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Phosphazene-Functionalized Cyclopentadienyl and Its Derivatives Ligated Rare-Earth Metal Alkyl Complexes: Synthesis, Structures, and Catalysis on Ethylene Polymerization

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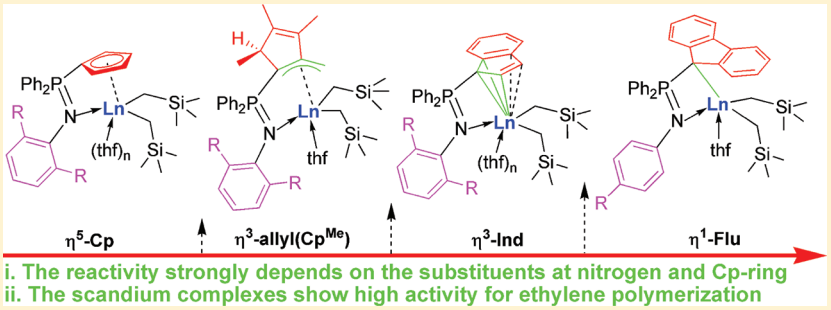
Supporting Information



ABSTRACT: Treatment of $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Sc, Y, and Lu) with 1 equiv of CpPN-type ligands $C_5H_4{=}PPh_2{-}NH{-}C_6H_3R_2$ (R = Me, **L^1(Me)**; R = ^{i}Pr, **L^1(^{i}Pr)**) at room temperature readily generated the corresponding CpPN-type bis(alkyl) complexes **1** and **2a**−**2c**. Addition of 3 equiv of $LiCH_2SiMe_3$ to a mixture of **L^1(^{i}Pr)** and $LnCl_3(thf)_2$ (Ln = Sm and Nd) also afforded the CpPN-type bis(alkyl) complexes **2d** and **2e**. The Cp moiety bonds to the central metal in a classical η^5 mode in all CpPN-type complexes **1** and **2**. In contrast, the Cp^{Me}PN-type ligands $C_5Me_4H{-}PPh_2{=}N{-}C_6H_3R_2$ (R = Me, **L^2(Me)**; R = ^{i}Pr, **L^2(^{i}Pr)**) behaved differently. **L^2(Me)** did not react with $Sc(CH_2SiMe_3)_3(thf)_2$. Similarly, **L^2(^{i}Pr)** was also inert to $Sc(CH_2SiMe_3)_3(thf)_2$ even at 50 °C. When the central metal was changed to yttrium, however, the equimolar reaction between $Y(CH_2SiMe_3)_3(thf)_2$ and **L^2(^{i}Pr)** in the presence of LiCl afforded two bis(alkyl) complexes **3a** and **3b**. In the main product **3a**, $[C_5HMe_3(\eta^3\text{-}CH_2){-}PPh_2{=}N{-}C_6H_3{}^iPr_2]Y(CH_2SiMe_3)_2(thf)$, the ligand bonds to the Y^{3+} ion in a rare η^3-allyl/κ-N mode, whereas in **3b**, $(C_5Me_4{-}PPh_2{=}N{-}C_6H_3{}^iPr_2)Y(CH_2SiMe_3)_2(LiCl)(thf)$, the Cp ring coordinates to the Y^{3+} ion in an η^5 mode, and a LiCl unit is located between the Y^{3+} ion and the nitrogen atom. When the central metal was changed to lutetium, a bis(alkyl) complex **4a**, $[C_5HMe_3(\eta^3\text{-}CH_2){-}PPh_2{=}N{-}C_6H_3{}^iPr_2]Lu(CH_2SiMe_3)_2(thf)$, and a bis(alkyl) complex **4b**, $(C_5Me_4{-}PPh_2{=}N{-}C_6H_3{}^iPr_2)Lu(CH_2SiMe_3)_2$, were isolated. The protonolysis reaction of the IndPN-type ligands $C_9H_7{-}PPh_2{=}N{-}C_6H_3R_2$ (R = Me, **L^3(Me)**; R = Et, **L^3(Et)**; R = ^{i}Pr, **L^3(^{i}Pr)**) with $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Sc, Y, and Lu) generated the IndPN-type bis(alkyl) complexes **5a**−**5c**, **6**, and **7a**−**7c**, selectively, where the Ind moiety tends to adopt an η^3-bonding fashion. The more bulky FluPN-type ligands $C_{13}H_9{-}PPh_2{=}N{-}C_6H_4R$ (R = H, **L^4(H)**; R = Me, **L^4(Me)**) were treated with $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Sc and Lu) to afford the FluPN-type bis(alkyl) complexes **8** and **9a** and **9b**, where the Flu moiety has a rare η^1-bonding mode. Complexes **1**−**9** were fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR; X-ray; and elemental analyses. Upon activation with AlR_3 and $[Ph_3C][B(C_6F_5)_4]$, the scandium complexes showed good to high catalytic activity for ethylene polymerization. The effects of the sterics and electronics of the ligand, the loading and the type of AlR_3, the polymerization temperature, and the polymerization time on the catalytic activity were also discussed.

INTRODUCTION

In the past decades, as the most commonly used ligands in the field of organometallic chemistry and polymerization, cyclopentadienyl (Cp), substituted Cp, and the indenyl (Ind) and fluorenyl (Flu) ligands have attracted considerable interest, because their related metal complexes not only exhibited interesting chemical structures and unique reactivities but also showed versatile catalytic activity and selectivity in the polymerizations of olefins or conjugated dienes.[1] In the rapid

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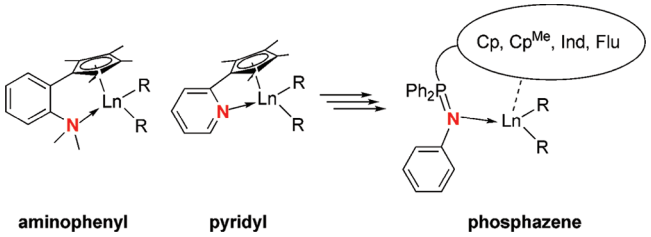
development of Cp-based complexes, to tune the steric and electronic properties around the central metal and control the orientation and rotation of the Cp-type ring, variation of the Cp substitution pattern has been extensively investigated. Introducing a soft or rigid heteroatom side arm on the Cp ring to form a constrained-geometry mode around the central metal is an efficient and tempting approach. Constrained-geometry complexes (CGCs), as one of the best developed classes of Cp-based complexes, were first reported by Bercaw and Okuda by using the dianionic cyclopentadienyl-silylamido (CpSiN) ligands, which showed excellent activity and selectivity toward olefin polymerization.[2−4] Since this breakthrough, by changing the nature of the Cp moieties,[5] the bridging units (soft or hard),[6] and the donating heteroatom types on the side arm,[7] various metal complexes based on monoanionic or dianionic CGC ligands have been extensively synthesized and have their reactivities investigated. In particular, as the isolobal analogue of the classical CpSiN-type ligands, the monoanionic phosphazene-functionalized cyclopentadienyl (CpPN) ligands have attracted increasing attention, owing to swift modification of their electronic properties and bulkiness by varying the substituents at the N and P atoms and Cp ring. Since 2005, we have presented the synthesis of some CpPN ligands and corresponding group 4 and rare-earth metal complexes by focusing mainly on the C_5Me_4═PMe_2−NH−Ad (Ad = 1-adamantyl) ligand.[8] The monoanionic IndPN- and FluPN-type ligand-attached rhodium and zirconium complexes have been also reported by Bourissou and co-workers.[9] However, to date, the study of the organometallic chemistry and polymerization of rare-earth metal CpPN, IndPN, and FluPN complexes is very limited, but promising, and needs to be further explored.

On the other hand, polyethylene (PE), which is the largest volume synthetic polymer applied in every aspect of our daily lives, such as packaging materials, pipes, textiles, etc., has been extensively studied in both academic and industrial fields. To date, catalyst systems for ethylene polymerization are mostly focused on transition metals or late transition metals,[10] those based on rare-earth metals are relatively explored less.[11] So far, both non-Cp,[12] such as N-type amino and imino ligands, and mono-Cp (or its derivatives)[13] attached rare-earth metal complexes, especially the scandium complexes, have been reported to initiate the polymerization of ethylene with good activity, although the scandium remains a model and may be difficult to apply in ethylene polymerization due to its prohibitive cost. Comparatively, the catalyst precursors based on CGC ligands that can polymerize ethylene were extremely limited, as far as we are aware.[6g,14]

Recently, we became interested in rare-earth metal complexes based on the monoanionic nitrogen-functionalized Cp ligands, and we have reported a series of rare-earth metal complexes based on aminophenyl-Cp^{Me} and pyridyl-Cp^{Me} ligands (Chart 1), which showed excellent reactivities and polymerization performances toward dienes and styrene monomers.[6a−f] In this contribution, therefore, we select a series of phosphazene-functionalized cyclopentadienyl (CpPN), tetramethylcyclopentadienyl (Cp^{Me}PN), indenyl (IndPN), and fluorenyl (FluPN) compounds as the monoanionic ancillary ligands. The synthesis and the detailed characterization and the diverse and interesting structures of a new family of rare-earth metal bis(alkyl) complexes are presented. More remarkably, we will demonstrate the strong influences of the central metals, the substituents at nitrogen, and the substituents on the Cp ring on the protonolysis reaction, while we also find that the pendent

Chart 1. Rare-Earth Metal Complexes Containing Various Nitrogen-Modified Cp Ligands

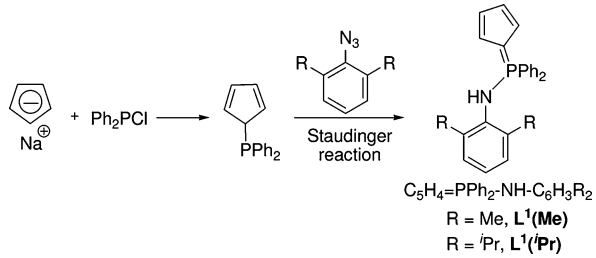


phosphazene side arm can enforce and modulate the low hapticity of Ind and Flu. The detailed study of ethylene polymerization shows that the scandium precursors provide the highest activity.

RESULTS AND DISCUSSION

Preparation of the CpPN-type Bis(alkyl) Complexes 1 and 2a−2e. We first focused on the less sterically crowded CpPN-type ligands. The ligand C_5H_4═PPh_2−NH−$C_6H_3{}^iPr_2$ ($\mathbf{L^1(^iPr)}$) synthesis via TlC_5H_4 and PPh_2Cl followed by a Staudinger reaction was reported by us.[8d] Herein, we successfully exchanged the highly toxic TlC_5H_5 with NaC_5H_5, which can be easily obtained from Na and dicyclopentadiene. The improved ligand synthesis, which is readily synthesized on a large scale using cheap starting materials, makes the CpPN-type ligand much more attractive. Therefore, the ligands C_5H_4═PPh_2−NH−$C_6H_3R_2$ (R = Me, $\mathbf{L^1(Me)}$; R = ^{i}Pr, $\mathbf{L^1(^iPr)}$) were prepared via NaC_5H_5 and PPh_2Cl, followed by a Staudinger reaction with 1.5 equiv of $C_6H_3R_2N_3$ in 83% and 63% yields, respectively (Scheme 1). The ^{1}H NMR spectrum of

Scheme 1. Synthesis of the CpPN-type Ligands $\mathbf{L^1(Me)}$ and $\mathbf{L^1(^iPr)}$



$\mathbf{L^1(Me)}$ shows a doublet at δ = 4.40 ppm with a coupling constant ($^2J_{PH}$ = 6.0 Hz) arising from the N*H* proton, but no allylic ring proton (Cp*H*) is observed. In addition, the ^{31}P NMR resonance of $\mathbf{L^1(Me)}$ (25.1 ppm) is similar to the chemical shift of compound $\mathbf{L^1(^iPr)}$ (28.9 ppm).[8d] The NMR spectroscopy suggests that $\mathbf{L^1(Me)}$, like $\mathbf{L^1(^iPr)}$, preferentially exists in its thermodynamically more favorable form of a *P*-amino-cyclopentadienyl-phosphorane (type **I**, Chart 2). The N*H* amino proton is of relative high kinetic acidity; therefore, ligands $\mathbf{L^1(Me)}$ and $\mathbf{L^1(^iPr)}$ can readily react with 1 equiv of $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Sc, Y, and Lu) at room temperature to straightforwardly generate the desired CpPN-type bis(alkyl) complexes **1** and **2a**−**2c** in high isolated yields (57−71%) (Scheme 2). In addition, it is well known that only a few rare-earth metal tris-alkyl precursors are of sufficient thermal stability.[1b] Therefore, we have used an alternative synthetic protocol to prepare the samarium and neodymium complexes.[15] Addition of 3 equiv of $LiCH_2SiMe_3$ to a mixture

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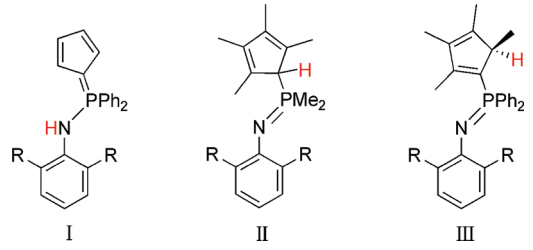
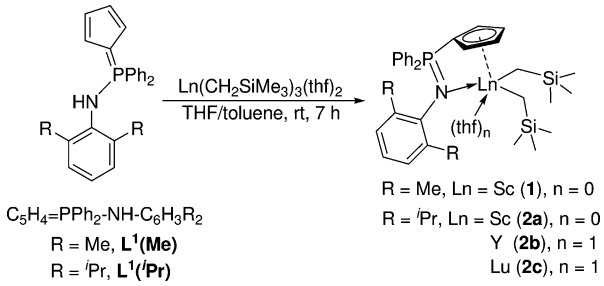
Chart 2. Preferred Tautomer of Different CpPN-type Ligands

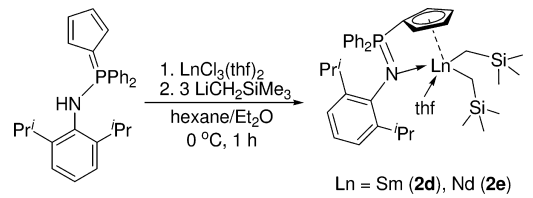


Scheme 2. Synthesis of the CpPN-type Complexes 1 and 2a–2c



of $\mathbf{L^1}(^i\mathbf{Pr})$ and $LnCl_3(thf)_2$ (Ln = Sm and Nd) at 0 °C readily afforded the CpPN-type bis(alkyl) complexes **2d** and **2e** (Scheme 3). Complexes **1** and **2a–2e** were fully characterized

Scheme 3. Synthesis of the CpPN-type Complexes 2d and 2e



by multinuclear NMR spectroscopy (^{1}H, ^{13}C, and ^{31}P), X-ray diffraction, and elemental analysis. The ^{1}H NMR spectra of scandium complexes **1** and **2a** exhibit a doublet at δ = 0.09 ppm and a broad singlet at δ = 0.20 ppm assigned to the Sc–CH_2SiMe_3 methylene protons, respectively. No THF coordination molecule is observed, which is unambiguously confirmed by the X-ray diffraction study as well. In contrast, the ^{1}H NMR spectra suggest that **2b–2e** with larger ionic radii contain one THF molecule in the structure, which is different from the THF-free rare-earth metal complexes η^5,η^1-$C_5Me_4PMe_2NAdLn(CH_2SiMe_3)_2$ (Ln has a bigger ionic radii, such as Pr and Ce) reported previously by us.[8a,b] We conclude that the less steric bulkiness of the Cp-ring leads to the coordination of THF. The yttrium and lutetium complexes **2b** and **2c** show the clear and similar ^{1}H NMR spectra. The ^{1}H NMR spectra of paramagnetic samarium and neodymium complexes **2d** and **2e** show some broad and some sharp signals. In addition, single sharp resonances with the chemical shifts of δ = 7.8, 11.1, 10.1, and 10.4 ppm in the ^{31}P NMR spectra refer to **1** and **2a–2c**, respectively, whereas ^{31}P NMR spectra of paramagnetic samarium and neodymium complexes **2d** and **2e** show broad signals at δ = 18.1 and −62.8 ppm, respectively. These resonances are in a good agreement with those found in η^5,η^1-$C_5Me_4PMe_2NAdLn(CH_2SiMe_3)_2$,[8a,b] but are shifted upfield in comparison with the free ligand ($\mathbf{L^1}$**(Me)**: δ = 25.12 ppm; $\mathbf{L^1}(^i\mathbf{Pr})$: δ = 28.9 ppm).[8d] Furthermore, X-ray studies of **1** and **2a–2e** reveal that the Cp ring coordinates to the metal center in a typical η^5 mode (Figures 1 and 2). In all structures,

