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Hydrosilylation Catalysis by C_2-Symmetric Bis(silylamido) Complexes of Yttrium

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The yttrium hydride $\{[\text{DADMB}]\text{YH(THF)}\}_2$ (**2**; DADMB = 2,2′-bis(*tert*-butyldimethylsilylamido)-6,6′-dimethylbiphenyl), conveniently generated in situ from $[\text{DADMB}]\text{YMe(THF)}_2$ (**1**), is an active olefin hydrosilylation catalyst. This system represents the first use of a d^0 metal complex with non-Cp ligands in the catalytic hydrosilylation of olefins. Studies of the reactivity and regio- and enantioselectivity for various olefins and silanes are presented. High preference for terminal addition in the case of aliphatic olefins is observed, while aromatic olefins exhibit preference for 2,1-addition. Both primary and secondary silanes have been employed. Preliminary studies of the enantioselectivity of the chiral catalyst show that 90% ee can be achieved in the hydrosilylation of norbornene with $PhSiH_3$. Kinetic studies support a mechanism consistent with the generally accepted one for hydrosilylation catalyzed by early transition metal species, involving rapid olefin insertion into a Y−H bond followed by a Si−C bond-forming σ-bond metathesis of the resulting yttrium alkyl with silane.

Introduction

We recently described studies on the structure and reactivity of alkyl and hydride yttrium complexes containing the $[\text{DADMB}]^{2-}$ ligand (DADMB = 2,2′-bis(*tert*-butyldimethylsilylamido)-6,6′-dimethylbiphenyl).[1] Chelating diamide complexes of this type have been investigated as catalysts for olefin polymerizations,[2−17] and we have been interested in their potential to function as silane dehydropolymerization catalysts.[18−22] While the yttrium−DADMB complexes were not active as olefin or silane polymerization catalysts, we have found that they can be used as olefin hydrosilylation catalysts. The hydrosilylation of olefins by early transition metal and lanthanide catalysts is a well-known process, and recently numerous studies have been devoted to investigating the reactivity and selectivity of such catalysts toward unsaturated organic substrates.[23−31] The mechanism and energetics of the hydrosilylation catalytic cycle has also been investigated.[23] As is usually the case in early transition metal chemistry, the ancillary ligands employed in these studies have been based on cyclopentadienide and its derivatives. The potential of noncyclopentadienyl ligand sets in hydrosilylation catalysis by d^0 metals has yet to be explored. In this paper we present our studies on the hydrosilylation chemistry of [DADMB]Y complexes. We also describe initial results on the use of a resolved chiral catalyst, (*S*)-$[\text{DADMB}]\text{YMe(THF)}_2$, in the enantioselective hydrosilylation of olefins.

Results and Discussion

The yttrium complexes **1** and **2** were prepared according to previously described methods.[1] In earlier

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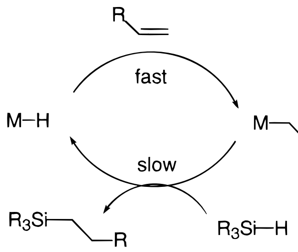
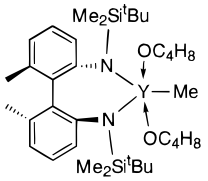
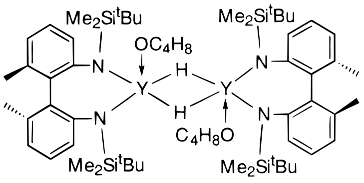
Scheme 1



studies on their reactivity, we observed that while these complexes do not appear to be promising as olefin polymerization catalysts, the yttrium hydride **2** reacts cleanly with olefins to give single-insertion alkyl products.[1] Further reactions with olefin are very slow, and measurable amounts of polyolefins were not observed. Complexes **1** and **2** were also found to be inactive as dehydropolymerization catalysts, and whereas **2** is inert toward silanes such as $PhSiH_3$, the yttrium alkyls **1** and $[DADMB]Y[CH(SiMe_3)_2](THF)(OEt_2)$ react with hydrosilanes in a metathesis-type reaction to form **2** and an alkylsilane. The latter observation of Si–C bond formation prompted us to investigate the possibility of catalytic hydrosilylation, since it was envisioned that the yttrium hydride **2** could react with an olefin via insertion, and then the resulting yttrium alkyl group might be transferred to a silane with regeneration of the yttrium hydride catalyst (Scheme 1). In fact, similar hydrosilylations are known to occur with other group 3 and lanthanide hydrides (e.g., $[Cp^*{}_2YH]_2$) or their precursors.[23–26,28]



1

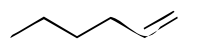
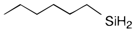
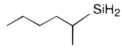
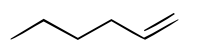
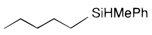
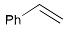
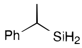
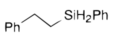
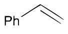
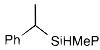
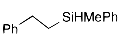
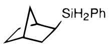


