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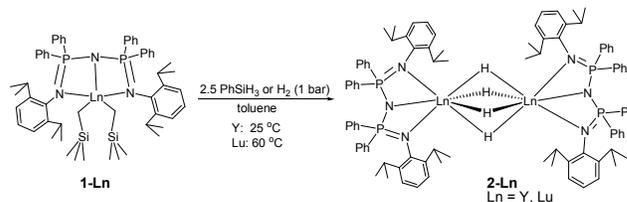
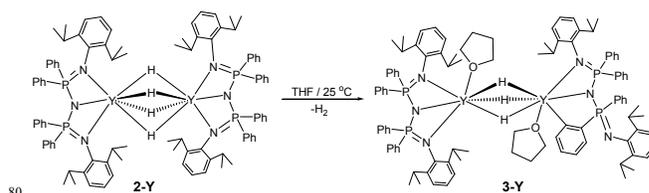
Neutral binuclear rare-earth metal complexes with four  $\mu_2$ -bridging hydrides†Weifeng Rong,<sup>a,b</sup> Dongliang He,<sup>a,d</sup> Meiyang Wang,<sup>c</sup> Zehuai Mou,<sup>a,b</sup> Jianhua Cheng,<sup>a</sup> Changguang Yao,<sup>a,b</sup> Shihui Li,<sup>a</sup> Alexander A. Trifonov\*,<sup>ef</sup> Dmitrii M. Lyubov,<sup>ef</sup> and Dongmei Cui\*<sup>a</sup>Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX  
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The first neutral rare-earth metal dinuclear dihydrido complexes [(NPNPN)LnH<sub>2</sub>]<sub>2</sub> (**2-Ln**; Ln = Y, Lu; NPNPN: N[Ph<sub>2</sub>PNC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>]<sub>2</sub>) bearing  $\mu_2$ -bridging hydride ligands have been synthesized. In the presence of THF, **2-Y** undergoes intramolecular activation of sp<sup>2</sup> C–H bond to form dinuclear aryl-hydride complex **3-Y** containing three  $\mu_2$ -bridging hydride ligands.

Metal hydride complexes occupy an important and unique position in organometallic chemistry<sup>1</sup> because of their peculiar and versatile applications, such as molecular models for hydrogen-storage material,<sup>2</sup> catalytic reduced reagent<sup>3</sup> and activation of small molecules.<sup>4</sup> Rare-earth metal hydrides have also witnessed a spectacular growth in the last three decades,<sup>5</sup> among which dihydride complexes bearing “LMH<sub>2</sub>” moiety have attracted a particular interest because of their fascinating structures and versatile reactivity.<sup>6</sup> However, most of the rare-earth dihydride species reported so far tend to assemble to polynuclear structures such as [LMH<sub>2</sub>]<sub>n</sub> (n ≥ 3) through ‘intermolecular’ metal-hydride interactions, especially for the non-Cp-type hydrido complexes, which may be ascribed to the steric unsaturation of the large f-element ions and their strong Lewis basic nature, as well as the small steric bulkiness of the hydride ligand.<sup>7</sup> The stoichiometric reactions of these polyhydrides show that different coordinate hydride ligands display different reactivity and the polynuclear skeletons usually

collapse to give complicated intermediates.<sup>6j</sup> Therefore, to synthesize the simple dinuclear and the finally targeted monomeric terminal rare-earth metal hydrides, is a challenging and promising project, as the simple structural hydride complexes are crucial factors to realize the cyclic catalysis. To date, the dinuclear rare-earth metal dihydrides are rather unstable and very scarce.<sup>7,8</sup> There is only one cationic rare-earth metal dihydrido complex bearing quadruply bridged hydrido ligands.<sup>9</sup> Herein we report the first neutral dimeric rare-earth metal hydride complexes containing quadruply bridged hydrido ligands and its reaction triggered by a THF molecule.

