876; f) T. K. Panda, A. Zulys, M. T. Gamer, P. W. Roesky, *J. Organomet. Chem.* **2005**, *690*, 5078–5089; g) T. K. Panda, M. T. Gamer, P. W. Roesky, *Inorg. Chem.* **2006**, *45*, 910–916; h) P. W. Roesky, *Inorg. Chem.* **2006**, *45*, 798–802.

[17] M. A. Munoz-Hernandez, T. S. Keizer, P. Wei, S. Parkin, D. A. Atwood, *Inorg. Chem.* **2001**, *40*, 6782–6787.

[18] a) M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* **2005**, *44*, 8004–8010; b) M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold, K. Phomphrai, *J. Am. Chem. Soc.* **2000**, *122*, 11845–11854; c) M. H. Chisholm, D. Navarro-Llobet, *Macromolecules* **2001**, *34*, 8851–8857; d) K. Majerska, A. Duda, *J. Am. Chem. Soc.* **2004**, *126*, 1026–1027; e) N. Nomura, T. Aoyama, R. Ishii, T. Kondo, *Macromolecules* **2005**, *38*, 5363–5366; f) Z. Zhong, P. J. Dijkstra, J. Feijen, *J. Am. Chem. Soc.* **2003**, *125*, 11291–11298; g) Z. Zhong, P. J. Dijkstra, J. Feijen, *Angew. Chem.* **2002**, *114*, 4692–4695; *Angew. Chem. Int. Ed.* **2002**, *41*, 4510–4513; h) N. Nomura, R. Ishii, M. Akakura, K. Aoi, *J. Am. Chem. Soc.* **2002**, *124*, 5938–5939.

[19] a) A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White, D. J. Williams, *Dalton Trans.* **2004**, *4*, 570–578; b) P. Hormnirun, E. L. Marshall, V. C. Gibson, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2004**, *126*, 2688–2689.

[20] a) M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 11583–11584; b) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238; c) T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 1316–1326; d) M. S. Hill, P. B. Hitchcock, *J. Chem. Soc. Dalton Trans.* **2002**, *24*, 4694–4702; e) C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc.* **2003**, *125*, 11350–11359; f) Z. Tang, X. Chen, X. Pang, Y. Yang, X. Zhang, X. Jing, *Biomacromolecules* **2004**, *5*, 965–970.

[21] a) T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 4072–4073; b) K. B. Aubrecht, K. Chang, M. A. Hillmyer, W. B. Tolman, *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 284–293.

[22] F. Bonnet, A. R. Cowley, P. Mountford, *Inorg. Chem.* **2005**, *44*, 9046–9055.

[23] a) H. Ma, T. P. Spaniol, J. Okuda, *Dalton Trans.* **2003**, 4770–4780; b) C. Cai, A. Amgoune, C. W. Lehmann, J. Carpentier, *Chem. Commun.* **2004**, 330–331; c) J. Gromada, J. Carpentier, A. Mortreux, *Coord. Chem. Rev.* **2004**, *248*, 397–410; d) H. Ma, J. Okuda, *Macro-*

molecules **2005**, *38*, 2665–2673; e) A. Amgoune, C. M. Thomas, T. Roisnel, J. Carpentier, *Chem. Eur. J.* **2005**, *11*, 169–179.

[24] a) W. J. Evans, H. Katsumata, *Macromolecules* **1994**, *27*, 2330–2332; b) M. Yamashita, Y. Takemoto, E. Ihara, H. Yasuda, *Macromolecules* **1996**, *29*, 1798–1806; c) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845–4856; d) G. R. Giesbrecht, G. D. Whiterer, J. Arnold, *J. Chem. Soc. Dalton Trans.* **2001**, 923–927.

[25] M. Save, M. Schappacher, A. Soum, *Macromol. Chem. Phys.* **2002**, *203*, 889–899.

[26] E. Marshall, V. Gibson, H. Rzepa, *J. Am. Chem. Soc.* **2005**, *127*, 6048–6051.

[27] S. Antonaroll, B. Crociani, *J. Organomet. Chem.* **1998**, *560*, 137–146.

[28] T. B. Rauchfuss, D. A. Wrobleski, *Inorg. Synth.* **1982**, *21*, 175–179.

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