Selective σ-Bond Metathesis in Alkyl−Aryl and Alkyl−Benzyl Yttrium Complexes. New Aryl− and Benzyl−Hydrido Yttrium Derivatives Supported by Amidopyridinate Ligands

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Yttrium dialkyl complexes coordinated by 6-aryl-substituted amidopyridinate ligands undergo selective intramolecular sp^2 or sp^3 C−H bond activation. Upon treatment with $PhSiH_3$ of the resulting Y−C(alkyl, aryl) or Y−C(alkyl,benzyl) systems, a σ-bond metathesis reaction takes place selectively at the Y−C(alkyl) bond, generating rare dimeric aryl−hydrido or benzyl−hydrido yttrium complexes, respectively.

Rare-earth-metal hydrides currently attract a great deal of attention due to the variety of their unique structural and chemical properties.[1] These compounds have proved to be promising catalysts in several olefin transformations[2] and have demonstrated extremely high reactivity in stoichiometric reactions, including C−F bond activation.[3] Rare-earth-metal hydrides are generally constituted by sandwich-[1] and half-sandwich-type ("constrained geometry")[4] complexes, and very few classes of cyclopentadienyl-free analogues have been systematically explored up to now.[5]

The reactivity of rare-earth-metal compounds is known to be defined by both the metal electrophilicity and the free coordination sites at the metal center and can be substantially modulated by tuning the electronic and steric properties of the ligand framework. This issue makes the design of new coordination environments crucial for generating a rational balance between the kinetic stability and the high reactivity of the resulting complexes. Recently the use of bulky amidopyridinate ligands has allowed us to synthesize and characterized a novel class of rare-earth alkyl−hydrido clusters containing highly reactive Ln−C and Ln−H bonds, that demonstrate an intriguing reactivity.[6]

In order to explore the potential of such a class of nitrogen-containing ligands for the synthesis of new alkyl and/or hydrido rare-earth complexes, we focused our attention on 6-aryl-substituted aminopyridinate systems which were straightforwardly prepared by reductive alkylation[7] of related iminopyridines (Schemes 1 and 2). The iminopyridine **1** was prepared according to a procedure reported in the literature,[8] while the new xylyl -substituted iminopyridyl ligand **2** was synthesized on a multigram scale through the five-step synthesis shown in Scheme 1.

All our attempts to synthesize yttrium bis(alkyl) species via monoalkane elimination by reacting $Y(CH_2SiMe_3)_3(THF)_2$[9] with the aminopyridine N_2H^{Ph} (**3**) in *n*-hexane at 0 °C resulted in

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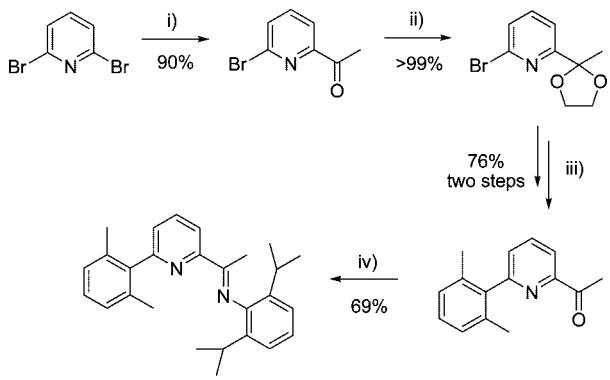
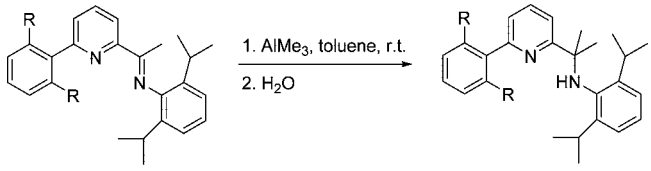
Scheme 1[a]



[a] Legend: (i) *t*-BuLi, *N*,*N*-dimethylacetamide, Et_2O, −78 °C; (ii) ethylene glycol, *p*-toluenesulfonic acid, benzene, reflux 12 h, Dean−Stark apparatus; (iii) Kumada coupling conditions, $Me_2(C_6H_3)MgBr$, $NiCl_2(PCy_3)_2$ cat., THF, 50 °C, 72 h and then HCl 2 M, 85 °C, 2 h; (iv) $iPr_2(C_6H_3)NH_2$, HCOOH cat., MeOH, reflux 62 h.

Scheme 2



the quantitative generation of the metallacyclic compound **5** as a result of an intramolecular sp^2-CH bond activation at one of the ortho positions of the phenyl substituent (Scheme 3). The ^1H and $^{13}C\{^1H\}$ NMR spectra for complex **5** were consistent with the expected yttrium coordination sphere. The ^1H NMR spectrum of **5**, which contains both Y−C(alkyl) and Y−C(aryl) bonds, shows one clear doublet centered at −0.54 ppm ($^2J_{YH}$ = 3.0 Hz), attributed to the hydrogen atoms of the methylene group attached to the yttrium. The $^{13}C\{^1H\}$ NMR spectrum contains a doublet for the sp^3 carbon atom centered at 30.3 ppm ($^1J_{YC}$ = 39.5 Hz), while a further doublet at 190.6 ppm ($^1J_{YC}$ = 41.2 Hz) is readily assigned to the sp^2 carbon of the phenyl ring *σ*-bonded to the metal center.

Unexpectedly, the xylyl-substituted aminopyridine system N_2H^{Xyl} (**4**) did not allow us to generate dialkyl species due to an intramolecular activation of the sp^3-hybridized C−H bond of one methyl group (Scheme 3). The reaction actually gave the mononuclear metallacyclic monoalkyl complex **6**, where the yttrium atom turned out to be five-coordinated by a tridentate aminopyridinate ligand, a residual (trimethylsilyl)methylene fragment, and a THF molecule.