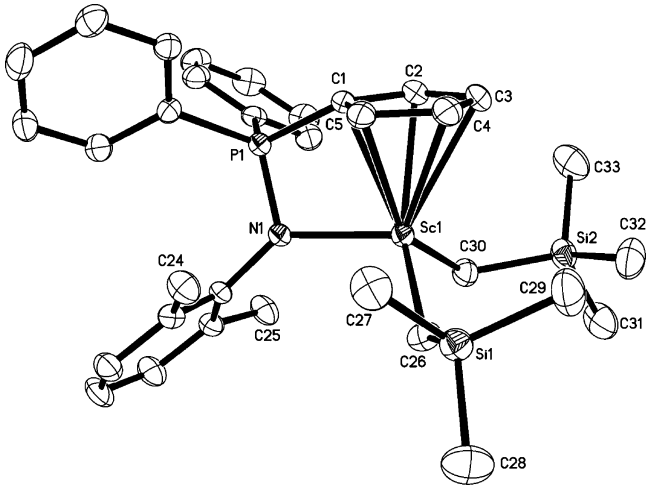


Figure 1. X-ray structure of **1** (40% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc1–Cp_{cent} 2.251, Sc1–C26 2.212(3), Sc1–C30 2.219(2), P1–C1 1.769(2), P1–N1 1.623(2), Sc1–N1 2.188(2); C1–P1–N1 99.2(1), Cp_{cent}–Sc1–N1 95.9, C26–Sc1–C30 102.9(1) (Cp_{Cent} is the centroid of the cyclopentadienyl ring).

the P–C1 bond lengths (1.757(4)–1.769(2) Å) are clearly longer than those in the $\mathbf{L^1}(^i\mathbf{Pr})$ ligand (1.718(1) Å); however, the P1–N1 bond distances (1.590(5)–1.625(3) Å) are shorter than those in the ligand (1.649(1) Å).[8d] Additionally, we observe that the Sc1–N1 bond distances (2.188(2)–2.214(3) Å) are comparable to those in NPN-type scandium complexes (2.175–2.203 Å).[16]

Noteworthy is that they are longer than the covalent Sc–N bond in the CpSiN-type complexes (2.071(6)–2.083(5) Å),[2d] but shorter than the coordination Sc–N bond (up to 2.47 Å).[6a,b,f,g,12a] These results suggest that the electrons in the complexes tend to delocalize within the N–P–Cp fragment. Despite the large difference in ionic radii of the central metals, the molecular structures of **2b**, **2d**, and **2e** are very similar (Figure 2). The notable structural feature is the larger Ln–N bond lengths in **2b** (2.469(3) Å), **2d** (2.533(6) Å), and **2e** (2.572(2) Å) compared with the analogous complexes η^5,η^1-$C_5Me_4PMe_2NAdLn(CH_2SiMe_3)_2$ (Y: 2.316(4) Å, Sm: 2.367(3) Å),[8b] demonstrating the lower basicity of $\mathbf{L^1}(^i\mathbf{Pr})$ in comparison with the $C_5Me_4PMe_2NHAd$ ligand. A consequence is the presence of a coordinated THF molecule. The most interesting feature in the structures of **2b**, **2d**, and **2e** is the rather small Cp_{cent}–Ln–N bite angles of 87.2(1), 85.2(1), and 85.0(1)°, respectively, which explains the coordination of the additional THF molecule.

Preparation of the Cp^{Me}PN-type Bis(alkyl) Complexes 3a, 3b and 4a, 4b. We have found that the structures of CpPN-type ligands exist either in their *P*-amino-cyclopentadienylidene-phosphorane (**I**-type, Chart 2) or in their *P*-cyclopentadienyl-iminophosphorane tautomeric form (**II**- and **III**-types, Chart 2).[8] The equilibrium between both tautomers strongly depends on the substituents at the N, P, and C(Cp) atoms as they influence the relative Brønsted acidity of the Cp–H and RN–H protons.[8d] For example, ligands $\mathbf{L^1}$**(Me)** and

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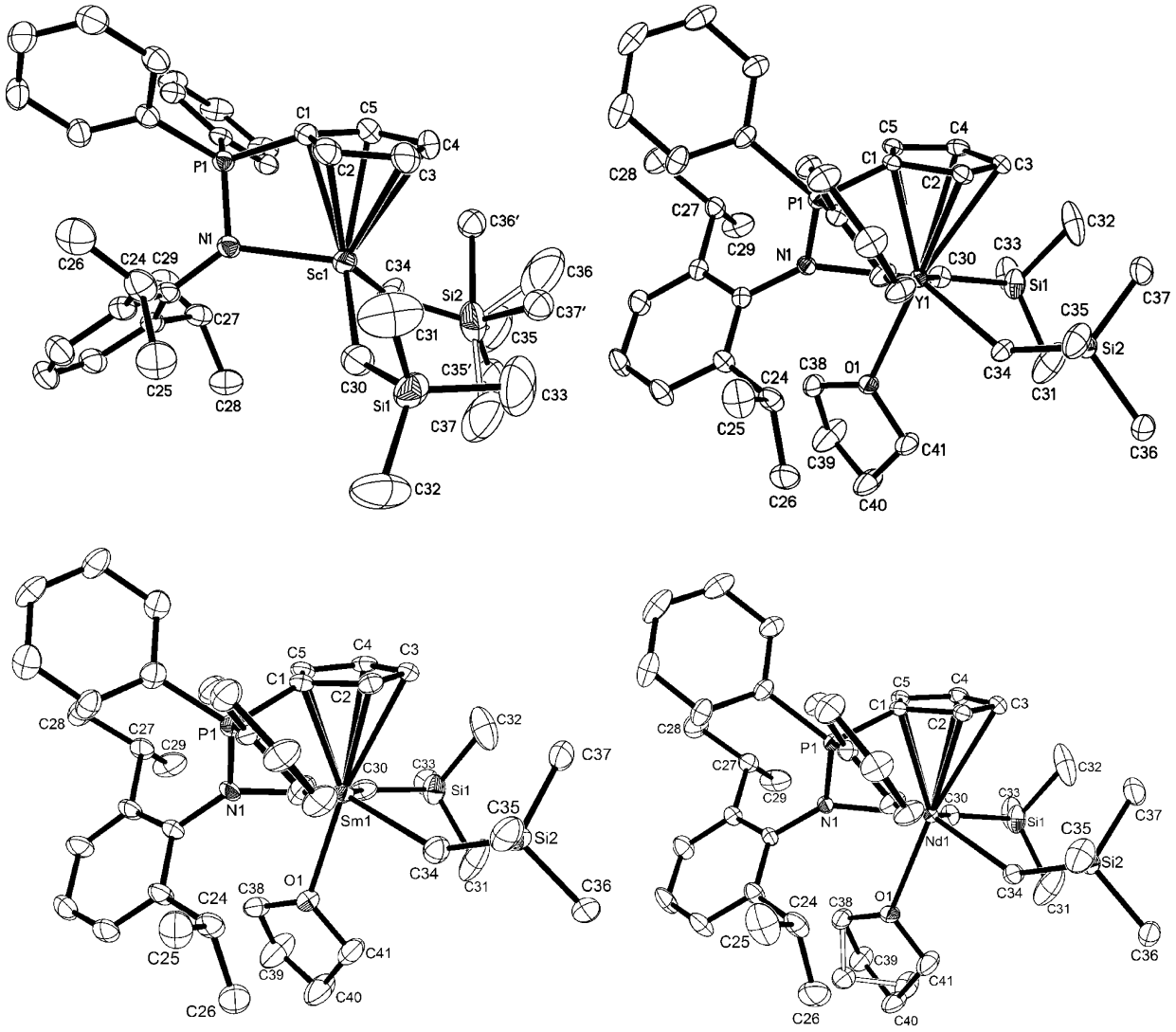

Figure 2. X-ray structures of **2a**, **2b**, **2d**, and **2e** (40% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **2a**: Sc1−Cp_{cent} 2.260, Sc1−C30 2.180(5), Sc1−C34 2.266(6), P1−C1 1.768(4), P1−N1 1.625(3), Sc1−N1 2.214(3); C1−P1−N1 99.0(2), Cp_{cent}−Sc1−N1 95.3, C34−Sc1−C30 103.1(2). **2b**: Y1−Cp_{cent} 2.460, Y1−C30 2.421(4), Y1−C34 2.419(4), P1−C1 1.757(4), P1−N1 1.611(3), Y1−O1 2.448(3), Y1−N1 2.469(3); Cp_{cent}−Y1−N1 87.2(1), C30−Y1−C34 109.7(1). **2d**: Sm1−Cp_{cent} 2.516, Sm1−C30 2.477(7), Sm1−C34 2.482(7), P1−C1 1.758(8), P1−N1 1.590(5), Sm1−O1 2.491(4), Sm1−N1 2.533(6); Cp_{cent}−Sm1−N1 85.2(1), C30−Sm1−C34 110.6(3). **2e**: Nd1−Cp_{cent} 2.551, Nd1−C30 2.498(2), Nd1−C34 2.504(3), P1−C1 1.767(3), P1−N1 1.608(2), Nd1−O1 2.543(2), Nd1−N1 2.572(2); Cp_{cent}−Nd1−N1 85.0(1), C30−Nd1−C34 110.2(1).

$L^1(^iPr)$ occur in the form of tautomer **I**, $C_5H_4{=}PPh_2{-}NH{-}Ar$ (Chart 2). Allylic iminophosphorane (type **II**) $C_5Me_4H{-}PMe_2{=}N{-}C_6H_3{}^iPr_2$ was observed as a product of kinetic control, which, upon prolonged heating under thermodynamic control, can rearrange to the **III**-type product. The new $Cp^{Me}PN$ ligands $C_5Me_4H{-}PPh_2{=}N{-}C_6H_3R_2$ (R = Me, $L^2(Me)$; R = ^{i}Pr, $L^2(^iPr)$) synthesized through prolonged heating of rather unreactive $C_5Me_4H{-}PPh_2$ with ArN_3 occur in the thermodynamically most favorable form of type **III**, which has a weak reactivity. In the ^{1}H NMR spectra of $L^2(Me)$ and $L^2(^iPr)$, a quartet signal is observed at δ = 3.11−3.14 ppm and δ = 3.10−3.13 ppm assigned to the C_5Me_4H proton, respectively, which is completely different from the doublet signal at δ = 3.37 ppm with a $^2J_{PH}$ coupling constant (26.8 Hz) assigned to the C_5Me_4H proton in the **II**-type $C_5Me_4H{-}PMe_2{=}N{-}C_6H_3{}^iPr_2$ ligand.[8d] Because of the absence of symmetry in both ligands, one doublet and three singlets are observed for the C_5Me_4 groups. Moreover, the resonance signal in the ^{31}P NMR spectrum is in the region of iminophosphoranes but is still shifted upfield (δ = −15.07 ppm for $L^2(^iPr)$) in comparison with the singlet at δ = −3.1 ppm for the **II**-type $C_5Me_4H{-}PMe_2{=}N{-}C_6H_3{}^iPr_2$ ligand.[8d] X-ray diffraction study further confirms that the ligands exist as the **III**-type (Figure 3). The bond lengths of C1−C2 (1.350(3) Å) and C3−C4 (1.336(4) Å) are much shorter than the bond lengths of C1−C5 (1.512(3) Å), C2−C3 (1.474(4) Å), and C4−C5 (1.498(4) Å), showing the nature of the double bond. In addition, C6 obviously deviates from the Cp (C1−C5) plane by 1.169 Å, suggesting that C5 is a sp^3-hybridized carbon atom. Because of the special position of the H proton in the $L^2(Me)$ and $L^2(^iPr)$ ligands, we became interested in their reaction chemistry and expected to give access to some novel structures. We first investigated the reactivity of the $L^2(Me)$ ligand. To our surprise, compared with the good reactivity of the $L^1(Me)$ ligand, reaction of 1 equiv of $L^2(Me)$ with Sc$(CH_2SiMe_3)_3(thf)_2$ at room temperature or higher (50 °C)

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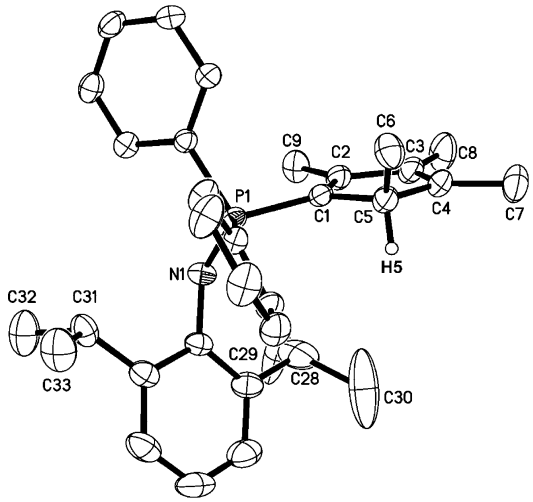
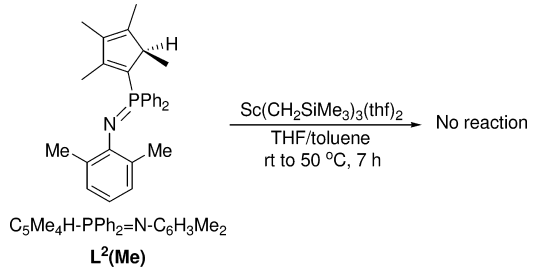


Figure 3. X-ray structure of the ligand $L^2(^iPr)$ (40% probability of thermal ellipsoids). Hydrogen atoms are partly omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2 1.350(3), C3−C4 1.336(4), C1−C5 1.512(3), C2−C3 1.474(4), C4−C5 1.498(4), C1−P1 1.793(2), P1−N1 1.562(2); C1−P1−N1 116.5(1), C1−C5−C4 102.6(2).

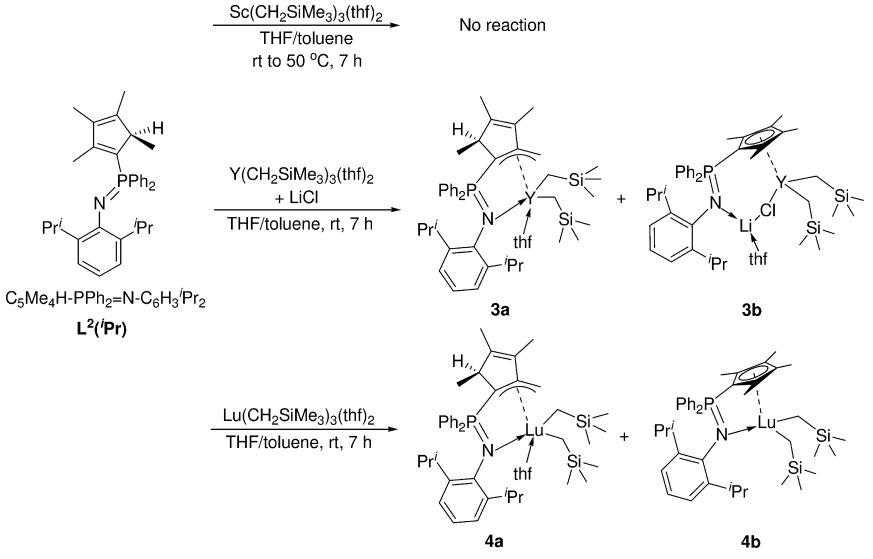
did not give the desired product (Scheme 4). The ^{1}H NMR spectrum also showed that no reaction happened. We conclude

Scheme 4. Unsuccessful Synthesis of the $Cp^{Me}PN$-type Complexes



that the reactive H proton of $L^2(Me)$ is a weaker acidic proton compared with the N*H* proton of $L^1(Me)$ and is shielded by neighboring groups, while the $Sc(CH_2SiMe_3)_3(thf)_2$ is of weaker reactivity than the $Y(CH_2SiMe_3)_3(thf)_2$ and $Lu(CH_2SiMe_3)_3(thf)_2$, both of which lead to no reaction between $L^2(Me)$ and $Sc(CH_2SiMe_3)_3(thf)_2$. Changing the $C_6H_3Me_2$ substituent at the nitrogen atom to the more bulky $C_6H_3{}^iPr_2$, some interesting reactions took place, which were strongly dependent on the type of central metals. Although the reaction of $Sc(CH_2SiMe_3)_3(thf)_2$ and the $L^2(^iPr)$ ligand did not take place as well (Scheme 5), $L^2(^iPr)$ reacted with $Y(CH_2SiMe_3)_3(thf)_2$ in the presence of LiCl to rapidly afford two bis(alkyl) products **3a** and **3b**, evidenced by the ^{1}H and ^{13}C NMR spectra (Scheme 5). The main product **3a** could first deposit from a toluene/hexane mixture as yellow crystalline solids, and then the remaining mother liquor afforded further crystals of complexes **3a** and **3b** when cooling to −30 °C for 2 days. In the ^{1}H NMR spectrum of **3a**, an AB spin system is observed at δ = −0.30 and −0.50 ppm, which can be attributed to the Y−C*H*$_2$SiMe$_3$ methylene protons. To our surprise, however, two singlets appearing at δ = 4.28 and 4.51 ppm in a 1:1 ratio, which correlate with the singlet at δ = 73.25 ppm (J_{YC} is not observed) in the ^{13}C NMR spectrum,[6a,b] may arise from the newly generated methylene (C*H*$_2$) protons. Meanwhile, a quartet is still found at δ = 3.27−3.30 ppm (^{13}C: δ = 52.98 ppm) assigned to the Cp*H* proton according to the NMR information of $L^2(^iPr)$ ligand. Consistently with these, there are signals attributable to three, rather than four, methyl groups on the Cp ring. To the best of our knowledge, these data could reveal that a hydrogen proton on the allylic methyl group rather than on the Cp ring was abstracted in the C−H bond activation reaction. Such unique behavior has been accidentally observed by us in a yttrium byproduct $(\eta^5{:}\kappa\text{-}C_5Me_4{-}C_5H_4N)[C_5HMe_3(\eta^3\text{-}CH_2){-}C_5H_4N\text{-}\kappa]Y(CH_2SiMe_3)$.[6b] The interesting NMR spectra of **3a** inspired us to study its structure, which was successfully resolved by X-ray diffraction to be an unusual $[C_5HMe_3(\eta^3\text{-}CH_2){-}PPh_2{=}N{-}C_6H_3{}^iPr_2]Y(CH_2SiMe_3)_2(thf)$ (Figure 4). The $Cp^{Me}PN$-type ligand bonds to the Y^{3+} ion in a rare κ-N/η^3-allylic mode. The C1−C5 (1.442(4) Å) and C5−C6 (1.369(4) Å) interatomic distances that form part of the allyl component bound to yttrium are not as similar as these

