

Scorpionate-Supported Dialkyl and Dihydride Lanthanide Complexes: Ligand- and Solvent-Dependent Cluster Hydride Formation**

Jianhua Cheng, Kuburat Saliu, Gong Y. Kiel, Michael J. Ferguson, Robert McDonald, and Josef Takats*

In memory of Jerry Trofimenko

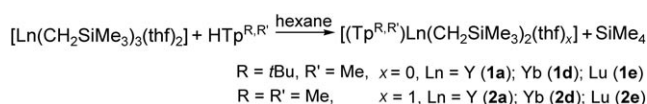
The synthesis, structure, and reactivity of trivalent Group 3 and lanthanide (Ln) metal alkyl and hydride complexes have occupied a central place in the organometallic chemistry of these elements. Not only are these functional groups of fundamental interest, they are also responsible for the versatile catalytic behavior of such complexes.^[1] For many years the area of rare earth metal alkyl compounds was almost the exclusive domain of bis(cyclopentadienyl) mono-alkyl complexes Cp₂MR (Cp = various C₅R₅ moieties, M = Group 3 metal, Ln). Recently, however, there has been intense interest and spectacular progress in the synthesis of rare earth metal dialkyl complexes bearing one anionic ancillary ligand (LMR₂), and aside from the ubiquitous bulky cyclopentadienyl ligands^[2] various non-cyclopentadienyl ligands have been successfully enlisted.^[3] However, most of the studies have focused on the Group 3 metals Sc and Y, and only the works of Hou et al.^[4] and Hessen et al.^[5] have included the range of lanthanide metals.

In a similar vein, although numerous metallocene mono-hydride complexes of the rare earth metals have been synthesized and studied since the first example reported by Evans et al. in the 1980s,^[6] only recently have Hou et al.^[7] reported an extensive series of monocyclopentadienyl rare earth metal dihydrides “[Cp₂Me₄SiMe₃LnH₂],”^[8] which exhibit remarkable reactivity, far different from that of metallocene monohydrides. Compared to the aforementioned compounds, cyclopentadienyl-free rare earth metal hydrides are relatively few,^[9] and no example of a dihydride “LLnH₂” has been reported.^[10]

Trofimenko's tris(pyrazolyl)borates (Tp^{R,R'}) are among the most versatile and widely used supporting ligands in inorganic chemistry.^[11] The steric demand of the Tp^{R,R'} ligands can be easily and judiciously adjusted by variation of the

substituents in the 3-positions of the pyrazolyl rings, a feature that is especially relevant to the large lanthanides. Surprisingly, only two mono-Tp^{R,R'} Group 3 metal alkyl complexes are known. Bianconi and Long synthesized [(Tp^{Me₂})YR₂(thf)] (R = CH₂SiMe₃, Ph) by salt metathesis between [(Tp^{Me₂})YCl₂(thf)] and LiR,^[12] and Piers et al. prepared the scandium analogues [(Tp^{Me₂})Sc(CH₂SiMe₃)₂(thf)] and [(Tp^{tBu,Me})Sc(CH₂SiMe₃)₂] by alkane elimination from [Sc(CH₂SiMe₃)₃(thf)₂] and HTp^{R,R'}.^[13] Herein we report the synthesis of [(Tp^{R,R'})Ln(CH₂SiMe₃)₂(thf)_x]^[14] complexes for the full range of lanthanides except La. We also disclose that elevated-pressure hydrogenolysis of [(Tp^{R,R'})Ln(CH₂SiMe₃)₂(thf)] (R = R' = Me, H) successfully leads to the first non-cyclopentadienyl lanthanide dihydrides “[(Tp^{R,R'})LnH₂(thf)_x],” the aggregation of which is ligand- and solvent-dependent.