Unlike the case for **5**, the ^1H NMR spectrum of **6** shows two sets of diastereotopic protons, one for the methylene group of the residual alkyl fragment attached to the yttrium atom (doublet of doublets at −0.92 and −0.76 ppm ($^2J_{HH}$ = 10.8 Hz, $^2J_{YH}$ = 3.0 Hz, respectively)) and one for the "benzylic" methylene $Me(C_6H_3)CH_2Y$ group (doublet of doublets at 1.81 and 2.00 ppm ($^2J_{HH}$ = 5.5 Hz, $^2J_{YH}$ = 2.0 Hz, respectively)). The corresponding $^{13}C\{^1H\}$ NMR spectrum contains a broad doublet centered at 27.3 ppm ($^1J_{YC}$ = 43.3 Hz) attributable to the Me_3SiCH_2Y group, while a doublet at 49.2 ppm ($^1J_{YC}$ = 22.8 Hz) is assigned to the "benzylic" sp^3 carbon. The two isopropyl fragments as well as the two methyl groups at the sp^3 carbon are not magnetically equivalent and show ^1H NMR and $^{13}C\{^1H\}$ NMR spectra distinguished by a set of eight distinct signals for the methyl groups and for the methyne protons, the latter providing two well-separated septets at 3.18 and 4.50 ppm, respectively. Such a situation reflects the existence of two possible conformations for **6** differing from each other in the location of the benzylic CH_2 group: above or below the amidopyridinate ligand plane, respectively.

Although inter- and intramolecular metalations of sp^2- and sp^3-hybridized C−H bonds have been previously documented for cyclopentadienyl[10] and cyclopentadienyl-free[11] lanthanide alkyl and hydride complexes, they still attract considerable interest for their ability to activate inert chemical bonds.

Crystallization by slow cooling of a concentrated *n*-hexane solution of **6** to −20 °C resulted in the formation of single crystals suitable for X-ray diffraction analysis. The molecular structure of the monomeric complex **6** is shown in Figure 1. The coordination environment of the yttrium atom is set up by two nitrogen atoms of the chelating aminopyridinate ligand, one sp^3 carbon atom from the residual alkyl group, one further sp^3 carbon atom from the "benzylic" group, and one oxygen atom from a THF molecule. Moreover, a close contact (2.9421(17) Å) between the yttrium and the ipso carbon on the "benzylic" group is finally observed, which increases the coordination number to 6. The $Y-C_{Alkyl}$ bond length (2.4139(17) Å) is comparable to the values reported for related yttrium systems (2.410(8)−2.439(3) Å),[12] while the $Y-C_{Bn}$ distance (2.4520(18) Å) is slightly longer than that measured for analogous C−H activation products ($Ap'(Ap_{-H}')Y(thf)$] (2.420(11) Å).[13] It is worth noting that the covalent Y−N bond (2.2015(14) Å) is evidently shorter than that measured in analogous six-coordinated yttrium complexes containing amidopyridinate ligands with a shorter backbone (2.273(3) Å).[14]

The most common synthetic route to rare-earth hydrido complexes is the reaction of alkyl derivatives with either dihydrogen[15] or phenylsilane.[16] We have found that, by treat-

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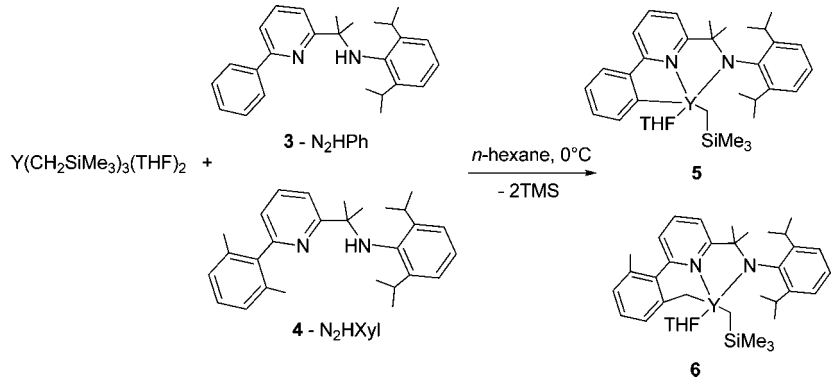
Scheme 3



ment with an equimolar amount of $PhSiH_3$ in *n*-hexane at 0 °C, **5** and **6** undergo rapid σ-bond metathesis of the residual $Y-CH_2SiMe_3$ bonds to give selectively the novel aryl−hydrido and benzyl−hydrido complexes **7** and **8** (Scheme 4). Surprisingly, the Y−C(Aryl) and Y−C(Bn) bonds in **5** and **6** did not react with $PhSiH_3$, even after 24 h at room temperature and in the presence of a 2-fold excess of silane. In fact, complexes **7** and **8** were recovered in the same yield with no appreciable decomposition. Complexes **5** and **6** were finally reacted with H_2 (1 bar) in toluene with the aim of exploring whether **7** and **8** were obtainable through this alternative way. All our attempts to react **5** and **6** with H_2 resulted in their decomposition with formation of an off-white material that does not contain any amidopyridinate ligand and is insoluble in common organic solvents. This result proves the effectiveness of phenylsilane as a highly selective reagent for the synthesis of hydride species **7** and **8**.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **7** and **8** (20 °C, C_6D_6) are consistent with binuclear species distinguised by an internal mirror plane. The hydride signals in **7** and **8** appear, in the ^1H NMR spectrum, as sharp, well-resolved triplets at 7.76 ppm ($^1J_{YH}$ = 27.4 Hz) and at 7.37 ppm ($^1J_{YH}$ = 26.5 Hz),

