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Hydrosilylation of dienes by yttrium hydrido complexes containing a linked amido-cyclopentadienyl ligand

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The dimeric hydrido complex $[Y(L)(THF)(\mu\text{-}H)]_2$ (**2**) containing the CH_2SiMe_2-linked amido-cyclopentadienyl ligand $L = C_5Me_4CH_2SiMe_2NCMe_3^{2-}$ catalyzed the hydrosilylation of 1,5-hexadiene, 1,7-octadiene and vinylcyclohexene by $PhSiH_3$. As demonstrated for 1,7-octadiene, the product distribution of the hydrosilylation strongly depends on the molar ratio of the reagents. In the absence of $PhSiH_3$, the stoichiometric reaction of **2** with 1,5-hexadiene gave the isolable crystalline cyclopentylmethyl complex $[Y(L)\{CH_2CH(CH_2)_4\}(THF)]$ (**3**). Internal olefins such as *trans*-stilbene and alkynes such as *tert*-butylacetylene were not hydrosilylated by **2**. *trans*-Stilbene was inserted into the yttrium–hydride bond of **2** to give the 1,2-diphenylethyl complex $[Y(L)\{CH(CH_2Ph)Ph\}(THF)]$ (**4**). *tert*-Butylacetylene reacted with **2** to give the dimeric acetylide $[Y(L)(C{\equiv}CCMe_3)]_2$ (**5**). In an attempt to detect the monomeric hydrido species as a DME adduct [Y(L)H(DME)], complex **2** was reacted with DME to form the sparingly soluble, dimeric 2-methoxyethoxy complex $[Y(L)(\mu\text{-}OCH_2CH_2OMe\text{-}\kappa O)]_2$ (**6**) under C–O splitting.

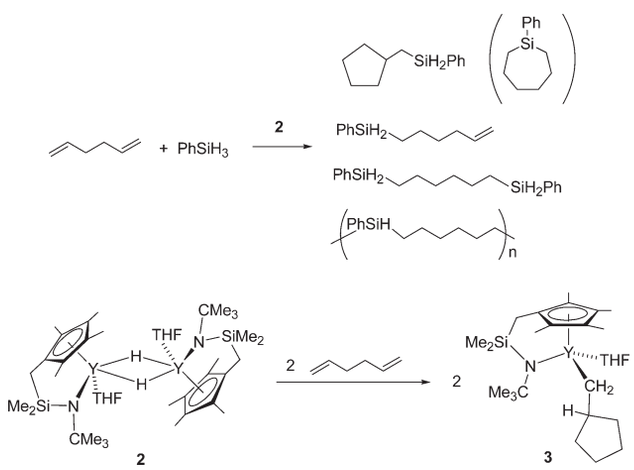
Introduction

In contrast to the metallocene alkyl and hydrido complexes of the rare-earth metals $[Ln(\eta^5\text{-}C_5R_5)_2X]$ (X = alkyl, H)[1] analogous complexes supported by the linked amido-cyclopentadienyl ligand system $[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4ZNR)X]$[2] have been used only to a limited degree as catalyst precursors for homogeneous alkene and alkyne hydrometalation reactions.[2d–f,3] We have recently reported that the hydrido yttrium complexes $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4ZNCMe_3)(THF)(\mu\text{-}H)]_2$ (Z = $SiMe_2$, CH_2SiMe_2) catalyze the hydrosilylation of 1-decene and styrene by $PhSiH_3$,[3a] previously reported for metallocene-based catalysts.[4] Extending the ancillary ligand backbone Z from the $SiMe_2$ link to the longer CH_2SiMe_2 significantly increased the reactivity,[5] although the ligand appears to be less "geometrically constrained".[6] We report here on the hydrosilylation of various dienes by $PhSiH_3$ catalyzed by the alkyl complex $[Y(L)(CH_2SiMe_3)(THF)]$ (**1**) with $L = (C_5Me_4CH_2SiMe_2NCMe_3)^{2-}$, which, in the presence of $PhSiH_3$, forms the dimeric hydrido complex $[Y(L)(THF)(\mu\text{-}H)]_2$ (**2**) *in situ*. In addition, we have studied the reactivity of the hydrido complex **2** towards various unsaturated substrates in order to compare the reactivity with that of the $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$[7] and to gain insight into the catalytically active species of the hydrosilylation reaction.

Results and discussion

Reaction of the hydrido complex 2 with dienes

The hydrido complex **2** catalyzed the hydrosilylation of 1,5-hexadiene with $PhSiH_3$ (1 : 1 molar ratio) under standard conditions (25 °C, 5 mol% **2** in hexane) to give an inseparable mixture of both linear (6-phenylsilyl-1-hexene, 1,6-bis(phenylsilyl)hexane) and cyclized products (1-phenylsilylmethylcyclopentane, 1-phenylsilacycloheptane) as well as involatile oligomer (Scheme 1). When the reaction of **2** with equimolar amounts of 1,5-hexadiene and $PhSiH_3$ in benzene-d_6 was monitored by NMR spectroscopy, the characteristic triplet at 5.50 ppm (J_{YH} = 26.8 Hz) was recorded upon addition of $PhSiH_3$, indicating regeneration of the dimeric hydride. At the same time, the multiplet due to the methylene protons of the $PhSiH_2CH_2$ group appeared at 1.16 ppm. The low chemoselectivity was somewhat unexpected, since other catalysts such as metallocenes appear to give selectively 1-phenylsilylmethylcyclopentane.[3a,4]



Scheme 1

Without $PhSiH_3$, however, the reaction of **2** with 1,5-hexadiene at 0 °C gives the cyclopentylmethyl complex $[Y(L)\{CH_2CH(CH_2)_4\}(THF)]$ (**3**) as a result of intramolecular cyclization, as previously reported for the analogous reaction of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ to give $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{CH_2CH(CH_2)_4\}(THF)]$.[7] Complex **3** was isolated as extremely air- and moisture-sensitive colorless crystals in 74% yield after crystallization from hexane at −30 °C. It is highly soluble in aliphatic and aromatic hydrocarbons and gradually decomposed in solution even under an atmosphere of argon at 0 °C over a period of one day.

The ^1H NMR spectrum of **3** at room temperature shows a doublet of doublets at −0.11 ppm with characteristic coupling constants ($^2J_{YH}$ = 3.3 Hz, $^3J_{HH}$ = 8.0 Hz) due to the two protons of the methylene group attached to the yttrium center. In the $^{13}C\{^1H\}$ NMR spectrum a resonance at 47.9 ppm with a large coupling constant $^1J_{YC}$ = 52.5 Hz is observed for the corresponding carbon atom ($^1J_{YC}$ = 54.7 Hz for $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{CH_2CH(CH_2)_4\}(THF)]$[7]). Variable-temperature ^1H and ^{13}C NMR spectroscopic data for **3** indicate the presence of a labile THF ligand over the temperature range of +25 to −70 °C, resulting in an apparent mirror plane within the molecule. No decoalescence of any of the diastereotopic signals was observed even at −70 °C.

