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Journal of Organometallic Chemistry 609 (2000) 21–28

Journal of Organometallic Chemistry

Early lanthanide organometallic hydrides: electronic and steric control of the stability

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Received 19 February 2000; received in revised form 16 April 2000

Abstract

Steric and electronic effects on the stability of early lanthanide, neodymium and samarium, organometallic hydrides are discussed. The instability of $(\text{tmp})_2\text{SmH}$ (tmp = tetramethylphospholyl) is attributed to electronic factors and the low stability of $(^t\text{BuC}_5\text{H}_4)_2\text{SmH}$ is related to steric reasons. The analogous neodymium hydride $(^t\text{BuC}_5\text{H}_4)_2\text{NdH}$, could not be obtained, whereas the more hindered triethylborohydride was formed. Access to bisphospholyl bridged heterobimetallic ruthenium–lanthanide hydrides is also related to the size of the lanthanide atom. The bimetallic structures are accessible for lanthanides of ionic radii smaller than 1 Å. The role of organometallic hydrides versus alkyls as catalysts for olefin or diene polymerization is discussed, a first and unique example of hex-1-ene and isoprene copolymerization is presented.

Keywords: Rare earth; Lanthanide; Hydride; Heterobimetallic; Neodymium; Samarium

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1. Introduction

Hydrides and polyhydrides of the d-transition metals have been isolated and characterized for more than 20 years [1]. The stability of the metal–hydrogen bond and the facile insertion of unsaturated molecules into this bond make these complexes the cornerstones in a great number of stoichiometric or catalytic reactions. An important step in the knowledge of the structure and the reactivity of these complexes was the discovery of non-classical hydrides [2].

Conversely, a relatively small number of organometallic rare earth hydrides have been synthesized; the known isolated hydrides were described in a recent well documented review [3]. Our objective was not to synthesize new stable hydrides, but to determine the accessibility to hydrides of the early lanthanides for catalytic use. Among the early lanthanides, the paramagnetic, but suitable for NMR studies, samarium and neodymium were chosen. These hydrides were obtained from precursors bearing non sterically demanding ligands or poor electron donating ligands. It was also of interest to establish, if for further applications, the use of the hydrides was the best choice, compared to the alkyl derivatives. This work was published in a series of papers [4], each one concerning a particular point; we give here a general presentation and try to determine the new trends of this chemistry. We discuss the identification of the hydride function, the access to undercoordinated hydrides and to bimetallic hydrides, the use of the hydrides in diene polymerization catalysis.

2. Characterization of the hydride function

The chemical behavior of the lanthanides is closely related to their ionic radii. The isolated hydrides of the large early lanthanides are stabilized by bulky and electron-donating ligands, pentamethylcyclopentadienyl (Cp*) [5] and related rings, indenyl [6] or tetramethylphospholyl [4g]; these bulky ligands preclude the rearrangement into triscyclopentadienyl derivatives. Few examples of sterically less hindered substituted cyclopentadienyls were reported [7]. By the yttrium derivatives, the medium size of the yttrium atom allows

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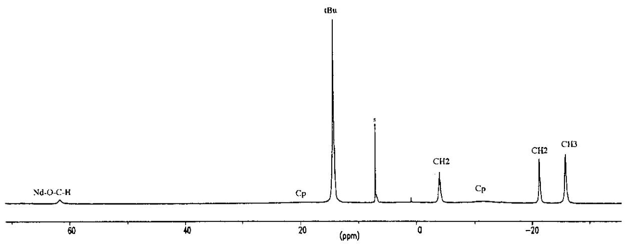
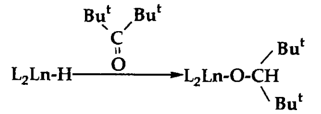


Fig. 1. ^{1}H-NMR (C_6D_6) spectrum of $(C_5H_4(CH_2)_2OCH_3)_2$-$NdOCH(^tBu)_2$ obtained by trapping the transient hydride formed by hydrogenolysis of $(C_5H_4(CH_2)_2OCH_3)_2NdCH(SiMe_3)_2$.

the use of non-bulky ligands [8]. For the smaller late lanthanides, cyclopentadienyl hydrides generally stabilized by ancillary ligands can be isolated [9]. Nowadays the synthesis of lanthanide hydrides is not a challenge, as at the end of the seventies, but the hydride function remains difficult to characterize.

