Group 3 Dialkyl Complexes with Tetradentate (L, L, N, O; L = N, O, S) Monoanionic Ligands: Synthesis and Reactivity

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Tripodal, tetradentate phenols, $(LCH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-OH (L = CH_2OCH_3 (**1**), CH_2NEt_2 (**2**), 2-C_5H_4N (**3**), CH_2SCMe_3 (**5**), CH_2NMe_2 (**6**)), were synthesized, and metalations were performed via alkane elimination from yttrium and scandium trialkyl complexes to generate the corresponding dialkyl complexes $[(LCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]MR_2 (M = Y, L = OCH_3, R = CH_2SiMe_2Ph (**7a**); M = Y, L = NEt_2, R = CH_2SiMe_2Ph (**7b**); M = Sc, L = OCH_3, R = CH_2SiMe_2Ph (**8a**); M = Sc, L = $SCMe_3$, R = CH_2SiMe_2Ph (**8b**); M = Y, L = OCH_3, R = CH_2SiMe_3 (**9**); M = Sc, L = OCH_3, R = CH_2SiMe_3 (**10**)). X-ray crystallographic studies show that **7a**,**b** and **8a** adopt, in the solid state, mononuclear structures of C_1 symmetry. The ^{1}H NMR spectra of these dialkyl complexes in benzene-d_6 at high temperatures reveal exchange processes involving the ether groups and the alkyl groups. The dynamic behavior of species **7a**, **8a**, and **10** in toluene-d_8 was investigated by variable-temperature ^{1}H NMR spectroscopy. The activation parameters of the fluxional processes for **7a**, **8a**, and **10** were determined by line-shape and Eyring analyses (for **7a**, $\Delta H^{\ddagger} = 7.3 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -16 \pm 1.4$ cal/(mol K); for **8a**, $\Delta H^{\ddagger} = 9.9 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -15.3 \pm 1.8$ cal/(mol K); for **10**, $\Delta H^{\ddagger} = 10.8 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = -11.4 \pm 1.9$ cal/(mol K)). These data establish that the dialkyl complexes **7a**, **8a**, and **10** undergo a nondissociative exchange process. The scandium dialkyl complex $[(C_5H_4N$-2-$CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]$Sc(CH_2SiMe_2Ph)_2$ (**11**) was found to undergo clean activation of a C−H bond of a methylene linking a pyridine to the central nitrogen donor. This process follows first-order kinetics ($k = [2.8(3)] \times 10^{-4}$ s^{-1} at 0 °C). The yttrium dialkyl complexes **7a** and **9** react with 1 equiv of $[PhNHMe_2]^+[B(C_6F_5)_4]^-$ in chlorobenzene-d_5, to generate a solution that slowly polymerizes ethylene. Compounds **7**−**10** also polymerize ethylene with low activity upon activation with MAO.

Introduction

Cationic alkyl complexes of group 4 metals are the most common single-site olefin polymerization catalysts.[1−3] Isoelectronic, neutral alkyl complexes of group 3 metals generally show much lower polymerization activity.[4] One approach to increasing polymerization activity involves the generation of cationic alkyl species. The most common route to cationic alkyl species involves alkide abstraction from neutral dialkyl or trialkyl complexes. Over the past few years the synthesis of dialkyl and trialkyl complexes of group 3 metals supported by multidentate ligands has been an area of increasing interest.[5−21] Recent reports indicate that, upon activation, the resulting cationic alkyl complexes display promising polymerization activities.[8−10,13,20] However, group 3 still remains a relatively unexplored part of the transition series in the context of olefin polymerization.[2,3]

As part of our continuing interest in developing novel polymerization catalysts, we have explored new ligand designs to support cationic group 3 alkyl complexes. Accordingly, a

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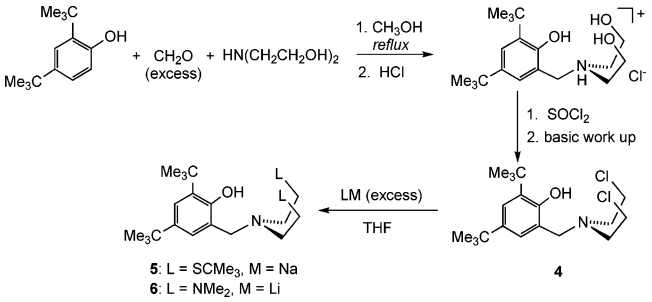
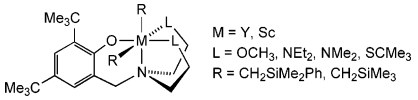
Scheme 1

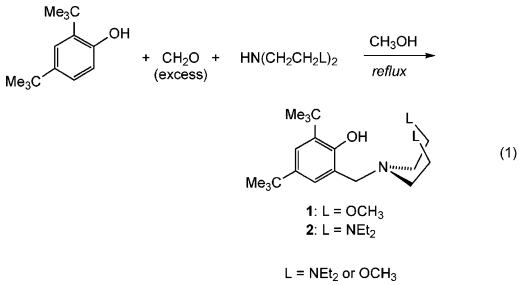


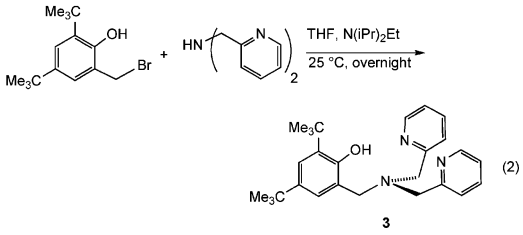
series of [L_2NO] (L = neutral donor; N = tertiary amine; O = phenolate) monoanionic, tripodal ligands was targeted. There is precedent in the literature for related [N_3O] monoanionic ligands to support zinc(II) and copper(I) complexes[22−25] as well as for [S_2NO] ligands to support copper(II) complexes.[26] Complexes supported by triazacyclononanes functionalized with one pendant phenolate arm have been reported as well.[15,27] Furthermore, related tetradentate amino phenolate ligands have been recently shown to support group 3−5 alkyl complexes.[15,28−34] Group 4 dialkyls supported by diphenolate ligands were reported to be active olefin polymerization catalysts when activated, and in some cases, isotactic poly-1-hexene and polypropylene are obtained.[34−36] These reports indicate that monoanionic [L_2NO] frameworks could be used as robust ancillary ligands. Inspired by the promising precedents, we prepared a new series of [L_2NO] ligands, and the ability of these to support group 3 dialkyl species was investigated (see below). This report describes the synthesis and reactivity of a series of yttrium and scandium alkyl complexes with such tetradentate phenolate ligands. After we started work on this project, two of the ligands described herein were reported by others to support early-metal complexes. Ligand **1**, $(CH_3OCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-OH, was recently reported by Kol et al. as part of a study of a number of zirconium complexes,[37] while ligand **2**, $(Et_2NCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-OH, was reported by Arnold et al. as part of a study of group 3 catalysts for the polymerization of lactide and ϵ-caprolactone.[38]



Results and Discussion

Ligand and Metal Dialkyl Complex Syntheses. (a) Synthesis of $(LCH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-OH (L = CH_2OCH_3, CH_2NEt_2, 2-C_5H_4N). A modification of the Mannich condensation used by Kol et al. to synthesize tetradentate diphenolate ligands was employed for the synthesis of tetradentate monophenolate ligands **1** and **2** (eq 1).[39] Using a related strategy,





compound **3** was prepared from the corresponding benzyl bromide and secondary amine (eq 2). Compounds **1**−**3** were synthesized using commercially available or easily accessible starting materials. These procedures afford the desired products in close to quantitative yields. The phenols obtained in this fashion do not require additional purification before metalation.

(b) Synthesis of $(LCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-OH (L = $SCMe_3$, NMe_2). An alternative route to [L_2NO] ligand frameworks involves nucleophilic substitution on dichloride **4** (Scheme 1). This synthetic route was developed to gain access to ligand precursors for which the appropriate secondary amine starting materials required for the Mannich condensation are not commercially available. Compound **4** has been readily prepared in two steps from commercially available starting materials via Mannich condensation followed by chlorination with thionyl chloride. The nucleophilic substitution step could present a problem due to the unprotected phenol functionality; however, the example shown affords the desired product **5** cleanly upon purification by precipitation from CH_3OH and compound **6** upon purification by column chromatography.

The ligand syntheses described here offer the possibility of altering the nature of the two L groups. Such ligand architecture allows for steric and electronic variations on both the phenol and the L donor fragments.

(c) Synthesis of Metal Dialkyl Complexes $[(LCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]MR_2 (M = Y, Sc; L = OCH_3, NEt_2, $SCMe_3$; R = CH_2SiMe_2Ph, CH_2SiMe_3). Using in situ generated yttrium and scandium trialkyl starting materials, the preparation of target metal dialkyl complexes was accomplished

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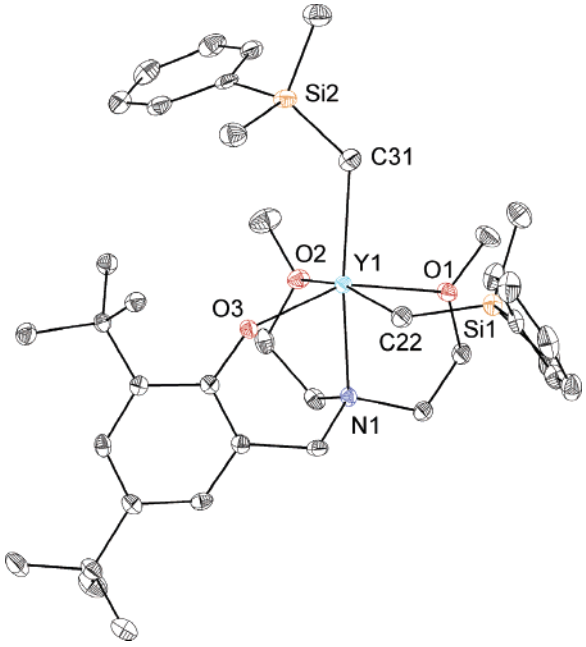
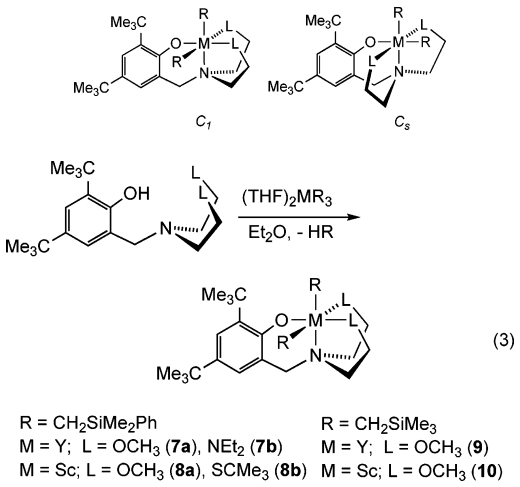


Figure 1. Structural drawing of $[(CH_3OCH_2CH_2)_2NCH_2\text{-}C_6H_2\text{-}3,5\text{-}(CMe_3)_2\text{-}2\text{-}O]Y(CH_2SiMe_2Ph)_2$ (**7a**) with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): $Y-O_3$, 2.1140(11); $Y-O_1$, 2.4038(11); $Y-O_2$, 2.5040(11); Y−N, 2.5345(14); $Y-C_{22}$, 2.4453(19); $Y-C_{31}$, 2.4557(19); $N-Y-O_1$, 69.30(4); $N-Y-O_2$, 65.89(4); $N-Y-O_3$, 78.55(4); $N-Y-C_{22}$, 99.28(6); O_3-Y-C_{22}, 94.48(6).

Chart 1



via alkane elimination (eq 3). The starting materials, $M(THF)_2(CH_2SiMe_2Ph)_3$ (M = Y, Sc) were expected to give more crystalline products,[17] while $M(THF)_2(CH_2SiMe_3)_3$ were preferred for ease of byproduct removal. For all compounds (eq 3) metalations occur cleanly with elimination of 1 equiv of $SiMe_3Ph$ or $SiMe_4$, on the basis of the ^1H NMR spectrum of the crude reaction mixture. The isolated yields are somewhat low, due to the high solubility of the products. In general, the reactions occur more cleanly when the reaction is started at low temperatures (<−70 °C) and then warmed to room temperature. Dialkyl complexes **7a**,**b** and **8a**,**b** can be separated from the alkane byproduct by recrystallization from petroleum ether−diethyl ether mixtures. On the other hand, when the more volatile byproduct $SiMe_4$ is formed, the purification is accomplished by removing the volatile materials under vacuum. All complexes are air- and water-sensitive.

