Review

Non-metallocene hydride complexes of the rare-earth metals

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Contents

Abstract

The chemistry of the hydride complexes of the rare-earth metals has been dominated by complexes with metallocene and half-sandwich ligand frameworks. In contrast to hydride complexes supported by cyclopentadienyl ligands, only relatively few examples of non-metallocene hydride complexes have been reported in the literature. Such complexes are potentially of some interest in view of their chemical reactivity and catalytic applications. This review surveys the chemistry of non-metallocene hydride complexes up to mid-2007, some spectroscopic and structural aspects as well as their reactivity.
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1. Introduction

Metal-hydrogen and metal-carbon bonds are at the pinnacle of organometallic chemistry. In particular many d-block transition metal hydride and alkyl complexes play a pivotal role as important homogeneous catalysts [1]. f-block metal hydride and alkyl complexes have also been investigated with the aim

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$[\mathbf{Ln}(L_n)H_3]$		
$[\mathbf{Ln}(L_n)H_2]^+$	$[\mathbf{Ln}(L_nX)H_2]$	
	$[Ln(\eta^5\text{-}C_5Me_4SiMe_3)H_2]_4$	
$[\mathbf{Ln}(L_n)H]^{2+}$	$[\mathbf{Ln}(L_nX)H]^+$	$[\mathbf{Ln}(L_nX)_2H]$
		$[Ln(\eta^5\text{-}C_5R_5)_2H]_2$
		$[Ln(\eta^5\text{-}C_5R_5)(H)(X)]_2$
		$[Ln(\eta^5\text{:}\eta^1\text{-}C_5Me_4ZNR)(H)(L)]_2$

Fig. 1. Systematics of molecular hydride complexes of rare-earth metals Ln. L_n is a neutral two-electron ligand; X is a monoanionic one-electron ligand. Known types of cyclopenta-dienyl hydride complexes of the rare-earth metals are shown.

of developing new homogeneous catalysts, but were mostly confined to those supported by the bis(η^5-cyclopentadienyl) or metallocene ligand framework [2]. As group 4 metal-based organometallic catalysts, e.g. for α-olefin polymerization, are currently increasingly utilizing non-metallocene ligand scaffolds ("post-metallocene catalysts") [3], it appears to be reasonable to apply these new types of supporting ligands to the group 3 metals and lanthanides and to expand their structural and reactivity patterns. However, electronic and steric control of the relatively large and highly electropositive rare-earth metal centers is not straightforward, as intramolecular ligand fluxionality and intermolecular scrambling may preclude stabilization of a defined (e.g. chiral) ligand sphere [4].

According to the so-called MLX scheme [5], possible compositions of rare-earth metal hydride complexes are compiled in Fig. 1. Mainly two families of molecular hydrides belonging to the class of neutral species of the type $[Ln(L_nX)_2H]$ have been reported. The first family includes metallocene hydrides $[Ln(\eta^5\text{-}C_5R_5)_2H]_2$ [6] or $[Ln(\eta^5\text{-}C_5H_4R')_2H]_2$ [7], whereas the second one dimeric hydride complexes featuring a dianionic linked amido-cyclopentadienyl ligand, the so-called "constrained geometry" ligand, $[Ln(\eta^5\text{:}\eta^1\text{-}C_5Me_4ZNR)(H)(L)]_2$ [8]. More recently, a number of highly

aggregated mono(cyclopentadienyl) dihydride complexes of the rare-earth metals have been studied in some detail [9].

It is interesting to note that so far only a very limited number of hydride complexes without a cyclopentadienyl ligand have been reported in the literature [10]. Not unexpectedly, there is not a single example for a structurally characterized complex exhibiting a terminal metal-hydride bond, as all known complexes form bridging hydride bonds. This is a consequence of a strongly polarized metal-hydride bond at the large rare-earth metal centers. The present review article compiles literature reports on non-metallocene rare-earth metal hydride complexes.

## 2. Hydride complexes containing monoanionic ligands

Monoanionic ancillary ligands for the non-metallocene hydride complexes of the rare-earth metals are in all cases hard Lewis bases. They include N,N donors such as benzamidinate (**L1**) [11] or guanidinate (**L2**) [12], N,N,N donors such as tris(pyrazolyl)borate ligand (**L3**) [13,14] or N,O donors such as (alkoxysilyl)amide (**L4**) [15] and salicylaldiminate (**L5**) [16] ligands as shown in Scheme 1. Hydride complexes with those ligands are hydrido-bridged dimers.

2.1. Amidinates

In 1993 Teuben et al. reported the preparation of the dimeric bis(*N,N'*-bis(trimethylsilyl)benzamidinate) yttrium hydride, $[Y\{PhC(NSiMe_3)_2\}_2(\mu\text{-}H)]_2$ (**1L1**), via hydrogenolysis of the corresponding alkyl complex $[Y\{PhC(NSiMe_3)_2\}_2\{CH(SiMe_3)_2\}]$ in benzene (Scheme 2) [11a]. In a similar manner the corresponding hydride complex with a *para*-methoxy-substituted benzamidinate ligand, $[Y\{p\text{-}MeOC_6H_4C(NSiMe_3)_2\}_2(\mu\text{-}H)]_2$ (**2L1**) was isolated [11b]. Compound **1L1** could also be synthesized via hydrogenolysis of the benzyl complex $[Y\{PhC(NSiMe_3)_2\}_2(CH_2Ph)(THF)]$, although the coordinated THF retarded the
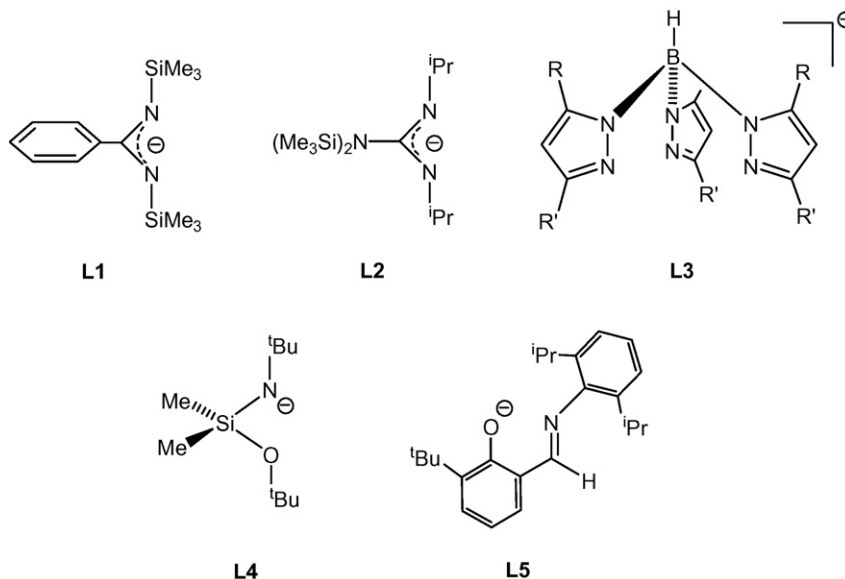
Scheme 1.

Scheme 2.
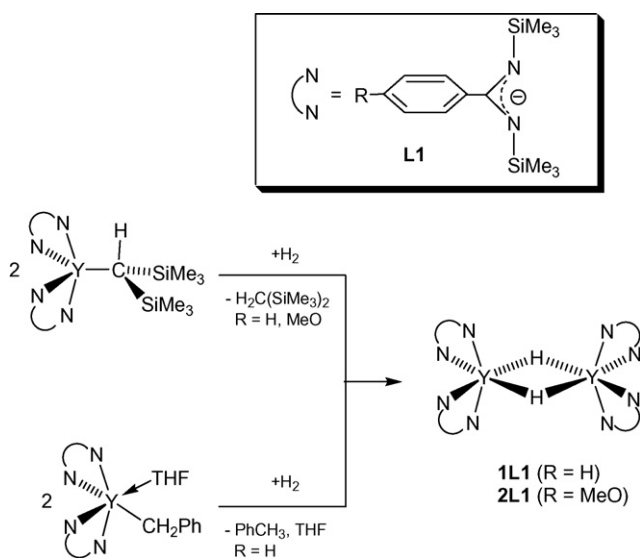
rate considerably. Arnold and Hagadorn reported the scandium analogue of **1L1** by hydrogenolysis of $[Sc\{PhC(NSiMe_3)_2\}_2(CH_2SiMe_3)]$ in hexane or benzene at r.t. to yield $[Sc\{PhC(NSiMe_3)_2\}_2(\mu\text{-}H)]_2$ (**3L1**) along with 1 equiv. of $SiMe_4$ [11d]. The preparation of **3L1** from the alkyl derivatives, $[Sc\{PhC(NSiMe_3)_2\}_2(Me)(THF)]$ and $[Sc\{PhC(NSiMe_3)_2\}_2(Mes)]$, was reported to require higher temperatures (ca. 70 °C). The benzamidinate ligand binds to a metal in a symmetrical fashion and the negative charge appears to be fully delocalized over the NCN fragment.