IR spectroscopy: the stretching Ln–H band is located in the range 1100–1300 cm^{-1}. Many peaks appear in this range and identification of Ln–H needs the H/D substitution, the shift of the Ln–D peak at a lower frequency allowing the attribution [1b,5b].

NMR spectroscopy: the ^{1}H chemical shifts of the M–H signal of late d transition metals are frequently recorded far upfield versus TMS whereas for the early transition metals, the M–H signals are generally located in the range 2–9 ppm. The hydrido signals of the diamagnetic lanthanides also appear in this range [3]. Most of the available data concern yttrium (Y–H coupling permits an easy identification of the signal) [9] and to a less extent, lutetium complexes [5b]. Very few results are reported for lanthanum [5b] and scandium derivatives [10]. Concerning the paramagnetic hydrides, only one Ce–H [11] and two Sm–H broad signals were reported [5a,12]. It is frequently assumed that the broadening of the H signal does not permit its location [5b]. Thus, an alternative and definite way to underscore the hydrido function is the chemical reactivity. Moreover, this offers the great advantage of working in solution and means one does not need to obtain the pure hydride but can check for the presence of the hydride in the reaction medium. Reactions with alcohols, or carbon tetrachloride have been used, but the more convincing reaction consists in trapping the hydride with a sterically hindered ketone, unable to react with alkyllanthanides [4b,e,h,13] (Eq. (1))



$$L_2Ln\text{-}H \xrightarrow{Bu^t_2C=O} L_2Ln\text{-}O\text{-}CH(Bu^t)_2 \quad (1)$$

The alkoxide thus obtained is easily evidenced by NMR which reveals, under the LnOC–H form, the presence of the previously undetected LnH (Fig. 1).

In the same way, it is also possible to trap the hydride by a borane (Eq. (2)), the new compound giving well defined ^{1}H or ^{11}B signals [4e,h,14] (Fig. 2).

$$L_2Ln\text{-}H \xrightarrow{BR_3} L_2Ln\text{-}H\text{-}BR_3 \quad R = H, BEt_3, B(C_6F_5)_3 \quad (2)$$

3. Factors of stability, access to under-coordinated hydrides

The large ionic radius of the lanthanides, from 0.85 (Lu) to 1.10 Å (La), and the very small size of the hydride ligand are important destabilizing factors. A ligand redistribution reaction of biscyclopentadienyl hydrides is frequently observed. The Cp^*_2LnH complexes

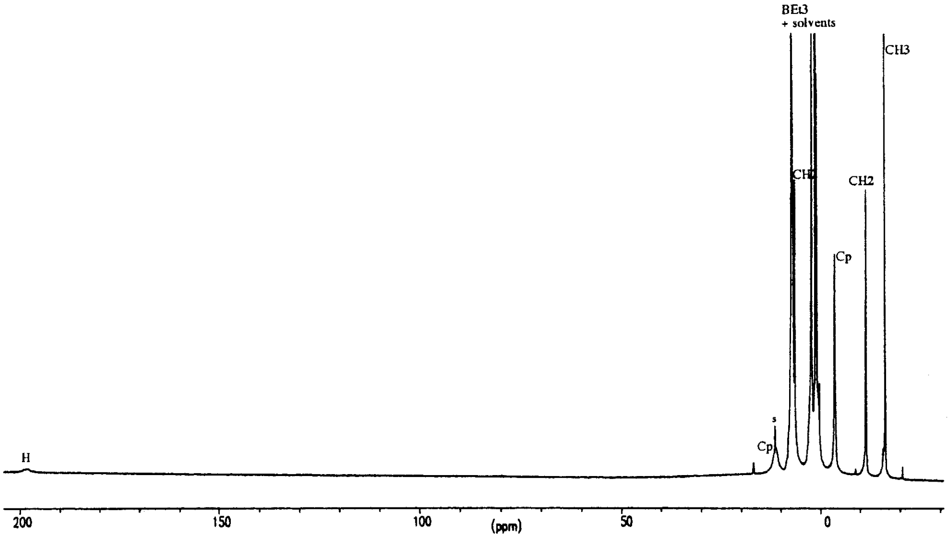
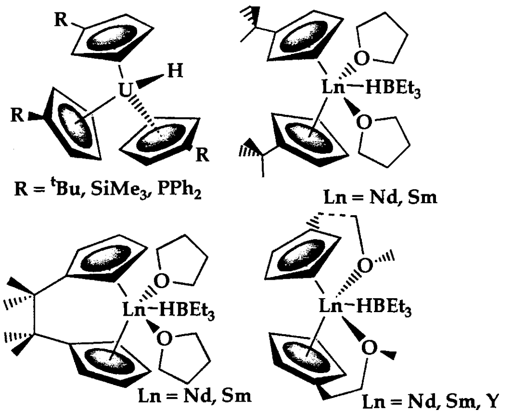


