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Journal of Organometallic Chemistry 692 (2007) 4690–4701
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

(+)-Neomenthyl- and (−)-phenylmenthyl-substituted cyclopentadienyl and indenyl yttrocenes as catalysts in asymmetric hydroamination/cyclization of aminoalkenes (AHA)

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Received 31 March 2007; received in revised form 4 May 2007; accepted 4 May 2007
Available online 22 May 2007

Dedicated to Gerhard Erker on the occasion of his 61st birthday.

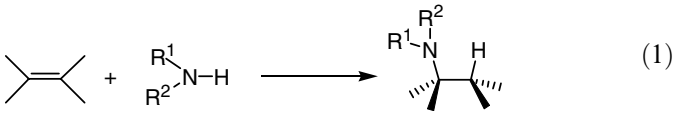
Abstract

The chiral, terpenoid-substituted yttrocene [(η^5-neomenthylCp)$_2$Y{*o*-$C_6H_4CH_2NMe_2$}] (**1**) can be prepared via facile arene elimination starting from [Y(*o*-$C_6H_4CH_2NMe_2)_3$]. Compound **1** retains a C_1-symmetric structure in solution on the NMR time scale, due to tight binding of the amine donor. The (−)-phenylmenthyl-substituted complexes [(η^5-(−)-phenylmenthylCp)$_2$Y(μ-Cl)$_2$Li(OEt_2)$_2$] (**5**) and [(η^5-(−)-phenylmenthylCp)$_2$YN($SiMe_3$)$_2$] (**6**) were prepared via salt metathesis. Reaction of YCl_3 with the planar chiral (1-neomenthylindenyl)lithium predominantly produced a single, C_2-symmetric, racemic-like diastereomer. The X-ray crystal structure analysis confirmed that [(η^5-(+)-NMInd)$_2$Y(μ-Cl)$_2$Li(Et_2O)$_2$] (**7**) represents the same p-*S*, p-*S* metallocene diastereomer and adopts a very similar conformation as observed by Erker in his zirconocene complexes. Complex **7** reacts with LiN($SiMe_3$)$_2$ to form [(η^5-(+)-NMInd)$_2$Y-N ($SiMe_3$)$_2$] (**8**) with retention of configuration. Complexes **1**, **6** and **8** showed moderate to good catalytic activity in asymmetric hydroamination/cyclizations of aminoalkenes, but enantioselectivities were limited to a maximum of 38% ee for the sterically most hindered catalyst **8**. The indenyl complex **8** is prone to protolytic loss of an indenyl ligand at low (≤0.5%) catalyst loading, if sterically undemanding aminoalkene substrates are applied.

Keywords: Asymmetric catalysis; Hydroamination; Yttrium; Metallocene complexes

1. Introduction

The hydroamination is a highly atom economical process in which an amine N–H bond is added to an unsaturated carbon–carbon bond (Eqs. (1) and (2)). This reaction is of great potential interest for the waste-free synthesis of basic and fine chemicals, pharmaceuticals and other industrially relevant building blocks starting from inexpensive precursors [1].



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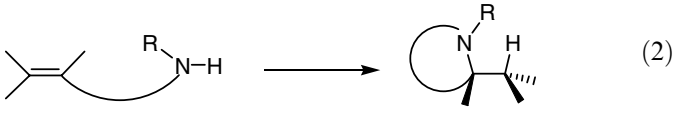

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Intensive research efforts from a growing number of research groups has led to the development of a large number of catalytic systems based on alkali or alkaline earth metals [1b,1e,1f,2], early (groups 3–5, as well as lanthanides and actinides) [1h,1i,1j,1k,1m] and late (groups 8–10) [1g,1l] transition metals. Many catalyst systems are limited

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doi:10.1016/j.jorganchem.2007.05.010

in their scope and reactivity, with rare earth metal based catalysts [3], pioneered by Marks and coworkers [1k,4], being still among the most reactive and versatile systems.

The generation of new stereogenic centers during the hydroamination process is an attractive application of this reaction and has found increased interest in recent years [5], but the development of chiral catalysts for the asymmetric hydroamination of alkenes (AHA) has remained challenging.

Marks and coworkers reported the first asymmetric hydroamination catalysts based on chiral rare earth metal lanthanocenes in 1992 (Fig. 1) [6]. Unfortunately, these C_1-symmetric chiral *ansa*-lanthanocenes underwent facile epimerization under the conditions of catalytic hydroamination via reversible protolytic cleavage of the metal cyclopentadienyl bond (Scheme 1) [6,7], limiting the utility of these catalyst systems in AHA.

Because of these limitations of chiral lanthanocene hydroamination catalysts, we [8] and others [9] have set out to develop efficient and configurationally stable catalysts for AHA based on non-cyclopentadienyl ligand sets. However, with the exception of binaphtholate rare earth metal based catalysts [8c,8d], these new non-metallocene type catalyst systems have remained inferior in catalytic activity in comparison to lanthanocene based catalysts. Therefore, we decided to investigate a number of C_2-symmetric chiral lanthanocene complexes with (+)-neomenthyl- or (−)-phenylmenthylcyclopentadienyl ligands [10–12]. Because these ligands are not planar chiral, the problem of diastereomeric lanthanocenes species can be avoided. As an alternative we sought to investigate sterically more encumbered (+)-neomenthylindenyl ligands [11,13,14], which should favor formation of a single diastereomer.

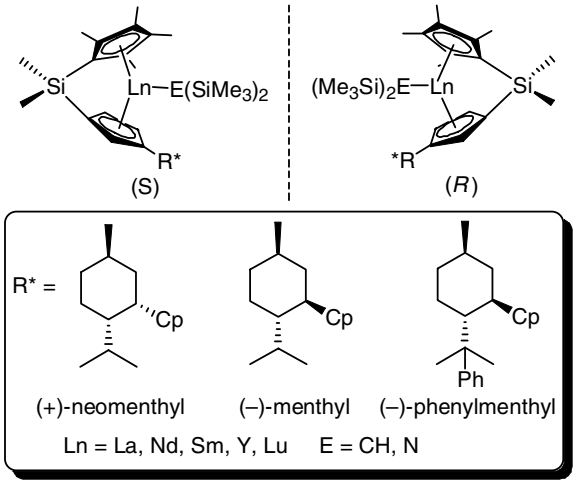
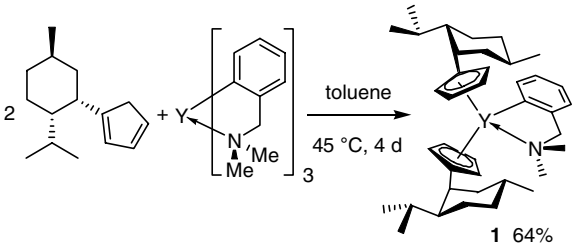


Fig. 1. C_1-symmetric chiral lanthanocene precatalysts for asymmetric hydroamination [6,7a].

2. Results and discussion

2.1. Synthesis of neomenthyl- and phenylmenthylcyclopentadienyl yttrium complexes

Lanthanocene complexes have been traditionally synthesized via salt metathesis [7,12,15], while amine or alkane elimination methodology [16] often helps to avoid the problem of *ate* complex formation concomitant with alkali metal salt incorporation. We therefore initially attempted to prepare neomenthyl-substituted yttrocene complexes via amine elimination reaction of (+)-neomenthylcyclopentadiene with either $[Y\{N(SiMe_3)_2\}_3]$ or $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$, however, under various reaction conditions we observed the formation of inseparable mixtures of the mono-, bis- and tris(cyclopentadienyl) complexes [17]. The readily available trisaryl complex $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$ [18] has been utilized in our laboratory as an alternative and convenient starting material for rare earth metal complex synthesis [8c,8d,19]. Indeed, arene elimination reaction of $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$ with 2.2 equiv. of (+)-neomenthylcyclopentadiene for 4 days at 45 °C led to the clean formation of the chiral yttrocene aryl complex **1** in 64% crystallized yield (Eq. (3)). The complexation of the cyclopentadienyl ligand proceeded stepwise and a mono(cyclopentadienyl) intermediate was observed spectroscopically.