It is noteworthy that the yttrium hydride **1L1** shows no tendency to form a THF adduct. However, in neat THF C–O bond activation was observed as revealed by the almost quantitative formation of ethane and the presence of olefinic resonances in the ^{1}H NMR spectrum, indicating formation of an yttrium enolate [Y]–OCH=CH$_2$ fragment [11c]. Furthermore, in spite of its extreme oxygen and moisture sensitivity, compound **1L1** was found to be thermally stable with no decomposition after several days at 100 °C in C_6D_6. Interestingly, unlike the dimeric metallocenes $[LnCp^*_2(\mu\text{-}H)]_2$ (Ln = Sc, Y, lanthanides; $Cp^* = \eta^5\text{-}C_5Me_5$) [6a,c,e,i–l], which commonly dissociate readily into the highly reactive monomers, no C–H bond activation of solvent molecules *i.e.* H/D scrambling and metallation of deuterated aromatic solvents was observed with the benzamidinato hydride complexes. This lack of intermolecular σ-bond metathesis reaction and also significantly lower hydrogenolysis rates of the alkyl derivatives compared with those found for $[Cp^*_2YR]$ $(R=CH(SiMe_3)_2)$ [6e] are postulated to be a consequence of the different electronic properties of the hard Lewis basic benzamidinate PhC(NSiMe$_3$)$_2$ ligand. Despite the comparable steric properties to Cp* systems, this ligand renders the metal center more electropositive than do softer cyclopentadienyl ligands in metallocenes. The high electropositivity of the lanthanide center in benzamidinato hydride complexes renders this system highly ionic resulting in strongly contracted metal orbitals and, as a consequence, in low tendency to engage in σ-bond metathesis reactions [11b].

As far as the reactivity of bis(benzamidinato) hydride complexes is concerned, a dominant reaction pathway is insertion of unsaturated substrates into the Ln–H bonds (Scheme 3). Thus, $[Y\{PhC(NSiMe_3)_2\}_2(\mu\text{-}H)]_2$ (**1L1**) was found to react with ethyne or *tert*-butylacetylene, yielding the corresponding dimeric alkynyl complex $[Y\{PhC(NSiMe_3)_2\}_2(\mu\text{-}C{\equiv}C\text{-}R)]_2$ (R = H, ^{t}Bu) [11a,b]. Furthermore, minor amounts of the intermediate $[\{Y[PhC(NSiMe_3)_2]_2\}_2(\mu\text{-}H)(\mu\text{-}C{\equiv}C\text{-}^tBu)]$ could be identified by ^{1}H NMR spectroscopy, suggesting a stepwise reaction with the alkyne. Reaction of the scandium analogue, $[Sc\{PhC(NSiMe_3)_2\}_2(\mu\text{-}H)]_2$ (**3L1**) with diphenylacetylene leads to formation of the single insertion product $[Sc\{PhC(NSiMe_3)_2\}_2(PhC{=}CHPh)]$ in moderate yield [11d]. An insertion pathway also occurs in the reaction of **1L1** with acetonitrile resulting in formation of the unstable complex $[Y\{PhC(NSiMe_3)_2\}_2(\mu\text{-}N{=}C(H)Me)]_2$. In contrast to $[YCp^*_2(\mu\text{-}H)]_2$, which is known to activate pyridine giving the pyridyl species $[YCp^*_2(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)]$ [17], the bis(benzamidinato) complex **1L1** was reported to give the 1,2-inserted product $[Y\{PhC(NSiMe_3)_2\}_2(NC_5H_6)]$, exemplifying again the highly nucleophilic character of the hydride ligand [11c]. Interestingly, this reactivity with pyridine resembles that of non-permethylated cyclopentadienyl complexes $[\{Y(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}H)(THF)\}_2]$ (R = H, Me) [18].

$[Y\{PhC(NSiMe_3)_2\}_2(\mu\text{-}H)]_2$ (**1L1**) was found to polymerize ethylene with rather low productivity, giving polyethylene with a relatively broad molecular weight distribution ($M_w/M_n = 5.2$) [11c]. With propylene and hex-1-ene **1L1** did not react. Monitoring the reaction by means of ^{1}H NMR spectroscopy revealed no other yttrium compounds than **1L1** and no resonances attributable to ethylene oligomers or mixed hydrido-alkyl species, as it was observed *e.g.* by Marks et al. for $[\{Ln(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)SiR_2\}_2(\mu\text{-}H)(\mu\text{-}R')]$ (Ln = Y, Lu; R = Me, Et; R′ = Et, ^{n}Pr, ^{n}Hex) [19] and by Schaverien for $[\{YCp^*(OAr)\}_2(\mu\text{-}H)(\mu\text{-}R)]$ (OAr = $OC_6H_3{}^tBu_2$-2,6; R = Et, ^{n}Pr, ^{n}Bu, ^{n}Hex) [20]. These observations show that, due to the high ionic character of the bis(benzamidinato) yttrium compound, activation of a precatalyst by dissociation and/or pre-complexation of ethylene is unfavorable. It is also believed that dissociation of **1L1** into the monomeric hydride is slow, accounting for the reduced activity. The yttrium hydride **1L1** was also reported to catalyze the hydroboration of hex-1-ene with catechol borane [21] and the dimerization of 1-alkynes [11a,c]. The latter reaction was found to be strongly dependent on the alkyne substituent R in HC≡CR. For 1-alkynes with small substituents (R = H, Me, ^{n}Pr) no dimerization was observed and the reaction gave dimeric acetylides, whereas for bulky substituents (R = Ph, SiMe$_3$, ^{t}Bu) catalytic dimerization took place. Furthermore, phenylacetylene and *tert*-butylacetylene gave head-to-tail dimers, while for trimethylsilylacetylene the regioselectivity reversed and head-to-head dimer was formed.

2.2. Guanidinates

Another type of ancillary N,N donor for the stabilization of hydride complexes of the type $[Ln(L_nX)_2H]$ is a tetrasubstituted guanidinate ligand **L2** reported by
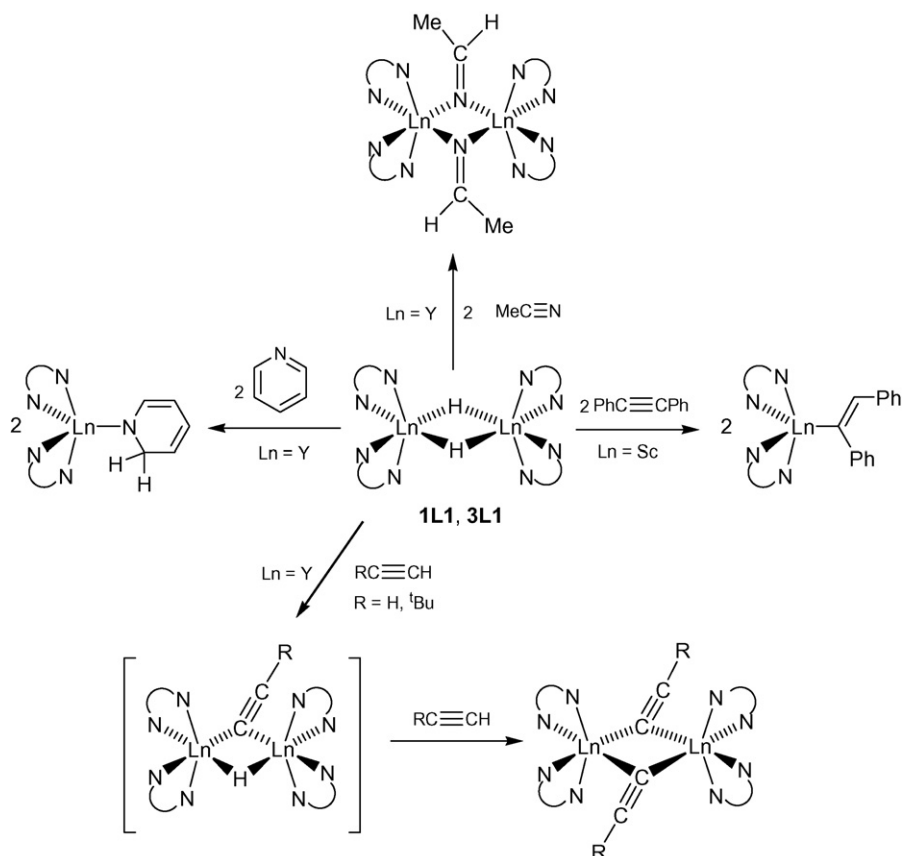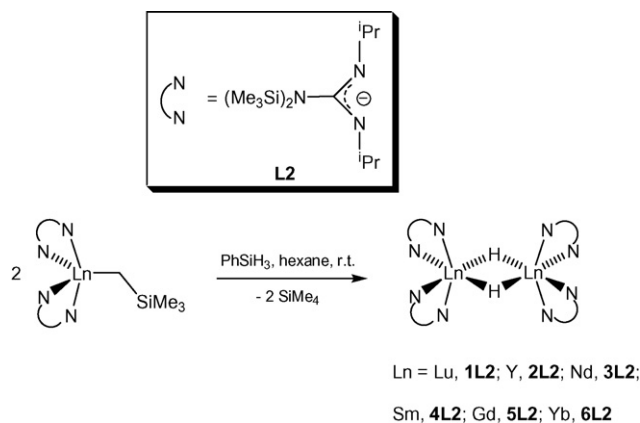
Scheme 3.

Trifonov et al. [12]. Reaction of the lutetium alkyl complex [Lu{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(CH$_2$SiMe$_3$)] with an equimolar amount of PhSiH$_3$ in hexane at r.t. resulted in formation of the dimeric hydride complex, [Lu{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$ (1L2) [12a]. Furthermore, the analogously prepared hydride complexes of some other lanthanides [Ln{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$ (Ln = Y, 2L2; Nd, 3L2; Sm, 4L2; Gd, 5L2 and Yb, 6L2) have also been reported (Scheme 4) [12b]. In contrast to the lutetium analogue 1L2, the guanidinate ligands in the yttrium complex 2L2 give a single set of signals in ^{1}H and ^{13}C NMR spec-

troscopy, indicating equivalence of both {(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$} ligands.

