

## Mini-Review

Variable nuclearity scorpionate-supported lanthanide polyhydrides:  $[(\text{Tp}^{\text{R,R'}})\text{LnH}_2]_n$  ( $n = 3, 4$  and  $6$ )

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## ABSTRACT

The synthesis and chemistry of monoligand lanthanide dihydrides,  $\text{LnH}_2$ , is a very active current area of research. Herein we summarize the status of our contributions utilizing various scorpionates,  $\text{Tp}^{\text{R,R'}}$ , as protective ancillary ligands and show that the nuclearity of the so obtained hydride clusters depends on the size of the scorpionate ligands and, in one instance, the solvent used in the synthesis. Following brief consideration of the synthesis of the various precursor dialkyl complexes,  $(\text{Tp}^{\text{R,R'}})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_{1/0}$ , the solid-state structures of the hydride clusters,  $[(\text{Tp}^{\text{R,R'}})\text{LnH}_2]_n$  ( $\text{R, R}' = \text{Me, Ln} = \text{Nd, Sm, Y, Yb}$  and  $\text{Lu, } n = 4$ ;  $\text{R, R}' = \text{H, Ln} = \text{Y, Yb}$  and  $\text{Lu, } n = 6$ ;  $\text{R, R}' = \textit{i}\text{Pr, Ln} = \text{Y}$  and  $\text{Lu, } n = 3$ ), obtained *via* hydrogenolysis, are described.

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## 1. Introduction

A major recent thrust in the development of organo-lanthanide chemistry has been the synthesis of monoligand lanthanide dialkyls,  $\text{LnR}_2$ , and their conversion to the corresponding dihydrides,  $\text{LnH}_2$ . The driving force behind the intense scrutiny is the reasonable assumption that the presence of *two* reactive functionalities could result in greater reactivity and possibly open new reaction channels and pave the way for the discovery of novel lanthanide based catalysts. Recent results have already amply demonstrated the validity of this assumption and bode well for the future of this area [1].

Successful synthesis of monoligand lanthanide dialkyls, mostly the trimethylsilylmethyls ( $\text{CH}_2\text{SiMe}_3$ ), has been achieved with the ubiquitous bulky cyclopentadienyl ligands [2–4], and there has been an impressive increase in the use of a variety of non-cyclopentadienyl ancillaries in this regard [5–11], however, it was only the work of Hessen et al. with bulky amidinates [12] and that of Hou et al. with bulky cyclopentadienyls [3] that included a wide range of lanthanide metals. It was also the pioneering work of Hou that showed that hydrogenolysis of the dialkyls leads to the corresponding dihydrides. Remarkably, the structure of these complexes

proved to be based on novel, polynuclear cluster framework, such as tetranuclear  $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{LnH}_2]_4(\text{THF})_{0-2}$  and hexanuclear  $[(\text{C}_5\text{Me}_5)\text{LnH}_2]_6$  [13,14] and, equally notable was the unprecedented reactivity of these polyhydrides, for example toward nitriles [15a] and carbon monoxide [15b].

More recently, Okuda and coworkers described trinuclear,  $[(\text{Me}_3\text{TACD})\text{LnH}_2]_3$  complexes ( $\text{Me}_3\text{TACDH} = 1,4,7\text{-trimethyl-1,4,7,10-tetraazacyclododecane}$ ;  $\text{Ln} = \text{Y, Ho, Lu}$ ) [16], and Kempe, Trifonov and coworkers disclosed the synthesis of trinuclear alkylpentahydrides,  $[(\text{Ap}^*\text{Ln})_3\text{H}_5(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$  ( $\text{Ap}^*\text{H} = (2,6\text{-diisopropylphenyl})[6-(2,4,6\text{-triisopropylphenyl})\text{pyridine-2-yl}]\text{amine}$ ;  $\text{Ln} = \text{Y, Lu}$ ) [17].

For many years we have utilized the steric protection offered by Trofimenko's bulky scorpionates for the synthesis of various  $(\text{Tp}^{\text{R,R'}})\text{Ln}(\text{II})/(\text{III})$  complexes [18,19], and recently turned our attention to the preparation of scorpionate anchored  $\text{Ln}(\text{III})$  dialkyls and their conversion to dihydrides. Herein we summarize the synthesis and structures of the currently available  $(\text{Tp}^{\text{R,R'}})\text{LnH}_2$  complexes.

