Yttrium Complexes of the Chelating, C_2-Symmetric, Bis(silylamido)biphenyl Ligand $[DADMB]^{2-}$ $(=\{[6,6'\text{-}Me_2\text{-}(C_6H_3)_2](2,2'\text{-}NSiMe_2{}^tBu)_2\}^{2-})$

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The yttrium bis(silylamido)biphenyl complex $[DADMB]YCl(THF)_2$ (**2**; DADMB = 2,2′-bis((*tert*-butyldimethylsilyl)amido)-6,6′-dimethylbiphenyl) was prepared from $Li_2[DADMB]\cdot 2THF$ and $YCl_3(THF)_3$, and its structure was determined by X-ray crystallography. Compound **2** reacts with MeLi and $(Me_3Si)_2CHLi$ to give the corresponding alkyl derivatives $[DADMB]YMe(THF)_2$ (**3**) and $[DADMB]Y[CH(SiMe_3)_2](THF)(OEt_2)$ (**5**), respectively. In the presence of silicone grease, the reaction of **2** with MeLi produces the yttrium trimethylsiloxide complex $[DADMB]Y(OSiMe_3)(THF)_2$ (**4**), which was also crystallographically characterized. Both **3** and **5** react with phenylsilane or H_2 to give the insoluble, dimeric yttrium hydride $\{[DADMB]Y(\mu\text{-}H)(THF)\}_2\cdot C_6H_6$ (**6**). The alkyl derivatives **3** and **5** exhibit only limited olefin polymerization activity; however, the hydride **6** reacts rapidly with ethylene or 1-hexene to give a single insertion product. The resulting yttrium ethyl complex **7** was structurally characterized. Compound **6** reacts with pyridine to produce a mixture of the isomeric 1,2- and 1,4-insertion products **9** and **10**, $[DADMB]Y(NC_5H_6)(pyr)_2$. Compound **9** converts quantitatively to **10** upon heating.

Introduction

The chemistry of d^0 early-transition-metal complexes has recently attracted considerable attention, as these species have been developed as catalysts for various transformations, including olefin polymerization, dehydropolymerization, hydrosilylation, and hydrogenation.[1−9] In much of this chemistry, it is widely appreciated that reaction pathways are readily controlled via changes in electronic and steric environments, and that much of the observed reactivity for these complexes derives from electrophilicity and coordinative unsaturation at the metal center.[2,3] Much of the work with d^0 metal complexes has featured cyclopentadienyl ligand sets. In an attempt to extend the possibility for modifying and controlling the reactivity of early-transition-metal complexes, recent research efforts have been directed toward development of alternative ligand sets that may increase the electrophilicity of the metal center and create a different steric environment at the reactive site.[10−17] In particular, the use of multidentate amido ligands has become an area of intensive study.[15,16,18−29]

Our previous work in this area led to the synthesis and investigation of a number of complexes of the bis(triisopropylsilyl)-*o*-phenylenediamido ligand $[o\text{-}C_6H_4(NSi^iPr_3)_2]^{2-}$.[30,31] A common structural feature for these

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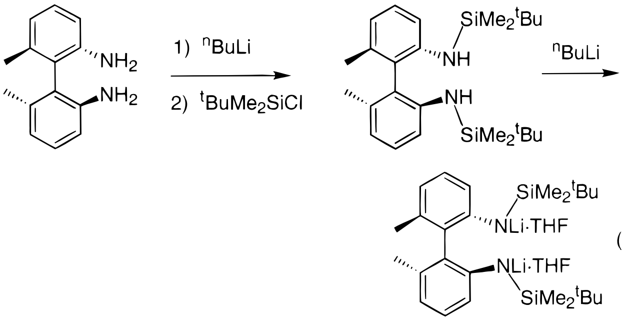
complexes is the presence of a secondary bonding interaction between the aromatic ring and the metal center. While confirming the electron-poor character of the metal center in complexes of this ligand, this donation of electron density from the ligand has the potentially undesirable effect of reducing electrophilicity at the metal. To reduce the possibility of such an interaction, and also to create a chiral environment at the reactive site, we began to explore alternative bis(silylamido) ligands based on C_2-symmetric biphenyl backbones.[32] Asymmetric early-transition-metal complexes, usually based on substituted cyclopentadienyl ligands, have found application as olefin polymerization catalysts for control of stereoregularity of the resulting polymer.[2,3,7,10,33,34] Group 3 and lanthanide metallocene complexes have also been used as regio- and stereoselective hydrosilylation catalysts, and the effect of varying the ancillary Cp-based ligands on the reactivity and selectivity of the catalyst has been studied extensively.[35−37] Even though many alternatives to cyclopentadienyl ligands in early-transition-metal chemistry have been explored,[10−29] the study of chelating diamides as ligands has been mostly restricted to symmetric systems.

We recently reported studies on a tantalum mixed amido−imido ligand system derived from a bis((trimethylsilyl)amino)biphenyl ligand.[32] Here we describe studies on a series of yttrium complexes with a related bis(silylamido)biphenyl ligand, using more sterically demanding *tert*-butyldimethylsilyl substituents. Unlike the tantalum system, where reactivity was dominated by reactions of the nitrogen−silicon bond, the yttrium complexes described here appear to possess more robust bis(silylamido) spectator ligands.

Results and Discussion

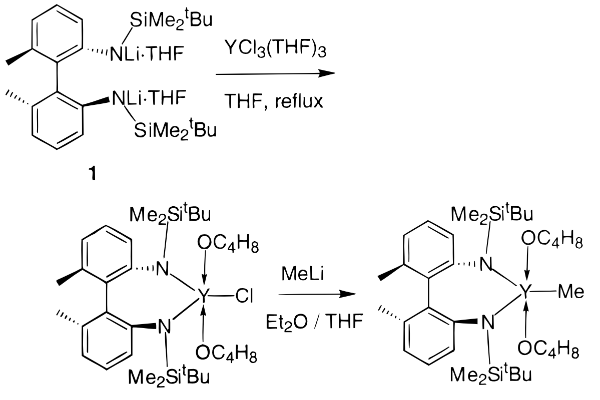
The starting material 2,2′-diamino-6,6′-dimethylbiphenyl was prepared according to the literature procedure.[38] Silylation of this diamine was achieved via deprotonation with ^{n}BuLi in THF, followed by reaction of the resulting dianion with ^{t}BuMe$_2$SiCl (eq 1). Lithiation of the silylamine in situ with ^{n}BuLi produced the lithium salt (**1**), isolated as a THF adduct in 84% yield from pentane.



(1)

1

Reaction of **1** with YCl$_3$(THF)$_3$ in refluxing THF yielded the yttrium complex **2** as a white crystalline solid, in 92% yield (eq 2).



(2)

2 **3**

Yttrium complex **2** (Figure 1) adopts a distorted-trigonal-bipyramidal coordination geometry, with the chelating diamide and chloride ligands in the equatorial plane and the two coordinated THF molecules in the axial positions. Selected bond distances and angles are given in Table 1. The molecule has an approximate (noncrystallographic) C_2 axis coincident with the Y−Cl bond. The ligand bite angle is 123.3(2)°, and the average Y−N distance is 2.25 Å. The dihedral angle between the phenyl planes is 84.8°. The short Y−C$_{ipso}$ (average 2.75 Å) and Y−C$_{ortho}$ (average 2.87 Å) distances, and the small Y−N−C$_{ipso}$ angles (average 94.6°), suggest the presence of Y−aromatic carbon bonding interactions, which are often observed in complexes of this type.[30,31]

The methyl derivative **3**, an off-white crystalline solid, was synthesized in 60% yield by reaction of **2** with MeLi in Et$_2$O/THF (eq 2). The methyl group of **3** gives rise to a doublet in the ^{1}H NMR spectrum at −0.42 ppm, and the coupling constant $^2J_{YH} = 1.8$ Hz is slightly smaller than those reported for Cp*$_2$YMe(THF) ($^2J_{YH} = 2.3$ Hz) and related complexes.[13,39] The $^1J_{CH} = 101$ Hz coupling (cf. 108.2 Hz in Cp*$_2$YMe(THF)[39] and 108 Hz in Cp*Y(OC$_6$H$_3$^{t}Bu$_2$)Me(THF)$_2$[13]) is lower than the typical 120−130 Hz for an sp^3 CH bond.[40−42]

The synthesis of **3** was found to be very sensitive to the presence of adventitious amounts of silicone grease, such that high yields require exclusive use of hydrocarbon grease in the Schlenkware used for the synthesis. In the presence of Dow Corning silicone grease, the reaction of **2** with MeLi resulted in formation of the yttrium trimethylsiloxide derivative **4** in 50% yield (as the only isolable product). Complex **4** was characterized by X-ray crystallography (Figure 2), and selected bond distances and angles are listed in Table 2. The structure is very similar to that of the chloride complex **2**, with an Y−N distance of 2.26 Å (average), a ligand bite angle of 118.8(1)°, and an almost linear Y−O−Si linkage of