Concerning the reactivity no detailed studies have been reported. Treatment of 2L2 in C$_6$D$_6$ with 0.2 equiv. of THF-d_8 at 20 °C resulted in formation of the unstable monomeric THF adduct, [Y{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(H)(THF)$_n$], as revealed by ^{1}H NMR spectroscopy. The yttrium complex 2L2 was found generally to be inert with respect to addition to multiple C–C bonds of substituted olefins, since no reaction with styrene, stilbene, tolane or bis(trimethylsilyl)acetylene was observed. A stoichiometric reaction of 2L2 with ethylene did not lead to an insertion product but resulted in the rapid formation of polyethylene. The hydride complexes of samarium 4L2, yttrium 2L2 and lutetium 1L2 were found to have high catalytic activity in ethylene polymerization, whereas the lutetium analogue catalyzed also the polymerization of propylene and styrene [12].

2.3. Tris(pyrazolyl)borates

Low coordinate, low valent hydride complexes of lanthanides could be stabilized by sterically demanding tridentate tris(pyrazolyl)borate ligands [13,14]. Bianconi and Long reported that the hydrogenolysis (8 atm, 0 °C, 24 h) of the yttrium bis(alkyl) complex [Y(Tp^{Me})(CH$_2$SiMe$_3$)$_2$(THF)] (Tp^{Me} = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) resulted in formation of the thermally unstable hydride 1L3 [13], for which a trimeric solution structure analogous to [{Er(η^5-


Ln = Lu, 1L2; Y, 2L2; Nd, 3L2; Sm, 4L2; Gd, 5L2; Yb, 6L2

Scheme 4.

$C_5H_5)_2H\}_3Cl]^-$ was postulated [22]. This aggregated structure is indicated by the presence of two inequivalent pyrazoles and a quartet at $\delta = 7.46$ ppm in the ^{1}H NMR spectrum ($^1J_{YH} = 16.2$ Hz). The hydride complex **1L3** was found to catalyze the polymerization of ethylene, giving linear polyethylene with very high molecular weights ($M_w = 10^6$) but with high polydispersity due to the presence of a large number of catalytic sites.

Ancillary ligand environment based on tris(pyrazolyl)borate ligand is versatile and its electronic and steric properties can be tuned by substitution of the 3-position of the pyrazole rings. Takats et al. successfully utilized the sterically more demanding hydrotris(3-tert-butyl-5-methyl-1-pyrazolyl)borate ligand (Tp^{tBu,Me}) [14]. Thus, hydrogenolysis of the divalent ytterbium trimethylsilylmethyl complex in pentane afforded the red crystalline hydride complex [Yb(Tp^{tBu,Me})(μ-H)]$_2$ (**2L3**) of the type [Ln(L$_2$X)H]$_2$. Noteworthy, carrying out this reaction in THF, benzene or toluene resulted in formation of other uncharacterized products. Moreover, the deuterium analogue of **2L3**, [Yb(Tp^{tBu,Me})(μ-D)]$_2$, could also be prepared. Despite substantial steric bulk of the *tert*-butyl groups the hydride complex **2L3** shows diverse reactivity pattern.

Detailed reactivity studies that were performed are summarized in Scheme 5. Thus, **2L3** was found to undergo (a)

reactions with Lewis bases and Lewis acids, (b) σ-bond metathesis reactions with protic substrates and (c) insertion reactions of unsaturated functional groups. The hydride **2L3** was reported to be stable for hours in benzene but its deuteride analogue underwent a H/D exchange in benzene with H$_2$ at r.t. to give **2L3**. Dissolution of **2L3** in THF resulted in rapid ligand redistribution to form [Yb(Tp^{tBu,Me})$_2$] and presumably {YbH$_2$(THF)$_n$}. Furthermore, reaction with one equivalent of B(C$_6$F$_5$)$_3$ or HB(C$_6$F$_5$)$_2$ did not result in hydride abstraction but in cleavage of **2L3** and coordination of the Lewis acid to form [Yb(Tp^{tBu,Me})(μ-H)B(C$_6$F$_5$)$_3$] and [Yb(Tp^{tBu,Me})(H)$_2$B(C$_6$F$_5$)$_2$], respectively [14c]. The exact bonding mode in the latter case has not been determined. In the former case two Yb–F interactions are present as revealed by X-ray crystallography, while in the latter case two bridging Yb–H–B hydrides and one Yb–F interaction were anticipated. On the other hand, [Yb(Tp^{tBu,Me})(μ-H)]$_2$ was found to rapidly undergo protonolysis/σ-bond metathesis reactions with H–L to eliminate dihydrogen and give quantitatively solvate-free [Yb(Tp^{tBu,Me})L] (L = *e.g.* N(SiMe$_3$)$_2$, OMes, C≡CSiMe$_3$, η^5-C$_5$H$_5$) derivatives (Scheme 5, **b**). Reaction in benzene with dipivaloylmethane, ^{t}BuC(O)CH$_2$C(O)^{t}Bu gave the β-diketonato complex (Scheme 5, **c**) [14c].
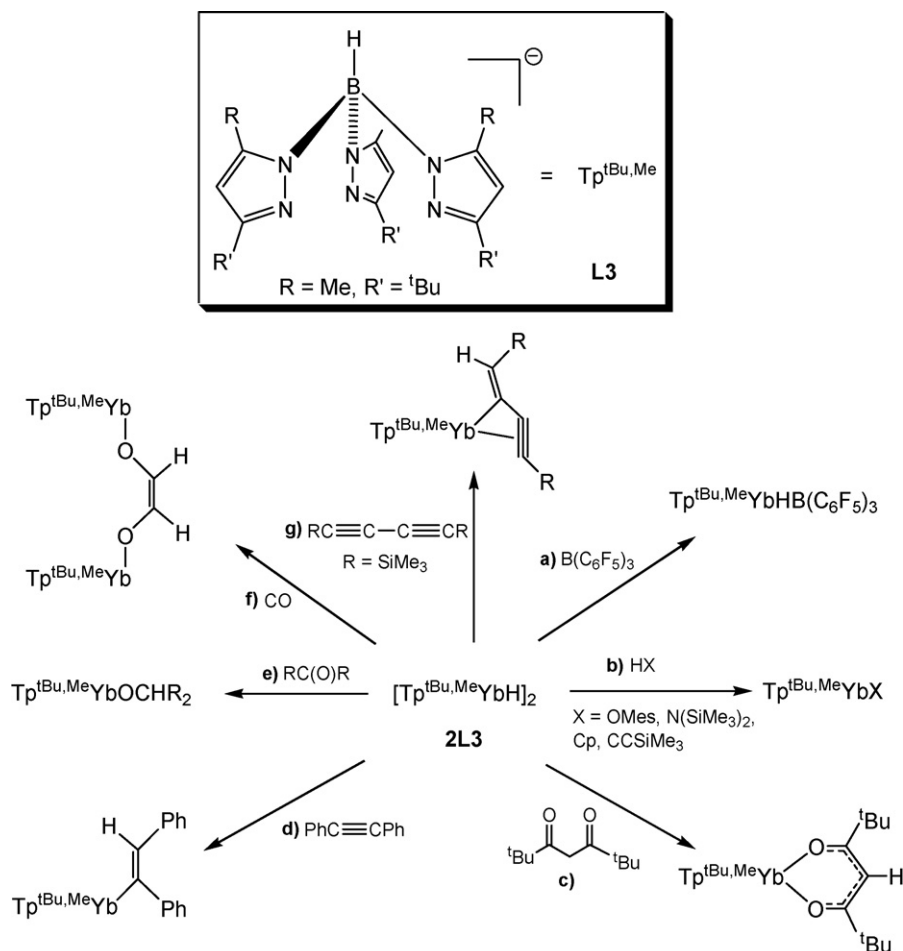
Scheme 5.
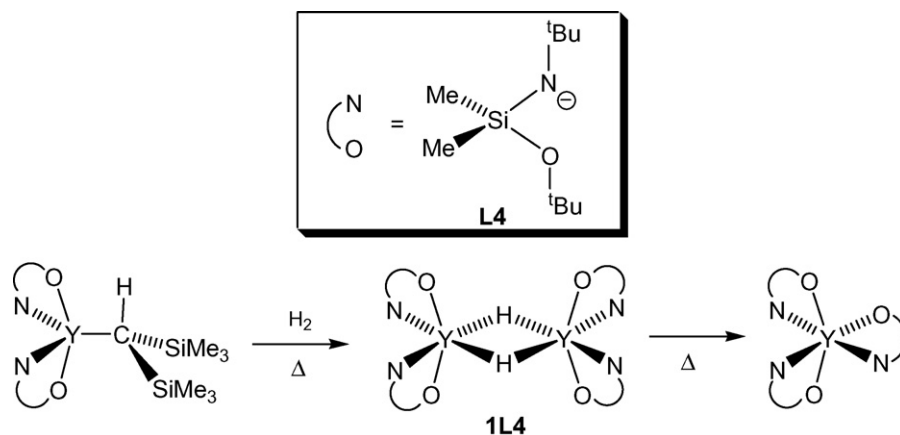
Scheme 6.

With regard to insertion reactions the reactivity of **2L3** resembles that of aforementioned Ln(III)-hydride complexes with hard donor ligands. Thus, reaction of **2L3** with diphenylacetylene follows an insertion pathway, analogously to [{Y(η^5-C$_5$H$_4$R)$_2$(μ-H)(THF)}$_2$] (R = H, Me) [18], to yield the *cis*-alkenyl complex [Yb(Tp^{tBu,Me})(CPh=CHPh)] (Scheme 5, **d**). Also ketones were found to insert into the Yb–H bond with formation of the alkoxide complexes (**e**), whereas in the case of CO a reductive coupling occurs, leading to the remarkable formation of the *cis*-enediolate complex, [(Tp^{tBu,Me})YbOCH=CHOYb(Tp^{tBu,Me})] (Scheme 5, **f**). The insertion of bis(trimethylsilyl) diacetylene gave the η^3-propargyl complex, [Yb(Tp^{tBu,Me}){η^3-(Me$_3$Si)C≡CC=CH(SiMe$_3$)}], showing that this type of bonding is viable for lanthanides (Scheme 5, **g**) [14c].

