

“Constrained geometry” catalysts of the rare-earth metals for the hydrosilylation of olefins

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Abstract

A series of yttrium and lutetium alkyl complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{ZNR}'\text{-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]$ ($\text{Ln} = \text{Y}, \text{Lu}$) was prepared by reacting the tris(trimethylsilylmethyl) precursor $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ with different linked amino-cyclopentadienes of the type $(\text{C}_5\text{Me}_4\text{H})\text{ZNHR}'$ ($\text{Z} = \text{SiMe}_2, \text{CH}_2\text{SiMe}_2$; $\text{R}' = t\text{Bu}, \text{Ph}, \text{C}_6\text{H}_4\text{-}t\text{Bu-4}, \text{C}_6\text{H}_4\text{-}n\text{Bu-4}$). The catalytic activity of these alkyl complexes in the hydrosilylation of 1-decene and styrene using PhSiH_3 as reagent was examined under standard conditions. A significant influence of the ligand structure on the catalytic property (turnover frequency, regioselectivity) was observed with the yttrium complex $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ being the most active for 1-decene hydrosilylation.

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Keywords: Rare-earth metal; Hydrosilylation; Olefins; Alkyl complex; Bidentate ligand

1. Introduction

Rare-earth metal complexes are known to be efficient homogeneous catalysts for a wide range of organic transformations [1]. While rare-earth metallocenes have been extensively studied for hydrosilylation of olefins [1,2,5b], mono(cyclopentadienyl) [3], and non-cyclopentadienyl [4] complexes that catalyze this reaction are still quite uncommon. In addition, the influence of the ligand structure on the activity and regioselectivity of the catalyst remains poorly understood [5]. We report here a systematic study of the hydrosilylation of 1-decene and styrene catalyzed by rare-earth alkyl complexes bearing a linked amido-cyclopentadienyl ligand (“constrained geometry” catalyst) of the general formula $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{ZNR}'\text{-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]$ [3c,3d]. Both electronic and steric characteristics of the ligand were varied in order to determine the factors that govern the efficiency and the regioselectivity of the catalysts. Different rare-earth metals were also

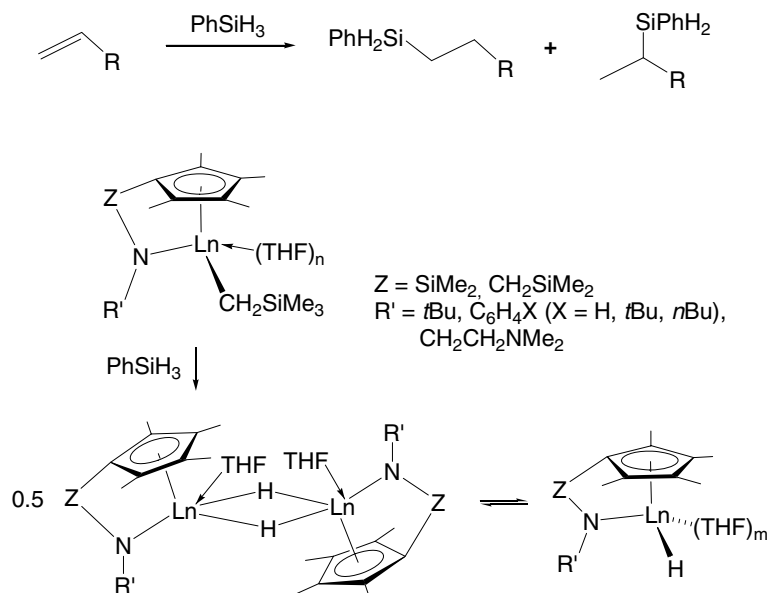
included to probe the influence of the ionic radius on the catalytic activity.

2. Results and discussion

2.1. General hydrosilylation procedure

All yttrium and lutetium complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{ZNR}'\text{-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]$ used in this work have been straightforwardly synthesized by the reaction of the corresponding tris(trimethylsilylmethyl) complex $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ ($\text{Ln} = \text{Y}, \text{Lu}$) with the linked amino-cyclopentadienes $(\text{C}_5\text{Me}_4\text{H})\text{ZNHR}'$ in pentane with concomitant formation of two equivalents of tetramethylsilane [3]. Depending on the ligand characteristics (length of the link Z and substituent at the amido-nitrogen R'), the products displayed very different solubility in organic solvents. Thus, $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_n\text{SiMe}_2\text{NPh-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ ($\text{Ln} = \text{Y}$ or Lu , $n = 0$ or 1) and $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2\text{-}\kappa\text{N},\text{N}')(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ [15] were found to be sparingly soluble in pentane (and could be isolated by simple filtration), but highly soluble in aromatic solvents. The other complexes were

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Scheme 1.

generally highly soluble both in aliphatic and aromatic hydrocarbons.

