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Alkylyttrium Complexes of Amidine−Amidopyridinate Ligands. Intramolecular C(sp^3)−H Activation and Reactivity Studies

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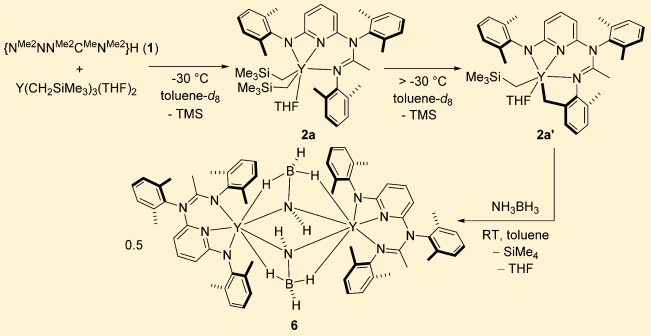
Supporting Information

ABSTRACT: The new multidentate amidine−aminopyridine proligand {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}H (**1**) was used in σ-bond metathesis reactions with the trialkyl precursors Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ and Y(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$. These reactions generate the dialkyl complexes {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}Y(CH$_2$SiMe$_3$)$_2$(THF) (**2a**) and {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}Y(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_2$ (**2b**), respectively, which were characterized by NMR spectroscopy and microanalysis (for **2b**). Complex **2a** is unstable at −30 °C in toluene and selectively undergoes intramolecular C(sp^3)−H activation to give {N^{Me2}NN^{Me2}C^{Me}N^{Me}−CH$_2$}Y(CH$_2$SiMe$_3$)(THF) (**2a′**), authenticated by X-ray crystallography, NMR spectroscopy, and elemental analysis. The reactivity of **2a′** toward a number of Lewis and Brønsted acids and bases as well as oxidants and reductants was explored. In the course of these studies, the new complexes {N^{Me2}NN^{Me2}C^{Me}N^{Me}CH$_2$B(C$_6$F$_5$)$_3$}Y(CH$_2$SiMe$_3$)(THF) (**3**), [{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH$_2$}Y(CH$_2$SiMe$_3$)(THF)$_x$]$^+$[BPh$_4$]$^-$ (**4**), {N^{Me2}NN^{Me2}C^{Me}N^{Me}CH$_2$}Y(*i*PrNC(PPh$_2$)N*i*Pr) (**5**), [{N^{Me2}NN^{Me2}C^{Me}N^{Me2}}Y{(μ_2-BH$_3$)(μ_2-NH)}]$_2$ (**6**), and [{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH$_2$(μ-O)}Y(CH$_2$SiMe$_3$)]$_2$ (**7**) were isolated and characterized by NMR spectroscopy and X-ray crystallography and microanalysis (for **6** and **7**). Complex **6** was found to be active in the ROP of *rac*-lactide, affording slightly heterotactic-enriched PLAs.



INTRODUCTION

Nitrogen-based donor ligands play a crucial role in modern non-metallocene polymerization catalysis.[1] Since the pioneering implementation of late-transition-metal catalysts incorporating α-diimine and bis(imino)pyridine ligand systems for the polymerization of olefins,[2] a stupendous amount of research has been directed toward the design of new polydentate ligand systems, and new efficient and stereoselective polymerization catalysts have been eventually created and intensely studied.[3] Several new classes of early-transition-metal polymerization catalysts have recently flourished, which incorporate N-based ligands with steric and electronic properties tunable almost at will, such as β-diketiminate,[4] tris(pyrazolyl)borate[5] and related ligands,[6] amidinate/guanidinate[7] and related aminopyridinates,[8] pyridyl−amido,[9] and some other scaffolds.[10]

Herein we report a new multidentate amidine−amidopyridinate ligand system derived from the parent bis(phenylamino)pyridine platform.[11] Due to the linear geometry and intrinsic multidentate coordination character, both the monoanionic and dianionic ligands, derived from the original bis(phenylamino)pyridine platform, essentially lead to di- and polymetallic bis(ligand) complexes. We anticipated that adding an auxiliary pendant donating group to the bis(phenylamino)pyridine ligand skeleton should give rise to a new perfectly chelating ligand system capable of stabilizing monometallic monoligand species, which would feature valuable reactivity. The coordination chemistry of the new amidine−amidopyridinate ligand system with yttrium, starting from yttrium tris-carbyl precursors, has been investigated. Special emphasis has been placed on (i) elucidation of intramolecular C−H activation reactions occurring in these yttrium alkyl complexes and (ii) exploration of the reactivity of these C−H activation products with different substrates. In addition, the efficacy of some complexes obtained during this study in representative polymerization reactions (vinyl polymerization of styrene and isoprene; ROP of *rac*-lactide) has been preliminarily investigated.

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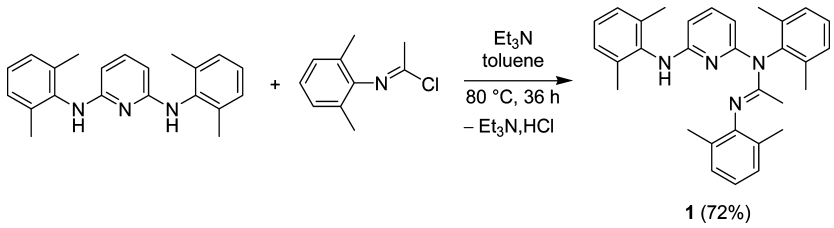
Scheme 1. Synthesis of Proligand 1



RESULTS AND DISCUSSION

Synthesis of Proligand {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}H (1). The amidine−aminopyridine proligand **1** was obtained straightforwardly by the one-step condensation of 2,6-bis(2,6-dimethylphenylamino)pyridine with *N*-(2,6-dimethylphenyl)-acetimidoyl chloride (Scheme 1). The product was isolated as an off-white solid in 72% yield and characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography.

Suitable crystals for X-ray diffraction studies of compound **1** were isolated by successive recrystallizations from diethyl ether. Figure 1 shows the molecular structure of **1**, along with selected metrical data. In the solid state, **1** adopts a geometry in which the amidine fragment deviates ca. 50° from the plane defined by the pyridine ring and the two adjacent nitrogen atoms (the dihedral angle between the plane of the Me−C(4)−N(3)−N(4) fragment and that of the pyridine ring is 50.0°). The C(2)−N(1), C(3)−N(3), and C(4)−N(3) bonds in **1** (1.373(3), 1.406(3), and 1.406(3) Å, respectively) are noticeably shorter than regular single C−N bonds (1.47−1.49 Å) observed in various organic compounds.[12] This is indicative of substantial n−π delocalization within the N(1)C(2)N(2)-C(3)N(3)C(4) fragment of **1**. The C(4)−N(4) distance of 1.276(3) Å is in agreement with double-bond character.

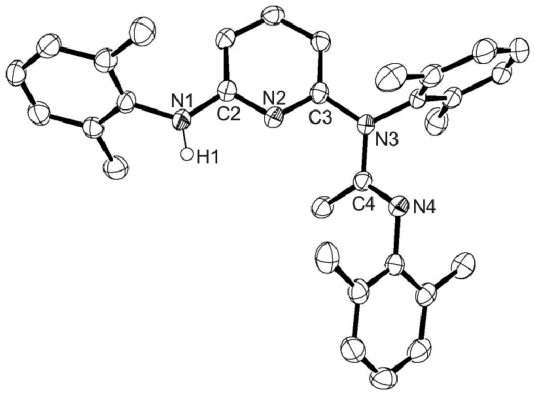


Figure 1. Molecular structure of {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}H (**1**). All hydrogen atoms, except that of the N−H group, are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): C(2)−N(1), 1.373(3); C(3)−N(3), 1.406(3); C(4)−N(3), 1.406(3); C(4)−N(4), 1.276(3); N(3)−C(4)−N(4), 117.3(2); N(1)−C(2)−N(2), 113.4(2); N(2)−C(3)−N(3), 114.6(2).

Synthesis of Dialkylyttrium Complexes. Recent studies of the chemistry of rare-earth metals have shown the alkane elimination approach, using homoleptic MR$_3$ precursors and amidine-based or related protio ligands, to be a straightforward route toward different classes of amidinate complexes.[13,14] In an attempt to obtain the corresponding bis(alkyl) complex incorporating a monoanionic {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}$^-$ ligand, the 1:1 reaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ and proligand **1** was conducted in toluene (Scheme 2). Unexpectedly, the standard workup led to the isolation in high yield of product **2a′**, which results from an intramolecular C−H activation of a methyl group of the amidine phenyl fragment.[15−17]

In situ monitoring by ^{1}H NMR spectroscopy showed that Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ reacts very slowly with 1 equiv of proligand **1** at −50 °C in toluene-d_8. Raising the temperature of the reaction to −30 °C led to its completion within several minutes, giving quantitatively {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}Y-(CH$_2$SiMe$_3$)$_2$(THF) (**2a**), with concomitant release of 1 equiv of SiMe$_4$ (Scheme 3). Due to its high instability, complex **2a** was rapidly characterized at this temperature by 1D and 2D (COSY, HMQC, and HMBC) ^{1}H NMR spectroscopic techniques. The ^{1}H NMR spectrum of **2a** (Figure S3; see the Supporting Information) contains two doublets of doublets (δ −0.50 and −0.36 ppm; $^2J_{H-H}$ = 11.5 Hz, $^2J_{Y-H}$ = 3.0 Hz) for the diastereotopic C*HH*SiMe$_3$ hydrogens and a series of singlet resonances for each of the Si*Me*$_3$ groups, the Me group of the imino unit, and the methyl groups of three 2,6-dimethylanilinic units, as well as two broadened signals for the α-CH$_2$ and β-CH$_2$ THF hydrogens. The aromatic region of the spectrum features characteristic doublets and one triplet ($^3J_{H-H}$ = 8.0 Hz) for the pyridine linker and multiplets for the aniline hydrogens. This pattern indicates an apparent C_s-symmetric coordination sphere around yttrium in **2a**.

Complex **2a** slowly undergoes intramolecular C−H activation at −30 °C following zero-order kinetics (k_{app} = (7.5 ± 0.4) × 10^{-3} M s^{-1}). The resulting product **2a′** is thermally quite robust and does not decompose even upon prolonged heating at elevated temperatures (up to 60 °C, days, benzene or toluene). Also, **2a′** is stable in pyridine-d_5 at room temperature; however, it rapidly reacts in this solvent at 70 °C to give a mixture of unidentified products.

The ^{1}H NMR spectrum of complex **2a′**, recorded in toluene-d_8 at room temperature (Figure S6; see the Supporting Information), is quite different from that of **2a**. Key resonances in the aliphatic region include (i) two doublets of doublets (δ −1.18 and −1.02 ppm, $^2J_{H-H}$ = 11.3 Hz, $^2J_{Y-H}$ = 3.0 Hz) for the diastereotopic hydrogens of the C*HH*SiMe$_3$ group and two doublets (δ 1.67 and 1.97 ppm; $^2J_{H-H}$ = 6.0 Hz, $^2J_{Y-H}$ = 2.0 Hz) for those of the C*HH*C$_6$H$_3$(CH$_3$)N group, (ii) one singlet for the Si*Me*$_3$ group, (iii) six singlets for methyl groups of the imino, the two 2,6-dimethylaniline, and one 6-methylaniline units, and (iv) two broad signals for the α-CH$_2$ and β-CH$_2$ THF hydrogens. In the ^{13}C{^{1}H} NMR spectrum, the *C*H$_2$SiMe$_3$ and *C*H$_2$C$_6$H$_3$(CH$_3$)N groups appear as two characteristic doublets (δ 23.1 ppm, $^1J_{Y-C}$ = 38.9 Hz; δ 43.7 ppm, $^1J_{Y-C}$ = 21.6 Hz, respectively).