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Table 1 Crystallographic and refinement parameters for complexes **3, 4** and **6**

Compound	**3**	**4**	**6**
Crystal data			
Empirical formula	$C_{26}H_{48}NOSiY$	$C_{34}H_{50}NOSiY$	$C_{38}H_{72}N_2O_4Si_2Y_2{\cdot}0.5C_4H_8O$
M/g mol^{-1}	507.65	605.77	891.04
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Crystal size/mm	0.45 × 0.30 × 0.08	0.50 × 0.45 × 0.13	0.18 × 0.14 × 0.12
a/Å	10.5235(7)	9.2905(5)	10.5434(7)
b/Å	17.119(1)	18.017(1)	14.0024(9)
c/Å	16.244(1)	20.250(1)	16.678(1)
α/°	90	86.247(6)	69.103(1)
β/°	104.359(1)	84.471(5)	80.809(1)
γ/°	90	79.076(6)	79.444(1)
V/Å^3	2835.0(3)	3308.8(3)	2249.4(2)
Z	4	4	2
D_c/g cm^{-3}	1.189	1.216	1.316
F(000)	1088	1288	944
μ/mm^{-1}	2.115	1.824	2.660
T/K	181(2)	293(2)	183(2)
Data collection			
$2\theta_{max}$/°	56.6	51.9	56.6
Index ranges	h, −14 to 14	h, 0 to 11	h, −14 to 14
	k, −22 to 22	k, −21 to 22	k, −18 to 18
	l, −21 to 21	l, −24 to 24	l, −22 to 22
Solution and refinement			
No. of rflns. measd	25422	13779	20801
No. of indep. rflns. (R_{int})	7000 (0.0584)	12943 (0.0608)	10853 (0.0548)
No. of parameters	278	715	473
GOF	0.911	0.976	0.872
Final R indices R_1, wR_2 (obsd. data)	0.0423/0.0948	0.0613/0.0966	0.0418/0.0729
Final R indices R_1, wR_2 (all data)	0.0959/0.1071	0.1911/0.1228	0.0944/0.0833
$\Delta\rho$/e Å^{-3}	0.593/−0.428	0.320/−0.476	0.624/−0.445

The molecular structure of **3** in the solid state was determined by a crystal structure analysis on colorless crystals obtained by slow cooling of a hexane solution to −30 °C. Crystallographic data are compiled in Table 1. Fig. 1 shows the molecular structure that is derived from a three-legged piano-stool configuration. The yttrium atom is coordinated in pseudo-tetrahedral fashion by the cyclopentadienyl ring, the chelating amido and cyclopentylmethyl ligands, as well as one THF molecule. Molecular parameters of **3** are comparable with those of [Y(L){CH_2SiMe_3}(THF)].[4] The Y–C17 bond distance of 2.423(3) Å is similar to the distance reported for the related trimethylsilylmethyl derivative (2.425(2) Å), but slightly longer than that in the complex [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] (2.388(7) Å).[7b] As expected, the length of the terminal Y–C bond in **3** is much shorter than the distances between yttrium and α-carbon atoms in dimeric complexes with bridging *n*-alkyl ligands of the type [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(μ-CH_2CH_2R)]$_2$.[7d] The slightly longer Y–O contact in **3** (2.344(2) Å) compared to the corresponding distance in [Y(L){CH_2SiMe_3}(THF)] (2.327(1) Å)[3a] may result from higher steric hindrance caused by the cyclopentylmethyl ligand. Compound **3** has a monomeric structure both in solution and in the crystalline state, probably due to an increased steric demand of the tertiary β-carbon atom compared with the secondary β-carbon atom.

The catalytic reaction of 1,7-octadiene with $PhSiH_3$ in the presence of 5 mol% of **2** did not give any cyclic organosilanes. We found that the hydrosilylation reaction was strongly influenced by the stoichiometric ratio of the diene to the silane $PhSiH_3$ as well as by the reaction time (Scheme 2).

When the reaction was carried out in the presence of a twofold molar excess of $PhSiH_3$, 1,7-octadiene was quantitatively converted within 48 h to the product of the double primary (anti-Markovnikov) addition, 1,8-bis(phenylsilyl)octane. The equimolar reaction of 1,7-octadiene with $PhSiH_3$ is less selective and resulted in the complete conversion of the starting material within 2 h to a 70 : 27-mixture of 8-phenylsilyl-1-octene and 1,8-bis(phenylsilyl)octane. When an equimolar reaction mixture of $PhSiH_3$ and 1,7-octadiene was left standing at room temperature for 72 h, a highly viscous pale-yellow oil was isolated in high yield instead of the volatile organosilanes.

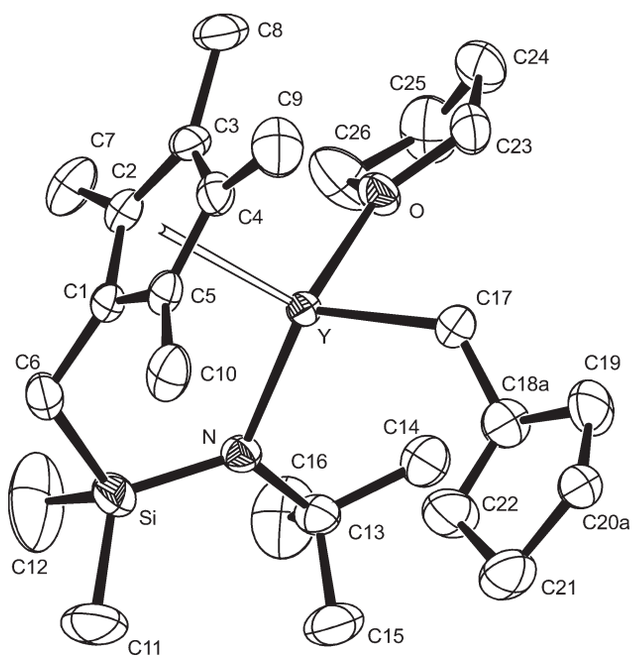
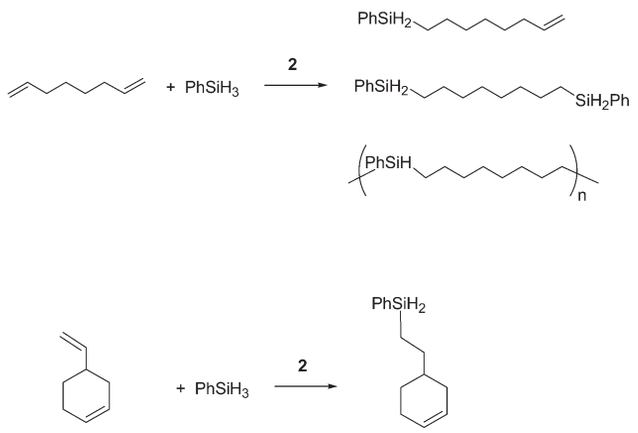


Fig. 1 ORTEP diagram of the molecular structure of [Y(L){$CH_2CH(CH_2)_4$}(THF)] (**3**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms as well as C18b and C20b (which are split positions due to disorder within this ligand) are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (°): Y–N 2.235(2), Y–C17 2.423(3), Y–C1 2.598(3), Y–C2 2.608(3), Y–C3 2.656(3), Y–C4 2.649(3), Y–C5 2.610(3), Y–O 2.344(2), Cp_{Cent}–Y 2.335(3); Cp_{Cent}–Y–N 106.1(1), Cp_{Cent}–Y–C17 113.4(1), Cp_{Cent}–Y–O 110.1(1), N–Y–C17 118.0(1), N–Y–O 111.58(8), O–Y–C17 97.5(1).