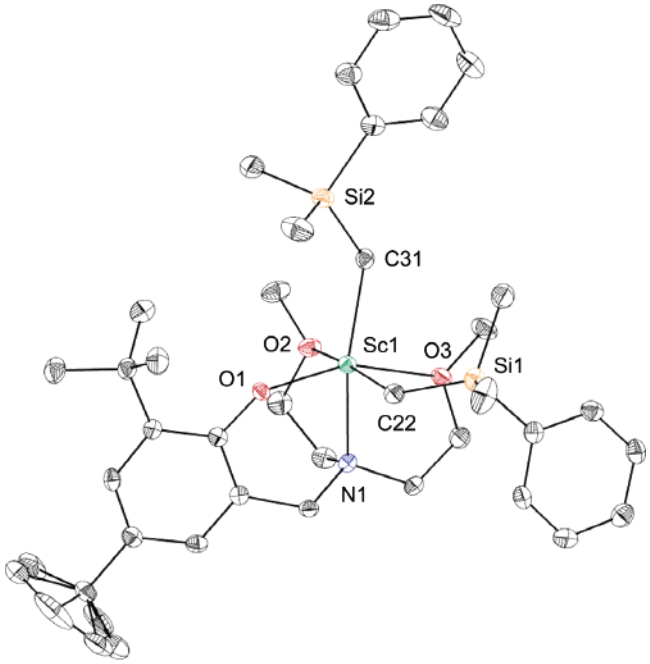


Figure 2. Structural drawing of $[(CH_3OCH_2CH_2)_2NCH_2\text{-}C_6H_2\text{-}3,5\text{-}(CMe_3)_2\text{-}2\text{-}O]Sc(CH_2SiMe_2Ph)_2$ (**8a**) with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): $Sc-O_1$, 1.9702(10); $Sc-O_2$, 2.3494(11); $Sc-O_3$, 2.3028(11); Sc−N, 2.3721(13); $Sc-C_{22}$, 2.2698(16); $Sc-C_{31}$, 2.2636(16); $N-Sc-O_1$, 82.50(4); $N-Sc-O_2$, 71.98(4); $N-Sc-O_3$, 70.16(4); $N-Sc-C_{22}$, 99.58(5); O_1-Sc-C_{22}, 95.90(5).

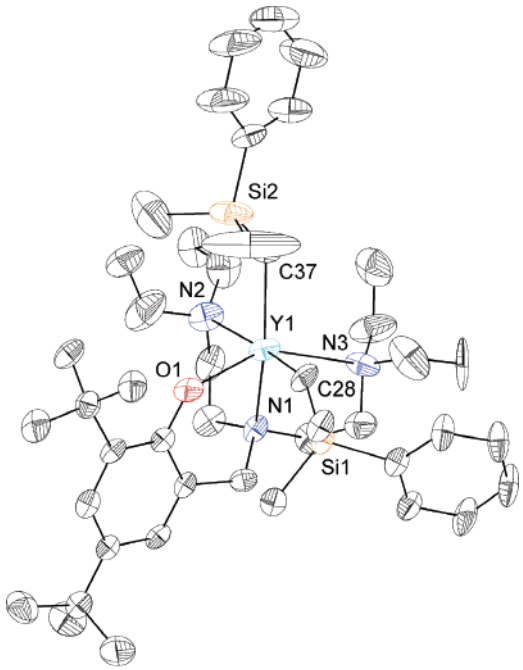


Figure 3. Structural drawing of $[(Et_2NCH_2CH_2)_2NCH_2\text{-}C_6H_2\text{-}3,5\text{-}(CMe_3)_2\text{-}2\text{-}O]Y(CH_2SiMe_2Ph)_2$ (**7b**), with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): $Y-O_1$, 2.104(4); $Y-N_1$, 2.538(4); $Y-N_2$, 2.832(5); $Y-N_3$, 2.594(5); $Y-C_{28}$, 2.425(5); $Y-C_{37}$, 2.430(5); N_1-Y-O_1, 76.55(13); N_1-Y-N_2, 66.81(14); N_1-Y-N_3, 71.62(14); N_1-Y-C_{28}, 114.41(16); O_1-Y-C_{37}, 112.95(16). Only one of the two positions calculated for the ethyl methyl groups is shown.

The reactions of the yttrium and scandium trialkyl complexes $M(THF)_2(CH_2SiMe_2Ph)_3$ with the ligand $(Me_2NCH_2CH_2)_2NCH_2\text{-}C_6H_2\text{-}3,5\text{-}(CMe_3)_2\text{-}2\text{-}OH$ (**6**) generate multiple, as yet

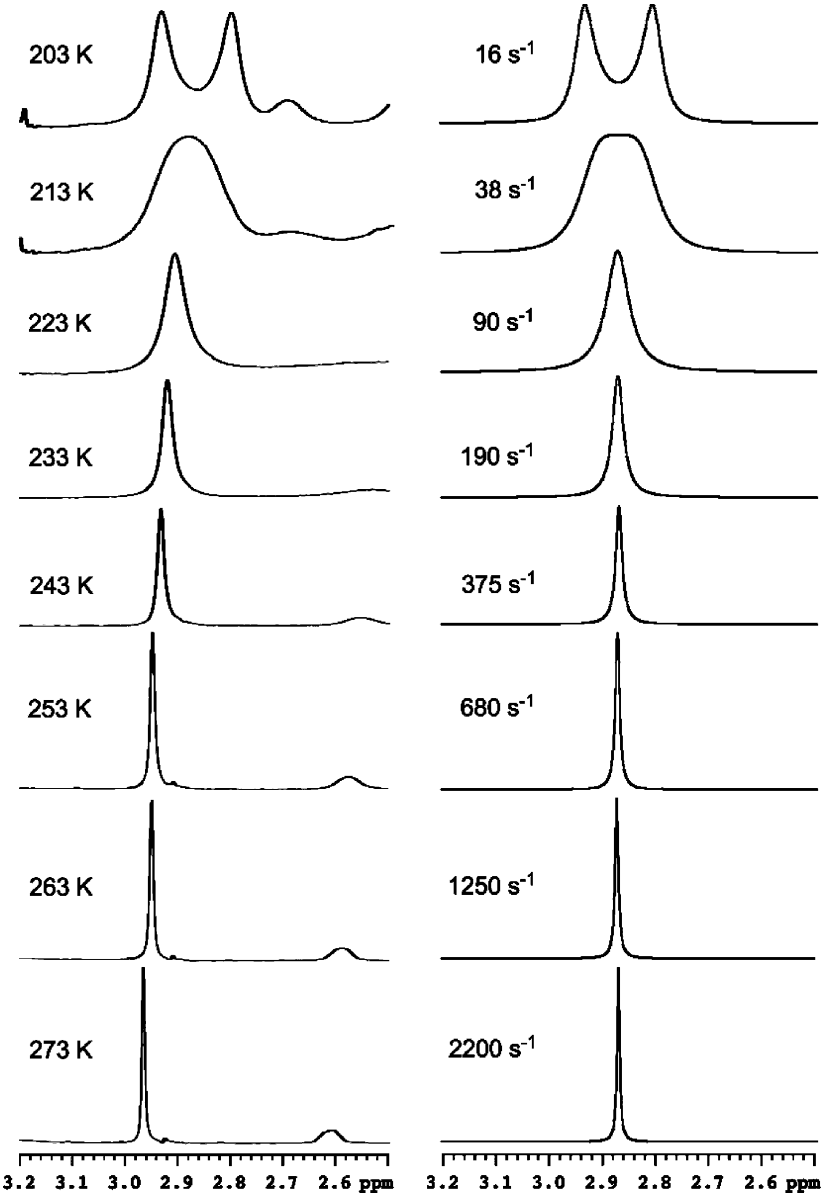


Figure 4. Experimental (left) and simulated (right) variable-temperature ^{1}H NMR spectra of [$(CH_3OCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]Y$(CH_2SiMe_2Ph)_2$ (**7a**), showing the OCH_3 (δ 2.94 and 2.8) resonances (toluene-d_8, 500 MHz). Best-fit first-order rate constants (k) are illustrated with the simulated spectra.

unidentified, products according to ^{1}H NMR spectroscopy. One possible decomposition pathway is the C−H activation of the methyl groups. A recent report indicates that group III complexes with pendant tertiary amine donors can undergo ligand C−H activation reactions.[21] The authors of this report state that the rate of this process is dependent on subtle ligand changes. If the reactions shown in eq 3 are similarly very dependent on ligand structure, we may reconcile why in some, but not all, cases the targeted dialkyl product (**7b**) can be isolated with pendant amine donors. Reaction of phenol **3** with metal trialkyls will be discussed in a later section.

Assuming the formation of hexacoordinate metal complexes, the dialkyl species could present C_1 or C_s symmetry (Chart 1). In order to determine the favored geometry in the solid state as well as in solution, single-crystal X-ray diffraction studies as well as variable-temperature ^{1}H NMR spectroscopic studies were performed. These are discussed in the following sections.

Solid-State Structures of Dialkyl Complexes. The solid-state structures of **7a**,**b** and **8a** were determined by single-crystal X-ray diffraction studies (Figures 1−3). In all three cases, a six-coordinate, distorted-octahedral, monomeric, C_1-symmetric structure is displayed. One alkyl group is trans to the linking (axial) nitrogen and the other trans to a pendant neutral donor, rather than a phenolate oxygen, possibly to avoid greater trans influence in the latter case. The metal−ether oxygen distances are larger that the metal−phenolate oxygen distances by 0.3−0.4 Å. Moreover, the M−O bonds to the ethers trans to the alkyls are longer than to the ethers trans to the phenolates by 0.05−0.1 Å, as anticipated for a greater trans influence for the alkyls. A similar trend is observed for the pendant amines, with a difference of more than 0.2 Å between the amine trans to the alkyl vs the amine trans to the phenolate. An analogous substantial bond length difference was observed for a related yttrium dialkyl triaminoamide complex reported recently.[21]

Solution Structure of Dialkyl Complexes. Despite their C_1 solid-state structures, the room-temperature (294 K) ^{1}H NMR spectra for both **7a** and **8a**, [$(CH_3OCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]M$(CH_2SiMe_2Ph)_2$ (M = Y, Sc), in toluene-d_8 feature, among other peaks, a singlet corresponding to Si$(CH_3)_2$-Ph, a singlet corresponding to MCH_2 (M = Y, Sc) and a singlet

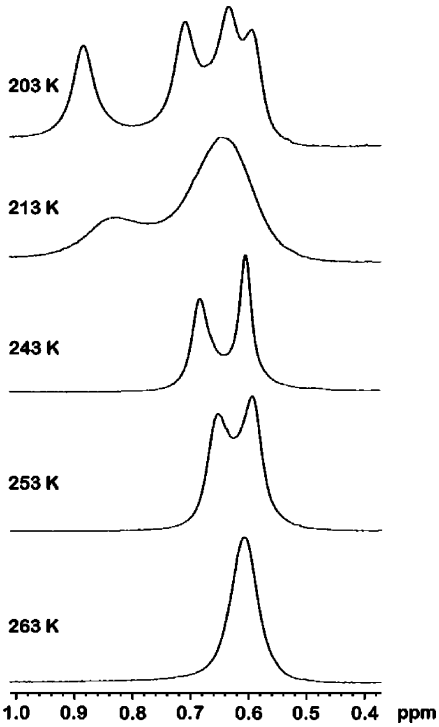


Figure 5. Variable-temperature ^{1}H NMR spectra of [$(CH_3OCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]Y$(CH_2SiMe_2Ph)_2$ (**7a**) showing the Si$(CH_3)_2$Ph peaks (toluene-d_8, 500 MHz).

corresponding to OCH_3. At temperatures below 203 K, the ^{1}H NMR spectra feature two singlets corresponding to the OCH_3 groups (Figure 4), along with four singlets for Si$(CH_3)_2$Ph (Figure 5) and four doublets for MCH_2 (some overlapping). When the temperature is increased, the peaks corresponding to the Si$(CH_3)_2$Ph groups collapse first into two singlets and then, at higher temperatures, into one singlet. Similar behavior is observed for **8b**, [$(Me_3CSCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]Sc$(CH_2SiMe_2Ph)_2$ (Figure 6). For compounds **9** and **10**, [$(CH_3OCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]M$(CH_2SiMe_3)_2$ (M = Y, Sc), with a different alkyl, the methyls bound to each silicon are equivalent and give rise to only two singlets at low temperature and one singlet at high temperature. At room temperature, compound **7b**, [$(Et_2NCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]Y$(CH_2SiMe_2Ph)_2$, displays only one set of peaks for the metal-bound alkyl groups; moreover, the four ethyl groups display only one broad triplet/quartet combination.

Given the small number of peaks corresponding to the [CH_2SiMe_2Ph] groups, the room-temperature spectra for **7a** and **8a** are consistent neither with C_s nor with C_1 structures (Chart 1). For the C_s structure, the two metal alkyl groups are chemically different and distinct peaks are expected in the ^{1}H NMR spectra—two singlets for the Si$(CH_3)_2$Ph protons and two singlets for MCH_2 (M = Y, Sc). On the other hand, for the C_1 structure, the silicon methyls are diastereotopic and should display four singlets. Furthermore, the Sc- or Y-bound methylene groups present diastereotopic hydrogens and should display four doublets in the ^{1}H NMR spectrum. The ether methyls are chemically different and should display two distinct singlets. Hence, the variable-temperature ^{1}H NMR spectroscopy data are indicative of an exchange process. The ^{1}H NMR spectra at low temperatures (vide infra) do indicate that the lowest energy structure is that having C_1 symmetry, as established for the solid-state structures. The ^{1}H NMR spectroscopy data for **8b**, **9**, and **10** indicate the presence of a similar exchange process and a C_1-symmetric ground-state structure.