2. Synthesis of the precursor  $(\text{Tp}^{\text{R,R'}})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_{1/0}$  complexes

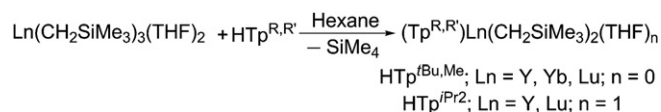
Preparation of the precursor dialkyls was pursued along two complementary synthetic strategies.

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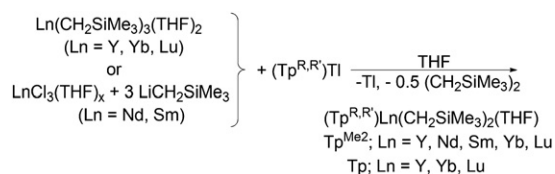
Protonolysis of lanthanide trialkyls,  $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ , is now a time-tested approach for replacement of one or two alkyl groups by various ancillaries, and was the method of choice by Hou et al. [3] and Hessen et al. [12] in their synthesis of lanthanide dialkyls with bulky cyclopentadienyl,  $\text{C}_5\text{Me}_4\text{SiMe}_3$ , and bulky amidinate,  $\text{PhC}(\text{NAr}^*)_2$  ( $\text{Ar}^* = 2,6\text{-diisopropylphenyl}$ ), ligands. A prerequisite of this approach is the availability of the acid form of the ligand. In the case of the hydrotris(pyrazolyl)borates, the accessibility and stability of the acid form,  $\text{HTp}^{\text{R,R'}}$ , is crucially dependent on the size of the R and R' substituents on the pyrazolyl ring and is conveniently available only with rather bulky  $\text{Tp}^{\text{R,R'}}$  ligands. The protonolysis reaction also requires pure, isolable lanthanide trialkyls and hence it is limited to the mid and late lanthanides, unless isolation of the delicate early lanthanide trialkyls is circumvented by the one-pot synthesis of Hessen [12], which allowed the isolation of  $\{\text{PhC}(\text{NAr}^*)_2\}\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_n$  complexes for the full-range of lanthanides.

In our hands, protonolysis of yttrium and late lanthanide trialkyls with  $\text{HTp}^{\text{tBu,Me}}$  [20] and very recently with  $\text{HTp}^{\text{iPr}_2}$  [21], gave the corresponding dialkyls in good yields, Scheme 1.



**Scheme 1.** Synthesis of the precursor  $(\text{Tp}^{\text{R,R'}})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_n$  complexes via protonolysis.

To obtain the  $\text{Tp}^{\text{Me}_2}$  and Tp anchored lanthanide dialkyls an alternative synthetic strategy was required and this was inspired by Parkin's observation that  $\text{TiTp}^{\text{R,R'}}$  can serve as useful alkyl abstractor agents from Mg [22a] and Al [22b] alkyl complexes. Fortunately the method is also applicable to lanthanide trialkyls, and indeed a one-pot approach was even successful for the large Sm and Nd metals, Scheme 2.



**Scheme 2.** Synthesis of the precursor  $(\text{Tp}^{\text{R,R'}})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$  complexes by alkyl abstraction.

### 3. Scorpionate anchored Ln(III) polyhydride clusters

With the availability of various scorpionate anchored lanthanide dialkyls the stage was set to carry out the hydrogenolysis reactions in an attempt to obtain scorpionate-supported trivalent lanthanide dihydrides.