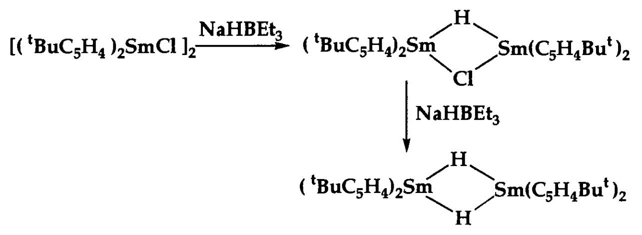
Fig. 2. ^{1}H-NMR spectrum (C_6D_6) of $(C_5H_4(CH_2)_2OCH_3)_2NdHBEt_3$ showing the Nd–H–B signal at 198 ppm.



Scheme 1.

Table 1
Chemical shifts of Ln–BH$_4$ and Ln–H–BEt$_3$ signals

Compound	δX = BH$_4$	δX = H–BEt$_3$
$Nd(BH_4)_3(THF)_3$	99	
$(C_5H_4(CH_2)_2OCH_3)_2NdX$	74	198
$({}^t\mathrm{BuC_5H_4})_2NdX(THF)_n$	90	210
$[C_5H_4(CMe_2)]_2NdX\ (THF)_n$	91	270
$Sm(BH_4)_3(THF)_3$	−10	–
$({}^t\mathrm{BuC_5H_4})_2SmX(THF)_n$	−8	−20
$[C_5H_4(CMe_2)]_2SmX(THF)_n$	−7	−23
$(C_5H_4(CH_2)_2OCH_3)_2SmX$	–	−23.4
$(C_5H_4(CH_2)_2OCH_3)_2YHBEt_3$	–	−0.56



Scheme 2.

are isolated under a dimeric form; in the presence of ancillary THF ligands a monomeric adduct is obtained for scandium [15] and yttrium only [9b]. For complexes of yttrium and of the late lanthanides [9,16] containing less sterically cyclopentadienyl or monosubstituted cyclopentadienyl ligands, the presence of ether groups allows one to obtain dimeric hydrides. Dimeric stable hydrides of the late lanthanides are also obtained, without ancillary ligands, by using mono substituted cyclopentadienyl ligands [17].

In order to establish if early lanthanide hydrides with mono substituted Cp ligand could be obtained or evidenced, we tried to synthesize samarium and neodymium hydrides from dimeric $[({}^t\mathrm{BuC_5H_4})_2LnCl]_2$ [18], $[C_5H_4(CMe_2)]_2LnCl(THF)]_2$ [19] and monomeric in the solid state $(C_5H_4(CH_2)_2OCH_3)_2LnCl$ [20], by reaction with hydride reagent or by hydrogenolysis of the corresponding alkyls.

3.1. Reactions with hydridic reagents

As hydride reagent, we tested the inorganic NaH, because it led to the formation of the structurally characterized yttrium hydride [16]. Different commercially available samples of NaH were used, the rearrangement into triscyclopentadienyl species was invariably observed (Eq. (3)).

$$(C_5H_4(CH_2)_2OCH_3)_2NdCl \xrightarrow[50°,\ 7\ \mathrm{days}]{\mathrm{NaH,\ THF}} (C_5H_4(CH_2)_2OCH_3)_3Nd \tag{3}$$

Soluble NaHBEt$_3$, commonly used in uranium chemistry to obtain hydrides [21] also reacted with lanthanide chlorides, but the results were quite different. For the lanthanides, harder Lewis acids than uranium, triethylborane was not released; a series of hydridotrialkylborane could be obtained [4b] (Scheme 1). The formation of the Ln–H–B species was evidenced by NMR. It is noteworthy that the Nd–H signal, which has never been reported, could be attributed unambiguously for these new hydrides. The Sm–H signal was recorded in the same range but at a significantly higher field than the corresponding borohydride signal. Table 1 reports on the chemical shifts of triethylborohydrides compared to analogous borohydrides.

In one case, in the absence of ancillary ligand, from the unsolvated dimer $[({}^t\mathrm{BuC_5H_4})_2SmCl]_2$, the formation of the dimeric hydride $[({}^t\mathrm{BuC_5H_4})_2SmH]_2$ was observed with triethylborane elimination. In this reaction, an intermediate could be characterized: after addition of one equivalent of hydride reagent, the hydridochloro bridged dimer was formed [4e] (Scheme 2).