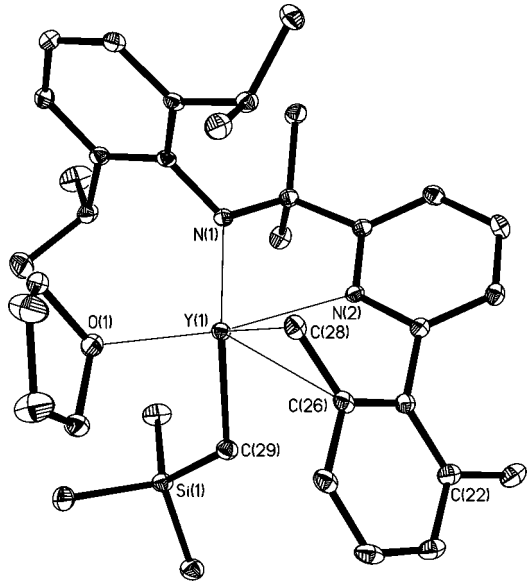
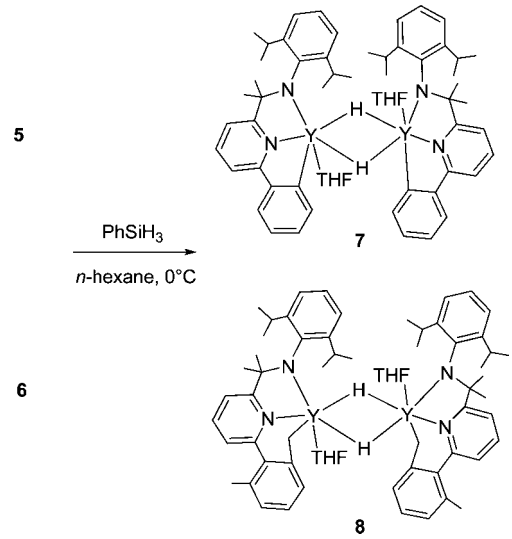


Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of complex **6** showing the numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)−N(1) = 2.2015(14), Y(1)−O(1) = 2.3422(13), Y(1)−C(29) = 2.4139(17), Y(1)−N(2) = 2.4200(14), Y(1)−C(28) = 2.4520(18), Y(1)−C(26) = 2.9421(17); C(29)−Y(1)−C(28) = 117.20(6), N(1)−Y(1)−N(2) = 70.00(5), C(28)−Y(1)−C(26) = 29.47(5).

Scheme 4



respectively, thus indicating the coupling of each hydride with two equivalent ^{89}Y nuclei. The $^{13}C\{^1H\}$ NMR signals of the carbon atoms bonded to yttrium appear as two doublets centered at 193.1 ppm ($^1J_{YC}$ = 46.2 Hz) and 51.3 ppm ($^1J_{YC}$ = 24.9 Hz) for complexes **7** and **8**, respectively.

Yellow single crystals of **7**, suitable for X-ray analysis, were prepared by slow cooling of an *n*-hexane solution of **7** down to −20 °C. The molecular structure of **7**is illustrated in Figure 2. The complex adopts a binuclear structure with two six-coordinate yttrium atoms. The metal coordination sphere is determined by the two nitrogen and one carbon atoms from the tridentate amidopyridinate ligand, two bridging hydrido ligands, and one oxygen atom from a residual THF molecule. The tetranuclear Y_2H_2 core is not planar; the dihedral angle between the Y(1)H(1)H(1A) and Y(1A)H(1)H(1A) planes is 20.1°. The Y−H bond lengths are 2.15(2) Å. It should be noted that N(1), N(2), and C(26) atoms lie in the same plane, though the entire chelating ligand is not planar.

The Y−C bond length in **7** (2.469(2) Å) is in good agreement with previously reported distances for similar six-coordinate yttrium aryl species,[17] while the Y−Y distance (3.5787(4) Å)

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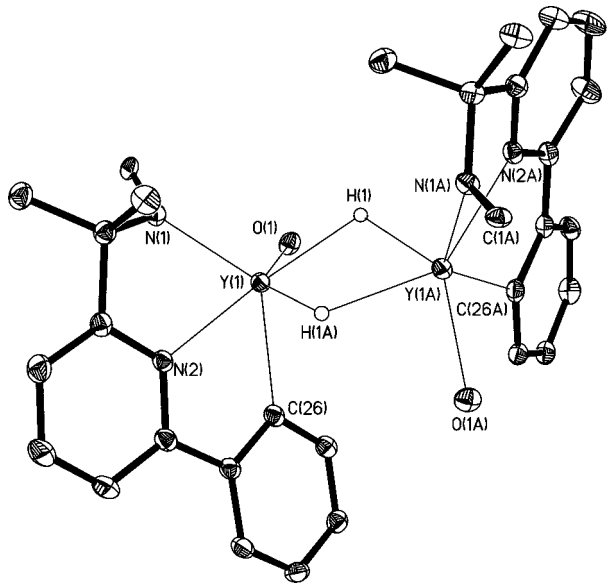

Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of complex **7** showing the numbering scheme. Hydrogen atoms, 2,6-diisopropylphenyl fragments, and methylene groups of the THF molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Y−H = 2.15(2), Y(1)−N(1) = 2.2205(18), Y(1)−O(1) = 2.3609(15), Y(1)−N(2) = 2.4252(17), Y(1)−C(26) = 2.469(2), Y(1)−Y(1A) = 3.5780(4); N(1)−Y(1)−N(2) = 68.24(6), N(1)−Y(1)−C(26) = 130.34(7), N(2)−Y(1)−C(26) = 68.43(7).

is significantly shorter than those measured in related binuclear yttrium hydrides.[5a,18]

In conclusion, we have reported the synthesis of new yttrium dialkyl complexes stabilized by amidopyridinate ligands which rapidly undergo intramolecular sp^2 or sp^3 C−H bond activation with the formation of alkyl−aryl or alkyl−benzyl complexes. We have also found that the residual Y−C(alkyl) bonds undergo selective σ-bond metathesis upon treatment with $PhSiH_3$, while the Y−C(aryl) and Y−C(benzyl) bonds do not react with the silane under analogous conditions. As a result, rare[19] binuclear aryl−hydrido and benzyl−hydrido yttrium complexes have been synthesized and characterized. Polymerization tests with both Y−alkyl and Y−hydrido complexes using ethylene and propene as monomer feeds are currently under investigation in our laboratories. Preliminary results for ethylene polymerization under standard conditions (10 bar of C_2H_4, 25 mL of toluene, 30 °C) indicate that both precursors do not generate very active catalytic systems, as the highest turnover frequency observed was 870 mol of C_2H_4 converted (mol of metal)$^{-1}$ h^{-1}.

