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Dihydrogen Addition in a Dinuclear Rare-Earth Metal Hydride Complex Supported by a Metalated TREN Ligand

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S Supporting Information

ABSTRACT: The dinuclear lutetium dihydride dication supported by metalated tripodal ligands undergoes facile hydrogenolysis with H_2 to form a trihydride dication. Molecular orbital analysis shows that the LUMO is a bonding Lu···Lu orbital that is poised to activate dihydrogen.

Interstitial rare-earth compounds such as $LaNi_5H_6$ have been recognized as hydrogen storage materials.[1] Molecular hydrides could act as model compounds toward understanding the mechanism of dihydrogen uptake and release.[2] Metallocene hydrides of the type $[Ln(\eta^5\text{-}C_5R_5)_2H]$[3] exist as monomers and exhibit high reactivity[4] but cannot change the number of hydride ligands. Half-sandwich rare-earth metal hydrides of varied nuclearity, $[Ln(\eta^5\text{-}C_5R_5)H_2]_x$,[5] as well as neutral rare-earth metal hydrides of the type $[Ln(L_nX)H_2]$[6] bearing a non-cyclopentadienyl monoanionic ligand (L_nX), have also been shown to be active in a wide range of stoichiometric and catalytic reactions[4−6] but fail to undergo dihydrogen addition and/or release.[7]

We report here that a dinuclear rare-earth metal hydrido cation supported by the anionic ligand $(Me_5TRENCH_2)^-$ (L_4X-type ligand derived from the neutral ligand tris{2-(dimethylamino)-ethyl}amine, Me_6TREN)[8,9] adds dihydrogen to give another hydride cation. Cationic hydrides can be expected to be less aggregated and to exhibit different reactivity patterns, but they are still rare.[10,11]

Me_6TREN reacts with $[Lu(CH_2SiMe_3)_2(THF)_x][X]$[12] to form the monocationic lutetium alkyl $[Lu(Me_6TREN)(CH_2SiMe_3)_2]$-$[X]$ ($X = B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4$, **1-Lu**, Scheme 1). **1-Lu** is thermally sensitive and decomposes at temperatures above 0 °C. The identity and purity of **1-Lu** were established by ^1H NMR spectroscopy. At room temperature, **1-Lu** is converted over a period of 3 days, yielding 91% of $[Lu(Me_5TRENCH_2)(CH_2SiMe_3)][X]$ (**2-Lu**) with concomitant elimination of $SiMe_4$. This transformation results from the metalation of one of the six methyl groups in Me_6TREN, forming the anionic $(Me_5TRENCH_2)^-$ ligand of L_4X-type. Similar metalations of NMe_2 groups by alkyl derivatives of rare-earth metals have been previously observed.[13] **2-Lu** is soluble in Et_2O, THF, and CH_2Cl_2, is stable at room temperature for several days both in the isolated state and in solution, and was characterized by elemental analysis and multinuclear NMR spectroscopy.

Single crystals suitable for X-ray diffraction (XRD) experiments were obtained for $[Lu(Me_5TRENCH_2)(CH_2SiMe_3)][B(C_6F_5)_4]$ (**2a-Lu**), synthesized in a method similar to the preparation of **2-Lu** (see Supporting Information (SI)). The Lu atom in **2a-Lu** is coordinated by the $(Me_5TRENCH_2)^-$ ligand in a $\kappa^4N{:}\kappa C$ manner (Figure 1). The overall geometry around the metal center can be considered as distorted trigonal bipyramidal. The $Lu{-}CH_2SiMe_3$ distance in **2a-Lu** is comparable to those found in other monocationic lutetium alkyls.[14,15]