Our first approach to scorpionate-supported lanthanide dialkyl complexes involved alkane elimination from [Ln(CH₂SiMe₃)₃(thf)₂] and HTp^{R,R'}. This strategy follows the successful application of the protonolysis protocol by Hou et al.^[4] and Hessen et al.^[5] for lanthanide dialkyl complexes with cyclopentadienyl and amidinate ligands. The reaction requires the use of pure, isolable lanthanide trialkyl complexes and hence is limited to the late lanthanides (Scheme 1).^[15,17] Attempts to emulate the one-pot synthesis of Hessen et al.^[5] with early lanthanides led to intractable mixtures.



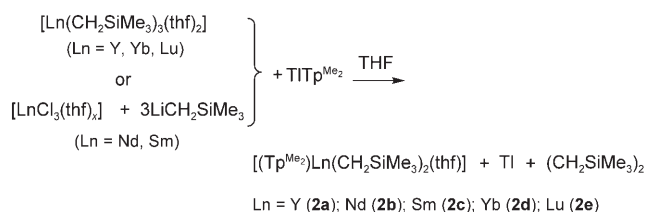
Scheme 1. Preparation of complexes **1a,d,e** and **2a,d,e** by alkane elimination.

Clearly an alternative strategy was needed to obtain the full range of scorpionate-supported lanthanide dialkyl complexes. The search for such a strategy was inspired by Parkin et al., who showed that TITp^{R,R'} can serve as a useful alkyl abstractor from Mg^[18] and Al^[19] alkyl compounds for the synthesis of (Tp^{R,R'})MR_n-type compounds (M = Mg, n = 1; M = Al, n = 2; R = Me, CH₂SiMe₃). Gratifyingly, the method is applicable to lanthanide trialkyl complexes (Scheme 2) and permits a one-pot approach for the large lanthanides Sm and Nd (i.e., without isolating their delicate alkyl complexes^[20]). The yield of products and their ease of isolation reflect their

[*] Dr. J. Cheng, K. Saliu, Dr. G. Y. Kiel, Dr. M. J. Ferguson, Dr. R. McDonald, Prof. Dr. J. Takats
 Department of Chemistry
 11227 Saskatchewan Drive
 University of Alberta
 Edmonton, AB, Canada T6G 2G2
 Fax: (+1) 780-492-4944
 E-mail: joe.takats@ualberta.ca

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Scheme 2. Preparation of complexes **2a–e** by alkyl abstraction.

position in the lanthanide series (ca. 80% for late Ln and 35% for Nd). Attempts to synthesize the La analogue failed.

Contrary to the clean and rapid alkyl abstraction with $\text{TiTp}^{\text{Me}_2}$, the reaction with $\text{TiTp}^{\text{tBu,Me}}$ proved problematic. Although $[(\text{Tp}^{\text{tBu,Me}})\text{Lu}(\text{CH}_2\text{SiMe}_3)_2]$ could be obtained in satisfactory yield, reactions with other lanthanides were slow and failed to give pure products. Thus, we have two complementary syntheses: $[(\text{Tp}^{\text{tBu,Me}})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2]$ via protonolysis with the easily obtainable $\text{HTp}^{\text{tBu,Me}}$, whereas alkyl abstraction with $\text{TiTp}^{\text{Me}_2}$ is the method of choice for $[(\text{Tp}^{\text{Me}_2})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})]$.

All the compounds were characterized by C,H,N elemental analysis, NMR spectroscopy (mostly for Y, Lu), and crystal structure determination. Representative structures are shown in Figure 1.

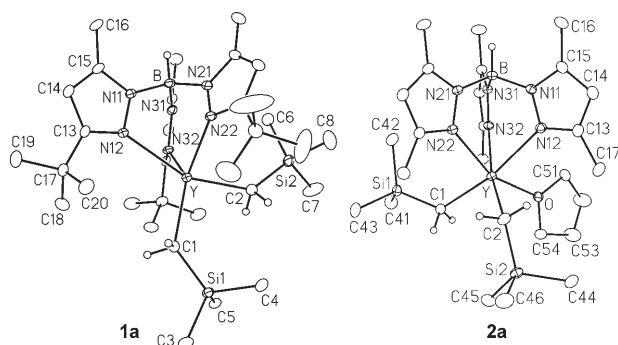


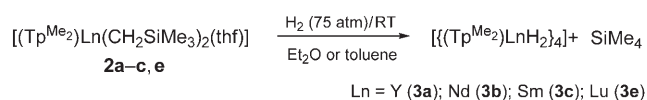
Figure 1. ORTEP drawings of the structures of **1a** and **2a**.