Scheme 5. Synthesis of the $Cp^{Me}PN$-type Complexes 3a, 3b and 4a, 4b



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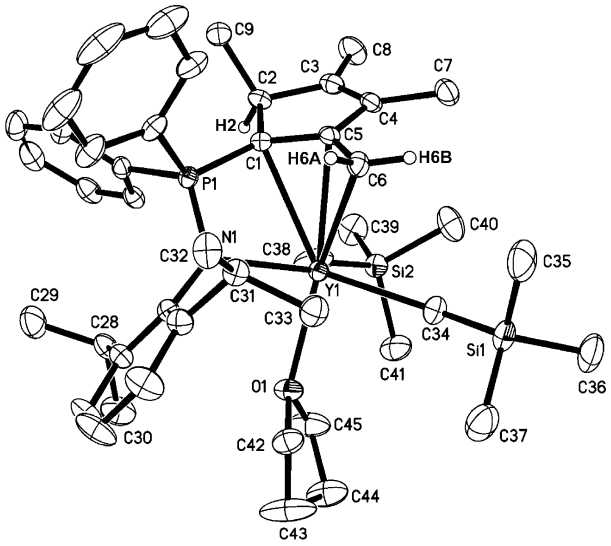

Figure 4. X-ray structure of **3a** (40% probability of thermal ellipsoids). Hydrogen atoms are partly omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C5 1.442(4), C5−C6 1.369(4), C1−C2 1.527(4), C2−C3 1.512(4), C3−C4 1.336(5), C4−C5 1.484(4), P1−C1 1.739(3), P1−N1 1.623(2), Y1−C1 2.749(3), Y1−C5 2.669(3), Y1−C6 2.724(3), Y1−N1 2.383(2), Y1−O1 2.388(2), Y1−C34 2.407(3), Y1−C38 2.408(4); C1−C5−C6 129.9(3), C1−P1−N1 106.2(1), C34−Y1−C38 103.4(2).

analogous distances, 1.391(3) and 1.392(3) Å, in $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$,[17] and 1.412(4) and 1.404(4) Å, in $(\eta^5{:}\kappa\text{-}C_5Me_4{-}C_5H_4N)[C_5HMe_3(\eta^3\text{-}CH_2){-}C_5H_4N\text{-}\kappa]Y(CH_2SiMe_3)$,[6b] but being comparable to the corresponding bond lengths in $(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)$ (1.380(2) and 1.434(2) Å).[18] In particular, the Y1−C(allyl) distances tend to be equal (2.749(3), 2.669(3), and 2.724(3) Å), which are similar to the close Y−C(allyl) distances (2.582(2), 2.582(2), and 2.601(2) Å) in $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$,[17] but different significantly from those Y−C(allyl) distances in $(\eta^5{:}\kappa\text{-}C_5Me_4{-}C_5H_4N)[C_5HMe_3(\eta^3\text{-}CH_2){-}C_5H_4N\text{-}\kappa]Y(CH_2SiMe_3)$ (2.961(3), 2.792(3), and 2.501(3) Å)[6b] and $(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)$ ((2.990(2), 2.699(2), and 2.450(2) Å)),[18] suggesting that the Y1−C(η^3-allyl) linkage in **3a** is almost symmetric. In addition, the P1−C1 bond length (1.739(3) Å) is shorter than that in the $\mathbf{L^2(^iPr)}$ ligand (1.793(2) Å), but the P1−N1 bond distance (1.623(2) Å) is longer than that in the neutral ligand (1.562(2) Å), indicating that the electrons tend to delocalize within the N−P−C(allyl) fragment. Moreover, the atoms C1, C5, C4, and C3 define a plane, whereas C2, a saturated sp^3-hybridized carbon, deviates from the plane by 0.168 Å, with the relatively stronger acid proton H2 remaining unaffected. This is consistent with the bond lengths: the C3−C4 bond (1.336(5) Å), for instance, is an obvious double bond, much shorter than the single bonds of C1−C2 (1.527(4) Å), C2−C3 (1.512(4) Å), and C4−C5 (1.484(4) Å), suggesting that the C1−C5 ring is not a delocalized pentahapto structure. Thus, we deduced that, in comparison with the cleavage of the conventional C−H bond on the Cp ring, cleavage of the C−H bond on the allylic methyl fragment not only was accidental but also was necessary, depending on the nature of ligand, although the C−H bond activation of this type was against the basic acid−base theory.

On the other hand, it is well known that the rare-earth metal bis(alkyl) complexes can be prepared by three methods: (i) the ligand-alkaline salts with rare-earth metal trichlorides and then with 2 equiv of alkyl lithium, (ii) the rare-earth metal trichlorides with 3 equiv of alkyl lithium (some rare-earth metal tris(alkyl)s are unstable and cannot be isolated) and then with the neutral ligand, and (iii) the alkyl abstraction of stable rare-earth metal tris(alkyl)s with the neutral ligand.[19] Yao and co-workers obtained the "Li"- and "Cl"-containing product $\{[ONNO]Gd(CH_2SiMe_3)(\mu\text{-}Li)(\mu\text{-}Cl)\}_2$ by using the (ii) method.[19b] Herein, in the presence of LiCl, we used the (iii) method to prepare the yttrium bis(alkyl) **3b**. The structure of **3b**, $(C_5Me_4{-}PPh_2{=}N{-}C_6H_3{}^iPr_2)Y(CH_2SiMe_3)_2(LiCl)(thf)$, was evidenced by X-ray diffraction (Figure 5). The LiCl unit,

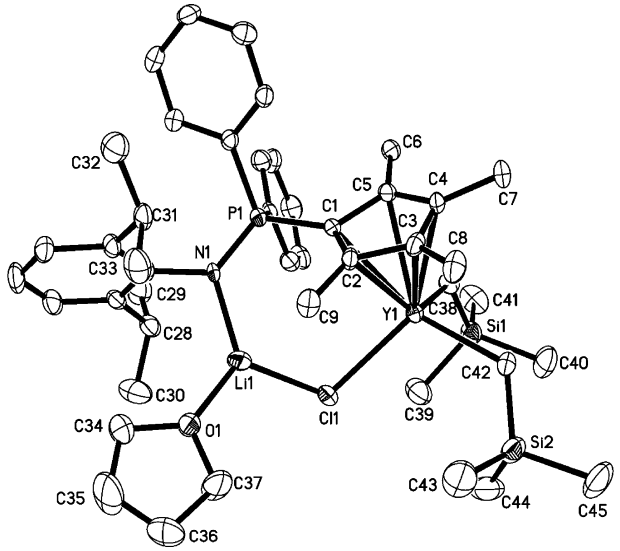

Figure 5. X-ray structure of **3b** (40% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.764(6), P1−N1 1.598(5), N1−Li1 1.969(11), Li1−Cl1 2.300(12), Y1−Cl1 2.624(2), Y1−Cp_{Cent} 2.405, Y1−C38 2.369(9), Y1−C42 2.373(6); C1−P1−N1 108.9(3), Y1−Cl1−Li1 107.7(3), C38−Y1−C42 99.8(3).

serving as a bridge, connects the yttrium atom and nitrogen atom. Of particular note is that the P1−C1 bond length (1.764(6) Å) in **3b** is between 1.739(3) Å (**3a**) and 1.793(2) Å ($\mathbf{L^2(^iPr)}$), while the P1−N1 bond length (1.598(5) Å) is within the range from 1.623(2) Å (**3a**) to 1.562(2) Å ($\mathbf{L^2(^iPr)}$).

Switching the central metal to lutetium, the equimolar reaction between $Lu(CH_2SiMe_3)_3(thf)_2$ and $\mathbf{L^2(^iPr)}$ in the absence of LiCl still generated a mixture of two bis(alkyl) products $[C_5HMe_3(\eta^3\text{-}CH_2){-}PPh_2{=}N{-}C_6H_3{}^iPr_2]Lu(CH_2SiMe_3)_2(thf)$ (**4a**) and $(C_5Me_4{-}PPh_2{=}N{-}C_6H_3{}^iPr_2)Lu(CH_2SiMe_3)_2$ (**4b**) in a 5:1 ratio (Scheme 5). The ^{1}H NMR spectrum shows that the structure of **4a** is analogous to that of **3a**, and so it is not discussed in detail. In particular, the Lu−CH_2SiMe_3 methylene protons of **4a** exhibit two doublets at δ = −0.51 and −0.40 ppm, but those of **4b** only present a broad singlet at δ = −0.62 ppm. The structure of **4b** was further identified by X-ray crystallography to be a THF-free monomer (Figure 6), which is different from these lutetium bis(alkyl)s (**2c**, **5c**, **7c**, and **9b**) that contain a solvent molecule (vide infra). On the basis of these results, in the absence of LiCl, we studied the reaction of $Y(CH_2SiMe_3)_3(thf)_2$ with $\mathbf{L^2(^iPr)}$, which also leads to the formation of a mixture of two bis(alkyl) products that are analogous to the **4a** and **4b**.

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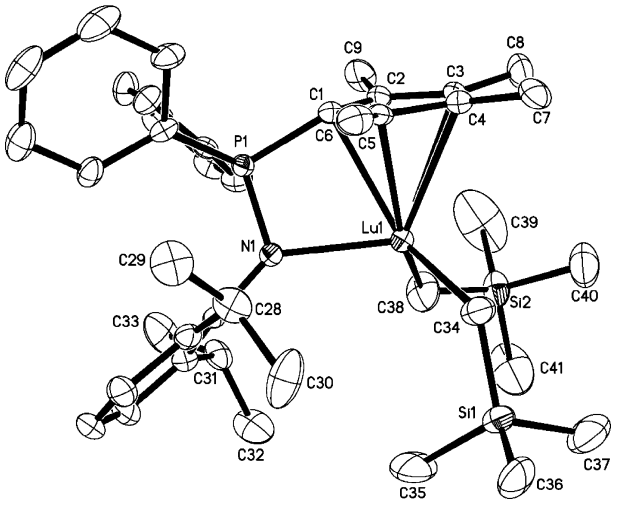


Figure 6. X-ray structure of **4b** (40% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu1−Cp_{cent} 2.362, Lu1−C34 2.327(8), Lu1−C38 2.338(8), P1−C1 1.774(7), P1−N1 1.627(5), Lu1−N1 2.297(5); C1−P1−N1 102.1(3), Cp_{cent}−Lu1−N1 94.2, C34−Lu1−C38 108.4(3).

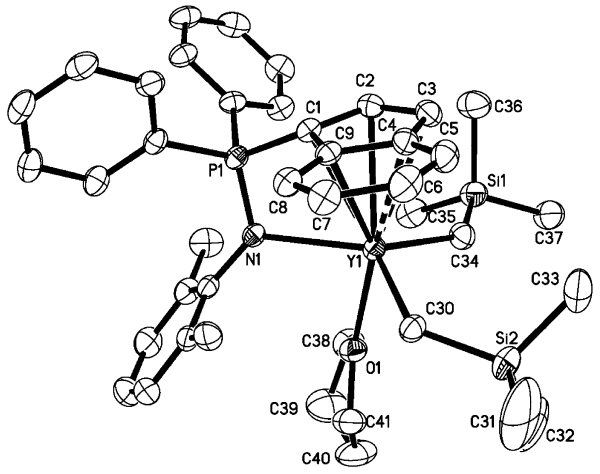
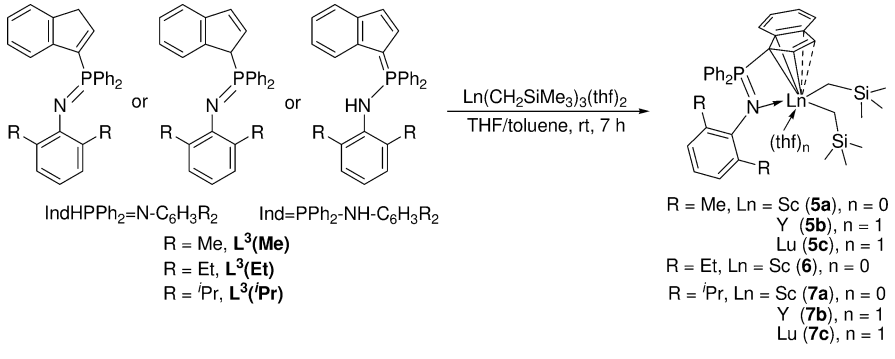


Figure 7. X-ray structure of **5b** (40% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.755(3), P1−N1 1.603(2), Y1−Cp_{cent} 2.538, Y1−C1 2.670(3), Y1−C2 2.759(3), Y1−C9 2.790(3), Y1−C3 2.899(3), Y1−C4 2.935(3), Y1−N1 2.472(2), Y1−O1 2.388(2), Y1−C30 2.404(3), Y1−C34 2.405(3); C1−P1−N1 103.5(1), Cp_{cent}−Y1−N1 88.54, C30−Y1−C34 109.8(1).

Preparation of the IndPN-type Bis(alkyl) Complexes 5a−5c, 6, and 7a−7c. The tremendous reactivity of CpPN-type ligands L^1(**Me**), L^1(^{i}**Pr**), L^2(**Me**), and L^2(^{i}**Pr**) with rare-earth metal tris(alkyl)s promoted us to investigate their indenyl derivatives, IndPN-type ligands C_9H_7−PPh_2=N−$C_6H_3R_2$ (R = Me, L^3(**Me**); R = Et, L^3(**Et**); R = ^{i}Pr, L^3(^{i}**Pr**)). So far, Ind-based ligands have shown versatile coordination modes (η^1, η^2, η^3, η^4, η^5, η^6, η^9) when attaching to transition metals,[9a,20] which further reinforced our interest in rare-earth metal complexes featuring diverse Ind coordination modes, whose number and variety remain limited to date. The straightforward protonolysis reaction of these ligands L^3(**Me**), L^3(**Et**), and L^3(^{i}**Pr**) with $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Sc, Y, and Lu) at room temperature generated the IndPN-type bis(alkyl) complexes **5a**−**5c**, **6**, and **7a**−**7c**, selectively (Scheme 6). The multinuclear spectra (^{1}H, ^{13}C, and ^{31}P) and X-ray diffraction clearly confirmed their structures. All these complexes were analogous; thus, only complexes **5b** and **6** were discussed in detail. X-ray diffraction analysis identified that the yttrium complex **5b** was a monomeric bis(alkyl)s coordinated by a THF molecule (Figure 7). The bond distances Y1−C1 (2.670(3) Å), Y1−C2 (2.759(3) Å), and Y1−C9 (2.790(3) Å) almost fall in the 2.617(8)−2.784(5) Å range for the η^5-indenyl-based yttrium complexes.[5b,21] However, it is noteworthy that the bond distances Y1−C3 (2.899(3) Å) and Y1−C4 (2.935(3) Å) are obviously longer, suggesting that the indenyl ligand, bonding to the yttrium center, tends to adopt an η^3-bonding fashion rather than an η^5-binding mode. The strong tendency of the η^3-coordination mode can also be reflected by the longer bond distance Y1−Cp_{cent} (2.538 Å), which is much longer than those analogous distances in (η^5-Ind-NHC)Y$(CH_2SiMe_3)_2$ (2.396 Å),[5b] [{(η^5-Ind)CMe_2(η^5-Ind)}Y{1,3-$(SiMe_3)_2C_3H_3$}] (2.331 and 2.341 Å),[21a] and [(η^5-Ind′)$_2$Y(μ-H)]$_2$ (2.343−2.368 Å).[21d] To the best of our knowledge, an η^3-indenyl-based yttrium complex, [(η^3:η^3-Ind-CMe_2-Ind)$_2$Y]$^-$[Li(thf)$_4$]$^+$(thf), was also reported by Carpentier, in which the bond distances between two carbon atoms (away from the metal center) and the yttrium center are 2.948(5) and 2.949(5) Å, respectively.[21c] As for the scandium complex **6**, the bond distances Sc1−C3 (2.668(5) Å) and Sc1−C4 (2.707(5) Å) are also beyond the distances, 2.468(5)−2.627(4) Å, in η^5-indenyl coordinated scandium complexes, indicating the trend of η^3-indenyl bonding mode as well (Figures 8 and 9).[5b,22]