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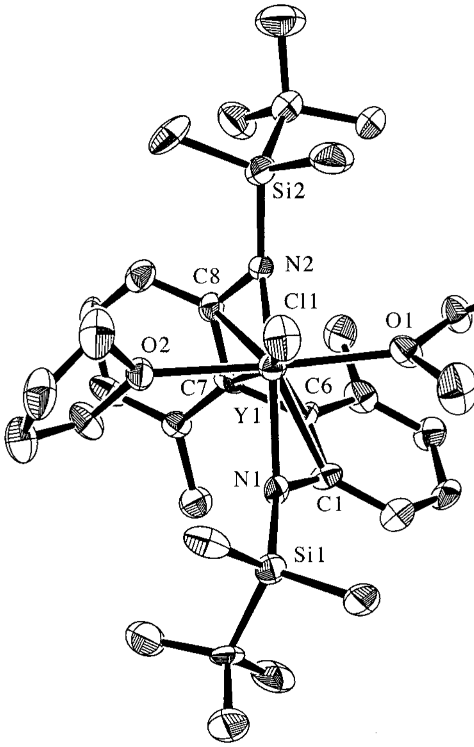

Figure 1. ORTEP diagram of [DADMB]YCl(THF)$_2$ (**2**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 2

Y(1)-Cl(1)	2.574(2)	Y(1)−C(1)	2.745(8)
Y(1)−N(1)	2.247(7)	Y(1)−C(6)	2.847(8)
Y(1)−N(2)	2.252(7)	Y(1)−C(7)	2.884(9)
Y(1)−O(1)	2.365(6)	Y(1)−C(8)	2.749(7)
Y(1)−O(2)	2.388(5)		
N(1)−Y(1)−N(2)	123.3(2)	N(1)−Y(1)−Cl(1)	116.9(2)
O(1)−Y(1)−O(2)	167.9(2)	N(2)−Y(1)−Cl(1)	119.8(2)
O(1)−Y(1)−Cl(1)	83.5(2)	Y(1)−N(1)−C(1)	94.5(5)
O(2)−Y(1)−Cl(1)	84.3(2)	Y(1)−N(2)−C(8)	94.6(5)

175.5(2)°. The dihedral angle between the phenyl planes is 92.0°. The Y−C$_{ipso}$ and Y−C$_{ortho}$ bonding interactions are again present, but the corresponding distances are longer (averages of 2.82 and 3.00 Å, respectively), and the Y−N−C$_{ipso}$ angles are larger (average 98.2°) than those observed for **2**. The mechanism of formation of **4** is unclear, but the methyl complex **3** was found to be unreactive toward silicone grease (benzene-d_6, 24 h, room temperature), suggesting that formation of **4** proceeds via trapping by silicone grease of an intermediate in the reaction of **2** with MeLi. Analogous reactivity was reported for the samarium hydride complex [(C$_5$Me$_5$)$_2$Sm(μ-H)]$_2$, which reacts with hexamethylcyclotrisiloxane to afford the dimeric siloxide [(C$_5$Me$_5$)$_2$-Sm(THF)]$_2$(μ-OSiMe$_2$OSiMe$_2$O).[43]

Exposure of **2** to C$_2$H$_4$ (80 psi) in the presence of MAO cocatalyst (500 equiv) in toluene produced only 0.06 g of polyethylene. The methyl derivative **3** was also found to be inert toward olefins, since no reaction was observed between **3** and 1-hexene in benzene-d_6 (24 h, room temperature). A benzene-d_6 solution of **3** under 5 psi of C$_2$H$_4$ appears to react very slowly, as indicated by formation of a cloudy precipitate, presumed to be polyethylene, over the course of a few days. During this time, only a small decrease in the amount of C$_2$H$_4$ was observed (by ^{1}H NMR spectroscopy), **3** remained unchanged after 3 days, and no new organoyttrium species were detected by ^{1}H NMR spectroscopy.

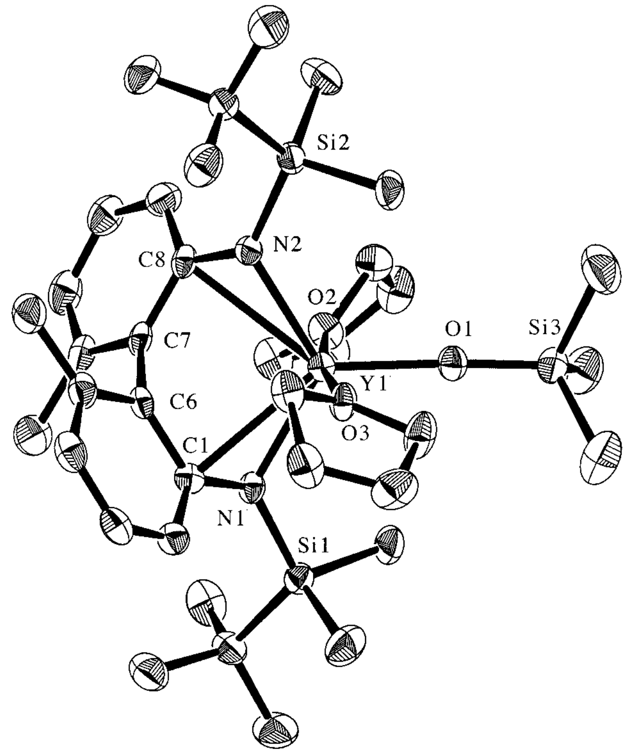

Figure 2. ORTEP diagram of [DADMB]Y(OSiMe$_3$)(THF)$_2$ (**4**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 4

Y(1)−O(1)	2.111(3)	Y(1)−C(1)	2.827(4)
Y(1)−N(1)	2.262(3)	Y(1)−C(6)	3.010(4)
Y(1)−N(2)	2.254(3)	Y(1)−C(7)	2.993(4)
Y(1)−O(2)	2.358(3)	Y(1)−C(8)	2.816(4)
Y(1)−O(3)	2.365(3)	O(1)−Si(3)	1.601(3)
Y(1)−O(1)−Si(3)	175.5(2)	N(1)−Y(1)−O(1)	120.4(1)
N(1)−Y(1)−N(2)	118.8(1)	N(2)−Y(1)−O(1)	120.8(1)
O(1)−Y(1)−O(2)	84.9(1)	Y(1)−N(1)−C(1)	98.3(2)
O(1)−Y(1)−O(3)	84.9(1)	Y(1)−N(2)−C(8)	98.1(2)

Reasoning that the coordinated THF ligands may act to greatly diminish the reactivity of **3** toward alkenes, we sought to introduce a bulkier alkyl group which might facilitate dissociation of THF with production of a more coordinatively unsaturated complex. The bis(trimethylsilyl)methyl derivative [DADMB]Y[CH(SiMe$_3$)$_2$]-(THF)(OEt$_2$) (**5**) was obtained by reaction of **2** with (Me$_3$Si)$_2$CHLi in diethyl ether. The incorporation of Et$_2$O into **5** suggests that the more crowded steric environment in **5** can indeed favor dissociation of coordinated solvent. A similar tendency toward THF dissociation in the presence of a bulky alkyl substituent has been observed for [NON]Y[CH(SiMe$_3$)$_2$](THF) ([NON]$^{2-}$ = [^{t}Bu-d_6-N-o-C$_6$H$_4$)$_2$O]$^{2-}$).[44] The YCH resonance in the ^{1}H NMR spectrum appears as a doublet at δ −0.94 ($^2J_{YH}$ = 2.1 Hz), and the corresponding resonance in the ^{13}C NMR spectrum appears at δ 39.4 ($^1J_{YC}$ = 35.6 Hz). The downfield chemical shift for the α-carbon is much closer

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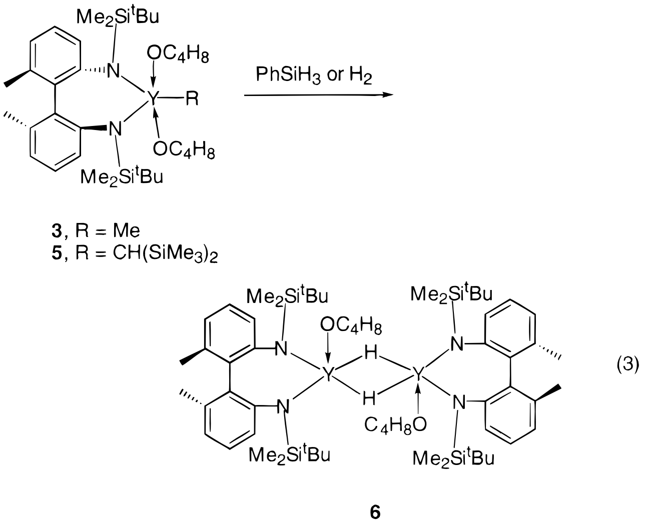
to those reported for [NON]Y[CH(SiMe$_3$)$_2$](THF)[44] (37.9 ppm) and [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$[11] (43.5 ppm) than to the one for Cp*$_2$YCH(SiMe$_3$)$_2$[45] (25.19 ppm) and can therefore be viewed as an indication of the high electrophilicity of the metal center in **5**. The small C−H coupling for the α-C−H bond ($^1J_{CH}$ = 80 Hz, cf. 88 Hz in [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$[11] and 84.2 Hz in Cp*$_2$YCH(SiMe$_3$)$_2$[45]) is consistent with the presence of an α-agostic interaction, as observed for many group 3 and lanthanide bis(trimethylsilyl)methyl complexes.[40,41]