After their isolation, the trimethylsilylmethyl complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{ZNR}'\text{-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]$ were directly used for hydrosilylation of 1-decene and styrene in NMR-scale experiments. The olefin and PhSiH_3 were subsequently added to the complex dissolved in C_6D_6 at 25 °C, and monitoring of the typical signals of $\text{PhSiH}_2\text{CH}_2\text{SiMe}_3$ in the ^1H NMR spectrum in all cases evidenced the immediate and complete formation of the catalytically active hydrido species $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{ZNR}'\text{-}\kappa\text{N})(\mu\text{-H})(\text{THF})_m]_2$. The kinetically competent species is assumed to be the mononuclear hydride species in equilibrium with the dimer [3a] (Scheme 1).

2.2. 1-Decene

Under standard conditions, 1-decene was exclusively transformed into the anti-Markovnikov (1,2-addition or

terminal) product in practically quantitative yield by all complexes under consideration (Table 1). The catalytic efficiency, as judged qualitatively by considering the turnover frequency (TOF) values in h^{-1} defined as mol substrate per mol metal and reaction time shows considerable dependence on the nature of the trimethylsilylmethyl complex employed. The regioselectivity agrees with the general tendency of α -olefins to give predominantly 1,2-insertion into the polarized metal–hydride bond [6].

2.2.1. Structure–activity relationship

2.2.1.1. Length of the link. According to the previous studies performed on rare-earth metallocenes in comparison with rare-earth ansa-metallocenes, the presence of a link between the two cyclopentadienyl-moieties has been shown to influence the reactivity and the regioselectivity of the corresponding catalysts significantly by creating a well defined space around the active site [7]. In the case of “constrained geometry” catalysts, the length of the link

Table 1
Hydrosilylation of 1-decene with PhSiH_3 catalyzed by rare-earth metal alkyl complex with various linked amido-cyclopentadienyl ligands; $R = \text{CH}_2\text{SiMe}_3$

Complex	Turnover frequency, TOF (h^{-1})	Regioselectivity (1,2)/(2,1)
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\text{R}(\text{THF})]$	2.9	100/0
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\text{R}(\text{THF})]$	0.49	100/0
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\text{R}(\text{THF})]$	20.0	100/0
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\text{R}(\text{THF})]$	10.0	100/0
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{R}(\text{THF})_2]$	4.0	100/0
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.45	100/0
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{R}(\text{THF})_2]$	1.33	100/0
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.20	100/0
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}t\text{Bu-4-}\kappa\text{N})\text{R}(\text{THF})_2]$	1.33	100/0
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}t\text{Bu-4-}\kappa\text{N})\text{R}(\text{THF})_{1.5}]$	0.20	100/0
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}n\text{Bu-4-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.56	100/0
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}n\text{Bu-4-}\kappa\text{N})\text{R}(\text{THF})_{1.5}]$	0.19	100/0
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2\text{-}\kappa\text{N},\text{N}')\text{R}(\text{THF})]$	<0.15	100/0

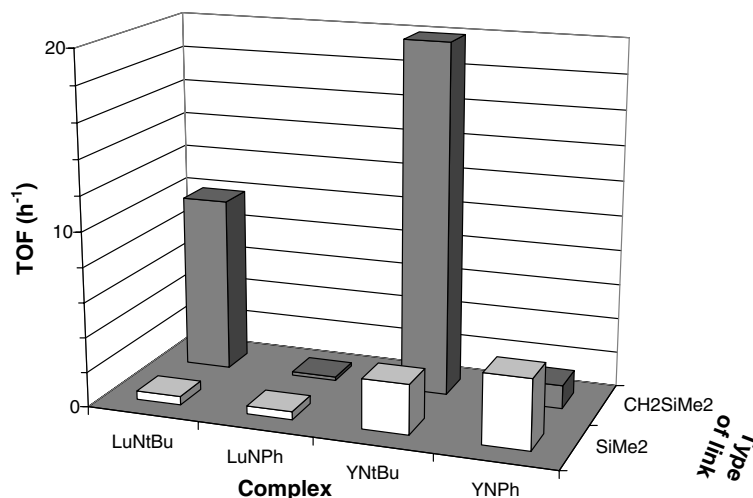


Fig. 1. Turnover frequencies (TOF, h^{-1}) for the 1-decene hydrosilylation by PhSiH_3 catalyzed by various rare-earth metal trimethylsilylmethyl complexes. The effect of the length of the link.