When an Et_2O solution of **2-Lu** was treated with a 4-fold excess of $PhSiH_3$ and allowed to stand for 24 h at room temperature, a colorless crystalline precipitate of $[Lu_2(Me_5TRENCH_2)$-$H_2][X]_2$ (**3-Lu**) was obtained in 76% yield (Scheme 1). **3-Lu** was characterized by elemental analysis, multinuclear NMR spectroscopy, and single-crystal XRD. **3-Lu** is the first example of a *cationic* rare-earth metal hydride featuring a $Ln_2(\mu\text{-}H)_2$ core.[3] Each of the metal centers is additionally coordinated by the anionic $(Me_5TRENCH_2)^-$ ligand in a $\kappa^4N{:}\kappa C$ manner (Scheme 1). The dicationic charge is balanced by two organoborate anions, $[B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]^-$. A characteristic feature in the ^1H NMR spectrum of **3-Lu** in THF-d_8 recorded at 24 °C is the appearance of two broad signals at δ 11.65 and 11.69 ppm for the bridging hydride ligands and two AB patterns at δ 1.13 and 1.76 ppm for the methylene protons of the $(Me_5TRENCH_2)^-$ ligand. Variable-temperature ^1H NMR and ^1H COSY studies indicate that **3-Lu** is present in solution as a diastereomeric mixture of centrosymmetric heterochiral (*meso*) and C_2-symmetric homochiral (*rac*) dimers (see SI). Similar observations have previously been made in the case of metallocene and half-sandwich rare-earth metal hydrides.[16] The solid-state structure of **3-Lu**·$2Et_2O$ was elucidated by single-crystal XRD. The dication consists of two Lu centers of opposite chirality bridged by two μ_2-hydride ligands (Figure 2). The two lutetium centers are separated by a distance of 3.5147(2) Å, which is comparable to the Lu···Lu distances in the neutral dimeric μ_2-bridged lutetium complexes.[17] Each of the Lu atoms is coordinated by the $(Me_5TRENCH_2)^-$ ligand. An inversion center exists between the two lutetium atoms, and hence the atoms are symmetry related. The Lu−N distances lie in the range of 2.397(2)−2.484(2) Å, and the Lu1−C1A distance is 2.328(5) Å; both these distances are slightly larger than the corresponding distances found in **2-Lu**.

When a THF-d_8 solution of **3-Lu** was treated with 1 bar of H_2 at room temperature for 24 h, one of the two $(Me_5TRENCH_2)^-$ ligands in **3-Lu** reverted to Me_6TREN, resulting in the formation of a dicationic tri(μ_2-hydride) complex, $[Lu(Me_5TRENCH_2)$-$(\mu_2\text{-}H)_3Lu(Me_6TREN)][X]_2$ (**4-Lu**, Scheme 1). This reaction was observed also in the absence of any solvent in the solid state. Notably, further hydrogenation of **4-Lu** was not observed even

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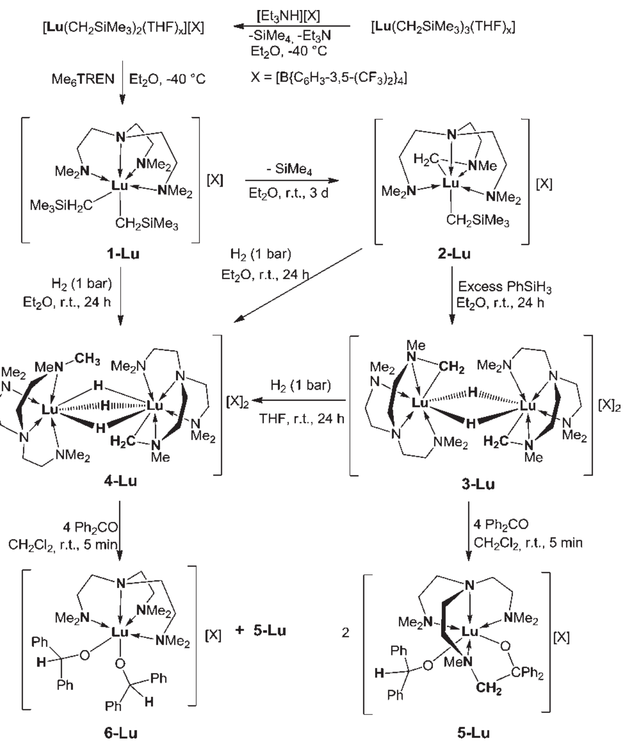
Scheme 1. Synthesis and Reactivity of Cationic Lutetium Hydrides