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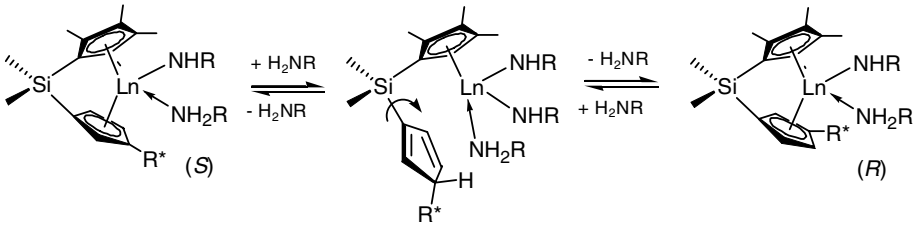


Scheme 1.

In contrast to previously characterized achiral yttrocenes of the type $[(C_5R_5)_2Y(o\text{-}C_6H_4CH_2NMe_2)]$ [20], complex **1** has a C_1-symmetric structure in solution with a tightly bound amine donor on the NMR times scale [21], as indicated by eight separate signals for the two diastereotopic cyclopentadienyl rings in the ^1H NMR spectrum. The signals for the benzylic methylene protons gave rise to a set of two doublets at 3.61 and 3.08 ppm with a geminal coupling constant $^2J_{H,H}$ of 13.4 Hz. The resonances for the *N*-methyl groups are shifted to higher field in comparison to $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$ (2.15 ppm [18]) and appear at 1.83 and 1.80 ppm. The $^{13}C\{^1H\}$ NMR spectrum is also in agreement with the C_1-symmetric structure, exhibiting 10 separate signals for the two non-equivalent cyclopentadienyl ligands. The *ipso*-carbon of the aryl ligand resonates at 184.7 ppm with a coupling constant $^1J_{Y,C}$ of 54.2 Hz typical for yttrium aryl complexes [8c,8d,18–21].

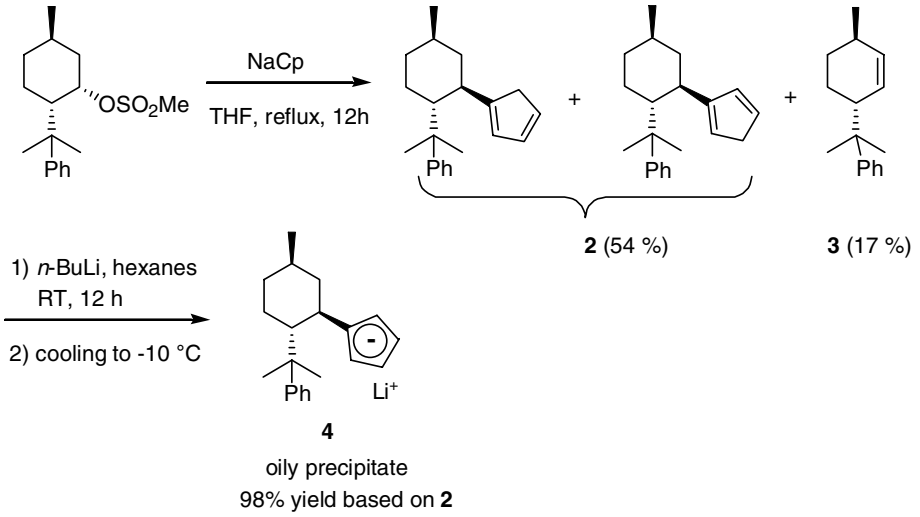
Complexes based on the sterically slightly more demanding (−)-phenylmenthyl-substituted cyclopentadienyl ligand **2** can be expected to possess improved stereodifferentiating ability in comparison to (+)-neomenthyl- or (−)-menthyl-derivatives. Complex **2** can be obtained in five steps starting from (*R*)-pulegone as a mixture of double bond isomers [22]. Unfortunately, **2** was contaminated with a significant amount of the elimination product **3**, formed in the nucleophilic substitution of cyclopentadienyl sodium and phenylmenthyl methansulfonate (Scheme 2). All attempts to separate **2** and **3** failed. Although reaction of 2 equiv. of **2** with $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$ cleanly formed the corresponding yttrocene aryl complex analogous to **1**, we were unable to separate this complex from the elimination by-product **3** via crystallization thus far. However, lithiation of **2** with *n*-BuLi in hexanes produced a biphasic system with an oily precipitate of the cyclopentadienyl lithium salt **4**. Careful decantation of the supernatant solution containing the olefinic impurity at −10 °C, followed by washing with cold pentane, produced the spectroscopically pure lithium salt **4**.

Salt-metathesis reaction of **4** with YCl_3 in THF at room temperature afforded the dichloro complex **5** after Et_2O exchange [7a] in moderate yield (Scheme 3). Note, in contrast to the previously isolated chloro bridged dimeric $[(\eta^5\text{-neomenthylCp})_2Y(\mu\text{-Cl})]_2$ [12], complex **5** forms the monomeric lithium chloride adduct as a result of the increased steric congestion around the metal center in the sterically more demanding phenylmenthyl-substituted yttrocene **5**.

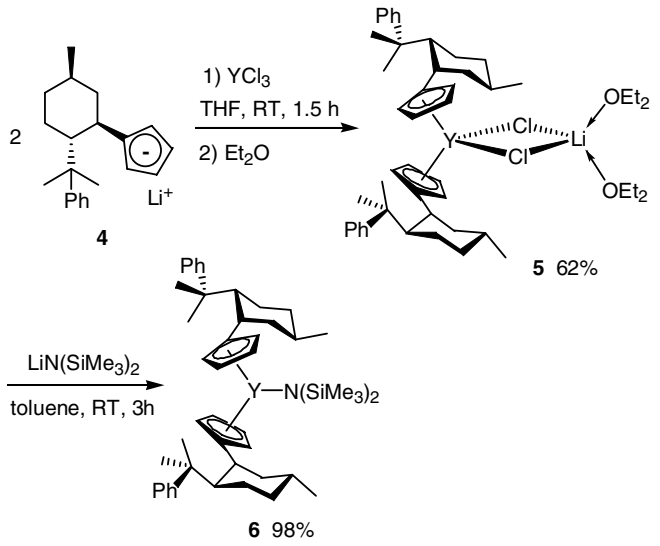
Reaction of **5** in toluene with $LiN(SiMe_3)_2$ furnished the corresponding bis(trimethylsilyl)amido complex **6** in high yield. The NMR spectra of **6** show the expected C_2-symmetry of the complex, as indicated by a single set of signals for the two cyclopentadienyl ligands in the ^1H and ^{13}C NMR spectra. The phenylmenthyl methine ring proton gave rise to a triplet of doublets ($^3J_{H,H} = 10.0$ Hz, $^3J_{H,H} = 2.5$ Hz), in agreement with the expected presence of two large vicinal axial–axial and a small vicinal axial–equatorial coupling in the phenylmenthyl moiety. The methyl resonance of the trimethylsilyl groups appeared as a singlet at 0.21 ppm in the ^1H NMR and 3.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

2.2. Synthesis of neomenthylindenyl yttrium complexes

In order to increase the steric congestion around the metal center further, we became interested in preparing neomenthylindenyl yttrocenes. Initial attempts to apply (+)-3-neomenthylindene in amine or arene elimination reactions were unsuccessful, most likely due to the lower acidity of indene (pK_a(indene) ~ 20 [23]) compared to cyclopentadiene (pK_a(cyclopentadiene) ~ 16 [24]) and steric hindrance of the ligand. However, reaction of (1-neomenthylindenyl)lithium [13a] with YCl_3 in THF successfully generated the desired bis(indenyl) complex **7** in high crystallized yield after Et_2O exchange (Scheme 4). Similar to observations made by Erker in the synthesis of the corresponding neomenthylindenyl zirconocenes [13], complex-



Scheme 2.