was proposed to influence the equilibrium between the dimeric and the monomeric forms of the active hydrido species [3a]. Thus, the longer CH_2SiMe_2 link would block more efficiently the space around the metal and allow the hydride to be sterically encumbered to shift the dissociation equilibrium towards the monomeric species [8]. We assume that the monomeric hydride is more catalytically efficient than the corresponding dimer, although in the case of metallocene hydrides the dimer was also shown to be active [5b]. The results of the hydrosilylation as function of the link are compiled in Fig. 1.

For the *t*BuN substituent all the catalysts with the longer CH_2SiMe_2 -bridge displayed a better activity than those with the shorter SiMe_2 -link. For the PhN substituent a decrease in reactivity was observed for all catalysts, when

exchanging the SiMe_2 - for the CH_2SiMe_2 -link. Possibly the combination of the longer link and the phenyl ring created too much steric bulk around the metal and hindered the approach of the substrate.

2.2.1.2. Substituent at the amido-nitrogen. The reactivity induced by the *t*Bu group being taken as a reference, the influence of different amido-nitrogen substituents was studied (Fig. 2). Changing the *t*Bu group against the phenyl ring had a detrimental effect on the catalytic activity. Because of its electron withdrawing ability, the phenyl ring renders the metal center more Lewis acidic (presence of two THF molecules on $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ [15] in contrast to one on $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ [12]). Therefore, a higher reactivity

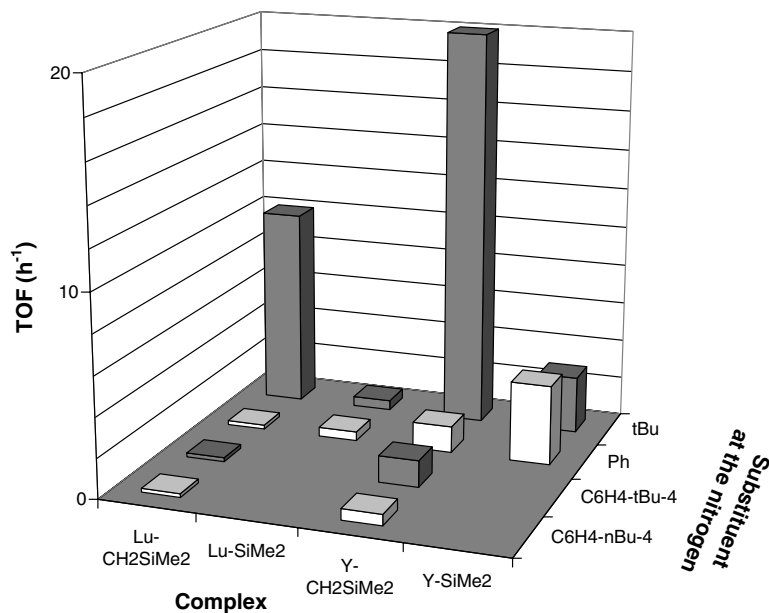


Fig. 2. Turnover frequencies (TOF, h^{-1}) for the 1-decene hydrosilylation by PhSiH_3 catalyzed by various rare-earth metal trimethylsilylmethyl complexes. The effect of the amido-substituent.

could be expected from the anilido derivatives towards electron-rich substrates. As the opposite effect was observed, the increased Lewis acidity of the metal possibly led to a more stable hydride dimer resulting in lower activity. The substitution of the phenyl ring at the *para* position by a *t*Bu group does not significantly influence the catalytic activity; the *t*Bu-group cannot interact neither with the metal center, nor with the substrate. When this *t*Bu group is exchanged for a *n*Bu one, a slight decrease in activity was noted.