Fortunately, based on our previous experience with the hydrogenolysis of divalent  $(\text{Tp}^{\text{tBu,Me}})\text{Yb}(\text{CH}_2\text{SiMe}_3)(\text{THF})$  complex, which required several hours at 1000 psi (68 atm) of hydrogen pressure to effect conversion to  $[(\text{Tp}^{\text{tBu,Me}})\text{YbH}]_2$  [23], we were cognizant that similar conditions might be needed to effect hydride formation with the trivalent  $(\text{Tp}^{\text{R,R'}})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_{1/0}$  complexes. These conditions are more rigorous than those necessary for the cyclopentadienyl based dialkyl systems of Hou, one atm of  $\text{H}_2$  and

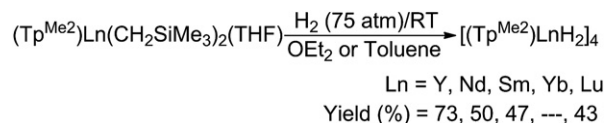
4–24 h of reaction time, and can be attributed to a combination of electronic factors and steric effects. The presence of the hard nitrogen donor scorpionate ligand may induce stronger Ln–C (alkyl) bonding in the scorpionate dialkyls, while the steric bulk of the ligand, centered around the metal, hinders approach of dihydrogen toward the reactive and highly polar Ln–C bonds; both factors conspiring to reduce the rate of hydrogenolysis.

To our delight, hydrogenolysis of various  $(\text{Tp}^{\text{R,R'}})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$  complexes under 1000–1200 psi of  $\text{H}_2$  (68–82 atm) for 24–70 h at room temperature proved successful. The observation that the smallest and most polarizing lanthanide, Lu, required the highest  $\text{H}_2$  pressure (1200 psi) and longest reaction time (70 h), provide qualitative support for both electronic and steric arguments, presented above, for the different conditions needed to effect hydride formation between the scorpionate and cyclopentadienyl supported lanthanide dialkyls. The nuclearity of the  $(\text{Tp}^{\text{R,R'}})\text{LnH}_2$  clusters depends on the size of the  $\text{Tp}^{\text{R,R'}}$  ligand and, in one case on the solvent used in the synthesis, and product yield is heavily dependent on the lanthanide metal.

In the next sections we describe the structures of three different classes of scorpionate anchored Ln(III) polyhydride clusters.

#### 3.1. Tetranuclear $[(\text{Tp}^{\text{Me}_2})\text{LnH}_2]_4$ Complexes

With the availability of a wide range of lanthanide metals, hydrogenolysis of the  $(\text{Tp}^{\text{Me}_2})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$  complexes was carried out first. As shown in Scheme 3, this led to the formation of tetranuclear clusters,  $[(\text{Tp}^{\text{Me}_2})\text{LnH}_2]_4$  (**1**) (Ln = Y, Nd, Sm, Yb and Lu) [20].