The structure of **1a** is similar to that of the scandium analogue.^[13] The bulky scorpionate ligand precludes coordination of THF and restricts Y to a five-coordinate, distorted trigonal-bipyramidal coordination sphere, with N22, N32, and C1 occupying the equatorial positions, and N12 and C2 the apical sites. The apical Y–N bond is more than 0.2 Å longer than the other two Y–N bonds. Like the scandium analogue, the compound is fluxional in solution. The room-temperature NMR spectrum shows only resonances for equivalent alkyl and pyrazolyl groups, whereas at low temperature signals for two different alkyl groups and two pyrazolyl rings are observed in a 2:1 ratio, in line with the almost C_s -symmetric solid-state structure.

The $[(\text{Tp}^{\text{Me}_2})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})]$ complexes **2a–e** are isostructural to the Sc analogue.^[21] The rare earth metal centers are six-coordinate in an octahedral fashion, with distortions from ideal geometry due to constraints imposed by the Tp^{Me_2} ligand. The average Ln–C1/C2 distances show

typical increases with increasing size of the lanthanide ion, from 2.376(2) Å (Lu) to 2.498(3) Å (Nd).^[22] The molecular symmetry approaches C_s , with O of the THF ring, Ln, B, and pyrazole (N21, N22) almost in a plane, and renders the two CH_2SiMe_3 moieties and the other two pyrazole rings nearly equivalent. This equivalence is seen in solution, even at -50°C , as the ^1H NMR spectrum of **2a** in $[\text{D}_8]\text{toluene}$ shows a well-defined doublet of doublets for the diastereotopic methylene protons at $\delta = -0.30$ and -0.09 ppm ($^2J_{\text{H,H}} = 11.3$ Hz, $^2J_{\text{Y,H}} = 2.8$ Hz). The 3-Me-Pz and 4-H-Pz moieties both give two signals in a 2:1 ratio, while the signals of the 5-Me-Pz groups accidentally coincide to a sharp singlet at $\delta = 2.15$ ppm.

Hydrogenolysis of the dialkyl complexes **2a–c,e** led to the isolation of the corresponding dihydrides (Scheme 3). They thus join the only other series of monoligated trivalent



Scheme 3. Preparation of dihydride complexes **3a–c,e**.

lanthanide dihydrides reported to date, namely, $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ln}(\mu\text{-H})_4(\text{thf})_n]$ (Ln = Sc, Y, Gd–Tm, Lu),^[7,8] and are the first lanthanide dihydrides with non-cyclopentadienyl ligands. In view of the hard scorpionate nitrogen donor set and the correspondingly stronger Ln–alkyl bond, it is not surprising that the requisite experimental conditions for hydrogenolysis are more rigorous and that longer reaction times are required than reported by Hou et al.^[7a] (75 atm H_2 and 48 h vs 1 atm H_2 and 4–24 h). The compounds are soluble and stable in toluene and THF, and moderately soluble in Et_2O . The yields of the dihydrides vary from reasonable for Y (73%) to moderate for Nd, Sm and Lu (ca. 50%).