On the other hand, the reaction of **1** with Y(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$, carried out under conditions identical with those used for the preparation of **2a′** (Scheme 3), resulted in the isolation in 85% yield of {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}Y(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_2$

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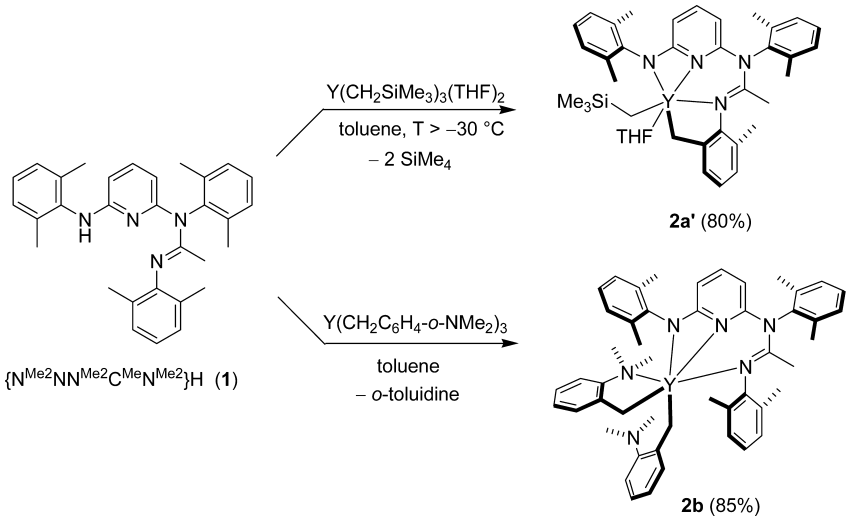
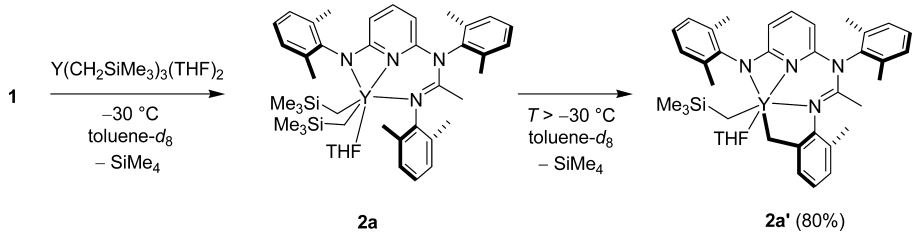
Scheme 2. Synthesis of Dialkylyttrium Complexes 2a′ and 2b



Scheme 3. Intramolecular C−H Activation of Complex 2a



(**2b**). Product **2b** is a yellow solid which appeared quite stable upon heating at elevated temperatures (up to 60 °C, days, aromatic hydrocarbons), not undergoing either C−H activation or other decomposition pathways. We assume that this stability may arise from the lower basicity of the benzyl group as compared to that of CH_2SiMe_3 and/or from the less sterically crowded coordination sphere in **2b**, notably due to the absence of coordinated THF molecule(s). The ^{1}H NMR spectrum of **2b**, in C_6D_6 at room temperature, is consistent with a dissymmetric structure on the NMR time scale (Figure S8; see the Supporting Information). In the $^{13}C\{^1H\}$ NMR spectrum (Figure S9; see the Supporting Information), two doublets are observed (δ 42.4 ppm, $^1J_{Y-C}$ = 32.0 Hz; δ 42.9 ppm, $^1J_{Y-C}$ = 26.3 Hz), which were assigned to the nonequivalent methylenic moieties. All attempts to obtain crystals of **2b** suitable for X-ray analysis failed.

Crystals of **2a′** suitable for X-ray diffraction studies were grown at room temperature from a toluene solution. The unit cell of **2a′** contains two crystallographically independent monomeric molecules, but those feature very similar geometries and overall organizations, and therefore the structural details of only one of them will be discussed. The molecular structure of complex **2a′** is shown in Figure 2. The coordination environment of the yttrium center in **2a′** is completed by three nitrogen atoms of the $\{N^{Me2}NN^{Me2}C^{Me}N^{Me}\}^{2-}$ ligand fragment, one oxygen atom from a THF molecule, one sp^3 carbon atom of the residual trimethylsilylmethyl group, and the sp^3 carbon atom of the "benzylic" group resulting from the C−H activation process. In addition, two close contacts (Y(1)···C(12), 2.845(5) Å; Y(1)···C(13), 2.907(5) Å) between the metal center and the sp^2 carbon atoms of the aromatic system of this "benzylic" group were identified. This may

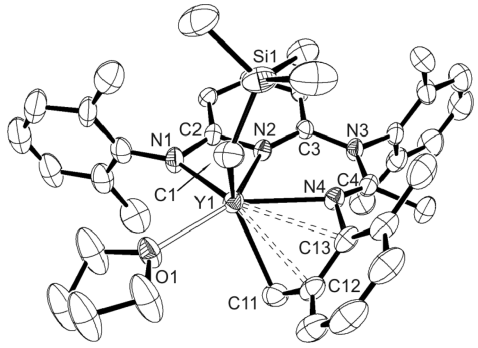


Figure 2. Molecular structure of $\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2\}Y(CH_2SiMe_3)(THF)$ (**2a′**). All hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Y(1)−N(1), 2.353(3); Y(1)−N(2), 2.344(3); Y(1)−N(4), 2.417(3); Y(1)−O(1), 2.389(3); Y(1)−C(11), 2.475(4); Y(1)−C(12), 2.845(5); Y(1)−C(13), 2.907(5); Y(1)−C(1), 2.418(4); C(2)−N(1), 1.343(5); C(2)−N(2), 1.378(5); C(3)−N(2), 1.338(5); C(3)−N(3), 1.434(5); C(4)−N(3), 1.388(6); C(4)−N(4), 1.280(5); N(1)−Y(1)−C(1), 109.9(1); Y(1)−C(11)−C(12), 89.4(3); N(3)−C(4)−N(4), 121.6(4).

increase the formal coordination number of yttrium in **2a′** up to 8 (vide infra). The amidopyridinato−amidinate ligand system in **2a′** is not strictly planar. The dihedral angle formed between the Y(1)N(1)N(2) plane and one of the pyridine rings is 168.2(4)°, while the dihedral angle between the NCN planes of the amidopyridinate and amidinate fragments is 161.9(4)°. The Y−C(carbyl) bond length in **2a′** (2.418(4) Å) is comparable with those reported for related yttrium systems (2.410(8)−2.439(3) Å).[18] These Y−C(alkyl) and the Y−C("benzyl") distances (2.418(4) and 2.475(4) Å, respectively)

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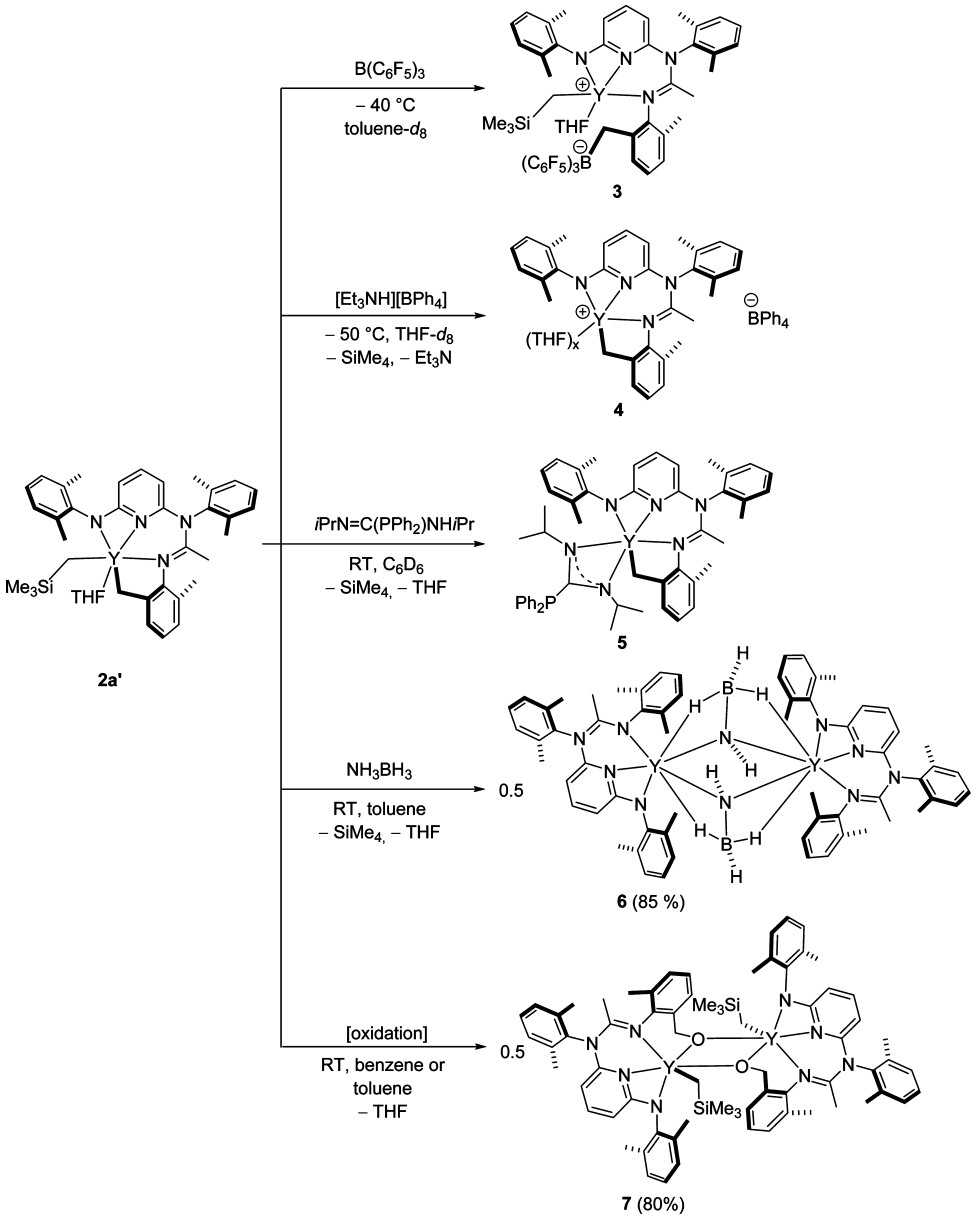
Scheme 4. Formation of Complexes 3−7



are quite comparable to those previously reported for an yttrium alkyl−benzyl species (2.4139(17) and 2.4520(18) Å, respectively) resulting from a related intramolecular C−H bond activation reaction.[17c] Among the Y−N bonds in **2a′**, that involving the amidinate nitrogen N(4) is the longest (2.417(3) Å). The bonding situation within the Y(1)N(1)N(2) fragment in **2a′** is quite different from those previously described in related yttrium amidopyridinate species, in which the two Y−N bond lengths are significantly different (ca. 0.1 Å).[17d,19] Here, the Y(1)−N(1) and Y(1)−N(2) bonds exhibit very similar lengths (2.353(3) and 2.344(3) Å, respectively).[20] The geometric parameters of the amidinate fragment in **2a′** prove its neutral state.[21] Also, the noticeable difference in the C(4)−N(3) and C(4)−N(4) bond lengths (1.281(5) and 1.389(5) Å, respectively) argues for the absence of charge delocalization within the NCN fragment.