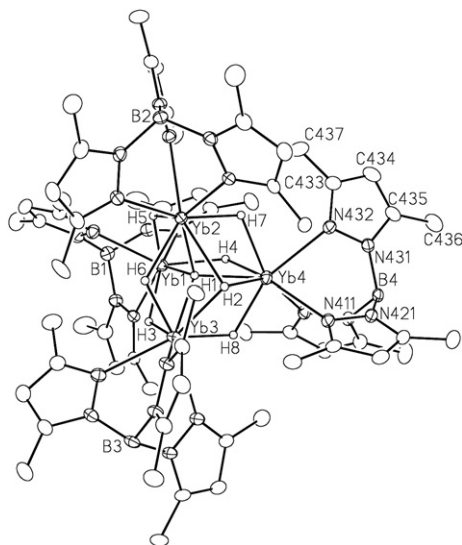


**Scheme 3.** Preparation of  $[(\text{Tp}^{\text{Me}_2})\text{LnH}_2]_4$  (**1**) complexes.

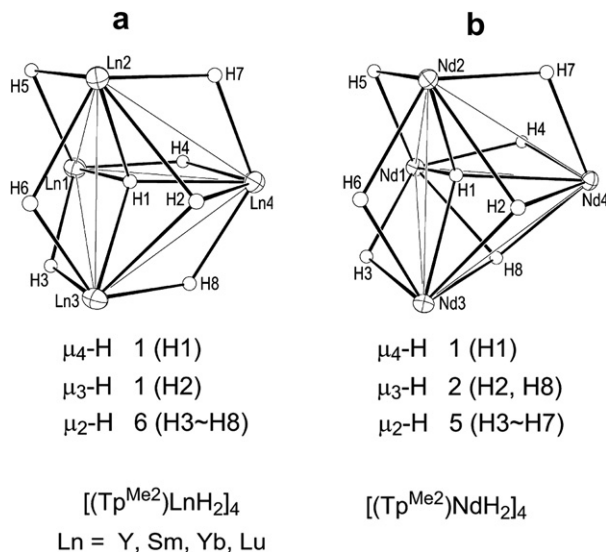
Notable features of the synthesis are the fact that it can be extended to the early and large neodymium, and also to the redox active samarium and ytterbium metals. The yields of the hydride clusters **1** range from reasonable (Y) to moderate (Nd, Sm and Lu), but poor for Yb. The complex **1-Yb** is unstable in solution and, during attempted crystallization deposits the very insoluble, purple divalent  $\text{Yb}(\text{Tp}^{\text{Me}_2})_2$  [24], formation of the latter is already observed during the hydrogenolysis reaction. Although analytically pure **1-Yb** could not be obtained the tetranuclear cluster formulation was corroborated by solid-state X-ray structure determination (*vide infra*). Small amounts of the similarly insoluble, purple  $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$  [24] was also observed in the synthesis of **1-Sm**, but the solution stability of this complex far exceeds that of **1-Yb**.

A distinguishing feature of the hydride clusters **1**, compared to their cyclopentadienyl analogs, is the lack of coordinated THF ligand, while the latter can retain up to two molecules of THF,  $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{LnH}_2]_4(\text{THF})_{0-2}$  [13]. Indeed single crystals of **1** for X-ray analysis were grown from concentrated THF solutions. The absence of coordinated THF is clearly the result of the bulkier nature of the scorpionate ligand and the greater steric protection it provides to the lanthanide centers.

The solid-state structure of **1-Yb** is shown in Fig. 1, while Fig. 2 compares the core structures of **1** (Ln = Y, Sm, Yb and Lu) with that of the larger lanthanide, **1-Nd**. Table 1 lists some relevant  $\text{Ln}\cdots\text{Ln}$  and  $\text{Ln}\cdots\text{H}$  distances.



**Fig. 1.** Perspective view of  $[(\text{Tp}^{\text{Me}_2})\text{YbH}_2]_4$  (**1-Yb**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms of the bridging hydrides, which have been refined, are shown with arbitrarily small thermal parameters; the remaining hydrogen atoms are not shown.



**Fig. 2.** View of the  $\text{Ln}_4\text{H}_8$  core of  $[(\text{Tp}^{\text{Me}_2})\text{LnH}_2]_4$  (**1**) complexes.

The structure consists of four lanthanide metals at the corners of a slightly distorted tetrahedron, with each lanthanide capped by a  $\kappa^3\text{-Tp}^{\text{Me}_2}$  ligand and the tetranuclear cluster held together by eight bridging hydrides. The overall structural motif is similar to that of Hou's cyclopentadienyl analogs and, interestingly both classes of hydride clusters encapsulate very rare example of a tetra coordinate bridging hydride at the body center of the tetranuclear core, H1. The remaining seven hydrides occupy face and edge bridging positions. Compounds **1** (Ln = Y, Sm, Yb, Lu) are isostructural and have the same  $\text{Ln}_4\text{H}_8$  core structure as the  $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{LnH}_2]_4$  complexes, with one of the seven remaining hydrides capping a triangular face (H2) and the rest edge bridging (H3–H8), Fig. 2a. The core structure of  $[(\text{Tp}^{\text{Me}_2})\text{NdH}_2]_4$  appears to be slightly different, with H8 showing more face-capping tendency than edge bridging and this is attributed to the larger size of Nd, Fig. 2b.