2.4. (Alkoxysilyl)amides

In 1997 Teuben et al. reported formation of the hydride complex bearing the N,O-bis(*tert*-butyl)(alkoxydimethylsilyl)amide ligand, [Y{Me$_2$Si(N^{t}Bu)(O^{t}Bu)}$_2$(μ-H)]$_2$ (**1L4**), via slow hydrogenolysis (2 days, 60 °C) of the corresponding bis(trimethylsilyl)methyl complex (Scheme 6) [15].

The reaction with dihydrogen was reported to give complicated mixtures, with only 10% of the hydride species formed. The hydride **1L4** was sufficiently stable in THF to be detected by ^{1}H NMR spectroscopy, which showed a characteristic ^{89}Y–H coupling pattern consistent with a symmetrical dimeric structure. However, the hydride could not be isolated due to ready ligand redistribution and only a disproportionation product, [Y{Me$_2$Si(N^{t}Bu)(O^{t}Bu)}$_3$] was formed in benzene. Moreover, the synthesis of the hydride through thermolysis of *in situ* prepared alkyl compounds or by salt metathesis of the chloro complex with *e.g.* NaH or LiAlH$_4$ also resulted in formation of [Y{Me$_2$Si(N^{t}Bu)(O^{t}Bu)}$_3$]. The (alkoxysilyl)amide ligand **L4** has comparable geometry and steric bulk with the benzamidinate ligand **L1**. However, calculations show that, while in the former case the negative charge is delocalized within the N–C–N fragment, in the latter case this charge is almost completely located at nitrogen of the N–Si–O fragment [15].

2.5. Salicylaldiminates

A further type of ancillary N,O donor for the stabilization of hydride complexes of the type [Ln(L$_n$X)$_2$H] is a salicylaldiminate ligand system reported by Piers et al. [16]. Thus, the yttrium bis(ligand)(dimethylphenylsilyl)methyl complex [YL$_2$(CH$_2$SiMe$_2$Ph)] (L = 2-*tert*-butyl-6-{(*E*)-[(2,6-diisopropylphenyl)imino]methyl}phenolate) was found to cleanly react with dihydrogen (4 atm, 24 h, r.t.) giving the bridging hydride dimer [YL$_2$(μ-H)]$_2$ (**1L5**) in 90% yield (Scheme 7). Complex **1L5** could also be synthesized, although less cleanly, by the reaction of [YL$_2$(CH$_2$SiMe$_2$Ph)] with PhSiH$_3$. Unlike the yttrium alkyl complex, the scandium analogue was found to react with dihydrogen under the same conditions with forma-
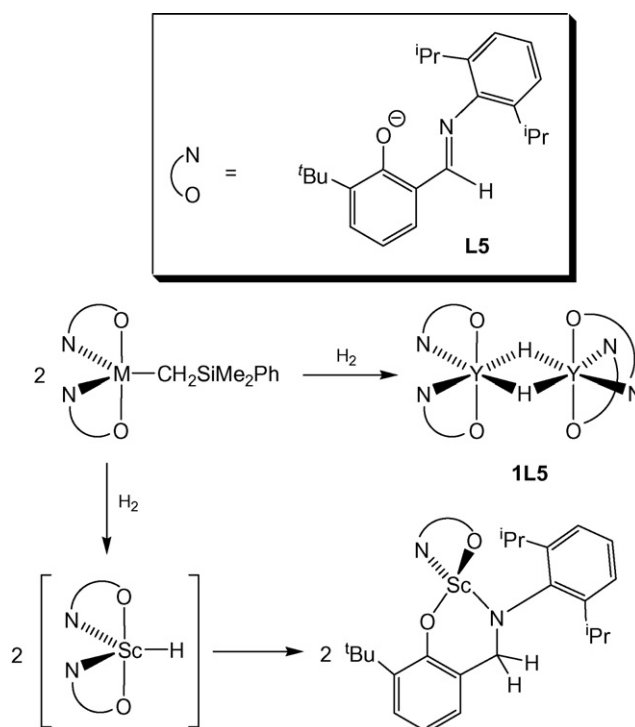
Scheme 7.
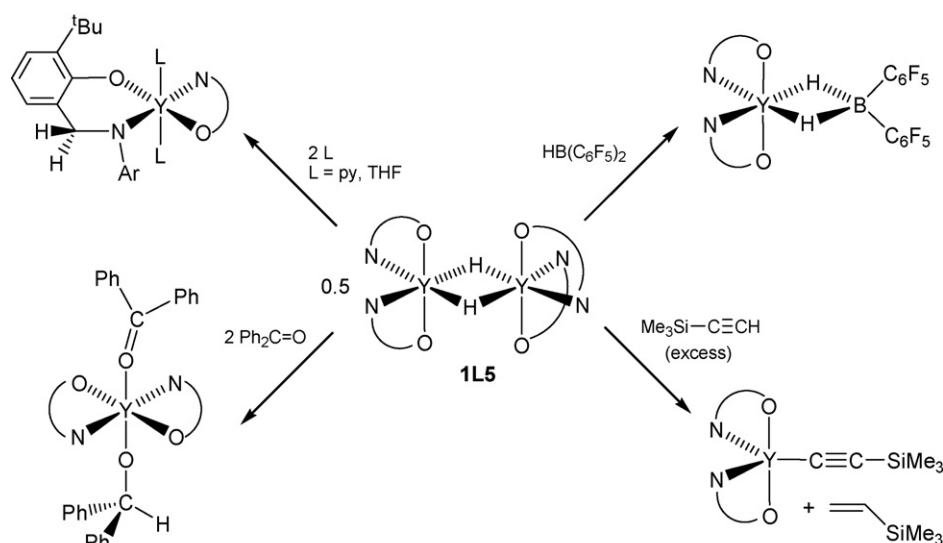
Scheme 8.

tion of a product derived from a 1,3-hydride migration to the aldimine carbon atom of the ligand. This is evidently due to the smaller ionic radius of scandium that prevents dimerization. In contrast to many metallocene and "constrained geometry" hydride complexes [23], complex **1L5** exhibited no evidence for dissociation and for H/D exchange with deuterated NMR solvents. Moreover, no formation of the $[(YL_2)_2(\mu\text{-H})(\mu\text{-D})]$ isotopomer was observed after mixing **1L5** with the deuteride complex in a 1:1 ratio in C_6D_6.

The reactivity of **1L5** is summarized in Scheme 8. Similarly to yttrium benzamidinato and (alkoxysilyl)amido hydride complexes, no or little ethylene polymerization activity was reported. This is indicative of considerably slow dissociation into the corresponding reactive monomer in solution. This observation was further supported by the slow reaction (8 days) of **1L5** with borane to form $[YL_2(\mu\text{-H})_2B(C_6F_5)_2]$. Unlike the yttrium benzamidinato hydride complex **1L1**, which was found to catalyze the dimerization of alkynes [11c], reaction of **1L5** with an excess of trimethylsilylacetylene at r.t. for 3 days gave the monomeric acetylide complex $[YL_2(C{\equiv}CSiMe_3)]$. The formation of vinyltrimethylsilane and the absence of H_2 in NMR experiments suggest an initial insertion of an alkyne rather than direct σ-bond metathesis between the C−H and Y−H bonds. The resulting yttrium vinyl species would then undergo σ-

bond metathesis with another equivalent of alkyne. On the other hand, benzophenone was found to insert into the Y−H bond to form the bis(ligand) alkoxy ketone compound [*trans*-$YL_2(OCHPh_2)(OCPh_2)$] characterized by NMR spectroscopy and X-ray crystallography. In reactions with Lewis bases slow insertion was reported to compete with the hydride migration to the ligand aldimine carbon atom, the latter pathway being represented by the reactions of **1L5** with pyridine or THF [16].

## 3. Hydride complexes containing dianionic ligands

There are only two types of the dianionic ancillary ligands for non-metallocene hydride complexes of the rare-earth metals reported in the literature. As shown in Scheme 9 one of them utilizes a hard N,N donor such as diamide (**L6**, **L7**) [24,25]. Recently, our group has introduced the first hydride complexes of lanthanides with mixed hard-soft OSO- (**L8**) or OSSO-type (**L9**) bis(phenolate) ligands [26].