Experimental Section

General Considerations. All air- and/or water-sensitive reactions were performed under either nitrogen or argon in flame-dried flasks using standard Schlenk-type techniques. THF was purified by distillation from sodium/benzophenone ketyl, after drying over KOH. Et_2O, benzene, *n*-hexane, and toluene were purified by distillation from sodium/triglyme benzophenone ketyl or were obtained by means of a MBraun solvent purification system, while MeOH was distilled over Mg prior to use. C_6D_6 was dried over sodium/benzophenone ketyl and condensed in vacuo prior to use, while CD_2Cl_2 and $CDCl_3$ were dried over activated 4 Å molecular sieves. Literature methods were used to synthesize the iminopyridine ligand N_2^{Ph} (**1**).[8] $Y(CH_2SiMe_3)_3(THF)_2$ was prepared according to literature procedures.[2] All the other reagents and solvents were used as purchased from commercial suppliers. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on either a Bruker ACP 200 (200.13 and 50.32 MHz, respectively) or a Bruker Avance DRX-400 (400.13 and 100.62 MHz, respectively). Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvent resonances (^1H and ^{13}C), and coupling constants are given in Hz. IR spectra were recorded as Nujol mulls or KBr plates on FSM 1201 and Bruker-Vertex 70 instruments. Lanthanide metal analyses were carried out by complexometric titration. The C, H elemental analyses were carried out in the microanalytical laboratory of the IOMC or at the ICCOM by means of a a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of ±0.4 unit on carbon (C), hydrogen (H), and nitrogen (N). Melting points were determined by using a Stuart Scientific SMP3 melting point apparatus.

Synthesis of 1-(6-Bromopyridin-2-yl)ethanone.[20] To a stirred solution of 2,6-dibromopyridine (7.11 g, 30.0 mmol) in Et_2O (130 mL) at −78 °C was added dropwise a 1.7 M solution of *t*BuLi (18.8 mL, 30.0 mmol) in *n*-pentane over 10 min. After 30 min of stirring at −78 °C, *N,N*-dimethylacetamide (3.1 mL, 33.0 mmol) was added and stirring maintained for 1.5 h. The resulting mixture was warmed to room temperature and treated with water (30 mL). The formed layers were separated, and the organic phase was washed with water (2 × 30 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a yellow oil that was dissolved in petroleum ether and cooled to −20 °C. After 6 h, small yellow pale crystals were separated by filtration (yield 90%). Mp: 44 °C. IR (KBr): ν 1695 cm^{-1} (C═O). ^1H NMR (200 MHz, $CDCl_3$, 293 K): δ 2.70 (s, 3H, C(O)Me), 7.68 (m, 2H, CH), 7.98 (dd, J = 6.5, 2.1, 1H, CH). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 293 K): δ 26.4 (1C, C(O)*Me*), 121.1 (1C, CH), 132.4 (1C, CH), 139.8 (1C, CH), 142.0 (1C, C), 154.9 (1C, C), 198.5 (1C, *C*(O)Me). Anal. Calcd for C_7H_6BrNO (200.03): C, 42.03; H, 3.02; N, 7.00. Found: C, 42.09; H, 2.90; N, 7.02.

Synthesis of 6-Bromo-2-(2′-methyl-1′,3′-dioxolan-2′-yl)pyridine.[21] A solution of 1-(6-bromopyridin-2-yl)ethanone (1.0 g, 5 mmol), 1,2-ethanediol (0.34 mL, 6 mmol), and *p*-toluenesulfonic acid hydrate (PTSA, 0.1 g, 0.5 mmol) in 15 mL of distilled benzene was heated for 24 h under reflux in a Dean−Stark apparatus. The mixture was cooled to room temperature and then treated with 5 mL of 0.5 M aqueous NaOH solution. The layers that formed were separated. The aqueous phase was washed with Et_2O (2 × 5 mL), and the combined organic extracts were dried over $NaSO_4$. After removal of the solvent under reduced pressure a white solid was obtained in pure form (yield >99%). Mp: 40−42 °C. ^1H NMR (200 MHz, $CDCl_3$, 293 K): δ 1.80 (s, 3H, Me), 3.95−4.20 (m, 4H, CH_2), 7.49 (dd, J = 7.7, 1.3, 1H, CH Ar), 7.58−7.65 (2H, m, CH Ar). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 298 K): δ 25.6 (1C, Me); 65.6 (2C, CH_2); 108.5 (1C, C Ar); 118.9 (1C, CH Ar); 128.1 (1C, CH Ar); 139.6 (1C, CH Ar); 142.5 (1C, CH Ar); 163.0 (1C, CH Ar). Anal. Calcd for $C_9H_{10}BrNO_2$ (244.09): C, 44.29; H, 4.13; N, 5.74. Found: C, 44.09; H, 4.22; N, 5.69.