Treatment of the phosphazene-ligated rare-earth dialkyl complexes **1-Ln** [(NPNPN)Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (Ln = Y, Lu)<sup>10</sup> with dihydrogen or phenylsilane in toluene or benzene at 25 °C (for Y complex) or at 60 °C (for Lu complex) afforded the dinuclear tetrahydride complexes **2-Ln** in moderate yields (Scheme 1). **2-Ln** were sparingly soluble in toluene and benzene but insoluble in hexane. In the <sup>1</sup>H NMR spectrum of complex **2-Y**, the Y–H signal was overlapped with the aromatic H signals;<sup>11</sup> but the hydride resonance in **2-Lu** was recorded at  $\delta$  10.26 ppm as a distinct singlet, which is consistent with the previous reports that the hydride ligands usually give downfield resonances such as [(Me-PNP<sup>i</sup>Pr)LuH<sub>2</sub>]<sub>3</sub> at  $\delta$  9.70 ppm,<sup>6c</sup> [(NCN)LuH<sub>2</sub>]<sub>2</sub>(THF)<sub>3</sub> at  $\delta$  8.72 ppm,<sup>7a</sup> [(NCN)LuH(THF)<sub>3</sub>][BPh<sub>4</sub>] at  $\delta$  12.28 ppm,<sup>7b</sup> and [(Ap\*Lu)<sub>3</sub>( $\mu_2$ -H)<sub>3</sub>( $\mu_3$ -H)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>] at  $\delta$  9.08, 12.25, and 12.37 ppm.<sup>11b</sup> Colorless single crystals of **2-Y** and **2-Lu** were

Scheme 1. Synthesis of neutral tetrahydrido complexes **2-Ln**.Scheme 2. Synthesis of neutral trihydrido complex **3-Y**.

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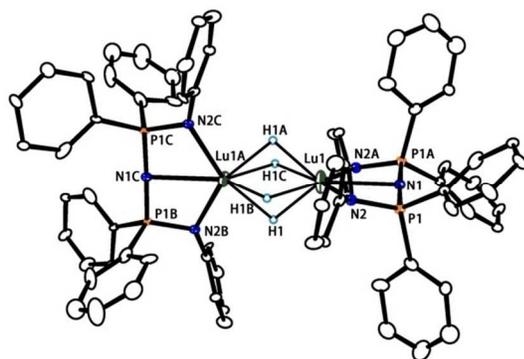
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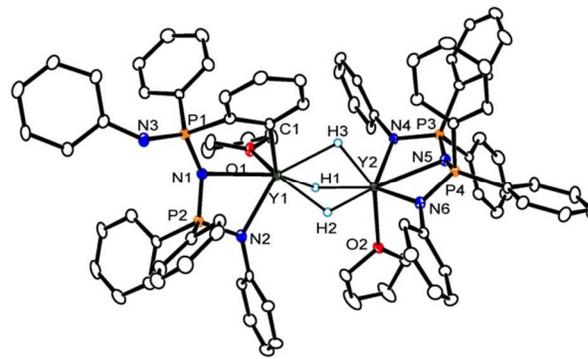
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† Electronic Supplementary Information (ESI) available: Experimental section, NMR, and crystallographic data. CCDC 1020089 (**2-Y**) 1020088 (**2-Lu**), 1020087 (**3-Y**). For ESI and crystallographic data in CIF See DOI: 10.1039/b000000x/



**Fig. 1** ORTEP plot of **2-Lu** with thermal ellipsoids at the 35% probability level. Hydrogen atoms except bridging hydrides and <sup>1</sup>Pr groups have been omitted for clarity. Selected bond distances (Å): Lu1–N2 2.276(12), Lu1–N1 2.507(15), Lu1...P1 2.982(4), Lu1...Lu1A 3.104(3), Lu1–H1 2.0622.