Preparation of the FluPN-type Bis(alkyl) Complexes 8 and 9a, 9b. The IndPN-type bis(alkyl) complexes **5a**−**5c**, **6**, and **7a**−**7c** demonstrate the propensity of the phosphazene side

Scheme 6. Synthesis of the IndPN-type Complexes 5a−5c, 6, and 7a−7c



IndHPPh$_2$=N-$C_6H_3R_2$ Ind=PPh$_2$-NH-$C_6H_3R_2$

R = Me, L^3(**Me**)
R = Et, L^3(**Et**)
R = ^{i}Pr, L^3(^{i}**Pr**)

R = Me, Ln = Sc (**5a**), n = 0
Y (**5b**), n = 1
Lu (**5c**), n = 1
R = Et, Ln = Sc (**6**), n = 0
R = ^{i}Pr, Ln = Sc (**7a**), n = 0
Y (**7b**), n = 1
Lu (**7c**), n = 1

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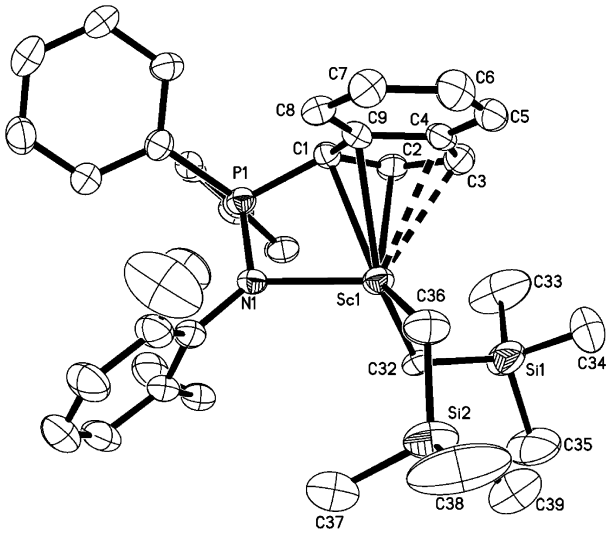


Figure 8. X-ray structure of **6** (40% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.748(5), P1−N1 1.606(4), Sc1−Cp_{cent} 2.287, Sc1−C1 2.457(5), Sc1−C2 2.529(5), Sc1−C9 2.564(5), Sc1−C3 2.668(5), Sc1−C4 2.707(5), Sc1−N1 2.195(4), Sc1−C32 2.204(5), Sc1−C36 2.197(6); C1−P1−N1 100.9(2), Cp_{cent}−Sc1−N1 96.8, C32−Sc1−C36 104.2(2).

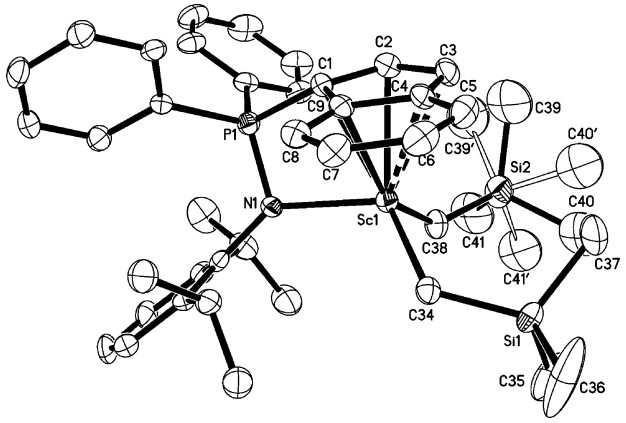
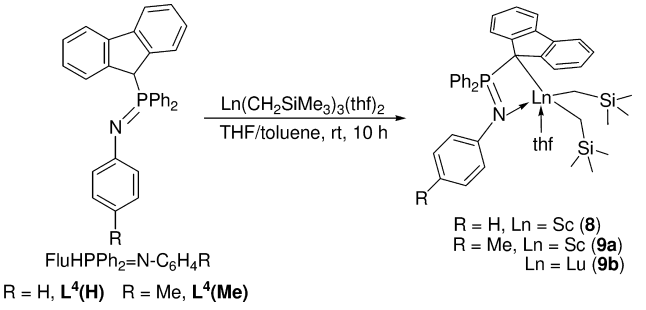


Figure 9. X-ray structure of **7a** (40% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.770(5), P1−N1 1.627(4), Sc1−Cp_{cent} 2.283, Sc1−C1 2.465(5), Sc1−C2 2.518(5), Sc1−C9 2.562(5), Sc1−C3 2.654(5), Sc1−C4 2.707(5), Sc1−N1 2.213(4), Sc1−C34 2.206(5), Sc1−C38 2.220(4); C1−P1−N1 100.4(2), Cp_{cent}−Sc1−N1 96.6, C34−Sc1−C38 103.9(2).

arm to enforce the low η^3-indenyl coordination even with the rare-earth metals. This greatly encouraged us to explore the possible low fluorenyl coordination. The FluPN-type ligands, therefore, were prepared by the Staudinger reaction of $C_{13}H_9$−PPh_2 with 1.5 equiv of ArN_3.[9a] We first synthesized one FluPN-type ligand $C_{13}H_9$−PPh_2=N−$C_6H_3{}^iPr_2$ featuring the 2,6-diisopropylphenyl (Dipp) substituent at the nitrogen atom, which unfortunately could not react with $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Sc, Y, and Lu) even at 50 °C. Aiming at probing the influence of the substituent at nitrogen, two less sterically demanding FluPN-type ligands $C_{13}H_9$−PPh_2=N−C_6H_4R (R = H, $\mathbf{L^4(H)}$; R = Me, $\mathbf{L^4(Me)}$) were further used. The acid−base reaction between $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Sc and Lu) and 1 equiv of ligands $\mathbf{L^4(H)}$ and $\mathbf{L^4(Me)}$ at room temperature at 10 h successfully took place and afforded the corresponding rare-earth metal bis(alkyl) complexes **8** and **9a**, **9b** in good yields, respectively (Scheme 7). The ^{1}H NMR spectroscopic

Scheme 7. Synthesis of the FluPN-type Complexes 8 and 9a, 9b



analysis reveals that the scandium complexes **8** and **9a** give two doublets at δ = 0.29 and 0.59 ppm and δ = 0.30 and 0.60 ppm, respectively, assigned to the methylene protons of the Sc−CH_2SiMe_3 groups, but the lutetium complex **9b** shows two overlapped singlets at δ = −0.25 and −0.36 ppm. In addition, the resonances from the coordinated THF molecules are also detected. It is of interest to note that the Flu quaternary carbon atoms C13 of **8** and **9a**, **9b** resonate at δ = 59.14, 59.17, and 60.65 ppm as a doublet (J_{PC} = 108.0−114.0 Hz), respectively, which are significantly lower than those resonances at δ = 79.0−93.49 ppm for η^3- or η^5-bonding fluorenyl rare-earth metal complexes, suggesting an unusual structure for **8** and **9a**, **9b**.[5a,6a,23] Complex **9b**, as a representative example, was subsequently identified by X-ray diffraction analysis. The lutetium center adopts a distorted trigonal-bipyramidal geometry in the solid state (Figure 10). Two alkyl groups and the C13 atom occupy the equatorial positions, while the oxygen and the nitrogen are located in the pseudoaxial positions. The bond distance of Lu1−C13 (2.584(4) Å) is

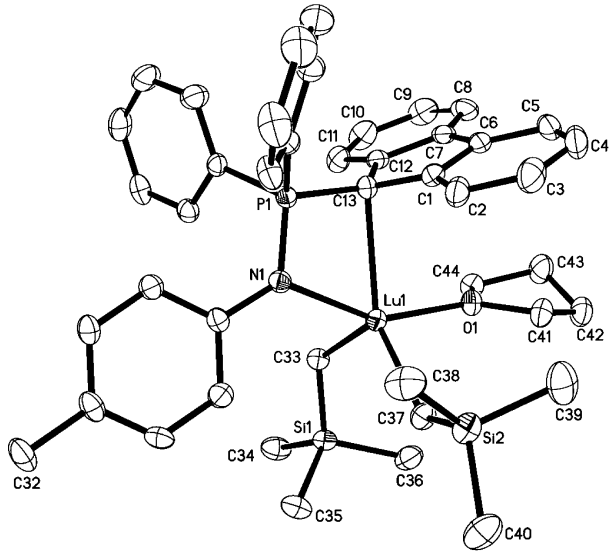


Figure 10. X-ray structure of **9b** (40% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C13 1.752(4), P1−N1 1.612(3), Lu1−C13 2.584(4), Lu1−N1 2.309(3), Lu1−C33 2.320(4), Lu1−C37 2.338(4); C13−P1−N1 104.2(2), C33−Lu1−C37 109.4(1).

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Table 1. Ethylene Polymerization by All Catalyst Precursors 1−9 under Various Conditions[a]

run	cat	AlR_3	T (°C)	yield (g)	productivity[b]	activity[c]	M_w[d] (10^3)	M_w/M_n[d]	T_m[e] (°C)
1	**1**		50	trace					
2	**1**	Al^iBu_3	50	0.27	14	162	10.6	5.34	126
3	**2a**	Al^iBu_3	25	0.38	19	228	14.4	2.11	130
4[f]	**2a**	Al^iBu_3	50	1.13	57	678	12.5	2.03	136
5	**2a**	Al^iBu_3	50	0.65	33	390	5.0	1.69	126
6[g]	**2a**	Al^iBu_3	50	0.42	21	252	1.6	2.31	115
7	**2a**	Al^iBu_3	80	0.72	36	432	3.3	1.38	124
8[h]	**2a**	Al^iBu_3	50	0.34	34	2040	4.2	1.75	127
9[i]	**2a**	Al^iBu_3	50	2.83	142	568	42.4	2.24	130
10	**5a**	$AlMe_3$	50	trace					
11	**5a**	$AlEt_3$	50	0.28	14	168	9.1	5.72	128
12	**5a**	Al^iBu_3	50	0.60	30	360	6.7	1.97	132
13	**6**	Al^iBu_3	50	0.20	10	120	4.2	2.34	133
14	**7a**	Al^iBu_3	50	0.44	22	264	5.8	2.65	132
15	**8**	Al^iBu_3	50	0.18	9	108	3.3	1.58	123
16	**9**	Al^iBu_3	50	0.36	18	216	14.1	2.07	125

[a]Polymerization conditions: Sc (20 μmol), [Sc]/AlR_3/[Ph_3C][$B(C_6F_5)_4$] = 1/10/1 (mol/mol/mol), toluene (50 mL), T_p = 50 °C, ethylene 1 bar, 5 min, unless otherwise noted. [b]Given in kg of PE (mol_{Sc} bar)$^{-1}$. [c]Given in kg of PE (mol_{Sc} h bar)$^{-1}$. [d]Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard. [e]Determined by DSC. [f]Al^iBu_3 (100 μmol, 5 equiv). [g]Al^iBu_3 (400 μmol, 20 equiv). [h]Sc (10 μmol), Al^iBu_3 (50 μmol, 5 equiv), 1 min. [i]Sc (20 μmol), Al^iBu_3 (100 μmol, 5 equiv), 15 min.

shorter than these analogous distances of the Lu−Cp(Flu) (2.638(3)−2.724(3) Å),[5a,6a] but all of these large distances between the remaining Flu carbon atoms (C1−C12) and the central lutetium exceed 3.104 Å, suggesting that the Flu ligand bonds to the metal center in a rare η^1 mode. In addition, the bond distance of Lu1−N1 (2.309(3) Å) is reasonably shorter than that of Lu1−N1 (2.360(2) Å) in (η^3-Flu−C_5H_4N)Lu-$(CH_2SiMe_3)_2$(thf),[6a] indicating that the presence of the phosphazene side arm, which interacts with the metal center by the nitrogen atom, enforces the low hapticity of the Flu ligand. As far as we are aware, to date, there are various bonding modes (η^1, η^2, η^3, η^5, η^6) of the Flu moiety in the zirconocenes and lanthanidocenes established by X-ray diffraction analysis,[5a,6a,23] but this type of η^1-bonding mode of the Flu moiety in **8** and **9a**, **9b** remains extremely limited for rare-earth metal complexes, which was only observed in [(FluSiMe_2N-^{t}Bu)YH-$(thf)_2]_2$.[24]

Ethylene Polymerization. All these complexes **1**−**9** have been preliminarily tested as the precatalysts for ethylene polymerization under various conditions (Table 1). It is found that the polymerization activity strongly depends on the ionic radius of the central metal. Upon activation with AlR_3 and [Ph_3C][$B(C_6F_5)_4$] together, only the smallest scandium complexes show high activity for the ethylene polymerization; those based on yttrium, lutetium, samarium, and neodymium ions are all inert.[12g,25] This can be attributed to the more Lewis acidic nature of the Sc^{3+} ion and non-THF coordination. In addition, the activity of these scandium complexes is influenced by both the sterics and the electronics of the ligand; thus, the activity follows the trend of **2a** (^{i}Pr) > **1** (Me) (runs 2 and 5), **9** (Me) > **8** (H) (runs 15 and 16), and **5a** (Me) > **7a** (^{i}Pr) > **6** (Et) (runs 12−14), respectively. The highest activity (TOF) can reach 2040 kg of PE (mol_{Sc} h bar)$^{-1}$ within 1 min (run 8), and the productivity (TON) can also be up to 142 kg of PE (mol_{Sc} bar)$^{-1}$ under a prolonging 15 min (run 9).

Noteworthy is that the presence of AlR_3 is essential to construct an active catalyst system (run 1), and its loadings and types have remarkable influences on the activity of the catalyst system and the molecular weight of polyethylene (PE). When the Al^iBu_3/**2a** ratio is 5:1, the polymerization shows the highest acitivity (run 4); however, addition of a larger excess amount of Al^iBu_3 (10 and 20 equiv) obviously decreases the catalyst activity, probably due to formation of a dormant state where the active site is blocked by a bridging aluminum species (runs 5 and 6).[26] In addition, the variation of catalytic activity caused by trialkylaluminum, which is in a trend of Al^iBu_3 > $AlEt_3$ ≫ $AlMe_3$ (**5a** is chosen as the precursor), may be attributed to the interaction between the scandium catalyst and the aluminum cocatalyst molecule (runs 10−12).[27] Meanwhile, the M_w clearly decreases with the increase of Al^iBu_3 (runs 4−6), showing the presence of a chain-transfer reaction between the scandium cation and the aluminum center.[12e,g] On the basis of the above results and the previous reports,[12c−e,g,r,26] the roles of AlR_3 in the process of polymerization are: (1) stabilizing the formed cationic active species, (2) a scavenger for removing impurities, and (3) a chain-transfer agent.

The resulting polyethylenes (PEs) are measured by GPC, which show that the weight-average molecular weight of these PE samples is much lower (M_w = (1.6−42.4) × 10^3). It can be attributed to the polymer chain transfer to the alkylaluminum cocatalyst.[28] The ^{1}H NMR spectra of the resultant PEs do not show any double bond signals, suggesting the absence of a β−H elimination reaction (see the Supporting Information).[28b] Meanwhile, the narrow and unimodal molecular weight distribution is indicative of the single-site nature of the active metal center, except for runs 2 and 11, which show a shoulder peak with a wide distribution likely due to the formation of two active species at high temperature. In the DSC curve, we also find that all of these PE samples show a sharp endothermic melting peak (T_m) in the range of 115−136 °C, which is lower than those of high-molecular-weight PEs (up to 141 °C).[28] In addition, the T_m clearly becomes lower with an increase of Al^iBu_3 (runs 4−6). Study on the copolymerization of ethylene and other monomers is in progress.

CONCLUSIONS

We have demonstrated the synthesis and full characterization of a new family of CpPN-type, Cp^{Me}PN-type, IndPN-type, and

FluPN-type rare-earth metal bis(alkyl) complexes bearing diverse η^5, η^3-allyl, η^3, and η^1 coordination modes. In particular, we find that these reactions strongly depend on the substituents at the nitrogen atom and Cp ring and the type of central metal. Reaction of the CpPN-type ligands with $Ln(CH_2SiMe_3)_3(thf)_2$ or with $LiCH_2SiMe_3$ and $LnCl_3(thf)_2$ readily gives the CpPN-type rare-earth metal bis(alkyl)s with the classical η^5-bonding mode; however, the Cp^{Me}PN-type ligands react with $Ln(CH_2SiMe_3)_3(thf)_2$ to generate the rare-earth metal bis(alkyl)s with an unusual η^3-allylic coordination mode, limiting to both the yttrium and the lutetium central metal. It is of interest to note that the obtained IndPN-type bis(alkyl) complexes tend to adopt an η^3-bonding fashion rather than an η^5-binding mode, whereas the more bulky FluPN-type bis(alkyl) complexes unexpectedly take a lower η^1 coordination mode, indicating that the strongly donating phosphazene side arm, which interacts with the metal center by the nitrogen atom, facilitates to enforce the low Ind and Flu hapticities. In addition, upon activation with AlR_3 and $[Ph_3C][B(C_6F_5)_4]$ together, only the scandium complexes show good to high catalytic activity for ethylene polymerization and produce polyethylene with low molecular weight. The catalytic activity clearly depends on the sterics and electronics of the ligand, the loading and the type of AlR_3 cocatalyst, the polymerization temperature, and the polymerization time.