The tetranuclear cluster structure, already suggested by the ^1H NMR spectrum of the Y complex (quintet at $\delta = 8.22$ ppm, $^1J_{\text{Y,H}} = 12.1$ Hz), was confirmed by X-ray analysis. Crystals were grown from concentrated THF solution. The lack of THF coordination to the lanthanide attests to the bulkier nature of the Tp^{Me_2} ligand compared to $\text{C}_5\text{Me}_4\text{SiMe}_3$, for which up to two THF molecules were retained by the cluster hydrides.^[7,8] The structure of the representative Y complex is shown in Figure 2. The structure consists of four Y ions located on the corners of a slightly distorted tetrahedron. Each Y is bonded to a $\kappa^3\text{-Tp}^{\text{Me}_2}$ ligand, and the hydride ligands form bridges between the Y atoms in three modes: one $\mu_4\text{-H1}$ at the center of the Y_4 unit, one face-capping $\mu_3\text{-H2}$, and six edge-bridging $\mu_2\text{-H}$. The Y···Y distances range from 3.5329(5) (Y3···Y4) to 3.7114(6) Å (Y1···Y2), and the shortest separation is associated with one of the three Y···Y edges bridged by three hydride ligands. These distances are almost 0.1 Å larger than in the cyclopentadienyl analogue $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Y}(\mu\text{-H})_2]_4$ (3.460 Å–3.621 Å),^[23] and this again reflects the bulkier nature of the Tp^{Me_2} ligand. The $\mu_2\text{-H–Y}$ bond lengths range from 1.94(4) (Y3–H6) to 2.36(4) Å (Y2–H5), which fall in the range found in dimeric yttrium hydrido complexes with bulky

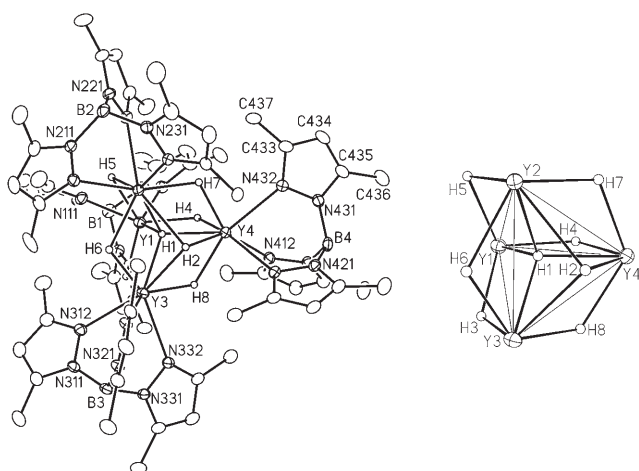
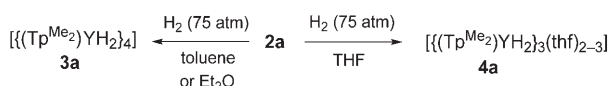


Figure 2. ORTEP drawing of the structure of **3a** (left) and a view of the Y₄H₈ core structure (right): μ_4 : H1, μ_3 : H2, μ_2 : H3–H8.

ligands.^[24] The μ_3 -H–Y distances (Y4–H2 2.17(4), Y3–H2 2.33(4), Y2–H2 2.47(4) Å) indicate an asymmetric bridging arrangement with a weaker bond to Y2. The μ_4 -H–Y bonds (2.18(4)–2.28(4) Å) are again slightly longer than those in $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Y}(\mu\text{-H})_2]_4$ (2.09(2)–2.26(2) Å).^[23] The complexes **3c** and **3e** are isostructural and have the same Ln₄H₈ core structure as $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Ln}(\mu\text{-H})_2]_4$ (Ln = Sc, Y, Lu). The core structure of **3b** appears to be slightly different, with H8 exhibiting a slightly more face-capping than edge-bridging tendency.

The ¹H NMR spectrum of the product of one of the yttrium hydrogenolysis reactions showed that it was a mixture of the usual tetranuclear Y₄ and a new trinuclear Y₃ cluster. We traced the culprit for this unusual observation to a less rigorously dried starting material **2a** which retained some THF of solvation. This hypothesis was verified when the hydrogenolysis reaction in Et₂O/THF (15/1) or THF alone gave pure trinuclear cluster **4a** (Scheme 4). The ¹H NMR



Scheme 4. Solvent effects on the hydrogenolysis of **2a**.

spectrum in C₆D₆ at room temperature showed a quartet at $\delta = 7.45$ ppm with $^1J_{\text{Y,H}} = 15.3$ Hz ($\delta = 7.06$ ppm, $^1J_{\text{Y,H}} = 15.6$ Hz, in [D₈]THF) and one set of signals for the Tp^{Me}₂ ligand indicating fluxional behavior in solution.^[25] Unfortunately, all crystallization attempts gave only small, poor-quality single crystals, and low-temperature ¹H NMR studies in [D₈]toluene led only to signal broadening without reaching the limiting spectrum. Hence, at the moment, the structure of the “Y₃H₆” cluster remains unresolved.