In solution, this dimeric hydride was moderately stable. It was not possible to increase its stability significantly by coordinating phosphine or ether ligand. This led to the formation of less stable monomeric forms which invariably rearranged into the tris $({}^t\mathrm{BuC_5H_4})_3Sm$.

The crude solutions of neodymium complexes were pumped off to eliminate the volatiles and the results were different, as a function of the nature of the ether moiety and of the ease of redistribution reaction. From $({}^t\mathrm{BuC_5H_4})_2NdHBEt_3(THF)_2$, only $({}^t\mathrm{BuC_5H_4})_3Nd$ was obtained. From $(C_5H_4(CH_2)_2OCH_3)_2NdHBEt_3$, stabilized by intramolecular chelation, only 30% of $(C_5H_4(CH_2)_2OCH_3)_3Nd$ were formed whereas the *ansa* derivative $[(C_5H_4CMe_2]NdHBEt_3(THF)_2$ remained quite unchanged. Therefore, the dimeric hydride $[({}^t\mathrm{BuC_5H_4})_2NdH]_2$ was never observed.

3.2. Alkyl precursors, hydrogenolysis experiments

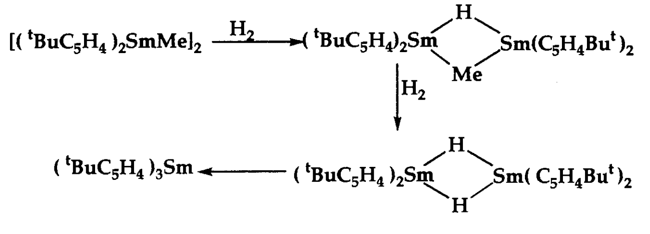
Hydrogenolysis of monomeric or dimeric lanthanide alkyls is the classical way to synthesize lanthanide hydrides. Hydrogenolysis generally takes place under atmospheric pressure of hydrogen and at room temperature (r.t.). The 'limiting step' is the synthesis of such alkyls. Unsolvated dimeric methyl compounds $[(^t\mathrm{BuC_5H_4})_2\mathrm{SmMe}]_2$ [4e] and $[(^t\mathrm{BuC_5H_4})_2\mathrm{NdMe}]_2$ [22] were available. By using bulky ligands such as $\mathrm{CH(SiMe_3)_2}$, one can expect the formation of monomeric species [9]. The $(^t\mathrm{BuC_5H_4})_2\mathrm{LnCH(SiMe_3)_2}$, Ln = Sm, Nd obtained in solution from the corresponding halides and $\mathrm{LiCH(SiMe_3)_2}$ was verified by NMR. But, after the usual work-up to isolate solid compounds, only the tris derivatives were obtained. As a consequence, hydrogenolyses were performed from $(^t\mathrm{BuC_5H_4})_2\mathrm{LnCH(SiMe_3)_2}$ made in situ.

Surprisingly, no stable compounds could be obtained with $\mathrm{CH_2SiMe_3Li}$. The presence of an additional ancillary ligand, $\mathrm{PMe_3}$, was necessary to obtain the alkyl complex $(^t\mathrm{BuC_5H_4})_2\mathrm{Sm(CH_2SiMe_3)(PMe_3)}$ in solution. The size of $\mathrm{CH_2SiMe_3}$ is intermediate between Me and $\mathrm{CH(SiMe_3)_2}$. Therefore, this group does not authorize the isolation of neither a monomeric nor a dimeric complex.

The dimeric methyl compounds reacted slowly with dihydrogen at r.t. and atmospheric pressure. $[(^t\mathrm{BuC_5H_4})_2\mathrm{SmMe}]_2$ led within 1 week to a small amount of the dimeric hydride and as the major product, to the mixed alkyl hydride (Scheme 3). In the same conditions, the reaction of $[(^t\mathrm{BuC_5H_4})_2\mathrm{NdMe}]_2$ run faster (48 h) but led to the formation of $(^t\mathrm{BuC_5H_4})_3\mathrm{Nd}$ only.

After addition of THF as additional ancillary ligand, the formation of a more reactive monomeric alkyl complex was expected. In fact, in the presence of THF $(^t\mathrm{BuC_5H_4})_2\mathrm{NdMe}]_2$ was found unstable and rearranged to the tris derivative $(^t\mathrm{BuC_5H_4})_3\mathrm{Nd}$.