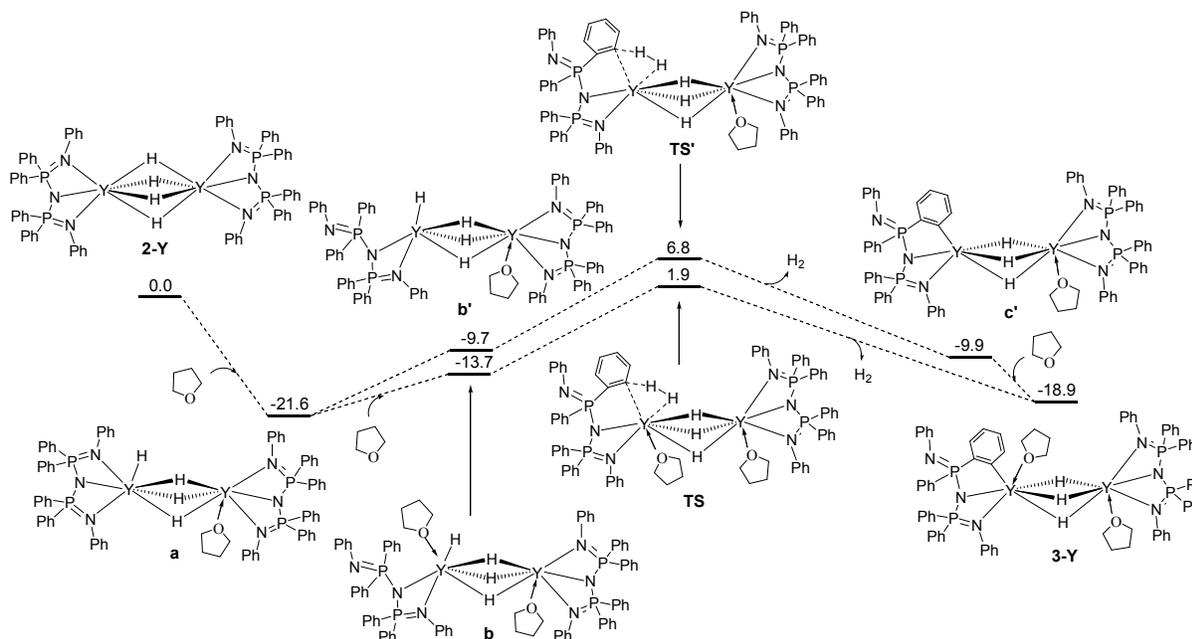


**Fig. 2** ORTEP plot of **3-Y** with thermal ellipsoids at the 35% probability level. Hydrogen atoms except bridging hydrides and <sup>1</sup>Pr groups have been omitted for clarity. Selected bond distances (Å): Y1...Y2 3.3681(8), Y1–C1 2.513(7), Y1–H1 2.12(6), Y1–H2 2.19(7), Y1–H3 2.30(6), Y2–H1 2.22(6), Y2–H2 2.18(7), Y2–H3 2.06(6).

obtained by slow evaporation of a mixture of toluene and benzene at room temperature. The X-ray diffraction study revealed that their lattice parameters were almost identical and their structures were refined in the uncommon space group I222.<sup>12</sup> Hence the final molecular structures were solved from one quarter initially after 222 symmetry operator.<sup>13</sup> The molecular structure of complex **2-Lu** is shown in Fig. 1 (Fig.S2 for **2-Y**), in which the two Lu<sup>3+</sup> are bridged by the unprecedented four  $\mu_2$ -H ligands, additionally, each Lu<sup>3+</sup> is coordinated by the anionic {N[Ph<sub>2</sub>PNC<sub>6</sub>H<sub>3</sub>(<sup>1</sup>Pr)<sub>2</sub>]<sub>2</sub>}<sup>-</sup> ligand in a  $\kappa^3$ -NNN mode. No THF was found to coordinate to the metal centers owing to the steric bulky NPNPN ligand. It is noteworthy that two NPNPN planes are almost perpendicular, as the thus staggered conformation is low energy and more stable. The Lu–H bond lengths are 2.062 Å and 2.112 Å, which are comparable with those found in [Cp<sup>\*</sup>LuH<sub>2</sub>]<sub>4</sub> (1.85(3)–2.44(6) Å),<sup>6h</sup> and [(NCN)LuH(THF)<sub>2</sub>]<sub>2</sub>[BPh<sub>4</sub>]<sub>2</sub> (2.01(5), 2.15(5) Å).<sup>7b</sup> The Lu...Lu distance (3.104(3) Å) is the shortest among the values reported for neutral hydride complexes, but longer than that in the cationic example (2.9270(6) Å).<sup>9</sup> So far, **2-Lu** represents the first binuclear neutral complex with four  $\mu_2$ -

bridging hydrides in rare-earth metal chemistry, although the similar structures [LM-( $\mu_2$ -H)<sub>4</sub>-ML] have been reported in Zr, Re, Ta and Hf complexes.<sup>14</sup>

The poor solubility of **2-Lu** in aromatic solvents arouse great difficulty in NMR characterization, so we could not provide the convincing <sup>13</sup>C NMR data. However **2-Y** turned out to be highly soluble in THF. Removal of the THF solvent and drying in vacuo gave a residue that was re-dissolved by THF-*d*<sub>8</sub>. The obtained <sup>1</sup>H NMR spectrum presented, surprisingly, a set of resonances different from that of **2-Y**, suggesting the formation of a new compound **3-Y** (Scheme 2). Similar to its congener **2-Y**, the Y–H signals of **3-Y** could not be distinguished from the aromatic H signals. Fortunately we successfully isolated high quality single crystals of **3-Y** suitable for the X-ray study, which allowed us to determine the structure of **3-Y** with defined hydride localization. Complex **3-Y** remains the dimeric structure like its congener but contains two THF molecules, where one Y<sup>3+</sup> ion is bonded to the monoanionic  $\kappa^3$ -NPNPN ligand while the other Y<sup>3+</sup> ion is coordinated by the dianionic  $\kappa^3$ -CPNPN ligand arising from the Ph–H (sp<sup>2</sup>) activation of the NPNPN ligand. The two Y<sup>3+</sup> ions are