2

Initial experiments were designed to test the activity of **2** as a hydrosilylation catalyst. Addition of a large excess of $PhSiH_3$ to a THF-d_8 solution of **2** did not result in reaction, but when the mixture was pressurized with ethylene (5 psi, room temperature), the clean formation of $PhEtSiH_2$ was immediately observed, and within 12 h all the $PhSiH_3$ had been consumed. 1-Hexene was also found to react with $PhSiH_3$ in the presence of **2**, to give $PhSiH_2(CH_2)_5CH_3$ as the major product. Under similar conditions cyclohexene did not undergo hydrosilylation, consistent with its observed lack of reactivity toward the hydride **2** (THF-d_8, 24 h, room temperature).

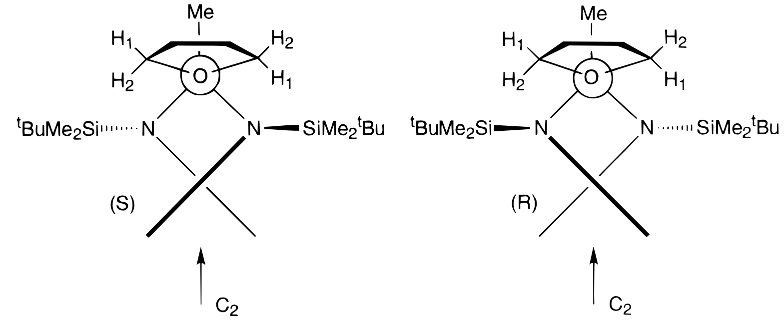
The insolubility of the hydride dimer in noncoordinating solvents required the use of THF for the hydrosilylation reactions. However, the yttrium methyl complex **1** can also be used as an active hydrosilylation catalyst, presumably because it first reacts with the silane to give a small concentration of reactive, monomeric hydride. Thus, hydrosilylations may be carried out in a nonpolar solvent such as benzene using **1** as the catalyst precursor. The active hydride species under these catalytic conditions has not been observed, as addition of a hydrosilane to **1** led to rapid disappearance of the resonances for **1** (by ^1H NMR spectroscopy) with formation of the methylsilane, but no yttrium hydride resonances could be detected (apparently due to the very low concentration of the active species).

Table 1. Results from the Hydrosilylation of Olefins Catalyzed by $[DADMB]YMe(THF)_2$ (1)

Olefin	Silane	Turnover rate, h^{-1}	Products	Product ratio
	$PhSiH_3$	~100		92%
				8%
	$PhMeSiH_2$	4.3		>99%
	$PhSiH_3$	0.66		76%
				24%
	$PhMeSiH_2$	0.12		64%
				36%
	$PhSiH_3$	~30		>99% (90% ee)

To probe the selectivity of this catalytic system, a range of olefins was tested, using $PhSiH_3$ and $PhMeSiH_2$ as representative primary and secondary silanes. The results are presented in Table 1. The steric bulk of the ligand apparently limits the reactivity of the catalyst such that only terminal olefins react at a measurable rate, and norbornene is the only disubstituted olefin observed to react. With both $PhSiH_3$ and $PhMeSiH_2$, no reaction was observed with cyclohexene, 1-phenyl-1-methylethene (α-methylstyrene), and *trans*-1,2-diphenylethene, and $PhMeSiH_2$ did not react with norbornene. As has been noted for other lanthanide and yttrium hydrosilylation catalysts,[23–25,28] both 1,2- and 2,1-additions of the silane to the double bond are observed, the ratio of the two isomers being controlled by steric and electronic effects. Aliphatic olefins give predominantly the terminal addition product, while styrene preferably gives benzylsilane derivatives. The latter effect has been observed with related catalysts and rationalized in terms of electronic interactions between the metal center and the aromatic ring of styrene, which directs the insertion reaction toward the α-phenylalkyl intermediate.[23] Our system seems to be less selective toward 2,1-addition in the case of aromatic olefins, compared to catalysts such as $Me_2Si(C_5Me_4)_2$-$SmCH(SiMe_3)_2$,[23] which gives near quantitative yields of the 2,1-addition products. In its selectivity toward terminal addition to aliphatic olefins, our catalyst is more similar to $Cp^*{}_2YCH(SiMe_3)_2$.[24] In terms of reactivity, the turnover rates (Table 1) observed for 1-hexene are within the range reported for Cp-based group 3 and lanthanide catalysts, while those for $PhCH{=}CH_2$ are lower (cf. 1-hexene + $PhSiH_3$, $N_t = 120$ h^{-1}, $PhCH{=}$

Scheme 2



CH_2 + $PhSiH_3$, $N_t = 25$ h^{-1}, both at 23 °C using $Me_2Si(C_5Me_4)_2SmCH(SiMe_3)_2$).[23] Most of the literature studies of hydrosilylation with d^0 metal catalysts employ $PhSiH_3$ as a representative primary silane, with a few reporting successful use of secondary silanes such as $PhMeSiH_2$[29] or Ph_2SiH_2.[30] In our system, however, the steric bulk of the secondary silane appears not to be a significant hindrance, and most of the olefins tested (norbornene being the only exception) were found to react with both $PhSiH_3$ and $PhMeSiH_2$. As expected, the secondary silane favors the terminal addition products more than does the primary silane.