The electronic structure of **2a′** was examined in more detail on the basis of DFT calculations. The overall geometry of this complex and that of proligand **1** thus computed are quite comparable with those observed in the solid state (see Computational Details in the Supporting Information). A natural population analysis (NPA) performed on the optimized structure of **2a′** revealed that no significant changes of the computed Wiberg bond indexes occurred for the C−N bonds in the dianionic $\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2\}^{2-}$ ligand skeleton, in comparison with those for the corresponding bonds and charges in the neutral proligand **1** (Table S2; see the Supporting Information). This result argues against distribution of the two negative charges over the entire ligand skeleton and, in particular, against considerable resonance of the nitrogen lone pair located on the N(3) atom into the π system of the ligand.[22] Very weak interactions between the sp^2 carbons C(12) and C(13) and the metal center were attested by the corresponding Wiberg bond indexes (0.06 and 0.05, respectively). A second-order perturbation NBO analysis also indicated weak interactions (highest stabilization energies of 2.5 and 3.9 kcal mol^{-1}, respectively) between these carbons and yttrium in **2a′**.[23] Thus, the coordination number at yttrium

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should be considered as more 6 than 8 (vide supra). Finally, the HOMO in **2a′** is localized mostly at the Y(1)−C(11) bond (Figure S21a; see the Supporting Information), while the HOMO-1 is predominantly the σ bond Y(1)−C(1) (Figure S21b; see the Supporting Information). On the basis of ground-state orbital control arguments, an electrophile (or an oxidant) would be predicted to attack initially at the HOMO: that is, via cleavage of the Y(1)−C("benzyl") bond.

Reactivity Studies of Complex 2a′. Given the dissimilar nature of the two alkyl groups in **2a′**, they may reveal different reactivity patterns toward appropriate substrates.[24] Hence, we set out to explore the reactivity of **2a′** with a variety of Lewis and Brønsted acids and bases, as well as oxidants and reductants (Scheme 4).

Instantaneous reaction of **2a′** with $B(C_6F_5)_3$ in toluene-d_8 solution was observed at −40 °C, as evidenced by ^{1}H NMR spectroscopy.[25] Formation of the zwitterionic complex **3** took place through chemoselective abstraction of the "benzylic" group $-CH_2C_6H_3(Me)N-$, while the CH_2SiMe_3 moiety remained intact. This is evidenced by the presence in the ^{1}H NMR spectrum of **3** (Figure S10; see the Supporting Information) of two doublets of doublets (δ −0.88 and −0.70 ppm, $^2J_{H-H}$ = 11.3 Hz, $^2J_{Y-H}$ = 3.3 Hz) for the diastereotopic hydrogens of the $CHHSiMe_3$ group and two broad signals integrating each for one hydrogen for the $(C_6F_5)_3BCHHC_6H_3(Me)N-$ moiety (δ 3.28 and 2.42 ppm; the latter overlaps with a methyl resonance). In the $^{13}C\{^1H\}$ NMR spectrum (Figure S13; see the Supporting Information), these two methylene groups appeared as a characteristic doublet (δ 39.6 ppm, $^1J_{Y-C}$ = 61.5 Hz) and a broadened signal (δ 23.5 ppm), respectively. The $^{19}F\{^1H\}$ NMR spectrum of **3** recorded at −40 °C (Figure S12; see the Supporting Information) contains a set of three broadened signals for the *o*-, *p*-, and *m*-F groups, which suggests possible dynamic processes. No evidence for nonvalent F···Y interactions was found.[26] Complex **3** rapidly decomposes in toluene solution above 0 °C, affording unidentified products.

Reaction of **2a′** with 1 equiv of $[Et_3NH]^+[BPh_4]^-$ in THF-d_8 does not take place below −20 °C.[25] Monitoring of the reaction by ^{1}H NMR spectroscopy at −10 °C showed that it follows first-order kinetics ($k_{app} = (1.1 \pm 0.1) \times 10^{-3}$ s^{-1}) and proceeds with concomitant evolution of Me_4Si. The major (>95%) product of this reaction, complex **4**, was characterized by a combination of NMR spectroscopic methods at 0 °C (Figures S14 and S15; see the Experimental Section and the Supporting Information) and appears overall as the protonolysis product of the CH_2SiMe_3 group in **2a′**.[27] The corresponding Y−C*HH*("benzyl") group appeared in the ^{1}H NMR spectrum as an AB system (δ 1.24 and 1.93 ppm, $^2J_{H-H}$ = 8.0 Hz) and as a doublet (δ 48.2 ppm, $^1J_{Y-C}$ = 26.0 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. Product **4** was found to be stable in THF solution at room temperature. However, all attempts to crystallize this compound have failed so far.

Reaction between **2a′** and 1 equiv of the phosphaguanidine *i*PrN═C(PPh$_2$)NH*i*Pr in C_6D_6 rapidly proceeded via selective protonolysis of the Y−CH_2SiMe_3 bond.[27] The corresponding product **5** formed quantitatively and was authenticated by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic studies (Figures S16−S18; see the Supporting Information). Complex **5** exists as a dissymmetric species in C_6D_6 solution, as evidenced by the presence in the ^{1}H NMR spectrum of six resonances from methyl groups of the $\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2\}$ ligand, two multiplets for the methine hydrogens, and four doublets for the methyl hydrogens of the nonequivalent *i*Pr groups of the phosphaguanidinate moiety. As in complex **4**, the Y−CH_2 group in **5** appears in the ^{1}H NMR spectrum as two doublets of doublets (δ 2.53 and 1.99 ppm, $^2J_{HH}$ = 5.9 Hz) and as a doublet (δ 47.0 ppm, $^1J_{Y-C}$ = 24.3 Hz) in the $^{13}C\{^1H\}$ NMR spectrum.

With the aim of synthesizing hydrido species with a monoanionic $\{N^{Me2}NN^{Me2}C^{Me}N^{Me2}\}^-$ ligand scaffold, efforts were made to explore the reactivity of **2a′** toward reagents such as H_2, $PhSiH_3$, and Ph_3SiH.[24,28] The reaction of **2a′** with H_2 (1 bar, 25 °C) in toluene-d_8 or in C_6D_6 (monitored by ^{1}H NMR spectroscopy) proceeded slowly over 5 days and afforded mixtures of unidentified products. Similarly, the reaction between equimolar amounts of **2a′** and $PhSiH_3$ in toluene-d_8 at room temperature resulted in rapid consumption of the initial reagents, however, giving rise to mixtures of unidentified products; no hydride resonance could be unambiguously identified. No reaction was observed between **2a′** and the more bulky Ph_3SiH in toluene-d_8 at room temperature over 1 day.

Amine−boranes $RNH_2{\cdot}BH_3$ (R = H, alkyl) have recently emerged as nonconventional sources of hydrogen for the synthesis of alkaline-earth-metal complexes having M−NH(R)·(μ-H)$_x$B(H)$_{3-x}$ bridging moieties.[29] In this study, the reaction of 1 equiv of $NH_3{\cdot}BH_3$[30] and **2a′** in toluene-d_8 at room temperature was monitored by ^{1}H NMR spectroscopy. Immediate release of Me_4Si was observed, while the product of this reaction, complex **6**, precipitated as a pale yellow crystalline solid. Compound **6** was resynthesized on a preparative scale by following this procedure. The very poor solubility of **6** in toluene and THF hampered its characterization by ^{13}C and ^{11}B NMR spectroscopy. Complex **6** was identified by ^{1}H NMR spectroscopy (Figure S19; see the Supporting Information), elemental analysis, and an X-ray crystallographic study.

Complex **6** crystallized as a toluene solvate (**6**·C_7H_8); its molecular structure and selected geometric parameters are given in Figure 3. The molecular structure of **6** consists of a centrosymmetric dimer, in which two $[(N^{Me2}NN^{Me2}C^{Me}N^{Me2})Y]$ moieties are bound by two μ-bridging dianionic NH·BH_3 fragments. The yttrium atoms are coordinated by three nitrogen atoms of the monoanionic $\{N^{Me2}NN^{Me2}C^{Me}N^{Me2}\}^-$ ligands and two nitrogens and two hydrogens of the NH·BH_3 groups, thus resulting in a formal coordination number of 7. In the BH_3 groups, two hydrogen atoms bridge both yttrium and boron atoms while the third remains terminal. The amidopyridinate fragment in **6** coordinates nearly symmetrically to the metal center, which is evidenced by the quite similar Y(1)−N(1) and Y(1)−N(2) bond lengths (2.403(2) and 2.377(2) Å, respectively), those being in the range reported for yttrium amidopyridinate complexes (2.289−2.554 Å).[8] The Y(1)−B(1) distance in **6** (2.767(3) Å) is longer than those reported for the borohydride complexes of yttrium incorporating anionic BH_4^- moieties (2.496−2.643 Å).[31]

Furthermore, **2a′** was found to be totally unreactive toward ethylene, propylene, and diphenylacetylene even upon prolonged heating at 60−80 °C in toluene-d_8. On the other hand, complex mixtures of products were obtained in the reactions of equimolar amounts of **2a′** and carbodiimide *i*PrN═C═N*i*Pr or isocyanate 3,4,5-$(CH_3O)_3C_6H_2N$═C═O, respectively, conducted in toluene at −50 °C.

During several independent attempts to recrystallize **2a′** from benzene or toluene solutions, crystals of the dimeric complex

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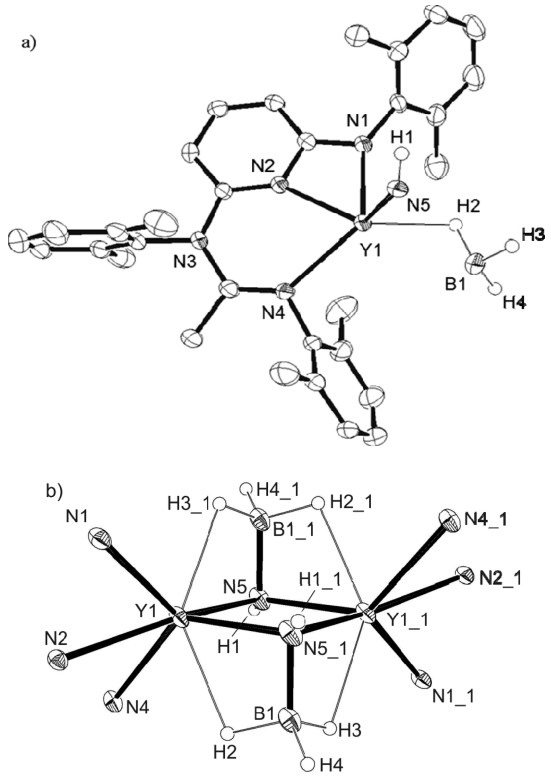

Figure 3. (a) Molecular structure of $[\{N^{Me2}NN^{Me2}C^{Me}N^{Me2}\}Y\{(\mu_2\text{-}BH_3)(\mu_2\text{-}NH)\}]_2\cdot C_7H_8$ (**6**·C_7H_8). Only the asymmetric unit is given. All hydrogen atoms and the solvent molecule are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. (b) Central bimetallic core of **6**·C_7H_8. Selected bond distances (Å) and angles (deg): Y(1)−N(1), 2.403(2); Y(1)−N(2), 2.377(2); Y(1)−N(4), 2.520(2); Y(1)−N(5), 2.243(2); Y(1)−B(1), 2.767(3); C(1)−N(1), 1.343(3); C(1)−N(2), 1.379(3); C(2)−N(2), 1.331(3); C(2)−N(3), 1.418(3); C(3)−N(3), 1.392(3); C(4)−N(4), 1.298(3); N(1)−C(1)−N(2), 111.2(2); N(2)−Y(1)−N(5), 101.40(8); N(5)−Y(1)−B(1), 82.78(9).