After removal of all volatiles *in vacuo*, the oil was purified by flash chromatography. The microanalytical data and the ^{1}H and ^{13}C NMR spectra indicate that it is an oligomer consisting of [$PhSiH(CH_2)_8$]$_n$ fragments. The degree of oligomerization was estimated to be $n \sim 20$, based on one sharp peak corresponding to M_w = 4500 in the gel permeation chromatogram. Apparently, the $PhSiH_2$ group of ini-



Scheme 2

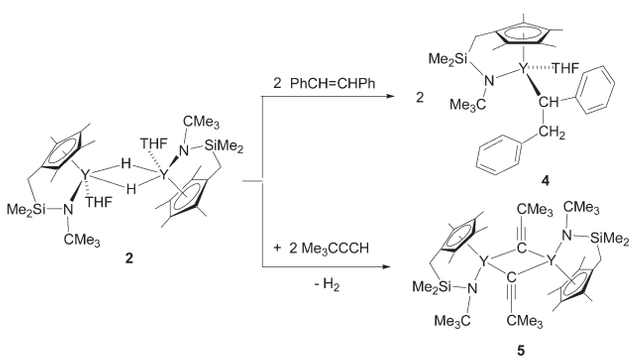
tially formed 8-phenylsilyl-1-octene reacted with the double bond of another 8-phenylsilyl-1-octene molecule under oligomerization.

^{1}H NMR spectroscopic monitoring of the reaction of the hydrido complex **2** with 1,7-octadiene at 0 °C indicated that the conversion was complete within 45 min to give the derivative with a cycloheptylmethyl ligand [Y(L){$CH_2CH(CH_2)_6$}(THF)]. The product is highly unstable in solution even at low temperatures and decomposed readily. All attempts to isolate the complex in analytically pure form failed.

Selective hydrosilylation of the vinylic double bond of 4-vinyl-1-cyclohexene was achieved in the presence of **2** using two equivalents of $PhSiH_3$. The reaction led to the primary (anti-Markovnikov) product 4-{2-(phenylsilyl)ethyl}cyclohex-1-ene[4a] in 93% yield after 18 h. The reaction of **2** with 4-vinyl-1-cyclohexene in toluene at 0 °C gave the insertion product which readily decomposed and could not be isolated.

Reactions of the hydrido complex 2 with *trans*-stilbene

In contrast to well known reactions of rare-earth metal hydrides with α-olefins,[1,8] the insertion of 1,2-disubstituted olefins into Ln–H bonds is less investigated. **2** did not catalyze the hydrosilylations of *trans*-stilbene. The yttrium hydrido complex [Y(η^5:η^1-$C_5Me_4SiMe_2CMe_3$)(THF)(μ-H)]$_2$ is inert against *trans*-stilbene even at 60–80 °C over several hours.[7b] However, the yttrium hydride **2** slowly reacted with an equimolar amount of *trans*-stilbene in benzene at room temperature over a period of 6 d (Scheme 3).



Scheme 3

The insertion product [Y(L){$CH(CH_2Ph)Ph$}(THF)] (**4**) was isolated as air- and moisture-sensitive crystals in 72% yield after crystallization from hexane at −30 °C. It is soluble in aliphatic and aromatic hydrocarbons. The crystal structure was determined by X-ray diffraction. The unit cell contains two crystallographically independent molecules of similar structure. An ORTEP diagram of the structure of one molecule is shown in Fig. 2. The monomeric complex contains a chiral yttrium center adopting a pseudo-tetrahedral geometry similar to that found in **3**, [Y(L){CH_2SiMe_3}(THF)], and [Y(L){CHMePh}(THF)].[3a] Although the Y–N bond length (Y1–N1 2.232(4) Å, Y2–N2 2.235(4) Å) and the Y–Cp_{Cent} distance (2.342(5) Å for both crystallographically independent molecules) are comparable to those observed in the complex mentioned above, the Y–O bond (Y1–O1 2.370(4) Å, Y2–O2 2.357(4) Å) is somewhat longer (2.350(8) Å for [Y(L){CHMePh}(THF)]). The Y–C bond in **4** (Y1–C17 2.519(5) Å, Y2–C51 2.478(5) Å) is similar to that in [Y(L){CHMePh}(THF)] (2.52(1) Å).[3a] A weak interaction between the yttrium atom and the *ipso* ring carbon atom of the α-phenyl group is indicated by the interatomic distance of 2.985(5) Å (Y1–C18) as well as of 3.064(5) Å (Y2–C52). Interaction between the yttrium atom and the aromatic ring is also indicated by the small angle of 93.7(3)° (Y1–C17–C18) as well as of 99.1(4)° (Y2–C51–C52) which is significantly smaller than that found for the η^1-bonded benzyl ligand in the complex [$Cp^*_2Y(CH_2Ph)(THF)$] (Y–C_{ipso} 3.444 Å, Y–$C_α$–C_{ipso} 118.3(4)°).[9] The bond distance between the *ipso*-carbon atom and the two *ortho*-carbon atoms of the ring atoms are slightly longer than the other bond lengths within the aromatic ring (C18–C23 1.402(7) Å and C18–C19 1.410(7) Å as well as C52–C57 1.397(8) Å and C52–C53 1.408(8) Å).