Dynamic Processes in 7a, 8a, and 10. In order to determine exchange rate constants, line-shape analyses were performed for **7a** (Figure 4), **8a**, and **10**. As shown in Figure 4, increasing the temperature from 203 to 273 K results in broadening and coalescence of the OCH_3 resonances followed by sharpening of the resulting coalesced signal. For **7a** and **8a**, line-shape analyses were performed only for the ether methyl groups. The activation parameters for exchange of methoxy groups were obtained from Eyring plots (Figures 7 and 8) over a temperature range of greater than 60 K: $\Delta H^{\ddagger} = 7.3 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -16.2 \pm 1.4$ cal/(mol K) for **7a** and $\Delta H^{\ddagger} = 9.9 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -15.3 \pm 1.8$ cal/(mol K) for **8a**. Compound **10**, [$(CH_3OCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]Sc$(CH_2SiMe_3)_2$, provides an opportunity to inspect independently the exchange rates for both the ether methyl groups and the silicon methyl groups, because both display only two singlets in the slow exchange limit. The activation parameters determined for the exchange of the ether methyl groups are $\Delta H^{\ddagger} = 10.6 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -12.3 \pm 1.4$ cal/(mol K), and those for the silicon methyl groups are $\Delta H^{\ddagger} = 11.1 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -10.4 \pm 2.3$ cal/(mol K), values that are not significantly different and indicative of a single process for exchange of both methoxy and alkyl groups.

The substantially negative values of the entropy of activation suggest that **7a**, **8a**, and **10** undergo a nondissociative exchange process. The proposed mechanism that accommodates the dynamic NMR behavior involves twisting of the trigonal faces of the pseudo-octahedron (Scheme 2), resulting in the interconversion of three facial groups via trigonal-prismatic intermediates. This type of mechanism has previously been proposed for dynamic processes in pseudo-octahedral complexes of titanium.[40]

Two reaction pathways are required from the ground-state structure (***A***): one involves rotation around the pseudo-C_3 axis passing through the $[R_1R_2O]$ and $[NL_2L_1]$ trigonal faces, and a second involves rotation around the pseudo-C_3 axis passing through the $[R_1R_2L_2]$ and $[NOL_1]$ trigonal faces followed by rotation around the pseudo-C_3 axis passing through the $[R_1L_1R_2]$ and $[NL_2O]$ trigonal faces. Other possible pseudo-C_3 rotations would necessarily change the nature of the tetradentate $[ONL_1L_2]$ coordination (N axial with O, L_1 and L_2 cis to N) and, thus, need not be considered for nondissociative processes. Twisting of the $[R_1R_2O]$ face (red-arrow pathway) leads to the C_1 structure ***C*** via the trigonal-prismatic intermediate ***B***. This process affords simultaneous exchange of the ligands L_1 and L_2 together with alkyls R_1 and R_2. However, this process does *not* exchange the diastereotopic groups of the alkyls (CH_2 and Si$(CH_3)_2$Ph). A pathway that interconverts these diastereotopic protons involves twisting of the $[R_1R_2L_2]$ face (green-arrow pathway) to access the C_s structure ***E***, which, upon subsequent twisting of the $[R_1L_1R_2]$ face (blue-arrow pathway), gives ***G*** (an enantiomer of ***A***). This process also interchanges L_1 and L_2 but does not change the chemical environment of the alkyl groups R_1 and R_2. Hence, either pathway can interconvert the neutral ligands L_1 and L_2, but neither one alone can exchange both the metal alkyl groups and the diastereotopic groups on each of the metal alkyls.

Significantly, for **7a**, [$(CH_3OCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-O]Y$(CH_2SiMe_2Ph)_2$, exchange of [Si$(CH_3)_2$Ph] methyl hydrogens occurs in two stages; first the four singlets collapse into two singlets and, at higher temperatures, into one singlet (Figure 5). This stepwise behavior suggests that the exchange involves two processes with different activation barriers. The

(40) Fay, R. C.; Lindmark, A. F. *J. Am. Chem. Soc.* **1983**, *105*, 2118.

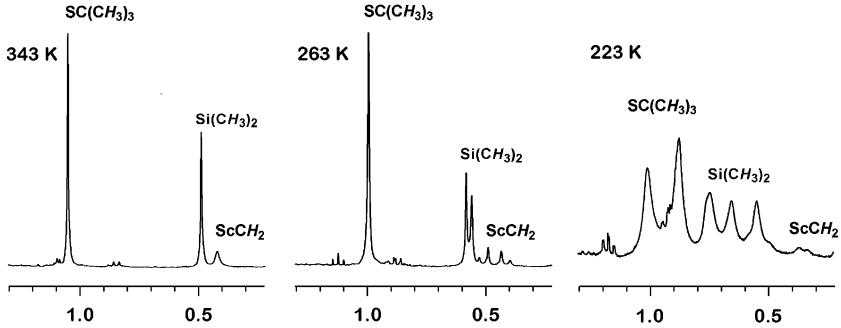


Figure 6. Selected aliphatic region of the ^{1}H NMR spectra of [(Me$_3$CSCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Sc(CH$_2$SiMe$_2$Ph)$_2$ (**8b**) at different temperatures (toluene-d_8, 300 MHz).

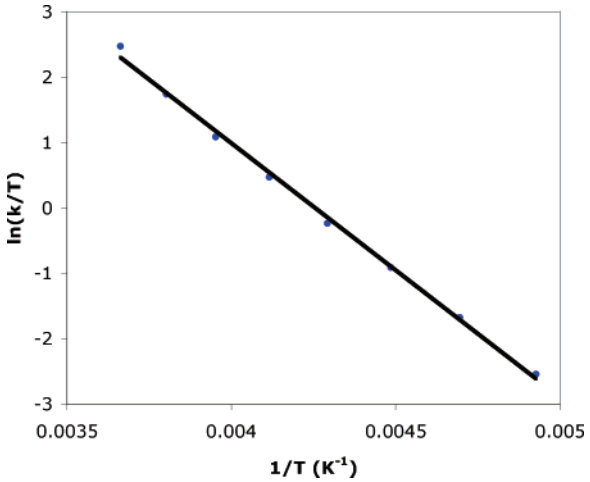


Figure 7. Eyring plot for [(CH$_3$OCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Y(CH$_2$SiMe$_2$Ph)$_2$ (**7a**) (toluene-d_8, 500 MHz).

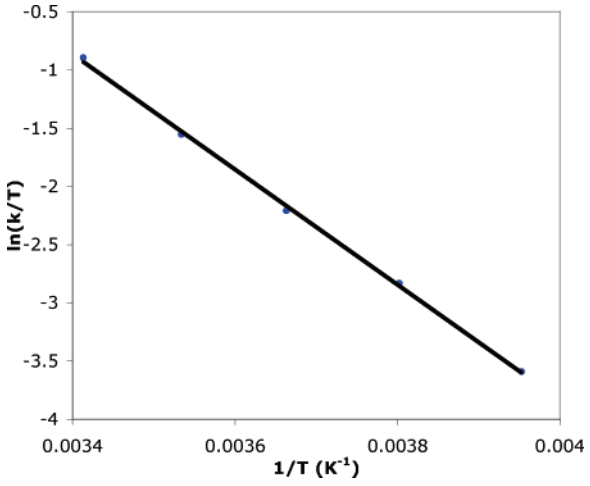


Figure 8. Eyring plot for [(CH$_3$OCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Sc(CH$_2$SiMe$_2$Ph)$_2$ (**8a**) (toluene-d_8, 300 MHz).

diastereotopic methylene hydrogens for these alkyls (both C*H*$_2$SiMe$_3$ and C*H*$_2$SiMe$_2$Ph derivatives) appear to also exhibit stepwise exchange behavior that in some cases changes from four doublets to a singlet by way of *two doublets*, although in most cases it is not possible to unambiguously identify these small signals at intermediate temperatures. The 263 K spectrum for **8b** [(Me$_3$CSCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Sc(C*H*$_2$SiMe$_2$Ph)$_2$ (Figure 6) does clearly show one set of these two resonances as an AB quartet indicative of the alkyls being in rapid exchange, but the individual diastereotopic hydrogens on the two methylenes Sc(C*H*$_a$*H*$_b$)$_2$SiMe$_2$Ph are in slow exchange and thus are still coupled to each other.[41] We infer, therefore, that the stepwise exchange of diastereotopic [Si(C*H*$_3$)$_2$Ph] groups gives rise to a similar situation: four singlets in slow exchange, followed by rapid alkyl exchange with slow diastereotopic [Si(C*H*$_3$)$_a$(C*H*$_3$)$_b$Ph] methyl exchange at intermediate temperatures giving rise to two singlets, and rapid alkyl and diastereotopic methyl exchange at high temperatures exhibiting one singlet. We attempted to simulate the observed spectra using two independent exchange rate constants at each temperature for the four peaks due to the Si(C*H*$_3$)$_2$Ph group of **7a**, but even for this relatively simple case we have been unsuccessful. Thus, we can conclude that the interconversion ***A*** ⇔ ***C*** is sometimes faster than ***A*** ⇔ ***E*** ⇔ ***G*** (this is the case for **8b**), but we are unable to quantify the differences in rates and barriers.

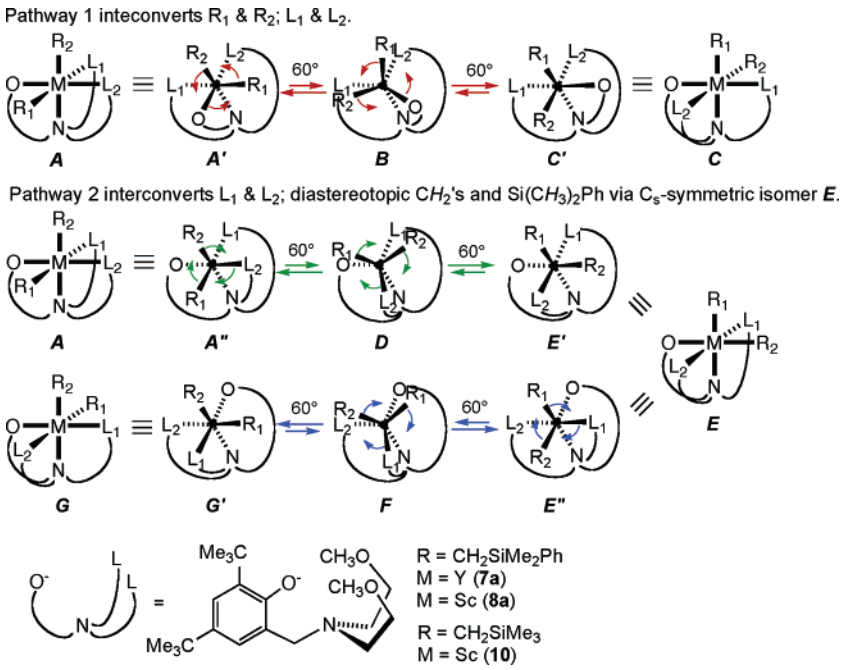
The activation enthalpy for the yttrium complex **7a** is smaller than that for the scandium analogue **8a**. Assuming that bond strengths are affected in a similar fashion along the reaction coordinate, it is likely that the larger yttrium center renders the complex more sterically open, facilitating access to the strained trigonal-prismatic intermediates. Supporting this hypothesis, increased steric bulk around the metal center has been shown to increase the activation enthalpy for a series of titanium/acac complexes that exchange via a similar mechanism.[40]

Interestingly, the room-temperature ^{1}H NMR spectrum of **7b**, [(Et$_2$NCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Y(CH$_2$SiMe$_2$Ph)$_2$, shows only one set of peaks for the ethyl groups, suggesting fast exchange of ethyls bound to the same nitrogen. The mechanism proposed here for the complexes with ether donors (Scheme 2) cannot account for this exchange. However, a mechanism involving amine dissociation followed by inversion and recoordination would provide a pathway for exchanging the ethyl groups on each pendant nitrogen donor. This type of mechanism has been proposed recently for a related yttrium dialkyl triaminoamide complex.[21] Furthermore, a related yttrium complex supported by the same ligand but with bulkier amide ligands (N(SiMe$_2$H)$_2$ instead of CH$_2$SiMe$_2$Ph) has been reported to coordinate only via one of the two pendant amines, suggesting that the amine coordination is not very strong.[38]

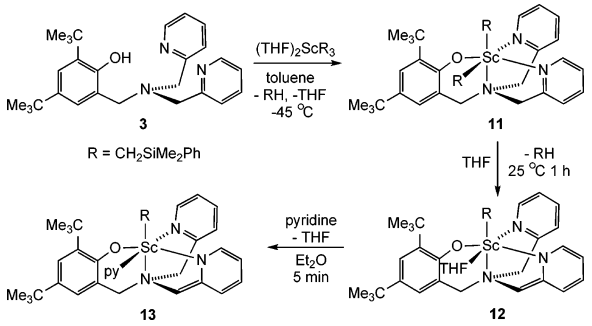
Metalation of (C$_5$H$_5$N-2-CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-OH (3) with a Scandium Trialkyl. Reaction of the scandium trialkyl Sc(THF)$_2$(CH$_2$SiMe$_2$Ph)$_3$ with the ligand (C$_5$H$_5$N-2-CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-OH (**3**) in diethyl ether, at room temperature, generates first a green solution that, within

(41) Cationic Zr species generated from the ligand precursor **1** were reported, at room temperature, to display ^{1}H NMR spectroscopy characteristics related to the phenomena reported here—the ether CH$_3$ groups show only one singlet, while the metal-bound benzyl group shows two doublets for the methylene groups.[33] This is consistent both with the C_s structure proposed by Kol et al., with the two benzyls reflecting into each other via the mirror plane, and with a dynamic process which, in this case, exchanges the ether groups (via ***B***), but not the diastereotopic hydrogens (via ***D***−***F***). A variable-temperature ^{1}H NMR spectroscopy study would distinguish between the two possibilities.