3.1. Diamides

In 1999 Tilley and Gountchev introduced a chelating dianionic silylamido ligand (DADMB: 2,2′-bis{(*tert*-
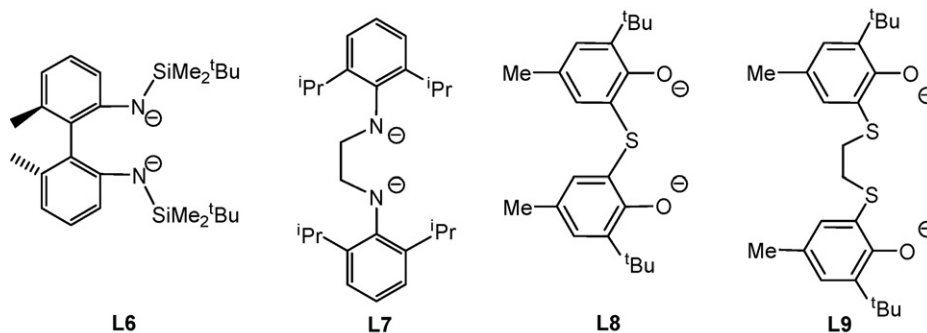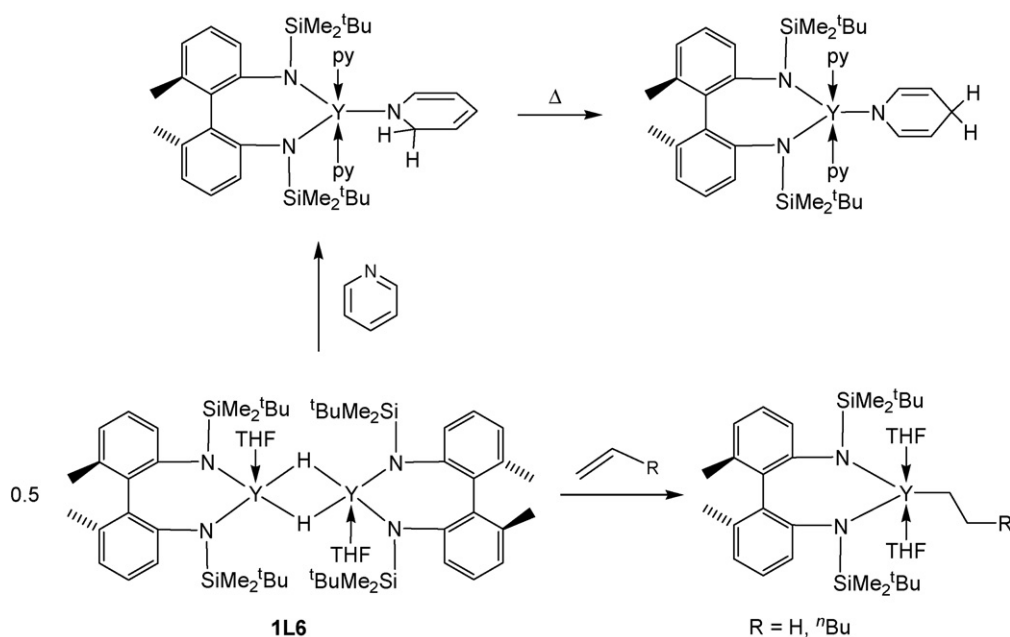

Scheme 9.
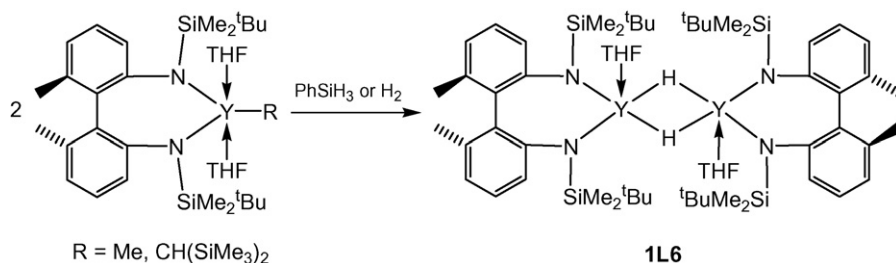
Scheme 10.

butyldimethylsilyl)amido}-6,6′-dimethylbiphenyl) based on a C_2-symmetrical biphenyl framework. Reaction of the yttrium bis(silylamido)biphenyl alkyl complexes [Y(DADMB)(R)(THF)$_2$] (R = Me, CH(SiMe$_3$)$_2$) with PhSiH$_3$ in benzene at r.t. resulted in formation of the yttrium hydride complex [Y(DADMB)(μ-H)(THF)]$_2$ (**1L6**) of the type [Ln(L$_n$X)H] along with PhMeSiH$_2$ or PhSiH$_2$CH(SiMe$_3$)$_2$ (Scheme 10) [24]. An X-ray diffraction analysis revealed a centrosymmetric dimeric structure of **1L6**.

The hydride **1L6** could also be prepared via hydrogenolysis in benzene. An exchange with deuterium from THF-d_8 was reported to take place as revealed by the disappearance of the hydride signal at r.t. within 4 days. Both the dimeric nature and the very low solubility of **1L6** in non-polar organic solvents restrict its reactivity. No polymerization activity was observed toward ethylene or hex-1-ene in C$_6$D$_6$. The lack of olefin polymerization activity, which is due to the high degree of ionicity of the yttrium–nitrogen bonding, is similar to the aforementioned low activity reported for the bis(benzamidinato) hydride complexes. Instead, when dissolved in THF, for both α-olefins insertion into the Y–H bond of [Y(DADMB)(μ-H)(THF)]$_2$ was observed to form the yttrium *n*-alkyl complexes [Y(DADMB)(R)(THF)$_2$] (R = Et, ^{n}Hex) (Scheme 11). Reaction

with hex-1-ene was found to be significantly slower and the product could be characterized only by means of NMR spectroscopy. However, no reaction with cyclohexene occurred. As shown in Scheme 11, **1L6** was also found to react with pyridine to give a mixture of 1,2-(major) and 1,4-(minor) insertion products. The former isomer could be completely converted into the latter one upon heating a benzene solution to 80 °C, indicating that the 1,4-insertion product is thermodynamically more stable, while the 1,2-product is kinetically generated [24]. Interestingly, the isomerization of the 1,2-product to the 1,4-product has been also reported by Evans et al. for [{Y(η^5-C$_5$H$_4$R)$_2$(μ-H)(THF)}$_2$] (R = H, Me) [18]. This emphasizes that the reactivity of non-permethylated cyclopentadienyl lanthanide hydride complexes resembles that of the non-cyclopentadienyl ones.

While the yttrium-DADMB hydride complex **1L6** was not active as olefin or silane polymerization catalyst, it was found to catalyze the hydrosilylation of olefins [27]. Also the yttrium methyl complex [Y(DADMB)(Me)(THF)$_2$] could be used as an active hydrosilylation catalyst, presumably because it first reacts with a silane to form a reactive, monomeric hydride. The ratio of two isomers, resulting from a 1,2- or 2,1-addition of the silane to a double bond, is controlled by electronic and steric effects. Thus, with both primary (PhSiH$_3$) and secondary silanes

Scheme 11.

1L7
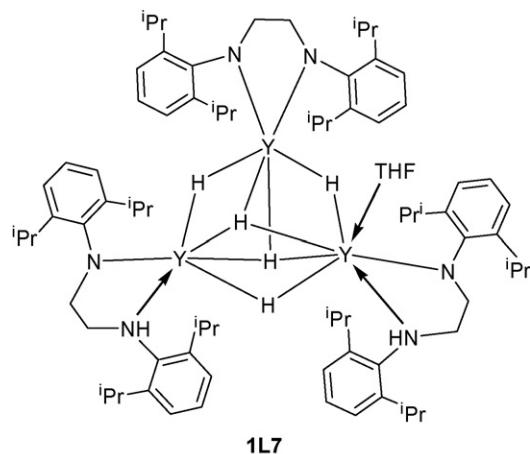
Scheme 12.

(PhMeSiH$_2$) aliphatic olefins such as ethylene or hex-1-ene gave over 90% of the terminal 1,2-addition product, whereas styrene gave benzylsilane derivatives (64–76%). The electronic interactions between yttrium and the aromatic ring, which direct the insertion reaction toward the α-phenylalkyl intermediate, may account for this 2,1-addition to styrene [28]. Furthermore, in the reaction with styrene the secondary silane favors the terminal addition products more than does the primary silane. Independently of the silane used no reaction was observed with cyclohexene, α-methylstyrene and *trans*-1,2-diphenylethene. Turnover numbers for hex-1-ene are comparable to those reported for d^0 metallocene-based catalysts. Norbornene could be enantioselectively hydrosilylated to *exo*-diastereomer with 90% ee in favour of the (1*S*)-enantiomer. The proposed mechanism is analogous to that generally accepted for other d^0 systems and consists of two steps: (a) fast, irreversible insertion of olefin into the metal-hydrogen bond to give an alkyl complex and (b) rate-determining transfer of an alkyl group to a silane with regeneration of the yttrium hydride complex [27].

In 2004 Cloke et al. reported an yttrium hydride complex with a chelating diamide ligand $\{ArN(CH_2)_2NAr\}^{2-}$ (Ar = C$_6$H$_3$^{i}Pr$_2$-2,6) of the type [Ln(LX)$_2$H][Ln(L$_2$X)H$_2$]$_2$. This complex was isolated via hydrogenolysis of the *in situ* generated alkyl complex [Y$\{ArN(CH_2)_2NAr\}\{CH(SiMe_3)_2\}$(THF)] in 9% yield [25]. An X-ray crystal structure analysis revealed the amido-amine complex [Y$_3$$\{ArNH(CH_2)_2NAr\}_2\{ArN(CH_2)_2NAr\}$(μ-H)$_3$(μ$_3$-H)$_2$(THF)] (**1L7**) with three different yttrium centers and an unusual mixture of bridging and face-capping hydrides as shown in Scheme 12. However, in C$_6$D$_6$ solution only the dimeric species [Y$\{ArN(CH_2)_2NAr\}$(μ-H)(THF)$_n$]$_2$ (**2L7**) was observed. The complex was not found to revert to the dimeric form from the amido-amine structure revealed by X-ray crystallography and this conventional dimeric hydride is considered to be a major component of the mixture. Interestingly, reaction of [Y$\{ArN(CH_2)_xNAr\}\{CH(SiMe_3)_2\}$(THF)] (*x* = 2, 3) with phenylsilane resulted in the unusual substitution of yttrium by silicon to form the organosilanes, Si$\{CH(SiMe_3)_2\}$PhH$_2$ and diamide, Si$\{ArN(CH_2)_xNAr\}$PhH (*x* = 2, 3).