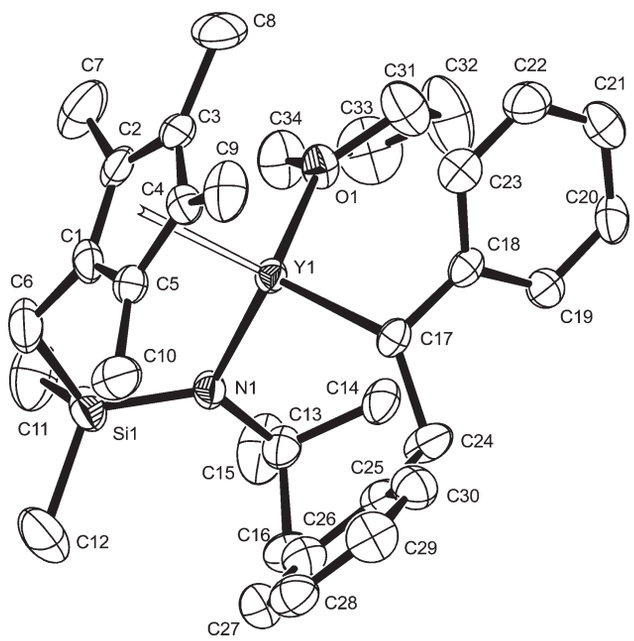


Fig. 2 ORTEP diagram of the molecular structure of [Y(L){$CH(CH_2Ph)Ph$}(THF)] (**4**). Thermal ellipsoids are drawn at the 30% probability level. Only one of the two crystallographically independent molecules is shown. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (°): Y1–N1 2.232(4), Y1–C17 2.519(5), Y1–C1 2.587(5), Y1–C2 2.606(5), Y1–C3 2.662(5), Y1–C4 2.680(5), Y1–C5 2.618(5), Y1–O1 2.370(4); N1–Y1–O1 97.5(2), N1–Y1–C17 114.3(2), O1–Y1–C17 119.6(2), Y1–C17–C18 93.7(3), Y1–C17–C24 125.5(4).

The ^{1}H NMR spectra at different temperatures indicate that the coordinated THF ligands in **4** are labile on the NMR time scale. ^{1}H and ^{13}C NMR spectroscopic data of **4** at room temperature show four distinct singlets for the cyclopentadienyl methyl groups as well as two singlets for the $SiMe_2$ group, as expected for a chiral molecule. The diastereotopic protons of the methylene group of the CH_2SiMe_2 link give rise to two signals at 2.14 and 2.22 ppm in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, the α-carbon atom of the $CH(CH_2Ph)Ph$ moiety bonded to the yttrium appears as a doublet at 58.0 ppm with $^1J_{YC}$ = 25.0 Hz. The proton bonded to this carbon atom is observed as a broadened multiplet at 2.75 ppm, while the protons of the methylene group appear as doublets of doublets at 3.45 and 3.70 ppm, as part of a higher-order ABX pattern.

Reactions of the hydrido complex 2 with *tert*-butylacetylene

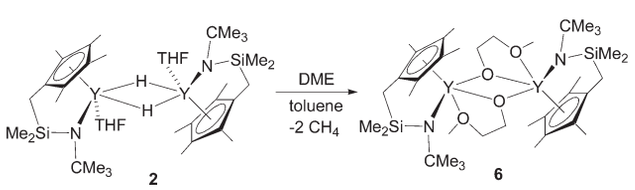
The lanthanide alkyls and hydrides are known to react with terminal alkynes to produce oligomeric acetylides which normally rearrange in solution to give carbon–carbon coupled products.[10] Since hydrosilylation of alkynes by $PhSiH_3$ was not observed using **2**, it

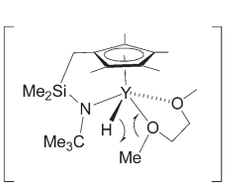
was assumed that a stoichiometric metalation reaction took place. Complex **2** readily reacted with *tert*-butylacetylene in benzene at room temperature under evolution of dihydrogen over a period of 30 min. The acetylide $[Y(L)(C{\equiv}CCMe_3)]_2$ (**5**) was isolated in 92% yield after crystallization from hexane (Scheme 3).

The colorless crystals of **5** are extremely air- and moisture-sensitive and highly soluble in aromatic solvents, but only sparingly soluble in aliphatic hydrocarbons. The NMR spectra at room temperature show C_{2h}-symmetry: two singlets are observed in the ^{1}H as well as in the ^{13}C NMR spectra in benzene-d_6 for the eight cyclopentadienyl methyl groups and one singlet is observed for the methyl groups as well as for the methylene group of the CH_2SiMe_2-bridge. The ^{13}C NMR spectrum shows a triplet at 126.7 ppm with $^1J_{YC}$ = 25.5 Hz for the α-carbon atom of the acetylide group. The splitting due to the Y–C coupling indicates a dimeric structure of **5** with two μ-bridging alkynyl ligands interacting with the two yttrium centers. In contrast to the metallocene acetylide derivatives of the rare earths,[10c–f] no evidence for the formation of carbon–carbon coupled products were found in the reaction mixture. The reactivity of the hydride **2** toward acetylene is similar to that of the bis(benzamidinato) complexes[10h,i] and is different from that of Cp^*_2LnR complexes. More recently, however, for the catalytic alkyne dimerization using $[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NPh)(CH_2SiMe_3)(THF)_2]$ (Ln = Y, Lu) alkynyl derivatives $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NPh)(C{\equiv}CR)]_2$ have been identified as the active species.[10j]

The reaction of the hydrido complex 2 with DME

Previously we argued that the higher reactivity of **2** compared to that of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ was due to the shift in the monomer–dimer equilibrium towards higher monomer concentration for **2**. More recently, the conversion of the dimeric alkyl complexes $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}CH_2CH_2R)]_2$ into the monomeric adducts $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}CH_2CH_2R)(L)]$ (L = THF, DME) have been observed by adding an excess of THF or DME.[7d] In an attempt to generate the monomeric yttrium hydride complex [Y(L)H(DME)], we have reacted **2** with 2 equivalents of DME in toluene at room temperature. The reaction occurred with cleavage of one of the C–O bonds of the DME molecule, resulting in the formation of sparingly soluble crystals of the bridging 2-methoxyethoxy complex $[Y(L)(\mu\text{-}OCH_2CH_2OMe\text{-}\kappa O)]_2$ (**6**) (Scheme 4). Evidently, the hydrido ligand as a strong nucleophile attacks the methoxy function of DME, activated by the Lewis-acidic yttrium center in [Y(L)H(DME)]. This is in analogy to the ether cleavage reaction promoted by reagents such as BBr_3 and Me_3SiI.[11]





Scheme 4

Crystallization of **6** from THF gave the THF hemi-solvate $[Y(L)(\mu\text{-}OCH_2CH_2OMe\text{-}\kappa O)]_2{\cdot}0.5THF$. Due to the low solubility of **6** even in polar organic solvents such as THF or pyridine, only ^{1}H NMR spectroscopic data could be obtained (with difficulty). Single crystals suitable for an X-ray diffraction analysis were obtained by slow cooling of a THF solution from 40 to 20 °C. Crystallographic data are compiled in Table 1. The unit cell contains two crystallographically independent molecules of similar structure. An ORTEP diagram of the structure of one molecule of **6** is shown in Fig. 3. Both molecules show crystallographic inversion symmetry. The yttrium atoms are coordinated by the linked amido-cyclopentadienyl ligands and are assembled by two 2-methoxyethoxy fragments forming an Y_2O_4 core with μ_2-bridging alkoxy oxygen atoms, while the ether oxygen atoms are bonded to each yttrium center. The bridging Y–O bonds are inequivalent with bond distances between 2.329(2) Å (Y1–O1) and 2.251(2) Å (Y1–O1′) as well as 2.339(2) Å (Y2–O3) and 2.242(2) Å (Y2–O3′) for the second crystallographically independent molecule. The Y–O distances in **6** are close to the bridging bonds in the dimeric enolate complex $[Y(\eta^5\text{-}MeC_5H_4)_2(\mu\text{-}OCH{=}CH_2)]_2$.[12] The coordinative bond between the methoxy oxygen atom and the yttrium center (Y1–O2 2.424(2) Å, Y2–O4 2.426(2) Å) is slightly shorter than the Y–O bond in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2CH_2CH_2CH_3)(DME)]$ (2.431(3) and 2.477(3) Å) or $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(C_4H_3O)(DME)]$ (2.387(2) and 2.473(2) Å).[7d]