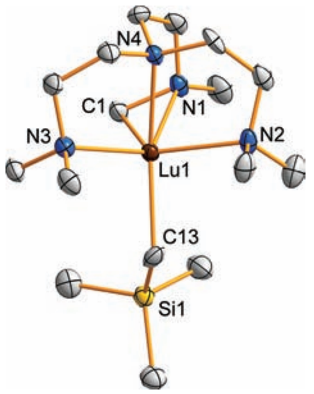


Figure 1. ORTEP diagram of the cationic part of **2a-Lu**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1−C1 2.298(5), Lu1−C13 2.347(5), N1−Lu1 2.376(4), N2−Lu1 2.420(4), N3−Lu1 2.405(4), N4−Lu1 2.464(4); C13−Lu1−N1 130.30(16), C13−Lu1−N4 151.62(16), N3−Lu1−N2 120.04(14).

with 7 bar of H_2 at 70 °C. **4-Lu** did not convert back to **3-Lu** when it was heated in THF-d_8 in a sealed NMR tube under vacuum for 3 days, but H_2 evolution was observed, accompanied by the formation of intractable Lu compounds. The hydrogenolysis from **3-Lu** to **4-Lu** resembles the reaction between [Ln(η^5-$C_5Me_4SiMe_3$)(η^5:η^1-$C_5Me_4SiMe_2CH_2$)(THF)] (Ln = Y, Nd, Sm, Dy, Lu) and H_2, wherein the "tucked-in" chelating methylene bridge undergoes σ-bond metathesis to form the metallocene hydride [Ln(η^5-$C_5Me_4SiMe_3$)$_2$H(THF)].[4a] **4-Lu** was characterized by NMR spectroscopy and elemental analysis and is the first example of a dicationic rare-earth metal trihydride. The signal for the three hydrides in the ^{1}H NMR spectrum of **4-Lu** in THF-d_8 appears as a singlet and is upfield shifted to δ 8.27 ppm as compared to those in **3-Lu**. The two signals for the diastereotopic methylene protons of the $(Me_5TRENCH_2)^-$ unit appear at δ 1.44 and 1.53 ppm.

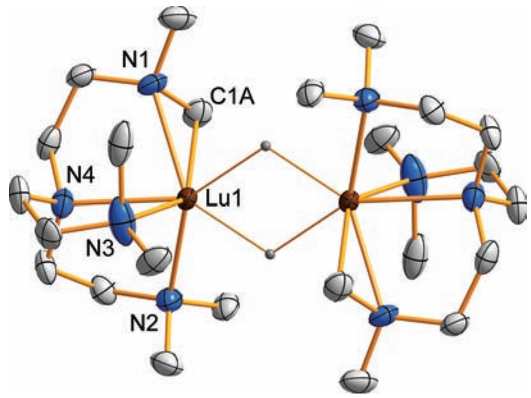


Figure 2. ORTEP diagram of the cationic part of **3-Lu**·2Et$_2$O. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1$\cdots$Lu1 3.5147(2), Lu1−C1A 2.328(5), Lu1−N1 2.397(2), Lu1−N2 2.398(2), Lu1−N3 2.459(2), Lu1−N4 2.484(2); C1A−Lu1−N1 36.23(14), N1−Lu1−N2 125.71(8), N1−Lu1−N3 103.26(10), N1−Lu1−N4 72.89(8), N2−Lu1−N3 104.28(9), N2−Lu1−N4 72.76(7), N3−Lu1−N4 71.79(9).