Scheme 3.

ation of the neomenthylindenyl ligand produced predominantly a single, *racemic*-like product, one of the three conceivable diastereomers (Fig. 2). An NMR scale reaction in THF-d_8 also showed **7** as the major product of the complexation reaction within minutes of mixing of the reagents and no significant change was observed in the NMR spectra after 15 h at 25 °C. Furthermore, isolated **7** did not show any signs of epimerization in non-polar solvents, such as C_6D_6.

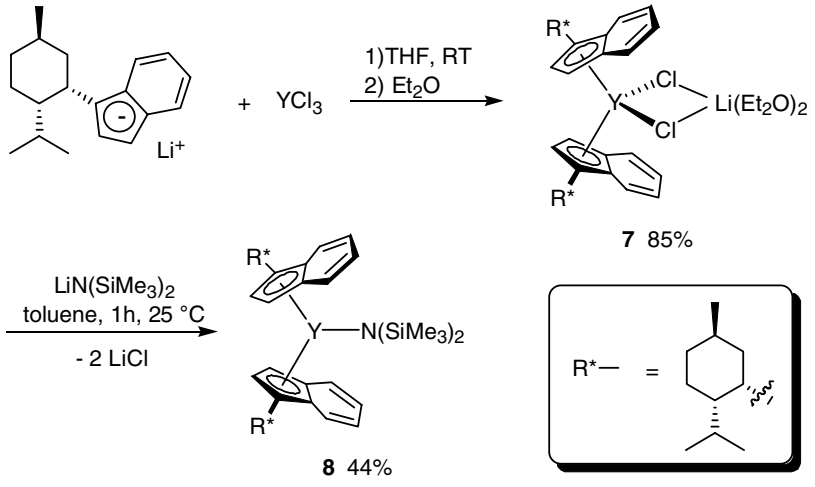
Similar to the C_2-symmetric phenylmenthylcyclopentadienyl complexes **5** and **6**, the NMR spectra of **7** are in agreement with a C_2-symmetric structure for a *racemic*-like form, which was later confirmed by X-ray crystallographic analysis (*vide infra*). ^{1}H and ^{13}C NMR spectra indicated a single set of signals for both neomenthylindenyl moieties.

Reaction of **7** with $LiN(SiMe_3)_2$ in toluene produced a single diastereomer of the bis(neomenthylindenyl)yttrium amido complex **8** within 1 h at 25 °C (Scheme 4). Crystallization from pentane furnished complex **8** in 44% crystallized yield.

The NMR spectra of **8** indicate that the C_2-symmetric structure of complex **7** has been retained. ^{1}H and ^{13}C NMR spectra show only a single set of signals for both neomenthylindenyl moieties and the bis(trimethylsilyl)amido methyl groups are characterized by one singlet at −0.05 ppm in the ^{1}H NMR spectrum and one signal at 3.6 ppm in the ^{13}C {^{1}H} NMR spectrum.

2.3. Molecular structure of the bis(neomenthylindenyl) yttrium complex 7

Clear, slightly yellow crystals of **7** suitable for X-ray diffraction analysis were obtained by crystallization from Et_2O at ambient temperature. The ORTEP diagram of **7**



Scheme 4.

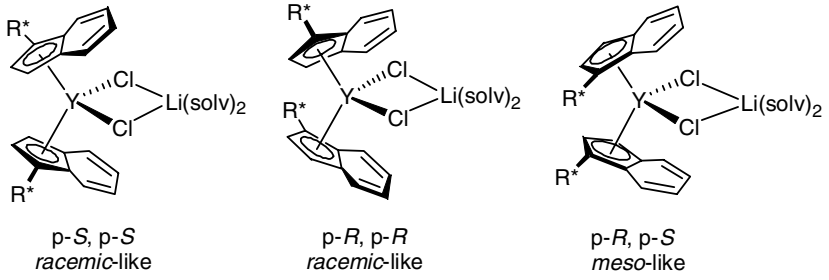


Fig. 2. Three possible diastereomeric bis(NMInd)yttrium complexes ($R*$ = (+)-neomenthyl).

is depicted in Fig. 3, selected bond lengths and angles are given in Table 1.

In the crystal, the structure of complex **7** resembles strongly that of Erker's *racemic*-like C_2-symmetric neomenthylindenyl zirconocene [13] and represents the same p-*S*,p-*S* metallocene diastereomer. The neomenthyl substituents are oriented towards the lateral sector of the bent yttrocene unit in an almost ideally antiperiplanar arrangement. The annulated aromatic six membered rings of the indenyl ligand are oriented toward the open front side of the bent yttrocene with an almost perfect orientation of the C16–C17 and C36–C37 vectors above Cl1 and Cl2, respectively (Fig. 4). The sterically demanding indenyl moiety occupies an axial position in the neomenthyl six-membered ring, while the isopropyl and the methyl substituent are placed in equatorial positions.

Yttrium is coordinated in a pseudotetrahedral fashion by two chloro-ligands and two η^5-bound indenyl ligands. The Cl–Y–Cl angle is 85.09(3)°, which is in the typical range of 82–87° for eight-coordinate complexes of the type $[(C_5R_5)_2Ln(\mu\text{-}Z)_2M(solv)_2]$ [15,25]. The Cp_{Cent}–Y–Cp_{Cent} angle is unusually small (124.66(4)°) in comparison to related yttrium biscyclopentadienyl and bisindenyl derivatives, such as $[(2,4,7\text{-trimethylindenyl})_2Y(\mu\text{-}H)]_2$ (132.40(4)° and 131.87(4)°) [26a], $[Cp^*_2YN(SiMe_3)_2]$ (132.4(2)°) [26b], (*R*,*R*)-Li[Y(η^5:η^1-C_5H_3tBuSiMe$_2$NCH$_2$CH$_2$NMe$_2$)$_2$] (128.9(1)°) [7c] or $[(t\text{BuC}_5\text{H}_4)_2\text{Y}(\text{C}_4\text{H}_7\text{S}_2\text{-}1,3)]\cdot\text{LiCl}\cdot 2\text{THF}$ (126.5(8)°) [26c]. This angle is also significantly smaller than those found in $[((+)\text{-neomenthylCp})_2\text{Y}(\mu\text{-Cl})]_2$ (128.9° and 132.0°) [12], but is closer to angles typical for *ansa*-yttrocenes (122–125°) [7a,7d,16a], in order to minimize repulsive interactions between the bulky neomenthyl substituents and the indenyl moiety of the other ligand.