Reaction of **5** with C_2H_4 (5 psi, benzene-d_6) also resulted in the very slow formation of insignificant amounts of polyethylene, with no new organoyttrium species observed in the ^{1}H NMR spectrum after 5 days. This low olefin polymerization activity for **3** and **5** should be compared to the behavior of other group 3 and lanthanide alkyl derivatives, some of which are reported to be active polymerization catalysts. Thus, Cp*$_2$YMe(THF),[39] Cp*$_2$ScMe,[46] [Tp^{Me}YR$_2$(THF)] (Tp^{Me} = tris(3,5-dimethyl-1-pyrazolyl)borohydride),[17] and R$_2$Si(η^5-C$_5$H$_4$)(η^5-C$_5$Me$_4$)LuCH(SiMe$_3$)$_2$[47] are reported to be active as olefin polymerization catalysts, whereas [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph(THF)[48] is moderately active and [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YCH(SiMe$_3$)$_2$,[12] Cp*$_2$MCH(SiMe$_3$)$_2$ (M = La, Nd, Lu),[49] and [NON]Y[CH(SiMe$_3$)$_2$](THF)[44] are inactive. The lack of olefin polymerization activity in such systems is usually attributed to steric hindrance (in the case of CH(SiMe$_3$)$_2$ derivatives), coordinated THF (which blocks coordination sites), or high ionicity in the bonding (which leads to more contracted vacant metal orbitals).[11,12,48]

To evaluate the activities of **3** and **5** toward σ-bond metathesis processes involving hydrosilanes, their interactions with PhSiH$_3$ were investigated. Both compounds **3** and **5** were found to react with PhSiH$_3$ in benzene at room temperature via Si−C bond formation, to give PhMeSiH$_2$ and PhSiH$_2$CH(SiMe$_3$)$_2$,[35] respectively. These reactions also produced a white crystalline precipitate, insoluble in pentane and benzene but soluble in THF, characterized as an yttrium hydride (eq 3). Hydride **6** was also produced by hydrogenolysis, upon exposure of **3** or **5** to H$_2$ gas in benzene-d_6 (5 psi, room temperature). The other products of these reactions (methane and (Me$_3$Si)$_2$CH$_2$,[50] respectively) were observed to form quantitatively (by NMR spectroscopy).



3, R = Me
5, R = CH(SiMe$_3$)$_2$

(3)

6

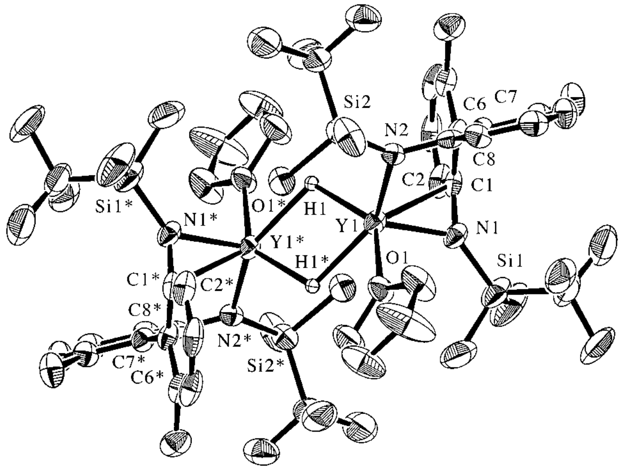


Figure 3. ORTEP diagram of {[DADMB]YH(THF)}$_2$·C$_6$H$_6$ (**6**).

The hydride resonance for **6** was observed in the ^{1}H NMR spectrum as a triplet at δ 5.88 ($^1J_{YH}$ = 28 Hz) in THF-d_8. The Y−H coupling constant is similar to that observed for other yttrium hydride dimers,[11,12,51,52] and the chemical shift is rather downfield compared to most yttrium hydrides with bis(cyclopentadienyl) ligands (δ 2.02−5.45).[47,51,53,54] However, the shift for **6** is not as low as those reported for bis(benzamidinato)yttrium hydrides (δ 8.28−8.31)[11] and {[Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(μ-H)}$_2$[12] (δ 6.80). This hydride signal was observed to decay slowly in intensity and completely disappear within 4 days at room temperature, indicating exchange with deuterium from the THF-d_8 solvent. In the IR spectrum of **6**, the Y−H absorption at 1240 cm^{-1} was obscured by strong ligand absorptions in the same region and could be assigned only by comparison with the spectrum of the deuterated analogue **6**-d_2 (obtained by hydride exchange with THF-d_8), which exhibits a Y−D absorption at 870 cm^{-1}. This frequency is, however, in good agreement with those reported for other dimeric yttrium hydride species.[50,51]

X-ray-quality crystals of **6** were grown by slow diffusion of PhSiH$_3$ (in benzene solution) layered above a benzene solution of **5**, and the molecular structure (Figure 3) may be described as a centrosymmetric dimer. The hydride atom, located in the Fourier difference map, was refined isotropically. Selected bond distances and angles are given in Table 3. The Y−H distance is 2.25(4) Å (average), and the Y−H−Y angle is 109(2)°. The

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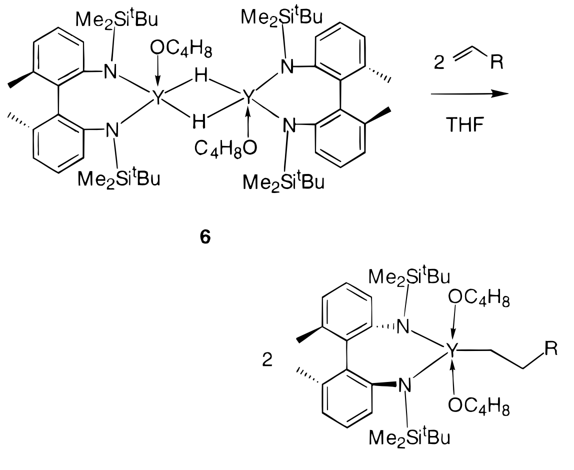
Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

Y(1)−Y(1)*	3.6652(8)	Y(1)−N(2)	2.228(4)
Y(1)−H(1)	2.27(4)	Y(1)−O(1)	2.329(3)
Y(1)−H(1)*	2.22(4)	Y(1)−C(1)	2.702(4)
Y(1)−N(1)	2.213(4)	Y(1)−C(8)	3.098(5)
Y(1)−H(1)−Y(1)*	109(2)	N(2)−Y(1)−O(1)	91.0(1)
H(1)−Y(1)−H(1)*	71(2)	Y(1)−N(1)−C(1)	93.4(2)
N(1)−Y(1)−N(2)	103.9(1)	Y(1)−N(2)−C(8)	114.6(3)
N(1)−Y(1)−O(1)	100.3(1)		

geometry of the four-membered ring is very similar to that found in other structurally characterized dimeric yttrium hydrides, $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}H)(THF)]_2$[52] (average 2.15(7) Å and 118(3)°), $[(MeC_5H_4)_2Y(\mu\text{-}H)(THF)]_2$[51] (2.18(8) Å and 114(3)°), and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$[11] (2.14(3) Å and 111.5(15)°). The N−Y−N ligand bite angle in **6** (103.9(1)°) is significantly lower than those of ca. 120° in the 5-coordinate complexes **2** and **4**, and only one of the ligand *ipso* carbons is in a close contact with the yttrium center (Y−C(1) = 2.702(4) Å, Y−C(6) = 3.069(5) Å, and Y−N(1)−C(1) = 93.4(2)°, whereas Y−C(8) = 3.098(5) Å, Y−C(7) = 3.409(4) Å, and Y−N(2)−C(8) = 114.6(3)°). The dihedral angle between the phenyl planes is 81.9°. These differences may be attributed to steric crowding in the hydride dimer relative to the monomeric complexes **2** and **4**.