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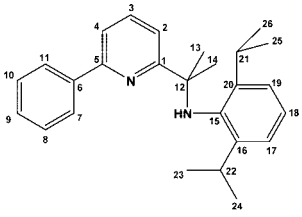
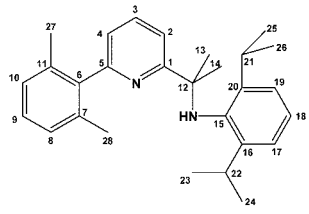
Synthesis of 1-(6-(2,6-Dimethylphenyl)pyridin-2-yl)ethanone.[22] To a solution of 6-bromo-2-(2′-methyl-1′,3′-dioxolan-2′-yl)pyridine (1.5 g, 6.14 mmol) in dry and degassed THF (40 mL) was added $NiCl_2(PCy_3)_2$ (0.29 g, 0.43 mmol) in one portion. A 1 M THF solution of $(2,6\text{-}Me_2C_6H_3)MgBr$ (7.4 mL, 7.4 mmol) was then added dropwise, and the resulting red solution was stirred at 50 °C for 72 h. Afterward, the mixture was cooled to room temperature and then treated with 30 mL of a saturated aqueous NH_4Cl solution. The layers that formed were separated, the aqueous phase was washed with Et_2O (3 × 25 mL), and the combined organic extracts were dried over $NaSO_4$. After removal of the solvent under reduced pressure a brown oil was obtained, and it was used in the next step without any further purification. The oil was then suspended in HCl 2 M (15 mL) and stirred at 80−85 °C for 2 h. The resulting mixture was then cooled in an ice bath, diluted with iced water (15 mL), and neutralized portionwise with solid $NaHCO_3$. A standard extractive workup with AcOEt (3 × 30 mL) gave, after removal of solvent, a crude slightly brown solid which was purified by filtration over a silica gel pad (AcOEt−petroleum ether, 10:90) to afford the expected compound as a pale yellow oil (yield 76%). ^{1}H NMR (200 MHz, CD_2Cl_2, 293 K): δ 1.98 (s, 6H, $(C_6H_3)(CH_3)_2$), 2.60 (s, 3H, $COCH_3$), 7.06−7.08 (2H, C*H* Ar), 7.16 (m, 1H, C_H Ar), 7.36 (dd, $^3J_{HH}$ = 7.8 Hz, 1H, C*H* Ar), 7.85 (t, $^3J_{HH}$ = 7.8 Hz, 1H, C*H* Ar), 7.92 (dd, $^3J_{HH}$ = 7.8 Hz, 1H, C*H* Ar).

Synthesis of [1-(6-(2,6-Dimethylphenyl)pyridin-2-yl)ethylidene]-(2,6-diisopropyphenyl)amine (2). A solution of 1-(6-(2,6-dimethylphenyl)pyridin-2-yl)ethanone (0.94 g, 4.17 mmol), 2,6-diisopropylaniline (2.4 mL, 12.5 mmol, 3 equiv) and a few drops of formic acid in MeOH (30 mL) was refluxed for 62 h. The reaction mixture was cooled to room temperature under stirring overnight and cooled for several hours to +4 °C to afford a yellow solid, which was filtered and washed several times with cold MeOH. Recrystallization from boiling MeOH gave a yellow solid in 69% yield. ^{1}H NMR (200 MHz, CD_2Cl_2, 293 K): δ 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 2.15 (s, 6H, $(C_6H_3)(CH_3)_2$), 2.19 (s, 3H, $CNCH_3$), 2.82 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, $CH(CH_3)_2$), 6.09−7.14 (m, 1H, C*H* Ar), 7.16−7.22 (4H, C*H* Ar), 7.23−7.29 (m, 1H, C*H* Ar), 7.38 (dd, $^3J_{HH}$ = 7.7 Hz, 1H, C*H* Ar), 7.93 (t, $^3J_{HH}$ = 7.7 Hz, 1H, C*H* Ar), 8.32 (dd, $^3J_{HH}$ = 7.7 Hz, 1H, C*H* Ar). ^{13}C{^{1}H} NMR (50 MHz, CD_2Cl_2, 293 K): δ 17.1 (1C, $CNCH_3$), 20.1 (2C, CH_3 Ar), 22.5 (2C, $CH(CH_3)_2$), 23.0 (2C, $CH(CH_3)_2$), 28.1 (2C, $CH(CH_3)_2$), 119.0 (1C, CH Ar), 122.9 (2C, CH Ar), 123.4 (1C, CH Ar), 125.7 (1C, CH Ar), 127.6 (2C, CH Ar), 127.8 (1C, CH Ar), 135.8 (1C, CH Ar), 136.0 (2C, C Ar), 136.6 (2C, C Ar), 140.4 (1C, C Ar), 146.5 (1C, C Ar), 156.3 (1C, C Ar), 158.4 (1C, C Ar), 167.5 (1C, CN). Anal. Calcd for $C_{27}H_{32}N_2$ (384.56): C, 84.33; H, 8.39; N, 7.28. Found: C, 84.19; H, 8.42; N, 7.39.





Synthesis of N_2H^{Ph} (3). A solution of the iminopyridine ligand N_2^{Ph} (**1**; 1.21 g, 3.4 mmol) in 35 mL of toluene was cooled to 0 °C in an ice bath and treated dropwise with a 2.0 M toluene solution of trimethylaluminum (TMA; 2.54 mL, 5.1 mmol). The reaction mixture was stirred at room temperature for 12 h and then was quenched with 30 mL of water. The aqueous phase was extracted with 3 × 25 mL of AcOEt, and the combined organic layers were dried over Na_2SO_4. Removal of the solvent under reduced pressure gave the amidopyridinate ligand as a crude dark white solid. The ligand was purified by crystallization from hot MeOH, by cooling the resulting solution to 4 °C overnight to afford white crystals in 93% yield (1.18 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)$, $H^{23,24,25,26}$), 1.53 (s, 6H, $C(CH_3)_2$, $H^{13,14}$), 3.38 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)$, $H^{21,22}$), 4.56 (bs, 1H, N*H*), 7,10 (bs, 3H, C*H* Ar, $H^{17,18,19}$), 7.45−7.54 (m, 4H, C*H* Ar, $H^{2,8,9,10}$), 7.71 (d, 1H, $^3J_{HH}$ = 7.5 Hz, C*H* Ar, H^4), 7.81 (t, 1H, $^3J_{HH}$ = 7.5 Hz, C*H* Ar, H^3), 8.14−8.16 (m, 2H, C*H* Ar, $H^{7,11}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 23.7 ($CH(CH_3)_2$, $C^{23,24,25,26}$), 28.2 ($CH(CH_3)_2$, $C^{21,22}$), 28.9 ($C(CH_3)_2$, $C^{13,14}$), 59.4 ($C(CH_3)_2$; C^{12}), 117.7 ($C^{2,4}$), 122.9 ($C^{17,19}$), 124.4 (C^{18}), 126.8 ($C^{7,11}$), 128.6 ($C^{8,10}$), 128.8 (C^9), 137.2 (C^3), 139.5 (C^6), 140.5 ($C^{16,20}$), 146.8 (C^{15}), 155.4 (C^5), 167.8 (C^1). Mp: 107.8 °C. Anal. Calcd for $C_{26}H_{32}N_2$ (372.55): C, 83.82; H, 8.66; N, 7.52. Found: C, 83.91; H, 8.62; N, 7.37.