The samarium analogue was stable in the same conditions, but no hydrogenolysis took place. The monomeric alkyls reacted smoothly at r.t. with dihydrogen. From the samarium complex, the formation of $[(^t\mathrm{BuC_5H_4})_2\mathrm{SmH}]_2$ (ca 30% yield) occurred within 6 h. Consumption of the starting material was complete after 2 days, but the initially formed hydride rearranged to finally give $(^t\mathrm{BuC_5H_4})_3\mathrm{Sm}$. The phosphine adduct of the hydride: $(^t\mathrm{BuC_5H_4})_2\mathrm{SmH(PMe_3)_2}$ was formed within 6 h in good yield (85–95%) indifferently from $(^t\mathrm{BuC_5H_4})_2\mathrm{Sm(CH_2SiMe_3)(PMe_3)}$ alone or from $(^t\mathrm{BuC_5H_4})_2\mathrm{LnCH(SiMe_3)_2}$ in the presence of $\mathrm{PMe_3}$.


Scheme 3.

Attempted hydrogenolysis of the ether stabilized complex $\mathrm{(C_5H_4(CH_2)_2OCH_3)_2NdCH_2SiMe_3}$ led to $\mathrm{(C_5H_4(CH_2)_2OCH_3)_3Nd}$ after 12 and 48 h when $\mathrm{PMe_3}$ was added. No intermediate hydride could be observed, but the transient formation of this hydride was evidenced when hydrogenolysis was carried out in the presence of pivalone (unable to insert into the Nd–C bond), the alkoxo complex $\mathrm{(C_5H_4(CH_2)_2\ OCH_3)_2}$-$\mathrm{NdOCH(^tBu)_2}$ was formed.

As a summary, only the formation of the dimeric $[(^t\mathrm{BuC_5H_4})_2\mathrm{SmH}]_2$ or monomeric $(^t\mathrm{BuC_5H_4})_2\mathrm{SmH}$-$\mathrm{(PMe_3)_2}$ samarium hydrides could be observed. Both were moderately stable in solution and could not be isolated.

It was not possible to establish the formation of the dimeric neodymium hydrides. Conversely, the analogous yttrium hydrides were isolated in good yield [16,17].

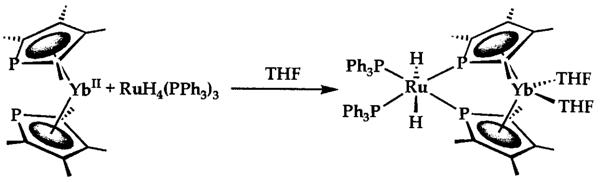
This behavior is a good illustration of the importance of steric factors in lanthanide chemistry, a small difference of ionic radius, 0.88 Å for yttrium versus 0.96 Å for samarium and 0.99 Å for neodymium induces a great difference of stability for analogous complexes.

Nevertheless, despite their instability, transient monomeric neodymium hydrides can be trapped by convenient reagents.

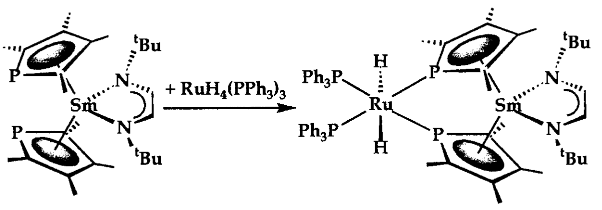
3.3. Electron poor hydrides, bimetallic hydrides

With a few exception, (inorganic hydrides [23]) all the characterized lanthanide hydrides were complexes of general formula $\mathrm{(C_5R_5)_2LnH(THF)}_n$. In order to distinguish between the electronic and steric effects, it is necessary to compare the properties of related complexes containing ligands of the same size, but of different electron donating ability. The tetramethylphospholyl ligand (tmp) is a bulky ligand, less electron donating than the ubiquitous pentamethylcyclopentadienyl Cp*. The presence of the phosphorous atom also allows the coordination of a late and soft d metal, and the synthesis of bimetallic complexes $\mathrm{[Ru][(tmp)_2LnH]}$ would lead to complexes in which the high withdrawing effect of the $\mathrm{[Ru](tmp)_2}$ group would increase the electron poor character of the LnH moiety. It should be possible to compare the reactivities of the electron rich $\mathrm{Cp^*_2LnH}$ and of the bridged analogue $\mathrm{[(C_5Me_4)SiMe_2}$-$\mathrm{(C_5Me_4)]LnH}$, to the reactivities of the electron poor $\mathrm{(tmp)_2LnH}$ and of a bridged $\mathrm{[Ru][(tmp)_2LnH]}$.