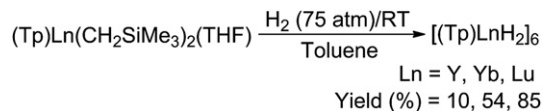
A comparison of the  $\text{Ln}\cdots\text{Ln}$  separations and  $\text{Ln}\text{-H}$  bond distances among complexes **1** and between **1** and the cyclopentadienyl analogs reveal the anticipated trends. The  $\text{Ln}\cdots\text{Ln}$  distances in **1** decrease from Nd to Lu, and so do the  $\text{Ln}\text{-H}$  bond lengths due to the lanthanide contraction. Furthermore the  $\text{Ln}\cdots\text{Ln}$  distances in **1** are some 0.1 Å longer than in the cyclopentadienyl analogs, while the  $\text{Ln}\text{-H}$  lengths are also somewhat longer. The expansion of the tetrahedral metal core is again due to the larger size of the  $\text{Tp}^{\text{Me}_2}$  ligand.

Finally we note that the relative order of the  $\text{Ln}\text{-H}$  distances also follows the unusual order seen in the cyclopentadienyl analogs. The expectation is that bond length should increase with coordination number, and in fact the  $\text{Ln}\text{-H}$  bond length increase from edge bridging ( $\mu_2\text{-H}$ ) to face bridging ( $\mu_3\text{-H}$ ), but there is a decrease in distances for the encapsulated  $\mu_4\text{-H}$ 1, Table 1. Hou et al. [25] ascribed this as being due to "tightness of the tetrahedral cavity" and complexes **1** provide further examples to support this conclusion.

### 3.2. Hexanuclear $[(\text{Tp})\text{LnH}_2]_6$ Complexes

As anticipated, hydrogenolysis of  $(\text{Tp})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ , anchored by the smallest scorpionate ligand, resulted in higher nuclearity clusters, namely the hexanuclear  $[(\text{Tp})\text{LnH}_2]_6$  (**2**) (Ln = Y, Yb, Lu) complexes, Scheme 4.

The synthesis is so far limited to Y and the late lanthanides, Yb and Lu. Already with the thermally delicate  $(\text{Tp})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$  complex, formation of mixtures was observed in the hydrogenolysis reaction, from which single crystals suitable for X-ray could be isolated but only in poor yield. Interestingly, and in contrast to the difficulties encountered with the unstable



**Scheme 4.** Preparation of  $[(\text{Tp})\text{LnH}_2]_6$  (**2**) complexes.

**Table 1**  
Comparison of the cluster core distances (Å) in  $[(\text{Tp}^{\text{Me}_2})\text{LnH}_2]_4$  (**1**) complexes.<sup>a,b</sup>

	Lu	Yb	Y	Sm	Nd
$\text{Ln}\cdots\text{Ln}^c$	3.433–3.593 (3.276–3.464)	3.456–3.620	3.533–3.711 (3.460–3.597)	3.661–3.893	3.713–3.948
$\text{Ln}\text{-}\mu_4\text{H1}$	2.05–2.27 (2.08–2.16)	2.11–2.21	2.18–2.28 (2.13–2.21)	2.16–2.36	2.24–2.40 2.33–2.49
$\text{Ln}\text{-}\mu_3\text{H2}$	2.17–2.34 (2.29–2.30)	2.15–2.34	2.17–2.47 (2.32–2.33)	2.32–2.47	2.517(3)
$\text{Ln}\text{-}\mu_3\text{H8}$					2.26–2.59
$\text{Ln}\text{-}\mu_2$ (H3–H8)	1.88–2.14 (2.10–2.16)	1.96–2.13	1.94–2.36 (2.12–2.19)	2.09–2.38	2.17–2.45

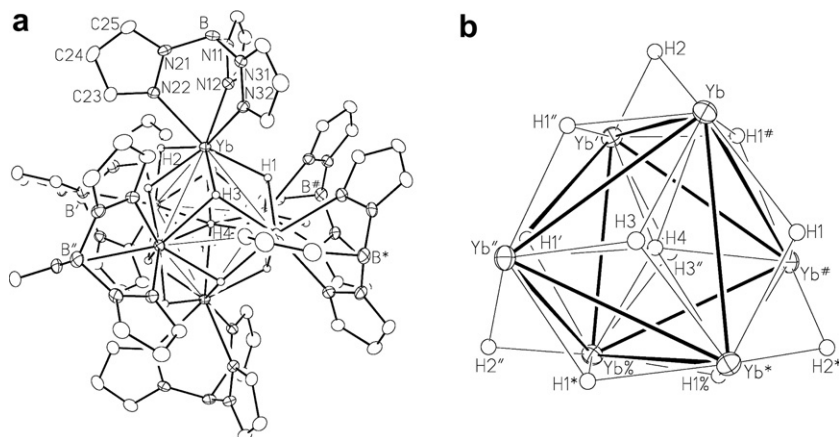
<sup>a</sup> Values in parenthesis are for the  $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{LnH}_2]_4$  analogs.