**Fig.3** Calculated energy profile from **2-Y** to **3-Y**.

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connected by three  $\mu_2$ -bridged hydride ligands, generating a  $Y_2H_3$  core (Fig. 2), which is similar to those found in the cationic complexes  $[(Me_5TRENCH_2)Lu(\mu_2-H)_3Lu(Me_6TREN)][X]_2^{8b}$  and  $[(Me_3TACD-CH_2)Lu(\mu_2-H)_3Lu(Me_4TACD)][A]_2^9$ . The  $Y \cdots Y$  distance is 3.368 Å, significantly shorter than those in the polynuclear hydrides ( $[Y(Me_3TACD)H_2]_3$ , 3.516(1) Å;<sup>6f</sup>  $[Tp^{Me_2}Y(\mu-H)_2]_4$ , 3.5329(5)–3.7114(6) Å;<sup>6g</sup>  $[(\eta^5-C_5Me_4SiMe_3)Y(\mu-H)_2]_4$ , 3.460–3.621 Å<sup>6i</sup>). Obviously, THF triggered the intramolecular phenyl C–H bond activation by the hydride ligand, leading to hydrogen extrusion and the formation of **3-Y**.

To gain more insight into the reaction pathways for **2-Y** transferring to **3-Y**, a DFT calculation was carried out using the B3PW91 functional (Fig. 3), where the isopropyl groups were neglected. The coordination of a THF molecule to the  $Y^{3+}$  ion of complex **2-Y** breaks one bridging H to give complex **a** bearing a terminal hydride ligand. Adopting a second THF generates complex **b**. The activation of the ortho C–H bond of phenyl substituent on P by the terminal hydride ligand via transition state **TS** releases  $H_2$  to afford complex **3-Y**. Alternatively, the rotation around P–N bond makes one phenyl group on P adjacent to Y–H bond (complex **b'**), which arouses dehydrogenation to give the final product via transition state **TS'** and the intermediate **c'**. The free energy of the transition state **TS** is 4.9 kcal/mol lower than that of **TS'**, indicating that the first reaction pathway is preferred.

In summary, we have demonstrated that the bulky  $N[Ph_2PNC_6H_3(Pr)_2]_2$  moiety can serve as an excellent supporting ligand to stabilize the rare-earth hydride species, resulting in the first neutral binuclear f-element metal based dihydride complexes bearing four  $\mu_2$ -bridging hydride ligands. In addition, THF can behave as a trigger to initiate the intramolecular activation of the very stable phenyl group  $sp^2$  C–H bond by releasing  $H_2$ , giving an unprecedented dinuclear aryl-hydride complex with three  $\mu_2$ -bridging hydride ligands.

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## Notes and references

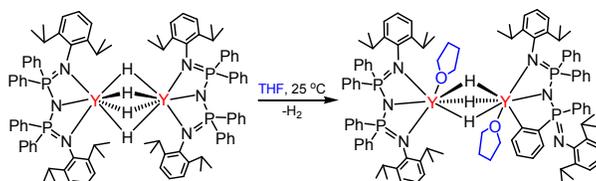
1. R. H. Crabtree. *The Organometallic Chemistry of The Transition Metals*, Ed. 6<sup>th</sup>. Wiley, 2014.
2. (a) S. Harder, *Chem Commun.*, 2012, **48**, 11165; (b) S. Harder, J. Spielmann, J. Intemann and H. Bandmann, *Angew. Chem., Int. Ed.*, 2011, **50**, 4156.
3. (a) S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna and A. Stasch, *Angew. Chem., Int. Ed.*, 2009, **48**, 2973; (b) C. Boone, I. Korobkov and G. I. Nikonov, *ACS Catal.*, 2013, **3**, 2336; (c) V. K. Chidara and G. Du, *Organometallics*, 2013, **32**, 5034; (d) B. Chatterjee and C. Gunanathan, *Chem. Commun.*, 2014, **50**, 888; (e) P.