The hemilabile $\text{CH}_2\text{CH}_2\text{NMe}_2$ group in $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{-CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2\text{-}\kappa\text{N,N}')\text{R}(\text{THF})]$ seemed to have an even stronger deactivating effect than the anilido groups, possibly because of the additional donor which coordinates at the metal center and blocks the active site. The double bond of the olefin might not be able to displace this pendant arm to efficiently access the metal center in order to insert into the Ln-H bond.

2.2.2. Regioselectivity

Even in the case of complexes containing a linked amido-cyclopentadienyl ligand, the coordination sphere around the metal appears to be encumbered. This observation is in accordance with the results obtained by Molander et al. in their study of the influence of parameters such as metal radius and ligand sterics on the regioselectivity of 1-decene hydrosilylation by rare-earth metallocenes [7]. They showed that a major condition for the increase in 2,1-regioisomer vs. 1,2-regioisomer was the accessible space at the active site of the catalyst and that the combination of a small metal with a sterically hindered ligand gave complete 1,2-regioselectivity. The linked amido-cyclopentadienyl complexes do not appear to offer sufficient space for the substrate to allow the 2,1-hydrosilylation of 1-decene. Factors other than steric ones may also play a role. This may include the nature of the monomer–dimer equilibrium and electronic factors.

2.3. Styrene

Hydrosilylation of styrene occurred at considerably lower rates of conversion in comparison to 1-decene for

the whole range of catalysts that were tested (Table 2). The ratio of anti-Markovnikov/Markovnikov isomer ranged from 4/96 to 46/54.

2.3.1. Structure–activity relationship

2.3.1.1. Length of the link. For the *t*BuN substituent, the trend observed for styrene was exactly the opposite to what was found for 1-decene, the differences being however less pronounced: the catalysts bearing the longer CH_2SiMe_2 -link were not always found to be more active than those with the shorter SiMe_2 -link.

As was found for 1-decene for the PhN substituent, a decrease in reactivity toward styrene was observed for all catalysts, when exchanging the short link for the long one (Fig. 3). Only $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{-(CH}_2\text{SiMe}_3\text{)}(\text{THF})_2]$ showed a higher activity than $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3\text{)}(\text{THF})_2]$ towards styrene.

2.3.1.2. Substituent at the amido-nitrogen. For the hydrosilylation of styrene, the same trend as for 1-decene is observed: the reactivity globally decreases as the steric bulk of the substituent increases with increasing electron-acceptor character. In general, the anilido derivatives are less active when compared with the *t*BuN derivatives (Fig. 4).

The tridentate ligand tested in this series, $[\text{C}_5\text{Me}_4\text{-CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2]^{2-}$, appeared to have a strong deactivating effect on the reactivity towards 1-decene, but gave a relatively active catalyst for styrene (total conversion within 7.5 h). Furthermore, the hydrosilylation was highly regioselective (96% of Markovnikov or branched regioisomer). This type of activity and regioselectivity are observed with sterically more “open” catalysts such as $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{NdCH}(\text{SiMe}_3)_2]$ [9], $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3\text{)}(\text{THF})]$ [3a], $[\text{K}(\text{THF})_2]_3[(\eta^5\text{-C}_5\text{Me}_5)_6\text{Sm}_6\text{H}_{15}]$ [3e] or $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{SmCH}(\text{SiMe}_3)_2]$ [5a]. The result obtained with the tridentate ligand [16] can be correlated with the observation that the product of styrene insertion into the yttrium–hydride bond shows no phenyl–metal interaction in $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{CHCH}_3\text{Ph})(\text{THF})]$ [3a], whereas such an

Table 2

Hydrosilylation of styrene with PhSiH_3 catalyzed by rare-earth metal alkyl complex with various linked amido-cyclopentadienyl ligands; $\text{R} = \text{CH}_2\text{SiMe}_3$

Complex	Turnover frequency, TOF (h^{-1})	Regioselectivity primary/secondary
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\text{R}(\text{THF})]$	4.0	12/88
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\text{R}(\text{THF})]$	0.18	11/89
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\text{R}(\text{THF})]$	2.5	40/60
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\text{R}(\text{THF})]$	0.17	46/54
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.22	37/63
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.17	31/69
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.87	25/75
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NPh-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.17	22/78
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}t\text{Bu-4-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.80	27/73
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}t\text{Bu-4-}\kappa\text{N})\text{R}(\text{THF})_{1.5}]$	0.17	30/70
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}n\text{Bu-4-}\kappa\text{N})\text{R}(\text{THF})_2]$	0.59	25/75
$[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}n\text{Bu-4-}\kappa\text{N})\text{R}(\text{THF})_{1.5}]$	0.16	20/80
$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2\text{-}\kappa\text{N,N}')\text{R}(\text{THF})]$	2.7	4/96