Synthesis of N_2H^{Xyl} (4). A solution of the iminopyridine ligand N_2^{Xyl} (**2**; 0.85 g, 2.2 mmol) in 20 mL of toluene was cooled to 0 °C in an ice bath and treated dropwise with a 2.0 M toluene solution of trimethylaluminum (TMA; 1.65 mL, 3.3 mmol). The reaction mixture was stirred at room temperature for 12 h and then was quenched with 20 mL of water. The aqueous phase was extracted with 3 × 25 mL of AcOEt, and the combined organic layers were dried over Na_2SO_4. Removal of the solvent under reduced pressure gave the amidopyridinate ligand as a crude dark white solid. The ligand was purified by crystallization from hot MeOH, by cooling the resulting solution to −20 °C overnight to afford white crystals in 89% yield (0.79 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 1.07 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)$, $H^{23,24,25,26}$), 1.49 (s, 6H, $C(CH_3)_2$, $H^{13,14}$), 2.12 (s, 6H, $C(CH_3)$, $H^{27,28}$), 3.23 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)$, $H^{21,22}$), 4.14 (bs, 1H, N*H*), 7,08 (bs, 3H, C*H* Ar, $H^{17,18,19}$), 7.14−7.17 (m, 4H, C*H* Ar, $H^{2,8,9,10}$), 7.57 (dd, 1H, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 0.9 Hz, C*H* Ar, H^4), 7.80 (t, 1H, $^3J_{HH}$ = 7.9 Hz, C*H* Ar, H^3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 20.1 ($C(CH_3)_2$, $C^{13,14}$), 23.7 ($CH(CH_3)_2$, $C^{23,24,25,26}$), 28.1 ($CH(CH_3)_2$, $C^{21,22}$), 29.1 ($C(CH_3)$, $C^{27,28}$), 58.9 ($C(CH_3)_2$; C^{12}), 116.9 (C^2), 122.1 (C^4), 122.9 ($C^{17,19}$), 124.2 (C^{18}), 127.4 ($C^{8,10}$), 127.6 (C^9), 135.9 (C^6), 136.5 ($C^{16,20}$), 140.8 (C^3), 141.0 (C^{15}), 146.3 ($C^{7,11}$), 158.3 (C^5), 168.5 (C^1). Mp: 109.6 °C. Anal. Calcd for $C_{28}H_{36}N_2$ (400.6): C, 83.95; H, 9.06; N, 6.99. Found: C, 83.7; H, 8.97; N, 7.02.

Synthesis of $N_2^{Ph}Y(CH_2SiMe_3)(THF)_2$ (5). A solution of $N_2^{Ph}H$ (**3**; 0.182 g, 0.49 mmol) in *n*-hexane (15 mL) was added to a solution of $(Me_3SiCH_2)_3Y(THF)_2$ (0.242 g, 0.49 mmol) in *n*-hexane (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The solution was concentrated under vacuum and was kept overnight at −20 °C. Complex **5** was isolated as a yellow microcrystalline solid in 87% yield (0.294 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ −0.54 (d, $^2J_{YH}$ = 3.0 Hz, 2H, YCH_2), 0.22 (s, 9H, $Si(CH_3)$), 1.07 (m, 8H, β-CH_2 THF), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CH(CH_3)$; $H^{23,24,25,26}$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CH(CH_3)$, $H^{23,24,25,26}$), 1.44 (s, 6H, $C(CH_3)_2$, $H^{13,14}$), 3.55 (m, 8H, α-CH_2 THF), 3.80 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)$, $H^{21,22}$), 6.76 (d, $^3J_{HH}$ = 7.9 Hz, 1H, C*H* Ar, H^2), 7.19 (m, together 2H, C*H* Ar, $H^{3,18}$), 7.27 (m, together 3H, C*H* Ar, $H^{10,17,19}$), 7.39 (t, $^3J_{HH}$ = 7.3 Hz, 1H, C*H* Ar, H^9), 7.45 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C*H* Ar, H^4), 7.79 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C*H* Ar, H^{11}), 8.15 (d, $^3J_{HH}$ = 6.8 Hz, 1H, C*H* Ar, H^8). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 4.6 (s, $Si(CH_3)_3$), 23.8 (s, $CH(CH_3)_2$, $C^{23,24,25,26}$), 24.7 (s, β-CH_2, THF), 27.5 (s, $CH(CH_3)_2$, $C^{3,24,25,26}$), 27.6 (s, $CH(CH_3)_2$, $C^{21,22}$), 30.3 (d, $^1J_{YC}$ = 39.5 Hz, YCH_2), 32.1 (s, $C(CH_3)_2$, $C^{13,14}$), 68.5 (s, $C(CH_3)_2$; C^{12}), 69.6 (s, α-CH_2 THF), 115.2 (s, C^4), 117.7 (s, C^2), 122.9 (s, C^{11}), 123.6 (s, $C^{17,19}$), 123.7 (s, C^{18}), 125.3 (s, C^{10}), 127.9 (s, C^9), 138.0 (s, C^8), 138.6 (s, C^3), 145.3 (s, C^6), 147.6 (s, C^{15}), 150.2 (s, $C^{16,20}$), 164.6 (s, C^5), 175.8 (s, C^1), 190.6 (d, $^1J_{YC}$ = 41.2 Hz, Y*C*, C^7). Anal. Calcd for $C_{38}H_{57}N_2O_2SiY$ (690.86): C, 66.06; H, 8.32; N, 4.05; Y, 12.87. Found: C, 66.38; H, 8.52; N, 4.09; Y, 12.64.