Since the yttrium centers involved in the catalysis are chiral, we examined the enantioselectivity of their catalytic action. A resolved version (S-**1**) of the methyl complex **1** was prepared using a sample of enantiopure 2,2′-diamino-6,6′-dimethylbiphenyl, following the previously reported synthetic procedure.[1] An unexpected confirmation of the preserved enantiopurity of the prepared complex S-**1** came from its ^{1}H NMR spectrum. While most chemical shifts for S-**1** were identical to those of racemic **1**,[1] two separate multiplets due to diastereotopic hydrogen atoms were observed for the α-H protons of the coordinated THF in S-**1**, as compared to a single multiplet in **1**. As shown in Scheme 2, coordination of THF to a chiral metal center places the CH_2 protons in chemically inequivalent environments. Since all THF coordination sites in an enantiopure system are of the same chirality, the exchange of THF between different molecules preserves the difference in chemical shift between the diastereotopic THF protons. In a racemic mixture, however, an exchange of THF between coordination sites of opposite chirality results in the exchange of environments for these protons. A variable-temperature NMR study of **1** further confirmed that the single multiplet observed at room temperature is due to a fast intermolecular exchange of THF between metal sites of opposite chirality, leading to an averaged signal. This exchange is slower at lower temperature such that two separate multiplets are observed (Figure 1). The transition temperature in toluene-d_8 was determined to be 280 K, from which an activation energy of $\Delta G^{\ddagger} = 54$ kJ mol^{-1} (13 kcal mol^{-1}) for THF dissociation can be calculated (rate constant $k = 1.8 \times 10^3$ s^{-1}).

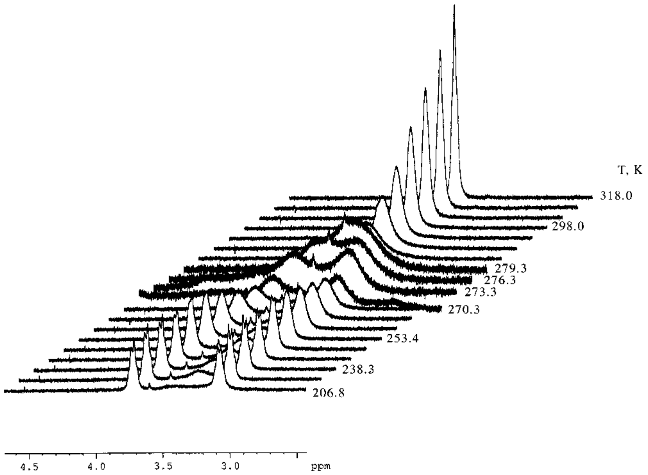


Figure 1. Temperature dependence of the chemical shift of the diastereotopic THF protons in **1**.

Evaluation of the catalyst enantioselectivity was hindered by the fact that most of the prochiral olefins tested did not react or gave a mixture of regioisomers (vide supra). The substrate chosen for enantioselectivity studies was norbornene, since it gives exclusively the exo-diastereoisomer on reaction with $PhSiH_3$. The enantiomeric excess of the $PhSiH_2$(norbornyl) product was found to be 90.4% (GC analysis with a chiral column), in favor of the 1S-enantiomer, as determined by oxidation of the silane to *exo*-norborneol following standard literature procedures.[23,25] For comparison, highly enantioselective hydrosilylation of norbornene and other olefins using late transition metal (Pd, Pt, Rh) catalysts has been previously reported, with ee's often exceeding 90%.[32−36] The only other study of enantioselective olefin hydrosilylation by early transition metal or lanthanide catalysts, however, utilized the chiral ansa-cyclopentadienyl complexes (*R*)-$Me_2Si(C_5Me_4)[(-)\text{-menthyl-}C_5H_4]SmCH(SiMe_3)_2$ and (*S*)-$Me_2Si(C_5Me_5)[(-)\text{-menthyl-}C_5H_4]SmCH(SiMe_3)_2$ and resulted in observation of enantiomeric excesses of 68% and 65%, respectively, for the hydrosilylation of $PhEtC{=}CH_2$ with $PhSiH_3$.[23]

The mechanism of hydrosilylation as catalyzed by early transition metal complexes has been studied for several cyclopentadienyl-based systems.[23,24] The active metal species is thought to be a monomeric d^0 metal hydride. The catalytic cycle is proposed to occur via fast, irreversible insertion of olefin into the metal−hydrogen bond to give an alkyl species, which then reacts with the silane in a slow, rate-determining step (Scheme 1). The overall reaction rate has been found to be zeroth-order in olefin and first-order in silane and catalyst precursor.[23]