$[\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2(\mu\text{−}O)\}Y(CH_2SiMe_3)]_2$ (**7**) were recurrently isolated in significant amounts. They were separated and authenticated by X-ray diffraction analyses, NMR spectroscopy, and microanalysis. Complex **7** crystallized as solvates containing either one molecule of toluene (**7**·C_7H_8) or two molecules of benzene (**7**·$2C_6H_6$). The molecular structure of **7**·C_7H_8 is depicted in Figure 4. Different space groups and cell parameters were determined for these two adducts, but the general atom connectivity and bonding features were similar. In both cases, **7** adopts centrosymmetric dimeric structures differing in the mutual disposition of the $[(N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2O)Y(CH_2SiMe_3)]$ fragments. Interestingly, in **7**·$2C_6H_6$ the $[(N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2O)Y(CH_2SiMe_3)]$ moieties are located in *trans* positions relative to the Y_2O_2 plane, while in **7**·C_7H_8 they are oriented *cis*. Two identical $[\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2O\}Y(CH_2SiMe_3)]$ fragments are linked by two bridging OCH_2 groups. In **7**·$2C_6H_6$, the Y_2O_2 core is nearly equilateral, with very similar Y−O distances (2.282(2) and 2.287(2) Å; compare with the corresponding distances in **7**·C_7H_8, 2.236(2) and 2.263(2) Å). The yttrium centers in both **7**·C_7H_8 and **7**·$2C_6H_6$ lie in a distorted-octahedral environment, coordinated by three nitrogens of the $\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2O\}$ ligands, two oxygens of the bridging OCH_2 groups, and one carbon of the carbyl group. The Y−C(carbyl) bond lengths in **7**·C_7H_8 and **7**·$2C_6H_6$ are only slightly different (2.396(3) and 2.362(4) Å, respectively) and compare well with that observed in **2a′** (2.418(4) Å). Also, the Y(1)−N(1), Y(1)−N(2), and Y(1)−N(4) bond distances in **7**·$2C_6H_6$ (2.469(3), 2.414(3), and 2.509(3) Å, respectively) are noticeably longer than those found in **7**·C_7H_8 (2.397(2), 2.379(2), and 2.4493(2) Å, respectively), but these distances remain comparable with the corresponding distances in **2a′** and **6**.

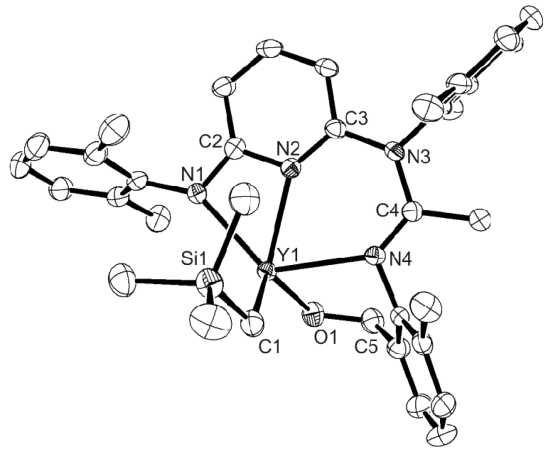

Figure 4. Molecular structure of $[\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2(\mu\text{-}O)\}Y(CH_2SiMe_3)]_2\cdot C_7H_8$ (**7**·C_7H_8). Only the asymmetric unit is given. All hydrogen atoms and the toluene molecule are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Y(1)−N(1), 2.397(2); Y(1)−N(2), 2.379(2); Y(1)−N(4), 2.493(2); Y(1)−O(1), 2.236(19); Y(1)−C(1), 2.396(3); C(5)−O(1), 1.406(3); C(2)−N(1), 1.342(3); C(2)−N(2), 1.379(3); C(3)−N(2), 1.342(3); C(3)−N(3), 1.417(3); C(4)−N(3), 1.397(4); C(4)−N(4), 1.292(3); N(4)−Y(1)−O(1), 76.93(7); N(1)−C(2)−N(2), 111.5(2).

The exogenous source of oxygen that resulted in the formation of **7** remained eventually unclear.[32] All attempts to generate in a controlled fashion a thio compound counterpart of complex **7** by reaction of **2a′** with both stoichiometric and substoichiometric amounts of S_8 in toluene-d_8 failed to afford the target product and led to the formation of intractable mixtures of unidentified materials.

Preliminary Polymerization Investigations. Due to the ongoing success of group 3 metal complexes applied in various catalytic polymerization processes,[1a,33] we sought to assess the abilities of some of the complexes obtained in this study in representative reactions.

First, no activity in isoprene and styrene polymerizations (bulk or toluene solutions, [monomer]/[Y] = 3000, T_{pol} = 25−60 °C) was observed with dialkyl complex **2a′**, employed as such or upon activation to generate in situ cationic systems: i.e., **2a′**/$B(C_6F_5)_3$/*i*Bu_3Al (1/1/200) and **2a′**/$[Ph_3C][B(C_6F_5)_4]$/*i*Bu_3Al (1/1/200). The inactivity of these systems may stem from either (i) the presence of a coordinated THF molecule in **2a′** which may impede monomer coordination or (ii) high instability of the cationic species under the given conditions.

We were also interested in assessing the performance of **6** as initiator/precatalyst of the ROP of *rac*-lactide, considering that this complex possesses original, potentially active nucleophilic $NHBH_3$ groups. Complex **6** actually proved to be moderately active at room temperature, especially in toluene, possibly reflecting solubility issues (Table 1, entry 1). Indeed, much better activity was observed in THF (entry 2). However, increasing the [*rac*-LA]/[Y] ratio appeared to be detrimental

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Table 1. Ring-Opening Polymerization of *rac*-Lactide Promoted by Complex 6

entry	compd	[LA]/[Ln]/[*i*PrOH]	solvent	time (min)[b]	conversn (%)[c]	M_n(calcd)[d] (10^3 g mol^{-1})	M_n(exptl)[e] (10^3 g mol^{-1})	M_w/M_n[e]	P_r[f]
1	**6**	100/1/0	toluene	1140	71	10.2	10.9	1.3	0.58
2	**6**	100/1/0	THF	5	62	8.9	13.0	1.3	0.56
3	**6**	500/1/0	THF	120	6	4.3	nd	nd	nd
4	**6**	1000/1/1	THF	1020	0	nd	nd	nd	nd

[a]General conditions: [*rac*-LA] = 2.0 mol L^{-1}, T = 25 °C. [b]Reaction times were not optimized. [c]Conversion of lactide as determined by ^{1}H NMR of the crude reaction mixture. [d]M_n values calculated considering one polymer chain per metal center from the relation: M_n(calcd) = conversion × [LA]/[Ln] × 144. [e]Experimental M_n and M_w/M_n values determined by GPC in THF vs PS standards and corrected with a factor of 0.58. [f]Determined by ^{1}H NMR; P_r is the probability of racemic linkage, as determined by ^{1}H NMR homodecoupling experiments.

and resulted in a significantly less active system (entry 3). The polymers formed had relatively narrow distributions and experimental molecular weights in good agreement with calculated values, assuming initiation of one polymer chain per $NHBH_3$ moiety (Table 1).[34] This observation hints at rather good initiation efficiency. The recovered PLAs were essentially atactic with a slight bias toward heterotacticity (P_r = 0.56−0.58). Surprisingly, addition of 1 equiv of *i*PrOH, a reagent often used as coinitiator to generate in situ alkoxide species,[35] did not improve the outcome of polymerization (entry 4).

CONCLUSIONS

A new multidentate ligand system combining amidopyridinate and amidine fragments into a chelating platform has been prepared. The reaction between the proligand $\{N^{Me2}NN^{Me2}C^{Me}N^{Me2}\}H$ (**1**) and $Y(CH_2SiMe_3)_3(THF)_2$ proceeds through the formation of dialkyl complex **2a**, which bears a monoanionic $\{N^{Me2}NN^{Me2}C^{Me}N^{Me2}\}^-$ ligand. The latter compound rapidly undergoes intramolecular C−H activation at a methylphenyl group, yielding selectively the hetero dialkyl species **2a′**, which bears a dianionic $\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2\}^{2-}$ ligand. On the other hand, a similar σ-bond metathesis reaction between **1** and $Y(CH_2C_6H_4$-*o*-$NMe_2)_3$ selectively afforded the stable dibenzyl species **2b**. The latter proved to be robust and does not undergo either intramolecular C−H activation reactions or other decomposition pathways.

Reactivity studies of hetero dialkyl **2a′** with various substrates revealed different patterns. In particular, **2a′** was found to react with Lewis and Brønsted acids as well as with (probably) dioxygen preferentially at the Y−("benzyl") bond. Thus, new complexes incorporating both monoanionic and dianionic multidentate ligands (products **3** and **6** and **4**, **5**, and **7**, respectively) have been synthesized and authenticated. The product of the reaction between **2a′** and $NH_3{\cdot}BH_3$, complex **6**, represents the first structurally characterized amidoborate derivative of group 3 metals. Complex **6** allowed the ring-opening polymerization of *rac*-lactide under mild conditions.

Ongoing studies in this field are focused on modifications of this amidine−amidopyridinate ligand system and elaboration of new polymerization catalysts derived thereof.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF, Et_2O) and Na/K alloy (toluene, hexane, and pentane) under nitrogen, degassed thoroughly, and stored under nitrogen prior to use. Deuterated solvents (benzene-d_6, toluene-d_8, THF-d_8; >99.5% D, Deutero GmbH and Euroisotop) were vacuum-transferred from Na/K alloy into storage tubes. $CDCl_3$ and CD_2Cl_2 were kept over calcium hydride and vacuum-transferred before use. The precursors *N*-(2,6-dimethylphenyl)acetimidoyl chloride,[36] Me_3SiCH_2Li,[37] $((CH_3)_3SiCH_2)_3Y(THF)_2$,[38] and $Y(CH_2C_6H_4$-*o*-$NMe_2)_3$[39] were prepared according to literature protocols. Styrene (99%, Acros) and isoprene (99%, Acros) were dried over CaH_2 and distilled under reduced pressure prior to experiments or stored at −30 °C under argon in the glovebox. *rac*-Lactide (Aldrich) was recrystallized once from *i*PrOH and twice from dry toluene and then dried under vacuum. Other starting materials were purchased from Acros, Strem, and Aldrich and used as received.

Instruments and Measurements. NMR spectra of complexes were recorded on Bruker AM-400 and AM-500 spectrometers in Teflon-valved NMR tubes at 25 °C, unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported in ppm vs $SiMe_4$ (δ 0.00), as determined by reference to the residual solvent peaks. ^{19}F and ^{31}P chemical shifts were determined by external reference to aqueous solutions of $NaBF_4$ and H_3PO_4, respectively. ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. Assignment of resonances was made from 2D ^{1}H−^{1}H COSY, ^{1}H−^{13}C HMQC, and HMBC NMR experiments. Coupling constants are given in hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations. Size exclusion chromatography (SEC) of PLAs was performed in THF (1 mL min^{-1}) at 20 °C using a Polymer Laboratories PL50 apparatus equipped with PLgel 5 μm MIXED-C 300 × 7.5 mm columns and combined RI and dual angle LS (PL-LS 45/90°) detectors. The number average molecular masses (M_n) and polydispersity indexes (M_w/M_n) of the polymers were calculated with reference to a universal calibration vs polystyrene standards. The M_n values of PLAs were corrected with a factor of 0.58 to account for the difference in hydrodynamic volumes between polystyrene and polylactide. The microstructure of PLAs was determined by homodecoupling ^{1}H NMR spectroscopy at 25 °C in $CDCl_3$ with a Bruker AC-500 spectrometer operating at 500 MHz.

***N,N′*-Bis(2,6-dimethylphenyl)pyridine-2,6-diamine.** This compound was prepared according to a modified literature procedure.[11b] 2,6-Dibromopyridine (8.00 g, 33.8 mmol) and 2,6-dimethylaniline hydrochloride (21.43 g, 136.0 mmol) were added in a 250 mL two-neck flask equipped with a stirring bar and a condenser. The mixture was heated to 220 °C. As the mixture melted, it turned dark orange. After 4 h of stirring under argon at this temperature, the reaction mixture was cooled. An aqueous solution of sodium carbonate (10%, 100 mL) was added to the mixture followed by extraction with Et_2O (100 mL). The organic phase was reduced to ca. 40 mL under reduced pressure, and then pentane (50 mL) was added. The crude precipitate was recrystallized from pentane to afford the analytically pure compound as an off-white solid (6.40 g, 20.2 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K):[40] δ 7.09 (m, 7H, *p*-Py and Ar), 6.19 (s, 2H, N*H*), 5.35 (d, $^3J_{H-H}$ = 7.9, 2H, *m*-Py), 2.26 (s, 12H, $(CH_3)_2C_6H_3N$).