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Synthesis of $N_2^{Xyl}Y(CH_2SiMe_3)(THF)$ (6). A solution of $N_2^{Xy}H$ (**4**; 0.215 g, 0.54 mmol) in *n*-hexane (15 mL) was added to a solution of $(Me_3SiCH_2)_3Y(THF)_2$ (0.266 g, 0.54 mmol) in *n*-hexane (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The solution was concentrated under vacuum and kept overnight at −20 °C. Complex **6** was isolated as an orange crystalline solid in 79% yield (0.274 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ −0.92 (dd, $^2J_{HH}$ = 10.8 Hz, $^2J_{YH}$ = 3.0 Hz, 1H, YCH_2SiMe$_3$), −0.76 (dd, $^2J_{HH}$ = 10.8 Hz, $^2J_{YH}$ = 3.0 Hz, 1H, YCH_2SiMe$_3$), 0.23 (s, 9H, Si(CH_3)$_3$), 0.96 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH(CH_3), H^{23,24,25,26}), 1.02 (br m, β-CH_2 THF), 1.15 (m, together 6H, CH(CH_3)$_2$ and C(CH_3)$_2$, H^{13,14,23,24,25,26}), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH(CH_3)$_2$, H^{23,24,25,26}), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH(CH_3)$_2$, H^{23,24,25,26}), 1.81 (dd, d, $^2J_{HH}$ = 5.5 Hz, $^2J_{YH}$ = 2.0 Hz, 1H, ArCH_2Y, H^{28}), 1.89 (s, 3H, ArCH_3, C^{27}), 2.00 (dd, d, $^2J_{HH}$ = 5.5 Hz, $^2J_{YH}$ = 2.0 Hz, 1H, ArCH_2Y, H^{28}), 2.20 (s, 3H, C(CH_3)$_2$, C^{13,14}), 3.00 (br m, 2H, α-CH_2, THF), 3.11 (br m, 2H, α-CH_2 THF), 3.18 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH(CH$_3$), H^{21,22}), 4.50 (sept, $^3J_{HH}$ = 6.3 Hz, 1H, CH(CH$_3$), H^{21,22}), 6.74 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH Ar, H^2), 6.80 (m, 2H, CH Ar, H^{4,8}), 6.98 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CH Ar, H^{10}), 7.05−7.22 (m, 5H, CH, H^{3,9,17,18,19}). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 4.7 (s, Si(CH_3)$_3$), 21.5 (s, C(CH_3)$_2$, C^{13,14}), 24.1 (s, CH(CH_3)$_2$, C^{23,24,25,26}), 24.8 (s, β-CH_2 THF), 24.9 (s, C(CH_3)$_2$, C^{13,14}), 25.6 (s, CH(CH_3)$_2$, C^{23,24,25,26}), 26.7 (s, CH(CH_3)$_2$, C^{23,24,25,26}), 27.2 (s, CH(CH$_3$)$_2$, C^{23,24,25,26}), 27.3 (d, $^1J_{YC}$ = 41.4 Hz, YCH_2Si), 27.4 (s, CH(CH$_3$)$_2$, C^{21,22}), 28.1 (s, CH(CH$_3$)$_2$, C^{21,22}), 40.8 (s, ArCH_3, C^{27}), 49.2 (d, $^1J_{YC}$ = 23.1 Hz, YCH_2, C^{28}), 65.4 (s, C(CH$_3$)$_2$, C^{12}), 69.5 (s, α-CH_2 THF), 115.5 (s, Ar, C^4), 119.8 (s, Ar, C^2), 122.8 (s, Ar, C^{10}), 123.5 (s, Ar, C^{17,19}), 123.6 (s, Ar, C^{17,19}), 123.7 (s, Ar, C^{18}), 124.0 (s, Ar, C^8), 130.5 (s, Ar, C^9), 136.5 (s, Ar, C^{11}), 139.0 (s, Ar, C^3), 145.6 (s, Ar, C^6), 149.3 (s, Ar, C^{15}), 150.0 (s, Ar, C^{16,20}), 150.2 (s, Ar, C^{16,20}) 150.6 (s, Ar, C^7), 158.3 (s, Ar, C^5), 176.0 (s, Ar, C^1). Anal. Calcd for $C_{36}H_{53}N_2OSiY$ (646.30): C, 66.85; H, 8.26; N, 4.33; Y, 13.76. Found: C, 66.63; H, 8.03; N, 4.29; Y, 13.64.