Scheme 2



Scheme 3



seconds, becomes deep red. The reaction occurs cleanly; only one set of peaks corresponding to the multidentate ligand is observed in the ^{1}H NMR spectrum at room temperature after 1 h. The reaction was repeated at low temperature (−45 °C) and the outcome investigated using ^{1}H, ^{1}H−^{1}H COSY, ^{13}C, DEPT, and HETCOR NMR spectroscopic studies. At −45 °C, the ^{1}H NMR spectrum shows only one set of peaks corresponding to the multidentate ligand, along with four singlets corresponding to Si(C*H*$_3$)$_2$Ph and four doublets corresponding to ScC*H*$_2$. The benzylic hydrogen atoms, [(C$_5$H$_5$N-2-C*H*$_2$)$_2$NC*H*$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O], show six doublets (two distinct doublets and four overlapped) that correlate with three *C*H$_2$ peaks (DEPT study) with chemical shifts between δ 60 and 63 ppm. One equivalent of PhSiMe$_3$, along with free THF released from the starting material, is observed as well. These data are consistent with the formation of dialkyl species **11** having a C_1 symmetry structure at −45 °C (Scheme 3), similar to the structures above.

The reaction mixture generated at −45 °C was warmed to room temperature and, after 1 h, was interrogated by NMR spectroscopy. The formation of an additional 1 equiv of PhSiMe$_3$ was observed. The ^{1}H NMR spectrum shows two singlets corresponding to Si(C*H*$_3$)$_2$Ph and two doublets corresponding to ScC*H*$_2$. In the benzylic region, four doublets and one singlet are observed. This singlet correlates with a methine carbon at 100.9 ppm, as determined by a HETCOR experiment. The $^1J_{C-H}$ value of 170 Hz is indicative of an sp^2 hybridized carbon.[42a] A tautomeric binding mode through the carbon is possible, but not consistent with the observed coupling constant. The THF peak is broadened and shifted, indicating ether coordination. These data are consistent with the decomposition of **11** via C−H activation of a methylene group linking a pyridine to the central nitrogen to give **12** with loss of another 1 equiv of silane. Confirmation that the activated methylene position does link a pyridine arm was made by quenching a THF solution of **12** with methanol-d_4 and checking for deuterium incorporation (^{2}H NMR spectroscopy) in the phenol found in the resulting mixture. A similar activation of a ligand benzylic C−H bond was reported as well for a tantalum system supported by a related tetradentate diphenolate ligand.[29] However, a scandium alkyl complex supported by a dianionic ligand displaying the same pyridine arm as that here was stable enough for isolation at room temperature.[15] THF may be displaced by addition of pyridine to afford **13** (Scheme 3), but not by softer donors such as ethylene, 2-butyne, and trimethylphosphine.[42b] Compound **12** is thermally unstable, decomposing in solution even at −35 °C over a few days.

Transformation of **11** into **12** was monitored by ^{1}H NMR spectroscopy in toluene-d_8 at 0 °C. Both the disappearance of **11** and the formation of **12** were followed over time by measuring the integrals for selected, baseline-separated proton peaks. As expected, these processes were found to follow first-order kinetics with similar rate constants (Figure 9 in the Supporting Information; $k = [2.8(3)] \times 10^{-4}$ s^{-1} for the decay of **11** and $k = [2.3(1)] \times 10^{-4}$ s^{-1} for the formation of **12**).

Attempts to cleanly metalate **3** with Y(THF)$_2$(CH$_2$SiMe$_2$Ph)$_3$ have been unsuccessful. NMR-scale reactions of the yttrium trialkyl complex and compound **3**, in toluene-d_8, when monitored by ^{1}H NMR spectroscopy at −35 °C, reveal multiple, unidentified products.

Generation of Cationic Alkyls for Ethylene Polymerizations. Generation and characterization of cationic monoalkyl

(42) (a) Silverstein, R. M.; Webster, F. X. *Spectroscopic Identification of Organic Compounds*, 6th ed; 1998. (b) Dialkyl complexes **7a** and **8a** do not show a reaction upon treatment with pyridine, suggesting that the intramolecular ether donors are preferred to the added base. While no reactivity was observed toward ethylene, **7b** reacts with acetonitrile and diphenylacetylene to afford multiple unidentified products.

Table 1. Crystal and Refinement Data for Complexes 7a,b and 8a

	7a	7b	8a
empirical formula	$C_{39}H_{62}NO_3Si_2Y$	$C_{45}H_{76}N_3OSi_2Y$	$C_{39}H_{62}NO_3Si_2Sc$
formula wt	737.99	820.18	694.04
T (K)	98(2)	100(2)	100(2)
a, Å	11.3640(4)	18.3292(16)	12.8434(5)
b, Å	14.2999(5)	10.1929(8)	18.7067(7)
c, Å	25.4993(9)	28.733(2)	33.6484(12)
α, deg			
β, deg	100.2310(10)	103.571(2)	
γ, deg			
V, Å^3	4077.9(2)	5218.2(8)	8084.3(5)
Z	4	4	8
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/c$	$Pbca$
d_{calcd}, g/cm^3	1.202	1.044	1.140
θ range, deg	1.62−28.41	1.46−22.49	1.99−28.50
μ, mm^{-1}	1.523	1.194	0.276
abs cor	none	none	none
GOF	1.446	2.059	2.272
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0323, 0.0535	0.0640, 0.1126	0.0447, 0.0693

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

yttrium species was attempted. In order to allow characterization by ^{1}H NMR spectroscopy, a stoichiometric activator, $[PhNHMe_2]^+[B(C_6F_5)_4]^-$, was utilized (eq 4). NMR-scale reactions of $[(CH_3OCH_2CH_2)_2NCH_2-C_6H_2$-3,5-$(CMe_3)_2$-2-O$]YR_2$ (R = CH_2SiMe_2Ph (**7a**), CH_2SiMe_3 (**9**)) with 1 equiv of anilinium salt in chlorobenzene-d_5 occur with formation of a major new species, but not cleanly (see the Supporting Information for the ^{1}H NMR spectrum) at −35 °C. For **9**, formation of $SiMe_4$ is observed, along with one major set of peaks corresponding to the phenoxide $C(CH_3)_3$ groups. The metal-bound alkyl group displays two doublets for YCH_2, while the ether groups display two singlets for the OCH_3 protons. Upon warming to room temperature, the doublets for the metal-bound methylene group collapse into a singlet, as do the two peaks for the ether methyl groups. These observations are consistent with the protonation of one of the alkyl groups to generate a C_1-symmetric monoalkyl species (**15**) at −35 °C. The $N(CH_3)_2$ resonances are shifted from those of free dimethylaniline, suggesting coordination to the metal center. Compound **15** seems to be involved in a dynamic process that exchanges the ether groups and the diastereotopic YCH_2 protons. The cationic species decomposes within hours at room temperature. Slow consumption of ethylene (7.5 equiv in 7 h) was observed with **15** generated at low temperature.

The dialkyl complexes were investigated for ethylene polymerization activity more generally. Medium-scale polymerizations with **7a** or **9** and activation with $[PhNHMe_2]^+[B(C_6F_5)_4]^-$ in a closed system with excess ethylene (initial pressure of 4 atm) led to the isolation of small amounts of polymer upon workup with MeOH/HCl. The polymerization was repeated as above, but with addition of excess MAO, as well as with MAO as sole activator. Only minor changes in polymerization activity arose on changing the nature of activator. Polymerization trials with dialkyls **7a**,**b**, **8a**,**b**, **9**, and **10** were performed upon activation with excess MAO (500 equiv), under 5 bar of ethylene, using 3.3×10^{-4} M concentrations of precatalyst. Under these conditions, all complexes serve as sluggish polymerization precatalysts, displaying productivities between 0.5 and 2.5 kg of PE/(mol M bar) (M = Y, Sc), after 1 h reaction times. The very low polymerization activities in these systems with pendant, unconstrained, donor groups may relate to the results reported by Hessen et al., who studied tetradentate monoanionic ligands based on one amide donor and three amine donors.[21] A system competent for ethylene polymerization was obtained when the neutral donors were linked in a macrocycle (1,4,7-triazacyclononane), but the polymerization activity decreases 20-fold when the NN macrocyclic linkage is removed. This reduction in activity was attributed to a reduced stability of the complexes with "open" triamine ligands, and, indeed, that may well be the case here.

Conclusions

Yttrium and scandium dialkyl complexes supported by readily available tetradentate, monoanionic phenolate ligands can be prepared by alkane elimination from trialkyl precursors. ^{1}H NMR spectroscopy studies show fluxional behavior in solution. C_1-Symmetric structures are favored for all alkyls in the solid state as well as in solution. The dynamic behavior of dialkyl complexes with pendant ether donors was investigated by variable-temperature ^{1}H NMR spectroscopy, and the fluxional rates and activation parameters were determined by line-shape analysis. A mechanism involving nondissociative ligand exchange was found, likely via trigonal-prismatic intermediates generated via twists of pseudooctahedral trigonal faces containing both alkyls and another donor ligand. The ligand with pendant pyridine donors $(C_5H_4N$-2-$CH_2)_2NCH_2-C_6H_2$-3,5-$(CMe_3)_2$-2-OH (**3**) presents a different reactivity. Low-temperature NMR studies indicate intermediate formation of dialkyl species at −45 °C, which decomposes cleanly by activation of a C−H bond of a methylene connecting the pyridine to the nitrogen linker position at 0 °C. The yttrium dialkyl complexes **7a** and **9** react quite cleanly (^{1}H NMR spectroscopy), at low temperatures with 1 equiv of $[PhNHMe_2]^+[B(C_6F_5)_4]^-$ in chlorobenzene-d_5 to generate 1 equiv of alkane and, presumably, a cationic monoalkyl species. Solutions of these cations slowly polymerize ethylene. Compounds **7**−**10** also polymerize ethylene upon activation with MAO, but with very low activities.

Experimental Section

General Considerations and Instrumentation. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a drybox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or by the method of Grubbs.[43] Benzene-d_6 was purchased from Cambridge Isotopes and distilled from sodium benzophenone ketyl. Chloroform-d and chlorobenzene-d_5 were purchased from Cambridge Isotopes and distilled from calcium hydride. 2-Hydroxy-3,5-di-*tert*-

(43) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

butylbenzyl bromide,[44] $LiCH_2SiMe_2Ph$,[17] and $M(THF)_2(CH_2SiMe_2Ph)_3$[17] (M = Sc, Y) were prepared according to the literature procedures. Other materials were used as received. ^1H and ^{13}C NMR spectra were recorded on Varian Mercury 300 and Varian INOVA-500 spectrometers at room temperature, unless otherwise indicated. Chemical shifts for ^1H and ^{13}C data are reported with respect to internal solvent: 7.16 and 128.38 (t) ppm (C_6D_6); 7.27 and 77.23 (t) ppm ($CDCl_3$). ^1H NMR data recorded in C_6D_5Cl were referenced with respect to the most upfield peak for Ph_2CH_2 (3.8 ppm) or with respect to the alkane byproduct, $Si(CH_3)_4$ (0 ppm), where appropriate. ^2H NMR spectra were recorded on a Varian INOVA-500 spectrometer, the chemical shifts being reported with respect to an external D_2O reference (4.8 ppm).