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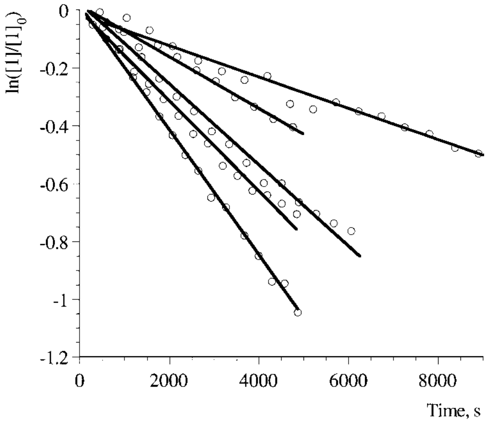

Figure 2. Pseudo-first-order plots for disappearance of **1** at different $PhMeSiH_2$ concentrations (298 K, benzene-d_6).

To probe the mechanism of hydrosilylation catalysis by [DADMB]Y complexes, we studied the kinetics of this process. The substrates chosen were 1-hexene and $PhMeSiH_2$, as the resulting reaction was found to proceed at a rate convenient to follow by NMR spectroscopy.

The mechanism of the catalyst initiation step (eq 1)

$$\underset{\mathbf{1}}{[DADMB]YMe(THF)_2} + PhMeSiH_2 \rightarrow PhMe_2SiH + \text{“[DADMB]YH”} \quad (1)$$

in benzene solution was studied by monitoring the disappearance of **1** at different concentrations of $PhMeSiH_2$, the silane being kept in large excess. This reaction may also represent a good model for the product-forming step in the proposed catalytic mechanism (Scheme 1). A linear decrease of ln[**1**] with time was observed, which is consistent with a rate law involving first-order dependence on **1** (Figure 2). A plot of the observed rate constant versus [$PhMeSiH_2$] was also found to be linear, consistent with the expected first-order dependence on silane concentration. The overall rate constant was found to be $k_H = 3.8(2) \times 10^{-4}$ L mol^{-1} s^{-1} at 298 K. To determine the isotope effect of this σ-bond metathesis process, several kinetic measurements were performed using deuterated silane ($PhMeSiD_2$), giving a rate constant $k_D = 3.4(3) \times 10^{-4}$ L mol^{-1} s^{-1}. Even though there is some scatter in the experimental data, the value of $k_H/k_D = 1.1(1)$ clearly indicates the absence of a significant primary kinetic isotope effect.

The actual hydrosilylation process was studied in benzene by monitoring the consumption of $PhMeSiH_2$ at different concentrations of 1-hexene (in most cases kept in at least 5-fold excess relative to the silane, so that the decrease in olefin concentration during the reaction was insignificant) and catalyst precursor **1** (typically about 5% relative to $PhMeSiH_2$). The linear dependence of ln[$PhMeSiH_2$] versus time over the whole range of initial concentrations of **1** and 1-hexene suggests a first-order rate law with respect to the silane, as expected from the mechanism of Scheme 1. The dependence of the overall rate on the olefin concentration was probed by conducting several kinetic runs at different 1-hexene concentrations (ranging from 0.33 to 4.01 mol L^{-1}). The observed rate constant was found to be practically independent of the olefin concentration,

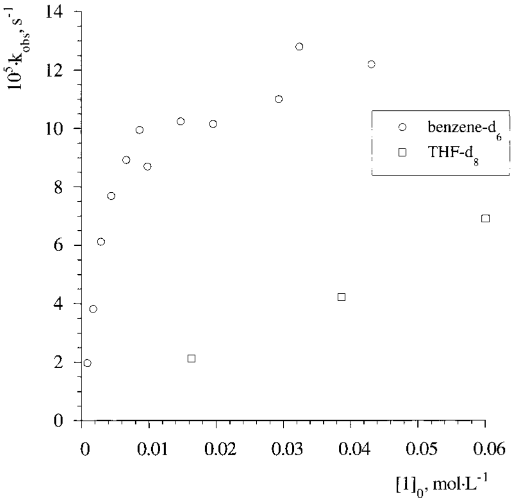

Figure 3. Observed pseudo-first-order rate constant for $PhMeSiH_2$ consumption as a function of catalyst precursor concentration, at constant initial 1-hexene concentration (298 K, benzene-d_6 or THF-d_8).