$(N^{Me2}NN^{Me2}C^{Me}N^{Me2})H$ (1). To a solution of *N,N′*-bis(2,6-dimethylphenyl)pyridine-2,6-diamine (2.38 g, 7.50 mmol) in toluene (30 mL) was added Et_3N (1.04 mL, 7.50 mmol) and *N*-(2,6-dimethylphenyl)acetimidoyl chloride (1.32 mL, 7.50 mmol) with rigorous stirring. The reaction mixture was stirred at 80 °C for 3 days. Then the solvent was removed in vacuo. The resulting solid residue was dissolved in diethyl ether (100 mL) and washed with Na_2CO_3.

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The organic layer was separated and dried with $MgSO_4$, the solvent was removed, and the solid residue was recrystallized from diethyl ether. Compound **1** was isolated as a pale yellow powder (2.58 g, 5.40 mmol, 72%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.03 (m, 5H, $(CH_3)_2C_6H_3N$), 6.90 (m, 5H, *p*-Py and $(CH_3)_2C_6H_3N$), 6.27 (d, $^3J_{H-H}$ = 7.7, 1H, *m*-Py), 5.57 (d, $^3J_{H-H}$ = 7.9, 1H, *m*-Py), 5.06 (s, 1H, N*H*), 2.26 (s, 6H, $(CH_3)_2C_6H_3N$), 2.08 (s, 6H, $(CH_3)_2C_6H_3N$), 2.01 (s, 6H, $(CH_3)_2C_6H_3N$), 1.82 (s, 3H, NC(CH_3)N). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ 156.4 (C═N), 156.1, 155.1 (*o*-Py), 148.4, 142.5, 138.8, 137.4, 137.2, 136.5, 128.4, 128.2, 127.3, 127.0, 126.4, 122.0 (*p*-Py), 104.4 (*m*-Py), 99.5 (*m*-Py), 18.6 (NC(CH_3)N), 18.5 ($(CH_3)_2C_6H_3N$), 18.2 ($(CH_3)_2C_6H_3N$), 18.0 ($(CH_3)_2C_6H_3N$). Anal. Calcd for $C_{31}H_{34}N_4$: C, 80.48; H, 7.41; N, 12.11. Found: C, 80.35; H, 7.53; N, 12.17.

Reaction of 1 with $Y(CH_2SiMe_3)_3(THF)_2$. *NMR Scale Synthesis of* ***2a****.* In the glovebox, a Teflon-valved NMR tube was charged with **1** (0.050 g, 0.11 mmol) and $Y(CH_2SiMe_3)_3(THF)_2$ (0.061 g, 0.11 mmol). To this mixture, toluene-d_8 (0.6 mL) was vacuum-transferred in and the tube was shaken for 15 min at −50 °C. Quantitative formation of **2a** was observed. ^{1}H NMR (500 MHz, toluene-d_8, 243 K): δ 7.11 (d, $^3J_{H-H}$ = 7.8, 3H, $(CH_3)_2C_6H_3N$), 6.98 (m, 2H, $(CH_3)_2C_6H_3N$), 6.92 (d, $^3J_{H-H}$ = 7.5, 2H, $(CH_3)_2C_6H_3N$), 6.73 (d, $^3J_{H-H}$ = 7.7, 2H, $(CH_3)_2C_6H_3N$), 6.44 (t, $^3J_{H-H}$ = 8.0, 1H, *p*-Py), 5.39 (d, $^3J_{H-H}$ = 8.0, 1H, *m*-Py), 4.73 (d, $^3J_{H-H}$ = 8.0, 1H, *m*-Py), 3.59 (br. s, 12H, α-CH_2 THF), 2.52 (s, 6H, $(CH_3)_2C_6H_3N$), 2.22 (s, 6H, $(CH_3)_2C_6H_3N$), 1.84 (s, 6H, $(CH_3)_2C_6H_3N$), 1.39 (br s, 12H, β-CH_2, THF), 0.95 (s, 3H, NC(CH_3)N), 0.21 (s, 18H, SiMe_3), −0.34 (dd, $^2J_{H-H}$ = 11.4, $^2J_{Y-H}$ = 3.0, 2H, CH*H*SiMe$_3$), −0.50 (dd, $^2J_{H-H}$ = 11.4, $^2J_{Y-H}$ = 3.0, 2H, C*H*HSiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, toluene-d_8, 243 K): δ 167.5 (*o*-Py), 161.6 (NC(CH_3)N), 145.6, 142.0 (*p*-Py) 141.5, 138.9, 135.7, 132.3, 131.4, 129.2, 128.4, 101.1 (*m*-Py), 93.4 (*m*-Py), 67.8 (α-CH_2 THF), 36.9 (CH_2SiMe_3), 25.1 (β-CH_2 THF), 19.5, 19.2 ($(CH_3)_2C_6H_3N$), 18.7 (NC(CH_3)N), 17.3 ($(CH_3)_2C_6H_3N$), 3.6 (CH_2Si*Me*$_3$).

($N^{Me2}NN^{Me2}C^{Me}N^{Me}$-$CH_2$)Y($CH_2SiMe_3$)(THF) (2a′). To a solution of **1** (1.30 g, 2.80 mmol) in toluene (10 mL) was added a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (1.40 g, 2.80 mmol) in toluene (25 mL). The reaction mixture was stirred at room temperature overnight. All volatiles were evaporated in vacuo, and the crude product was recrystallized from toluene to give yellow crystals of **2a′** (1.60 g, 2.20 mmol, 80%). ^{1}H NMR (500 MHz, toluene-d_8, 298 K): δ 7.07 (m, 2H, $(CH_3)_2C_6H_3N$), 7.04 (d, $^3J_{H-H}$ = 7.4, 1H, $(CH_3)_2C_6H_3N$), 7.00 (s, 1H, $CH_2(CH_3)C_6H_3N$), 6.92 (m, 2H, $CH_2(CH_3)C_6H_3N$), 6.86 (d, $^3J_{H-H}$ = 7.5, 1H, $(CH_3)_2C_6H_3N$), 6.78 (d, $^3J_{H-H}$ = 7.4, 1H, $(CH_3)_2C_6H_3N$), 6.73 (d, $^3J_{H-H}$ = 7.3, 1H, $(CH_3)_2C_6H_3N$), 6.63 (t, $^3J_{H-H}$ = 8.2, 1H, *p*-Py), 5.37 (d, $^3J_{H-H}$ = 8.2, 1H, *m*-Py), 4.84 (d, $^3J_{H-H}$ = 8.2, 1H, *m*-Py), 3.56 (br s, 9H, α-CH_2 THF), 2.46 (s, 3H, $(CH_3)_2C_6H_3N$), 2.26 (s, 3H, $(CH_3)_2C_6H_3N$), 2.25 (s, 3H, $CH_2(CH_3)$-C_6H_3N), 2.18 (s, 3H, $(CH_3)_2C_6H_3N$), 1.97 (dd, $^2J_{H-H}$ = 6.0, $^2J_{Y-H}$ = 0.5, 1H, C*H*H$(CH_3)C_6H_3N$), 1.86 (s, 3H, $(CH_3)_2C_6H_3N$), 1.67 (dd, $^2J_{H-H}$ = 6.0, $^2J_{Y-H}$ = 2.0, 1H, CH*H*$(CH_3)C_6H_3N$), 1.39 (s, 3H, NC(CH_3)N), 1.34 (br s, β-CH_2 THF), 0.12 (s, 9H, SiMe_3), −1.02 (dd, $^2J_{H-H}$ = 11.3, $^2J_{Y-H}$ = 3.0, 1H, CH*H*SiMe$_3$), −1.18 (dd, $^2J_{H-H}$ = 11.3, $^2J_{Y-H}$ = 3.0, 1H, C*H*HSiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, toluene-d_8, 298 K): δ 167.5 (*o*-Py), 158.4 (NC(CH_3)N), 149.9 (NCN), 147.0 ($(CH_3)_2C_6H_3N$), 141.7 (*p*-Py), 140.8, 139.3, 137.1, 136.9, 136.8, 133.3, 132.8, 131.9, 130.6, 129.2, 128.8, 128.1, 123.1, 123.0, 119.3, 99.9 (*m*-Py), 93.6 (*m*-Py), 63.9 (α-CH_2 THF), 43.7 (d, $^1J_{Y-C}$ = 21.6, $CH_2(CH_3)C_6H_3N$), 25.1 (β-CH_2 THF), 23.1 ($^1J_{Y-C}$ = 38.9, CH_2SiMe_3), 19.5, 19.2, 19.1($CH_3)_2C_6H_3N$), 18.9 (NC(CH_3)N), 17.4 ($(CH_3)_2C_6H_3N$), 17.0 ($CH_2(CH_3)C_6H_3N$), 4.7 (SiMe_3). Anal. Calcd for $C_{78}H_{102}N_8O_2Si_2Y_2$: C, 65.99; H, 7.38; N, 7.89. Found: C, 65.73; H, 7.50; N, 7.96.

($N^{Me2}NN^{Me2}C^{Me}N^{Me2}$)Y($CH_2C_6H_4$-*o*-$NMe_2$)$_2$ (2b). To a solution of **1** (0.47 g, 0.99 mmol) in toluene (10 mL) was added a solution of $Y(CH_2C_6H_4$-*o*-$NMe_2)_3$ (0.50 g, 0.99 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature overnight. All volatiles were evaporated in vacuo, and the crude product was recrystallized from toluene to afford pure **2b** as a yellow solid (0.69 g, 0.84 mmol, 85%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.09 (d, $^3J_{H-H}$ = 7.5, 3H, $(CH_3)_2C_6H_3N$), 7.03 (m, 2H, C_6H_4-*o*-NMe_2), 6.99−6.87 (m, 14H, $(CH_3)_2C_6H_3N$ and C_6H_4-*o*-NMe_2), 6.79 (t, $^3J_{H-H}$ = 8.0, 2H, C_6H_4-*o*-NMe_2), 6.72 (d, $^3J_{H-H}$ = 8.0, 1H, C_6H_4-*o*-NMe_2), 6.61 (m, 2H, C_6H_4-*o*-NMe_2, *p*-Py), 6.45 (d, $^3J_{H-H}$ = 8.5, 1H, C_6H_4-*o*-NMe_2), 5.34 (d, $^3J_{H-H}$ = 8.0, 1H, *m*-Py), 4.79 (d, $^3J_{H-H}$ = 8.0, 1H, *m*-Py), 2.44 (s, 9H, $(CH_3)_2C_6H_3N$), 2.33 (s, 3H, $(CH_3)_2C_6H_3N$), 2.28 (br s, 6H, $(CH_3)_2C_6H_3N$), 2.24 (s, 3H, $(CH_3)_2C_6H_3N$), 2.23 (br m, 1H, CH*H*C_6H_4-*o*-NMe_2), 2.18 (s, 3H, C_6H_4-*o*-NMe_2), 1.89 (s, 3H, C_6H_4-*o*-NMe_2),1.85 (br d, $^2J_{H-H}$ = 10.2, 1H, C*H*HC_6H_4-*o*-NMe_2), 1.83 (br m, 1H, C*H*HC_6H_4-*o*-NMe_2), 1.77 (s, 3H, C_6H_4-*o*-NMe_2), 1.66 (s, 3H, C_6H_4-*o*-NMe_2), 1.35 (s, 3H, NC(CH_3)N), 0.91 (d, $^2J_{H-H}$ = 10.2, 1H, CH*H*C_6H_4-*o*-NMe_2). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 298 K): δ 167.9 (*o*-Py), 158.7 (NCN), 152.8, 149.8, 146.1, 144.8 (C^4aro), 141.6 (*p*-Py), 139.2, 138.9, 137.2, 136.9, 136.8, 134.4, 132.7, 132.2, 132.1 (C^4, $(CH_3)_2C_6H_3N$)), 131.1 ($(CH_3)_2C_6H_3N$), 130.7 (C^4, C_6H_4-*o*-NMe_2), 129.2, 129.1, 129.1, 128.8 (C_6H_4-*o*-NMe_2), 128.2, 126.4, 124.5, 123.4, 122.7 ($(CH_3)_2C_6H_3N$), 120.1, 119.0, 118,5, 118.2 (C_6H_4-*o*-NMe_2), 99.8 (*m*-Py), 93.2 (*m*-Py), 45.4 ($(CH_3)_2C_6H_3N$), 43.8 ($(CH_3)_2C_6H_3N$), 42.9 (d, $^1J_{Y-C}$ = 26.3, $CH_2C_6H_4$-*o*-NMe_2), 42.4 ($^1J_{Y-C}$ = 32.0, $CH_2C_6H_4$-*o*-NMe_2), 41.8 ($(CH_3)_2C_6H_3N$), 18.9 ($(CH_3)_2C_6H_3N$), 18.8 (NC(CH_3)N), 18.4 ($(CH_3)_2C_6H_3N$), 18.1, 17.4, 17.0, 16.9 (C_6H_4-*o*-NMe_2). Anal. Calcd for $C_{49}H_{57}N_6Y$: C, 71.87; H, 7.02; N, 10.26; Y, 10.86. Found: C, 71.65; H, 7.15; N, 10.30; Y, 10.95.