Synthesis of $(MeOCH_2CH_2)_2NCH_2$-C_6H_2-3,5-$(CMe_3)_2$-2-OH (1). A methanol (10 mL) solution of 2,4-di-*tert*-butylphenol (2 g, 9.7 mmol, 1 equiv), bis(2-methoxyethyl)amine (1.3 g, 9.7 mmol, 1 equiv), and formaldehyde (3.5 g of a 37% aqueous solution, 38.9 mmol, 4 equiv) was refluxed. After the mixture was cooled to room temperature, volatile material was removed via rotary evaporation. The resulting pale yellow oil was placed under high vacuum for 6 h to remove remaining excess amine. The resulting material was pure by ^1H NMR spectroscopy (3.08 g, 8.7 mmol, 90%). HRMS (*m*/*z*): calcd, 351.2773 (M^+); found, 351.2766. ^1H NMR (300 MHz, C_6D_6; δ): 1.37 (s, 9H, $C(CH_3)_3$), 1.73 (s, 9H, $C(CH_3)_3$), 2.60 (t, 4H, J = 5.7 Hz, NCH_2CH_2O), 3.21 (t, 4H, J = 5.7 Hz, NCH_2CH_2O), 3.01 (s, 6H, OCH_3), 3.63 (s, 2H, aryl CH_2), 6.94 (d, 1H, J = 2.4 Hz, aryl *H*), 7.51 (d, 1H, J = 2.4 Hz, aryl *H*), 10.91 (s, 1H, O*H*). ^1H NMR (300 MHz, $CDCl_3$; δ): 1.29 (s, 9H, $C(CH_3)_3$), 1.43 (s, 9H, $C(CH_3)_3$), 2.82 (t, 4H, J = 5.7 Hz, NCH_2CH_2O), 3.54 (t, 4H, J = 5.7 Hz, NCH_2CH_2O), 3.33 (s, 6H, OCH_3), 3.85 (s, 2H, aryl CH_2), 6.74 (d, 1H, J = 2.4 Hz, aryl *H*), 7.21 (d, 1H, J = 2.4 Hz, aryl *H*), 10.59 (br s, 1H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 29.8 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 34.3 (CMe_3), 35.0 (CMe_3), 53.5 (CH_2), 59.0 (OCH_3), 59.7 (CH_2), 70.6 (CH_2), 121.7 (*aryl*), 123.0 (*aryl*−H), 123.7 (*aryl*−H), 135.8 (*aryl*), 140.5 (*aryl*), 154.5 (*aryl*).

Synthesis of $(Et_2NCH_2CH_2)_2NCH_2-C_6H_2$-3,5-$(CMe_3)_2$-2-OH (2). A methanol (15 mL) solution of 2,4-di-*tert*-butylphenol (3.68 g, 17.8 mmol, 1.1 equiv), *N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine (3.9 g, 90% purity, 16.2 mmol, 1 equiv), and formaldehyde (5.3 g 37% aqueous solution, 64.8 mmol, 4 equiv) was refluxed for 14 h. After the mixture was cooled to room temperature, volatile material was removed via rotary evaporation. An 8 mL portion of HCl (36.5%) was added to the reaction mixture. The aqueous phase was washed with petroleum ether (3 × 50 mL). The aqueous layer was neutralized with KOH solution and extracted with diethyl ether (3 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$. The volatile materials were removed via rotary evaporation to yield the desired product as a yellow oil (6.56 g, 15.2 mmol, 94%). ^1H NMR data in C_6D_6 match those in the literature report.[38] ^1H NMR (300 MHz, $CDCl_3$; δ): 0.97 (t, J = 7.1 Hz, 12H, CH_2CH_3), 1.27 (s, 9H, $C(CH_3)_3$), 1.41 (s, 9H, $C(CH_3)_3$), 2.48 (q, J = 7.1 Hz, 8H, CH_2CH_3), 2.57−2.64 (m, 8H, NCH_2CH_2N), 3.73 (s, 2H, aryl CH_2), 6.83 (d, J = 2.3 Hz, 1H, aryl *H*), 7.18 (d, J = 2.3 Hz, 1H, aryl *H*), 10.56 (br s, 1H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 11.8 (NCH_2CH_3), 29.8 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 35.0 (CMe_3), 47.4 (NCH_2), 50.6 (NCH_2), 52.3 (NCH_2), 59.0 (NCH_2), 122.0 (*aryl*), 122.9 (*aryl*−H), 123.9 (*aryl*−H), 135.7 (*aryl*), 140.4 (*aryl*), 154.3 (*aryl*).

Synthesis of $(C_5H_4N$-2-$CH_2)_2NCH_2-C_6H_2$-3,5-$(CMe_3)_2$-2-OH (3). A THF (20 mL) solution of 2-hydroxy-3,5-di-*tert*-butylbenzyl bromide (1.49 g, 5.0 mmol, 1 equiv) was added dropwise to a THF (20 mL) solution of bis(2-picolyl)amine (0.99 g, 5.0 mmol, 1 equiv) and *N*,*N*-diisopropylethylamine (0.62 g, 5.0 mmol, 1 equiv). The reaction mixture was stirred at room temperature overnight. The volatile materials were removed via rotary evaporation. A solution of NaOH was added to the reaction mixture, and the organic phase was extracted with CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$. The volatile materials were removed via rotary evaporation to yield a golden oil (1.77 g, 4.2 mmol, 84%). HRMS (*m*/*z*): calcd, 418.2858 (MH^+); found, 418.2852. ^1H NMR (500 MHz, C_6D_6; δ): 1.36 (s, 9H, $C(CH_3)_3$), 1.77 (s, 9H, $C(CH_3)_3$), 3.68 (s, 2H, aryl CH_2N), 3.82 (s, 4H, $NCH_2C_5H_4N$), 6.52−6.56 (m, 2H, aryl *H*), 6.95−7.01 (m, 3H, aryl *H*), 7.12 (d, 2H, aryl *H*), 7.53 (d, J = 2.4 Hz, 1H, aryl *H*), 8.41−8.44 (m, 2H, aryl *H*), 11.07 (s, 1H, O*H*). ^1H NMR (300 MHz, $CDCl_3$; δ): 1.28 (s, 9H, $C(CH_3)_3$), 1.48 (s, 9H, $C(CH_3)_3$), 3.82 (s, 2H, aryl CH_2N), 3.89 (s, 4H, $NCH_2C_5H_4N$), 6.90 (d, J = 2.4 Hz, 1H, aryl *H*), 7.13−7.19 (m, 2H, aryl *H*), 7.22 (d, J = 2.4 Hz, 1H, aryl *H*), 7.39 (d, 2H, aryl *H*), 7.60−7.67 (m, 2H, aryl *H*), 8.57 (m, 2H, aryl *H*), 10.66 (s, 1H, O*H*). ^1H NMR (300 MHz, CD_2Cl_2; δ): 1.26 (s, 9H, $C(CH_3)_3$), 1.44 (s, 9H, $C(CH_3)_3$), 3.78 (s, 2H, aryl CH_2N), 3.83 (s, 4H, $NCH_2C_5H_4N$), 6.90 (d, 1H, aryl *H*), 7.13−7.21 (m, 3H, aryl *H*), 7.33 (d, 2H, aryl *H*), 7.63 (td, 2H, aryl *H*), 8.54 (m, 2H, aryl *H*), 10.67 (s, 1H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 29.8 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 34.3 (CMe_3), 35.2 (CMe_3), 58.4 (NCH_2), 59.7 (NCH_2), 121.8 (*aryl*), 122.4 (*aryl*−H), 123.3 (*aryl*−H), 123.8 (*aryl*−H), 124.7 (*aryl*−H), 135.7 (*aryl*), 136.8 (*aryl*−H), 140.5 (*aryl*), 149.2 (*aryl*−H), 154.0 (*aryl*), 158.3 (*aryl*).

Synthesis of $(ClCH_2CH_2)_2NCH_2-C_6H_2$-3,5-$(CMe_3)_2$-2-OH (4). A methanol (40 mL) solution of 2,4-di-*tert*-butylphenol (20.3 g, 98.3 mmol, 1 equiv), diethanolamine (15.5 g, 147.4 mmol, 1.5 equiv), and formaldehyde (31.9 g of a 37% aqueous solution, 393.1 mmol, 4 equiv) was refluxed overnight. After the mixture was cooled to room temperature, the volatile material was removed via rotary evaporation. The oily residue was dissolved in 200 mL of diethyl ether and treated with 14 mL of concentrated hydrochloric acid (37%). Abundant precipitation of a white solid was observed. The product was collected on the sintered-glass funnel and washed with diethyl ether and water. The solid prepared by the above procedure was dissolved in CH_2Cl_2. Thionyl chloride (46.5 mL, 75.8 g, 637.5 mmol, 6.5 equiv) was added via volumetric pipet, and the reaction mixture was stirred overnight. A 10% solution of KOH was added to the reaction mixture until basic pH. The organic phase was extracted with CH_2Cl_2 (3 × 400 mL). The organic phase was dried over anhydrous $MgSO_4$. The volatile materials were removed via rotary evaporation to yield a yellowish solid (26.7 g, 74.2 mmol, 75%). HRMS (*m*/*z*): calcd, 359.1783 (M^+); found, 359.1765. ^1H NMR (300 MHz, C_6D_6; δ): 1.35 (s, 9H, $C(CH_3)_3$), 1.68 (s, 9H, $C(CH_3)_3$), 2.28 (t, 4H, J = 6.6 Hz, NCH_2CH_2Cl), 2.97 (t, 4H, J = 6.6 Hz, NCH_2CH_2Cl), 3.22 (s, 2H, aryl CH_2), 6.82 (d, 1H, J = 2.7 Hz, aryl *H*), 7.50 (d, 1H, J = 2.7 Hz, aryl *H*), 9.61 (s, 1H, O*H*). ^1H NMR (300 MHz, $CDCl_3$; δ): 1.31 (s, 9H, $C(CH_3)_3$), 1.45 (s, 9H, $C(CH_3)_3$), 3.00 (t, 4H, J = 6.6 Hz, NCH_2CH_2Cl), 3.64 (t, 4H, J = 6.6 Hz, NCH_2CH_2Cl), 3.87 (s, 2H, aryl CH_2), 6.87 (d, 1H, J = 2.4 Hz, aryl *H*), 7.28 (d, 1H, J = 2.4 Hz, aryl *H*), 9.45 (br s, 1H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 29.8 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 34.4 (CMe_3), 35.1 (CMe_3), 41.2 (CH_2), 55.9 (CH_2), 59.5 (CH_2), 120.8 (*aryl*), 123.8 (*aryl*−H), 123.9 (*aryl*−H), 136.4 (*aryl*), 141.3 (*aryl*), 153.9 (*aryl*).

Synthesis of $(Me_3CSCH_2CH_2)_2NCH_2-C_6H_2$-3,5-$(CMe_3)_2$-2-OH (5). A THF (∼50 mL) solution of Me_3CSH (3.3 g, 36.7 mmol, 3.3 equiv) was added under an argon atmosphere to a suspension of sodium hydride (1.3 g, 53.3 mmol, 4.8 equiv) in THF (∼50 mL). A THF (∼60 mL) solution of **4** (4 g, 11.1 mmol, 1 equiv) was added to the reaction mixture, and this mixture was stirred overnight. The reaction mixture was quenched with distilled water (150 mL) and extracted with diethyl ether (3 × 100 mL). The organic fraction was dried over $MgSO_4$ and filtered. Volatile materials were removed via rotary evaporation. The resulting yellow solid was recrystallized from methanol to give a white solid (2.8 g, 6.1 mmol, 55%). HRMS

(44) Sokolowski, A.; Muller, J.; Weyhermuller, T.; Schnepf, R.; Hildebrandt, P.; Hildenbrand, K.; Bothe, E.; Wieghardt, K. *J. Am. Chem. Soc.* **1997**, *119*, 8889−8900.

(*m*/*z*): calcd, 466.3177 ([MH^+] − H_2); found, 466.3161. ^{1}H NMR (300 MHz, C_6D_6; δ): 1.13 (s, 18H, SC(CH_3)$_3$), 1.36 (s, 9H, aryl C(CH_3)$_3$), 1.70 (s, 9H, aryl C(CH_3)$_3$), 2.46−2.61 (m, 8H, NCH_2CH_2S), 3.43 (s, 2H, aryl CH_2), 6.88 (d, J = 2.4 Hz, 1H, aryl *H*), 7.48 (d, J = 2.4 Hz, 1H, aryl *H*), 10.39 (s, 1H, O*H*). ^{1}H NMR (300 MHz, $CDCl_3$; δ): 1.26 (s, 18H, SC(CH_3)$_3$), 1.28 (s, 9H, aryl C(CH_3)$_3$), 1.43 (s, 9H, aryl C(CH_3)$_3$), 2.62−2.82 (m, 8H, NCH_2CH_2S), 3.80 (s, 2H, aryl CH_2), 6.84 (d, J = 2.6 Hz, 1H, aryl *H*), 7.22 (d, J = 2.6 Hz, 1H, aryl *H*), 10.20 (br s, 1H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 25.8 (*C*H_2), 29.8 (C(*C*H_3)$_3$), 31.2 (C(*C*H_3)$_3$), 31.9 (C(*C*H_3)$_3$), 34.3 (*C*Me$_3$), 35.0 (*C*Me$_3$), 42.5 (*C*Me$_3$), 54.7 (*C*H_2), 59.3 (*C*H_2), 121.4 (*aryl*), 123.3 (*aryl*−H), 123.7 (*aryl*−H), 136.0 (*aryl*), 141.0 (*aryl*), 154.2 (*aryl*).