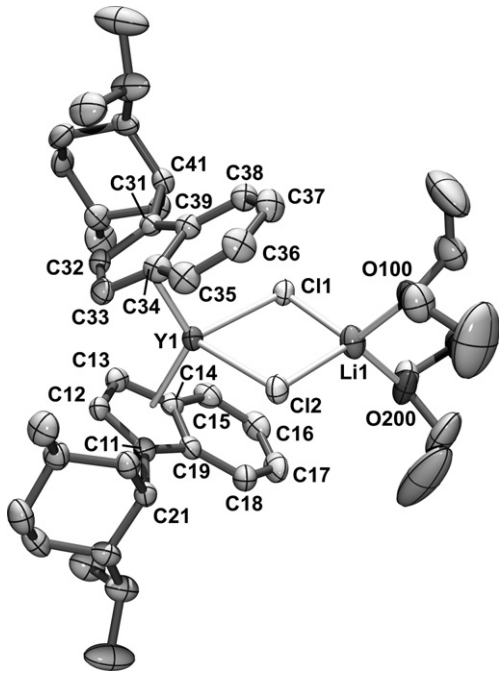


Fig. 3. ORTEP diagram of the molecular structure of **7**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms have been omitted for the sake of clarity.

Table 1
Selected bond lengths (Å), atomic distances (Å) and angles (°) for **7**

Y1–C11	2.672(4)	Li1–Cl1	2.350(8)
Y1–C12	2.639(4)	Li1–Cl2	2.393(8)
Y1–C13	2.633(4)	Li1–O100	1.947(8)
Y1–C14	2.695(4)	Li1–O200	1.945(9)
Y1–C19	2.712(4)	Cp_{cent}–Y1–Cp_{cent}	124.66(4)
Y1–C31	2.662(4)	Cl1–Y1–Cl2	85.09(3)
Y1–C32	2.639(4)	Y1–Cl1–Li1	89.61(19)
Y1–C33	2.626(4)	Y1–Cl2–Li1	88.71(19)
Y1–C34	2.689(4)	O100–Li1–O200	104.2(4)
Y1–C39	2.697(4)	Cl1–Li1–Cl2	96.5(3)
Y1···Cp_{cent}(1)	2.378(4)	Cl1–Li1–O100	122.1(4)
Y1···Cp_{cent}(2)	2.372(4)	Cl2–Li1–O200	123.6(4)
Y1–Cl1	2.6181(10)	Cl1–Li1–O200	106.3(3)
Y1–Cl2	2.6171(11)	Cl2–Li1–O100	105.7(3)
Y1···Li1	3.506(8)		

$Cp_{cent}(1)$ = C11–C12–C13–C14–C19; $Cp_{cent}(2)$ = C31–C32–C33–C34–C39.

The two chlorides and the η^5-indenyl subunits are not equivalent by crystallographic symmetry. The five yttrium-ring carbon bond lengths are not completely equidistant (see Table 1). The Y–C bonds between yttrium and the annulated ring carbon atoms C14/C19/C34/C39 (2.69–2.71 Å) are longer than the corresponding distances to the unsubstituted carbon atoms C12/C13/C32/C33 (2.63–2.64 Å), while the distances to C11 and C31 fall in between (~2.67 Å), indicating that the large terpenoid groups attached to C11 and C31 result in some steric constrains. Nevertheless, the distances of yttrium to the cyclopentadienyl ring carbons (2.62–2.71 Å) are within the normal range of Y–Cp distances [7c]. Also, the bonds of yttrium to the bridging chlorides (2.6171(11) and 2.6181(10) Å) are consistent with bond lengths found in heterobimetallic structures of the general type $[L_2Y(\mu\text{-Cl})_2Li(solv)_2]$ (2.62–2.70 Å) [15].

2.4. Hydroamination/cyclization using chiral yttrocenes

Complexes **1**, **6** and **8** were utilized in catalytic intramolecular hydroamination/cyclization reactions of nonactivated terminal aminoalkenes (Table 2). Addition of the aminoalkene substrates to complexes **1** and **6** resulted in immediate and irreversible liberation of benzylamine, respectively $HN(SiMe_3)_2$. In the case of the C_1-symmetric precatalyst **1** an increase in symmetry to C_2 in the resulting catalytic species was observed via NMR spectroscopy, as indicated by only one set of signals for both cyclopentadienyl ligands.

The reactivity of the substrates followed the trends predicted by the Thorpe–Ingold effect [27]. Among the substrates present in Table 2, the most reactive was 2-allyl-2-methyl-pent-4-enylamine (**9c**), followed by 2,2-dimethyl-pent-4-enylamine (**9b**), while the unsubstituted **9a** was cyclized only at elevated temperatures. Cyclization of **9b** with **1** proceeded at 25 °C ca. six times slower ($N_t = 3.3\ h^{-1}$) relative to $[Me_2Si(C_5Me_4)(neomenthylCp)YN(SiMe_3)_2]$

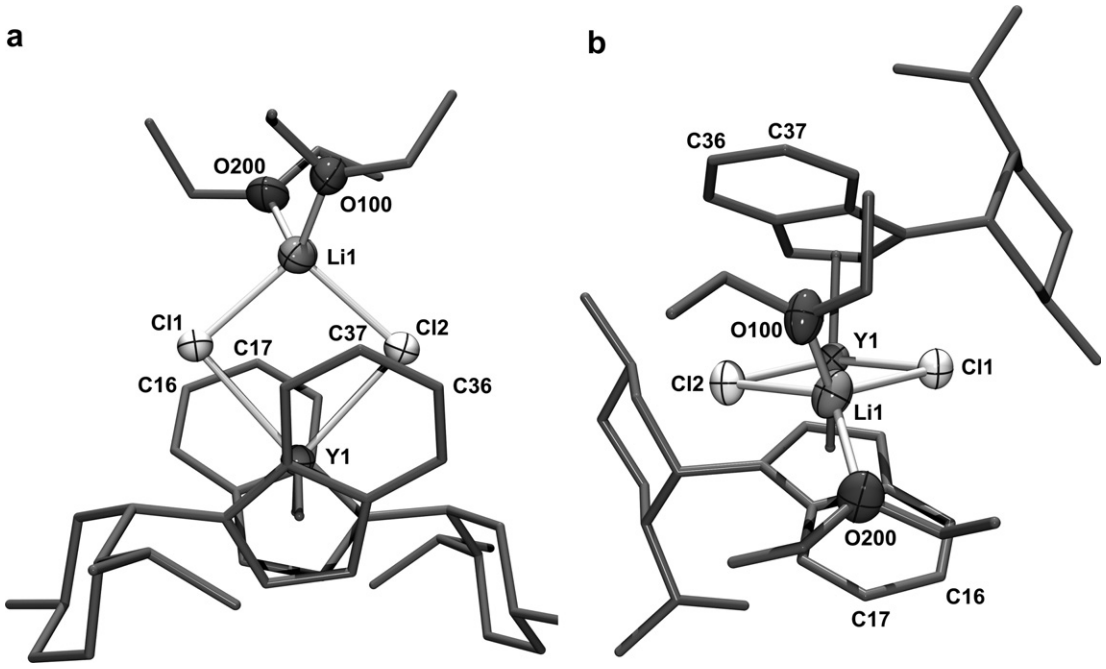


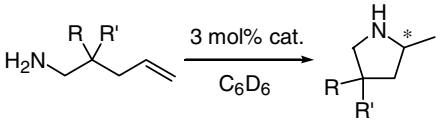
Fig. 4. Two views of the molecular geometry of the bis(NMInd)yttrium dichloride complex **7**. (a) Top view; (b) front view.

($N_t = 21\ h^{-1}$) [6b], due to the sterical more open coordination sphere around the metal in the *ansa*-lanthanocene. The same transformation using catalyst precursor **6** was sluggish at ambient temperature but an appreciable turnover frequency ($N_t = 48\ h^{-1}$) was observed at 60 °C.

The neomenthylindenyl complex **8** showed the highest catalytic activity in the cyclization of **9c** ($N_t = 225\ h^{-1}$), followed by the neomenthylcyclopentadienyl complex **1** ($N_t = 16\ h^{-1}$). Unfortunately, all catalyst displayed similar poor diastereoselectivities for this substrate as noted before [8,19].