3.2. Bis(phenolates)

Another alternative non-metallocene ancillary ligands to stabilize hydride complexes of lanthanides are bis(phenolate) ligands with an OSO or OSSO framework, which were investigated by our group. [26]. Thus, lutetium alkyl complexes [LuL(CH$_2$SiMe$_3$)(THF)$_n$] (L = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolate) (tbmp), *n* = 2; 1,4-dithiabutanediyl-bis(6-*tert*-butyl-4-methylphenolate) (etbmp), *n* = 1) were found to react smoothly at r.t. with PhSiH$_3$ to form the corresponding hydride complexes [LuL(μ-H)(THF)$_n$]$_2$ (L = tbmp **1L8**; etbmp **1L9**) of the [Ln(L$_n$X)H]-type (Scheme 13). Complex **1L9** with 1,4-dithiabutanediyl-bridged ligand could also be prepared in 83% yield from [Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$] in a one-pot procedure. A dimeric form of **1L8** in the solid state was revealed by an X-ray diffraction analysis. According to the ^{1}H NMR spectra two phenyl groups of the bis(phenolate) ligands were found to be symmetrical and only the fluxionality of the ethylene bridge in **1L9** was frozen out on the NMR time scale.

The reactivity of lutetium hydride complexes **1L8** and **1L9** resembles that of benzamidinato hydride complexes **1L1**–**3L1**, where the dominant pathway is insertion into the Ln−H bond (Scheme 14). Reactions with benzophenone and pyridine led to formation of the insertion products, [Lu(tbmp)(OCHPh$_2$)(THF)$_3$] and [Lu(etbmp)(NC$_5$H$_6$)(NC$_5$H$_5$)], respectively. However, no reaction with diphenylacetylene was observed. Moreover, no evidence was found for a dissociation process and for H/D scrambling with D$_2$. Reaction of **1L8** with phenylacetylene led to the corresponding acetylide complex [Lu(tbmp)(CCPh)(THF)$_2$]. On the other hand, styrene was found to react regioselectively yielding the 2-phenylethyl complex [Lu(etbmp)$\{CH(Ph)CH_3\}$(THF)], as revealed by ^{1}H and ^{13}C NMR spectroscopy. The catalytic potential of the hydride complex **1L9** was tested in a hydrosilylation reaction. Thus, monitoring the reaction of hex-1-ene with PhSiH$_3$ in C$_6$D$_6$ at 25 °C in the presence of **1L9** ([Lu]$_0$/[PhSiH$_3$]$_0$/[Alk]$_0$ = 1:20:20) revealed formation of the *anti*-Markovnikov product, PhSiH$_2$(CH$_2$)$_5$CH$_3$, with 81% conversion after 4 days and with 98% selectivity. At 60 °C conversion of 82% with maintained high selectivity could be achieved after 21 h [26].

4. Spectroscopic and structural features of the hydride complexes

As shown in Table 1, the hydride resonances for the yttrium hydride complexes **1L1**, **2L1**, **2L2**, **1L4**, **1L5**, **1L6**, **2L7** were observed in the ^{1}H NMR spectra as a triplet, thus indicating a dimeric structure in solution. The coupling constants are similar to those observed for other dimeric yttrium hydrides (see Table 1). The hydride resonances are low-field shifted (5.9–8.3 ppm) in comparison with those for the yttrium hydrides **A**–**D** with cyclopentadienyl ligands (2.0–5.5 ppm). Analogous observation has been made for lutetium complexes (5.9–9.9 ppm for cyclopentadienyl(Cp)-stabilized complexes **E**–**G** versus
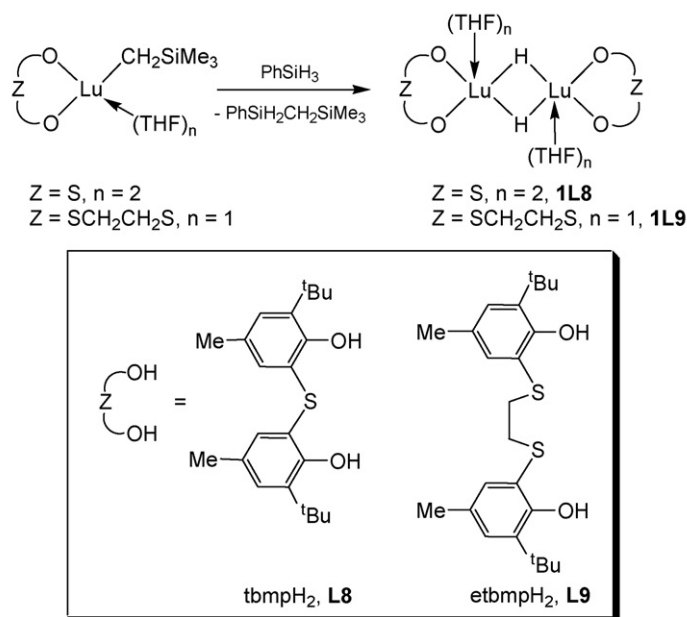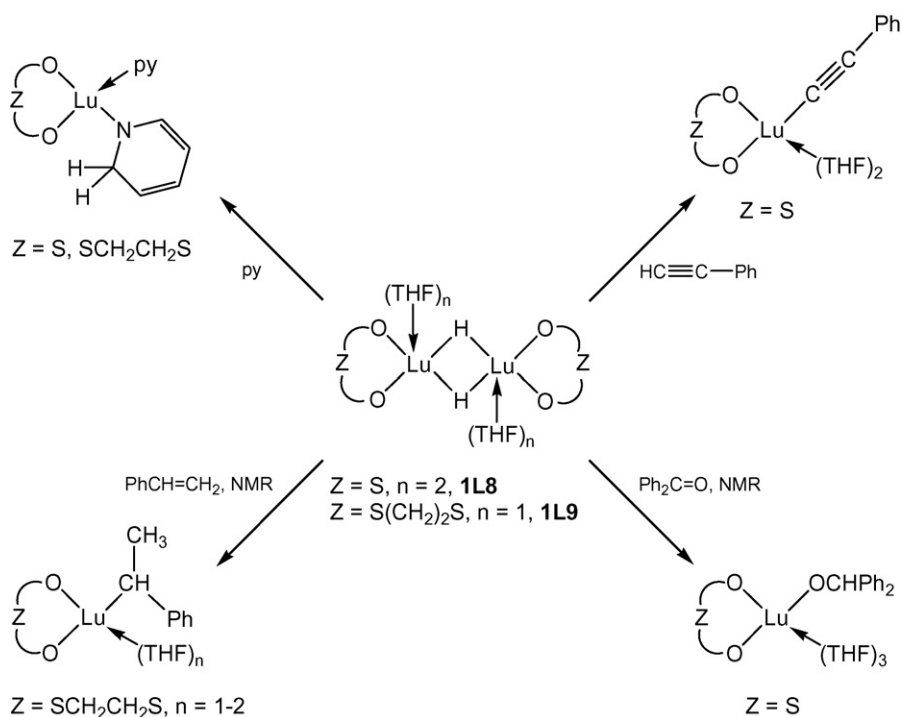
Scheme 13.

11.3–13.0 for complexes **1L2**, **1L8**, **1L9**). Compared to Cp-containing hydrides, this greater low-field shift of the hydride resonances for the complexes with electron-withdrawing benzamidinate, guanidinate or salicylaldiminate ligand framework reflects a strong ionic component of a metal-ligand bonding.

The crystallographic features of the non-metallocene hydride complexes of lanthanides are summarized in Table 2.

All the structures reveal a dimeric form of hydride complexes in the solid state. Generally, the central atom adopts a distorted octahedral or prismatic coordination geometry with two bridging hydrido ligands co-planar with two lanthanide atoms as it is exemplified in Fig. 2 for the lutetium hydride complex **1L8**.

Interesting structural features have been observed in a series of hydride complexes with two guanidinate ligands, $[\text{Ln}\{(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^i\text{Pr})_2\}_2(\mu\text{-H})]_2$ [12]. While in the lutetium

Scheme 14.

Table 1
Selected ^{1}H NMR spectroscopic data of yttrium and lutetium hydride complexes

	Complex	Solvent	δ Ln−H (ppm)	$^1J_{YH}$ (Hz)	Ref.
1L1	[Y{PhC(NSiMe$_3$)$_2$}$_2$(μ-H)]$_2$	C$_6$D$_6$	8.28, t	27.6	[11b]
2L1	[Y{p-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$}$_2$(μ-H)]$_2$	C$_6$D$_6$	8.31, t	27.8	[11b]
1L2	[Lu{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$	C$_6$D$_6$	12.96, s	−	[12a]
2L2	[Y{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$	C$_6$D$_6$	7.95, t	26.0	[12b]
1L4	[Y{Me$_2$Si(N^{t}Bu)(O^{t}Bu)}$_2$(μ-H)]$_2$	THF-d_8	6.80, t	31.0	[15]
1L5	[YL$_2$(μ-H)]$_2$[a]	C$_6$D$_5$CD$_3$	7.54, t	32.0	[16]
1L6	[Y(DADMB)(μ-H)(THF)]$_2$	THF-d_8	5.88, t	28.0	[24]
2L7	[Y{ArN(CH$_2$)$_2$NAr}(μ-H)(THF)$_n$]$_2$[b]	C$_6$D$_6$	5.91, t	28.0	[25]
1L8	[Lu(tbmp)(μ-H)(THF)$_2$]$_2$	THF-d_8	11.29, s	−	[26]
1L9	[Lu(etbmp)(μ-H)(THF)$_2$]$_2$	THF-d_8	11.41, s	−	[26]
A	[Y(^{t}BuC$_5$H$_4$)$_2$(μ-H)]$_2$	C$_6$D$_6$	3.09, t	32.8	[7b]
B	[YCp$_2$(THF)(μ-H)]$_2$	THF-d_8	2.02, t	27.0	[7a]
C	[Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(THF)(μ-H)]$_2$	C$_6$D$_5$CD$_3$	5.50, t	26.8	[29]
D	[Y{Et$_2$Si(η^5-C$_5$H$_4$)(η^5-C$_5$Me$_4$)}(μ-H)]$_2$	C$_6$D$_6$	3.03, t	35.3	[19]
E	[Lu(^{t}BuC$_5$H$_4$)$_2$(μ-H)]$_2$	C$_6$D$_6$	5.91, s	−	[7b]
F	[Lu{Et$_2$Si(η^5-C$_5$H$_4$)(η^5-C$_5$Me$_4$)}(μ-H)]$_2$	C$_6$D$_5$CD$_3$	5.87, s	−	[19]
G	[Lu(η^5:η^1-C$_5$Me$_4$SiMe$_2$N^{t}Bu)(THF)(μ-H)]$_2$	C$_6$D$_5$CD$_3$	9.90, s	−	[30]