In an effort to investigate the influence of ligands on cluster hydride formation, hydrogenolysis of **1a** and **1e** was investigated. Although the alkyl ligands were eliminated, the ¹H NMR spectrum of the products showed the presence of a mixture of compounds. We attribute this to possible metal-

ation of the *t*Bu substituents. Since the bulky Tp^{*t*Bu,Me} ligand proved problematic we decided to turn to Trofimenko's first-generation and smallest scorpionate Tp (cone angle 184°). The desired $[(\text{Tp})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})]$ (Ln = Y, **5a**; Yb, **5d**; Lu, **5e**) were obtained in moderate yields (56–66%) by following the alkyl-abstraction protocol with TITp. The reaction and isolation of the products were carried out at room temperature for Ln = Yb, Lu, but for the more delicate Y complexes low temperature was necessary.^[22]

Hydrogenolysis of **5a** and **5e** delivered the corresponding dihydrides in yields reflecting the stability of the dialkyl complexes. The moderately stable Lu dialkyl complex gave the dihydride in high yield (ca. 85%). The ¹H NMR spectrum in C₆D₆ at room temperature showed a broad hydride singlet at $\delta = 11.92$ ppm and one set of signals for the Tp ligand in the requisite ratio. The thermally delicate Y dialkyl complex gave mixtures from which single crystals suitable for X-ray analysis could be isolated in very poor yields. Unfortunately, a clean ¹H NMR spectrum of the NMR-active Y dihydride could not be obtained, and determination of the nuclearity of these dihydrides was left to X-ray analysis. The molecular structure of $[(\text{Tp})\text{LuH}_2]_6$ is shown in Figure 3; the Y complex is

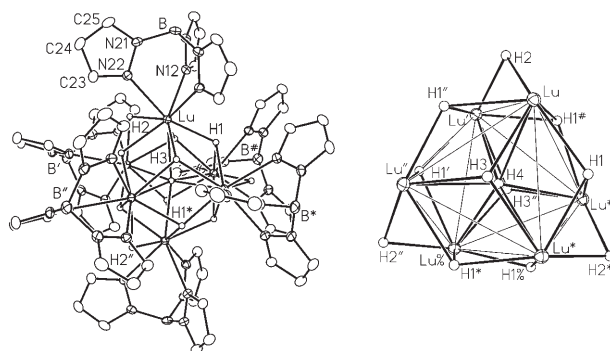


Figure 3. ORTEP drawing of the structure of $[(\text{Tp})\text{LuH}_2]_6$ (left) and a view of the Lu₆H₁₂ core structure (right): μ_6 : H4, μ_3 : H3, H3'', μ_2 : H2, H2'', H2''', μ_3 : H1, H1'', H1*, H1', H1#, H1%.

isostructural. The structure consists of six “(Tp)LuH₂” units forming a hexanuclear cluster held together by twelve bridging hydride ligands.^[26] Also shown in Figure 3 is the hexanuclear Lu₆H₁₂ frame. The six Lu centers are disposed in a trigonal-antiprismatic arrangement with *D*₃ point symmetry, which results in one crystallographically unique Lu atom and “top” and “bottom” equilateral triangular faces bridged by Lu, Lu*, Lu' and Lu', Lu#, Lu%, respectively.