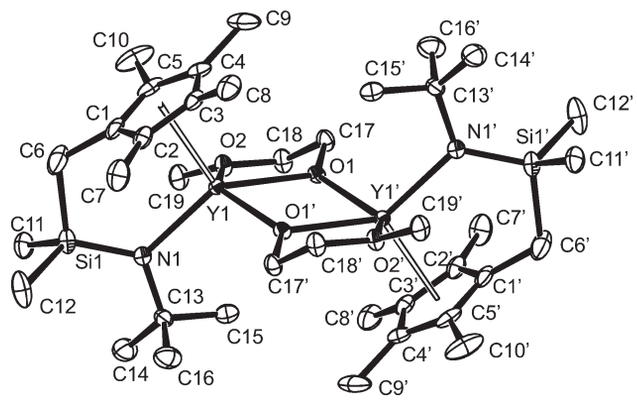


Fig. 3 ORTEP drawing and numbering scheme of the molecular structure of $\{[Y(L)(\mu^2\text{-}OCH_2CH_2OCH_3)\}_2(THF)_{0.5}$ (**6**) with thermal ellipsoids drawn at the 30% probability level. Only one of two crystallographically independent molecules is shown. Hydrogen atoms are omitted for the sake of clarity. The atoms marked with a prime (′) correspond to the symmetry equivalent positions ($-x$, $1-y$, $1-z$). Selected bond lengths (Å) and bond angles (°): Y1–O1 2.329(2), Y1–O1′ 2.251(2), Y1–N1 2.299(3), Y1–O2 2.424(2), Y1–C1 2.653(3), Y1–C2 2.658(3), Y1–C3 2.704(3), Y1–C4 2.678(3), Y1–C5 2.650(3), Y1–Y1′ 3.8000(7); O1′–Y1–N1 107.78(8), O1–Y1–O1′ 67.88(8), O1′–Y1–O2 131.37(7).

Conclusion

The hydride complex $[Y(L)(THF)(\mu\text{-}H)]_2$ (**2**) when compared with the more "constrained" analogue $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$[7] shows high reactivity towards terminal olefinic double bonds, and as shown for *trans*-stilbene, even towards an internal double bond. This may be ascribed to the more open coordination sphere around the yttrium center despite the longer CH_2SiMe_2 link in the backbone of the ligand. Moreover, the σ-bond metathesis of the initially formed alkyl complex by $PhSiH_3$ seems to be sufficiently fast so that even in the case of 1,5-hexadiene, the cyclization to give 1-phenylsilylmethylcyclopentane is not a predominant reaction.

Experimental

General considerations

All operations were performed under an inert atmosphere of argon and by using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Complexes **1** and **2** were prepared as reported earlier.[3a] All other commercially available chemicals were used after appropriate purification. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 101 MHz) in C_6D_6 at 25 °C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally according to the residual solvent resonances and reported relative to tetramethylsilane. Gas chromatographic analyses were performed on a Fisons GC 8000 Top instrument using a capillary column (30 m × 0.32 mm). Elemental

analyses were performed by the Microanalytical Laboratory in the Chemistry Department of Mainz University.

Hydrosilylation of 1,5-hexadiene (molar ratio C_6H_{10} : $PhSiH_3$ = 1 : 1)

To a solution of **1** (25.5 mg, 50 μmol) in 0.5 mL of hexane were added sequentially $PhSiH_3$ (108 mg, 1.00 mmol) and 1,5-hexadiene (82 mg, 1.00 mmol) The reaction mixture was stirred at ambient temperature. Small aliquots were taken for GC analysis and the reaction was found to be complete after 2 h. The reaction mixture was quenched with 0.5 mL of methanol, diluted with hexane, and filtered. The volatiles were removed *in vacuo* to give a pale yellow oil. The oil was purified by flash chromatography (silica gel, eluent: pentane) and distilled *in vacuo* (250 °C/4 × 10^{-2} mmHg). Distillation afforded 110 mg (58%) of volatile products, shown by GC and NMR to be a mixture consisting of 6-phenylsilyl-1-hexene, 1,6-bis(phenylsilyl)hexane, 1-phenylsilylmethylcyclopentane, and 1-phenylsilacycloheptane. The residue was identified as a mixture of oligomers, 80 mg (42%) (Found: C, 75.42; H, 9.71. $C_{12}H_{18}Si$ requires C, 75.77; H, 9.46); δ_H ($CDCl_3$, 25 °C) 0.79 (m, 4 H, CH_2Si), 1.29–1.39 (m, 8 H, CH_2), 4.27 (m, 1 H), 7.25 (m, 3 H), 7.50 (m, 2 H).

Hydrosilylation of 1,7-octadiene (molar ratio C_8H_{14} : $PhSiH_3$ = 1 : 2)

To a solution of **1** (25.5 mg, 50 μmol) in 0.5 mL of hexane were sequentially added $PhSiH_3$ (217 mg, 2.00 mmol) and 1,7-octadiene (110 mg, 1.00 mmol). The reaction mixture was stirred at ambient temperature and small aliquots were taken for GC analysis. The reaction was found to be complete after 48 h. The reaction mixture was quenched with 0.5 mL of methanol, diluted with hexane, and filtered. The volatiles were removed *in vacuo* to give a pale-yellow oil. Purification by flash chromatography (silica gel, eluent: pentane) and Kugelrohr distillation *in vacuo* (230 °C/10^{-2} mmHg) gave 299 mg (94%) of 1,8-bis(phenylsilyl)octane as a colorless oil (Found: C, 73.74; H, 9.52. $C_{20}H_{30}Si_2$ requires C, 73.60; H, 9.19); δ_H ($CDCl_3$, 25 °C) 1.02 (m, 4 H, CH_2Si), 1.34 (m, 4 H, CH_2), 1.42 (m, 4 H, CH_2), 1.54 (m, 4 H, CH_2), 4.38 (t, $^3J_{HH}$ = 3.6 Hz, $^1J_{SiH}$ = 96 Hz, 4 H, SiH_2), 7.47 (m, 6 H), 7.66 (m, 4 H). δ_C ($CDCl_3$, 25 °C) 10.3 (CH_2Si), 25.3 (CH_2), 29.4 (CH_2), 33.1 (CH_2), 128.2, 129.7, 133.0, 135.5 (C_6H_5). EI MS *m*/*z* (%): 326 (8%, M^+), 249 (32%, $C_{14}H_{25}Si_2^+$) 248 (100%, $C_{14}H_{24}Si_2^+$), 170 (93%, $C_8H_{18}Si_2^+$), 139 (47%, $C_8H_{15}Si^+$).