Reaction of 2a′ with $B(C_6F_5)_3$. *NMR Scale Synthesis of* ***3****.* In the glovebox, a Teflon-valved NMR tube was charged with **2a′** (0.040 g, 0.056 mmol) and $B(C_6F_5)_3$ (0.032 g, 0.056 mmol). To this mixture, toluene-d_8 (0.6 mL) was vacuum-transferred in and the tube was shaken for 15 min at −50 °C. The progress of the reaction was monitored at −40 °C by NMR spectroscopy. ^{1}H NMR indicated that **3** formed quantitatively after 1−2 min. ^{1}H NMR (400 MHz, toluene-d_8, 233 K): δ 7.62 (d, $^3J_{H-H}$ = 8.0, 1H, $(CH_3)_2C_6H_3N$), 7.14 (s, 1H, $CH_2(CH_3)C_6H_3N$), 7.06 (s, 1H, $CH_2(CH_3)C_6H_3N$), 6.99 (s, 1H, $CH_2(CH_3)C_6H_3N$), 6.92 (t, $^3J_{H-H}$ = 7.6, 1H, $(CH_3)_2C_6H_3N$), 6.71 (m, 2H, $(CH_3)_2C_6H_3N$), 6.58 (t, $^3J_{H-H}$ = 8.4, 2H, $(CH_3)_2C_6H_3N$), 6.33 (t, $^3J_{H-H}$ = 8.2, 1H, *p*-Py), 5.29 (d, $^3J_{H-H}$ = 8.2, 1H, *m*-Py), 4.75 (d, $^3J_{H-H}$ = 8.2, 1H, *m*-Py), 3.50 (br m, $^2J_{H-H}$ = 6.4, 2H, α-CH_2 THF), 3.37 (br m, $^2J_{H-H}$ = 6.4, 2H, α-CH_2 THF), 3.28 (br s, 1H, C*H*HB(C_6F_5)), 2.42 (br s, 1H, CH*H*B(C_6F_5) and 3H, $(CH_3)_2C_6H_3N$), 2.36 (s, 3H, $CH_2(CH_3)C_6H_3N$), 2.00 (s, 3H, $(CH_3)_2C_6H_3N$), 1.89 (s, 3H, $(CH_3)_2C_6H_3N$), 1.74 (s, 3H, $(CH_3)_2C_6H_3N$), 1.25 (s, 3H, NC(CH_3)-N), 1.11 (br m, $^2J_{H-H}$ = 6.0, 4H, β-CH_2 THF), 0.08 (s, 9H, SiMe_3), −0.70 (dd, $^2J_{H-H}$ = 11.3, $^2J_{Y-H}$ = 3.3, 1H, CH*H*SiMe$_3$), −0.88 (dd, $^2J_{H-H}$ = 10.6, $^2J_{Y-H}$ = 2.2, 1H, C*H*HSiMe$_3$). ^{13}C{^{1}H} NMR (100 MHz, toluene-d_8, 233 K) (signals from carbons of the C_6F_5 moieties in the aromatic region were not identified): δ 168.5 (NCN), 159.6 (NC(CH_3)N), 147.8 NCN, 144.7 (Caro), 144.6 (*p*-Py), 136.8, 135.5, 133.2, 132.1, 131.9, 131.3, 130.8, 130.5, 130.1, 130.0, 129.5 ($(CH_3)_2C_6H_3N$), 129.3, 129.1, 128.4 ($CH_2(CH_3)C_6H_3N$), 126.5, 126.2, 125.2 ($(CH_3)_2C_6H_3N$), 102.7, 95.4 (*m*-Py), 71.9 (α-CH_2 THF), 39.6 (d, $^1J_{Y-C}$ = 61.5, CH_2SiMe_3), 25.7 (β-CH_2THF), 23.5 (br s, $CH_2B(C_6F_5)$), 21.8 ($(CH_3)_2C_6H_3N$), 21.5 ($CH_2(CH_3)C_6H_3N$), 20.2 (NC(CH_3)N), 19.6 ($(CH_3)_2C_6H_3N$), 18.6 ($(CH_3)_2C_6H_3N$), 17.0 ($(CH_3)_2C_6H_3N$), 5.00 (SiMe_3). ^{11}B NMR (128 MHz, toluene-d_8, 233 K): δ −12.6. ^{19}F{^{1}H} NMR (376 MHz, toluene-d_8, 233 K): δ −133.1 (br m, 6F, *o*-F), −160.1 (br m, 3F, *p*-F), −164.2 (br m, 6F, *m*-F).

Reaction of 2a′ with $[HNEt_3]^+[BPh_4]^-$. *NMR Scale Synthesis of* ***4****.* In the glovebox, a Teflon-valved NMR tube was charged with **2a′** (0.040 g, 0.056 mmol) and $[HNEt_3]^+[BPh_4]^-$ (0.024 g, 0.056 mmol). To this mixture, THF-d_8 (0.6 mL) was vacuum-transferred in and the tube was shaken for 15 min at −70 °C. The progress of the reaction was monitored at −50 °C by NMR spectroscopy. ^{1}H NMR indicated that **4** formed quantitatively after 2 min. ^{1}H NMR (400 MHz, THF-d_8, 273 K): δ 7.36 (m, 2H, $(CH_3)_2C_6H_3N$), 7.31 (br m, 8H, B(C_6H_5)), 7.11−7.04 (m, 4H, *p*-Py and $(CH_3)_2C_6H_3N$), 6.95−6.91 (m, 4H, $CH_2(CH_3)C_6H_3N$ and $(CH_3)_2C_6H_3N$), 6.88 (t, $^3J_{H-H}$ = 7.4, 8H, B(C_6H_5)), 6.74 (t, $^3J_{H-H}$ = 7.1, 4H, B(C_6H_5)), 6.58 (d, $^3J_{H-H}$ = 7.0, 1H, $CH_2(CH_3)C_6H_3N$), 5.48 (d, $^3J_{H-H}$ = 8.6, *m*-Py), 5.10 (d, $^3J_{H-H}$ = 7.8, *m*-Py), 2.49 (q, $^3J_{H-H}$ = 7.1, 6H, CH_2, Et_3N), 2.37 (s, 3H,

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(CH_3)$_2$C$_6$H$_3$N), 2.23 (s, 3H, (CH_3)$_2$C$_6$H$_3$N), 2.20 (s, 3H, CH$_2$(CH_3)-C$_6$H$_3$N), 2.17 (s, 3H, (CH_3)$_2$C$_6$H$_3$N), 2.05 (s, 3H, (CH_3)$_2$C$_6$H$_3$N), 1.93 (d, $^2J_{H-H}$ = 8.0, 1H, CH_2(CH$_3$)C$_6$H$_3$N), 1.87 (s, 3H, NC(CH_3)N), 1.24 (d, $^2J_{H-H}$ = 8.0, 1H, CH_2(CH$_3$)C$_6$H$_3$N), 1.02 (t, $^3J_{H-H}$ = 7.1, 9H, CH_3, Et$_3$N). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 273 K): δ 166.9 (*o*-Py), 164.2 (B(C$_6$H$_5$), 161.8 (NC(CH$_3$)N), 147.2 ((CH_3)$_2$C$_6$H$_3$N), 144.8 (CH$_2$(CH_3)C$_6$H$_3$N), 141.8 (*p*-Py), 138.8 ((CH_3)$_2$C$_6$H$_3$N), 137.5 (CH$_2$(CH_3)C$_6$H$_3$N), 136.7, 135.8, 132.5, 129.7, 128.8, 128.2, 127.6, 124.5 ((CH_3)$_2$C$_6$H$_3$N), 122.6 (CH$_2$(CH_3)C$_6$H$_3$N), 120.1 ((CH_3)$_2$C$_6$H$_3$N), 101.8 (*o*-Py), 93.4 (*o*-Py), 48.2 (d, $^1J_{Y-C}$ = 26.0, CH_2(CH$_3$)C$_6$H$_3$N), 47.3 (CH_2, Et$_3$N), 20.6 (NC(CH_3)-N), 18.6 (CH$_2$(CH_3)C$_6$H$_3$N), 17.6 ((CH_3)$_2$C$_6$H$_3$N), 17.0 ((CH_3)$_2$C$_6$H$_3$N), 11.5 (CH_3, Et$_3$N). ^{11}B NMR (128 MHz, THF-d_8, 273 K): δ −6.6.