<sup>b</sup> The esd's on the  $\text{Ln}\cdots\text{Ln}$  and  $\text{Ln}\text{-H}$  distances are ca. 0.0004 and 0.05 Å, respectively.

<sup>c</sup> Non-bonded distances.

$[(\text{Tp}^{\text{Me}_2})\text{YbH}_2]_4$ , the hexanuclear ytterbium dodecahydride, **2-Yb**, was isolated in moderate yield and did not show a tendency to undergo reductive decomposition to form  $[\text{Yb}(\text{Tp})_2]$ .

Complexes **2** are isostructural, Fig. 3 shows the previously unreported **2-Yb** complex together with a view of the  $\text{Yb}_6\text{H}_{12}$  core structure.



**Fig. 3.** (a) Perspective view of  $[(\text{Tp})\text{YbH}_2]_6$  (**2-Yb**) showing the atom labeling scheme. (b) View of the  $\text{Yb}_6(\mu_3\text{-H})_8(\mu_2\text{-H})_3(\mu_6\text{-H})$  core, with the view direction just slightly offset from along the threefold rotational axis.

The solid-state structures exhibit some notable features. To begin with, the complexes crystallize in the relatively rare trigonal space group. The occupation of a special position imposes  $D_3$  point symmetry on the cluster, and results in one unique Yb atom. The six symmetry related ytterbium atoms are disposed in a trigonal antiprismatic arrangement, with parallel “top” and “bottom” faces, formed by Yb, Yb\*, Yb'' and Yb', Yb#, Yb%, respectively, rotated by  $10.5^\circ$  from being eclipsed. As a result, the interplane Yb...Yb distances are unequal (Yb...Yb' = 3.2400(5) and Yb...Yb# = 3.6360(6) Å), and the unique Yb...Yb distance within each “top/bottom” equilateral triangular faces is 3.6055(5) Å. The cluster metal framework is held together by twelve bridging hydrides, which, due to symmetry, sort into four types. Once again, there is an interstitial hydride, H4, which, in this case is six-coordinate and located at the intersection of the threefold and twofold axes. The “top” and “bottom” faces are bridged by three  $\mu_2$ -edge bridging hydrides (H2, H2\*, H2''), sitting on twofold rotational axes, and six  $\mu_3$ -face bridging hydrides (H1 and related), which are not on a symmetry element but related by them. Finally, there are two  $\mu_3$ -bridging hydrides on the “top/bottom” faces (H3, H3'') sitting on the threefold rotation axis.

The presence of different types of hydrides in the same complexes, offers yet again the opportunity to examine the relationship between M–H bond distances and coordination number. In complexes **2** the trend returns to normal, that is, the shortest distance is to the edge bridging, two coordinate  $\mu_2$ -hydrides H2

(1.99(6) Å) and followed by the face bridging, three coordinate  $\mu_3$ -hydrides H1 and H3 (2.17–2.37(7) Å), with the bond length of the six-coordinate,  $\mu_6$ -hydride H4 being the longest at 2.4894(3) Å. The same trend is seen with the analogous Y and Lu complexes and provide further support of the conclusion of Hou et al. [25] that the anomalous trend and the shorter  $\mu_4$ -hydride distances seen in the

tetranuclear cyclopentadienyl and, by extension, in the scorpionate hydride clusters is due to the “tightness of the tetrahedral cavity”.