Hydrosilylation of 1,7-octadiene (molar ratio C_8H_{14} : $PhSiH_3$ = 1 : 1)

To a solution of **1** (25.5 mg, 50 μmol) in 0.5 mL of hexane were added sequentially $PhSiH_3$ (108 mg, 1.00 mmol) and 1,7-octadiene (110 mg, 1.00 mmol). The reaction mixture was stirred at ambient temperature. Small aliquots were taken for GC analysis and the reaction was found to be complete after 2 h. The reaction mixture was quenched with 0.5 mL of methanol, diluted with hexane, and filtered. The volatiles were removed *in vacuo* to give a pale-yellow oil. The oil was purified by flash chromatography (silica gel, eluent: pentane). Two products were separated by vacuum distillation. The first product: (160 °C/10^{-2} mmHg) 8-phenylsilyl-1-octene, colorless oil, 152 mg (70%). δ_H ($CDCl_3$, 25 °C) 0.93 (m, 2 H, CH_2Si), 1.24–1.45 (m, 8 H, CH_2), 2.02 (m, 2 H, $CH_2CH{=}CH_2$), 4.27 (m, 2 H, SiH_2), 4.96 (m, 2 H, $CH_2{=}CH$), 5.78 (m, 1 H, $CH_2{=}CH$), 7.38 (m, 3 H), 7.57 (m, 2 H). δ_C ($CDCl_3$, 25 °C) 9.8 (CH_2Si), 24.8 (CH_2), 28.6 (CH_2), 28.9 (CH_2), 32.5 (CH_2), 33.6 ($CH_2CH{=}CH_2$), 114.0 ($CH_2{=}CH$), 127.7, 129.3, 132.6, 135.0 (C_6H_5), 138.9 ($CH_2{=}CH$). EI MS *m*/*z* (%): 218 (15%, M^+), 217 (22%, $C_{14}H_{21}Si^+$), 189 (34%, $C_{12}H_{17}Si^+$), 140 (21%, $C_8H_{17}Si^+$), 107 (100%, $C_6H_7Si^+$). Anal. Calc. for $C_{14}H_{22}Si$: C, 77.05; H, 10.08. Found: C, 77.48; H, 10.18. The second product (230 °C/10^{-2} mmHg) was 1,8-bis(phenylsilyl)octane, colorless oil, 60 mg (27%).

Silanolytic oligomerization of 1,7-octadiene

To a solution of 25.5 mg (50 μmol) of **1** in 0.5 mL of hexane were added sequentially $PhSiH_3$ (108 mg, 1.00 mmol) and 1,7-octadiene (110 mg, 1.00 mmol), and the reaction mixture was stirred at ambient temperature for 72 h. The resulting viscous solution was quenched with 0.5 mL of methanol, diluted with hexane, and filtered. The solvent was removed *in vacuo* to give a highly viscous pale-yellow oil. The oil was purified by flash chromatography (silica gel, eluent pentane) and heated in dynamic vacuum (190 °C/10^{-2} mmHg) to remove all volatiles. 190 mg (87%) of the oligomer was obtained as a pale-yellow oil (Found: C, 77.02; H, 10.11. $C_{14}H_{22}Si$ requires C, 77.05; H, 10.07); δ_H ($CDCl_3$, 25 °C) 0.84 (m, 4 H, CH_2Si), 1.22–1.44 (m, 12 H, CH_2), 4.24 (qnt, $^3J_{HH}$ = 3.6 Hz, $^1J_{SiH}$ = 92.4 Hz) and 4.28 (t, $^3J_{HH}$ = 3.6 Hz) (together 1 H (ratio 4.7 : 1)), 7.34 (m, 3 H), 7.55 (m, 2 H). δ_C ($CDCl_3$, 25 °C) 11.5 (CH_2Si), 24.3 (CH_2), 28.9 (CH_2), 32.7 (CH_2), 127.6, 129.2, 134.4, 135.9 (ring C).

Hydrosilylation of 4-vinyl-1-cyclohexene

To a solution of **1** (25.5 mg, 50 μmol) in 0.5 mL of hexane were added sequentially $PhSiH_3$ (108 mg, 1.00 mmol) and 4-vinyl-1-cyclohexene (108 mg, 1.00 mmol). The reaction mixture was stirred at ambient temperature. Small aliquots were taken for GC analysis and the reaction was found to be complete after 18 h. The reaction mixture was quenched with 0.5 mL of methanol, diluted with hexane, and filtered. The volatiles were removed *in vacuo* to give a pale-yellow oil. Purification by flash chromatography (silica gel, eluent pentane) and Kugelrohr distillation *in vacuo* (160 °C/10^{-2} mmHg) gave 200 mg (93%) of 4-{2-(phenylsilyl)ethyl}cyclohex-1-ene[4a] as a colorless oil (Found: C, 77.32; H, 9.04. $C_{14}H_{20}Si$ requires C, 77.76; H, 9.24); δ_H ($CDCl_3$, 25 °C) 0.97 (m, 2 H, CH_2Si), 1.17 (m, 1 H), 1.41 (m, 2 H), 1.57 (m, 1 H), 1.62 (m, 1 H), 1.72 (m, 1 H), 2.01 (m, 2 H), 2.12 (m, 1 H), 4.25 (t, $^3J_{HH}$ = 3.6 Hz, $^1J_{SiH}$ = 96 Hz, 2 H, SiH_2Ph), 5.62 (d, $^3J_{HH}$ = 10.4 Hz, 1 H, HC=CH), 5.64 (d, $^3J_{HH}$ = 10.4 Hz, 1 H, HC=CH), 7.35 (m, 3 H, C_6H_5), 7.55 (m, 2 H, C_6H_5). δ_C ($CDCl_3$, 25 °C) 7.4 (CH_2Si), 25.5 (CH_2CH_2Si), 28.7 (CH_2), 31.7 (CH_2), 32.1 (CH_2), 36.4 (CH), 126.7 (HC=), 127.3 (HC=), 128.2, 129.7, 132.9, 135.4 (C_6H_5). EI MS *m*/*z* (%): 216 (15%, M^+), 215 (66%, $C_{14}H_{19}Si^+$), 137 (29%, $C_8H_{13}Si^+$), 107 (100%, $PhSiH_2^+$).