Compound **6** represents a rare example of an yttrium hydride that contains no cyclopentadienyl ligands. We are aware of only one other structurally characterized non-Cp yttrium hydride, the bis(benzamidinato) complex $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$.[11] Other examples of such hydrides are the unstable species $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}H)\}_2$[12] and the (tris(pyrazolyl)borato)yttrium hydride $Tp^{Me}YH_2(THF)_4$,[17] for which a trimeric solution structure was suggested. All of the structurally characterized yttrium hydrides are dimers[11,33,47,51,52] or trimers[52] in the solid state, although more complicated aggregates have also been observed in anionic or heterometallic species.[54]

The reactivity of **6** appears to be restricted by its dimeric nature (preserved even in THF solution, as suggested by the ^1H NMR spectrum) and its very low solubility in nonpolar organic solvents. No polymerization activity was observed toward 1-hexene or C_2H_4 (5 psi) in benzene-d_6 at room temperature, and heating these mixtures at 80 °C for 2 h resulted in decomposition of the hydride with precipitation of only a small amount of polyethylene. However, when dissolved in THF, compound **6** was found to rapidly insert ethylene at room temperature, to give the yttrium ethyl complex **7** (eq 4).



6

7, R = H
8, R = C_4H_9

(4)

At longer reaction times (6−7 h), compound **7** seems to undergo a slow insertion of a second molecule of C_2H_4, but positive identification of multiple insertion products was hindered by their decomposition, and no formation of polyethylene was observed even at elevated pressure (80 psi, THF, 48 h at room temperature). Decomposition of **7** to unidentified products was also found to occur in the solid state, under N_2, over the period of a few months. The ethyl group of **7** gives rise to a broad multiplet at 0.0 ppm (YCH_2CH_3, 2 H) and a triplet of doublets at 1.67 ppm (YCH_2CH_3, 3 H) in the ^1H NMR spectrum. The $^3J_{YH}$ coupling constant of 1.9 Hz for the CH_3 protons of the ethyl ligand is very similar to the related value ($^3J_{YH}$ = 1.4 Hz) reported for $(\eta^5\text{-}CH_3C_5H_4)_2Y(CH_2CH_3)(THF)$,[54] and the $^1J_{CH}$ coupling constant of 120 Hz is typical for an sp^3 C−H bond. Although β-agostic interactions are often observed in early-transition-metal ethyl complexes,[40−42,46,55−57] their existence cannot be determined on the basis of the (averaged) $^1J_{CH}$ coupling constant only. The IR spectrum of **7** does not contain evidence for agostic C−H bonds (no low-energy C−H bands were detected). The relatively small $^1J_{CH}$ coupling constant of 70−80 Hz (multiplet broadness prevents accurate measurement) for the α-protons, however, is consistent with the presence of an α-agostic interaction with the metal center,[40,41,58−60] analogous to that reported for some bis(trimethylsilyl)methyl yttrium complexes (vide supra). In the ^{13}C NMR spectrum of **6**, the α-carbon appeared as a doublet at 35.5 ppm, with a coupling of 50 Hz to yttrium.

The solid-state structure of **7** was determined by X-ray crystallography (Figure 4 and Table 4). The molecule lies on a crystallographic C_2 symmetry axis, and the ethyl group is disordered between two symmetry-related positions. Unfortunately, this disorder does not allow us to positively determine the presence or absence of agostic interactions, although the rather large Y−C(1)−C(2) angle of 148(1)° may be consistent with α-CH coordination. The ligand geometry is very similar to that in compounds **2** and **4**, with a ligand bite angle of 119.8(3)°, and close Y−C$_{ipso}$ contacts (Y(1)−C(3) = 2.809(7) Å, Y(1)−N(1)−C(3) = 97.4(4)°). The dihedral angle between the phenyl planes is 88.2°.

In THF-d_8 solution, the slower insertion of 1-hexene into the Y−H bond of **6** was observed (eq 4) to give the 1-hexyl derivative **8** (by ^1H NMR spectroscopy). No reaction occurred between **6** and cyclohexene, however. Single insertion of terminal olefins to give yttrium alkyl

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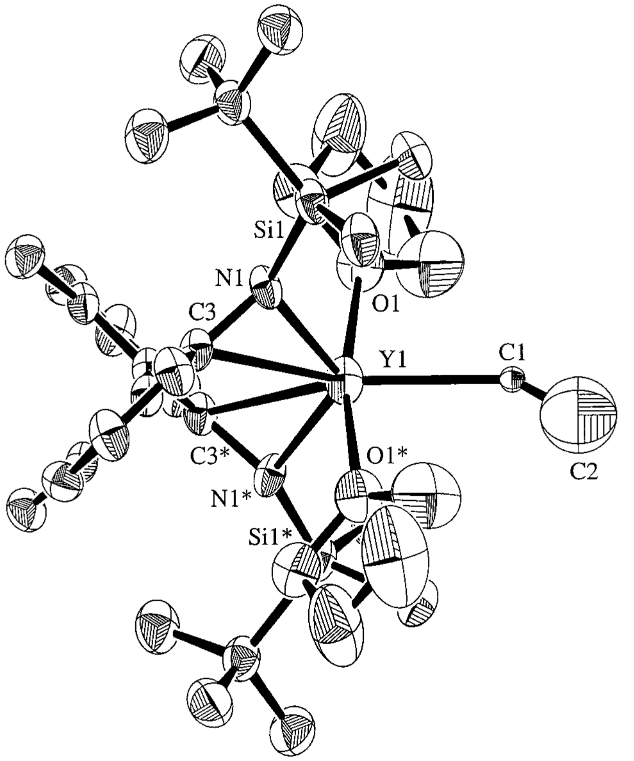


Figure 4. ORTEP diagram of [DADMB]YEt(THF)$_2$ (**7**).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 7

Y(1)−N(1)	2.251(5)	Y(1)−C(3)	2.809(7)
Y(1)−O(1)	2.371(5)	Y(1)−C(4)	2.996(7)
Y(1)−C(1)	2.464(9)		
C(1)−C(2)	1.13(2)	Y(1)−N(1)−C(3)	97.4(4)
N(1)−Y(1)−N(1)*	119.8(3)	Y(1)−C(1)−C(2)	148(1)
O(1)−Y(1)−O(1)*	169.1(3)		

complexes has been reported for [(η^5-RC$_5$H$_4$)$_2$YH(THF)]$_2$ (R = H, Me).[54] The lack of olefin polymerization activity for compound **6** can be contrasted with the high catalytic activity of certain dimeric group 3 and lanthanide hydrides of the type [Cp*$_2$MH]$_2$ (M = La, Nd, Sm, Lu)[49] but is similar to the reported low activity for {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$[11] and {[Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(μ-H)}$_2$.[12] Other dimeric hydrides have been reported to undergo single, reversible olefin insertion to give mixed hydrido−alkyl complexes (e.g., [Cp*Y(OC$_6$H$_3$-^{t}Bu$_2$)]$_2$(μ-H)(μ-alkyl)[13] and [Et$_2$Si(η^5-C$_5$H$_4$)(η^5-C$_5$Me$_4$)M]$_2$(μ-H)(μ-CH$_2$CH$_3$) for M = Lu, Y[45]), but we have not been able to observe such species in reactions of **6** with olefins.

As shown in eq 5, yttrium hydride **6** was found to react with pyridine to give a mixture of pyridine insertion products, **9** (major) and **10** (minor), in variable ratios. The structure of **9**, confirmed by X-ray crystallography (Figure 5), is again based on a distorted-trigonal-bipyramidal geometry, with neutral donors (pyridine) occupying the axial positions. The ligand bite angle is 118.9°, and the two *ipso* carbons are in close contact with yttrium (average distance 2.77 Å). The dihedral angle between the phenyl planes is 92.8°. The third pyridine unit attached to the metal center has been reduced via 1,2-insertion, as can be deduced from the changes in the C−C bond lengths (Table 5) and a puckering of the pyridine ring.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 9

Y(1)−N(1)	2.281(5)	N(1)−C(1)	1.424(8)
Y(1)−N(2)	2.255(4)	C(1)−C(2)	1.46(1)
Y(1)−N(3)	2.253(4)	C(2)−C(3)	1.36(1)
Y(1)−N(4)	2.482(4)	C(3)−C(4)	1.372(9)
Y(1)−N(5)	2.486(4)	C(4)−C(5)	1.369(8)
Y(1)−C(6)	2.717(5)	C(5)−N(1)	1.397(7)
Y(1)−C(13)	2.822(5)		
N(1)−Y(1)−N(2)	119.5(2)	C(1)−C(2)−C(3)	115.8(6)
N(1)−Y(1)−N(3)	121.4(2)	C(2)−C(3)−C(4)	119.8(6)
N(2)−Y(1)−N(3)	118.9(1)	C(3)−C(4)−C(5)	119.6(6)
N(4)−Y(1)−N(5)	170.8(2)	C(4)−C(5)−N(1)	122.3(6)
N(1)−C(1)−C(2)	115.2(6)	C(1)−N(1)−C(5)	109.6(5)