There are four crystallographically unique hydride ligands. Three of them (H2, H2*, H2''), located on twofold rotational axes, bridge the top/bottom faces in μ_2 fashion on alternating edges. There are two μ_3 -bridging hydride ligands on the top/bottom faces (H3, H3'') sitting on a threefold rotation axis, while the remaining six hydride ligands (H1 and related) cap the other faces in a μ_3 fashion; these hydride ligands are not on a symmetry element. The last hydride ligand, H4, binds in a μ_6 -H–Ln fashion and is located at the intersection of the threefold and twofold axes. The parallel top/bottom faces are rotated by 11.6° away from being

eclipsed, and hence the Lu...Lu distances between planes are unequal (3.2008(3) and 3.6411(3) Å for Lu...Lu' and Lu...Lu[#], respectively), the unique Lu...Lu distance within each equilateral triangular face is 3.5961(3). For the same reason, there are two unequal distances to the hydride ligands that bridge the faces between the top/bottom planes (Lu–H1, 2.15(4), Lu–H1'' 2.24(4) Å); the distance to H3 is 2.27(3) Å. The shortest Lu–H distance is that to the μ_2 edge-bridging hydride H2 (and symmetry related ligands), 2.07(4) Å, while the distance to μ_6 -H4 is significantly longer (2.480(2) Å) and is also longer than the μ_4 -H–Lu distance (2.05(3)–2.27(3) Å) in the tetranuclear cluster **3e**.

In summary, we have presented two complementary protocols for the synthesis of a wide range of scorpionate-supported rare earth metal dialkyl complexes. Protonolysis of [Ln(CH₂SiMe₃)₃(thf)₂] with HTp^{tBu,Me} is the method of choice to obtain lanthanide(III) dialkyl complexes with the bulky Tp^{tBu,Me} scorpionate (Ln = Y, Yb, Lu), whereas alkyl abstraction with thallium pyrazolylborates allows the synthesis of the full range of [(Tp^{Me2})Ln(CH₂SiMe₃)₂(thf)] (Ln = Y, Nd, Sm, Yb, Lu) and even [(Tp)Ln(CH₂SiMe₃)₂(thf)] (Ln = Y, Yb, Lu) complexes. Hydrogenolysis of [(Tp^{R,R'})Ln(CH₂SiMe₃)₂(thf)] (R = R' = Me, H) successfully led to the isolation of the first non-cyclopentadienyl lanthanide dihydrides [(Tp^{R,R'})LnH₂]_n. The structure of the dihydrides can be described as a polynuclear cluster framework which is maintained in solution and the nuclearity of which depends on the ligand and even the solvent used in their synthesis. Work is continuing to explore the reactivity of these dialkyl and dihydride complexes.^[27]