again consistent with the proposed mechanism, which implies zeroth order with respect to olefin. The dependence of the observed rate constant on the initial concentration of **1**, however, was found to deviate significantly from the expected linear correlation for a first-order rate law with respect to yttrium catalyst (Figure 3). However, the precipitation of insoluble yttrium hydride dimer at later stages of the reaction, which can irreversibly remove some of the active catalyst from solution, is a possible cause for the saturation behavior observed at higher catalyst concentrations. Alternatively, an order of 1/2 would lead to qualitatively similar behavior, and this can be explained if the concentration of the active yttrium species in the rate-determining step is controlled by an equilibrium leading to dimer formation. An example of such half-order dependence on catalyst concentration has been reported for the hydrogenation of olefins catalyzed by Cp*−organolanthanide complexes,[37] a mechanistically similar process. In the latter hydrogenation, the half-order dependence was rationalized by invoking a fast equilibrium between the reactive metal alkyl intermediate and an inactive dimeric (alkyl bridged) species. Interestingly, the corresponding catalytic hydrosilylation process, using the same catalysts, is reported to exhibit regular first-order dependence on catalyst concentration.[23] Although in our system no evidence is available to suggest that **1** could form a dimer in solution, the dimeric nature of the hydride **2**, as well as the existence of many examples of dimeric alkyl and mixed hydrido−alkyl yttrium species in the literature,[37−39] suggests that such equilibria could be operative. The complexity of the system, however, and uncertainty in the structure of the active species prevent us from formulating a more detailed mechanistic picture at this time.

To avoid the potential effects of the insolubility of the yttrium hydride dimers in benzene on the kinetics of

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the hydrosilylation process, several runs were also performed using THF-d_8 as solvent. The consumption of $PhMeSiH_2$ was followed at different yttrium catalyst precursor concentrations, while keeping the 1-hexene concentration constant. A plot of ln[$PhMeSiH_2$] versus time, however, showed that an observable decrease in the reaction rate occurs after some period of time, which is likely due to catalyst decomposition in the THF solvent. Unlike the approximately half-order rate law observed in benzene, however, the dependence of the observed rate constant on the catalyst precursor concentration in the initial period was found to be linear, suggesting a first-order rate law ($k = 1.1(1) \times 10^{-3}$ L mol^{-1} s^{-1} at 298 K) with respect to catalyst precursor when the reaction is conducted in THF. The observed rate constants in THF are lower than those in benzene (Figure 3), which is consistent with the idea that the catalytically active species is a coordinatively unsaturated complex, and THF coordination can inhibit its reactivity.

Conclusions

We have explored the hydrosilylation activity of two yttrium complexes with bis(silylamido)biphenyl ligands and have performed kinetic and mechanistic investigations of this catalytic process. Although hydrosilylation catalysis by d^0 complexes is well-known, previous research on such catalysts has been based on cyclopentadienyl complexes. Our system is the first to demonstrate the use of non-Cp ligands in the catalytic hydrosilylation of olefins by a d^0 metal. Mechanistic investigations indicate that this hydrosilylation occurs by the mechanism generally accepted to operate for other d^0 systems, involving fast olefin insertion into the reactive metal hydride bond, followed by a slow metathesis reaction with the silane. As with the Cp-based systems studied earlier, the diamido catalyst **1** exhibits a high regioselective preference for terminal addition in the case of aliphatic olefins. However, a lower preference for 2,1-addition in the case of aromatic olefins was observed, presumably due to the different steric requirements of the bis(silylamido)biphenyl ligand as compared to the bis-Cp systems. The [DADMB]Y catalyst is also reactive enough to allow a secondary silane such as $PhMeSiH_2$ to be used in the hydrosilylation, in addition to the more typically employed $PhSiH_3$. Significantly, the enantioselectivity observed with the chiral [DADMB]Y catalyst in the hydrosilylation of norbornene (90% ee) is impressively high for an unoptimized system and compares favorably with some of the best late transition metal-based catalysts known.

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 and tetrahydrofuran-d_8 were distilled from Na/K alloy. Commercial silanes, 1-hexene, and $PhCH{=}CH_2$ were dried over molecular sieves and distilled before use. Deuterated phenylmethylsilane was obtained by reduction of $PhMeSiCl_2$ with $LiAlD_4$ (98% D). The syntheses of **1** and **2** have been reported elsewhere.[1] Enantiopure (*S*)-2,2′-diamino-6,6′-dimethylbiphenyl (99.9+% ee as determined by polarimetry and HPLC) was provided by Prof. A. Togni (ETH-Zurich). NMR spectra were recorded at 300 or 500 MHz (^1H) with Bruker AMX-300 and DRX-500 spectrometers or at 100 MHz ($^{13}C\{^1H\}$) with an AMX-400 spectrometer, at ambient temperature and in benzene-d_6, unless otherwise noted. Signal multiplicities are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet. GC/MS data was obtained with a HP 6890 GC/MS system, equipped with a JW DB-XLB column.