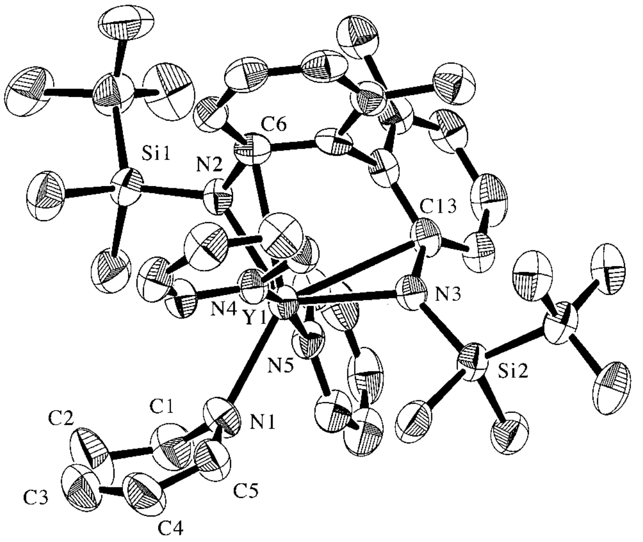
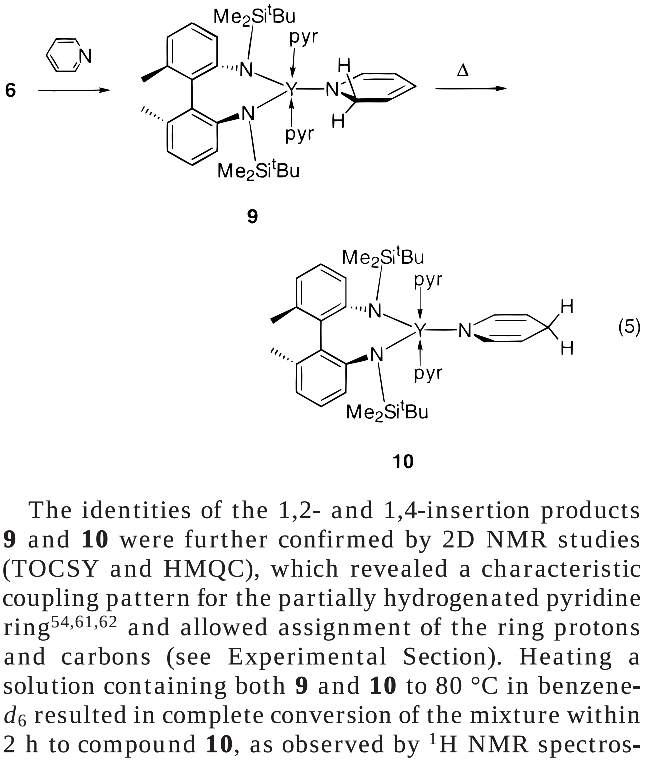


Figure 5. ORTEP diagram of [DADMB]Y(NC$_5$H$_6$)(NC$_5$H$_5$)$_2$·C$_5$H$_{12}$ (**9**).



The identities of the 1,2- and 1,4-insertion products **9** and **10** were further confirmed by 2D NMR studies (TOCSY and HMQC), which revealed a characteristic coupling pattern for the partially hydrogenated pyridine ring[54,61,62] and allowed assignment of the ring protons and carbons (see Experimental Section). Heating a solution containing both **9** and **10** to 80 °C in benzene-d_6 resulted in complete conversion of the mixture within 2 h to compound **10**, as observed by ^{1}H NMR spectroscopy. This indicates that **10** is the thermodynamically

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more stable isomer, while **9** is kinetically generated. This reactivity toward pyridine has precedent in a number of previously reported reactions for yttrium hydride and alkyl complexes. Metalation of pyridine via CH activation has been reported for $[Cp^*_2YH]_2$,[63] $Cp^*_2YCH(SiMe_3)_2$,[50] and $Cp^*_2YMe(THF)$,[50] while 1,2-insertion of pyridine followed by rearrangement to the 1,4-insertion product has been reported for $[(\eta^5\text{-}C_5H_4R)_2YH(THF)]_2$ (R = H, CH_3).[54] Also, an analogous 1,2- to 1,4-isomer rearrangement has been observed for the bis(alkoxysilylamido)yttrium derivative $[Me_2Si(NCMe_3)(OCMe_3)]_2YNC_5H_6$.[61] The bis(trimethylsilyl)benzamidinate complexes $\{[PhC(NSiMe_3)_2]_2YH\}_2$ and $[PhC(NSiMe_3)_2]_2YCH_2Ph(THF)$ have also been reported to undergo the 1,2-insertion of pyridine,[48] but no further isomerization was noted in these cases. The reactivity of **6** toward pyridine is thus different from that of similar (pentamethylcyclopentadienyl)yttrium complexes and is more similar to that of other known yttrium hydrides and alkyls with monosubstituted Cp, or noncyclopentadienyl, ligands.

Conclusions

We have synthesized and characterized a series of novel yttrium complexes with bis(silylamido)biphenyl ligands. The structures and reactivities of the chloride, alkyl, and hydrido derivatives have been investigated. In their reactivity, these complexes resemble more closely some benzamidinate[11] and alkoxysilylamido[12] yttrium species, rather than the more fully investigated cyclopentadienylyttrium derivatives.[45,47,52,54,64] The high degree of ionicity in the yttrium−nitrogen bonding appears to result in a highly electrophilic metal center, which leads to lower reactivity toward olefin polymerization and σ-bond metathesis, perhaps resulting from more contracted vacant metal orbitals which are less effective in substrate binding.[11,12,48] The reactivity of the hydride is also inhibited by the high stability of the bridged yttrium hydride unit and the insolubility of the dimer in noncoordinating solvents. Very low olefin polymerization activity is exhibited by the MAO-activated chloride and the alkyl and the hydride complexes. A single insertion of olefins into the Y−H bond, reminiscent of the reactivity of some monosubstituted-Cp yttrium hydrides,[54] results in formation of yttrium alkyl species, and the ethyl complex is sufficiently stable to be isolated and characterized. The reactivity of the yttrium hydride **6** toward pyridine also resembles that observed for related hydride derivatives containing benzamidinate and alkoxysilylamido ancillary ligands.

The yttrium derivatives studied represent another example of noncyclopentadienyl early-transition-metal complexes. This study further contributes to an understanding of the factors behind the reactivity of such d^0 complexes. As has been already suggested, in addition to the electrophilicity of the metal center, other possibly important factors include the degree of ionicity in the metal−ligand bonds, and the steric environment created by the ligand. The latter affects not only the accessibility of the metal center by the substrate but also the ease of dimer formation, which is particularly important in the case of hydride derivatives. Although apparently not promising in terms of olefin polymerization activity, these (silylamido)yttrium species exhibit reactivity patterns which are distinct from those known for more traditional cyclopentadienyl derivatives. The possible use of these yttrium complexes as catalysts for other transformations, such as catalytic hydrosilylation, is currently under investigation.

Experimental Section

General Considerations. All reactions with air-sensitive compounds were performed under dry nitrogen, using standard Schlenk and glovebox techniques. Reagents were obtained from commercial suppliers and used without further purification, unless otherwise noted. Olefin-free pentane, benzene, and toluene were prepared by pretreating with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, $NaHCO_3$, and finally anhydrous $MgSO_4$. Solvents (pentane, diethyl ether, benzene, toluene, tetrahydrofuran) were distilled under nitrogen from sodium benzophenone ketyl. Benzene-d_6 was distilled from Na/K alloy. Commercial silanes were distilled and dried over molecular sieves before use. ^{n}BuLi was used as a 1.6 M solution in hexanes, as supplied by Aldrich, and MeLi as a 1.6 M solution in Et_2O, as supplied by Alfa Aesar. 2,2′-Diamino-6,6′-dimethylbiphenyl,[38] $YCl_3(THF)_3$,[45] and $LiCH(SiMe_3)_2$[65] were prepared according to published literature procedures. NMR spectra were recorded at 300 or 500 MHz (^{1}H) with Bruker AMX-300 and DRX-500 spectrometers, or at 100 MHz (^{13}C{^{1}H}) with an AMX-400 spectrometer, at ambient temperature and in benzene-d_6, unless otherwise noted. CH coupling constants were obtained from nondecoupled HMQC experiments. Signal multiplicities are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet. Elemental analyses were performed by the Microanalytical Laboratory at UC Berkeley, E+R Microanalytical Laboratory, or Desert Analytics. Infrared spectra were recorded with a Mattson Infinity 60 MI FTIR spectrometer, as KBr pellets.