Reaction of 2a′ with *i*PrN═C(PPh$_2$)N(H)*i*Pr. *NMR Scale Synthesis of* **5**. In the glovebox, a Teflon-valved NMR tube was charged with **2a′** (0.040 g, 0.057 mmol) and *i*PrN═C(PPh$_2$)-N(H)*i*Pr (0.017 g, 0.057 mmol). To this mixture, C$_6$D$_6$ (0.6 mL) was vacuum-transferred in and the tube was shaken for 15 min at room temperature. ^{1}H NMR indicated that **5** formed quantitatively. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ 7.46 (m, 4H, P(C$_6H_5$)$_2$), 7.29 (d, $^3J_{H-H}$ = 7.8, 1H, (CH_3)$_2$C$_6H_3$N), 7.24−7.18 (m, 4H, (CH_3)$_2$C$_6H_3$N and P(C$_6H_5$)$_2$), 7.13−7.07 ((CH_3)$_2$C$_6H_3$N and CH$_2$(CH_3)C$_6H_3$N), 7.03 (d, $^3J_{H-H}$ = 6.9, 2H, CH$_2$(CH_3)C$_6H_3$N), 7.00 (m, 2H, (CH_3)$_2$C$_6H_3$N), 6.93 (t, $^3J_{H-H}$ = 7.5, 2H, (CH_3)$_2$C$_6H_3$N), 6.84 (d, $^3J_{H-H}$ = 7.7, 1H, (CH_3)$_2$C$_6H_3$N), 6.77 (d, $^3J_{H-H}$ = 7.4, 1H, (CH_3)$_2$C$_6H_3$N), 7.73 (d, $^3J_{H-H}$ = 7.2, 1H, (CH_3)$_2$C$_6H_3$N), 6.63 (t, $^3J_{H-H}$ = 8.0, 1H, *p*-Py), 5.45 (d, $^3J_{H-H}$ = 8.0, 1H, *m*-Py), 4.81 (d, $^3J_{H-H}$ = 8.0, 1H, *m*-Py), 4.24 (br sept, $^3J_{H-H}$ = 6.2, 1H, CH(CH_3)$_2$), 3.48 (br sept, $^3J_{H-H}$ = 5.9, 1H, CH(CH_3)$_2$), 2.53 (d, $^2J_{H-H}$ = 5.7, 1H, CHH(CH_3)C$_6$H$_3$N), 2.43 (s, 3H, (CH_3)$_2$C$_6$H$_3$N), 2.41 (s, 3H, (CH_3)$_2$C$_6$H$_3$N), 2.15 (s, 3H, CH$_2$(CH_3)C$_6$H$_3$N), 2.12 (s, 3H, (CH_3)$_2$C$_6$H$_3$N), 1.99 (d, $^2J_{H-H}$ = 5.7, 1H, CHH(CH$_3$)C$_6$H$_3$N), 1.81 (s, 3H, (CH_3)$_2$C$_6$H$_3$N), 1.40 (s, 3H, NC(CH_3)N), 1.09 (d, $^3J_{H-H}$ = 6.2, 3H, CH(CH_3)$_2$), 0.95 (d, $^3J_{H-H}$ = 6.2, 3H, CH(CH_3)$_2$), 0.92 (d, $^3J_{H-H}$ = 5.9, 3H, CH(CH_3)$_2$), 0.24 (d, $^3J_{H-H}$ = 5.9, 3H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 298 K): δ 171.1 (d, $^1J_{P-C}$ = 55.8, NC(PPh$_2$)N), 167.8 (*o*-Py), 159.7 (NC(CH$_3$)N), 149.7 (*o*-Py), 146.5 ((CH_3)$_2$C$_6$H$_3$N), 141.8, 141.5, 139.0, 137.1, 136.5, 135.3, 135.2, 134.5, 134.3, 134.1, 133.9 (d, $^2J_{P-C}$ = 19.5, PPh_2), 133.1 (d, $^2J_{P-C}$ = 19.5, PPh_2), 132.2 (d, $^2J_{P-C}$ = 16.5, PPh_2), 131.8 (d, $^2J_{P-C}$ = 16.5, PPh_2), 133.4, 133.2, 133.1(CH_3)$_2$C$_6$H$_3$N, 131.3, 129.4, 129.1, 128.9, 128.4 (CH$_2$(CH_3)C$_6$H$_3$N), 126.6, 125.8, 123.1, 119.8 ((CH_3)$_2$C$_6$H$_3$N), 100.1 (*m*-Py), 93.0 (*m*-Py), 48.9, 48.7 (CH(CH_3)$_2$), 47.0 (d, $^1J_{Y-C}$ = 24.3, CH_2(CH$_3$)C$_6$H$_3$N), 26.8, 25.7, 24.6, 24.5 (CH(CH_3)$_2$), 19.7 (NC(CH_3)N), 19.4 (CH$_2$(CH_3)C$_6$H$_3$N), 19.2 ((CH_3)$_2$C$_6$H$_3$N), 19.0 ((CH_3)$_2$C$_6$H$_3$N), 17.2 ((CH_3)$_2$C$_6$H$_3$N), 17.1 ((CH_3)$_2$C$_6$H$_3$N). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 298 K): δ −19.5 (d, J_{Y-P} = 6.6, 1P).

[{N^{Me2}NN^{Me2}C^{Me}N^{Me2}}Y{(μ_2-BH$_3$)(μ_2-NH)}]$_2$ (6). *Protocol A.* In the glovebox, a Teflon-valved NMR tube was charged with **2a′** (0.040 g, 0.056 mmol) and NH$_3$BH$_3$ (0.0017 g, 0.056 mmol). To this mixture, toluene-d_8 (0.6 mL) was vacuum-transferred in and the tube was shaken for 15 min at room temperature. NMR indicated quantitative conversion of the reagents to **6**.

Protocol B. To a solution of **2a′** (0.200 g, 0.28 mmol) in toluene (3 mL) was added NH$_3$·BH$_3$ (0.0087 g, 0.28 mmol) in toluene (2 mL). The crude product was precipitated from toluene to give pure **6** as yellow crystals (0.69 g, 0.84 mmol, 85%). ^{1}H NMR (500 MHz, toluene-d_8, 298 K): δ 7.09 (d, $^3J_{H-H}$ = 7.4, 2H, (CH_3)$_2$C$_6H_3$N), 6.90 (m, 3H, (CH_3)$_2$C$_6H_3$N), 6.77 (d, $^3J_{H-H}$ = 7.7, 3H, (CH_3)$_2$C$_6H_3$N), 6.58 (t, $^3J_{H-H}$ = 8.5, 1H, *p*-Py), 5.39 (d, $^3J_{H-H}$ = 8.2, 1H, *m*-Py), 4.71 (d, $^3J_{H-H}$ = 7.9, 1H, *m*-Py), 2.44 (s, 6H, (CH_3)$_2$C$_6$H$_3$N), 2.26 (s, 6H, (CH_3)$_2$C$_6$H$_3$N), 1.92 (s, 6H, (CH_3)$_2$C$_6$H$_3$N), 1.08 (s, 3H, NC(CH_3)-N), 0.20 (br m, 2H, BH), 0.12 (br m, 2H, BH). Due to the very low solubility of **6** in toluene-d_8 and THF-d_8, no informative ^{13}C NMR spectrum could be recorded. Anal. Calcd for C$_{38}$H$_{45}$N$_5$BY: C, 67.97; H, 6.75; N, 10.43; Y, 13.24. Found: C, 67.78; H, 6.86; N, 10.47; Y, 13.59.

Isolation of [{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH$_2$(μ-O)}Y(CH$_2$SiMe$_3$)]$_2$ (7).[32] To a solution of **1** (0.43 g, 0.93 mmol) in toluene (25 mL) was added a solution of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.46 g, 0.93 mmol) in hexane (10 mL). The reaction mixture was stirred for 1 h at 0 °C. All volatiles were evaporated in vacuo, and a mixture of toluene/hexane (3/1) was vacuum-transferred onto the crude solid product. Yellow crystals of **7** rapidly grew from this solution at room temperature (0.55 g, 0.74 mmol, 80%). ^{1}H NMR (500 MHz, toluene-d_8, 333 K): δ 7.32 (d, $^3J_{H-H}$ = 7.3, 1H, (CH_3)$_2$C$_6H_3$N), 7.14 (d, $^3J_{H-H}$ = 7.6, 1H, (CH_3)$_2$C$_6H_3$N), 7.11 (s, 2H, C$_6H_5$CH$_3$), 7.06 (d, $^3J_{H-H}$ = 7.4, 1H, CH$_2$(CH_3)C$_6H_3$N), 7.03 (s, 2H, CH$_2$(CH_3)C$_6H_3$N), 7.01 (s, 3H, C$_6H_5$CH$_3$), 6.96 (t, $^3J_{H-H}$ = 6.0, 2H, (CH_3)$_2$C$_6H_3$N), 6.92 (d, $^3J_{H-H}$ = 6.7, 2H, (CH_3)$_2$C$_6H_3$N), 6.79 (t, $^3J_{H-H}$ = 7.5, 1H, (CH_3)$_2$C$_6H_3$N), 6.65 (t, $^3J_{H-H}$ = 8.2, 1H, *p*-Py), 5.38 (d, $^3J_{H-H}$ = 8.2, 1H, *m*-Py), 4.8 (d, $^3J_{H-H}$ = 8.2, 1H, *m*-Py), 4.62 (d, $^2J_{H-H}$ = 12.1, 1H, OCH_2), 4.28 (d, $^2J_{H-H}$ = 12.1, 1H, OCH_2), 2.64 (s, 3H, (CH_3)$_2$C$_6H_3$N), 2.34 (s, 3H, (CH_3)$_2$C$_6H_3$N), 2.31 (s, 3H, CH$_2$(CH_3)C$_6H_3$N), 2.19 (s, 6H, (CH_3)$_2$C$_6H_3$N), 2.13 (m, 3H, C$_6H_5CH_3$), 1.10 (s, 3H, NC(CH_3)N), 0.28 (s, 9H, SiMe_3), −0.39 (dd, $^2J_{H-H}$ = 11.7, $^2J_{Y-H}$ = 3.1, 1H, CHHSiMe$_3$), −1.02 (dd, $^2J_{H-H}$ = 11.7, $^2J_{Y-H}$ = 3.1, 1H, CHHSiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, toluene-d_8, 333 K): δ 167.8 (*o*-Py), 159.8 (NC(CH$_3$)N), 147.7 ((CH_3)$_2$C$_6H_3$N), 145.1 (CH$_2$(CH_3)C$_6H_3$N), 141.0 (*p*-Py), 140.4 ((CH_3)$_2$C$_6H_3$N), 137.3 (CH$_2$(CH_3)C$_6H_3$N), 136.7 (C$_6H_5$CH$_3$), 130.7 ((CH_3)$_2$C$_6H_3$N), 128.7 (C$_6H_5$CH$_3$), 127.9 (CH$_2$(CH_3)C$_6H_3$N), 127.7 ((CH_3)$_2$C$_6H_3$N), 124.9 ((CH_3)$_2$C$_6H_3$N), 122.8 ((CH_3)$_2$C$_6H_3$N), 100.4 (*m*-Py), 92.9 (*m*-Py), 65.2 (OCH_2), 29.4 (CH_2SiMe$_3$), 19.6 (NC(CH_3)N), 19.4, 18.9 ((CH_3)$_2$C$_6H_3$N), 18.2 (CH$_2$(CH_3)C$_6H_3$N), 18.1 (C$_6H_5$CH$_3$), 17.6 ((CH_3)$_2$C$_6H_3$N), 4.6 (SiMe_3). Anal. Calcd for C$_{84}$H$_{102}$N$_8$O$_2$Si$_2$Y$_2$: C, 67.63; H, 7.03; N, 7.51; Y, 11.92. Found: C, 67.45; H, 7.14; N, 7.57; Y, 11.95.

Crystal Structure Determination of 1, 2a′, 6, and 7. Diffraction data were collected at 150(2) or 250(2) K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal structures were solved by direct methods; the remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SIR97 and SHELXL-97).[41] Many hydrogen atoms could be located from the Fourier difference analysis. Other hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom positions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and details of data collection and structure refinement for the different compounds are given in Table S1 (see the Supporting Information). Detailed crystallographic data (excluding structure factors) are available as Supporting Information, as CIF files.

Typical Procedure for Polymerization of *rac*-Lactide. In a typical experiment (Table 1, entry 2), in the glovebox, a Schlenk flask was charged with a solution of **6** (11.0 mg, 14.7 μmol) in toluene (0.728 mL). *rac*-Lactide (0.21 g, 1.47 mmol, 100 equiv vs Y) was added rapidly to this solution. The mixture was immediately stirred with a magnetic stir bar at 20 °C for the appropriate time. The reaction was quenched by adding ca. 1 mL of a 10% H$_2$O solution in THF, and the polymer was precipitated from CH$_2$Cl$_2$/pentane (ca. 2 mL/100 mL) five times. The polymer was then filtered and dried in vacuo to constant weight.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving details of the computations, representative NMR spectra of proligand **1** and yttrium complexes, and crystallographic data for **1**, **2a′**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews see: (a) Gromada, J.; Carpentier, J.-F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397−410. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−315.

(2) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203. (b) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745−1776.

(3) Budagumpia, S.; Kimb, K.-H.; Kim, I. *Coord. Chem. Rev.* **2011**, *255*, 2785−2809.

(4) (a) Hamaki, H.; Takeda, N.; Nabika, M.; Tokitoh, N. *Macromolecules* **2012**, *45*, 1758−1769. (b) Li, D.; Li, S.; Cui, D.; Zhang, X. *Organometallics* **2010**, *29*, 2186−2193. (c) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132−2133. (d) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3065.

(5) Hasumi, S.; Itagaki, K.; Zhang, S.; Nomura, K. *Macromolecules* **2011**, *44*, 773−777 and references cited therein.

(6) Chen, C.; Lee, H.; Jordan, R. F. *Organometallics* **2010**, *29*, 5373−5381 and references cited therein.