(*S*)-[DADMB]YMe(THF)$_2$ (S-1). To a cold (0 °C) solution of (*S*)-2,2′-diamino-6,6′-dimethylbiphenyl (0.68 g, 3.20 mmol) in THF (50 mL) was added dropwise 4.0 mL (6.4 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 $^tBuMe_2SiCl$ (1.01 g, 6.72 mmol) in 10 mL of THF was then added dropwise. The mixture was heated at reflux for 1 h, which resulted in the formation of a white precipitate. After cooling to room temperature, a second portion of ^{n}BuLi (4.0 mL, 6.4 mmol) was added, and the mixture was stirred overnight at room temperature. The THF was removed under vacuum to give an oily white solid. Extraction with hexane (2 × 50 mL) gave a light yellow solution, which was concentrated in vacuo until crystals appeared and then cooled to −78 °C to obtain 1.53 g (83% yield) of (*S*)-Li_2[DADMB]·(THF)$_2$ as colorless crystals. ^1H NMR: δ 7.06 (d, 2 H, $J = 7.7$ Hz), 6.96 (t, 2 H, $J = 7.7$ Hz), 6.48 (d, 2 H, $J = 7.1$ Hz biphenyl H's), 3.26 (m, 4 H, THF), 3.06 (m, 4 H, THF), 1.99 (s, 6 H, *Me*), 1.24 (m, 8 H, THF), 1.17 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.50 (s, 6 H, ^{t}Bu*Me*$_2$Si), 0.10 (s, 6 H, ^{t}Bu*Me*$_2$Si). $^{13}C\{^1H\}$ 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). A portion of this product (1.28 g, 2.15 mmol) was mixed with 0.91 g (2.22 mmol) of $YCl_3(THF)_3$ in 50 mL of THF, and the solution was heated at reflux for 3 h. The solvent was removed in vacuo, and the resulting white powder was extracted with hexane/THF mixture. The filtrate was concentrated to about 15 mL, and more hexane (20 mL) was added to initiate crystallization of the product as a white precipitate. After cooling to −78 °C, the solution was filtered, and the product was then dried in vacuo to obtain 1.01 g (66% yield) of (*S*)-[DADMB]YCl(THF)$_2$ as a white crystalline powder. ^1H NMR: δ 7.07 (d, 2 H), 6.95 (t, 2 H), 6.56 d, 2 H, aromatic H), 3.73 (m, 4 H, THF), 3.42 (m, 4 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). $^{13}C\{^1H\}$ NMR: δ 152.4, 142.4, 130.5, 130.0, 123.5, 120.1 (aromatic C), 71.6 (THF), 28.3 (*Me*$_3$C), 25.5 (THF), 22.3 (*Me*Ar), 21.5 (Me$_3$*C*), 1.8, −1.5 (*Me*$_2$Si). A portion of this product (0.82 g, 1.15 mmol) was dissolved in 50 mL of THF, the solution was cooled in an ice bath, and MeLi (0.72 mL, 1.15 mmol) was added. The resulting pale yellow solution was allowed to warm to room temperature and was stirred overnight, the solvents were removed in vacuo, and the oily residue was extracted with 2 × 30 mL of hexane. The (*S*)-[DADMB]YMe(THF)$_2$ product was isolated by crystallization at −78 °C (0.34 g, 43% yield) as a white crystalline powder, mp 128−132 °C (cf. 145−150 °C for racemic **1**). ^1H NMR: δ 7.07 (m, 2 H), 6.96 (m, 2 H), 6.57 (m, 2 H, aromatic H), 3.66 (m, 4 H, THF), 3.29 (m, 4 H, THF), 1.88 (s, 6 H, Me), 1.24 (m, 8 H, THF), 1.14 (s, 18 H, ^{t}*Bu*Me$_2$Si), 0.53, 0.41 (s, 6 H each, ^{t}Bu*Me*$_2$Si), −0.42 (d, 3 H, Y*Me*). $^{13}C\{^1H\}$ 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).

Hydrosilylation of Ethylene with $PhSiH_3$. A sample of **1** (ca. 5 mg) was dissolved in benzene-d_6 in a J. Young NMR tube. The tube was evacuated briefly and refilled with C_2H_4

(5−10 psi) several times. An excess of $PhSiH_3$ (ca. 50 μL) was added. After 20 min at room temperature, the silane was completely consumed and formation of $PhH_2SiCH_2CH_3$ was observed. The NMR spectrum of $PhH_2SiCH_2CH_3$ was consistent with the literature data.[40] A control sample not containing **1** revealed no reaction between $PhSiH_3$ and C_2H_4 after 8 h.

Hydrosilylation of 1-Hexene with $PhSiH_3$. A sample of **1** (9.6 mg, 0.014 mmol) was dissolved in 0.8 mL of benzene-d_6. To this solution were added 1-hexene (35 μL, 0.28 mmol) and $PhSiH_3$ (35 μL, 0.28 mmol). Monitoring the reaction by ^{1}H NMR spectroscopy showed that 80% conversion to products had occurred within the first 10 min after mixing, corresponding to a turnover rate of about 100 h^{-1}. The spectrum of the hydrosilylation product was consistent with that reported for the $PhH_2Si(CH_2)_5CH_3$ isomer.[23] Analysis of the products was also performed by GC/MS, after quenching and diluting the reaction mixture with pentane, which revealed the presence of a small amount (ca. 8%) of the $PhSiH_2(CH)(CH_3)(CH_2)_3CH_3$ isomer.