Synthesis of (Me$_2$NCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-OH (6). Compound **4** (4 g, 11.2 mmol, 1 equiv) and lithium dimethylamide (2.9 g, 56.2 mmol, 5 equiv) were placed in a Schlenk tube, in the drybox. THF (∼50 mL) was vacuum-transferred over the starting materials. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was then quenched with water and extracted with diethyl ether. The organic fraction was dried over $MgSO_4$ and filtered. Volatile materials were removed via rotary evaporation. The resulting oil consists of three species. A diethyl ether solution of the product mixture was acidified with hydrochloric acid. The aqueous layer was washed with diethyl ether and then basified with sodium hydroxide and extracted with diethyl ether. The organic fraction was dried over $MgSO_4$ and filtered, and then the volatile materials were removed via rotary evaporation. The resulting material consists of a mixture of only two species. Purification by column chromatography with ethyl acetate as eluent provided pure product (0.4 g, 0.9 mmol, 8%). Because this phenol did not give clean metalation reactions, no optimization was attempted. HRMS (*m*/*z*): calcd, 332.2828 (M − [$HNMe_2$]); found, 332.2818. ^{1}H NMR (300 MHz, C_6D_6; δ): 1.39 (s, 9H, C(CH_3)$_3$), 1.75 (s, 9H, C(CH_3)$_3$), 1.86 (s, 12H, NCH_3), 1.96 (t, 4H, J = 5.7 Hz, NCH_2CH_2N), 2.24 (t, 4H, J = 5.7 Hz, NCH_2CH_2N), 3.59 (s, 2H, aryl CH_2), 6.93 (d, 1H, J = 2.4 Hz, aryl *H*), 7.52 (d, 1H, J = 2.4 Hz, aryl *H*), 11.61 (br s, 1H, O*H*). ^{1}H NMR (300 MHz, $CDCl_3$; δ): 1.27 (s, 9H, C(CH_3)$_3$), 1.41 (s, 9H, C(CH_3)$_3$), 2.18 (s, 12H, NCH_3), 2.45 (t, 4H, J = 5.9 Hz, NCH_2CH_2N), 2.65 (t, 4H, J = 5.9 Hz, NCH_2CH_2N), 3.73 (s, 2H, aryl CH_2), 6.83 (d, 1H, J = 2.4 Hz, aryl *H*), 7.18 (d, 1H, J = 2.4 Hz, aryl *H*), 10.51 (br s, 1H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 29.8 (C(*C*H_3)$_3$), 31.9 (C(*C*H_3)$_3$), 34.3 (*C*Me$_3$), 35.0 (*C*Me$_3$), 45.6 (N*C*H_3), 46.1 (N*C*H_2), 53.6 (N*C*H_2), 58.4 (N*C*H_2), 122.3 (*aryl*), 122.9 (*aryl*−H), 123.3 (*aryl*−H), 135.9 (*aryl*), 140.4 (*aryl*), 155.0 (*aryl*).

Synthesis of [(LCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]M-(CH$_2$SiMe$_2$Ph)$_2$ (M = Y, Sc; L = OMe, NEt$_2$, SCMe$_3$). In a typical procedure, a THF (5 mL) solution of phenol (1 equiv) was added dropwise to an in situ generated THF (5 mL) solution of M(THF)$_2$(CH$_2$SiMe$_2$C$_6$H$_5$)$_3$ (1 equiv) and stirred for 4 h at room temperature. ^{1}H NMR spectra of the crude reaction mixtures show clean formation of the desired yttrium and scandium dialkyl products along with $SiMe_3Ph$. The volatile materials were removed under vacuum. Diethyl ether (5 mL) was added, and the mixture was filtered through Celite to remove insoluble salts. The filtrate was concentrated under vacuum.

Synthesis of [(MeOCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Y-(CH$_2$SiMe$_2$Ph)$_2$ (7a). Recrystallization from petroleum ether or petroleum ether/diethyl ether mixtures, followed by collection on a sintered-glass funnel and washing with cold petroleum ether, provided the desired product as a white solid (57% yield) carrying only traces of alkane impurity. Anal. Calcd for $C_{39}H_{62}NO_3Si_2Y$: C, 63.47; H, 8.47; N, 1.90. Found: C, 64.46; H, 9.01; N, 2.08. ^{1}H NMR (300 MHz, C_6D_6; δ): −0.38 (d, $^2J_{YH}$ = 2.9 Hz, 4H, YCH_2), 0.65 (s, 12H, Si(CH_3)$_2$), 1.43 (s, 9H, C(CH_3)$_3$), 1.82 (s, 9H, C(CH_3)$_3$), 1.39, 2.24, 2.33, 2.60 (br m, 8H, NCH_2CH_2O), 3.24 (br s, 2H, aryl CH_2), 2.94 (s, 6H, OCH_3), 6.86 (d, 1H, J = 2.4 Hz, aryl *H*), 7.59 (d, 1H, J = 2.4 Hz, aryl *H*), 7.23 (t, 2H, *p*-Ph *H*), 7.31 (t, 4H, *m*-Ph *H*), 7.88 (d, 4H, *o*-Ph *H*). ^{13}C NMR (75 MHz, C_6D_6; δ): 3.5 (s, Si(*C*H_3)$_2$), 27.6 (d, Y*C*H_2, $^1J_{YC}$ = 39.8 Hz), 30.6 (C(*C*H_3)$_3$), 32.6 (C(*C*H_3)$_3$), 34.6 (*C*Me$_3$), 36.0 (*C*Me$_3$), 52.6, 61.3, 63.6, 72.0 (OCH_3, aryl *C*H_2, NCH_2*C*H_2O), 123.7, 125.1, 125.9, 127.9, 128.0, 134.3, 136.8, 137.5, 148.3 (*aryls*), 162.2 (d, $^2J_{YC}$ = 3.1 Hz, *C*OY). ^{1}H NMR (500 MHz, $C_6D_5CD_3$, −75 °C; δ): −0.51 (br app d, 1H, YCH_2), −0.35 (br app t, 2H, YCH_2), −0.24 (br app d, 1H, YCH_2), 0.63 (s, 3H, SiCH_3), 0.67 (s, 3H, SiCH_3), 0.75 (s, 3H, SiCH_3), 0.95 (s, 3H, SiCH_3), 1.51 (s, 9H, C(CH_3)$_3$), 1.92 (s, 9H, C(CH_3)$_3$), 1.06, 1.37, 1.74, 2.20, 2.36, 2.47, 2.70 (m, 9H, NCH_2CH_2O and aryl CH_2), 2.80 (br s, 3H, OCH_3), 2.94 (br s, 3H, OCH_3), 3.84 (br app d, 1H, aryl CH_2), 6.92 (s, 1H, aryl *H*), 7.23 (br s, 4H, aryl *H*), 7.40 (br s, 2H, aryl *H*), 7.62 (s, 1H, aryl *H*), 7.73 (br s, 2H, aryl *H*), 8.00 (br s, 2H, aryl *H*).

Synthesis of [(Et$_2$NCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Y-(CH$_2$SiMe$_2$Ph)$_2$ (7b). Recrystallization from petroleum ether, followed by collection on a sintered-glass funnel and washing with cold petroleum ether, provides the desired product as a white solid (32% yield) carrying only traces of alkane residue. Anal. Calcd for $C_{45}H_{76}ON_3Si_2Y$: C, 65.90; H, 9.34; N, 5.12. Found: C, 66.20; H, 8.85; N, 5.49. ^{1}H NMR (300 MHz, C_6D_6, 40 °C; δ): −0.21 (d, $^2J_{YH}$ = 2.7 Hz, 4H, YCH_2), 0.57 (s, 12H, Si(CH_3)$_2$), 0.68 (t, 12H, NCH$_2$CH_3), 1.43 (s, 9H, C(CH_3)$_3$), 1.81 (s, 9H, C(CH_3)$_3$), 2.36 (q, 8H, NCH_2CH$_3$), 1.20−1.32, 1.88−2.10, 2.14−2.22 (m, 8H, NCH_2CH_2N), 3.34 (br s, 2H, aryl CH_2), 6.95 (d, J = 2.6 Hz, 1H, aryl *H*), 7.58 (d, J = 2.6 Hz, 1H, aryl *H*), 7.18−7.30 (m, 6H, *p*-Ph *H* and *m*-Ph *H*), 7.80 (d, 4H, *o*-Ph *H*). ^{13}C NMR (75 MHz, C_6D_6, 40 °C; δ): 3.4 (Si(*C*H_3)$_2$), 9.7 (NCH$_2$*C*H$_3$), 31.4 (d, $^1J_{YC}$ = 41.9 Hz, Y*C*H$_2$), 31.0 (C(*C*H_3)$_3$), 32.5 (C(*C*H_3)$_3$), 34.6 (*C*Me$_3$), 36.1 (*C*Me$_3$), 46.4 (N*C*H$_2$), 49.3 (N*C*H$_2$), 51.0 (N*C*H$_2$), 61.4 (N*C*H$_2$), 123.4, 125.1, 125.7, 127.9, 128.0, 134.3, 137.3, 138.0, 147.9 (*aryls*), 161.5 (d, $^2J_{YC}$ = 3.3 Hz, *C*OY). ^{1}H NMR (300 MHz, $C_6D_5CD_3$, −75 °C, selected peaks; δ): −0.52 (br app d, 1H, YCH_2), −0.33 (br app d, 1H, YCH_2), −0.13 (br app d, 1H, YCH_2), 0.10 (br app d, 1H, YCH_2), 1.50 (s, 9H, C(CH_3)$_3$), 1.95 (s, 9H, C(CH_3)$_3$).

Synthesis of [(MeOCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]-Sc(CH$_2$SiMe$_2$Ph)$_2$ (8a). Recrystallization from diethyl ether, followed by collection on a sintered-glass funnel and washing with cold diethyl ether, provides the desired product as a white solid (26% yield) carrying only traces of alkane byproduct. Anal. Calcd for $C_{39}H_{62}NO_3Si_2Sc$: C, 67.49; H, 9.00; N, 2.02. Found: C, 67.81; H, 8.66; N, 2.31. ^{1}H NMR (300 MHz, C_6D_6, 55 °C; δ): −0.03 (s, 4H, ScCH_2), 0.59 (s, 12H, Si(CH_3)$_2$), 1.40 (s, 9H, C(CH_3)$_3$), 1.81 (s, 9H, C(CH_3)$_3$), 1.43−1.54, 2.33−2.59, 2.72−2.80, 3.21−3.44 (m, 10H, NCH_2CH_2O and aryl CH_2), 3.07 (s, 6H, OCH_3), 6.83 (d, J = 2.4 Hz, 1H, aryl *H*), 7.56 (d, J = 2.4 Hz, 1H, aryl *H*), 7.17−7.24 (m, 2H, *p*-Ph *H*), 7.25−7.32 (m, 4H, Ph *H*), 7.82 (m, 4H, Ph *H*). ^{13}C NMR (75 MHz, C_6D_6, 55 °C; δ): 3.1 (Si(*C*H_3)$_2$), 30.7 (Sc*C*H$_2$), 30.8 (C(*C*H_3)$_3$), 32.5 (C(*C*H_3)$_3$), 34.6 (*C*Me$_3$), 36.0 (*C*Me$_3$), 53.4 (br s, O*C*H$_3$), 61.9 (*C*H$_2$), 64.1 (*C*H$_2$), 71.9 (*C*H$_2$), 123.9, 124.9, 125.3, 127.9, 128.0, 134.4, 136.7, 138.2, 148.0 (*aryls*), 161.8 (*C*OSc). ^{1}H NMR (300 MHz, $C_6D_5CD_3$, −60 °C, selected peaks; δ): −0.22 (br app d, 1H, ScCH_2), −0.05 (br app d, 1H, ScCH_2), 0.16 (br app d, 1H, ScCH_2), 0.70 (br app d, 1H, ScCH_2), 0.53 (s, 3H, SiCH$_3$), 0.62 (s, 3H, SiCH$_3$), 0.80 (s, 3H, SiCH$_3$), 0.90 (s, 3H, SiCH$_3$), 1.48 (s, 9H, C(CH_3)$_3$), 1.92 (s, 9H, C(CH_3)$_3$), 2.80 (s, 3H, OCH_3), 3.10 (s, 3H, OCH_3).