Li_2[DADMB]·2THF (1). To a cold (0 °C) solution of 2,2′-diamino-6,6′-dimethylbiphenyl (4.00 g, 18.8 mmol) in THF (100 mL) was added dropwise 25.0 mL (40 mmol) of 1.6 M ^{n}BuLi. A white precipitate formed initially but dissolved completely after all of the ^{n}BuLi had been added. The solution was allowed to warm to room temperature and was then stirred for 3 h. A solution of ^{t}BuMe$_2$SiCl (6.22 g, 41.2 mmol) in 20 mL of THF was then added dropwise. The mixture was heated at reflux for 5 h, which resulted in the formation of a white precipitate. After the mixture was cooled to room temperature, a second portion of ^{n}BuLi (25.0 mL, 40 mmol) was added and this mixture was stirred overnight at room temperature. The THF was removed under vacuum to give an oily white solid. Extraction with pentane (2 × 100 mL) gave a light yellow solution, which was concentrated in vacuo until crystals appeared and then cooled to −78 °C. The resulting crystalline product was recrystallized from pentane and dried to afford 9.45 g (15.8 mmol, 84% yield) of colorless crystals. ^{1}H NMR: δ 7.06 (d, 2 H, $J = 7.7$ Hz), 6.95 (t, 2 H, $J = 7.7$ Hz), 6.48 (d, 2 H, $J = 7.1$ Hz biphenyl H's), 3.14 (m, 8 H, THF), 1.99 (s, 6 H, *Me*), 1.25 (m, 8 H, THF), 1.16 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.49 (s, 6 H, ^{t}Bu*Me*$_2$Si), 0.09 (s, 6 H, ^{t}Bu*Me*$_2$Si). ^{13}C{^{1}H} NMR: δ 157.5, 140.1, 133.2, 128.0, 121.8, 116.6, 68.6 (THF), 28.7 (C*Me*$_3$), 25.4 (THF), 21.8, 21.7 (*Me*; *C*Me$_3$), 1.0, −0.5 (^{t}Bu*Me*$_2$Si). IR (cm^{-1}): 3039 (w), 2951 (s), 2923 (s), 2879 (s), 2848 (s), 1575 (s), 1559 (s), 1460 (s), 1440 (s), 1288 (s), 1250 (s), 1049 (s), 968 (m), 899 (m), 842 (s), 824 (s), 769 (s), 668 (m), 605 (m), 457 (m), 419 (m). Anal. Calcd for $C_{34}H_{58}N_2Li_2O_2Si_2$: C, 68.42; H, 9.79; N, 4.69. Found: C, 68.18; H, 9.85; N, 4.56.

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[DADMB]YCl(THF)$_2$ (2). A solution of **1** (3.00 g, 5.03 mmol) and YCl$_3$(THF)$_3$ (2.10 g, 5.10 mmol) in 100 mL of THF was heated at reflux for 4 h, resulting in formation of a white precipitate. The solvent was removed in vacuo, and the resulting white powder was extracted with a mixture of 60 mL of pentane and 25 mL of THF. The filtrate was concentrated to about 15 mL, and more pentane (20 mL) was added to initiate crystallization of the product as a white precipitate. After it was cooled to −78 °C, the solution was filtered and the product was then dried in vacuo to obtain 3.28 g (92% yield) of white crystalline powder. ^{1}H NMR: δ 7.07 (d, 2 H), 6.95 (t, 2 H), 6.55 d, 2 H, aromatic H), 3.70−3.46 (br m, 8 H, THF), 1.88 (s, 6 H, Me), 1.24 (m, 8 H, THF), 1.11 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.52, 0.50 (s, 6 H each, ^{t}Bu*Me*$_2$Si). ^{13}C{^{1}H} NMR: δ 152.4, 142.4, 130.5, 129.9, 123.5, 120.1 (aromatic C), 68 (THF), 28.3 (*Me*$_3$C), 25.5 (THF), 22.3 (*Me*Ar), 21.5 (Me$_3$*C*), 1.8, −1.6 (*Me*$_2$Si). IR (cm^{-1}): 3040 (w), 2949 (s), 2925 (s), 2882 (s), 2851 (s), 1578 (m), 1558 (m), 1471 (m), 1461 (m), 1441 (s), 1387 (w), 1356 (w), 1272 (s), 1248 (s), 1085 (w), 1048 (s), 1021 (m), 963 (m), 872 (m), 830 (s), 777 (s), 708 (m), 668 (m), 568 (m), 440 (m). Anal. Calcd for $C_{34}H_{58}N_2O_2Si_2YCl$: C, 57.73; H, 8.26; N, 3.96. Found: C, 57.61; H, 8.44; N, 3.85.

[DADMB]YMe(THF)$_2$ (3). Compound **2** (1.16 g, 1.64 mmol) was dissolved in 100 mL of Et$_2$O, and MeLi (1.10 mL, 1.76 mmol) was added at room temperature. To the reaction mixture was added a small amount of THF, to bring the remaining undissolved **2** into solution. The resulting pale yellow solution was stirred overnight, the solvents were removed in vacuo, and the oily residue was extracted with 2 × 50 mL of pentane. The product was isolated by crystallization at −78 °C in two crops (0.67 g, 60% yield) as a white crystalline powder. ^{1}H NMR: δ 7.07 (m, 2 H), 6.96 (m, 2 H), 6.56 (m, 2 H, aromatic H), 3.43 (m, 8 H, THF), 1.89 (s, 6 H, Me), 1.24 (m, 8 H, THF), 1.14 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.52, 0.40 (s, 6 H each, ^{t}Bu*Me*$_2$Si), −0.42 (d, 3 H, $^2J_{YH} = 1.8$ Hz, $^1J_{CH} = 101$ Hz, Y*Me*). ^{13}C{^{1}H} NMR: δ 153.2, 142.1, 131.1, 129.4, 123.4, 119.5, 70.9 (THF), 28.4 (*Me*$_3$C), 25.5 (THF), 22.4 (*Me*Ar), 21.7 (Y*Me*), 21.7 (Me$_3$*C*), 2.0, −1.9 (*Me*$_2$Si). IR (cm^{-1}): 3038 (w), 3043 (m), 2951 (s), 2890 (s), 2851 (s), 1906 (w), 1577 (s), 1555 (s), 1460 (s), 1440 (s), 1398 (m), 1358 (m), 1271 (s), 1243 (s), 1085 (m), 1048 (s), 1031 (s), 981 (s), 880 (m), 830 (s), 784 (s), 769 (s), 708 (m), 673 (m), 661 (m), 607 (w), 567 (w), 454 (m), 436 (w). Anal. Calcd for $C_{35}H_{61}N_2Si_2O_2Y$: C, 61.20; H, 8.95; N, 4.08. Found: C, 59.74; H, 9.48; N, 3.87.

[DADMB]Y(OSiMe$_3$)(THF)$_2$ (4). Compound **2** (0.54 g, 0.76 mmol) and 0.3 g of Dow Corning silicone grease were dissolved in 100 mL of Et$_2$O, and MeLi (0.5 mL, 0.8 mmol) was added at room temperature. To the reaction mixture was added a small amount of THF, to bring the remaining undissolved **2** into solution. The resulting pale yellow solution was stirred overnight, the solvents were removed in vacuo, and the oily residue was extracted with 2 × 40 mL of pentane. The product was isolated by crystallization from pentane at −78 °C (0.29 g, 50% yield) as a white crystalline powder. ^{1}H NMR: δ 7.04 (m, 2 H), 6.96 (m, 2 H), 6.57 (m, 2 H, aromatic H), 3.46 (m, 8 H, THF), 1.91 (s, 6 H, Me), 1.28 (m, 8 H, THF), 1.14 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.50, 0.29 (s, 6 H each, ^{t}Bu*Me*$_2$Si), 0.26 (s, 9 H, *Me*$_3$SiO). ^{13}C{^{1}H} NMR: δ 153.6, 142.2, 131.2, 129.4, 123.2, 119.4, 70.7 (THF), 28.5 (*Me*$_3$C), 25.4 (THF), 22.4 (*Me*Ar), 21.6 (Me$_3$*C*), 4.0 (*Me*$_3$SiO), 1.7, −1.3 (*Me*$_2$Si). IR (cm^{-1}): 3078 (w), 3043 (m), 2951 (s), 2890 (s), 2851 (s), 1906 (w), 1577 (s), 1555 (s), 1460 (s), 1440 (s), 1398 (m), 1358 (m), 1271 (s), 1243 (s), 1085 (m), 1048 (s), 1031 (s), 981 (s), 880 (m), 830 (s), 784 (s), 769 (s), 708 (m), 673 (m), 661 (m), 607 (w), 567 (w), 454 (m), 436 (w). Anal. Calcd for $C_{37}H_{67}N_2Si_3O_3Y$: C, 58.39; H, 8.87; N, 3.68. Found: C, 58.66; H, 9.25; N, 3.58.