[a] L = (2-^{t}BuC$_6$H$_3$O)HC=N(2,6-^{i}PrC$_6$H$_3$).
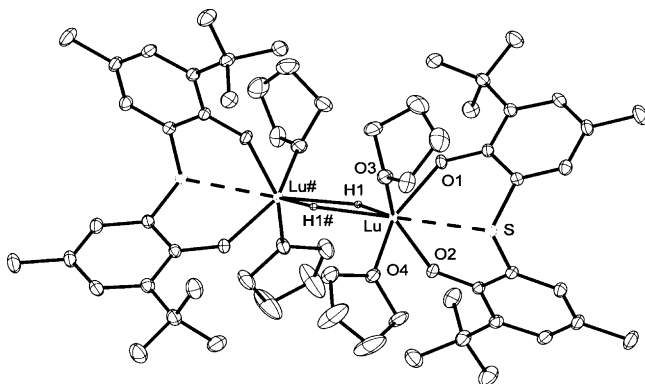[b] Ar = C$_6$H$_3$^{i}Pr$_2$-2,6.

Fig. 2. Molecular structure of **1L8** shown with 40% thermal ellipsoids. Hydrogen atoms except for the bridging ones have been omitted for clarity [26].

complex **1L2** both {(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$} ligands were found to be equivalent (Y−N, 2.349(2) and 2.365(2) Å), the crystal structure of the yttrium analogue, [Y{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$ (**2L2**) showed substantial difference of the Y−N bond

lengths for both moieties (2.304(3), 2.315(3) Å versus 2.266(3), 2.372(5) Å). Furthermore, these complexes can be divided into two groups, according to the mutual orientation of the Ln{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$ moieties in the dimer. For smaller lanthanides such as Lu (**1L2**), Y (**2L2**) and Yb (**6L2**) the planes defined by the centroid carbon atoms of two guanidinate ligands and the metal atom are nearly orthogonal (dihedral angle ca. 87°), resulting in a staggered conformation. On the other hand, with larger atoms (Nd, **3L2**; Sm, **4L2**; Gd, **5L2**) co-planarity of both planes can be observed (dihedral angle ca. 7.6°) and the dimers adopt an eclipsed conformation.

In the case of the salicylaldimine hydride complex **1L5** the two O−Y−O vectors are twisted relative to each other by approx. 30–40° in order to minimize unfavorable steric interactions between opposing ^{i}Pr and ^{t}Bu groups of the ligand [16].

An X-ray crystal structure analysis of the amido-amine complex [Y$_3${ArNH(CH$_2$)$_2$NAr}$_2${ArN(CH$_2$)$_2$NAr}(μ-H)$_3$(μ$_3$-H)$_2$(THF)] (**1L7**) reveals that three bridging hydrides are located at alternate apices of a Y−H hexagon, while two other μ$_3$-bridging hydrides cap opposite faces of the hexagon.

Table 2
Comparison of structurally characterized non-metallocene hydride complexes of lanthanides

	Complex	Ln−H (Å)	Ln−Ln (Å)	Ref.
1L1	[Y{PhC(NSiMe$_3$)$_2$}$_2$(μ-H)]$_2$	2.11(3), 2.16(3), 2.19(3), 2.17(3)	3.565	[11b]
3L1	[Sc{PhC(NSiMe$_3$)$_2$}$_2$(μ-H)]$_2$	1.92(3), 1.87(3), 2.00(3), 1.98(3)	3.30	[11d]
1L2	[Lu{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$	2.12(4) 2.03(4)	3.58	[12a]
2L2	[Y{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$	2.15(3) 2.50(4)	3.68	[12b]
4L2	[Sm{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$	2.33(2), 2.40(2), 2.40(2), 2.31(2)	3.81	[12b]
5L2	[Gd{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$	2.53(2), 2.60(2), 2.57(2), 2.54(2)	3.81	[12b]
6L2	[Yb{(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$}$_2$(μ-H)]$_2$	2.15(3) 2.14(3)	3.60	[12b]
1L5	[YL$_2$(μ-H)]$_2$[a]	2.11(3), 2.16(2), 2.25(3), 2.17(3)	3.63	[16]
1L6	[Y(DADMB)(μ-H)(THF)]$_2$	2.27(4) 2.22(4)	3.66	[24]
1L7	[Y$_3${ArNH(CH$_2$)$_2$NAr}$_2${ArN(CH$_2$)$_2$NAr}(μ-H)$_3$(μ$_3$-H)$_2$(THF)][b]	1.94(12)–2.39(8)	−	[25]
1L8	[Lu(tbmp)(μ-H)(THF)$_2$]$_2$	2.09(3)	3.55	[26]

[a] L = (2-^{t}BuC$_6$H$_3$O)HC=N(2,6-^{i}PrC$_6$H$_3$).
[b] Ar = C$_6$H$_3$^{i}Pr$_2$-2,6.
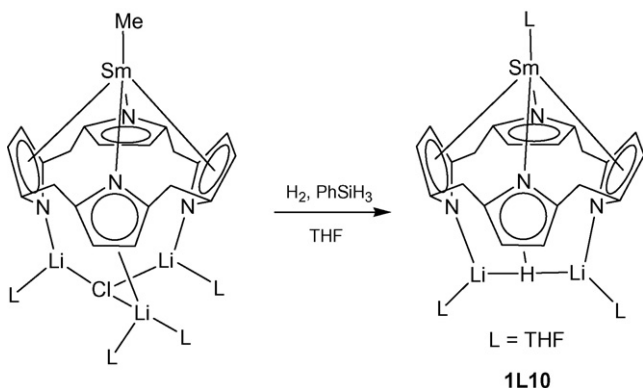
Scheme 15. Ethyl groups attached to the ring have been omitted for clarity.

There is a considerable asymmetry about the face-capping hydrides (Y−H: 1.94(12)–2.39(8) Å). The bond distances for the other three hydrides range from 1.98(6) to 2.18(6) Å [25].

5. Other ligands

5.1. Calix-tetrapyrroles

In 2000 Gambarotta et al. utilized the calix-tetrapyrrole ligand as an alternative to Cp-based ligands for stabilizing samarium alkyl and hydride complexes [31]. Reaction of [(Et$_8$-calix-pyrrole)SmMe(μ_3-Cl){Li(THF)}$_2${Li(THF)$_2$}] with H$_2$ or PhSiH$_3$ in THF at r.t. rapidly led to formation of the hydride complex [(Et$_8$-calix-pyrrole)Sm(μ-H)(THF){Li(THF)}$_2$]·3THF (**1L10**) (Scheme 15). This complex could also be synthesized from [(Et$_8$-calix-pyrrole)SmCl{Li$_2$(THF)$_3$}] with either LiAlH$_4$ or NaBEt$_3$H. The formation of the hydride was confirmed by ^{1}H NMR spectroscopy, showing a very broad resonance at 7.91 ppm that was absent in the spectrum of the deuteride analogue. An X-ray crystal structure analysis revealed a hydride in the middle of

the SmLi$_2$ triangle and placed coaxial to the Sm−O$_{THF}$ vector. The Sm−H distance of 2.25(7) Å is in the range of bond lengths reported for other hydrido-bridged lanthanide complexes (see Table 2).

As far as the reactivity of **1L10** is concerned, no exchange with D$_2$ was observed. However, it reacts rapidly with ethylene at r.t. with unusual σ-bond metathesis reaction to form a vinyl derivative. The formation of vinyl species has been also reported by Bercaw et al. in the reaction of [ScCp$_2^*$CH$_3$] with *para*-substituted styrenes [6f]. Noteworthy, isolation of the vinyl species was possible only when **1L10** was generated *in situ*, thus in the presence of LiCl as a reaction by-product.

The versatility of the calix-tetrapyrrole ligand is illustrated by the fact that it can also stabilize polynuclear samarium hydrides. The reaction of the dinuclear alkyl ate complex, [(Et$_8$-calix-pyrrole)Sm$_2${(μ-Me)$_2$Li(THF)$_2$}$_2$] with PhSiH$_3$ in THF resulted in a mixture of **1L10** and a minor amount (<10%) of [(Et$_8$-calix-pyrrole)Sm(μ-H)(THF)(μ-OCH=CH$_2$)$_2$Li$_4$(THF)$_2$] (**2L10**) (Scheme 16) [32]. The formation of two lithium enolate moieties Li(OCH=CH$_2$) is presumably due to the cleavage of THF, resulting from the attack on it by LiMe that is released during the reaction. Moreover, hydrogenolysis of the alkyl ate complex resulted in the exclusive formation of **1L10** and no formation of the enolate complex **2L10** was observed.