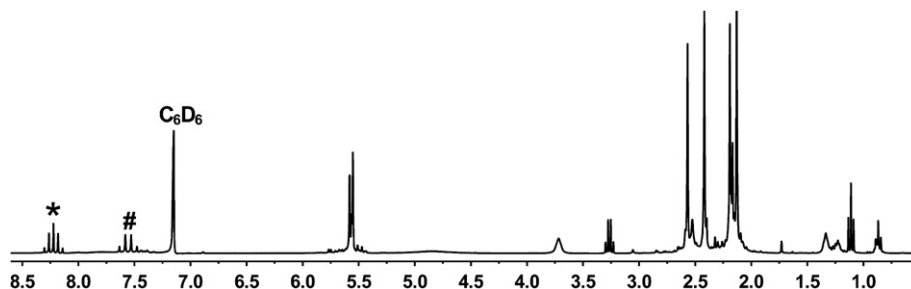
### 3.3. Quest for lower nuclearity $(\text{Tp}^{\text{R,R'}})\text{LnH}_2$ complexes

Structurally interesting, with an embedded interstitial hydride ligand and various hydride bridges, preliminary reactivity studies of polyhydrides **1** and **2** have, so far, proved disappointing and certainly not able to mimic the exquisite and unique reaction chemistry displayed by Hou's  $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{LnH}_2]_4(\text{THF})$  complexes toward unsaturated small molecules [13]. The reduced reactivity can undoubtedly be traced to the greater steric bulk of the tripodal scorpionate ligands and enhanced steric protection, which impede approach to the lanthanide centers by reagent molecules, as testified by the lack of coordinated THF ligands in complexes **1** and **2**.

In our quest to obtain more reactive scorpionate anchored polyhydrides, serendipity and then a rational approach came to the rescue.

#### 3.3.1. Serendipity at work: $[(\text{Tp}^{\text{Me}_2})\text{YH}_2]_3(\text{THF})_x$ complex

In one of the hydrogenolysis of  $(\text{Tp}^{\text{Me}_2})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ , we noticed that the  $^1\text{H}$  NMR spectrum of the product showed, a quartet in the hydride region, in addition to the NMR signature of **1-Y**, a quintet due to hydride coupling to four yttrium nuclei ( $^{89}\text{Y}$ , 100%  $I = 1/2$ ). The quartet was indicative of the presence of a trinuclear hydride cluster. The  $^1\text{H}$  NMR spectrum of this sample is shown in Fig. 4.



**Fig. 4.**  $^1\text{H}$  NMR spectrum of the crude reaction product of the hydrogenolysis of  $(\text{Tp}^{\text{Me}_2})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$  showing the presence of both tetranuclear  $[(\text{Tp}^{\text{Me}_2})\text{YH}_2]_4$  (**1-Y**) and trinuclear  $[(\text{Tp}^{\text{Me}_2})\text{YH}_2]_3(\text{THF})_x$  (**3**)#.