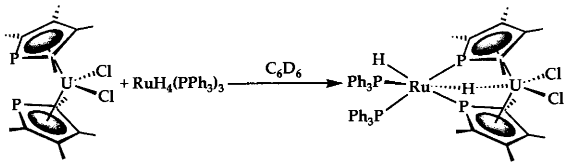
Because the synthesis of early late heterobimetallic hydrides had received considerable attention [24], we



Scheme 4.



Scheme 5.



Scheme 6.

decided that the [Ru] moiety would be a hydride one. The fragment $RuH_2(PPh_3)_2$ should be able to coordinate the lone phosphorus pairs of $[(tmp)_2Ln]$ complexes.

The synthesis of a bridged heterobimetallic Ru–Zr complex was easy [4c], and in the same manner, we have obtained the analogous ytterbium (II) complex (see Scheme 4). The difference of the ionic radii 0.93 Å for ytterbium (II) versus 0.74 Å for zirconium(IV) did not impede this synthesis [4a,d].

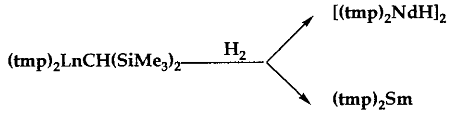
The analogous bisphospholylsamarium $[(tmp)_2Sm]_n$ was also available [25], but from this complex no bimetallic could be formed. By using a ligand able to induce an intramolecular electron transfer, the diazadiene ligand ^{t}BuN=C–C=N^{t}Bu [26], we succeeded in building a heterobimetallic complex, with the same ruthenium *trans* dihydride structure [4f]. The spectroscopic properties were close to those of a samarium(III) diazadienyl complex (Scheme 5): the chemical shifts of the phosphorous atoms of the phospholyl ligands is related to the oxidation state of the complexes. For Sm(III) complexes the resonance of the ^{31}P is positive, recorded in the range, 50–150 ppm [27], and for Sm(II) complexes, the resonance is negative, in the range 400–600 ppm [25,28]. The observed ^{31}P resonances were $(tmp)_2Sm$, $\delta = -540$ ppm (THF); $(tmp)_2Sm$(diazadienyl), $\delta = 200$ ppm (C_6D_6); bimetallic, $\delta = 254$ ppm (C_6D_6).

The thus determined limit of the tolerable ionic radius of the lanthanide atom allowing the formation of a bimetallic structure was between 0.96 (Sm(III)) and 1.11 Å (Sm(II)). In the same conditions, from $(tmp)_2Nd^{III}X$, (Nd(III) radius 0.99 Å) X = chloride or alkyls, the formation of a bimetallic species did not occur. Thus, the limit of ionic radius to get a Ru–Ln bimetallic compound seems to be ca. 1 Å.

In the range of the allowed size, from uranium(IV) (0.93 Å), bimetallic complexes were readily obtained [4a] (Scheme 6). The geometry of the Ru–U bimetallics was related to the electronic density around the metal: in the case of the chloride derivative, a 'back' donation is made to the early metal by the formation of a Ru–H–U bridge, from the *cis*-dihydridoruthenium moiety (^{1}H-NMR, Ru–H–U, $\delta = 530$ ppm). This bimetallic did not react with a non hindered ketone, then despite the high chemical shift denoting a strong influence of the paramagnetic metal, the reactivity of the bimetallic dihydride was similar to that of a ruthenium hydride.

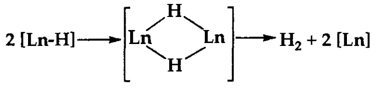
When the chloride ligands are replaced by a more electron donating BH_4 ligand, two isomeric dihydrides (ratio *cis*/*trans* = 80/20) are formed [4a].