Although the increased steric demand of the phenylmenthyl-substituent in **6** was slightly beneficial for catalyst selectivity in comparison to the neomenthyl-substituted

Table 2
Hydroamination reactions catalyzed by chiral yttrocenes **1**, **6**, and **8**[a]



9a R = R' = H
9b R = R' =Me
9c R = Me, R' = $CH_2CH{=}CH_2$

10a-c

Entry	Substrate	Cat.	T (°C)	t (h)	Conv. (%)	N_t (h^{-1})[b]	%ee (config.);[c] dr
1	**9a**	**1**[d]	65	65	96	0.4	22 (*R*)
2	**9a**	**6**	100	65	82	0.8	35 (*S*)
3	**9b**	**1**	25	12.7	96	3.8	21 (*R*)
4	**9b**	**6**	25	115	74	0.3	28 (*S*)
5	**9b**	**6**	60	1	97	48	26 (*S*)
6	**9b**	**8**	25	6.25	80	nd	11 (*S*)
7	**9c**	**1**	25	2.6	100	16	5/21; 1.36:1
8	**9c**	**6**	25	68	100	0.5	13/27; 1.18:1
9	**9c**	**8**[e]	25	0.5	96	225	38/25; 1.55:1
10	**9c**	**8**[f]	25	2.3	68	112	nd; 1.34:1

[a] Reaction conditions: 3 mol% cat., C_6D_6, Ar atm.
[b] N_t calculated from the linear part of the kinetic plot, generally at least one half-life.
[c] Enantiomeric excess determined by ^{19}F NMR spectroscopy of the Mosher amides of the corresponding pyrrolidine products.
[d] 4 mol% cat.
[e] 1.5 mol%.
[f] 0.5 mol% cat. nd = not determined.

complex **1**, it was detrimental for catalyst activity. The overall enantioselectivities are rather low (up to 22% ee for **1**, 35% ee for **6**, and 38% ee for **8**). Following the trends observed by Marks and coworkers for chiral *ansa*-lanthanocenes [6b], the (+)-neomenthyl-substituted complex **1** generally produced (*R*)-pyrrolidines, while the (−)-phenylmenthyl-substituted complex **6** generated (*S*)-pyrrolidines. However, the (+)-neomenthylindenyl complex **8** preferentially gave the (*S*)-pyrrolidine, indicating that the planar chirality of the indenyl moiety is overriding the directing effect of the chiral auxiliary.

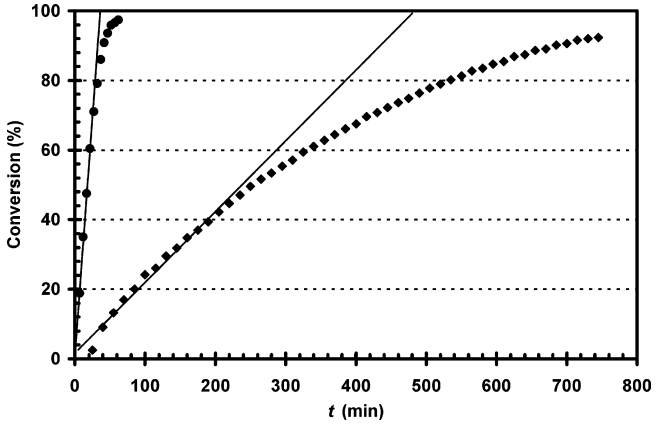


Fig. 5. Conversion of substrate as a function of time for the hydroamination/cyclization of 2,2-dimethyl-pent-4-enylamine (**9b**) using 3 mol% [(neomenthylCp)$_2$Y(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] (**1**) in C$_6$D$_6$ at 25 °C (◆) and [(phenylmenthylCp)$_2$YN(SiMe$_3$)$_2$] (**6**) in C$_6$D$_6$ at 60 °C (●). The line represents the least-squares fit to the initial linear part of the data.

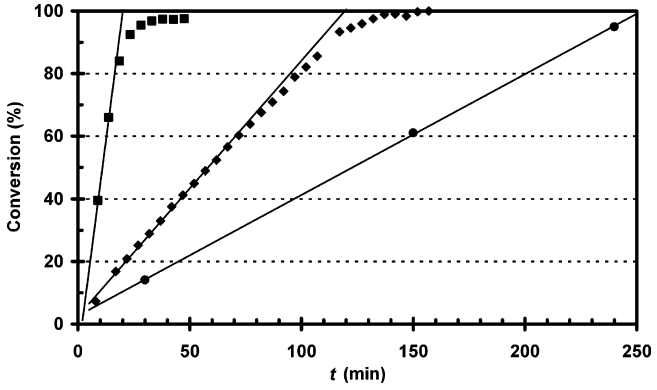


Fig. 6. Conversion of substrate as a function of time for the hydroamination/cyclization of 2-allyl-2-methyl-pent-4-enylamine (**9c**) in C$_6$D$_6$ at 25 °C using 3 mol% [(neomenthylCp)$_2$Y(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] (**1**) (◆), 3 mol% [(phenylmenthylCp)$_2$YN(SiMe$_3$)$_2$] (**6**) (•), and 1.5 mol% [(NMInd)$_2$YN(SiMe$_3$)$_2$] (**8**) (■). The line represents the least-squares fit to the initial linear part of the data.

Figs. 5 and 6 show representative kinetic data of the catalytic reactions mediated by **1**, **6**, and **8**.

The cyclizations of **9b** and **9c** showed initially zeroth-order dependence on substrate concentration. After approximately one half-life, the rate of cyclization of dimethyl-substituted aminoalkene **9b** deviated from the zeroth order linearity (Fig. 5), while for **9c** deviation became apparent only at high ($\geqslant$90%) conversion (Fig. 6). Non-zeroth-order kinetics in substrate concentration were observed previously for lanthanocene-catalyzed hydroamination/cyclization reactions [4,6], which has been attributed to competitive product inhibition; a reasonable explanation also in the present systems. The sterically more demanding pyrrolidine **10c** is supposed to bind weaker to the catalyst than pyrrolidines **10a** and **10b** with less bulky substituents. Therefore, the cyclization of **9c** showed kinetic plots very close to a zeroth-order rate dependence on substrate concentration. In addition, the phenyl groups in **6** increase the steric congestion around the metal in the catalytically active species in comparison to the neomenthyl Cp-based catalyst **1**. Hence, deviations from linearity are more pronounced for reactions mediated by **1**.

Although complex **8** was very active in the cyclization of **9c**, NMR spectroscopy indicated incomplete (44%) activation of the precatalyst based on free HN(SiMe$_3$)$_2$ relative to unreacted precatalyst **8**. Apparently, **8** is in equilibrium with the catalytically active species. Indeed, when the cyclization of **9c** was performed with lower catalyst loading (Table 2, entry 10), complete activation of **8** was observed, but presumably also partial protonation of the NMInd ligand. Thus, protonation of the indenyl ligand resulted in catalyst deactivation (*vide infra*) and the reaction showed significant deviation from zero-order kinetics.