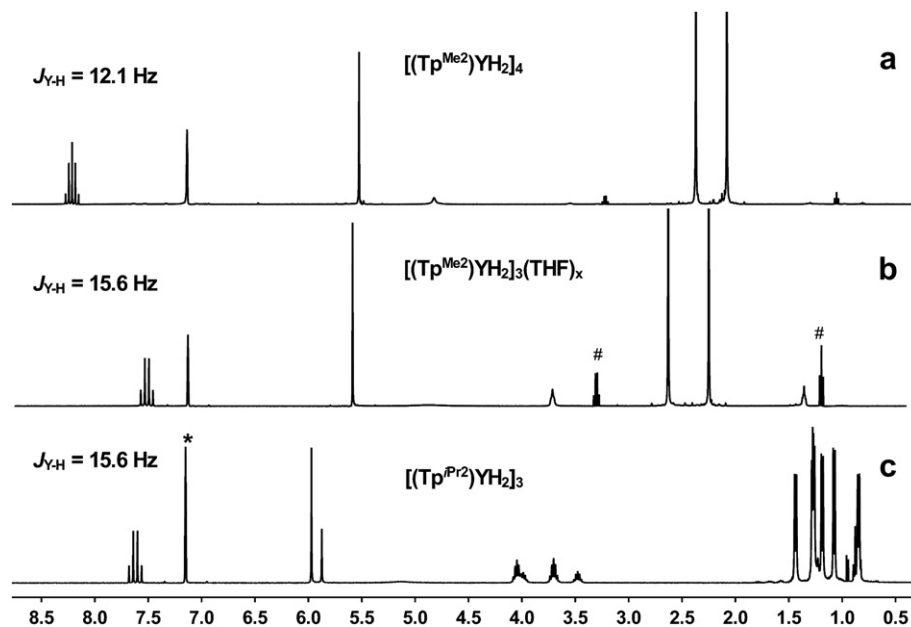


Fig. 6. Comparison of the  $^1\text{H}$  NMR spectra of (a)  $[(\text{Tp}^{\text{Me}_2})\text{YH}_2]_4$  (**1-Y**), (b)  $[(\text{Tp}^{\text{Me}_2})\text{YH}_2]_3(\text{THF})_x$  (**3**), (c)  $[(\text{Tp}^{\text{iPr}_2})\text{YH}_2]_3$  (**4**). (#:  $\text{Et}_2\text{O}$ ; \*:  $\text{C}_6\text{D}_6$ ).

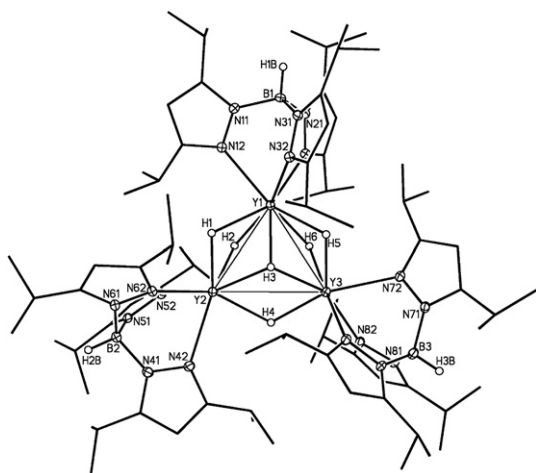


Fig. 7. Molecular structure of  $[(\text{Tp}^{\text{iPr}_2})\text{YH}_2]_3$  (**4**); simplified ball-and-stick diagram.

#### 4. Conclusions

Hydrogenolysis of scorpionate anchored lanthanide dialkyl complexes, under moderate pressure of  $\text{H}_2$ , successfully led to the corresponding dihydrides,  $(\text{Tp}^{\text{R,R}})\text{LnH}_2$ . The structure of the complexes is based on interesting cluster framework, the nuclearity of which depends on the size of the scorpionate ligand. The smallest, first generation Trofimenko scorpionate, Tp, gives the hexanuclear hydride cluster,  $[(\text{Tp})\text{LnH}_2]_6$ , while the bulkier  $\text{Tp}^{\text{Me}_2}$  ligand restricts the cluster size to tetranuclear,  $[(\text{Tp}^{\text{Me}_2})\text{LnH}_2]_4$  or trinuclear,  $[(\text{Tp}^{\text{Me}_2})\text{YH}_2]_3(\text{THF})_x$ , when  $\text{Et}_2\text{O}/\text{THF}$  is used in the synthesis. Increasing the bulk of the scorpionate to  $\text{Tp}^{\text{iPr}_2}$  results in exclusive formation of the trinuclear cluster hydride,  $[(\text{Tp}^{\text{iPr}_2})\text{LnH}_2]_3$ .

The higher nuclearity clusters contain interstitial hydrides,  $\mu_6\text{-H}$  and  $\mu_4\text{-H}$ , respectively; although the steric protection offered by the scorpionate ligands appears to severely limit their reactivity. Preliminary studies indicate that the reactivity of the trinuclear hydride clusters is greater.

It is tempting to speculate that the nuclearity and reactivity of lanthanide polyhydrides can be further fine tuned by judicious changes in the substitution profile of the scorpionate ligands, the solvent used for hydrogenolysis, and the size of the lanthanide metal center. Work along these lines is being pursued in our laboratories.

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#### Appendix A. Supplementary material

Crystallographic data for complexes **1-Yb** (CCDC 785144), **2-Yb** (CCDC 785145) and **5** (CCDC 785146) have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from, The Director, CCDC, 12 union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>) or via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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