EXPERIMENTAL SECTION

General Procedures and Materials. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. All solvents were purified from the MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed with paraffin film. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV600 (FT, 600 MHz for ^1H; 150 MHz for ^{13}C) spectrometer. ^{31}P NMR spectra were recorded on a Bruker AV400 (FT, 162 MHz) spectrometer. NMR assignments were confirmed by $^1H-^1H$ COSY and $^1H-^{13}C$ HMQC experiments when necessary. Elemental analyses were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). These ligands **L^1(Me)**, **L^1(^{i}Pr)**, **L^2(Me)**, **L^2(^{i}Pr)**, **L^3(Me)**, **L^3(Et)**, **L^3(^{i}Pr)**, **L^4(H)**, and **L^4(Me)** were prepared by following the known procedure.[8,9] $Ln(CH_2SiMe_3)_3(thf)_2$[29] was synthesized as described earlier. Organoborate $[Ph_3C][B(C_6F_5)_4]$ was synthesized following the literature procedures.[30] Toluene was distilled from sodium/benzophenone under nitrogen and degassed thoroughly prior to use. Polymerization grade ethylene was dried by passing through a column filled with activated molecular sieves (4 Å). The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polyethylene were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C. 1,2,4-Trichlorobenzene (TCB), containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol (BHT), was employed as the solvent at a flow rate of 1.0 mL min^{-1}. The calibration was made by polystyrene standard Easi Cal PS-1 (PL Ltd.). T_m of polyethylene was measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 10 °C min^{-1} (temperature range: 25−300 °C).

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[31] The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[32] The structures were solved by using the SHELXTL program.[33] Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

By the way, crystals of **2d** (Sm) and **2e** (Nd) were measured on a Stoe IPDS2 diffractometer at 100 or 180 K. Data were processed using the XAREA program system.[34] **2d** was solved by using the SIR-92 program,[35] **2e** by using SHELXS-97.[36] Refinements were performed by using SHELXL-97.[36]

Synthesis of the Ligand $C_5H_4{=}PPh_2{-}NH{-}C_6H_3{}^iPr_2$ (L^1(^{i}Pr)). To 4.48 g of NaC_5H_5 (50.9 mmol, 1.08 equiv) in 150 mL of pentane at 0 °C was added 10.42 mL of PPh_2Cl (47.2 mmol, 1.00 equiv). The mixture was stirred for 16 h at room temperature, and then 5 mL of ethane-1,2-diol was added. The solution was decanted from the precipitate, the precipitate was washed twice with 20 mL of pentane, and the solvent of the transferred solution was evaporated in vacuum. The residue was dissolved in 150 mL of THF, and 10.35 g of $C_6H_3(^iPr_2)N_3$ (50.9 mmol, 1.08 equiv) was added at 0 °C and stirred for 16 h at 50 °C. All volatiles were removed under vacuum, and the residue was crystallized out of 50 mL of hexane. The powder was filtered, washed with 2 × 10 mL of hexane, and dried under vacuum in 63% yield (12.7 g) as a pale yellow powder.

Synthesis of the Ligand $C_5H_4{=}PPh_2{-}NH{-}C_6H_3Me_2$ (L^1(Me)). Following a similar procedure described for the preparation of ligand **L^1(^{i}Pr)**, the ligand **L^1(Me)** was isolated from the Staudinger reaction of $C_5H_5{-}PPh_2$ (2.50 g, 10 mmol) with 1.5 equiv of $C_6H_3(Me_2)N_3$ (2.20 g, 15 mmol) as pale yellow powder in a 83% yield (3.07 g). ^1H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 2.01 (s, 6H, Ar−CH_3), 4.40 (d, $^2J_{PH}$ = 6.0 Hz, 1H, N*H*), 6.71−6.72 (d, $^2J_{HH}$ = 6.0 Hz, 2H, C_5H_4), 6.78−6.80 (quart, 2H, C_5H_4), 6.81−6.87 (m, 5H, Ph-*H* and Ar-*H*), 6.90−6.92 (m, 2H, Ph-*H*), 6.97−7.00 (m, 2H, Ph-*H*), 7.34−7.37 ppm (m, 4H, Ph-*H*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 25.12 ppm (s).

Synthesis of the Ligand $C_5Me_4H{-}PPh_2{=}N{-}C_6H_3Me_2$ (L^2(Me)). Following a similar procedure described for the preparation of ligand **L^1(^{i}Pr)**, the ligand **L^2(Me)** was isolated from the Staudinger reaction of $C_5Me_4H{-}PPh_2$ (3.06 g, 10 mmol) with 1.5 equiv of $C_6H_3(Me_2)N_3$ (2.20 g, 15 mmol) as a pale white powder in a 47% yield (2.00 g). ^1H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.80 (d, $^3J_{HH}$ = 6.0 Hz, 3H, C_5Me_4H), 1.48 (s, 3H, C_5Me_4H), 1.60 (s, 3H, C_5Me_4H), 1.67 (s, 3H, C_5Me_4H), 2.32 (s, 6H, Ar−CH_3), 3.11−3.14 (quart, 1H, C_5Me_4H), 6.89−7.11 (m, 7H, Ar-*H*), 7.19 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*), 7.68−7.72 (m, 2H, Ar-*H*), 7.92−7.96 ppm (m, 2H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 10.57 (s, 1C, C_5Me_4), 11.08 (s, 1C, C_5Me_4), 12.17 (s, 1C, C_5Me_4), 15.02 (s, 1C, C_5Me_4), 21.61 (s, 2C, Ar-CH_3), 53.57 (d, $^2J_{PC}$ = 10.5 Hz, 1C, C_5Me_4), 118.76 (s, 2C, Ar-*C*), 127.43 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 128.35 (s, 2C, Ar-*C*), 130.64 (s, 1C, Ar-*C*), 130.96 (d, $^3J_{PC}$ = 4.5 Hz, 2C, Ar-*C*), 131.80 (d, $^3J_{PC}$ = 7.5 Hz, 2C, Ar-*C*), 131.99 (d, $^2J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 132.79 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 135.21 (s, 1C, Ar-*C*), 135.42 (d, $^2J_{PC}$ = 13.5 Hz, 1C, C_5Me_4), 135.94 (s, 1C, Ar-*C*), 136.79 (s, 1C, Ar-*C*), 137.46 (s, 1C, Ar-*C*), 140.91 (d, $^3J_{PC}$ = 7.5 Hz, 1C, C_5Me_4), 148.74 (d, $^3J_{PC}$ = 6.0 Hz, 1C, C_5Me_4), 149.03 (s, 1C, C_5Me_4), 157.27 ppm (d, $^2J_{PC}$ = 10.5 Hz, 1C, Ar-*C*). Anal. Calcd for $C_{29}H_{32}NP$: C, 81.85; H, 7.58; N, 3.29. Found: C, 82.22; H, 7.45; N, 3.20.

Synthesis of the Ligand $C_5Me_4H{-}PPh_2{=}N{-}C_6H_3{}^iPr_2$ (L^2(^{i}Pr)). Following a similar procedure described for the preparation of ligand **L^1(^{i}Pr)**, the ligand **L^2(^{i}Pr)** was isolated from the Staudinger reaction of $C_5Me_4H{-}PPh_2$ (3.06 g, 10 mmol) with 1.5 equiv of $C_6H_3(^iPr_2)N_3$ (3.05 g, 15 mmol) as a white powder in a 58% yield (2.78 g). ^1H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.78 (d, $^3J_{HH}$ = 12.0 Hz, 3H, C_5Me_4H), 1.11 (d, $^3J_{HH}$ = 6.0 Hz, 6H, Ar−CH(CH_3)$_2$), 1.21 (d, $^3J_{HH}$ = 12.0 Hz, 6H, Ar−CH(CH_3)$_2$), 1.52 (s, 3H, C_5Me_4H), 1.61 (s, 3H, C_5Me_4H), 1.70 (s, 3H, C_5Me_4H), 3.10−3.13 (quart, 1H, C_5Me_4H), 3.64−3.71 (sept, 2H, Ar−C*H*(CH$_3$)$_2$), 7.01−7.09 (m, 4H, Ar-*H*), 7.13−7.15 (m, 3H, Ar-*H*), 7.23 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*), 7.59−7.63 (m, 2H, Ar-*H*), 7.93−7.96 ppm (m, 2H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 10.56 (s, 1C, C_5Me_4), 12.17 (s, 1C, C_5Me_4), 14.73 (s, 1C, C_5Me_4), 15.08 (s, 1C, C_5Me_4), 23.89 (s, 2C,

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Ar−CH(CH_3)$_2$), 24.43 (s, 2C, Ar−CH(CH_3)$_2$), 28.93 (s, 2C, Ar-CH(CH_3)$_2$), 53.68 (d, $^2J_{PC}$ = 21.0 Hz, 1C, C_5Me_4), 119.68 (s, 1C, Ar-C), 123.15 (s, 2C, Ar-C), 128.39 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-C), 128.50 (s, 1C, Ar-C), 130.58 (s, 1C, Ar-C), 131.03 (s, 1C, Ar-C), 131.84 (d, $^2J_{PC}$ = 10.5 Hz, 2C, Ar-C), 132.19 (s, 1C, Ar-C), 132.87 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-C), 134.35 (s, 1C, Ar-C), 135.10 (s, 1C, Ar-C), 135.37 (d, $^2J_{PC}$ = 15.0 Hz, 1C, C_5Me_4), 136.36 (s, 1C, Ar-C), 137.00 (s, 1C, Ar-C), 143.09 (d, $^3J_{PC}$ = 6.0 Hz, 1C, C_5Me_4), 145.72 (s, 1C, C_5Me_4), 148.75 (d, $^3J_{PC}$ = 6.0 Hz, 1C, C_5Me_4), 157.38 ppm (d, $^2J_{PC}$ = 10.5 Hz, 1C, Ar-C). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ −15.07 ppm (s). Anal. Calcd for $C_{33}H_{40}NP$: C, 82.29; H, 8.37; N, 2.91. Found: C, 82.62; H, 8.24; N, 2.82.

Synthesis of the Ligand $C_{13}H_9$−PPh_2=N−C_6H_4Me (L^4(Me)). Following a similar procedure described for the preparation of ligand L^4(H) (ref), the ligand L^4(Me) was prepared from the Staudinger reaction of $C_{13}H_9$−PPh_2 (3.50 g, 10 mmol) with 1.5 equiv of $C_6H_4MeN_3$ (1.99 g, 15 mmol) as a white powder in a 87% yield (3.93 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 2.20 (s, 3H, Ar−CH_3), 5.16 (d, $^2J_{PH}$ = 6.0 Hz, Flu-H), 6.80−6.83 (m, 4H, Ar-H), 6.90 (t, $^3J_{HH}$ = 12.0 Hz, 2H, Ar-H), 6.99−7.10 (m, 8H, Ar-H), 7.34 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-H), 7.41−7.44 (m, 4H, Ar-H), 7.73 ppm (t, $^3J_{HH}$ = 12.0 Hz, 2H, Ar-H).

Synthesis of the Complex (C_5H_4−PPh_2=N−$C_6H_3Me_2$)Sc-(CH_2SiMe_3)$_2$ (1). Under a nitrogen atmosphere, to a mixture of THF and a toluene solution (10 mL) of Sc(CH_2SiMe_3)$_3$(thf)$_2$ (0.451 g, 1.0 mmol) was added 1 equiv of ligand L^1(Me) (0.369 g, 1.0 mmol) slowly at room temperature. The mixture was stirred for 7 h to afford a pale yellow solution. Evaporation of the solvent left complex **1** as pale yellow crystalline solids (0.332 g, 56%). Recrystallization from a mixture of toluene and hexane gave pale yellow single crystals suitable for X-ray analysis. ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.09 (d, $^2J_{HH}$ = 6.0 Hz, 4H, CH_2SiMe_3), 0.31 (s, 18H, CH_2SiMe_3), 2.03 (s, 6H, Ar−CH_3), 6.68−6.69 (quart, 2H, C_5H_4), 6.85−6.89 (m, 7H, C_5H_4 and Ph-H and Ar-H), 6.96−6.99 (m, 4H, Ph-H), 7.40−7.43 ppm (m, 4H, Ph-H). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 3.91 (s, 6C, CH_2SiMe_3), 21.58 (br s, 2C, Ar-CH_3), 41.76 (br s, 2C, CH_2SiMe_3), 92.03 (d, J_{PC} = 120.0 Hz, 1C, *ipso*-C_5H_4), 117.95 (d, $^2J_{PC}$ = 12.0 Hz, 2C, C_5H_4), 118.84 (d, $^3J_{PC}$ = 15.0 Hz, 2C, C_5H_4), 124.61 (d, $^4J_{PC}$ = 4.5 Hz, 2C, Ar-C), 128.35 (s, 4C, Ph-C), 128.70 (d, J_{PC} = 12.0 Hz, 2C, *ipso*-Ph-C), 128.96 (s, 1C, Ar-C), 129.50 (d, $^4J_{PC}$ = 3.0 Hz, 2C, Ph-C), 132.76 (d, $^2J_{PC}$ = 10.5 Hz, 4C, Ph-C), 135.23 (d, $^3J_{PC}$ = 6.0 Hz, 2C, Ar-C), 142.94 ppm (d, $^2J_{PC}$ = 9.0 Hz, 1C, *ipso*-Ar-C). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 7.82 ppm (s). Anal. Calcd for $C_{33}H_{45}NPScSi_2$: C, 67.43; H, 7.72; N, 2.38. Found: C, 67.87; H, 7.78; N, 2.29.

Synthesis of the Complex (C_5H_4−PPh_2=N−$C_6H_3{}^iPr_2$)Sc-(CH_2SiMe_3)$_2$ (2a). Following a similar procedure described for the preparation of complex **1**, complex **2a** was isolated from the acid−base reaction of Sc(CH_2SiMe_3)$_3$(thf)$_2$ (0.451 g, 1.0 mmol) with 1 equiv of ligand L^1(^{i}Pr) (0.425 g, 1.0 mmol) in a 71% yield (0.459 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.20 (br s, 4H, CH_2SiMe_3), 0.37 (br s, 24H, CH_2SiMe_3 and Ar−CH(CH_3)$_2$), 1.23 (br s, 6H, Ar−CH(CH_3)$_2$), 3.40−3.46 (sept, 2H, Ar−CH(CH$_3$)$_2$), 6.78−6.79 (quart, 2H, C_5H_4), 6.87−6.91 (m, 4H, Ph-H), 6.96−7.03 (m, 6H, C_5H_4 and Ph-H and Ar-H), 7.05−7.08 (m, 1H, Ar-H), 7.40−7.43 ppm (m, 4H, Ph-H). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 3.91 (s, 6C, CH_2SiMe_3), 23.77 (br s, 2C, Ar−CH(CH_3)$_2$), 26.35 (br s, 2C, Ar−CH(CH_3)$_2$), 28.80 (s, 2C, Ar-CH(CH_3)$_2$), 42.01 (s, 2C, CH_2SiMe_3), 92.75 (d, J_{PC} = 120.0 Hz, 1C, *ipso*-C_5H_4), 118.38 (d, $^2J_{PC}$ = 12.0 Hz, 2C, C_5H_4), 119.19 (d, $^3J_{PC}$ = 15.0 Hz, 2C, C_5H_4), 124.87 (d, $^4J_{PC}$ = 3.0 Hz, 2C, Ar-C), 125.33 (d, $^5J_{PC}$ = 4.5 Hz, 1C, Ar-C), 127.71 (d, J_{PC} = 12.0 Hz, 2C, *ipso*-Ph-C), 128.75 (d, $^3J_{PC}$ = 12.0 Hz, 4C, Ph-C), 132.83 (d, $^4J_{PC}$ = 1.5 Hz, 2C, Ph-C), 133.57 (d, $^2J_{PC}$ = 9.0 Hz, 4C, Ph-C), 139.82 (d, $^2J_{PC}$ = 9.0 Hz, 1C, *ipso*-Ar-C), 145.86 ppm (d, $^3J_{PC}$ = 6.0 Hz, 2C, Ar-C). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 11.11 ppm (s). Anal. Calcd for $C_{37}H_{53}NPScSi_2$: C, 69.01; H, 8.30; N, 2.18. Found: C, 69.28; H, 8.19; N, 2.21.