- Jochmann and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2013, **52**, 9831.
- (a) T. Shima, S. Hu, G. Luo, X. Kang, Y. Luo and Z. Hou, *Science*, 2013, **340**, 1549. (b) S. Hu, T. Shima and Z. Hou, *Nature*, 2014, **512**, 413; (c) W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2011, **133**, 9708.
- (a) M. Konkol and J. Okuda, *Coord. Chem. Rev.* 2008, **252**, 1577; (b) P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, *Chem. Rev.*, 2006, **106**, 2404; (c) Z. Hou and Y. Wakatsuki, *Coord. Chem. Rev.*, 2002, **231**, 1. (d) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851; (e) S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953.
- For examples of rare-earth dihydride complexes, see: (a) T. Shima, M. Nishiura and Z. Hou, *Organometallics*, 2011, **30**, 2513; (b) M. Nishiura, J. Baldamus, T. Shima, K. Mori and Z. Hou, *Chem. Eur. J.*, 2011, **17**, 5033; (c) J. Cheng, T. Shima and Z. Hou, *Angew. Chem., Int. Ed.*, 2011, **50**, 1857; (d) D. M. Lyubov, C. Doring, S. Y. Ketkov, R. Kempe and A. A. Trifonov, *Chem. Eur. J.*, 2011, **17**, 3824; (e) J. Cheng, M. J. Ferguson and J. Takats, *J. Am. Chem. Soc.*, 2010, **132**, 2; (f) M. Ohashi, M. Konkol, I. Del Rosal, R. Poteau, L. Maron and J. Okuda, *J. Am. Chem. Soc.*, 2008, **130**, 6920; (g) J. Cheng, K. Saliu, G. Y. Kiel, M. J. Ferguson, R. McDonald and J. Takats, *Angew. Chem., Int. Ed.*, 2008, **47**, 4910; (h) O. Tardif, M. Nishiura and Z. Hou, *Organometallics*, 2003, **22**, 1171; (i) Y. Luo, J. Baldamus, O. Tardif and Z. Hou, *Organometallics*, 2005, **24**, 4362; (j) D. Cui, O. Tardif and Z. Hou, *J. Am. Chem. Soc.*, 2004, **126**, 1312.
- (a) J. Cheng, H. Wang, M. Nishiura and Z. Hou, *Chem. Sci.*, 2012, **3**, 2230; (b) J. Cheng and Z. Hou, *Chem. Commun.*, 2012, **48**, 814.
- (a) J. Zhou, J. Chu, Y. Zhang, G. Yang, X. Leng and Y. Chen, *Angew. Chem., Int. Ed.*, 2013, **52**, 4243; (b) A. Venugopal, W. Fegler, T. P. Spaniol, L. Maron and J. Okuda, *J. Am. Chem. Soc.*, 2011, **133**, 17574.
- W. Fegler, A. Venugopal, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.*, 2013, **52**, 7976.
- W. Rong, D. Liu, H. Zuo, Y. Pan, Z. Jian, S. Li and D. Cui, *Organometallics*, 2013, **32**, 1166.
- (a) E. Lu, Y. Chen and X. Leng, *Organometallics*, 2011, **30**, 5433; (b) D. M. Lyubov, C. Döring, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, R. Kempe and A. A. Trifonov, *Organometallics*, 2008, **27**, 2905.
- We did not deeply discuss the structure of **2-Y** here because the checkif report of **2-Y** has a mistake in level A (Supporting Information).
- Point group 222 has three mutually-perpendicular two-fold rotation axes.
- (a) H. Kulinna, T. P. Spaniol, L. Maron and J. Okuda, *Inorg. Chem.*, 2012, **51**, 12462; (b) S. C. Mayo, M. Bown and V. K. Lloyd, *Acta Crystallogr. Sect. C* 1994, **50**, 367; (c) J. Ballmann, F. Pick, L. Castro, M. D. Fryzuk and L. Maron, *Organometallics*, 2012, **31**, 8516; (d) M. D. Fryzuk, S. A. Johnson and S. J. Rettig, *Organometallics*, 2000, **19**, 3931; (e) J. G. Hinman, K. Abdur-Rashid, A. J. Lough and R. H. Morris, *Inorg. Chem.*, 2001, **40**, 2480; (f) F. A. Cotton and R. L. Luck, *Inorg. Chem.*, 1989, **28**, 4522.

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## Neutral binuclear rare-earth metal complexes with four $\mu_2$ -bridging hydrides

Weifeng Rong, Dongliang He, Meiyang Wang, Zehuai Mou, Jianhua Cheng, Changguang Yao, Shihui Li, Alexander A. Trifonov\*, Dmitrii M. Lyubov and Dongmei Cui\*



The first neutral dimeric rare-earth metal hydride complexes containing quadruply bridged hydrido ligands were prepared, in which the intramolecular activation of the stable phenyl group  $sp^2$  C–H bond triggered by a THF molecule has been observed.