In separate experiments, treatment of either **1-Lu** or **2-Lu** with 1 bar of H_2 in Et_2O for 24 h also resulted in the precipitation of **4-Lu** as colorless crystals in 70% yield. The pathway from **1-Lu** to give **4-Lu** possibly involves $[(Me_6TREN)LuH_2]^+$ as an intermediate, which, during dimerization, loses dihydrogen to form **4-Lu**. However, there is no experimental evidence for the formation of this type of mononuclear intermediate with terminal hydrides. The transformation from **2-Lu** to **4-Lu** can occur either via this intermediate or via **3-Lu**. An isostructural yttrium complex **4-Y** has also been obtained in 69% yield using an analogous synthetic procedure (see SI), but a hydride cation analogous to **3-Lu** was not observed. The solid-state structure of **4-Lu**·2Et$_2$O was confirmed by single-crystal XRD. The dication consists of two lutetium metal atoms which are μ_2-bridged by three hydride ligands (Figure 3). The Lu_2H_3 core in **4-Lu** resembles those found in the monocations $[Ln_2(\text{Me-PNP}^{iPr})_2H_3(THF)_2]^+$ (Ln = Y, Lu).[11] The Lu$\cdots$Lu distance of 3.2775(4) Å in **4-Lu** is shorter by 0.24 Å than the Lu$\cdots$Lu distance in **3-Lu** and comparable to that in $[Lu_2(\text{Me-PNP}^{iPr})_2H_3(THF)_2][BPh_4]$ (3.2174(4) Å).[11] While one of the Lu atoms in **4-Lu** is coordinated by the neutral Me$_6$TREN, the other is coordinated by the anionic $(Me_5TRENCH_2)^-$ ligand. The Lu−N and Lu−C distances are slightly larger than corresponding distances found in **2-Lu** and **3-Lu**.

In order to gain further insight into the bonding as well as the relative stability of each of the complexes, DFT calculations on both the lutetium and yttrium compounds were carried out (see SI). The geometry of the complexes **3-Lu** and **4-Lu** as well as **3-Y** and **4-Y** was optimized. In **3-Lu**, the optimized Lu$\cdots$Lu and Lu−CH$_2$N distances are 3.57 and 2.29 Å, in excellent agreement with the experimental values. The Lu−H distances are found to be 2.13 Å, indicating a symmetrical coordination of the bridging hydrides. A close analysis of the molecular orbitals shows that

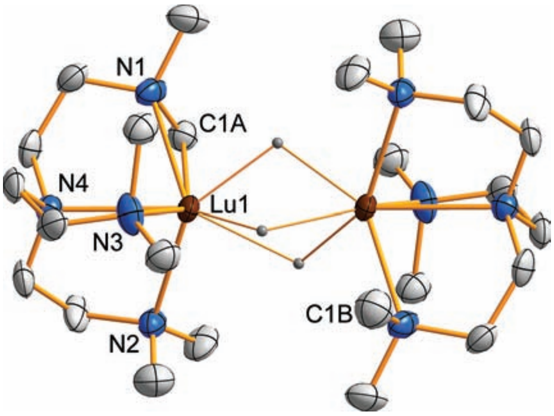


Figure 3. ORTEP diagram of the cationic part of **4-Lu**·2Et_2O. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1···Lu1 3.2775(4), Lu1−C1A 2.441(12), Lu1−N1 2.448(2), Lu1−N2 2.448(2), Lu1−N3 2.482(2), Lu1−N4 2.539(2); C1A−Lu1−N1 33.9(3), N2−Lu1−N1 117.75(8), N1−Lu1−N3 107.05(9), N1−Lu1−N4 71.52(8), N2−Lu1−N3 105.68(9), N2−Lu1−N4 71.61(8), N3−Lu1−N4 70.75(8).

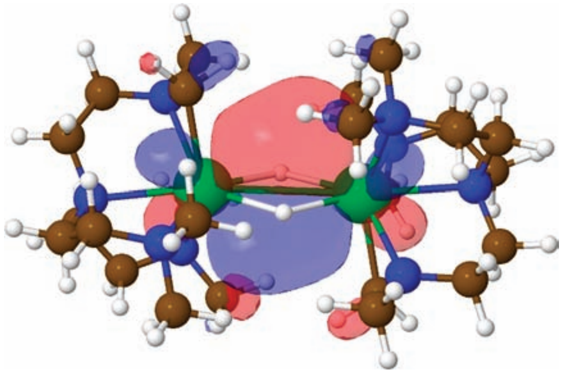


Figure 4. LUMO of **3-Lu**.