Synthesis of the Complex (C_5H_4−PPh_2=N−$C_6H_3{}^iPr_2$)Y-(CH_2SiMe_3)$_2$(thf) (2b). Following a similar procedure described for the preparation of complex **1**, complex **2b** was isolated from the acid−base reaction of Y(CH_2SiMe_3)$_3$(thf)$_2$ (0.495 g, 1.0 mmol) with 1 equiv of ligand L^1(^{i}Pr) (0.425 g, 1.0 mmol) in a 66% yield (0.501 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.45 (br s, 4H, CH_2SiMe_3), 0.45 (s, 18H, CH_2SiMe_3), 0.76 (br s, 12H, Ar−CH(CH_3)$_2$), 1.18−1.24 (m, 4H, thf), 3.18−3.24 (sept, 2H, Ar−CH(CH$_3$)$_2$), 3.70−3.72 (m, 4H, thf), 6.74−6.76 (quart, 2H, C_5H_4), 6.92−6.95 (m, 6H, Ph-H), 6.98−7.01 (m, 3H, C_5H_4 and Ar-H), 7.07−7.08 (m, 2H, Ar-H), 7.46−7.49 ppm (m, 4H, Ph-H). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.67 (s, 6C, CH_2SiMe_3), 24.58 (br s, 4C, Ar−CH(CH_3)$_2$), 25.03 (s, 2C, thf), 29.07 (s, 2C, Ar-CH(CH_3)$_2$), 32.09 (d, J_{YC} = 39.0 Hz, 2C, CH_2SiMe_3), 70.07 (s, 2C, thf), 94.45 (d, J_{PC} = 124.5 Hz, 1C, *ipso*-C_5H_4), 115.77 (d, $^2J_{PC}$ = 13.5 Hz, 2C, C_5H_4), 119.01 (d, $^3J_{PC}$ = 15.0 Hz, 2C, C_5H_4), 124.29 (d, $^4J_{PC}$ = 4.5 Hz, 2C, Ar-C), 124.50 (d, $^5J_{PC}$ = 3.0 Hz, 1C, Ar-C), 128.35 (s, 4C, Ph-C), 128.58 (d, J_{PC} = 12.0 Hz, 2C, *ipso*-Ph-C), 132.37 (br s, 2C, Ph-C), 133.19 (d, $^2J_{PC}$ = 9.0 Hz, 4C, Ph-C), 143.03 (d, $^2J_{PC}$ = 9.0 Hz, 1C, *ipso*-Ar-C), 145.28 ppm (d, $^3J_{PC}$ = 6.0 Hz, 2C, Ar-C). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 10.07 ppm (s). Anal. Calcd for $C_{41}H_{61}NPOYSi_2$: C, 64.80; H, 8.09; N, 1.84. Found: C, 65.18; H, 8.14; N, 1.76.

Synthesis of the Complex (C_5H_4−PPh_2=N−$C_6H_3{}^iPr_2$)Lu-(CH_2SiMe_3)$_2$(thf) (2c). Following a similar procedure described for the preparation of complex **1**, complex **2c** was isolated from the acid−base reaction of Lu(CH_2SiMe_3)$_3$(thf)$_2$ (0.580 g, 1.0 mmol) with 1 equiv of ligand L^1(^{i}Pr) (0.425 g, 1.0 mmol) in a 62% yield (0.527 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.50 (br s, 4H, CH_2SiMe_3), 0.39 (s, 18H, CH_2SiMe_3), 0.78 (br s, 12H, Ar−CH(CH_3)$_2$), 1.38 (s, 4H, thf), 3.33−3.39 (sept, 2H, Ar−CH(CH$_3$)$_2$), 3.60 (s, 4H, thf), 6.75−6.76 (quart, 2H, C_5H_4), 6.89−6.93 (m, 6H, Ph-H), 6.96−7.04 (m, 5H, C_5H_4 and Ar-H), 7.42−7.46 ppm (m, 4H, Ph-H). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.49 (s, 6C, CH_2SiMe_3), 24.81 (br s, 4C, Ar−CH(CH_3)$_2$), 25.65 (s, 2C, thf), 28.92 (s, 2C, Ar-CH(CH_3)$_2$), 40.21 (s, 2C, CH_2SiMe_3), 68.34 (s, 2C, thf), 92.47 (d, J_{PC} = 121.5 Hz, 1C, *ipso*-C_5H_4), 117.76 (d, $^2J_{PC}$ = 13.5 Hz, 2C, C_5H_4), 117.96 (d, $^3J_{PC}$ = 13.5 Hz, 2C, C_5H_4), 124.67 (d, $^4J_{PC}$ = 3.0 Hz, 2C, Ar-C), 125.14 (d, $^5J_{PC}$ = 3.0 Hz, 1C, Ar-C), 128.35 (s, 4C, Ph-C), 128.70 (d, J_{PC} = 12.0 Hz, 2C, *ipso*-Ph-C), 132.76 (br s, 2C, Ph-C), 133.38 (d, $^2J_{PC}$ = 10.5 Hz, 4C, Ph-C), 140.07 (d, $^2J_{PC}$ = 12.0 Hz, 1C, *ipso*-Ar-C), 145.74 ppm (d, $^3J_{PC}$ = 6.0 Hz, 2C, Ar-C). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 10.39 ppm (s). Anal. Calcd for $C_{41}H_{61}NPOLuSi_2$: C, 58.21; H, 7.27; N, 1.66. Found: C, 58.45; H, 7.21; N, 1.64.

Synthesis of the Complex (C_5H_4−PPh_2=N−$C_6H_3{}^iPr_2$)Sm-(CH_2SiMe_3)$_2$(thf) (2d). To a suspension of $SmCl_3$(thf)$_2$ (0.400 g, 1.0 mmol) and L^1(^{i}Pr) (0.425 g, 1.0 mmol) in ether was added dropwise at 0 °C a solution of $LiCH_2SiMe_3$ (3.04 mmol) in hexane. The reaction mixture was stirred at 0 °C for another 1 h and concentrated in vacuo to half of the original volume. Formed LiCl was filtered off over Celite. The solvent was stripped off, and the residue was extracted with hexane. Crystallization occurred by storage at −30 °C. Filtration and drying in a vacuum resulted in isolation of yellow microcrystalline solids in a 29% yield (0.220 g). ^{1}H NMR (300 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.27 (br s, 12H, Ar−CH(CH_3)$_2$), 0.27 (br s, 6H, Sm−CH_2 or thf), 0.61 (s, 18H, CH_2SiMe_3), 1.89 (br s, 2H, C_5H_4), 2.16 (br s, 6H, Sm−CH_2 or thf), 2.95 (sept, 2H, Ar−CH(CH$_3$)$_2$), 5.85 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-DippH), 6.07 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-DippH), 7.33−7.38 (m, 2H, Ph-H), 7.44−7.49 (m, 4H, Ph-H), 9.18−9.24 (m, 4H, Ph-H), 9.80 ppm (br s, 2H, C_5H_4). ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): δ 18.1 ppm (br s). Anal. Calcd for $C_{41}H_{61}NPOSmSi_2$: C, 59.95; H, 7.49; N, 1.71. Found: C, 59.24; H, 7.24; N, 1.85.

Synthesis of the Complex (C_5H_4−PPh_2=N−$C_6H_3{}^iPr_2$)Nd-(CH_2SiMe_3)$_2$(thf) (2e). To a suspension of $NdCl_3$(thf)$_2$ (0.360 g, 1.0 mmol) and L^1(^{i}Pr) (0.425 g, 1.0 mmol) in ether was added dropwise at 0 °C a solution of $LiCH_2SiMe_3$ (3.04 mmol) in hexane. The reaction mixture was stirred at 0 °C for another 1 h and concentrated in vacuo to half of the original volume. Formed LiCl was filtered off over Celite. The solvent was stripped off, and the residue was extracted with hexane. Crystallization occurred by storage at −30 °C. Filtration and drying in a vacuum resulted in isolation of blue

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microcrystalline solids in a 34% yield (0.231 g). ^{1}H NMR (500 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −20.91 (br s, 2H, C_5H_4), −6.74 (br s, 2H, C_5H_4), −4.26 (br s, 4H, Nd−CH_2 or thf), −1.79 (br s, 6H, Ar−$CH(CH_3)_2$), −1.61 (br s, 4H, Nd−CH_2 or thf), 1.36 (br s, 6H, Ar−$CH(CH_3)_2$), 2.45 (s, 18H, CH_2SiMe_3), 3.68 (br s, 1H, *p*-Dipp*H*), 4.46 (d, $^3J_{HH}$ = 6.9 Hz, 2H, *m*-Dipp*H*), 8.33 (t, $^2J_{HH}$ = 7.5 Hz, 2H, Ph-*H*), 8.92 (d, $^2J_{HH}$ = 5.5 Hz, 4H, Ph-*H*), 14.83 ppm (br s, 4H, Ph-*H*). ^{31}P NMR (202.5 MHz, C_6D_6, 25 °C): δ −62.8 ppm (br s). Anal. Calcd for $C_{41}H_{61}NPONdSi_2$: C, 60.40; H, 7.54; N, 1.72. Found: C, 59.77; H, 7.34; N, 1.89.

Synthesis of the Complexes [$C_5HMe_3(\eta^3$-$CH_2)$−PPh_2=N−$C_6H_3{}^iPr_2$]Y($CH_2SiMe_3)_2$(thf) (3a) and (C_5Me_4−PPh_2=N−$C_6H_3{}^iPr_2$)Y($CH_2SiMe_3)_2$(LiCl)(thf) (3b). Under a nitrogen atmosphere, to a mixture of THF and a toluene solution (10 mL) of Y($CH_2SiMe_3)_3$(thf)$_2$ (0.495 g, 1.0 mmol) and LiCl (0.043 g, 1.0 mmol) was added 1 equiv of ligand $\mathbf{L^2(^iPr)}$ (0.482 g, 1.0 mmol) slowly at room temperature. The mixture was stirred for 7 h to afford a yellow solution. Evaporation of the solvent left a mixture of complexes **3a** and **3b** as yellow crystalline solids. Recrystallization from a mixture of toluene and hexane at −30 °C within 12 h first gave pure complex **3a** as yellow crystalline solids in high yield (0.324 g); then the remaining mother liquor was further recrystallized at −30 °C within 2 days to afford the mixture of complexes **3a** and **3b** (**3a**: 0.133 g; **3b**: 0.069 g).

*Complex **3a**:* ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.30, −0.50 (AB, $^2J_{HH}$ = 12.0 Hz, 4H, YCH_2SiMe$_3$), 0.33 (d, $^3J_{HH}$ = 6.0 Hz, 3H, Ar−CH(CH_3)$_2$), 0.36 (s, 18H, YCH$_2$SiMe_3), 0.45 (d, $^3J_{HH}$ = 6.0 Hz, 3H, Ar−CH(CH_3)$_2$), 0.53 (d, $^3J_{HH}$ = 12.0 Hz, 3H, C_5Me_3HCH$_2$), 1.19 (d, $^3J_{HH}$ = 12.0 Hz, 3H, Ar−CH(CH_3)$_2$), 1.30 (d, $^3J_{HH}$ = 6.0 Hz, 3H, Ar−CH(CH_3)$_2$), 1.33 (m, 4H, thf), 1.68 (s, 3H, C_5Me_3HCH$_2$), 1.88 (s, 3H, C_5Me_3HCH$_2$), 2.93−2.99 (sept, 1H, Ar−C*H*(CH$_3$)$_2$), 3.27−3.30 (quart, 1H, C_5Me_3*H*CH$_2$), 3.76 (m, 4H, thf), 3.79−3.85 (sept, 1H, Ar−C*H*(CH$_3$)$_2$), 4.28 (s, 1H, C_5Me_3HCH_2−Y), 4.51 (s, 1H, C_5Me_3HCH_2−Y), 6.94−7.16 (m, 11H, Ar-*H*), 7.36 (br s, 1H, Ar-*H*), 7.95 ppm (very br s, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.77 (s, 6C, CH$_2$SiMe_3), 11.04 (s, 1C, C_5Me_3HCH$_2$), 13.25 (s, 1C, C_5Me_3HCH$_2$), 20.40 (s, 1C, C_5Me_3HCH$_2$), 21.65 (s, 1C, Ar−CH(CH$_3$)$_2$), 24.40 (s, 1C, Ar−CH(CH$_3$)$_2$), 25.29 (s, 2C, thf), 25.43 (s, 1C, Ar−CH(CH$_3$)$_2$), 28.10 (s, 1C, Ar−CH(CH$_3$)$_2$), 28.60 (s, 1C, Ar-CH(CH$_3$)$_2$), 29.70 (s, 1C, Ar-CH(CH$_3$)$_2$), 34.16 (d, J_{YC} = 39.0 Hz, 2C, YCH$_2$SiMe$_3$), 52.98 (d, $^2J_{PC}$ = 15.0 Hz, 1C, C_5Me_3HCH$_2$), 70.52 (s, 2C, thf), 73.25 (s, 1C, C_5Me_3HCH$_2$−Y), 124.04 (d, J_{PC} = 27.0 Hz, 2C, Ar-*C*), 124.90 (s, 2C, Ar-*C*), 128.35 (s, 2C, Ar-*C*), 128.82 (s, 1C, Ar-*C*), 131.21 (s, 2C, Ar-*C*), 131.63 (s, 2C, Ar-*C*), 132.64 (d, $^3J_{PC}$ = 15.0 Hz, 1C, Ar-*C*), 133.01 (d, $^2J_{PC}$ = 7.5 Hz, 2C, Ar-*C*), 133.62 (s, 1C, Ar-*C*), 134.21 (s, 1C, Ar-*C*), 135.01 (br s, 1C, Ar-*C*), 142.34 (d, $^2J_{PC}$ = 9.0 Hz, 1C, C_5Me_3HCH$_2$), 145.22 (d, $^3J_{PC}$ = 6.0 Hz, 1C, C_5Me_3HCH$_2$), 145.90 (d, $^3J_{PC}$ = 4.5 Hz, 1C, C_5Me_3HCH$_2$), 153.03 (d, J_{PC} = 12.0 Hz, 1C, C_5Me_3HCH$_2$), 163.65 ppm (d, $^2J_{PC}$ = 12.0 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 14.04 ppm (s). Anal. Calcd for $C_{45}H_{69}ONPSi_2Y$: C, 66.23; H, 8.52; N, 1.72. Found: C, 66.63; H, 8.61; N, 1.63.

*Complex **3b**:* ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.40 (br s, 4H, YCH_2SiMe$_3$), 0.36 (s, 18H, YCH$_2$SiMe_3), 1.00 (d, $^3J_{HH}$ = 6.0 Hz, 12H, Ar−CH(CH_3)$_2$), 1.24 (m, 4H, thf), 2.22 (s, 6H, C_5Me_4), 2.24 (br s, 6H, C_5Me_4), 3.45 (m, 4H, thf), 3.79−3.85 (sept, 2H, Ar−C*H*(CH$_3$)$_2$), 6.82−7.13 (m, 11H, Ar-*H*), 7.34−7.38 ppm (m, 2H, Ar-*H*).

Synthesis of the Complexes [$C_5HMe_3(\eta^3$-$CH_2)$−PPh_2=N−$C_6H_3{}^iPr_2$]Lu($CH_2SiMe_3)_2$(thf) (4a) and (C_5Me_4−PPh_2=N−$C_6H_3{}^iPr_2$)Lu($CH_2SiMe_3)_2$ (4b). Under a nitrogen atmosphere, to a mixture of THF and a toluene solution (10 mL) of Lu($CH_2SiMe_3)_3$(thf)$_2$ (0.580 g, 1.0 mmol) was added 1 equiv of ligand $\mathbf{L^2(^iPr)}$ (0.482 g, 1.0 mmol) slowly at room temperature. The mixture was stirred for 7 h to afford a yellow solution. Evaporation of the solvent left a mixture of complexes **4a** and **4b** as yellow crystalline solids. Recrystallization from a mixture of toluene and hexane at −30 °C within 12 h first gave pure complex **4a** as yellow crystalline solids in high yield (0.312 g); then the remaining mother liquor was further recrystallized at −30 °C within 2 days to afford the mixture of complexes **4a** and **4b** (**4a**: 0.129 g; **4b**: 0.083 g).