[DADMB]YCH(SiMe$_3$)$_2$(THF)(Et$_2$O) (5). A mixture of **2** (1.24 g, 1.75 mmol) and LiCH(SiMe$_3$)$_2$(Et$_2$O)$_{0.1}$ (0.30 g, 1.76 mmol) was dissolved in 80 mL of Et$_2$O. The reaction mixture was kept in an ice bath for 30 min then allowed to warm to room temperature and stirred for 8 h. The cloudy yellow solution was filtered, the clear filtrate was concentrated to about 15 mL, and 20 mL of pentane was then added. Further concentration and cooling to −78 °C resulted in the formation of a white crystalline precipitate, which was isolated by filtration and dried in vacuo to give 0.59 g of product (43% yield). The product can be purified by recrystallization from pentane. ^{1}H NMR: δ 7.23 (m, 1 H), 6.85 (m, 3 H), 6.70 (m, 1 H), 6.59 (m, 1 H, aromatic H's), 3.52 (m, broad, 4 H, THF), 3.24 (q, 6 H, Et$_2$O), 1.88 (s, 3 H, *Me*Ar), 1.84 (s, 3 H, *Me*Ar), 1.38 (m, 4 H, THF), 1.11 (t, 4 H, Et$_2$O), 1.10 (s, 9 H, *Me*$_3$C, overlaps with Et$_2$O), 1.08 (s, 9 H, *Me*$_3$C), 0.60 (s, 3 H, *Me*$_2$Si), 0.32 (s, 3 H, *Me*$_2$Si), 0.31 (s, 3 H, *Me*$_2$Si), 0.29 (s, 9 H, *Me*$_3$Si, overlaps *Me*$_2$Si), 0.26 (s, 3 H, *Me*$_2$Si), 0.25 (s, 9 H, *Me*$_3$Si), −0.94 (d, 1 H, $^2J_{YH} = 2.1$ Hz, $^1J_{CH} = 80$ Hz, YC*H*). ^{13}C NMR: δ 150.3, 141.7, 138.6, 129.3, 120.1, 113.4, (biphenyl), 71.7, 68.5, 66.2 (THF, Et$_2$O), 39.4 (Y*C*H, $^1J_{YC} = 35.6$ Hz), 28.7, 27.9, 26.0, 25.3 (*Me*$_3$C), 26.5 (THF), 22.4 (*Me*Ar), 21.2, 20.6 (Me$_3$*C*), 15.9 (Et$_2$O), 5.7, 4.8 (*Me*$_3$Si), 1.28, −0.51 (*Me*$_2$Si). IR (cm^{-1}): 3043 (w), 2952 (s), 2887 (s), 2851 (s), 1577 (m), 1559 (m), 1462 (s), 1443 (s), 1387 (w), 1247 (s), 1091 (w), 1044 (s), 1006 (m), 963 (m), 836 (s), 793 (m), 768 (m), 711 (w), 661 (m), 594 (w), 427 (w). Anal. Calcd for $C_{41}H_{79}N_2O_2Si_2Y$: C, 63.36; H, 10.25; N, 3.60. Found: C, 63.07; H, 10.45; N, 3.76.

{[DADMB]YH(THF)}$_2$·C$_6$H$_6$ (6). To a solution of **5** (1.05 g, 1.35 mmol) in 50 mL of benzene was added 0.6 mL (5.5 mmol) of PhSiH$_3$. The mixture was left undisturbed at room temperature for 5 days, resulting in formation of a highly crystalline, colorless precipitate. The product was then isolated by filtration, washed with benzene (30 mL) and pentane (30 mL), and briefly dried in vacuo (0.53 g, 61% yield). ^{1}H NMR (THF-d_8): δ 6.99 (m, 4 H, aromatic H), 6.54 (m, 2 H, aromatic H), 5.88 (t, 1 H, $J = 28$ Hz, Y*H*), 3.61 (m, THF), 1.77 (m, THF), 1.69 (s, 6 H, *Me*Ar), 0.90 (s, 18 H, *Me*$_3$C), 0.35 (s, 6 H, *Me*$_2$Si), 0.21 (s, 6 H, *Me*$_2$Si). ^{13}C{^{1}H} NMR (THF-d_8): δ 152.7, 142.6, 130.8, 130.3, 124.0, 120.3 (aromatic C), 129.2 (C_6H_6), 68.4 (THF), 28.3 (*Me*$_3$C), 26.5 (THF), 22.2 (*Me*Ar), 21.7 (Me$_3$*C*), 1.5 (*Me*$_2$Si), −1.7 (*Me*$_2$Si). IR (cm^{-1}): 3038 (m), 2949 (s), 2926 (s), 2881 (s), 2850 (s), 2703 (w), 1564 (m), 1462 (s), 1441 (s), 1388 (m), 1359 (m), 1251 (s, broad), 1087 (m), 1047 (s), 1014 (s), 966 (s), 865 (s), 834 (s, broad), 791 (s), 767 (s), 707 (m), 682 (s), 662 (s), 617 (m), 595 (m), 567 (m), 464 (m), 431 (m). A sample of the deuterated analogue (**6**-d_2) was obtained by allowing a THF-d_8 solution of **6** to stand at room temperature for 4 days, followed by removal of the solvent in vacuo, which resulted in complete exchange of the Y−hydride with deuterium. Subtraction of the IR spectrum of **6**-d_2 showed the presence of a strong Y−H absorption at 1240 cm^{-1}, overlapping with a strong ligand absorption. Anal. Calcd for $C_{66}H_{108}N_4O_2Si_4Y_2$: C, 61.94; H, 8.51; N, 4.38. Found: C, 61.95; H, 8.55; N, 4.19.

[DADMB]YEt(THF)$_2$ (7). A sample of the yttrium hydride **6** (0.184 g, 0.144 mmol) was dissolved in 15 mL of THF. The reaction flask was filled with C$_2$H$_4$ at 5−10 psi, and the solution was stirred for 30 min. The solvent was removed under vacuum, and the solid residue was extracted into 20 mL of hexane. The extract was filtered, and the filtrate was then concentrated to 5 mL and cooled to −35 °C overnight, to give **7** as a white crystalline solid (0.121 g, 60% yield). ^{1}H NMR: δ 7.07, 6.95, 6.56 (m, 2 H each, aromatic H), 3.49 (m, 8 H, THF), 1.88 (s, 6 H, *Me*Ar), 1.67 (dt, $^3J_{HH} = 7.4$ Hz, $^3J_{YH} = 1.9$ Hz, $^1J_{CH} = 70{-}80$ Hz, 3 H, YCH$_2$C*H*$_3$), 1.25 (m, 8 H, THF), 1.13 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.53, 0.37 (s, 6 H each, ^{t}Bu*Me*$_2$Si), 0.0 (br m, $^1J_{CH} = 120$ Hz, 2 H, YC*H*$_2$CH$_3$). ^{13}C NMR: δ 153.1, 141.9, 131.4, 129.3, 123.5, 119.7 (biphenyl C), 72 (THF), 35.5, (d, $J = 50$ Hz, Y*C*H$_2$CH$_3$), 28.4 (*Me*$_3$C), 25.5 (THF), 22.4 (*Me*Ar), 21.6 (Me$_3$*C*), 15.7 (YCH$_2$*C*H$_3$), 1.7, −1.9 (*Me*$_2$Si). IR (cm^{-1}): 3043 (w), 3034 (w), 2953 (s), 2851 (s), 1578 (m), 1555 (m), 1461 (m), 1440 (m), 1268 (s), 1048 (s), 964 (m), 829 (s), 785 (m), 768 (m), 662 (w). Anal. Calcd for $C_{36}H_{63}N_2Si_2O_2Y$: C, 61.68; H, 9.06; N, 4.00. Found: C, 61.08; H, 8.96; N, 4.05. Slow decomposition of **7** at room temperature, even in the solid