Hydrosilylation of 1-Hexene with $PhMeSiH_2$. A sample of **1** (10.0 mg, 0.015 mmol) was dissolved in benzene-d_6 (0.8 mL). To this solution were added 1-hexene (36 μL, 0.29 mmol) and $PhMeSiH_2$ (40 μL, 0.29 mmol). An initial turnover rate of 4.3 h^{-1} was determined by following the disappearance of the starting materials by ^{1}H NMR spectroscopy for the first 7000 s. The ^{1}H NMR spectrum and the GS/MS data indicated exclusive formation of a single hydrosilylation product, identified as $PhMeHSi(CH_2)_5CH_3$. ^{1}H NMR: δ 7.50 (m, 2 H, Ph), 7.20 (m, 3 H, Ph), 4.58 (m, 1 H, Si*H*), 1.10−1.30 (m, 8 H, CH_2), 0.87 (t, 3 H, CH_3), 0.70−0.80 (m, 2 H, CH_2), 0.26 (d, $^3J_{HH}$ = 3.8 Hz, Si*Me*).

Hydrosilylation of $PhCH{=}CH_2$ with $PhSiH_3$. A sample of **1** (9.6 mg, 0.014 mmol) was dissolved in 0.8 mL of benzene-d_6. To this solution were added $PhCH{=}CH_2$ (34 μL, 0.30 mmol) and $PhSiH_3$ (35 μL, 0.28 mmol). An initial turnover rate of 0.66 h^{-1} was determined by following the disappearance of the starting materials by ^{1}H NMR spectroscopy for the first 12 000 s. After 3 days, ca. 80% conversion was observed. Complete consumption of the starting materials was observed after 1 week. The product ratio $PhCH(CH_3)SiH_2Ph$ to $PhCH_2CH_2SiH_2Ph$ as determined by ^{1}H NMR integration was 3.1:1. The NMR spectrum was consistent with the literature data.[23] The identity of the products was also confirmed by GC/MS (m/z = 212).

Hydrosilylation of $PhCH{=}CH_2$ with $PhMeSiH_2$. A sample of **1** (9.3 mg, 0.013 mmol) was dissolved in 0.8 mL of benzene-d_6. To this solution were added $PhCH{=}CH_2$ (31 μL, 0.27 mmol) and $PhMeSiH_2$ (37 μL, 0.27 mmol). An initial turnover rate of ca. 0.12 h^{-1} was determined by following the disappearance of the starting materials by ^{1}H NMR spectroscopy over the first 80 000 s. After 2 days, 50% conversion was observed. Starting materials were still present even after 10 days. The product ratio $PhCH(CH_3)SiHMePh$ to $PhCH_2CH_2SiHMePh$ as determined by ^{1}H NMR integration was 1.8:1. The identity of the products was also confirmed by GC/MS (m/z = 226), which also showed the presence of both diastereoisomers of $PhCH(CH_3)SiHMePh$, in 1.2:1 ratio. ^{1}H NMR (some peaks overlap): δ 7.45 (m, 2 H, Ph), 7.32 (m, 2 H, Ph), 6.95−7.20 (m, 6 H, Ph), 4.50−4.55 (m, 2 H, Si*H*), 2.60 (t, 2 H, PhCH_2CH$_2$SiHMePh), 2.28−2.35 (m, 1 H, PhC*H*(CH$_3$)SiHMePh), 1.30 (m, 3 H, PhCH(CH_3)SiHMePh), 1.05−1.10 (m, 2 H, PhCH$_2$CH_2SiHMePh), 0.19 (d, Si*Me*(H), overlaps with $PhMeSiH_2$), 0.12 (d, SiH*Me*, 3 H).

Preparative Scale Hydrosilylation of Norbornene with $PhSiH_3$. To a solution of **1** (0.248 g, 0.36 mmol) and norbornene (1.13 g, 12.0 mmol) in 30 mL of C_6H_6 was added 1.50 mL of $PhSiH_3$ (12.0 mmol), and the mixture was stirred at room temperature for 48 h. The cloudy solution was diluted with 50 mL of Et_2O, and the resulting mixture was poured into 75 mL of saturated aqueous NH_4Cl. The organic layer was separated, the aqueous layer was extracted with Et_2O (3 × 50 mL), and the combined Et_2O extracts were dried over $MgSO_4$ and then concentrated under vacuum. The resulting oil was redissolved in 30 mL of hexane and filtered through a short silica column. Removal of the volatiles with a rotovap produced 2.80 g of *exo*-phenylsilylnorbornane as a colorless oil (quantitative yield). Only the exo-isomer was produced, as identified by NOESY ^{1}H NMR spectroscopy and GC/MS (m/z = 202). The NMR spectrum was in agreement with the published literature data.[24]