*Complex **4a**:* ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.51 (d, $^2J_{HH}$ = 12.0 Hz, 2H, LuCH_2SiMe$_3$), −0.40 (d, $^2J_{HH}$ = 12.0 Hz, 2H, LuCH_2SiMe$_3$), 0.35 (s, 18H, LuCH$_2$SiMe_3), 0.39 (d, $^3J_{HH}$ = 6.0 Hz, 3H, Ar−CH(CH_3)$_2$), 0.40 (d, $^3J_{HH}$ = 6.0 Hz, 3H, Ar−CH(CH_3)$_2$), 0.49 (d, $^3J_{HH}$ = 12.0 Hz, 3H, C_5Me_3HCH$_2$), 1.30 (d, $^3J_{HH}$ = 12.0 Hz, 3H, Ar−CH(CH_3)$_2$), 1.37 (m, 4H, thf), 1.40 (d, $^3J_{HH}$ = 12.0 Hz, 3H, Ar−CH(CH_3)$_2$), 1.64 (s, 3H, C_5Me_3HCH$_2$), 1.77 (s, 3H, C_5Me_3HCH$_2$), 3.00−3.12 (sept, 1H, Ar−C*H*(CH$_3$)$_2$), 3.14−3.19 (quart, 1H, C_5Me_3*H*CH$_2$), 3.76 (m, 4H, thf), 3.90−4.00 (sept, 1H, Ar−C*H*(CH$_3$)$_2$), 4.23 (s, 1H, C_5Me_3HCH_2−Lu), 4.35 (s, 1H, C_5Me_3HCH_2−Lu), 6.93−7.10 (m, 11H, Ar-*H*), 7.24 (br s, 1H, Ar-*H*), 7.97 ppm (very br s, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.89 (s, 6C, CH$_2$SiMe_3), 11.12 (s, 1C, C_5Me_3HCH$_2$), 12.96 (s, 1C, C_5Me_3HCH$_2$), 19.86 (s, 1C, C_5Me_3HCH$_2$), 21.75 (s, 1C, Ar−CH(CH$_3$)$_2$), 24.04 (s, 1C, Ar−CH(CH$_3$)$_2$), 25.42 (s, 2C, thf), 26.34 (s, 1C, Ar−CH(CH$_3$)$_2$), 27.81 (s, 1C, Ar−CH(CH$_3$)$_2$), 28.61 (s, 1C, Ar-CH(CH$_3$)$_2$), 29.96 (s, 1C, Ar-CH(CH$_3$)$_2$), 40.64 (s, 2C, LuCH$_2$SiMe$_3$), 52.46 (d, $^2J_{PC}$ = 21.0 Hz, 1C, C_5Me_3HCH$_2$), 70.21 (s, 2C, thf), 70.98 (s, 1C, C_5Me_3HCH$_2$−Lu), 124.06 (s, 2C, Ar-*C*), 124.56 (s, 2C, Ar-*C*), 124.86 (s, 2C, Ar-*C*), 128.98 (s, 1C, Ar-*C*), 131.38 (s, 2C, Ar-*C*), 131.73 (s, 2C, Ar-*C*), 132.88 (d, $^3J_{PC}$ = 9.0 Hz, 1C, Ar-*C*), 133.18 (d, $^2J_{PC}$ = 13.5 Hz, 2C, Ar-*C*), 133.81 (s, 1C, Ar-*C*), 135.12 (d, $^3J_{PC}$ = 13.5 Hz, 2C, Ar-*C*), 141.57 (d, $^2J_{PC}$ = 13.5 Hz, 1C, C_5Me_3HCH$_2$), 145.45 (d, $^3J_{PC}$ = 7.5 Hz, 1C, C_5Me_3HCH$_2$), 146.13 (d, $^3J_{PC}$ = 9.0 Hz, 1C, C_5Me_3HCH$_2$), 152.50 (d, J_{PC} = 16.5 Hz, 1C, C_5Me_3HCH$_2$), 165.43 ppm (d, $^2J_{PC}$ = 18.0 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 14.95 ppm (s). Anal. Calcd for $C_{45}H_{69}ONPSi_2Lu$: C, 59.91; H, 7.71; N, 1.55. Found: C, 60.33; H, 7.61; N, 1.47.

*Complex **4b**:* ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.62 (br s, 4H, LuCH_2SiMe$_3$), 0.36 (s, 18H, LuCH$_2$SiMe_3), 1.19 (d, $^3J_{HH}$ = 6.0 Hz, 12H, Ar−CH(CH_3)$_2$), 2.02 (s, 6H, C_5Me_4), 2.20 (s, 6H, C_5Me_4), 3.78−3.85 (sept, 2H, Ar−C*H*(CH$_3$)$_2$), 6.83−7.14 (m, 9H, Ar-*H*), 7.34−7.38 (m, 2H, Ar-*H*), 7.63−7.66 ppm (m, 2H, Ar-*H*).

Synthesis of the Complex (Ind−PPh_2=N−$C_6H_3Me_2$)Sc($CH_2SiMe_3)_2$ (5a). Following a similar procedure described for the preparation of complex **1**, complex **5a** was isolated from the acid−base reaction of Sc($CH_2SiMe_3)_3$(thf)$_2$ (0.451 g, 1.0 mmol) with 1 equiv of ligand $\mathbf{L^3(Me)}$ (0.419 g, 1.0 mmol) in a 49% yield (0.294 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.33 (br s, 2H, ScCH_2SiMe$_3$), −0.19 (br s, 2H, ScCH_2SiMe$_3$), 0.24 (s, 18H, CH$_2$SiMe_3), 2.26 (s, 6H, Ar−CH_3), 6.88−7.02 (m, 11H, Ar-*H*), 7.18 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.24 (t, $^3J_{HH}$ = 12.0 Hz, 1H, Ar-*H*), 7.50−7.53 (m, 5H, Ar-*H*), 7.79 ppm (d, $^3J_{HH}$ = 12.0 Hz, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 3.82 (s, 6C, CH$_2$SiMe_3), 22.26 (s, 2C, Ar-CH_3), 45.32 (br s, 2C, ScCH_2SiMe$_3$), 74.93 (d, J_{PC} = 121.5 Hz, 1C, Ind-*C*), 111.18 (d, $^2J_{PC}$ = 9.0 Hz, 1C, Ind-*C*), 121.58 (s, 1C, Ar-*C*), 122.62 (s, 1C, Ar-*C*), 123.45 (s, 1C, Ar-*C*), 123.66 (s, 1C, Ar-*C*), 124.04 (s, 1C, Ar-*C*), 124.75 (s, 2C, Ar-*C*), 125.90 (d, $^3J_{PC}$ = 13.5 Hz, 1C, Ind-*C*), 128.35 (s, 2C, Ar-*C*), 128.73 (d, $^3J_{PC}$ = 12.0 Hz, 2C, Ar-*C*), 129.00 (d, $^2J_{PC}$ = 12.0 Hz, 2C, Ar-*C*), 129.82 (s, 2C, Ar-*C*), 131.30 (s, 1C, Ar-*C*), 132.50 (d, $^2J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 132.80 (s, 1C, Ar-*C*), 133.45 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 135.50 (d, $^3J_{PC}$ = 10.5 Hz, 1C, Ar-*C*), 135.78 (s, 1C, Ar-*C*), 142.77 ppm (d, $^2J_{PC}$ = 9.0 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 6.35 ppm (s). Anal. Calcd for $C_{37}H_{47}NPSi_2Sc$: C, 69.67; H, 7.43; N, 2.20. Found: C, 70.13; H, 7.34; N, 2.14.

Synthesis of the Complex (Ind−PPh_2=N−$C_6H_3Me_2$)Y($CH_2SiMe_3)_2$(thf) (5b). Following a similar procedure described for the preparation of complex **1**, complex **5b** was isolated from the acid−base reaction of Y($CH_2SiMe_3)_3$(thf)$_2$ (0.495 g, 1.0 mmol) with 1 equiv of ligand $\mathbf{L^3(Me)}$ (0.419 g, 1.0 mmol) in a 53% yield (0.401 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −1.07 (d, $^2J_{HH}$ = 6.0 Hz, 2H, YCH_2SiMe$_3$), −0.70 (d, $^2J_{HH}$ = 6.0 Hz, 2H, YCH_2SiMe$_3$), 0.35 (s, 18H, CH$_2$SiMe_3), 1.10 (br s, 4H, thf), 2.10 (s, 6H, Ar−CH_3), 3.50 (br s, 4H, thf), 6.78−6.80 (m, 1H, Ar-*H*), 6.84 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*), 6.87−6.90 (m, 2H, Ar-*H*), 7.00−7.08 (m, 4H, Ar-*H*), 7.16 (s, 1H, Ar-*H*), 7.18 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.24 (t, $^3J_{HH}$ = 12.0 Hz, 1H,

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Ar-*H*), 7.31 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.38−7.41 (m, 2H, Ar-*H*), 7.46 (d, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.56−7.59 (m, 2H, Ar-*H*), 7.87 ppm (d, $^3J_{HH}$ = 12.0 Hz, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.57 (s, 6C, CH_2SiMe_3), 22.75 (s, 2C, Ar-CH_3), 36.39 (d, J_{YC} = 39.0 Hz, 2C, YCH_2SiMe_3), 25.02 (br s, 2C, thf), 69.90 (br s, 2C, thf), 75.59 (d, J_{PC} = 130.5 Hz, 1C, Ind-*C*), 110.87 (d, $^2J_{PC}$ = 12.0 Hz, 1C, Ind-*C*), 121.58 (s, 1C, Ar-*C*), 122.44 (s, 1C, Ar-*C*), 122.80 (s, 1C, Ar-*C*), 123.45 (s, 1C, Ar-*C*), 124.40 (s, 1C, Ar-*C*), 125.48 (d, $^3J_{PC}$ = 13.5 Hz, 1C, Ind-*C*), 128.35 (s, 2C, Ar-*C*), 128.40 (s, 1C, Ar-*C*), 128.85 (d, $^3J_{PC}$ = 12.0 Hz, 2C, Ar-*C*), 129.44 (d, $^3J_{PC}$ = 3.0 Hz, 2C, Ar-*C*), 132.15 (d, $^2J_{PC}$ = 7.5 Hz, 2C, Ar-*C*), 132.42 (s, 2C, Ar-*C*), 132.71 (s, 1C, Ar-*C*), 132.87 (d, $^2J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 133.30 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 135.13 (d, $^2J_{PC}$ = 6.0 Hz, 1C, Ar-*C*), 136.67 (d, $^3J_{PC}$ = 10.5 Hz, 1C, Ar-*C*), 145.86 ppm (d, $^2J_{PC}$ = 7.5 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 6.34 ppm (s). Anal. Calcd for $C_{41}H_{55}ONPSi_2Y$: C, 65.32; H, 7.35; N, 1.86. Found: C, 65.53; H, 7.24; N, 1.74.

Synthesis of the Complex (Ind−PPh$_2$=N−C$_6$H$_3$Me$_2$)Lu(CH$_2$SiMe$_3$)$_2$(thf) (5c). Following a similar procedure described for the preparation of complex **1**, complex **5c** was isolated from the acid−base reaction of $Lu(CH_2SiMe_3)_3(thf)_2$ (0.580 g, 1.0 mmol) with 1 equiv of ligand **L^3(Me)** (0.419 g, 1.0 mmol) in a 50% yield (0.424 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.72 (d, $^2J_{HH}$ = 12.0 Hz, 2H, $LuCH_2SiMe_3$), −0.58 (d, $^2J_{HH}$ = 12.0 Hz, 2H, $LuCH_2SiMe_3$), 0.27 (s, 18H, CH_2SiMe_3), 1.24 (br s, 4H, thf), 2.31 (s, 6H, Ar−CH_3), 3.40 (br s, 4H, thf), 6.85−7.14 (m, 12H, Ar-*H*), 7.26 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.33 (d, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.39−7.43 (m, 4H, Ar-*H*), 7.73 ppm (d, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.44 (s, 6C, CH_2SiMe_3), 22.45 (s, 2C, Ar-CH_3), 25.28 (br s, 2C, thf), 44.73 (s, 2C, $LuCH_2SiMe_3$), 69.46 (br s, 2C, thf), 72.64 (d, J_{PC} = 121.5 Hz, 1C, Ind-*C*), 114.28 (br s, 1C, Ar-*C*), 118.94 (d, $^2J_{PC}$ = 7.5 Hz, 1C, Ind-*C*), 121.40 (s, 1C, Ar-*C*), 122.48 (s, 1C, Ar-*C*), 122.79 (s, 1C, Ar-*C*), 124.32 (s, 2C, Ar-*C*), 128.35 (s, 2C, Ar-*C*), 128.75 (d, $^3J_{PC}$ = 12.0 Hz, 2C, Ar-*C*), 129.73 (s, 2C, Ar-*C*), 130.99 (s, 1C, Ar-*C*), 131.61 (s, 1C, Ar-*C*), 132.13 (s, 1C, Ar-*C*), 132.19 (s, 1C, Ar-*C*), 132.39 (s, 1C, Ar-*C*), 132.96 (d, $^2J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 133.07 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 135.65 (d, $^2J_{PC}$ = 6.0 Hz, 2C, Ar-*C*), 138.67 (br s, 1C, Ar-*C*), 143.88 ppm (d, $^2J_{PC}$ = 7.5 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 9.15 ppm (s). Anal. Calcd for $C_{41}H_{55}ONPSi_2Lu$: C, 58.62; H, 6.60; N, 1.67. Found: C, 58.98; H, 6.44; N, 1.61.

Synthesis of the Complex (Ind−PPh$_2$=N−C$_6$H$_3$Et$_2$)Sc(CH$_2$SiMe$_3$)$_2$ (6). Following a similar procedure described for the preparation of complex **1**, complex **6** was isolated from the acid−base reaction of $Sc(CH_2SiMe_3)_3(thf)_2$ (0.451 g, 1.0 mmol) with 1 equiv of ligand **L^3(Et)** (0.447 g, 1.0 mmol) in a 43% yield (0.290 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.17 (s, 4H, $ScCH_2SiMe_3$), 0.24 (br s, 18H, CH_2SiMe_3), 0.91 (t, $^3J_{HH}$ = 12.0 Hz, 6H, Ar−CH_2CH_3), 1.23−1.27 (m, 2H, Ar−CH_2CH_3), 2.75−2.79 (m, 2H, Ar−CH_2CH_3), 6.85−7.08 (m, 11H, Ar-*H*), 7.20 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.24 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.46−7.62 (m, 5H, Ar-*H*), 7.81 ppm (d, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 3.75 (s, 6C, CH_2SiMe_3), 25.09 (s, 2C, Ar−CH_2CH_3), 44.77 (br s, 2C, $ScCH_2SiMe_3$), 50.46 (s, 2C, Ar-CH_2CH_3), 75.72 (d, J_{PC} = 129.0 Hz, 1C, Ind-*C*), 109.84 (d, $^2J_{PC}$ = 12.0 Hz, 1C, Ind-*C*), 121.29 (s, 1C, Ar-*C*), 123.03 (s, 1C, Ar-*C*), 123.32 (s, 1C, Ar-*C*), 123.77 (s, 1C, Ar-*C*), 124.38 (s, 1C, Ar-*C*), 124.62 (s, 2C, Ar-*C*), 125.86 (d, $^3J_{PC}$ = 13.5 Hz, 1C, Ind-*C*), 128.35 (s, 2C, Ar-*C*), 128.49 (d, $^3J_{PC}$ = 12.0 Hz, 2C, Ar-*C*), 129.03 (d, $^2J_{PC}$ = 12.0 Hz, 2C, Ar-*C*), 129.89 (s, 2C, Ar-*C*), 131.71 (s, 1C, Ar-*C*), 132.40 (d, $^2J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 132.86 (s, 1C, Ar-*C*), 133.58 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 134.82 (d, $^3J_{PC}$ = 12.0 Hz, 1C, Ar-*C*), 138.41 (s, 1C, Ar-*C*), 141.39 ppm (d, $^2J_{PC}$ = 9.0 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 7.03 ppm (s). Anal. Calcd for $C_{39}H_{51}NPSi_2Sc$: C, 70.34; H, 7.72; N, 2.10. Found: C, 70.76; H, 7.61; N, 2.01.

Synthesis of the Complex (Ind−PPh$_2$=N−C$_6$H$_3$^{i}Pr$_2$)Sc(CH$_2$SiMe$_3$)$_2$ (7a). Following a similar procedure described for the preparation of complex **1**, complex **7a** was isolated from the acid−base reaction of $Sc(CH_2SiMe_3)_3(thf)_2$ (0.451 g, 1.0 mmol) with 1 equiv of ligand **L^3(^{i}Pr)** (0.475 g, 1.0 mmol) in a 50% yield (0.349 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.10 (br s, 10H, $ScCH_2SiMe_3$ and Ar−$CH(CH_3)_2$), 0.47 (br s, 18H, CH_2SiMe_3), 1.03 (s, 3H, Ar−$CH(CH_3)_2$), 1.33 (s, 3H, Ar−$CH(CH_3)_2$), 3.44 (br s, 1H, Ar−$CH(CH_3)_2$), 3.95 (br s, 1H, Ar−$CH(CH_3)_2$), 6.86 (br s, 2H, Ar-*H*), 6.99−7.10 (m, 10H, Ar-*H*), 7.17−7.22 (m, 3H, Ar-*H*), 7.60−7.62 (m, 3H, Ar-*H*), 7.79 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*), 7.83 ppm (d, $^3J_{HH}$ = 6.0 Hz, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 3.68 (s, 6C, CH_2SiMe_3), 23.44, 24.32, 25.51, 26.61, 27.24, 28.50 (s, 6C, Ar−$CH(CH_3)_2$ and Ar-$CH(CH_3)_2$), 43.59 (br s, 1C, $ScCH_2SiMe_3$), 46.93 (br s, 1C, $ScCH_2SiMe_3$), 76.53 (d, J_{PC} = 123.0 Hz, 1C, Ind-*C*), 109.62 (d, $^2J_{PC}$ = 10.5 Hz, 1C, Ind-*C*), 123.62 (s, 1C, Ar-*C*), 124.22 (s, 1C, Ar-*C*), 124.68 (s, 1C, Ar-*C*), 125.20 (d, $^2J_{PC}$ = 15.0 Hz, 2C, Ar-*C*), 125.46 (s, 1C, Ar-*C*), 125.78 (s, 1C, Ar-*C*), 126.58 (d, $^3J_{PC}$ = 13.5 Hz, 1C, Ind-*C*), 128.45 (s, 2C, Ar-*C*), 129.15 (d, $^3J_{PC}$ = 12.0 Hz, 2C, Ar-*C*), 130.53 (s, 1C, Ar-*C*), 131.20 (s, 1C, Ar-*C*), 132.71 (s, 2C, Ar-*C*), 132.95 (s, 2C, Ar-*C*), 133.16 (d, $^2J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 134.48 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 135.15 (d, $^2J_{PC}$ = 13.5 Hz, 1C, Ar-*C*), 139.33 (d, $^3J_{PC}$ = 9.0 Hz, 1C, Ar-*C*), 145.64 (br s, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 10.13 ppm (s). Anal. Calcd for $C_{41}H_{55}NPSi_2Sc$: C, 70.96; H, 7.99; N, 2.02. Found: C, 71.34; H, 7.87; N, 1.94.