Table 6. Crystallographic Data for Compounds 2, 4, 6, 7, and 9

	2	4	6	7	9
(a) Crystal Parameters					
formula	$C_{34}H_{58}N_2ClO_2Si_2Y$	$C_{37}H_{67}N_2O_3Si_3Y$	$C_{33}H_{54}N_2Si_2OY$	$C_{36}H_{63}N_2Si_2O_2Y$	$C_{46}H_{70}N_5Si_2Y$
fw	707.37	761.11	639.88	700.98	838.17
size (mm)	0.1 × 0.07 × 0.06	0.2 × 0.1 × 0.08	0.1 × 0.1 × 0.1	0.2 × 0.12 × 0.08	0.2 × 0.15 × 0.25
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$Pca2_1$ (No. 29)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$C2/c$ (No. 15)
a (Å)	17.1765(5)	11.3639(2)	10.7444(5)	17.516(4)	23.8332(1)
b (Å)	10.5593(3)	17.3411(2)	19.0747(8)	13.777(3)	11.8922(1)
c (Å)	20.7010(7)	21.7183(3)	17.7776(8)	15.927(3)	33.2391(3)
α, β, γ (deg)	90, 90, 90	90, 102.836(1), 90	90, 106.838(1), 90	90, 99.19(3), 90	90, 91.062(1), 90
V (Å$^{3)}$	3754.6(2)	4172.9(1)	3487.2(2)	3794(1)	9419.3(1)
Z	4	4	4	4	8
D_{calcd} (g cm^{-3})	1.251	1.211	1.219	1.227	1.182
F_{000}	1504.00	1632.00	1364.00	1504	3584.00
μ(Mo Kα) (cm^{-1})	17.20	15.19	17.69	16.34	13.26
(b) Data Collection					
temp (°C)	−120	−110	−155	−141	−110
unique/total no. of rflns	5472/12 491	7636/19 613	5153/14 444	3525/9055	7098/19 732
R_{int}	0.067	0.047	0.049	0.070	0.052
empirical abs cor	0.05	0.07	0.3	0.05	0.5
μR, $T_{min}-T_{max}$	0.828−0.886	0.786−0.879	0.473−0.547	0.824−0.919	0.216−0.270
(c) Refinement					
no. of observns ($I > 3\sigma(I)$)	3431	4655	3213	1627	4366
no. of variables	379	416	357	192	488
rflen/param ratio	9.05	11.19	9.00	8.47	8.95
R^a	0.047	0.042	0.038	0.055	0.045
$R_w{}^b$	0.052	0.047	0.044	0.058	0.055
goodness of fit^c	1.63	1.66	1.51	1.60	1.79
max and min peaks in final diff map (e/Å^3)	0.41/−0.54	0.41/−0.47	0.51/−0.37	0.79/−0.75	0.48/−0.41

[a] $R = \sum(|F_o| - |F_c|)^2/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$. [c] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

state, is probably responsible for the slight deviation in the percentage of observed carbon.

[DADMB]Y(*n*-C_6H_{13})(THF)$_2$ (8). A sample of **6** (ca. 10 mg) was dissolved in THF-d_8 (0.5 mL), and ca. 0.05 mL of 1-hexene was added. After 30 min, the YH signals had nearly disappeared, and after 5 h a complete conversion to product was observed. ^{1}H NMR: δ 6.9−7.0 (m, 4 H), 6.54 (m, 1 H), 6.47 (m, 1 H, biphenyl H), 1.65 (s, 6 H, *Me*Ar), 1.46 (m, 2 H, YCH_2CH_2), 1.33−1.38 (m, overlaps with 1-hexene, $YCH_2CH_2(CH_2)_3CH_3$), 0.89 (s, 18 H, *Me*$_3$C), 0.85 (m, overlaps, $Y(CH_2)_5CH_3$), 0.38 (s, 6 H, *Me*$_2$Si), 0.16 (s, 6 H, *Me*$_2$Si), −0.32 (m, 2 H, YCH_2).

[DADMB]Y(NC_5H_6)(pyr)$_2$·C_5H_{12} (Mixture of 9 and 10). A sample of **6** (0.36 g, 2.8 mmol) was dissolved in 20 mL of pyridine at room temperature. The dark yellow solution was stirred for 2 days, and the volatile material was then removed by vacuum transfer. The remaining solid was extracted with 2 × 75 mL of pentane, and then the combined yellow extracts were concentrated to 20 mL. Cooling the solution to −35 °C produced bright yellow crystals (0.14 g, 30% yield). ^{1}H NMR: compound **9**, δ 8.23 (m, 4 H, pyr), 7.27 (d, 1 H, NC_5H_6 vinylic), 6.83−6.54 (m, pyr and aromatic H), 6.47 (t, 1 H, NC_5H_6 vinylic), 5.40 (m, 1 H, NC_5H_6 vinylic), 5.04 (m, 1 H, NC_5H_6 vinylic), 4.30 (dd, 1 H, NC_5H_6 methylene), 4.04 (dd, 1 H, NC_5H_6 methylene), 2.03 (s, 6 H, *Me*), 1.05 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.23 (s, 6 H, ^{t}Bu*Me*$_2$Si), 0.18 (s, 6 H, ^{t}Bu*Me*$_2$Si); compound **10**, δ 8.32 (m, 4 H, pyr), 6.92 (m, 2 H, aromatic H), 6.71 (d, 2 H, NC_5H_6 vinylic), 6.63−6.58 (m, pyr and aromatic H), 4.55 (m, 2 H, NC_5H_6 vinylic), 3.69 (m, 2 H, NC_5H_6 methylene), 2.02 (s, 6 H, *Me*), 1.04 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.20 (s, 6 H, ^{t}Bu*Me*$_2$Si), 0.13 (s, 6 H, ^{t}Bu*Me*$_2$Si). ^{13}C{^{1}H} NMR: compound **9**, δ 152.3, 150.4, 146.4, 141.0, 132.9, 129.3 (aromatic C), 125.8 (NC_5H_6), 124.0, 120.4 (aromatic C), 113.4 (NC_5H_6), 102.2 (NC_5H_6), 96.8 (NC_5H_6), 47.9 (NC_5H_6 methylene), 28.6 (*Me*$_3$C), 22.3 (*Me*Ar), 21.4 (Me$_3$*C*), 0.9 (^{t}Bu*Me*$_2$Si), −0.8 (^{t}Bu*Me*$_2$Si); compound **10**, 152.3, 150.5, 141.0 (aromatic C), 137.0 (NC_5H_6), 133.0, 129.7, 129.6, 125.8, 124.1, 120.5 (aromatic C), 95.2 (NC_5H_6), 28.6 (*Me*$_3$C), 25.5 (NC_5H_6), 21.4 (Me$_3$*C*), 0.8 (^{t}Bu*Me*$_2$Si), −0.9 (^{t}Bu*Me*$_2$Si). Assignment of the NMR signals is based on 2D NMR studies (TOCSY and HMQC). Heating the NMR sample (product mixture of **9** and **10)** to 80 °C resulted in complete conversion of the mixture within 2 h to compound **10**. IR (cm^{-1}): 3040 (m), 2952 (s), 2926 (s), 2888 (s), 2852 (s), 2795 (m), 1645 (m), 1603 (s), 1579 (s), 1557 (m), 1506 (w), 1489 (w), 1471 (m), 1461 (m), 1443 (s), 1387 (w), 1359 (w), 1304 (w), 1268 (s), 1248 (s), 1231 (m), 1152 (w), 1100 (m), 1067 (m), 1046 (s), 1038 (s), 1007 (m), 998 (m), 965 (s), 932 (w), 867 (w), 829 (s), 786 (m), 769 (m), 752 (m), 702 (s), 661 (w), 627 (m), 567 (w), 536 (w), 432 (w). Anal. Calcd for $C_{46}H_{70}N_5Si_2Y$: C, 65.92; H, 8.42; N, 8.36. Found: C, 65.21; H, 8.03; N, 8.31. The inclusion of pentane in the crystal lattice of these compounds suggests that desolvation is probably responsible for the slight deviation in the percentage of observed carbon.

X-ray Structure Determinations. X-ray diffraction measurements were made on a Siemens SMART diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation. The crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range $4 < 2\theta < 45°$. The frame data were integrated using the program SAINT (SAX Area-Detector Integration Program; V4.024; Siemens Industrial Automation, Inc.: Madison, WI, 1995). An empirical absorption correction based on measurements of multiply redundant data was performed using the programs XPREP (part of the SHELXTL Crystal Structure Determination Package; Siemens Industrial Automation, Inc.: Madison, WI, 1995) or SADABS. Equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. A secondary extinction correction was applied if appropriate. The structures were solved using the teXsan crystallographic software package of the Molecular Structure Corp., using direct methods, and expanded with Fourier techniques. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions but not refined unless otherwise noted. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a *p*-factor to downweight the intense reflections. Crystallographic data are summarized in Table 6.

For 2. Crystals were grown from a 10:1 pentane/THF solution of **2** at −35 °C. The Flack parameter of the structure was 0.009(2), suggesting that the correct enantiomorph was chosen. The other enantiomorph was also tested, but this structure resulted in $R = 9.64\%$ with a Flack parameter of 0.88.

For 4. Crystals were grown from a pentane solution of **4** at −35 °C.

For 6. Crystals were grown by slow diffusion of $PhSiH_3$ (0.3 mL dissolved in 20 mL of benzene) into a solution of **5** (0.16 g in 20 mL of benzene), the two solutions being separated with a layer of neat benzene, at room temperature for 4 days. The non-hydrogen atoms were refined anisotropically. The hydride H was located on the Fourier difference map and refined isotropically; the rest of the hydrogen atoms were included in calculated positions.

For 7. Crystals were grown from a dilute hexane solution of **7** at −35 °C. The non-hydrogen atoms were refined anisotropically, except for those of the disordered ethyl group, which were refined isotropically.

For 9. Crystals were grown from a pentane solution of a mixture of **9** and **10** at −15 °C. The single crystal selected was found to be compound **9**. The non-hydrogen atoms were refined anisotropically, except for those of the solvating pentane, which were disordered and refined isotropically.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **2**, **4**, **6**, **7,** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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