[Y(η⁵:η¹-$C_5Me_4CH_2SiMe_2NCMe_3$){$CH_2CH(CH_2)_4$}(THF)] (3)

To a suspension of **2** (114 mg, 13 μmol) in hexane (5 mL), was added at 0 °C a solution of 1,5-hexadiene (22 mg, 26 μmol) in hexane (1 mL). The reaction mixture was stirred for 30 min, concentrated, and cooled to −30 °C to give 97 mg (74%) of colorless crystals (Found: C, 61.06; H, 9.96; N, 3.22. $C_{26}H_{48}NOSiY$ requires C, 61.56; H, 9.24; N 2.75); δ_H (C_7D_8, 25 °C) −0.11 (dd, $^2J_{YH}$ = 4 Hz, $^3J_{HH}$ = 7 Hz, 2 H, YCH_2), 0.44 (s, 6 H, $SiCH_3$), 1.22 (m, 4 H, β-CH_2, THF), 1.24 (m, 2 H, C_5H_9, α-CH_2), 1.40 (s, 9 H, $C(CH_3)_3$), 1.71, 1.87 (m, 2 H, C_5H_9, β-CH_2), 1.97 (m, 2 H, C_5H_9, α-CH_2), 2.02, 2.08 (s, 2 × 6 H, ring CH_3), 2.15 (s, 2 H, CH_2Si), 2.31 (m, 1 H, YCH_2CH), 3.36 (m, 4 H, α-CH_2, THF). δ_C (C_7D_8, 25 °C) 7.8 ($NSiCH_3$), 10.7, 13.8 (ring CH_3), 17.4 (CH_2Si), 22.5 (β-CH_2, THF), 24.2, 25.2 (C_5H_9, β-CH_2), 31.4 (C_5H_9, α-CH_2), 34.6 ($C(CH_3)_3$), 40.1 (C_5H_9, α-CH_2), 43.1 (CH_2CH), 47.9 (d, $^1J_{YC}$ = 52.5 Hz, YCH_2), 53.0 ($C(CH_3)_3$), 69.7 (α-CH_2, THF), 114.2, 114.9, 122.6 (ring C), 136.9 (ring C attached to CH_2).

[Y(η⁵:η¹-$C_5Me_4CH_2SiMe_2NCMe_3$){$CH(CH_2Ph)Ph$}(THF)] (4)

To a solution of **2** (126 mg, 148 μmol) in benzene (5 mL) was added at room temperature, a solution of *trans*-stilbene (53 mg, 295 μmol) in benzene (1 mL). The reaction mixture was stirred for 6 days at room temperature. The solvent was evaporated *in vacuo* and the resulting pale yellow solid residue was dissolved in hexane (10 mL). The solution was concentrated (~5 mL) and cooled to −30 °C to give 128 mg (72%) of pale yellow crystals (Found: C, 67.64; H, 8.40; N, 2.70. $C_{34}H_{50}NOSiY$ requires C, 67.46; H, 8.25; N 2.31); δ_H (C_7D_8, 25 °C) 0.43, 0.59 (s, 2 × 3 H, $SiCH_3$), 0.90 (br s, 4 H, β-CH_2, THF), 1.30 (s, 9 H, $C(CH_3)_3$), 1.91, 1.97, 2.16, 2.27 (s, 4 × 3 H, ring CH_3), 2.14, 2.22 (s, 2 × 1 H, CH_2Si), 2.75 (m, 1 H, $YCHPhCH_2Ph$), 3.17 (br s, 4 H, α-CH_2, THF), 3.45 (dd, 1 H, YCHPhCHHPh), 3.70 (dd, 1 H, YCHPhCHHPh), 6.40 (br t, 1 H, $^3J_{HH}$ = 7.2 Hz, C_6H_5), 6.64 (br d, 2 H, $^3J_{HH}$ = 7.2 Hz, C_6H_5), 6.97 (br t, 2 H, $^3J_{HH}$ = 7.2 Hz, C_6H_5), 7.19–7.36 (m, 3 H, C_6H_5), 7.54 (br d, 2 H, $^3J_{HH}$ = 7.2 Hz, C_6H_5). δ_C (C_7D_8, 25 °C)

8.2, 8.6 (NSiCH_3), 11.0, 11.4, 11.9, 13.3 (ring CH_3), 17.9 (CH_2Si), 24.7 (β-CH_2, THF), 34.0 (C(CH_3)$_3$), 38.2 (CH_2Ph), 53.7 (C(CH_3)$_3$), 58.0 (d, $^1J_{YC}$ = 25.0 Hz, YCH), 71.7 (α-CH_2, THF), 114.6 (C_6H_5), 116.1, 116.3, 117.2 (C_5Me_4 ring C), 119.0, 124.8, 125.3, 126.1, 131.0, (C_6H_5), 137.8 (C_5Me_4 ring C attached to CH_2), 146.7, 152.7 (*ipso*-C, C_6H_5).

[Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(C≡CCMe_3)]$_2$ (5)

To a solution of **2** (300 mg, 352 μmol) in benzene (5 mL) was added at room temperature a solution of *tert*-butylacetylene (58 mg, 706 μmol) in benzene (1 mL). Evolution of a hydrogen gas was observed. The reaction mixture was stirred for 1 h, benzene was evaporated *in vacuo*, and the resulting off-white solid was recrystallized from hexane at 0 °C; colorless microcrystals, yield 281 mg (92%) (Found: C, 60.14; H, 8.29. $C_{22}H_{38}NSiY$ requires C, 60.53; H, 8.77%); δ_H (C_6D_6, 25 °C) 0.55 (s, 6 H, $SiMe_2$), 1.12 (s, 9 H, C(CH_3)$_3$), 1.62 (s, 9 H, C(CH_3)$_3$), 2.13, 2.21 (s, 2 × 6 H, ring CH_3), 2.23 (s, 2 H, CH_2Si). δ_C (C_6D_6, 25 °C) 8.7 (NSiCH_3), 12.2, 13.2 (ring CH_3), 18.2 (CH_2Si), 28.7 (C≡CC(CH_3)$_3$), 31.2 (C(CH_3)$_3$), 37.7 (C(CH_3)$_3$), 54.5 (NC(CH_3)$_3$), 116.7, 118.2, 129.3 (ring C), 126.7 (t, $^1J_{YC}$ = 25.5 Hz, YC≡C), 127.0 (s, YC≡C), 136.8 (ring C attached to CH_2).

[Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(μ-OCH_2CH_2OMe-κO)]$_2$ (6)

To a solution of **2** (300 mg, 0.35 mmol) in 5 mL of toluene was added at room temperature a solution of DME (63 mg, 0.70 mmol) in 0.5 mL of toluene. Over a period of 72 h, a colorless precipitate formed and was isolated from the mother-liquor. Recrystallization from THF gave colorless crystals as a THF solvate; yield 0.26 g (83%) (Found: C, 53.53; H, 8.45; N, 3.09. $C_{40}H_{76}N_2O_{4.5}Si_2Y_2$ requires C, 53.95; H, 8.53; N 3.14%); δ_H (pyridine-d_5, 55 °C) 0.48, 0.52 (s, 2 × 3 H, $SiCH_3$), 1.44 (s, 9 H, C(CH_3)$_3$), 1.67 (m, 2 H, β-CH_2, free THF), 2.02 (br s, 7 H, $OCH_2CH_2OCH_3$), 2.10, 2.13 (s, 2 × 6 H, ring CH_3), 2.16 (s, 2 H, CH_2Si), 3.69 (m, 2 H, α-CH_2, free THF). ^{13}C NMR spectra could not be obtained due to low solubility.