Synthesis of the Complex (Ind−PPh$_2$=N−C$_6$H$_3$^{i}Pr$_2$)Y(CH$_2$SiMe$_3$)$_2$(thf) (7b). Following a similar procedure described for the preparation of complex **1**, complex **7b** was isolated from the acid−base reaction of $Y(CH_2SiMe_3)_3(thf)_2$ (0.495 g, 1.0 mmol) with 1 equiv of ligand **L^3(^{i}Pr)** (0.475 g, 1.0 mmol) in a 46% yield (0.371 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.89 (br s, 2H, YCH_2SiMe_3), −0.54 (br s, 2H, YCH_2SiMe_3), 0.35 (s, 18H, CH_2SiMe_3), 0.63 (br s, 4H, thf), 1.18 (s, 12H, Ar−$CH(CH_3)_2$), 3.51 (s, 4H, thf), 3.69 (br s, 2H, Ar−$CH(CH_3)_2$), 6.84−6.87 (m, 2H, Ar-*H*), 6.97−7.10 (m, 10H, Ar-*H*), 7.22 (t, $^3J_{HH}$ = 12.0 Hz, 2H, Ar-*H*), 7.30 (br s, 2H, Ar-*H*), 7.54 (br s, 2H, Ar-*H*), 7.83 ppm (d, $^3J_{HH}$ = 12.0 Hz, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.48 (s, 6C, CH_2SiMe_3), 25.20 (s, 4C, Ar−$CH(CH_3)_2$), 25.75 (br s, 2C, thf), 28.51 (s, 2C, Ar-$CH(CH_3)_2$), 37.30 (d, J_{YC} = 43.5 Hz, 2C, YCH_2SiMe_3), 69.97 (s, 2C, thf), 75.60 (d, J_{PC} = 129.0 Hz, 1C, Ind-*C*), 111.22 (br s, 1C, Ind-*C*), 121.05 (s, 1C, Ar-*C*), 122.61 (s, 1C, Ar-*C*), 122.73 (s, 1C, Ar-*C*), 124.36 (s, 1C, Ar-*C*), 124.72 (s, 1C, Ar-*C*), 124.88 (s, 2C, Ar-*C*), 126.74 (d, $^3J_{PC}$ = 12.0 Hz, 1C, Ind-*C*), 128.35 (s, 2C, Ar-*C*), 128.43 (s, 1C, Ar-*C*), 128.90 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 131.80 (s, 1C, Ar-*C*), 132.17 (s, 2C, Ar-*C*), 132.45 (s, 2C, Ar-*C*), 133.39 (d, $^2J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 133.58 (d, $^3J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 137.07 (d, $^2J_{PC}$ = 12.0 Hz, 1C, Ar-*C*), 141.53 (d, $^3J_{PC}$ = 9.0 Hz, 1C, Ar-*C*), 145.81 (br s, 1C, Ar-*C*). Anal. Calcd for $C_{45}H_{63}ONPSi_2Y$: C, 66.72; H, 7.84; N, 1.73. Found: C, 67.13; H, 7.69; N, 1.67.

Synthesis of the Complex (Ind−PPh$_2$=N−C$_6$H$_3$^{i}Pr$_2$)Lu(CH$_2$SiMe$_3$)$_2$(thf) (7c). Following a similar procedure described for the preparation of complex **1**, complex **7c** was isolated from the acid−base reaction of $Lu(CH_2SiMe_3)_3(thf)_2$ (0.580 g, 1.0 mmol) with 1 equiv of ligand **L^3(^{i}Pr)** (0.475 g, 1.0 mmol) in a 55% yield (0.491 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.60 (br s, 2H, $LuCH_2SiMe_3$), −0.41 (br s, 2H, $LuCH_2SiMe_3$), 0.31 (s, 18H, CH_2SiMe_3), 0.49 (br s, 6H, Ar−$CH(CH_3)_2$), 1.17 (s, 4H, thf), 1.42 (br s, 6H, Ar−$CH(CH_3)_2$), 3.37 (s, 4H, thf), 3.93 (br s, 2H, Ar−$CH(CH_3)_2$), 6.90−7.11 (m, 14H, Ar-*H*), 7.29 (very br s, 4H, Ar-*H*), 7.72 ppm (d, $^3J_{HH}$ = 12.0 Hz, 1H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.44 (s, 6C, CH_2SiMe_3), 23.73 (br s, 2C, Ar−$CH(CH_3)_2$), 25.19 (s, 2C, thf), 26.58 (br s, 2C, Ar−$CH(CH_3)_2$), 28.61 (s, 2C, Ar-$CH(CH_3)_2$), 45.58 (s, 2C, $LuCH_2SiMe_3$), 69.89 (s, 2C, thf), 73.13 (d, J_{PC} = 121.5 Hz, 1C, Ind-*C*), 114.64 (br s, 1C, Ind-*C*), 119.09 (s, 1C, Ar-*C*), 121.52 (s, 1C, Ar-*C*), 122.34 (s, 1C, Ar-*C*), 122.87 (s, 1C, Ar-*C*), 124.98 (s, 3C, Ar-*C*), 125.14 (s, 2C, Ar-*C*), 128.35 (s, 2C, Ar-*C*), 128.90 (d, $^3J_{PC}$ = 12.0 Hz, 2C, Ar-*C*), 131.22 (s, 1C, Ar-*C*), 131.79 (s, 2C, Ar-*C*), 132.10 (s, 2C, Ar-*C*), 132.38 (s, 2C, Ar-*C*), 133.44 (d, $^2J_{PC}$ = 6.0 Hz, 2C, Ar-*C*), 138.75 (br s, 1C, Ar-*C*), 140.51 (d, $^3J_{PC}$ = 9.0 Hz, 1C, Ar-*C*), 146.22 (s, 1C, Ar-*C*). Anal. Calcd for $C_{45}H_{63}ONPSi_2Lu$: C, 60.31; H, 7.09; N, 1.56. Found: C, 60.73; H, 6.99; N, 1.50.

Synthesis of the Complex [(η^1-Flu)−PPh$_2$=N−C$_6$H$_5$]Sc(CH$_2$SiMe$_3$)$_2$(thf) (8). Following a similar procedure described for

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the preparation of complex **1**, complex **8** was isolated from the acid−base reaction of $Sc(CH_2SiMe_3)_3(thf)_2$ (0.451 g, 1.0 mmol) with 1 equiv of ligand L^4**(H)** (0.442 g, 1.0 mmol) in a 55% yield (0.401 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.29 (d, $^2J_{HH}$ = 12.0 Hz, 2H, $ScCH_2SiMe_3$), 0.36 (s, 18H, CH_2SiMe_3), 0.59 (d, $^2J_{HH}$ = 12.0 Hz, 2H, $ScCH_2SiMe_3$), 0.86 (br s, 4H, thf), 2.53 (br s, 4H, thf), 6.83−6.86 (m, 4H, Ar-*H*), 6.92−6.96 (m, 3H, Ar-*H*), 6.98 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*), 7.07−7.12 (m, 4H, Ar-*H*), 7.23 (t, $^3J_{HH}$ = 18.0 Hz, 2H, Ar-*H*), 7.61−7.64 (m, 4H, Ar-*H*), 7.76 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*), 7.94 ppm (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 3.99 (s, 6C, CH_2SiMe_3), 24.93 (s, 2C, thf), 46.32 (br s, 2C, CH_2SiMe_3), 59.14 (d, J_{PC} = 108.0 Hz, 1C, Flu-*C*), 71.55 (s, 2C, thf), 119.73 (s, 2C, Ar-*C*), 119.90 (s, 2C, Ar-*C*), 120.83 (s, 2C, Ar-*C*), 122.15 (s, 1C, Ar-*C*), 124.58 (d, $^2J_{PC}$ = 14.5 Hz, 2C, Ar-*C*), 125.45 (s, 2C, Ar-*C*), 128.57 (s, 1C, Ar-*C*), 128.88 (d, $^2J_{PC}$ = 12.0 Hz, 4C, Ar-*C*), 129.18 (s, 2C, Ar-*C*), 129.67 (s, 1C, Ar-*C*), 132.18 (s, 2C, Ar-*C*), 133.65 (d, $^2J_{PC}$ = 9.0 Hz, 4C, Ar-*C*), 134.90 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 141.32 (d, $^2J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 147.87 ppm (d, $^2J_{PC}$ = 4.5 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 11.53 ppm (s). Anal. Calcd for $C_{43}H_{53}NPOSi_2Sc$: C, 70.56; H, 7.30; N, 1.91. Found: C, 71.04; H, 7.38; N, 1.84.

Synthesis of the Complex [(η^1-Flu)−PPh_2=N−C_6H_4Me]Sc-$(CH_2SiMe_3)_2$(thf) (9a). Following a similar procedure described for the preparation of complex **1**, complex **9a** was isolated from the acid−base reaction of $Sc(CH_2SiMe_3)_3(thf)_2$ (0.451 g, 1.0 mmol) with 1 equiv of ligand L^4**(Me)** (0.454 g, 1.0 mmol) in a 48% yield (0.357 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.30 (d, $^2J_{HH}$ = 12.0 Hz, 2H, $ScCH_2SiMe_3$), 0.37 (br s, 18H, CH_2SiMe_3), 0.60 (d, $^2J_{HH}$ = 12.0 Hz, 2H, $ScCH_2SiMe_3$), 0.86 (br s, 4H, thf), 2.13 (s, 3H, Ar−CH_3), 2.53 (br s, 4H, thf), 6.85−6.88 (m, 4H, Ar-*H*), 6.95 (t, $^3J_{HH}$ = 12.0 Hz, 2H, Ar-*H*), 7.00 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*), 7.07−7.12 (m, 6H, Ar-*H*), 7.63−7.66 (m, 4H, Ar-*H*), 7.69 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*), 7.95 ppm (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.02 (s, 6C, CH_2SiMe_3), 20.75 (s, 1C, Ar-CH_3), 24.93 (s, 2C, thf), 46.28 (br s, 2C, CH_2SiMe_3), 59.17 (d, J_{PC} = 108.0 Hz, 1C, Flu-*C*), 71.53 (s, 2C, thf), 119.75 (s, 2C, Ar-*C*), 119.88 (s, 2C, Ar-*C*), 120.77 (s, 2C, Ar-*C*), 124.48 (d, $^2J_{PC}$ = 14.5 Hz, 2C, Ar-*C*), 125.43 (s, 2C, Ar-*C*), 128.85 (d, $^2J_{PC}$ = 12.0 Hz, 4C, Ar-*C*), 129.33 (s, 1C, Ar-*C*), 129.80 (s, 2C, Ar-*C*), 129.89 (s, 1C, Ar-*C*), 131.21 (s, 1C, Ar-*C*), 132.13 (s, 2C, Ar-*C*), 133.71 (d, $^2J_{PC}$ = 9.0 Hz, 4C, Ar-*C*), 134.87 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 141.39 (d, $^2J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 145.26 ppm (d, $^2J_{PC}$ = 4.5 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 11.27 ppm (s). Anal. Calcd for $C_{44}H_{55}NPOSi_2Sc$: C, 70.84; H, 7.43; N, 1.88. Found: C, 71.23; H, 7.54; N, 1.76.

Synthesis of the Complex [(η^1-Flu)−PPh_2=N−C_6H_4Me]Lu-$(CH_2SiMe_3)_2$(thf) (9b). Following a similar procedure described for the preparation of complex **1**, complex **9b** was isolated from the acid−base reaction of $Lu(CH_2SiMe_3)_3(thf)_2$ (0.580 g, 1.0 mmol) with 1 equiv of ligand L^4**(Me)** (0.454 g, 1.0 mmol) in a 43% yield (0.381 g). ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ −0.25 and −0.36 (overlapped s, 4H, $LuCH_2SiMe_3$), 0.36 (br s, 18H, CH_2SiMe_3), 0.88 (br s, 4H, thf), 2.10 (s, 3H, Ar−CH_3), 2.44 (br s, 4H, thf), 6.86−6.89 (m, 4H, Ar-*H*), 6.97 (t, $^3J_{HH}$ = 18.0 Hz, 2H, Ar-*H*), 7.02 (t, $^3J_{HH}$ = 18.0 Hz, 4H, Ar-*H*), 7.10 (t, $^3J_{HH}$ = 12.0 Hz, 2H, Ar-*H*), 7.17 (t, $^3J_{HH}$ = 12.0 Hz, 2H, Ar-*H*), 7.53 (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*), 7.61−7.65 (m, 4H, Ar-*H*), 7.96 ppm (d, $^3J_{HH}$ = 6.0 Hz, 2H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 4.56 (s, 6C, CH_2SiMe_3), 20.74 (s, 1C, Ar-CH_3), 25.12 (br s, 2C, thf), 44.21 (br s, 1C, CH_2SiMe_3), 60.65 (d, J_{PC} = 114.0 Hz, 1C, Flu-*C*), 70.33 (br s, 2C, thf), 118.32 (s, 2C, Ar-*C*), 119.97 (s, 2C, Ar-*C*), 120.39 (s, 2C, Ar-*C*), 124.50 (d, $^2J_{PC}$ = 14.5 Hz, 2C, Ar-*C*), 125.85 (s, 2C, Ar-*C*), 128.93 (d, $^2J_{PC}$ = 10.5 Hz, 4C, Ar-*C*), 129.89 (s, 1C, Ar-*C*), 130.00 (s, 2C, Ar-*C*), 130.45 (s, 1C, Ar-*C*), 131.20 (s, 1C, Ar-*C*), 132.24 (s, 2C, Ar-*C*), 133.48 (d, $^2J_{PC}$ = 10.5 Hz, 4C, Ar-*C*), 134.08 (d, $^3J_{PC}$ = 10.5 Hz, 2C, Ar-*C*), 140.61 (d, $^2J_{PC}$ = 9.0 Hz, 2C, Ar-*C*), 144.76 ppm (d, $^2J_{PC}$ = 4.5 Hz, 1C, Ar-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 9.65 ppm (s). Anal. Calcd for $C_{44}H_{55}NPOSi_2Lu$: C, 60.33; H, 6.33; N, 1.60. Found: C, 60.74; H, 6.27; N, 1.54.

Ethylene Polymerization. A detailed polymerization procedure is described as a typical example (Table 1, run 5). In a glovebox, a toluene solution (30 mL) of complex **2a** (6.4 mg, 10 μmol) was charged into a two-neck flask with a magnetic stir bar. The flask was taken outside of the glovebox and set in a water bath and connected to a well-purged Schlenk ethylene line with a mercury-sealed stopper by use of a three-way cock. Ethylene (1.0 bar) was introduced into the system and was saturated in the solution at 50 °C by stirring for 5 min. The toluene solution of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) and Al^iBu_3 (0.1 mL, 100 μmol, 1.0 M in toluene) was then added through a syringe under vigorous stirring. The mixture was stirred under constant ethylene pressure (1.0 bar) for 5 min. After that, methanol (2 mL) was added to terminate the reaction. The reaction mixture was added to acidified methanol (20 mL of concentrated HCl in 500 mL of ethanol). Polyethylene was obtained by filtration, washed with methanol, and dried at 40 °C for 24 h in vacuum.

CCDC-851548 (**1**), 851549 (**2a**), 857591 (**2b**), 872989 (**2d**), 791780 (**2e**), 851550 (**3a**), 851551 (**3b**), 851552 (**4b**), 851553 (**5b**), 851554 (**6**), 851555 (**7a**), 851556 ($L^2(^iPr)$), and 670404 (**9b**) 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all complexes, ^{1}H NMR spectra of polyethylene, and the crystallographic data and structure refinement details for complexes **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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