At the same time, we looked at the synthesis of the $(tmp)_2LnH$ complexes. Hydrogenolysis of the alkyl led to the expected hydride $(tmp)_2NdH$, whereas the samarium alkyl $(tmp)_2SmCH(SiMe_3)_2$ led to $(tmp)_2Sm$ [4g]. The easy reduction of the transient hydride is illustrative of the accessibility of samarium(II) species (Eq. (4)).



$$(tmp)_2LnCH(SiMe_3)_2 \xrightarrow{H_2} \begin{cases} [(tmp)_2NdH]_2 \\ (tmp)_2Sm \end{cases} \qquad (4)$$

The mechanistic pathway for the reduction of the putative $(tmp)_2SmH$ was not established, nevertheless a bimolecular route as described for the reduction of cyclopentadienyluranium hydrides [29] could be invoked ((Eq. (5))).



$$2\,[Ln\text{-}H] \longrightarrow \left[Ln \overset{H}{\underset{H}{\diamond}} Ln \right] \longrightarrow H_2 + 2\,[Ln] \qquad (5)$$

It is noteworthy that this hydride is not stable even under 1 atm of dihydrogen. The Cp_2^*SmH complex is moderately stable in solution, and the reported spectrum of the bridged (and strained) complex $[(C_5Me_4)SiMe_2(C_5Me_4)]LnH$ was recorded under hydrogen [12].

On the other hand, $(tmp)_2Sm$ was able to activate dihydrogen when coordinated to a strong Lewis base [4f]. By heating at 60°C under 1 atm of dihydrogen, the carbene adduct of $(tmp)_2Sm$ decomposes slowly within 12 h, leading to $(tmp)_2Sm$ and to a 'dihydrogenocarbene' (Scheme 7). This 'dihydrogenocarbene' was also obtained after a two step reaction, with a protic and then a hydride reagent.

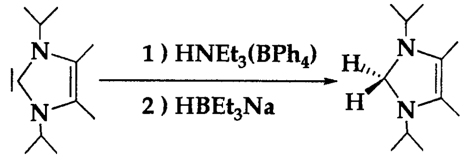
Owing to the poor stability of the samarium(III) hydride, an heterolytic cleavage of H_2 might be invoked instead of the classical four center homolytic cleavage. In a second step, the protonated carbene (stable when associated to a non coordinating anion such as BPh_4) reacts with the nucleophilic samarium species (Scheme 8).

The neodymium hydride $(tmp)_2NdH$, stored at r.t., did not show any marked decomposition after several weeks. Unfortunately, for the above developed steric reasons, it was not possible to gain access to a bridged heterobimetallic species [H–Ru–Nd–H].

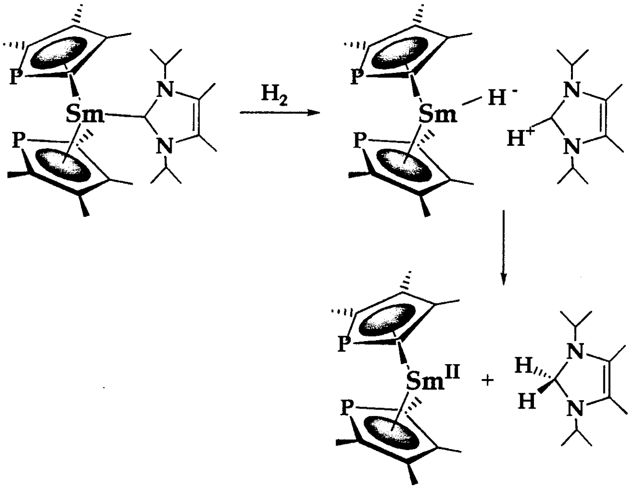
3.4. Reactivity

The organometallic lanthanide hydrides are extremely reactive species. They can rearrange to give the triscyclopentadienyl species or can be reduced as mentioned above. More stable pentamethylcyclopentadienyls react with themselves by abstraction of a proton from the Cp* ring [30].

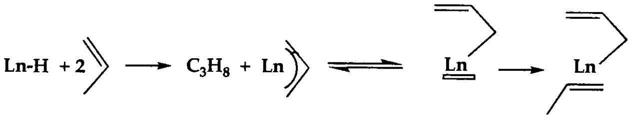
They react with aromatic solvents [31]. This reaction greatly favors the H/D exchanges [32] and could explain the impossibility of locating the hydride signal of some hydrides. Many saturated functional groups, halogenoalkanes, alcohols, oxiranes, amines, etc. react very rapidly with the hydrides to afford more stable Ln–X, Ln–N or Ln–O bonds. Unsaturated compounds, aldehydes, ketones, nitriles, etc. and also carbon monoxide insert into the Ln–H bond [3].



Scheme 7.



Scheme 8.