The less reactive substrate **9a** could not be cyclized using **8**, even at elevated temperatures. Careful analysis of ^{1}H

Table 3
Ligand-exchange processes of **8** with *n*-PrNH$_2$

$$(NMInd)_2YN(SiMe_3)_2 \underset{+\ HN(SiMe_3)_2}{\overset{+\ n\text{-}PrNH_2}{\underset{-\ n\text{-}PrNH_2}{\overset{-\ HN(SiMe_3)_2}{\rightleftharpoons}}}} (NMInd)_2YNHPr \underset{+\ (NMInd)H}{\overset{+\ n\text{-}PrNH_2}{\underset{-\ n\text{-}PrNH_2}{\overset{-\ (NMInd)H}{\rightleftharpoons}}}} (NMInd)Y(NHPr)_2 \underset{+\ (NMInd)H}{\overset{+\ n\text{-}PrNH_2}{\underset{-\ n\text{-}PrNH_2}{\overset{-\ (NMInd)H}{\rightleftharpoons}}}} \text{"}Y(NHPr)_3\text{"}$$

Equiv. *n*-PrNH$_2$	Free HN(SiMe$_3$)$_2$[a] (%)	(NMInd)H (%)
1	25	20
2	58	44
5	100	72

[a] Relative to N(SiMe$_3$)$_2$ amido signal.

NMR spectra revealed the presence of free neomenthylindene, suggesting catalyst decomposition. The simple primary amine, *n*-$PrNH_2$ was used as a model system to verify the stability of complex **8** in the presence of a sterically undemanding, weak proton source (Table 3). Reaction of **8** with one equiv. of *n*-$PrNH_2$, resulted in simultaneous formation of $HN(SiMe_3)_2$ (25%) and (NMInd)H (20%). Subsequent addition of *n*-$PrNH_2$ led to further protonolysis of both ligands. Although the exchange with the silylamido group is more facile, significant proton transfer to the NMInd ligand was observed. Similar to diamidoamine catalyst systems [19], loss of the NMInd ligands results in catalytic inactivity of precatalyst **8** in the cyclization of **9a**.

3. Conclusion

Herein, we have reported the synthesis, characterization, and catalytic application of a variety of terpenoid-substituted yttrocene complexes. In particular, we could show that complexation of neomenthylindenyl to yttrium yields the same diastereomer as has been observed by Erker for the corresponding neomenthylindenyl zirconocene analogue. All complexes displayed good to moderate catalytic activity in the asymmetric hydroamination of aminoalkenes (AHA), though enantioselectivities have remained low (up to 38% ee). One significant limitation of chiral lanthanocene based hydroamination catalysts is the protolytic loss of a chiral spectator ligand, especially in the regime of low catalyst concentration ($\leqslant$0.5 mol%) in the presence of sterically undemanding primary aminoalkene substrates.

4. Experimental

4.1. General procedures

All operations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexanes, pentane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous YCl_3 (Aldrich) was used as received. [Y(*o*-$C_6H_4CH_2NMe_2)_3$] [18], (+)-neomenthylcyclopentadiene [28], (−)-phenylmenthylcyclopentadiene [22], (1-neomenthylindenyl)lithium [13a], pent-4-enylamine (**9a**) [4], 2,2-dimethyl-pent-4-enylamine (**9b**) [29] and 2-allyl-2-methyl-pent-4-enylamine (**9c**) [8a] were synthesized as described in the literature. (*R*)-(+)-α-Methoxy-α-trifluoro-methylphenylacetic acid (>99% ee, from Reuter Chemische Apparatebau KG (RCA), Freiburg, Germany) was transformed to its acid chloride using oxalyl chloride/DMF in hexanes [30]. All other chemicals were commercially available and used as received. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 300 or Avance 400 spectrometer. Assignments of proton and carbon signals are based on $^1H,^1H$-COSY and $^1H,^{13}C$-COSY spectra. The enantiomeric excess of the hydroamination/cyclization reactions were determined via ^{19}F NMR spectroscopy of the Mosher amides as described earlier [2c,8d]. Elemental analyses were performed by the Microanalytical Laboratory of this department. Although metal complexes were combusted with V_2O_5 as burning aid, some analyses gave low carbon content repeatedly, presumably due to carbide formation. Catalytic asymmetric hydroamination reactions and kinetic studies were performed as described earlier [8d].

4.2. [(η^5-NeomenthylCp)$_2$Y{*o*-$C_6H_4CH_2NMe_2$}] (**1**)

A 25 mL Schlenk-tube was charged with (+)-neomenthylcyclopentadiene (568 mg, 2.78 mmol) and [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (608 mg, 1.24 mmol). Toluene (6 mL) was added via a syringe under a flush of nitrogen to the reaction flask. The mixture was stirred for 4 days at 45 °C. The solvent was removed *in vacuo* and the residue was dissolved in a minimum amount of pentane and allowed to crystallize at −30 °C to give **1** as a crop of white crystals in 64% yield (500.7 mg). ^1H NMR (400 MHz, C_6D_6): $\delta = 7.86$ (d, $^3J_{H,H} = 6.7$ Hz, 1 H, aryl-H), 7.29 (dd, $^3J_{H,H} = 6.7$ Hz, $^3J_{H,H} = 6.9$ Hz, 1H, aryl-H), 7.20 (ddd, $^3J_{H,H} = 7.4$ Hz, $^3J_{H,H} = 6.9$ Hz, $^4J_{H,H} = 1.2$ Hz, 1H, aryl-H), 6.94 (d, $^3J_{H,H} = 7.4$ Hz, 1H, aryl-H), 6.47 (m, 1H, C_5H_4, ring 1), 6.30 (m, 1H, C_5H_4, ring 2), 6.25 (m, 1H, C_5H_4, ring 2), 6.18 (m, 1H, C_5H_4, ring 1), 6.06 (m, 1H, C_5H_4, ring 1), 5.97 (m, 1H, C_5H_4, ring 2), 5.93 (m, 1H, C_5H_4, ring 1), 5.84 (m, 1H, C_5H_4, ring 2), 3.61 (d, $^2J_{H,H} = 13.4$ Hz, 1H, CH_2NMe_2), 3.37 (br s, 1H, H-1′, neomenthyl), 3.13 (br s, 1H, H-1′), 3.08 (d, $^2J_{H,H} = 13.4$ Hz, 1H, CH_2NMe_2), 1.83 (s, 3H, NCH_3), 1.80 (s, 3H, NCH_3), 1.6–0.8 (m, 18H, H-2′ to H-6′ and $CH(CH_3)$, neomenthyl), 1.04 (d, $^3J_{H,H} = 6.3$ Hz, 3H, $CHCH_3$), 1.00 (d, $^3J_{H,H} = 6.12$ Hz, 3H, $CHCH_3$), 0.98 (d, $^3J_{H,H} = 6.5$ Hz, 3H, $CHCH_3$), 0.94 (d, $^3J_{H,H} = 5.8$ Hz, 3H, $CHCH_3$), 0.65 (d, $^3J_{H,H} = 6.7$ Hz, 3H, CH_3), 0.62 (d, $^3J_{H,H} = 6.8$ Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta = 184.7$ (d, $^1J_{Y,C} = 54.2$ Hz), 144.4 (2-C_6H_4), 131.0, 129.3, 125.4, 125.14, 125.09 (C_6H_4), 124.96, 124.92 (C_{ipso}, C_5H_4) 113.8 (C_5H_4, ring 1), 113.7 (C_5H_4, ring 2), 113.4 (C_5H_4, ring 1), 112.1 (C_5H_4, ring 2), 110.8, 110.3, 110.0, 109.8 (C_5H_4), 69.5 (NCH_2), 49.8, 49.5 (C-1′), 48.9, 47.9 (NCH_3), 42.8, 42.2 (C-6′), 38.6, 38.5 (C-2′), 36.33, 36.27 (C-3′), 30.11, 30.10 ($CH(CH_3)_2$), 28.7, 28.3 (C-5′), 24.14, 24.07 (C-4′), 23.8, 23.7 ($CH(CH_3)_2$), 22.7 (2C, $CH(CH_3)_2$), 20.4, 20.3 (CH_3). Anal. Calc. for $C_{39}H_{58}NY$ (629.80): C, 74.38; H, 9.28; N, 2.22. Found: C, 73.53; H, 9.30; N, 2.20%.