Synthesis of $[N_2^{Ph}Y(\mu\text{-}H)(THF)]_2$ (7). $PhSiH_3$ (0.035 g, 0.318 mmol) was added to a solution of **5** (0.220 g, 0.318 mmol) in *n*-hexane (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and kept overnight at room temperature. The solution was concentrated under vacuum and was kept overnight at −20 °C. Complex **7** was isolated as a yellow microcrystalline solid in 69% yield (0.117 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 1.03 (br s, 8H, β-CH_2 THF), 1.18 (br m, 12H, CH(CH_3); H^{23,24,25,26}), 1.35 (br m, 12H, CH(CH_3), H^{23,24,25,26}), 1.55 (s, 12H, C(CH_3)$_2$, H^{13,14}), 3.21 (br m, together 12H, α-CH_2 THF and CH(CH$_3$), H^{21,22}), 6.84 (d, $^3J_{HH}$ = 7.6 Hz, 2H, CH Ar, H^2), 6.95 (d, $^3J_{HH}$ = 7.5 Hz, 2H, CH Ar, H^{18}), 7.04 (d, $^3J_{HH}$ = 7.5 Hz, 4H, CH Ar, C^{17,19}), 7.23 (m, together 4H, CH Ar, H^{3,10}), 7.36 (t, $^3J_{HH}$ = 7.0 Hz, 2H, CH Ar, H^9), 7.47 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH Ar, H^4), 7.76 (t, $^1J_{YH}$ = 27.7 Hz, 2H, Y(μ-H)), 7.85 (d, $^3J_{HH}$ = 7.8 Hz, 2H, CH Ar, H^{11}), 8.07 (d, $^3J_{HH}$ = 6.5 Hz, 2H, CH Ar, H^8). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 24.8 (s, β-CH_2 THF), 25.6 (s, CH(CH_3)$_2$, C^{23,24,25,26}), 27.5 (s, CH(CH_3)$_2$, C^{23,24,25,26}), 28.3 (s, CH(CH$_3$)$_2$, C^{21,22}), 29.2 (s, C(CH_3)$_2$, C^{13,14}), 66.2 (s, C(CH$_3$)$_2$, C^{12}), 70.0 (s, α-CH_2 THF), 115.2 (s, C^2), 115.5 (s, C^4), 122.2 (s, C^{18}), 122.8 (s, C^{17,19}), 123.1 (s, C^{11}), 125.1 (s, C^{10}), 126.9 (s, C^9), 138.0 (s, C^8), 138.6 (s, C^3), 147.8 (s, C^6), 148.1 (s, C^{15}), 148.9 (s, C^{16,20}), 164.0 (s, C^5), 176.0 (s, C^1), 193.1 (d, $^1J_{YC}$ = 46.2 Hz, YC). Anal. Calcd for $C_{60}H_{78}N_4O_2Y_2$ (1065.10): C, 67.66; H, 7.38; N, 5.26; Y, 16.69. Found: C, 67.23; H, 7.42; N, 5.15; Y, 16.43.

Synthesis of $[N_2^{Xyl}Y(\mu\text{-}H)(THF)]_2$ (8). $PhSiH_3$ (0.048 g, 0.444 mmol) was added to a solution of **6** (0.287 g, 0.444 mmol) in *n*-hexane (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and kept overnight at room temperature. The solution was concentrated under vacuum and was kept overnight at −20 °C. Complex **8** was isolated as an orange microcrystalline solid in 63% yield (0.157 g). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 1.03 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH(CH_3), H^{23,24,25,26}), 1.08 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH(CH_3), H^{23,24,25,26}), 1.13 (m, together 12H, CH(CH_3)$_2$ and C(CH_3)$_2$, H^{13,14,23,24,25,26}), 1.27 (br m, together 14H, CH(CH_3)$_2$ and β-CH_2 THF, H^{23,24,25,26}), 1.76 (d, $^2J_{HH}$ = 5.5 Hz, 2H, ArCH_2Y, H^8), 1.87 (d, $^2J_{HH}$ = 5.5 Hz, 2H, ArCH_2Y, H^{28}), 2.15 (s, 6H, C(CH_3)$_2$, C^{13,14}), 2.18 (s, 6H, ArCH_3, H^{27}) 2.83 (sept, $^3J_{HH}$ = 6.5 Hz, 2H, CH(CH$_3$), H^{21,22}), 2.92 (br m, 4H, α-CH_2 THF), 3.17 (br m, 4H, α-CH_2 THF), 4.33 (sept, $^3J_{HH}$ = 6.5 Hz, 2H, CH(CH$_3$), H^{21,22}), 6.32 (d, $^3J_{HH}$ = 6.5 Hz, 2H, CH Ar, H^2), 6.76 (d, $^3J_{HH}$ = 8.5 Hz, 2H, CH Ar, H^4), 6.81 (m, 4H, CH Ar, H^{9,10}), 6.88 (d, $^3J_{HH}$ = 7.8 Hz, 2H, CH Ar, H^8), 7.06 (m, 4H, CH Ar, H^{17,19}), 7.15 (m, 4H, CH Ar, H^{3,18}), 7.37 (t, $^1J_{YH}$ = 26.5 Hz, 2 H, YH). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 21.3 (s, C(CH_3)$_2$, C^{13,14}), 24.6 (s, CH(CH_3)$_2$, C^{23,24,25,26}), 24.5 (s, CH(CH$_3$)$_2$, C^{23,24,25,26}), 25.2 (s, C(CH_3)$_2$, C^{13,14}), 25.4 (s, CH(CH_3)$_2$, C^{23,24,25,26}), 25.5 (s, β-CH_2 THF), 26.3 (s, CH(CH_3)$_2$, C^{23,24,25,26}), 26.9 (s, CH(CH$_3$)$_2$, C^{21,22}), 27.7 (s, CH(CH$_3$)$_2$, C^{21,22}), 43.3 (s, ArCH_3, C^{27}), 51.3 (d,$^1J_{YC}$ = 24.9 Hz, YCH_2), 63.6 (s, C(CH$_3$)$_2$, C^{12}), 69.3 (s, α-CH_2 THF), 113.1 (s, C^4), 118.0 (s, C^2), 122.0 (s, C^{10}), 122.9 (s, C^{17,19}), 123.0 (s, C^{17,19}), 123.2 (s, C^{18}), 123.7 (s, C^8), 128.7 (s, C^9), 134.5 (s, C^3), 137.8 (s, C^{11}), 146.7 (s, C^6) 147.8 (s, C^{15}), 148.5 (s, C^{16,20}), 148.7 (s, C^{16,20}), 150.8 (s, C^7), 159.0 (s, C^5), 176.0 (s, C^1). Anal. Calcd for $C_{64}H_{86}N_4O_2Y_2$ (1121.20): C, 68.56; H, 7.73; N, 5.00; Y, 15.86. Found: C, 68.41; H, 7.33; N, 4.92; Y, 15.76.

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Supporting Information Available: Tables and CIF files giving crystallographic data for the compounds $N_2^{Xyl}Y(CH_2SiMe_3)(THF)$ (**6**) and $[N_2^{Ph}Y(\mu\text{-}H)(THF)]_2$ (**7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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