Oxidation of *exo*-Phenylsilylnorbornane to *exo*-Norborneol. The racemic product from the hydrosilylation of norbornene (2.80 g, ca. 12.0 mmol) was dissolved in $CHCl_3$ (140 mL), the solution was cooled with an ice bath, and 4.1 mL of $HBF_4{\cdot}Et_2O$ was added. The reaction mixture was stirred for 3 h, the volatiles were removed under vacuum, and the residue was redissolved in a 1:1 CH_3OH/THF mixture (200 mL). To this solution were added KF (3.75 g), $KHCO_3$ (6.7 g), and 33 mL of 30% H_2O_2. The mixture was stirred for 1 h at room temperature and then refluxed overnight, which resulted in the formation of a white precipitate. After reducing the volume of the solution, it was poured into 400 mL of concentrated aqueous NaCl, and the mixture was extracted with Et_2O (3 × 100 mL). Removal of volatiles produced a pale yellow oil, which was purified by flash chromatography on silica using a 3:1 pentane/Et_2O mixture to give 0.75 g of racemic *exo*-norborneol as a white powder. Under the same reaction conditions, oxidation of the enantio-enriched *exo*-phenylsilylnorbornane product (0.94 g) afforded 0.20 g of *exo*-norborneol. The enantiomeric excess of the produced *exo*-norborneol was measured to be 90.4%, as determined by GC analysis with a chiral column (Supelco beta-DEX 120, at 80 °C, He eluent at 1.4 mL/min flow)[32] at the laboratory of Prof. A. Togni at the ETH-Zürich.

Kinetic Measurements. Reactions were monitored by ^{1}H NMR spectroscopy, with a Bruker AMX300 spectrometer, using 5 mm Wilmad NMR tubes, equipped with J. Young Teflon screw caps. Liquid reagents were measured using a 100 μL Hamilton gastight syringe. The total volume of the reaction solution was determined by measuring its height in the precalibrated NMR tube. The samples were frozen in liquid N_2 immediately after preparation and defrosted just before being placed in the preshimmed probe, which was preheated at 25 °C. Single scan spectra were acquired automatically at preset time intervals. The peaks were integrated relative to ferrocene as an internal standard. Rate constants were obtained by nonweighted linear least-squares fits of the integrated first-order rate law in logarithmic form, $\ln C = \ln C_0 - k_{obs}t$.

Kinetic Study of the Reaction of 1 with $PhMeSiH_2$. Samples of **1** (12.3−15.5 mg, 0.0179−0.0226 mmol) and Cp_2Fe (1.0−3.0 mg) were weighed into an NMR tube and dissolved in benzene-d_6 (0.9 mL). To the solution was added a known amount of $PhMeSiH_2$. The disappearance of the YMe signal as integrated with respect to the ferrocene standard was monitored. Five kinetic runs were performed, using different amounts of silane. The overall rate constant was determined by plotting the observed pseudo-first-order rate constant for the consumption of **1** versus the concentration of $PhMeSiH_2$.

Kinetic Study of the Hydrosilylation of 1-Hexene with $PhMeSiH_2$ in Benzene-d_6. Samples of **1** (9.6−32.7 mg, 0.014−0.048 mmol) and Cp_2Fe (0.5−3.0 mg) were weighed into an NMR tube and dissolved in benzene-d_6 (ca. 0.6 mL). Alternatively, for accurate measuring of the amount of the catalyst precursor at low concentrations, a standard solution of **1** was prepared by dissolving 30.6 mg (0.0445 mmol) of **1** in 3.0 mL of benzene-d_6, and aliquots of this solution (50−800 μL) were used to prepare the NMR sample. To the solution were added known volumes of 1-hexene (36.4−500 μL) and

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[40] Bissinger, P.; Paul, M.; Jürgen, R.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 2579.

$PhMeSiH_2$ (20−44 μL). The consumption of $PhMeSiH_2$ was monitored by integrating the SiH_2 signal against ferrocene. The observed pseudo-first-order rate constants for silane disappearance were determined at different olefin or yttrium methyl initial concentrations by plotting ln[$PhMeSiH_2$] versus time.

Kinetic Study of the Hydrosilylation of 1-Hexene with $PhMeSiH_2$ in THF-d_8. Samples of **1** (8.2−18.6 mg, 0.012−0.042 mmol) and Cp_2Fe (0.5−2.0 mg) were weighed into an NMR tube and dissolved in THF-d_8 (ca. 0.5 mL). To this solution were added 1-hexene (150 μL, 1.20 mmol) and $PhMeSiH_2$ (40 μL, 0.29 mmol). The consumption of $PhMeSiH_2$ was monitored by integrating the CH_3 signal against ferrocene.

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Supporting Information Available: Tables and plots of kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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