4.3. ((−)-Phenylmenthylcyclopentadienyl)lithium (**4**)

To a solution of **2** (1.690 g, contaminated with elimination product **3**, ≈4.80 mmol of **2**) in pentane (20 mL) was added a solution of *n*-BuLi (2 mL, 2.4 M solution in hexanes, 4.80 mmol) at −78 °C. After warming to room temperature and stirring for 1 h, the clear yellow solution turned to a pale suspension, which was stirred overnight to give a pale yellow oil that separated from the supernatant.

The latter was decanted at −10 °C and the remaining product was washed once with pentane (10 mL) at the same temperature. The remaining solvent was then removed completely *in vacuo* and the resulting colorless solid foam was stirred under dynamic vacuum for 1 h to give **4** in 97% yield (1.350 g), which was used without further purification. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.17$ (d, 2H, 2,6-C_6H_5, obscured by solvent signal), 7.03 (pt, $^3J_{H,H} = 7.6$ Hz, 2H, 3,5-C_6H_5), 6.86 (t, $^3J_{H,H} = 7.3$ Hz, 1H, 4-C_6H_5), 5.66 (s, 4H, Cp), 2.57 (dt, $^3J_{(ax,ax\ (H\text{-}1,H\text{-}6\ and\ H\text{-}1,H\text{-}2))} = 10.0$ Hz, $^3J_{(ax,eq.\ (H\text{-}1,H\text{-}6))} = 3.3$ Hz, 1H, H-1, Phmenthyl), 1.89 (m, 2H, Phmenthyl), 1.63 (m, 1H, Phmenthyl), 1.35–1.53 (m, 2H, Phmenthyl), 1.23–1.35 (m, 1H, Phmenthyl), 1.00–1.07 (m, 1H, Phmenthyl), 1.21 (s, 3H, C(Ph)CH_3), 1.08 (d, $^3J_{H,H} = 6.3$ Hz, 3H, CH_3), 0.89–0.94 (m, 1H, Phmenthyl), 0.97 (s, 3H, C(Ph)CH_3); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 153.0$, 138.3 (q), 130.1 (q), 126.3 (2C), 125.3, 104.7 (2C), 101.3 (2C), 52.1, 49.4, 42.1, 41.3, 35.7, 33.6, 29.5, 29.3, 24.4, 22.9.

4.4. [(η^5-(−)-phenylmenthylCp)$_2$Y(μ-Cl)$_2$Li(OEt$_2$)$_2$] (5)

A 50 mL Schlenk-flask was charged with YCl_3 (464 mg, 2.38 mmol) and **4** (1.35 g, 4.71 mmol). The reaction flask was cooled to −78 °C and THF (25 mL) was added via a syringe. After warming back to room temperature YCl_3 had dissolved. The mixture was stirred for 1.5 h and then THF was removed *in vacuo*. The foam-like solid product was repetitively treated with Et_2O until complete replacement of coordinated THF. The solvent was removed *in vacuo* and finally pentane was added (2 × 10 mL) to extract the title compound. After removing the solvent, **5** was obtained in the form of a white powder in 62% yield (1.274 g). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.22$ (br s, 4H, 2,6-C_6H_5), 7.20 (br s, 4H, 3,5-C_6H_5), 7.07 (m, 2H, 4-C_6H_5), 6.45 (dd, $^3J_{H,H} = 4.8$ Hz, $^4J_{H,H} = 2.3$ Hz, 2H, Cp), 6.33 (br q, 2H, Cp), 6.28 (br q, 2H, Cp), 6.22 (dd, $^3J_{H,H} = 5.0$ Hz, $^4J_{H,H} = 2.5$ Hz, 2H, Cp), 3.25 (q, $^3J_{H,H} = 7.0$ Hz, 8H, Et_2O), 2.57 (dt, $^3J_{(ax,ax(H\text{-}1,H\text{-}6\ and\ H\text{-}1,H\text{-}2))} = 10.0$ Hz, $^3J_{(ax,eq.(H\text{-}1,H\text{-}6))} = 2.5$ Hz, 2H, H-1, Phmenthyl), 1.64–1.79 (m, 4H, Phmenthyl), 1.47–1.55 (m, 2H, Phmenthyl), 1.30–1.43 (m, 6H, Phmenthyl), 1.27 (s, 6H, C(Ph)CH_3), 1.11 (t, $^3J_{H,H} = 7.0$ Hz, 12H, Et_2O), 0.92–1.04 (m, 2H, Phmenthyl), 0.91 (d, 6H, CH_3, obscured by other signal), 0.90 (s, 6H, C(Ph)CH_3); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 152.4$, 136.2, 128.2 (2,6-C_6H_5), 125.9 (3,5-C_6H_5), 125.3 (4-C_6H_5), 114.0, 113.0, 111.9, 110.9 (Cp), 65.9 (Et_2O), 54.9 (C-1), 47.4 (C-6), 41.8 (C-2), 41.6 (C-8), 35.7 (C-3), 33.3 (C-5), 30.0 (C-4), 29.6 (CH_3), 22.8 (CH_3), 22.5 (CH_3), 15.5 (Et_2O). Anal. Calc. for $C_{50}H_{74}Cl_2LiO_2Y$ (873.89) C, 68.72; H, 8.54. Found: C, 67.36; H, 8.32%.

4.5. [(η^5-(−)-PhenylmenthylCp)$_2$YN(SiMe$_3$)$_2$] (6)

A 50 mL Schlenk flask was charged with complex **5** (874 mg, 1.00 mmol) and $LiN(SiMe_3)_2$ (167 mg, 1.00 mmol). Toluene (20 mL) was added via a syringe at room temperature and the resulting milky suspension was stirred for 3 h in the glove box. The LiCl precipitate was filtered off and the solvent was removed *in vacuo* to give **6** as a solid foam-like product in 98% yield (793 mg), which was clean according to NMR spectroscopy. The high solubility of the compound in pentane even at −78 °C has prohibited further purification thus far. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.20$ (br s, 2H, C_6H_5), 7.19 (br s, 2H, C_6H_5), 7.18 (br s, 4H, 3,5-C_6H_5), 7.06 (m, 2H, 4-C_6H_5), 6.31 (br q, 2H, C_5H_4), 6.30 (br q, 2H, C_5H_4), 6.05 (dd, $^3J_{H,H} = 5.0$ Hz, $^4J_{H,H} = 2.3$ Hz, 2H, C_5H_4), 5.80 (d, $^3J_{H,H} = 5.6$ Hz, $^4J_{H,H} = 2.8$ Hz, 2H, C_5H_4), 2.71 (dt, $^3J_{(ax,ax(H\text{-}1,H\text{-}6\ and\ H\text{-}1,H\text{-}2))} = 10.0$ Hz, $^3J_{(ax,eq.(H\text{-}1,H\text{-}6))} = 2.8$ Hz, 2H, H-1, Phmenthyl), 1.90 (m, 2H, Phmenthyl), 1.65 (m, 2H, Phmenthyl), 1.54 (m, 2H, Phmenthyl), 1.30–1.42 (m, 6H, Phmenthyl), 1.28 (s, 6H, C(Ph)CH_3), 0.98–1.20 (m, 2H, Phmenthyl), 0.93 (d, $^3J_{H,H} = 6.2$ Hz, 6H, CH_3), 0.78–0.82 (m, 2H, Phmenthyl), 0.75 (s, 6H, C(Ph)CH_3), 0.21 (s, 18H, $SiCH_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 152.5$, 135.6, 127.8 (2,6-C_6H_5) 125.8 (3,5-C_6H_5), 125.3 (4-C_6H_5), 115.2, 113.9, 112.0, 110.7 (Cp), 55.0 (C-1), 48.0 (C-6), 42.3 (C2), 41.5 (C-8), 35.7 (C-3), 33.6 (C-5), 30.3 (C-4), 29.5, 22.5, 22.0 (CH_3), 3.7 ($SiCH_3$).