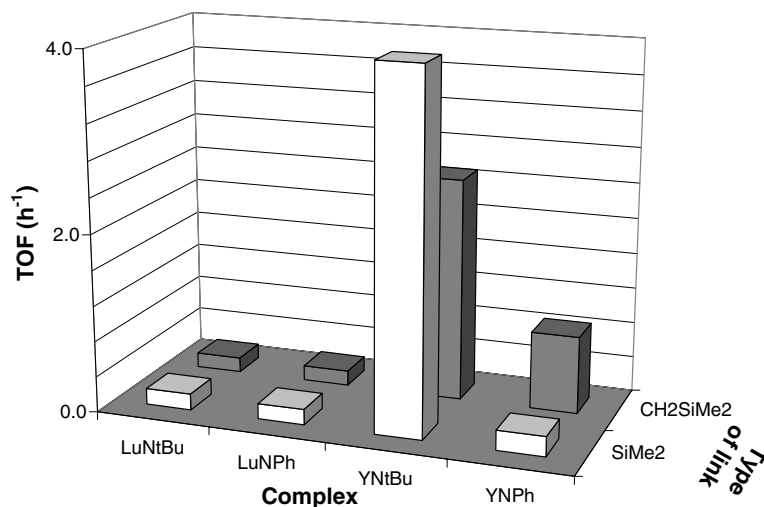


Fig. 3. Turnover frequencies (TOF, h⁻¹) for the styrene hydrosilylation by PhSiH₃ catalyzed by various rare-earth metal trimethylsilylmethyl complexes. The effect of the length of the link.