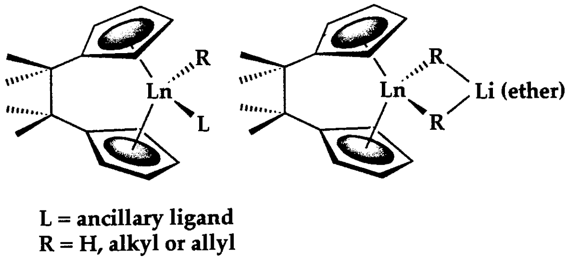
Scheme 9.

Mono or biscyclopentadienyllanthanide hydrides have been tested since their discovery as catalysts for many purposes and continue to focus the interest for H/D exchange [32], but essentially as homogeneous catalysts for hydrogenation of alkenes, chiral derivatives giving interesting results for asymmetric hydrogenation [33]. They were also used for alkenes isomerization [34], hydrocyclization [35], hydroboration [36], hydrosilylation [37], or hydroamination [38] reactions. The latter two reactions are now performed from alkyl [39] or bis(trimethylsilylamido) [40] complexes.

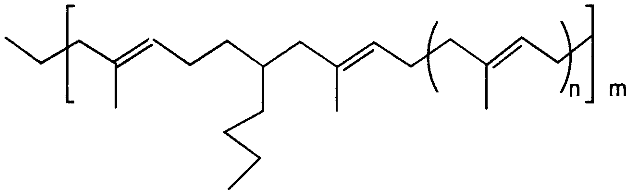
Olefin polymerization and oligomerization continue to be an exciting subject and numerous papers [6,41] or patents [42] report the catalytic activity of lanthanide hydrides, and also of alkyl or allyl complexes, in the polymerization of olefins and of polar monomers, terbutylacrylate and acrylonitrile [41b,43]. The hydrides react with α-olefins (or dienes) to give the corresponding alkyls (or allyls) and subsequent insertions of olefins in the lanthanide–carbon bond afford polymeric chains. Therefore, hydrides act as initiators only, the real catalysts involved in the catalytic cycles for olefin or diene polymerization are alkyl and allyl complexes, respectively. Thus these will be used rather than hydrides because they are more stable and more easily synthesized. Nevertheless sterically hindered alkyls or allyls are unable to insert olefins, and hydrogenolysis of these complexes is necessary to generate in situ the hydride initiator [41a,44]. In an other way, polymerization under hydrogen pressure permits the cleavage of the polymeric chain and the regeneration of the hydride initiator.

Very few organolanthanide systems are able to act as efficient catalysts for α-olefin polymerization. From pentamethylcyclopentadienyl complexes, elimination of a H atom of the coordinated propene occurs leading to an allylic compound, stable towards further insertion of the monomer. Coordination and subsequent insertion of a second molecule of monomer requires a vacant site, provided by isomerization of the π-allyl to a σ-allyl complex. The formation of the latter is favored by the presence of electron donating substituents on the cyclopentadienyl rings, but such hindered and electron rich complexes do not present a high affinity for the α-olefins (Scheme 9).

Monosubstituted, sterically less hindered cyclopentadienyl complexes, would also be less electron rich and could offer a good compromise between the contradictory requirements for an efficient α-olefin polymerization.



Scheme 10.



Scheme 11.

In the lanthanide series, small structural differences can induce important differences of reactivity. From this point of view, *ansa*-neodymium or samarium derivatives of general formula $C_5H_4CMe_2C_5H_4LnR$ (R = H, alkyl, allyl) would be good candidates for α-olefin polymerization (Scheme 10).

Of course, the synthesis of a hydride species would not be necessary if olefin insertion could occur into a more stable Ln–allyl complex. To check this point, we synthesized and tested the monoallylsamarium derivative. This compound was not active towards hex-1-ene polymerization, but was an efficient one site catalyst for isoprene polymerization affording *trans*-polyisoprene in high yield. Unexpectedly, it was possible to obtain an isoprene-hex-1-ene copolymerization (Scheme 11), with one-by-one insertion of *n*-hexyl moieties in the *trans*-polyisoprene chain [45].

As expected, the coordination of the diene was preferred but the olefin could compete and about 10% of hex-1-ene was incorporated. After insertion of one hex-1-ene molecule, only the diene, which is a better ligand, is able to coordinate the metal and to insert into the lanthanide–carbon bond.

4. Conclusion

Both steric and electronic factors which allow one to obtain and assume the stability of early lanthanide hydrides are defined. All lanthanide hydrides are extremely reactive species, but there appears a general trend, every time that it is possible, alkyls analogues are used instead of hydrides. If the catalytic cycle needs the hydride step, the latter will be synthesized or regenerated in situ by hydrogenolysis.

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