5.2. Dipyrrolides

A pyrrolide anion is electronically and sterically similar to a cyclopentadienyl anion. Gambarotta et al. studied the behavior of divalent samarium derivatives of diphenylmethyldipyrrolide dianion, structurally resembling the linked bis(cyclopentadienyl) ligand in an *ansa*-metallocene system. When the samarium precursor [{Ph$_2$C(C$_4$H$_3$N)$_2$}SmCl] was reduced with sodium in THF, the paramagnetic complex
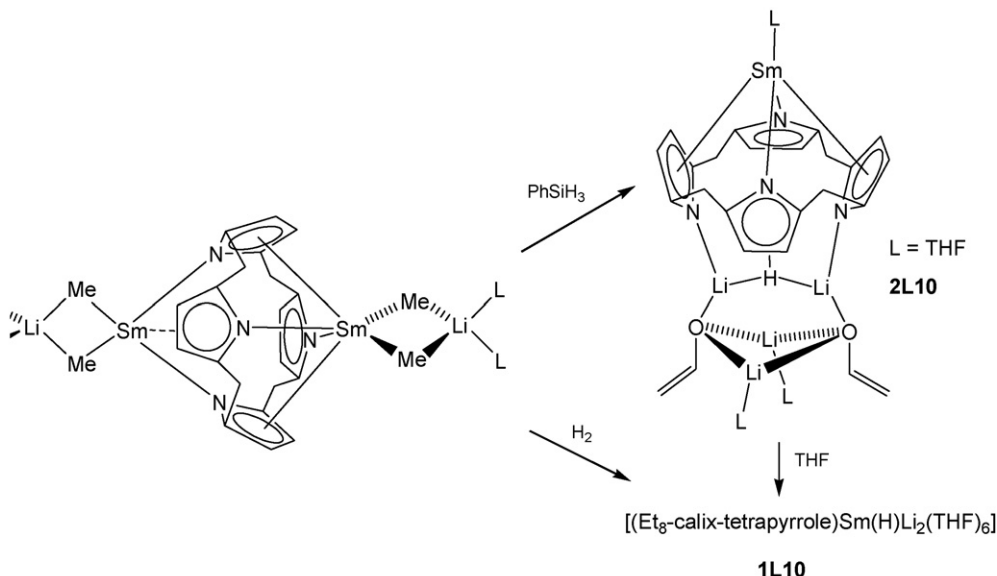
Scheme 16.
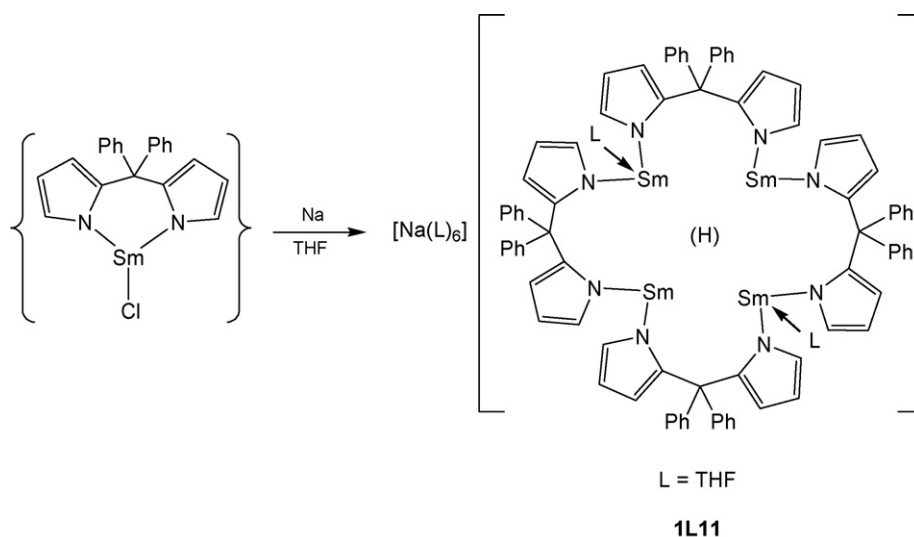
Scheme 17.

[Na(THF)$_6$]-[{Ph$_2$C(C$_4$H$_3$N)$_2$Sm}$_4$(H)(THF)$_2$] (**1L11**) could be isolated and identified by X-ray crystallography (Scheme 17) [33]. A broad peak at −3.91 ppm in the ^{1}H NMR spectrum was assigned to the hydride resonance. Upon H/D exchange in THF-d_8 this resonance was also detected in the ^{2}H NMR spectrum. The source of the hydride in this divalent tetrasamarium monohydride complex is believed to be resulting from THF cleavage.

5.3. Heterobimetallic hydride complexes

Mountford et al. reported the synthesis of mixed transition metal-ytterbium(II) hydride complexes of the formula [{W(PMe$_3$)$_3$H$_5$}$_2$Yb{(MeOCH$_2$CH$_2$)$_2$O}] (**1L12**) and [{Nb(η^5-C$_5$H$_5$)$_2$H$_2$}$_2$Yb{(MeOCH$_2$CH$_2$)$_2$O}] (**1L13**) [34a,b]. Both complexes were prepared from YbI$_2$ with K[W(PMe$_3$)$_3$H$_5$] and K[Nb(η^5-C$_5$H$_5$)$_2$H$_2$], respectively, and were characterized by X-ray crystallography. In the former case each tungsten center is bonded to ytterbium by three hydrogen atoms via two-electron three-center bonds, with possibly a small contribution from direct W−Yb interaction (av. W−Yb: 3.24 Å). However, on the basis of the structural and spectroscopic data an alternative formula with two bridging hydrides, *e.g.* [(PMe$_3$)$_3$H$_3$W(μ-H)$_2$Yb(μ-H)$_2$WH$_3$(PMe$_3$)$_3$], cannot be ruled out. Previously, related mixed metal complexes have been described for ytterbocene derivatives [34c].

5.4. Alkynyl-hydride complexes

In 1981 Evans et al. reported the first organolanthanide hydride complexes prepared by cocondensation of rare-earth metal vapors (Yb, Eu, Sm) and hex-1-yne at low temperatures [35]. For ytterbium divalent mixed alkynyl-hydride complexes of the formula [Yb(C≡C^{n}Bu)$_{1.5}$H$_{0.5}$]$_n$ (**1L14**) were postulated as the primary products, based on the analytical, magnetic, and chemical (quantitative protolytic and deuterolytic decomposition reactions) data. Alternative reac-

tion pathways such as α-CH$_2$ metallation and addition to the triple bond were found to be of minor importance. In the cases of samarium and erbium trivalent complexes were formed, with the formula represented as [Ln(C$_6$H$_9$)$_{2−x}$(C$_6$H$_8$)$_x$H$_{1−x}$]$_n$ (0 < x < 0.5) (Sm, **1L15**; Er, **1L16**), showing the increased amount of dimetallation. The latter two alkynyl-hydride complexes were found to catalyze hydrogenation of hex-3-yne to form *cis*-hex-3-ene (>96%), however, the reaction rates were low.

5.5. "Ligand-free" hydride complexes

Reaction of the ytterbium naphthalene complex [Yb(C$_{10}$H$_8$)(THF)$_3$] with dihydrogen was reported by Bochkarev et al. to yield the molecular dihydride complex, [YbH$_2$(THF)]$_n$ [36]. The analogous reaction with Ph$_3$GeH gives [Yb(Ph$_3$Ge)$_2$(THF)$_4$] as revealed by X-ray crystallographic studies. However, both structure and bonding mode remain obscure and either the existence of μ$_2$-hydride ligands, a formally zerovalent ytterbium and the absence of direct Yb−Ge bonds or a three-center two-electron bond with divalent ytterbium is possible. The analogous molecular dihydrides of divalent samarium and europium synthesized by hydrogenolysis of the corresponding naphthalene and stilbene complexes were also reported [37]. Both hydrides were found to react readily with Et$_3$GeBr in THF to give Et$_3$GeH, small amounts of Et$_3$GeGeEt$_3$ (<10%) and LnBr$_2$(THF)$_2$ (Ln = Sm, Eu). Molecular hydrides of ytterbium, samarium and europium were reported to exhibit high activity in styrene polymerization, yielding PS with high molecular weights (1.5×10^5 to 1×10^6) [38].

6. Conclusion

The present article indicates that the area of non-metallocene hydride complexes of the rare-earth metals leaves space for further development in the near future. As synthetic method using

σ-bond metathesis of the alkyl complex without any stabilizing cyclopentadienyl ligand has now been well established, the introduction of newly designed ligands is "reduced" to synthesizing the starting alkyl complex precursors in the most efficient way.

The first systematic trend recognizable at this early stage of development relates to the dinuclear monohydride complexes of the type $[Ln(L_nX)_2H]_2$ that contain either two monoanionic L_nX-type ligands or one chelating dianionic ligand of the $(L_nX)_2$-type (Fig. 1). At this time no example for a dihydride complex that contains only one monoanionic ligand $[Ln(L_nX)H_2]$ has been reported, not to mention a neutral trihydride complex that only contains a neutral ligand $[Ln(L_n)H_3]$. Both types can be expected to be highly aggregated and to exhibit interesting "cluster" structures. Another family entirely unknown is that of cationic hydride complexes. Molecular hydride complexes of the rare-earth metals are expected to attract attention in the near future. Not only do they form a link to the interstitial hydride compounds $[LnH_n]$ ($n = 2, 3$) of interest as hydrogen storage material, but they may show new reactivity patterns hitherto unknown for the well-established metallocene hydride complexes. Already, discrete hydride complexes within a non-metallocene framework have occasionally been implied as active intermediates during ethylene polymerization [39]. In general, it appears at this early stage that non-metallocene hydride complexe with relatively hard donors in the ancillary ligand tend to be less susceptible to σ-bond metathesis and comparable to metallocene complexes of the type $[Ln(\eta^5-C_5H_4R')_2H]_2$ (R' = H, Me) [7] rather than the permethylmetallocene systems $[Ln(\eta^5-C_5Me_5)_2H]_2$ [6].

Acknowledgment

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