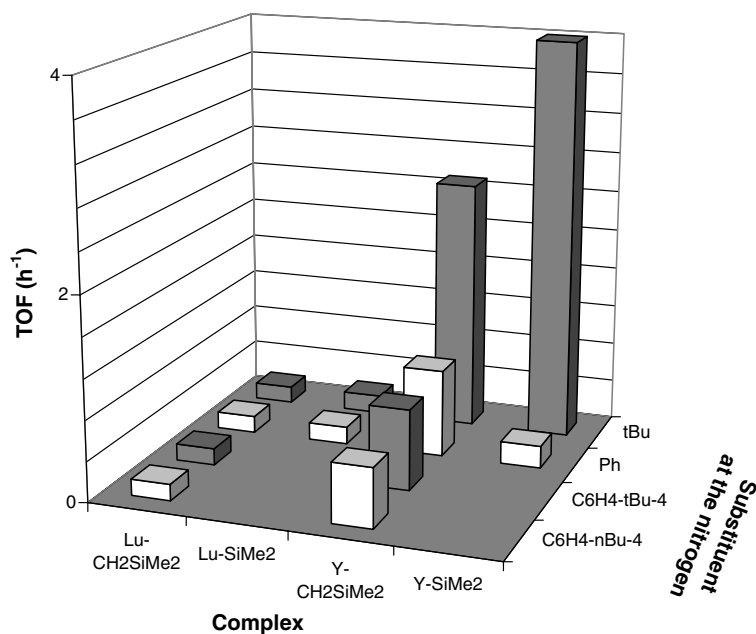


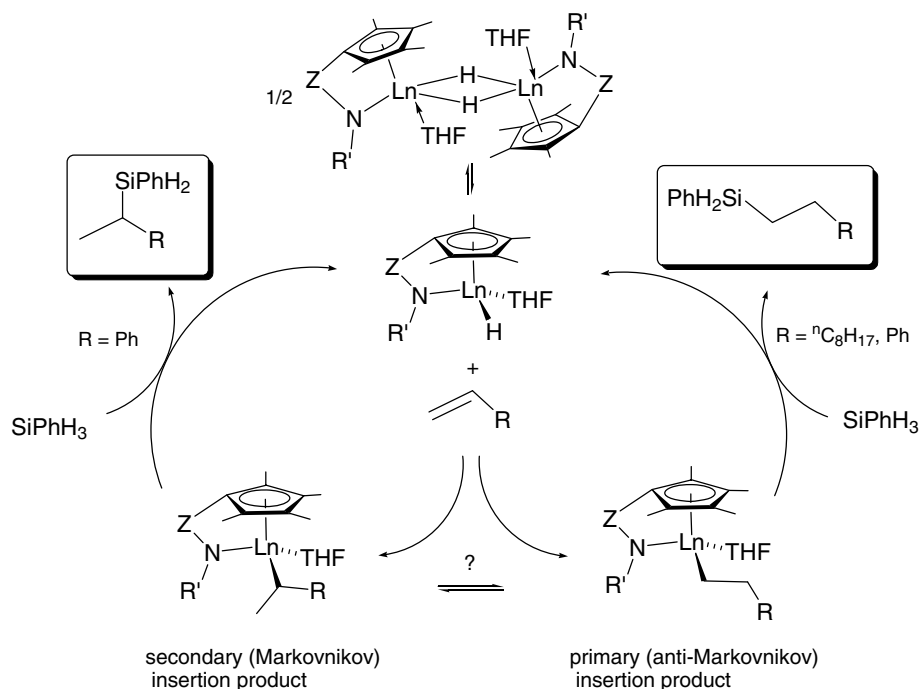
Fig. 4. Turnover frequencies (TOF, h⁻¹) for the styrene hydrosilylation by PhSiH₃ catalyzed by various rare-earth metal trimethylsilylmethyl complexes. The effect of the amido-substituent.

interaction is found in [Y(η^5 -C₅Me₄CH₂SiMe₂CH₂CH₂-NMe₂- κ N,N')(CHCH₃Ph)] [16] as well as in [Y(η^5 -C₅Me₄-SiMe₂N*t*Bu- κ N)(CHCH₃Ph)] [12b].

2.3.2. Regioselectivity

The formation of both regioisomers suggests a situation, which is not only governed by the sterics of both catalyst and substrate, but also by the electronic properties of styrene. [Y(η^5 -C₅Me₄CH₂SiMe₂NCH₂CH₂NMe₂- κ N,N')(CH₂SiMe₃)(THF)] is the only complex that displayed a very high regioselectivity for the branched isomer (96%). The fact that the proportion of Markovnikov regioisomer did not reach 100% might be due to at least two factors. These may be the steric bulk of the ligand and the ionic

radius of the metal used. For metallocenes or ansa-metallocenes, the regioselectivity for the Markovnikov product can be increased up to 99% for the larger metal centers such as Nd or Sm [5a,9]. For the complex bearing the tridentate ligand with an additional pendant arm at the amido-nitrogen [Y(η^5 -C₅Me₄CH₂SiMe₂CH₂CH₂NMe₂- κ N,N')(CH₂-SiMe₃)(THF)], the high selectivity for the Markovnikov product must be related to the hemilabile nature of the ligand. It is well known that styrene shows a strong preference for secondary insertion into the metal–hydride bonds [10], potentially leading to an η^3 -coordination at a Lewis-acidic/electrophilic metal center. This may be due to the η^n -coordination between the π -electron system of the styrene and the Lewis-acidic/electrophilic metal center. This



Scheme 2.

stabilization of rare-earth metal by aromatic ring has been shown to be quite common [5a,11,12b] in benzyl and other arene-containing complexes. Since the Markovnikov (primary) regioisomer was observed in non-negligible quantities in every experiment, a parallel reaction pathway involving a primary insertion must exist (Scheme 2). Under kinetic control, this energetically favored interaction results in the preference for secondary regioisomer. At longer reaction time (in the case of less active catalysts) the primary hydrosilylation product tends to increase. Interestingly the related scandium hydride complex $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\mu\text{-H})(\text{PMe}_3)_2]$ [8,17] gave a the bis(insertion) product $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})\{\text{CH}(\text{Ph})\text{-CH}_2\text{CH}_2\text{CH}_2\text{Ph}\}(\text{PMe}_3)]$ as a result of primary insertion followed by a secondary insertion.

3. Conclusion

The following general trends for the hydrosilylation activity of olefins using “constrained geometry” catalysts of the rare earth metals yttrium and lutetium can be recognized:

The apparently slight decrease in the ionic radius from Y to Lu (3.75% for coordination number 6) [13] results in a rather significant drop in hydrosilylation activity towards both 1-decene and styrene.