Synthesis of [(Me$_3$CSCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]-Sc(CH$_2$SiMe$_2$Ph)$_2$ (8b). Recrystallization from petroleum ether, followed by collection on a sintered-glass funnel and washing with cold petroleum ether, provides desired product as a white solid (16% yield) carrying only traces of alkane residue. Anal. Calcd for $C_{45}H_{74}NOS_2Si_2Sc$: C, 66.70; H, 9.20; N, 1.73. Found: C, 67.70;

H, 8.99; N, 1.76. ^{1}H NMR (300 MHz, C_6D_6; δ): 0.49 (br d, J = 12 Hz, 2H, ScCH_2), 0.58 (br d, J = 12 Hz, 2H, ScCH_2), 0.62 (s, 6H, Si(CH_3)$_2$), 0.64 (s, 6H, Si(CH_3)$_2$), 1.01 (s, 18H, SC(CH_3)$_3$), 1.40 (s, 9H, C(CH_3)$_3$), 1.81 (s, 9H, C(CH_3)$_3$), 1.93−2.16, 2.19−2.32, 2.34−2.47 (m, 8H, NCH_2CH_2N), 3.17 (br s, 2H, aryl CH_2), 6.85 (d, J = 2.4 Hz, 1H, aryl *H*), 7.54 (d, J = 2.4 Hz, 1H, aryl *H*), 7.19−7.29 (m, 6H, Ph *H*), 7.79 (m, 4H, Ph *H*). ^{1}H NMR (300 MHz, C_6D_6, 70 °C; δ): 0.48 (br s, 4H, ScCH_2), 0.55 (s, 12H, Si(CH_3)$_2$), 1.06 (s, 18H, SC(CH_3)$_3$), 1.38 (s, 9H, C(CH_3)$_3$), 1.76 (s, 9H, C(CH_3)$_3$), 2.07−2.43, 2.45−2.60 (m, 8H, NCH_2CH_2N), 3.23 (s, 2H, aryl CH_2), 6.84 (d, J = 2.4 Hz, 1H, aryl *H*), 7.51 (d, J = 2.4 Hz, 1H, aryl *H*), 7.17−7.26 (m, 6H, Ph *H*), 7.74 (m, 4H, Ph *H*). ^{13}C NMR (75 MHz, C_6D_6, 70 °C; δ): 3.1 (s, Si(*C*H_3)$_2$), 27.6 (Sc*C*H_2), 31.0 (C(*C*H_3)$_3$), 31.1 (C(*C*H_3)$_3$), 32.5 (C(*C*H_3)$_3$), 34.7 (*C*Me$_3$), 36.0 (*C*Me$_3$), 40.5 (br s, S*C*Me$_3$), 46.3 (*C*H_2), 51.6 (*C*H_2), 60.8 (*C*H_2), 123.3 (*aryl*), 124.9 (*aryl*−H), 125.4 (*aryl*−H), 128.0 (*aryl*−H), 128.1 (*aryl*−H), 134.4 (*aryl*−H), 137.5 (*aryl*), 146.9 (*aryl*), 160.8 (*C*OSc). ^{1}H NMR (300 MHz, $C_6D_5CD_3$, −50 °C, selected peaks; δ): 0.35 (br app d, 1H, ScCH_2), 0.55 (br s, 3H, SiCH_3), 0.66 (br s, 3H, SiCH_3), 0.75 (br s, 3H, SiCH_3), 0.88 (s, 9H, SC(CH_3)$_3$), 1.01 (s, 9H, SC(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 1.86 (s, 9H, C(CH_3)$_3$).

Synthesis of [(MeOCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Y(CH$_2$SiMe$_3$)$_2$ (9). A thawing THF (5 mL) solution of the phenol (MeOCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-OH (0.36 g, 1.0 mmol, 1 equiv) was added dropwise to an in situ generated thawing THF (5 mL) solution of Y(THF)$_2$(CH$_2$SiMe$_3$)$_3$ (1 equiv), and the mixture was stirred for 4 h at room temperature. The volatile materials along with the byproduct, tetramethylsilane, were removed under vacuum. ^{1}H NMR spectra of the crude reaction mixtures show clean formation of the desired yttrium dialkyl product. Diethyl ether (5 mL) was added, and the mixture was filtered through Celite to remove insoluble salts. The filtrate was concentrated under vacuum. Recrystallization from petroleum ether, followed by collection on a sintered-glass funnel and washing with cold petroleum ether, provided the desired product as a white solid (0.24 g, 0.4 mmol, 38%). Anal. Calcd for $C_{29}H_{58}NO_3Si_2Y$: C, 56.74; H, 9.52; N, 2.28. Found: C, 55.62; H, 9.34; N, 2.36. ^{1}H NMR (300 MHz, C_6D_6, 40 °C; δ): −0.58 (d, $^2J_{YH}$ = 2.7 Hz, 4H, YCH_2), 0.44 (s, 18H, Si(CH_3)$_3$), 1.41 (s, 9H, C(CH_3)$_3$), 1.79 (s, 9H, C(CH_3)$_3$), 1.56−1.67, 2.44−2.58, 2.76−2.85 (m, 8H, NCH_2CH_2O), 3.48 (br s, 2H, aryl CH_2), 3.19 (s, 6H, OCH_3), 6.90 (d, J = 2.6 Hz, 1H, aryl *H*), 7.56 (d, J = 2.6 Hz, 1H, aryl *H*). ^{13}C NMR (75 MHz, C_6D_6, 40 °C; δ): 5.1 (Si(*C*H_3)$_3$), 30.8 (d, Y*C*H_2, $^1J_{YC}$ = 40.1 Hz), 30.7 (C(*C*H_3)$_3$), 32.6 (C(*C*H_3)$_3$), 34.6 (*C*Me$_3$), 36.0 (*C*Me$_3$), 52.9 (br s, O*C*H_3), 61.4 (*C*H_2), 63.8 (*C*H_2), 72.1 (*C*H_2), 123.5, 125.2, 125.9, 137.0, 137.4 (*aryls*), 162.4 (d, $^2J_{YC}$ = 3.3 Hz, *C*OY).

Synthesis of [(MeOCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Sc(CH$_2$SiMe$_3$)$_2$ (10). A thawing THF (5 mL) solution of the phenol (MeOCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-OH (**1**; 0.30 g, 0.9 mmol, 1 equiv) was added dropwise to the in situ generated thawing THF (5 mL) solution of Sc(THF)$_2$(CH$_2$SiMe$_3$)$_3$ (1 equiv), and the mixture was stirred for 4 h at room temperature. The volatile materials along with the byproduct, tetramethylsilane, were removed under vacuum. ^{1}H NMR spectra of the crude reaction mixtures show clean formation of the desired yttrium dialkyl product. Diethyl ether (5 mL) was added, and the mixture was filtered through Celite to remove insoluble salts. The filtrate was concentrated under vacuum. Recrystallization from petroleum ether, followed by collection on a sintered-glass funnel and washing with cold petroleum ether, provided the desired product as a white solid (0.22 g, 0.4 mmol, 45%). Anal. Calcd for $C_{29}H_{58}NO_3Si_2Sc$: C, 61.12; H, 10.26; N, 2.46. Found: C, 58.66; H, 9.01; N, 2.22. ^{1}H NMR (300 MHz, C_6D_6, 60 °C; δ): −0.22 (s, 4H, ScCH_2), 0.38 (s, 18H, Si(CH_3)$_3$), 1.39 (s, 9H, C(CH_3)$_3$), 1.79 (s, 9H, C(CH_3)$_3$), 1.62−1.72, 2.63, 2.86−2.95 (m, 8H, NCH_2CH_2O), 3.56 (br s, 2H, aryl CH_2), 3.19 (s, 6H, OCH_3), 6.89 (d, J = 2.7 Hz, 1H, aryl *H*), 7.54 (d, J = 2.7 Hz, 1H, aryl *H*). ^{13}C NMR (75 MHz, C_6D_6, 60 °C; δ): 4.7 (Si(*C*H_3)$_3$), 30.7 (Sc*C*H_2), 30.9 (C(*C*H_3)$_3$), 32.5 (C(*C*H_3)$_3$), 34.6 (*C*Me$_3$), 36.0 (*C*Me$_3$), 53.5 (br s, O*C*H_3), 61.9 (*C*H_2), 64.3 (*C*H_2), 72.0 (*C*H_2), 123.8, 125.0, 125.3, 136.8, 138.0 (*aryls*), 162.0 (*C*OSc). ^{1}H NMR (300 MHz, $C_6D_5CD_3$, −50 °C, selected peaks; δ): −0.35 (br app d, 1H, ScCH_2), −0.22 (br app d, 1H, ScCH_2), −0.15 (br app d, 1H, ScCH_2), −0.08 (br app d, 1H, ScCH_2), 0.45 (s, 9H, Si(CH_3)$_3$), 0.64 (s, 9H, Si(CH_3)$_3$), 1.46 (s, 9H, C(CH_3)$_3$), 1.89 (s, 9H, C(CH_3)$_3$), 2.85 (s, 3H, OCH_3), 3.20 (s, 3H, OCH_3), 6.93 (br d, 1H, aryl *H*), 7.61 (br d, 1H, aryl *H*).

Synthesis of [(C$_5$H$_4$N-2-CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Sc(CH$_2$SiMe$_2$Ph)$_2$ (11). Under a nitrogen atmosphere, a toluene-d_8 solution (0.4 mL) of Sc(CH$_2$SiMe$_2$Ph)$_3$(THF)$_2$ (68.4 mg, 0.1074 mmol, 1 equiv) was frozen in a J-Young tube. Toluene-d_8 (0.1 mL) was added to separate the toluene-d_8 solution (0.4 mL each) of the trialkyl complex from the phenol (C$_5$H$_4$N-2-CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-OH (**3**) (44.8 mg, 0.1074 mmol, 1 equiv). Before the ^{1}H NMR spectrum was recorded, the sample was warmed for 5−10 s and mixed. After the ^{1}H and ^{13}C NMR spectra were recorded, the sample was warmed up room temperature and stirred for 1 h. The ^{1}H NMR spectrum shows formation of one species containing the phenolate ligand. The kinetics of this process were studied by ^{1}H NMR spectroscopy at 0 °C. NMR spectra used to characterize **11** and **12** are presented in the Supporting Information. ^{1}H NMR (300 MHz, $C_6D_5CD_3$, −45 °C; δ): 0.21 (s, 9H, PhSi(CH_3)$_3$, 1 equiv), −0.09 (br app d, J = 11.2 Hz, 1H, ScC*H*H), 0.17 (br app d, J = 11.2 Hz, 1H, ScC*H*H), 0.45 (br app d, J = 11.2 Hz, 1H, ScC*H*H), 0.64 (br app d, J = 11.2 Hz, 1H, ScC*H*H), 0.29 (s, 3H, SiCH_3), 0.54 (s, 3H, SiCH_3), 0.92 (s, 3H, SiCH_3), 0.96 (s, 3H, SiCH_3), 1.40 (m, 17H, C(CH_3)$_3$ and O(CH$_2$CH_2)$_2$, THF, 2 equiv), 1.65 (s, 9H, C(CH_3)$_3$), 3.57 (t, 8H, O(CH_2CH$_2$)$_2$, THF, 2 equiv), 2.60−2.83 (m, 4H, NCH_2), 4.01 (d, J = 14.4 Hz, 1H, NCH_2), 4.37 (d, J = 11.1 Hz, 1H, NCH_2), 5.76 (d, 1H, aryl *H*), 6.21 (t, 1H, aryl *H*), 6.36−6.48 (m, 4H, aryl *H*), 6.72−7.63 (15H, aryl *H*), 8.17 (d, 2H, aryl *H*), 8.66 (d, 1H, aryl *H*), 8.91 (d, 1H, aryl *H*). ^{13}C NMR (75 MHz, $C_6D_5CD_3$, −45 °C; δ): −1.3 (PhSi(*C*H_3)$_3$), 2.3 (Si*C*H_3), 2.6 (Si*C*H_3), 2.7 (Si*C*H_3), 3.8 (Si*C*H_3), 25.6 (O(CH$_2$*C*H$_2$)$_2$, THF), 28.7 (br, Sc*C*H_2), 30.3 (br, Sc*C*H_2), 30.5 (C(*C*H_3)$_3$), 32.1 (C(*C*H_3)$_3$), 34.0 (*C*Me$_3$), 35.3 (*C*Me$_3$), 60.3 (N*C*H$_2$), 61.9 (N*C*H$_2$), 62.3 (N*C*H$_2$), 67.6 (O(*C*H$_2$CH$_2$)$_2$, THF), 119.9, 121.8, 122.7, 123.4, 123.5, 127.9, 129.0, 133.4, 133.5, 133.8, 134.1, 134.3, 135.1, 136.4, 136.9, 137.7, 138.8, 139.9, 147.4, 147.6, 149.5, 156.6, 156.7, 161.3 (*aryls* and *C*$_6$H$_5$SiMe$_3$).