Crystal structure analysis of 3, 4 and 6

Relevant crystallographic data for **3, 4** and **6** are summarized in Table 1. The data of **3** and **6** were collected with a Bruker AXS diffractometer, reduced and corrected for absorption with the program system SMART.[13] The data of **4** were collected with an Enraf Nonius CAD4 diffractometer and the program system WinGX was used for the data reduction and absorption correction using psi-scans.[14] The structures were solved by Patterson and difference Fourier syntheses (SHELXS-86).[15] Complexes **4** and **6** crystallize with two independent molecules in the unit cell. The lattice of **6** contains disordered thf. All hydrogen atoms were included into calculated positions with torsional refinement of the methyl groups. Only the hydrogen atoms attached to C17 and C51, which belong to the two crystallographically independent molecules of **4**, were refined in their position. All independent reflections were used in the refinement by full-matrix least-squares against all F_o^2 data (SHELXL-97).[16] The non-hydrogen atoms were refined with anisotropic thermal parameters. In the crystal structure of **3**, split positions for the atoms C18 and C20 of the cyclopentylmethyl ligand where introduced which were refined with isotropic thermal parameters. For the graphical representation, the program ORTEP-III was used as implemented in the program system WINGX.

CCDC reference numbers 236764, 236765 and 236766 for **3, 4** and **6**, respectively.

See http://www.rsc.org/suppdata/dt/b4/b406071g/ for crystallographic data in CIF or other electronic format.

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References

1 (*a*) G. A. Molander and J. A. C. Romero, *Chem. Rev.*, 2002, **102**, 2161; (*b*) H. Yasuda, *J. Organomet. Chem.*, 2002, **647**, 128; (*c*) P. L. Watson and G. Parshall, *Acc. Chem. Res.*, 1985, **18**, 51; (*d*) C. J. Schaverien, *Adv. Organomet. Chem.*, 1994, **36**, 283; (*e*) F. T. Edelmann, in *Comprehensive Organometallic Chemistry* II, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, UK, 1995, vol. 4, p. 11; (*f*) P. J. Chirik and J. E. Bercaw, *Metallocenes*, ed. R. L. Halterman and A. Togni, Wiley-VCH, Weinheim, Germany, 1998, p. 111.

2 (*a*) P. J. Shapiro, E. E. Bunel, W. P. Schaefer and J. E. Bercaw, *Organometallics*, 1990, **9**, 867; (*b*) W. E. Piers, P. J. Shapiro, E. E. Bunel and J. E. Bercaw, *Synlett*, 1990, 74; (*c*) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1994, **116**, 4623; (*d*) For recent reviews, see: S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953; (*e*) J. Okuda, *Dalton Trans.*, 2003, 2367; (*f*) Z. Hou, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 2253.

3 (*a*) A. A. Trifonov, T. P. Spaniol and J. Okuda, *Organometallics*, 2001, **20**, 4869; (*b*) O. Tardif, M. Nishiura and Z. Hou, *Tetrahedron*, 2003, **59**, 10525.

4 (*a*) G. A. Molander and P. J. Nichols, *J. Org. Chem.*, 1992, **57**, 6347; (*b*) G. A. Molander and P. J. Nichols, *J. Am. Chem. Soc.*, 1995, **117**, 4415; P. F. Fu, L. Brard, Y. Li; (*c*) S. Onozawa, T. Sakakura and M. Tanaka, *Tetrahedron Lett.*, 1994, **35**, 8177; (*d*) T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 157.

5 P. Voth, T. P. Spaniol and J. Okuda, *Organometallics*, 2003, **22**, 3921.

6 For recent work on the effect of various bridges in group 4 "geometrically constrained" catalysts, see: K. Kunz, G. Erker, S. Doering, S. Bredeau, G. Kehr and R. Froehlich, *Organometallics*, 2002, **21**, 1031.

7 (*a*) K. C. Hultzsch, T. P. Spaniol and J. Okuda, *Angew. Chem., Int. Ed.*, 1999, **38**, 227; (*b*) K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol and J. Okuda, *Organometallics*, 2000, **19**, 228; (*c*) S. Arndt, K. C. Hultzsch, P. Voth, T. P. Spaniol and J. Okuda, *Organometallics*, 2000, **19**, 4690; (*d*) P. Voth, S. Arndt, T. P. Spaniol, J. Okuda, L. J. Ackerman and M. L. H. Green, *Organometallics*, 2003, **22**, 65.

8 X. Zhou and M. Zhu, *J. Organomet. Chem.*, 2002, **647**, 28.

9 A. Mandel and J. Magull, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1913.

10 (*a*) W. J. Evans and A. L. Wayda, *J. Organomet. Chem.*, 1980, **202**, C6; (*b*) T. J. Marks and R. D. Ernst, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982, ch. 21; (*c*) K. H. Den Haan, Y. Wielstra and J. H. Teuben, *Organometallics*, 1987, **6**, 2053; (*d*) W. E. Evans, R. A. Keyer and J. W. Ziller, *Organometallics*, 1993, **12**, 2618; (*e*) C. M. Forsyth, S. P. Nolan, S. L. Stern and T. J. Marks, *Organometallics*, 1993, **12**, 3618; (*f*) H. J. Heeres, J. Nijhoff and J. H. Teuben, *Organometallics*, 1993, **12**, 2609; (g) T. Dubé, J. Guan, S. Gambarotta and G. P. A. Yap, *Chem. Eur. J.*, 2001, **7**, 374; (*h*) R. Duchateau, C. T. van Wee and J. H. Teuben, *Organometallics*, 1996, **15**, 2291; (*i*) R. Duchateau, C. T. van Wee, A. Meetsma and J. H. Teuben, *J. Am. Chem. Soc.*, 1993, **115**, 4931; (*j*) M. Nishiura, Z. Hou, Y. Wakatsuki, T. Yamaki and T. Miyamoto, *J. Am. Chem. Soc.*, 2003, **125**, 1184.

11 M. V. Bhatt and S. U. Kulkarni, *Synthesis*, 1983, 249.

12 W. J. Evans, R. Dominguez and T. P. Hanusa, *Organometallics*, 1986, **5**, 1291.

13 Siemens, ASTRO, SAINT and SADABS: Data Collection and Processing Software for the SMART System, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1996.

14 L. J. Farrugia, WinGX—Version 1.64.02, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-crystal X-Ray Diffraction Data, *J. Appl. Crystallogr.*, 1999, **32**, 837.

15 G. M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, University of Göttingen: Göttingen, Germany, 1986.

16 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen: Göttingen, Germany, 1997.