The activity trends do not follow simple structure–activity relationship, evidently due to some subtle effects, both steric and electronic, on the hydride dimer–monomer equilibrium. At this time we cannot exclude the possibility that the hydride dimer itself may insert olefin to give a μ -alkyl species [17]. The effect of amido-substituents remain also

somewhat obscure; the specific role of *tert*-amido group in titanium based “constrained geometry” catalysts has been noted before [18].

The regioselectivity for 1-decene hydrosilylation is perfect for anti-Markovnikov (1,2) product, whereas for styrene both regioisomers are observed, with the Markovnikov product preferred in all cases examined.

In order to elucidate further the structure–activity relationship for these “constrained geometry” catalysts, detailed kinetic analysis is required. However, as was suggested earlier [3a], the rather qualitative concept of “opening up” the reaction site to increase reactivity is much more intricate than in the case of the metallocenes.

4. Experimental section

All experiments were performed under an inert atmosphere of argon using standard Schlenk-line techniques. Pentane and THF were distilled from sodium/benzophenone ketyl. Anhydrous yttrium and lutetium trichloride (STREM) were used as received. The following products were prepared according to published procedures: $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ [12], $[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ [8], $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ [3a], $[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ [14], $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ [15], $[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ [15], $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NPh-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ [14], $[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NPh-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ [14], $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}t\text{Bu-4-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$ [14], $[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NC}_6\text{H}_4\text{-}t\text{Bu-4-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)$

(THF)_{1.5}] [14], [Y(η^5 -C₅Me₄CH₂SiMe₂NC₆H₄-*n*Bu-4- κ N)(CH₂SiMe₃)(THF)₂] [14], [Lu(η^5 -C₅Me₄CH₂SiMe₂-NC₆H₄-*n*Bu-4- κ N)(CH₂SiMe₃)(THF)_{1.5}] [14], [Y(η^5 -C₅Me₄-CH₂SiMe₂NCH₂CH₂NMe₂- κ N,N') (CH₂SiMe₃)(THF)] [16]. NMR spectra were recorded on Varian Gemini 200 and Varian Unity 500 spectrometers at 25 °C. Chemical shifts for ¹H NMR and ¹³C NMR were reported in ppm relative to tetramethylsilane, using residual solvent resonances as reference. Deuterated solvents were dried over sodium, distilled and degassed prior to use.

4.1. Typical procedure for complex synthesis

To a pentane suspension of [Ln(CH₂SiMe₃)₃(THF)₂] cooled to -78 °C was added a pentane solution of one equivalent of the linked amino-cyclopentadiene. After the addition, the solution was stirred for 1 h, and then slowly allowed to warm to 0 °C. Additional stirring at this temperature for 2.5 h followed by filtration (complexes insoluble or sparingly soluble in pentane) or reduction of the solvent (pentane soluble complexes) afforded the desired products after standing for one night at -32 °C. The compounds already described in the literature were identified by ¹H NMR, all new complexes were fully characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis, and metal titration.

4.2. Hydrosilylation procedure

In the glove-box, 25 μ mol of the complex were dissolved in 0.5 mL of C₆D₆ in an NMR tube equipped with a Young valve. To that solution was first added 20 equivalents of the olefin, and then 21 equivalents of phenylsilane. The total volume of the solution was then increased to 0.75 mL, and the tube was closed and vigorously shaken. The reaction was monitored by ¹H NMR spectroscopy on a 200 MHz spectrometer at 25 °C. The reaction time was defined as being the total time required for the olefin to be entirely hydrosilylated by the catalyst. The proportions of Markovnikov and anti-Markovnikov regioisomers were calculated by integration of the appropriate signals in the ¹H NMR spectra. All experiments were repeated at least twice.