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- [1] F. T. Edlmann in *Comprehensive Organometallic Chemistry III*, Vol. 4.01 (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, **2006**, pp. 1–199.
- [2] D. M. Cui, M. Nishiura, Z. Hou, *Macromolecules* **2005**, *38*, 4089–4095.
- [3] D. M. Lyubov, G. K. Fukin, A. A. Trifonov, *Inorg. Chem.* **2007**, *46*, 11450–11456, and references therein.
- [4] Y. J. Luo, M. Nishiura, Z. Hou, *J. Organomet. Chem.* **2007**, *692*, 536–544.
- [5] S. Bambirra, M. W. Bouwkamp, A. Meetsma, B. Hessen, *J. Am. Chem. Soc.* **2004**, *126*, 9182–9183.
- [6] W. J. Evans, J. H. Meadows, A. L. Wayda, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1982**, *104*, 2008–2014.
- [7] a) O. Tardif, M. Nishiura, Z. Hou, *Organometallics* **2003**, *22*, 1171–1173; b) Z. Hou, M. Nishiura, T. Shima, *Eur. J. Inorg. Chem.* **2007**, 2535–2545.
- [8] [(C₅Me₅SiMe₂R)YH₂]₄(thf)₂ (R = Me, Ph) have also been synthesized: K. C. Hultsch, P. Voth, T. P. Spaniol, J. Okuda, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1272–1276.
- [9] W. E. Piers, D. J. H. Emslie, *Coord. Chem. Rev.* **2002**, *233*, 131–155.
- [10] M. Konkol, J. Okuda, *Coord. Chem. Rev.* **2007**, DOI: 10.1016/j.ccr.2007.09.019.
- [11] S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, London, Imperial College Press, **1999**.
- [12] D. P. Long, P. A. Bianconi, *J. Am. Chem. Soc.* **1996**, *118*, 12453–12454.
- [13] J. Blackwell, C. Lehr, Y. M. Sun, W. E. Piers, S. D. Pearce-Batchelder, M. J. Zaworotko, V. G. Young, *Can. J. Chem.* **1997**, *75*, 702–711.
- [14] a) R = tBu, R' = Me, Ln = Y, Yb, Lu, x = 0; R = R' = Me, Ln = Y, Nd, Sm, Yb, Lu, x = 1; R = R' = H, Ln = Y, Yb, Lu, x = 1; b) a series of [(Tp^{R,R'})Ln(CH₂SiMe₂Ph)₂(thf)_x] complexes has also been synthesized.
- [15] The salt-elimination route appears to be accompanied by LiTp^{R,R'} formation;^[13,16] in our hands, repeated preparation of [(Tp^{Me2})Y(CH₂SiMe₃)₂(thf)] also resulted in the formation of 5–10% of LiTp^{Me2}.
- [16] F. A. Kunrath, O. L. Casagrande, L. Toupet, J. F. Carpentier, *Polyhedron* **2004**, *23*, 2437–2445.
- [17] [(Tp^{Me2})Y(CH₂SiMe₃)₂(thf)] was also prepared through protonolysis by Casagrande and Carpentier: J.-F. Carpentier, personal communication.
- [18] R. Han, G. Parkin, *Organometallics* **1991**, *10*, 1010–1020.
- [19] A. Looney, G. Parkin, *Polyhedron* **1990**, *9*, 265–276.
- [20] H. Schumann, D. M. M. Freckmann, S. Dechert, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2422–2426.
- [21] The structure of **2e** has also been determined: G. W. Rabe, A. L. Rheingold, *Cambridge Structural Database* **2007**, CCDC REF CODE: VIFREI.
- [22] See the Supporting Information for synthetic, characterization, and structural details of these and other compounds.
- [23] Y. Luo, J. Baldamus, O. Tardif, Z. Hou, *Organometallics* **2005**, *24*, 4362–4366.
- [24] a) J. P. Mitchell, S. Hajela, S. K. Brookhart, K. I. Hardcastle, L. M. Henling, J. E. Bercaw, *J. Am. Chem. Soc.* **1996**, *118*, 1045–1053; b) A. A. Trifonov, T. P. Spaniol, J. Okuda, *Organometallics* **2001**, *20*, 4869–4874; c) K. C. Hultsch, H. P. Spaniol, J. Okuda, *Angew. Chem.* **1999**, *111*, 163–165; *Angew. Chem. Int. Ed.* **1999**, *38*, 227–230; d) A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, N. A. Skorodumova, G. K. Fukin, E. V. Baranov, V. N. Glushakova, *Chem. Eur. J.* **2006**, *12*, 5320–5327.
- [25] Trinuclear [(Tp^{Me2})YH₂(thf)₃] was briefly mentioned by Bianconi and Long,^[12] characterized as “very thermally unstable” and with ¹H NMR signatures somewhat different from ours: two inequivalent pyrazole moieties and Y–H (quartet at δ = 7.45 ppm with ¹J_{Y,H} = 16.25 Hz).
- [26] The related [(C₅Me₅)LnH₂]₆ compounds have been obtained and briefly mentioned by Hou et al.^[7b]
- [27] Note added in proof: Non-cyclopentadienyl supported lanthanide dialkyls and dihydrides with a monomeric [NNNN] ligand have been reported: M. Ohashi, M. Konkol, I. Del Rosal, R. Poteau, L. Maron, J. Okuda, *J. Am. Chem. Soc.* **2008**, DOI: 10.1021/ja801771u.