4.6. [(η^5-(+)-NMInd)$_2$Y(μ-Cl)$_2$Li(Et$_2$O)$_2$] (7)

To a solid mixture of (1-neomenthylindenyl)lithium (521 mg, 2.00 mmol) and anhydrous YCl_3 (197 mg, 1.01 mmol) was added THF (10 mL) at −78 °C. The mixture was allowed to warm to room temperature and then stirred overnight. The solvent was removed *in vacuo*. The resulting yellowish oily solid residue was treated with Et_2O (5 × 5 mL) and the remaining solution was filtered off from the LiCl precipitate. The clear solution was concentrated *in vacuo*. The product was redissolved in Et_2O to give 697 mg (85%) of large needle-like white crystals of **5** at room temperature. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.77$ (d, $^3J_{H,H} = 8.5$ Hz, 2H, H-7), 7.64 (d, $^3J_{H,H} = 8.3$ Hz, 2H, H-4), 7.01 (dd, $^3J_{H,H} = 8.3$ Hz, $^3J_{H,H} = 6.9$ Hz, 2H, H-5), 7.05 (d, $^3J_{H,H} = 3.4$ Hz, 2H, H-2), 6.86 (dd $^3J_{H,H} = 8.5$, $^3J_{H,H} = 6.9$ Hz, 2H, H-6), 6.37 (d, $^3J_{H,H} = 3.4$ Hz, 2H, H-3), 3.80 (m, 2H, H-1′, neomenthyl), 3.16 (q, 8H, Et_2O), 2.38 (m, 2H, neomenthyl), 2.24 (m, 2H, neomenthyl), 2.09 (m, 2H, neomenthyl), 1.40–1.65 (m, 10H, neomenthyl), 1.3 (d, $^3J_{H,H} = 6.3$ Hz, 6H, CH_3), 0.95 (m, 2H, neomenthyl), 0.99 (t, 12H, Et_2O), 0.84 (d, $^3J_{H,H} = 6.3$ Hz, 6H, CHCH_3), 0.15 (d, $^3J_{H,H} = 6.3$ Hz, 6H, CHCH_3); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta =$ 129.1, 128.6, 124.4, 122.8, 121.6, 120.1, 119.9, 119.7, 95.7 (C_6H_9), 65.9 (Et_2O), 49.1 (C-1′), 42.3 (C-6′), 36.2 (*C*H(CH_3)$_2$), 35.9 (C-3′), 30.1 (C-2′), 29.4 (C-5′), 23.8 (CH_3), 23.5 (CH*C*H_3), 22.8 (C-4′), 18.3 (CH*C*H_3), 15.2 (Et_2O). Anal. Calc. for $C_{46}H_{70}Cl_2LiO_2Y$ (821.81) C, 67.23; H, 8.59. Found: C, 66.07; H, 8.61%.

4.7. [(η^5-(+)-NMInd)$_2$YN(SiMe$_3$)$_2$] (**8**)

A 10 mL Schlenk-flask was charged with complex **7** (343 mg, 0.42 mmol) and 1 equiv. of LiN(SiMe$_3$)$_2$ (80.0 mg, 0.48 mmol). Toluene (5 mL) was added and the mixture was then stirred at ambient temperature for 1 h. The solvent was removed *in vacuo* and pentane (5 mL) was transferred onto the resulting yellowish oil. The mixture was filtered and the colorless precipitate was extracted once with pentane (1 mL). The combined extracts were concentrated *in vacuo* and cooled to −30 °C. No crystallization occurred under these conditions and the solvent was evaporated to give a viscous oil in 79% crude yield (249 mg). The product was dissolved again in pentane (2–3 mL). Slow evaporation of the solvent led to formation of colorless crystals, which were dried *in vacuo* to give complex **8** in 44% yield (140 mg). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.55$ (d, $^3J_{H,H} = 6.4$ Hz, 2H, H-7), 7.28 (dd, $^3J_{H,H} = 6.7$ Hz, $^4J_{H,H} = 1.8$ Hz, 2H, H-4), 7.23 (d, $^3J_{H,H} = 3.3$ Hz, 2H, H-3), 6.95 (m, 4H, H-5, H-6), 6.08 (d, $^3J_{H,H} = 3.3$ Hz, 2H, H-2), 3.44 (m, 2H, H-1′, neomenthyl), 2.37 (m, 2H, neomenthyl), 2.08 (m, 2H, neomenthyl), 1.94 (m, 2H, neomenthyl), 1.57 (m, 2H, neomenthyl), 1.43 (m, 6H, neomenthyl), 1.29 (m, 2H, neomenthyl), 1.18 (d, $^3J_{H,H} = 6.4$ Hz, 6 H, CH_3), 1.01 (m, 2H, neomenthyl), 0.68 (d, $^3J_{H,H} = 6.7$ Hz, 6H, CHCH_3), −0.05 (s, 18H, SiCH_3), −0.17 (d, $^3J_{H,H} = 6.7$ Hz, 6H, CHCH_3); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 130.2$, 129.9, 124.8, 123.3, 123.1, 122.8, 122.0, 119.6, 97.0 (C_9H_6), 49.0 (C-1′), 41.8 (C-6′), 36.6 (C-8), 35.2 (C-3′), 29.5 (C-2′), 29.2 (C-5′), 23.8 (CH_3), 23.2 (CHCH_3), 22.0 (C-4′), 17.5 (CHCH_3), 3.6 (SiCH_3). Anal. Calc. for $C_{44}H_{68}YNSi_2$ (756.11) C, 69.90; H, 9.06; N, 1.85. Found: C, 69.43; H, 9.13; N, 2.29%.

4.8. X-ray crystal structure analysis of 7

Clear, colorless crystals of **7**, $C_{46}H_{70}Cl_2LiO_2Y$, 821.81 g mol^{-1}, were obtained from a concentrated Et_2O solution at 25 °C. Crystal size $0.15 \times 0.15 \times 0.15$ mm, orthorhombic, $P2_12_12_1$, $a = 11.5907(3)$ Å, $b = 19.3686(4)$ Å, $c = 20.1307(6)$ Å, $V = 4519.3(2)$ Å^3, $Z = 4$, $\mu = 1.442$ mm^{-1}. Data were collected on a Nonius KappaCCD area detector at 173(2) K up to $2\theta_{max} = 55.0°$ (Mo Kα radiation). 10241 reflections were collected, 10241 were unique [$R_{int} = 0.0000$] of which 7451 were observed [$I > 2\sigma(I)$]. $R_1 = 0.0541$, $wR_2 = 0.1347$ (obsd. data), goodness-of-fit on $F^2 = 1.019$; absolute structure parameter −0.029(6), residual electron density (max/min) 0.835/−0.451 e Å^{-3}. Cell parameters were obtained from 10 frames using a 10° scan and refined with 5627 reflections. Lorentz, polarization, and empirical absorption corrections were applied [31a,31b]. The space group was determined from systematic absences and subsequent least-squares refinement. The structures were solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on F^2 using SHELXL-97 [31c]. Hydrogen atoms were fixed in idealized positions using a riding model. Non-hydrogen atoms were refined anisotropically. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature [31d].

5. Supplementary material

CCDC 642037 contains the supplementary crystallographic data for **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

Generous financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. K.C.H. is a DFG Emmy Noether fellow (2001–2007) and thanks Professor John A. Gladysz for his continual support.

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