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References

- [1] (a) G.A. Molander, Chem. Rev. 92 (1992) 29–68; (b) G.A. Molander, J.A.C. Romero, Chem. Rev. 102 (2002) 2161–2185; (c) R. Anwander, second ed., in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 2, Wiley-VCH, Germany, 2002, pp. 974–1014.
- [2] (a) S. Onozawa, T. Sakakura, M. Tanaka, Tetrahedron Lett. 35 (1994) 8177–8180; (b) G.A. Molander, J. Winterfeld, J. Organomet. Chem. 524 (1996) 275–279; (c) G.A. Molander, W.H. Retsch, J. Am. Chem. Soc. 119 (1997) 8817–8825; (d) H. Schumann, M.R. Keitsch, J. Winterfeld, S. Mühle, G.A. Molander, J. Organomet. Chem. 559 (1998) 181–190; (e) G.A. Molander, C.P. Corrette, Organometallics 17 (1998) 5504–5512; (f) H. Schumann, M.R. Keitsch, J. Demtschuk, G.A. Molander, J. Organomet. Chem. 582 (1999) 70–82.
- [3] (a) A.A. Trifonov, T.P. Spaniol, J. Okuda, Organometallics 20 (2001) 4869–4874; (b) A.A. Trifonov, T.P. Spaniol, J. Okuda, Dalton Trans. (2004) 2245–2250; (c) S. Arndt, J. Okuda, Chem. Rev. 102 (2002) 1953–1976; (d) J. Okuda, Dalton Trans. (2003) 2367–2378; (e) Z. Hou, Y. Zhang, O. Tardif, Y. Wakatsuki, J. Am. Chem. Soc. 123 (2001) 9216–9217; (f) O. Tardif, M. Nishiura, Z. Hou, Tetrahedron 59 (2003) 10525–10539.
- [4] (a) T.I. Gountchev, T.D. Tilley, Organometallics 18 (1999) 5661–5667; (b) K. Takaki, K. Sonoda, T. Kousaka, G. Koshiji, T. Shishido, K. Takehira, Tetrahedron Lett. 42 (2001) 9211–9214; (c) Y. Horino, T. Livinghouse, Organometallics 23 (2004) 12–14.
- [5] (a) P.-F. Fu, L. Brard, Y. Li, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 7157–7168; (b) A.Z. Voskoboinikov, A.K. Shestakova, I.P. Beletskaya, Organometallics 20 (2001) 2794–2801.
- [6] (a) G.A. Molander, M. Julius, J. Org. Chem. 57 (1992) 6347–6351; (b) K. Takaki, K. Komeyama, K. Takehira, Tetrahedron 59 (2003) 10381–10395.
- [7] G.A. Molander, E.D. Dowdy, B.C. Noll, Organometallics 17 (1998) 3754–3758.
- [8] S. Arndt, P. Voth, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 4690–4700.
- [9] T. Sakakura, H.-J. Lautenschlager, M. Tanaka, J. Chem. Soc., Chem. Commun. 1 (1991) 40–41.
- [10] (a) A. Zambelli, P. Longo, C. Pellecchia, A. Grassi, Macromol. 20 (1987) 2037–2039; (b) B.J. Burger, B.D. Santarsiero, M.S. Trimmer, J.E. Bercaw, J. Am. Chem. Soc. 110 (1988) 3134–3146; (c) J.E. Nelson, J.E. Bercaw, J.A. Labinger, Organometallics 8 (1989) 2484–2486; (d) A.M. Lapointe, F.C. Rix, M. Brookhart, J. Am. Chem. Soc. 119 (1997) 906–917.
- [11] (a) E.A. Mintz, K.G. Moloy, T.J. Marks, V.W. Day, J. Am. Chem. Soc. 104 (1982) 4692–4695; (b) W.J. Evans, T.A. Ullbarri, J.W. Ziller, J. Am. Chem. Soc. 112 (1990) 219–223.
- [12] (a) K.C. Hultsch, T.P. Spaniol, J. Okuda, Angew. Chem., Int. Ed. 38 (1999) 227–230; (b) K.C. Hultsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 228–243.
- [13] R.D. Shannon, Acta Cryst. A 32 (1976) 751–767.
- [14] P. Voth, D. Robert, T.P. Spaniol, J. Okuda (in preparation).
- [15] (a) M. Nishiura, Z. Hou, Y. Wakatsuki, T. Yamaki, T. Miyamoto, J. Am. Chem. Soc. 125 (2003) 1184–1185; (b) M. Nishiura, Z. Hou, J. Mol. Catal. A 213 (2004) 10–106; (c) W.-Z. Zhang, M. Nishiura, Z. Hou, J. Am. Chem. Soc. 127 (2005) 16788–16789.
- [16] P. Voth, T.P. Spaniol, J. Okuda, Organometallics 22 (2003) 3921–3926.
- [17] (a) P. Voth, S. Arndt, T.P. Spaniol, J. Okuda, M.L.H. Green, L.J. Ackerman, Organometallics 22 (2003) 65–76; (b) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.
- [18] J. Okuda, K. Musikabhumma, P.-J. Sinnema, Isr. J. Chem. 42 (2002) 383–392.