(7) (a) Epshteyn, A.; Trunkley, E. F.; Kissounko, D. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **2009**, *28*, 2520−2526 and references cited therein. (b) Volkis, V.; Lisovskii, A.; Tumanskii, B.; Shuster, M.; Eisen, M. S. *Organometallics* **2006**, *25*, 2656−2666 and references cited therein. (c) Collins, S. *Coord. Chem. Rev.* **2011**, *255*, 118−138.

(8) (a) Haas, I.; Kretschmer, W. P.; Kempe, R. *Organometallics* **2011**, *30*, 4854−4861. (b) Hafee, M.; Kretschmer, W. P.; Kempe, R. *Eur. J. Inorg. Chem.* **2011**, *36*, 5512−5522. (c) Noor, A.; Kretschmer, W. P.; Glatz, G.; Meetsma, A.; Kempe, R. *Eur. J. Inorg. Chem.* **2008**, *32*, 5088−5098.

(9) (a) Luconi, L.; Rossin, A.; Tuci, G.; Tritto, I.; Boggioni, L.; Klosin, J. J.; Theriault, C. N.; Giambastiani, G. *Chem. Eur. J.* **2012**, *18*, 681−687 and references cited therein. (b) Zuccaccia, C.; Busico, V.; Cipullo, R.; Talarico, G.; Froese, R. D. G.; Vosejpka, P. C.; Hustad, P. D.; Macchioni, A. *Organometallics* **2009**, *28*, 5445−5458 and references cited therein..

(10) Zimmermann, M.; Tornroos, K. W.; Waymouth, R. M.; Anwander, R. *Organometallics* **2004**, *27*, 4310−4317 and references cited therein.

(11) (a) Huang, Y.-L.; Lu, D.-Y.; Yu, H.-C.; Yu, J.-S. K.; Hsu, C.-W.; Kuo, T.-S.; Lee, G.-H.; Tsai, Y.-C. *Angew. Chem., Int. Ed.* **2012**, *51*, 7781−7785. (b) Cotton, F. A.; Daniels, L. M.; Alei, P.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2001**, *40*, 2778−2784. (c) Polamo, M. *Acta Crystallogr.* **1996**, *CS2*, 2980−2982.

(12) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(13) For recent references on rare-earth amidinate chemistry, see: (a) Bambirra, S.; Perazzolo, F.; Boot, S. J.; Sciarone, T. J. J.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 704−712. (b) Bambirra, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3454−3462. (c) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182−9183. (d) Harder, S. *Dalton Trans.* **2010**, *39*, 6677−6681. (e) Bambirra, S.; Van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2003**, 522−523.

(14) Sinenkov, M.; Kirillov, E.; Roisnel, T.; Fukin, G.; Trifonov, A. A.; Carpentier, J.-F. *Organometallics* **2011**, *30*, 5509−5523.

(15) For examples of C−H bond activation reactions involving Cp rare-earth complexes, see: (a) Evans, W. J.; Champagne, T. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2006**, *128*, 14270−14271. (b) Evans, W. J.; Perotti, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 1068−1069. (c) Okuda, J. *Dalton Trans.* **2003**, 2367−2378. (d) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276−277. (e) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G. *Organometallics* **1996**, *15*, 2720−2726. (f) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291−2302. (g) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1989**, *8*, 2454−2461. (h) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203−219. (i) den Haan, K. H.; Wiestra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053−2060. (j) Watson, P. L.; Parshall, G. B. *Acc. Chem. Res.* **1985**, *18*, 51−56. (k) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491−6493.

(16) For examples of C−H bond activation reactions involving Cp-free rare-earth complexes, see: (a) Sigiyama, H.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R.; Thiele, S. K.-H. *Organometallics* **2004**, *23*, 5054−5061. (b) Emslie, D. J. H.; Piers, W. E.; Parvez, M. *Dalton Trans.* **2003**, 2615−2620. (c) Emslie, D. J. H.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 4226−4240. (d) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; Van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511−3522. (e) Duchateau, R.; Van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931−4932. (f) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2026−2036.

(17) For recent reports on C−H bond activation reactions with yttrium complexes, see: (a) Lu, E.; Gan, W.; Chen, Y. *Dalton Trans.* **2011**, *40*, 2366−2374. (b) Luconi, L.; Lyubov, D. M.; Bianchini, C.; Rossin, A.; Faggi, C.; Fukin, G. K.; Cherkasov, A. V.; Shavyrin, A. S.; Trifonov, A. A.; Giambastiani, G. *Eur. J. Inorg. Chem.* **2010**, 608−620. (c) Lyubov, D. M.; Fukin, G. K.; Cherkasov, A. V.; Shavyrin, A. S.; Trifonov, A. A.; Luconi, L.; Bianchini, C.; Meli, A.; Giambastiani, G. *Organometallics* **2009**, *28*, 1227−1232. (d) Skvortsov, G. G.; Fukin, G. K.; Trifonov, A. A.; Noor, A.; Döring, C.; Kempe, R. *Organometallics* **2007**, *26*, 5770−5773.

(18) (a) Wang, D.; Cui, D.; Miao, M.; Huang, B. *Dalton Trans.* **2007**, 4576−4581. (b) Liu, X.; Shang, X.; Tang, T.; Hu, N.; Pei, F.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 2747−2757. (c) Cai, C.-X.; Toupet, L.; Lehmann, C. W.; Carpentier, J.-F. *J. Organomet. Chem.* **2003**, *683*, 131−136. (d) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 782−785.

(19) Lyubov, D. M.; Döring, C.; Fukin, G. K.; Cherkasov, A. V.; Shavyrin, A. S.; Kempe, R.; Trifonov, A. A. *Organometallics* **2008**, *27*, 2905−2907.

(20) Such an unusual situation is apparently caused by formation of the Y−C bond, resulting in redistribution of the 2− negative charge over the entire $\{N^{Me2}NN^{Me2}C^{Me}N^{Me}CH_2\}^{2-}$ skeleton.

(21) For comparison, see: (a) Edelmann, F. T. *Chem. Soc. Rev.* **2009**, *38*, 2253−2268. (b) Edelmann, F. T. *Adv. Organomet. Chem.* **2008**, *57*, 183−352. (c) Coles, M. P. *Dalton Trans.* **2006**, 985−1001. (d) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481. (e) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300.

(22) The planarity of the N(3) atom is most likely due to the steric crowding provided by the bulky aryl substituents.

(23) These include donor−acceptor interactions between the core electrons of electron-donating carbon atoms C(12) and C(13) and the accepting LP* (one-center valence antibonding lone pair) and RY* (one-center Rydberg) orbitals of yttrium.

(24) Amidopyridinate complexes of yttrium, incorporating CH_2SiMe_3 and another σ-bonded (benzyl, aryl, and heteroaryl) pendant group, exhibited different reactivities toward $PhSiH_3$ and H_2.[17d]

(25) A similar reaction between **2a′** and 1 equiv of $[Ph_3C]^+[B(C_6F_5)_4]^-$, monitored by NMR spectroscopy in the −50 to 0 °C temperature range in toluene-d_8, afforded unidentified products.

(26) Intramolecular (ortho aryl)C−F···Zr interactions in zwitterionic metallocene $[C_4H_6{-}B(C_6F_5)_3]$ complexes have been identified by ^{19}F NMR spectroscopy in solution from unusually strong upfield shifts of the signals for the corresponding F groups (−208 to −212 ppm). See: Erker, G. *Acc. Chem. Res.* **2001**, *34*, 309−317 and references cited therein.

(27) The global outcome of this protonolysis reaction does not contradict the aforementioned orbital control rule if the reaction is assumed to proceed stepwise: i.e., (i) protolytic cleavage of the Y(1)−C("benzyl") bond in **2a′** and formation of the monoalkyl complex and (ii) intramolecular C−H bond activation in this intermediate, resulting in release of the final product by re-forming the Y(1)−C("benzyl") bond with concomitant elimination of $SiMe_4$. Formation of **4** via such a stepwise process or by direct protonolysis of the CH_2SiMe_3 group in **2a′** still remains an open question.
(28) (a) Konkol, M.; Okuda, J. *Coord. Chem. Rev.* **2008**, *252*, 1577−1591. (b) Trifonov, A. A. *Russ. Chem. Rev.* **2007**, *76*, 1051−1072. (c) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193−2242. (d) Nishiura, M.; Hou, Z. *Nat. Chem.* **2010**, *2*, 257−268. (e) Hou, Z.; Nishiura, M.; Shima, T. *Eur. J. Inorg. Chem.* **2007**, 2535−2545. (f) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193−2242.
(29) (a) Bellham, P.; Hill, M. S.; Kociok-Kohn, G.; Liptrot, D. J. *Dalton Trans.* **2013**, *42*, 737−745. (b) Hill, M. S.; Hodgson, M.; Liptrot, D. J.; Mahon, M. F. *Dalton Trans.* **2011**, *40*, 7783−7790. (c) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; McDougall, D. J. *Chem. Eur. J.* **2010**, *16*, 8508−8515. (d) Spielmann, J.; Harder, S. *J. Am. Chem. Soc.* **2009**, *131*, 5064−5065. (e) Spielmann, J.; Bolte, M.; Harder, S. *Chem. Commun.* **2009**, 6934−6936.
(30) The analogous reaction of **2a′** with tBuNH$_2$·BH$_3$ in toluene was essentially not selective, giving an intractable mixture of unidentified products.
(31) (a) Demir, S.; Siladke, N. A.; Ziller, J. W.; Evans, W. J. *Dalton Trans.* **2012**, *41*, 9659−9666. (b) Jenter, J.; Roesky, P. W.; Ajellal, N.; Guillaume, S. M.; Susperregui, N..; Maron, L. *Chem. Eur. J.* **2010**, *16*, 4629−4638.
(32) It is worth noting that cleavage of the THF molecule, which could serve as a source of oxygen, would be highly unlikely. Although the origin of the oxygen atom in complex **7** could not be conclusively identified, it seems that its likely source is when both toluene and hexane solvents were vacuum-transferred onto solid **2a′** in order to eventually recrystallize it (see the Experimental Section), which apparently contaminated the medium with trace amounts of adventitious oxygen. At the same time, attempts to obtain selectively complex **7** by deliberately introducing small amounts of pure oxygen in the toluene solution of **2a′** during the recrystallization step resulted in the formation of intractable mixtures.
(33) For leading reviews on the ROP of cyclic esters with complexes of group 3 metals, see: (a) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176. (b) Wu, J.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *205*, 602. (c) Thomas, C. M. *Chem. Soc. Rev.* **2010**, *39*, 165. (d) Buffet, J.-C.; Okuda, J. *Polym. Chem.* **2011**, *2*, 2758.
(34) The ROP of lactide, initiated by the Y−NHBH$_3$ functions and followed by acidic workup, should afford PLAs bearing −CH(CH$_3$)OH and −C(═O)NH$_2$ end groups. Only signals from −CH(CH$_3$)OH termini were unambiguously identified in the ^{1}H NMR spectra of polymers prepared with complex **6** (Table 1, entries 1 and 2).
(35) (a) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39−48. (b) Ajellal, N.; Carpentier, J.-F.; Guillaume, C.; Guillaume, S.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalton Trans.* **2010**, *39*, 8363−8376.
(36) (a) Hill, M. S.; Hitchcock, P. B.; Mansell, S. M. *Dalton Trans.* **2006**, 1544−1553. (b) Whitener, G. D.; Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1249−1255.
(37) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664−4670.
(38) (a) Lappert, M. F.; Pearce, R. J. *J. Chem. Soc., Chem. Commun.* **1973**, 126−127. (b) Schumann, H.; Freckmann, D. M.; Dechert, S. Z. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2422−2426.
(39) Harder, S. *Organometallics* **2005**, *24*, 373−379.
(40) Faust, A.; Wolff, O.; Waldvogel, S. R. *Synthesis* **2009**, 155−159.
(41) (a) Sheldrick, G. M. *SHELXS-97, Program for the Determination of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997. (c) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.