Spectroscopic Characterization of 12. ^{1}H NMR (300 MHz, $C_6D_5CD_3$; δ): 0.20 (s, 18H, PhSi(CH_3)$_3$, 2 equiv), 0.27 (d, J = 11 Hz, 1H, ScC*H*H), 0.41 (d, J = 11 Hz, 1H, ScC*H*H), 0.61 (s, 3H, SiCH_3), 0.62 (s, 3H, SiCH_3), 1.36 (m, 17H, C(CH_3)$_3$ and O(CH$_2$CH_2)$_2$, THF, 2 equiv), 1.65 (s, 9H, C(CH_3)$_3$), 3.72 (br s, 8H, O(CH_2CH$_2$)$_2$, THF, 2 equiv), 2.91 (d, J = 14.8 Hz, 1H, NCH*H*), 3.32 (d, J = 13.5 Hz, 1H, NCH*H*), 3.86 (d, J = 13.5 Hz, 1H, NCH*H*), 4.19 (d, J = 14.8 Hz, 1H, NCH*H*), 4.08 (s, 1H, NC*H*), 5.01 (t, 1H, aryl *H*), 5.74 (d, 1H, aryl *H*), 6.05−6.12 (m, 1H, aryl *H*), 6.16−6.24 (d, 1H, aryl *H*), 6.24−6.30 (t, 1H, aryl *H*), 6.56−6.63 (td, 1H, aryl *H*), 7.02 (d, 1H, aryl *H*), 7.16−7.23 (m, 7H, aryl *H*), 7.28−7.35 (t, 2H, aryl *H*), 7.39−7.46 (m, 5H, aryl *H*), 7.52 (d, 1H, aryl *H*), 7.90 (dd, 2H, aryl *H*), 8.72 (d, 1H, aryl *H*). ^{13}C NMR (75 MHz, $C_6D_5CD_3$; δ): −1.2 (PhSi(*C*H_3)$_3$), 3.0 (Si*C*H_3), 3.1 (Si*C*H_3), 25.6 (O(CH$_2$*C*H$_2$)$_2$, THF), 27.7 (Sc*C*H_2), 30.3 (C(*C*H_3)$_3$), 32.1 (C(*C*H_3)$_3$), 34.3 (*C*Me$_3$), 35.5 (*C*Me$_3$), 62.1 (N*C*H$_2$), 64.4 (N*C*H$_2$), 68.8 (br s, O(*C*H$_2$CH$_2$)$_2$, THF), 96.6 (*aryl*−H), 100.9 (N*C*H, $^1J_{C-H}$ = 170 Hz), 114.0 (*aryl*−H), 122.3, 122.5, 123.7, 123.9, 124.9, 127.7, 127.8, 128.0, 129.0, 131.0, 133.5, 136.6, 137.9, 138.3, 140.2, 143.5, 143.8, 146.9, 149.0, 151.9, 159.8, 160.3 (*aryls*

and $C_6H_5SiMe_3$). A diethyl ether solution of **12** was quenched with CD_3OD and filtered through alumina. The volatile materials were removed under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$, peaks in the 3.5−4.0 ppm region; δ): 3.80 (d, J = 13.5 Hz, 1H, aryl C*H*H), 3.83 (d, J = 13.5 Hz, 1H, aryl C*H*H), 3.86 (br s, 1H, NC*H*DC$_5$H$_4$N), 3.88 (br s, 2H, NCH_2C$_5$H$_4$N). ^{2}H NMR (75 MHz, CH_2Cl_2; δ): 3.83.

Synthesis of 13. Under a nitrogen atmosphere, dry pyridine (10.7 μL, 0.13 mmol, 1 equiv) was added dropwise to a diethyl ether solution (3 mL) of **12** (1 equiv) previously generated. The reaction mixture was stirred for 5 min. The volatile materials were removed under vacuum. The ^{1}H NMR spectrum shows formation of one species containing the phenolate ligand. ^{1}H NMR (300 MHz, $C_6D_5CD_3$; δ): 0.42 (d, J = 11 Hz, 1H, ScC*H*H), 0.60 (d, J = 11 Hz, 1H, ScC*H*H), 0.31 (s, 3H, SiCH_3), 0.38 (s, 3H, SiCH_3), 1.33 (m, 9H, C(CH_3)$_3$), 1.73 (s, 9H, C(CH_3)$_3$), 2.98 (d, J = 14.4 Hz, 1H, NCH*H*), 3.12 (br d, J = 14.4 Hz, 1H, NCH*H*), 3.61 (br d, J = 14.4 Hz, 1H, NCH*H*), 4.20 (d, J = 14.4 Hz, 1H, NCH*H*), 4.07 (s, 1H, NC*H*), 5.07 (br t, 1H, aryl *H*), 5.78 (d, 1H, aryl *H*), 6.12−6.23 (m, 2H, aryl *H*), 6.30 (t, 1H, aryl *H*), 6.48 (br t, 2H, C$_5H_5$N), 6.63 (t, 1H, aryl *H*), 6.78 (br t, 1H, C$_5H_5$N), 6.88 (br s, 1H, aryl *H*), 7.17−7.46 (m, 4H, aryl *H*), 7.65 (br s, 1H, aryl *H*), 7.73 (br s, 2H, aryl *H*), 8.77 (d, 1H, aryl *H*), 8.97 (br s, 2H, C$_5H_5$N). ^{13}C NMR (75 MHz, $C_6D_5CD_3$; δ): −1.2 (PhSi(*C*H$_3$)$_3$), 2.3 (Si*C*H$_3$), 2.5 (Si*C*H$_3$), 30.4 (C(*C*H$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 32.2 (Sc*C*H$_2$), 34.2 (*C*Me$_3$), 35.6 (*C*Me$_3$), 62.7 (N*C*H$_2$), 64.4 (N*C*H$_2$), 101.4 (N*C*H), 96.9 (*aryl*−H), 114.2 (*aryl*−H), 122.3, 122.5, 123.8, 124.9, 125.2, 127.6, 128.0, 129.0, 131.1, 133.5, 133.8, 135.7, 136.6, 137.9, 138.3, 138.6, 140.2, 144.0. 146.9, 149.0, 150.8, 151.8, 152.7, 159.8, 160.4 (*aryls*, C_5H_5N, and $C_6H_5SiMe_3$).

Activation of 7a with [PhNHMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and NMR-Scale Ethylene Polymerizations. Under a nitrogen atmosphere, a chlorobenzene-d_5 solution (0.4 mL) of an yttrium dialkyl complex (13.5 mg, 0.018 mmol, 1 equiv) was frozen in a J-Young tube. A chlorobenzene-d_5 solution (0.3 mL) of diphenylmethane (3.1 mg, 0.018 mmol, 1 equiv) was added as an internal standard and to separate the chlorobenzene-d_5 solution (0.4 mL each) of the yttrium dialkyl complex from the solution of the stoichiometric activator [PhNHMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (14.6 mg, 0.018 mmol, 1 equiv). Before the ^{1}H NMR spectrum was recorded, the sample was warmed for 5−10 s and mixed. The ^{1}H NMR spectrum shows formation of mainly one species containing the phenolate ligand along with the alkane byproduct. After activation, ethylene (0.166 mmol, 9.3 equiv) was condensed in the J-Young tube. Using diphenylmethane as internal standard, slow consumption of ethylene (<4 equiv) was observed over 6 h.

Spectroscopic Characterization of 14. ^{1}H NMR (300 MHz, C_6D_5Cl, −40 °C; δ): tentatively assigned to the activated species (major), −0.75 (br d, J = 10.8 Hz, 1H, YCH*H*), −0.54 (br d, J = 10.8 Hz, 1H, YCH*H*), 0.37 (br s, 3H, SiCH_3), 0.49 (br s, 3H, SiCH_3), 1.36 (s, 9H, C(CH_3)$_3$), 1.68 (s, 9H, C(CH_3)$_3$), 2.09−3.50 (m, NCH_2CH_2O and aryl CH_2; overlapping broad peaks), 3.11 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 2.62 (s, 6H, C$_6$H$_5$N(CH_3)$_2$); not assigned, 0.85 (t, 1H), 0.89 (t, 1H), 1.61 (s, not C(CH_3)$_3$ from the starting material), 6.55−7.79 (aryl *H* peaks for YCH$_2$SiMe$_2$C$_6H_5$, C$_6H_2$-OY, C$_6H_5$SiMe$_3$, and C$_6H_5$NMe$_2$). ^{1}H NMR (300 MHz, C_6D_5Cl; δ): tentatively assigned to the activated species (major), −0.60 (br s, 2H, YCH_2), 0.40 (br s, 6H, Si(CH_3)$_2$), 1.32 (s, 9H, C(CH_3)$_3$), 1.57 (br s, 9H, C(CH_3)$_3$), 2.08−3.08 (br m, 10H, NCH_2CH_2O and aryl CH_2), 3.23 (s, 6H, OCH_3), 2.65 (s, 6H, C$_6$H$_5$N(CH_3)$_2$), remaining peaks are broad and overlapped; not assigned, 0.85 (m, ∼2H), 1.22 (s, not C(CH_3)$_3$ from the starting material), 6.67−7.71 (aryl *H* peaks for YCH$_2$SiMe$_2$C$_6H_5$, C$_6H_2$-OY, C$_6H_5$SiMe$_3$, and C$_6H_5$NMe$_2$).

Activation of 9 with [PhNHMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and NMR-Scale Ethylene Polymerizations. Under a nitrogen atmosphere, a chlorobenzene-d_5 solution (0.4 mL) of an yttrium dialkyl complex (9.1 mg, 0.015 mmol, 1 equiv) was frozen in a J-Young tube. A chlorobenzene-d_5 solution (0.3 mL) of diphenylmethane (2.5 mg, 0.015 mmol, 1 equiv) was added as an internal standard and to separate the chlorobenzene-d_5 solution (0.4 mL each) of the yttrium dialkyl complex from the stoichiometric activator [PhNHMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (11.9 mg, 0.015 mmol, 1 equiv). Before the ^{1}H NMR spectrum was recorded, the sample was warmed for 5−10 s and mixed. The ^{1}H NMR spectrum shows the formation of mainly one species containing the phenolate ligand, along with the alkane byproduct. After activation, ethylene (0.166 mmol, 11.1 equiv) was condensed into the J-Young tube. Using diphenylmethane as an internal standard, slow consumption of ethylene (<7.5 equiv) was observed over 7 h.

Spectroscopic Characterization of 15. ^{1}H NMR (300 MHz, C_6D_5Cl, −40 °C; δ): tentatively assigned to the activated species (major), −0.98 (br d, J = 11.1 Hz, 1H, YCH*H*), −0.77 (br d, J = 11.1 Hz, 1H, YCH*H*), 0.19 (br s, 9H, Si(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 1.60 (s, 9H, C(CH_3)$_3$), 1.70−3.00 (br m, NCH_2CH_2O and aryl CH_2), 3.15 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 2.59 (s, 6H, C$_6$H$_5$N(CH_3)$_2$); not assigned, 0.83 (m), 1.22 (s), 6.54−7.62 (aryl *H* peaks for C$_6H_2$-OY, and C$_6H_5$NMe$_2$). ^{1}H NMR (300 MHz, C_6D_5Cl; δ): tentatively assigned to the activated species (major), −0.81 (br s, 2H, YCH_2), 0.15 (br s, 9H, Si(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 1.58 (br s, 9H, C(CH_3)$_3$), 1.80−4.00 (br m, NCH_2CH_2O and aryl CH_2; overlapping broad peaks), 3.33 (s, 6H, OCH_3), 2.69 (s, 6H, C$_6$H$_5$N(CH_3)$_2$); not assigned, 0.84 (m), 1.22, 6.67−7.51 (aryl *H* peaks for C$_6H_2$-OY, and C$_6H_5$NMe$_2$).

Line Shape and Eyring Analysis. NMR spectral simulations were performed using gNMR version 3.6. The chemical shifts observed in the slow limit exchange (203 K) were used to set up the spin systems. The relative population ratio was fixed at 1:1 for **7a**, **8a**, and **10**. Lorentzian line shapes with line widths of 2 Hz were utilized. Small changes to the line width did not visibly affect the activation parameters of the exchange process. As the chemical shifts of the different hydrogens vary slightly with temperature, the difference in the chemical shifts was used to compare simulated with experimental spectra. For different temperatures, the exchange rate was varied to get the best fit between the simulated and the experimental spectra. Activation parameters were determined by a standard Eyring analysis, and the standard deviations from the χ^2 fit were used to estimate the uncertainties in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Ethylene Polymerizations. Ethylene polymerizations were performed in a high-pressure glass vessel equipped with a magnetic stirrer. In a typical procedure, under a nitrogen atmosphere, solid MAO (48.3 mg, 0.833 mmol, 500 equiv) was added to 4.5 mL of chlorobenzene. The mixture was pressurized to 1 bar of ethylene. A chlorobenzene (0.5 mL) solution of catalyst precursor (1.67 μmol, 1 equiv) was added by syringe. The ethylene pressure was immediately increased to 5 bar, and the solution was stirred for 1 h. The polymerization was stopped by venting of the vessel and quenching with a mixture of 37% HCl solution and methanol (1:12 v/v). The polymer was collected by filtration, washed with methanol (3 × 10 mL), and dried under high vacuum overnight. The amounts of polymer obtained are tabulated in the Supporting Information.

X-ray Crystal Data: General Procedure. Crystals grown from diethyl ether (**7a** and **8a**) or a mixture of diethyl ether and petroleum ether (**7b**) at −35 °C were removed quickly from a scintillation vial to a microscope slide coated with Paratone N oil. Samples were selected and mounted on a glass fiber with Paratone N oil. Data collection was carried out on a Bruker Smart 1000 CCD diffractometer. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Some details regarding refined data and cell parameters are available in Table 1. Selected bond distances and angles are supplied in the captions of Figures 3−5.

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Supporting Information Available: NMR spectra for experiments involving **7a**, **8a**, **10**−**12**, and **15**, kinetic plots for the conversion of **11** into **12**, tabulated results of the ethylene polymerization trials, Eyring plots for **10**, and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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