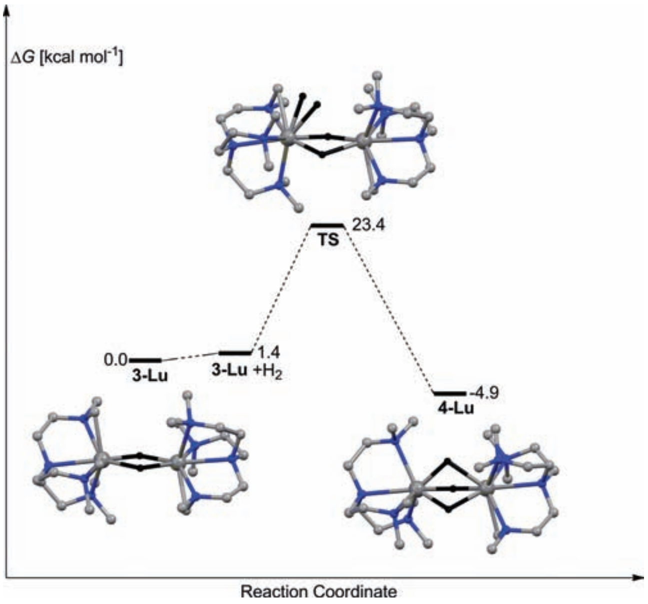


Figure 5. Proposed activation of dihydrogen in **3-Lu**.

the LUMO is a bonding Lu···Lu orbital that is poised to activate dihydrogen prior to σ-bond metathesis (Figure 4).

This has further been demonstrated by computing the entire free energy pathway (Figure 5). The reaction of **3-Lu** with H_2 to give **4-Lu** is predicted to be exergonic by 4.9 kcal·mol^{-1}. The activation barrier is predicted to be 23.4 kcal·mol^{-1}. In the transition state, the two hydrogen and two lutetium atoms are no longer coplanar. This bending allows the d-orbital of Lu, involved in a bonding interaction in the LUMO, to interact with the σ-orbital of H_2. The observed H···H distance of 0.96 Å is typically found in a σ-bond metathesis transition state. In **4-Lu**, the Lu···Lu distance is reduced to 3.28 Å (experimentally observed 3.278 Å) as compared to that in **3-Lu**. The Lu−CH_2N distance of 2.31 Å is in agreement with the experimental value. The three hydrogen atoms in **4-Lu** are no longer symmetrically bonded to the lutetium atoms. Lu−H distances vary between 2.15 and 2.27 Å.

Reactivity studies of **3-Lu** and **4-Lu** toward benzophenone were performed to confirm the nucleophilic property of the hydride ligands despite the overall positive charge.[18] **3-Lu** reacted with 4 equiv of benzophenone, leading to CO insertion between two Lu−H and two Lu−CH_2N bonds, resulting in the formation of [Lu($Me_5TRENCH_2CPh_2O$)($OCHPh_2$)][X] (**5-Lu**). The reaction of **4-Lu** with 4 equiv of benzophenone led to CO insertion between three Lu−H bonds and one Lu−CH_2N bond to give a 1:1 mixture of **5-Lu** and [Lu(Me_6TREN)$(OCHPh_2)_2$][X] (**6-Lu**). Similar reactivity has been observed in the case of **4-Y**. Both insertion reactions resulted in quantitative yields of the corresponding products, which have been fully characterized (see SI).

In conclusion, facile dihydrogen addition to a cationic hydrido lanthanide complex **3-Lu** has been found. Although clean dihydrogen release has not been observed, dihydrogen evolution is observed upon heating **4-Lu** under vacuum. Currently, we are investigating other ligand systems in order to achieve reversible dihydrogen activation.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthesis and characterization of all new compounds; ^{1}H NMR spectra of **1-Lu**, **2-Lu**, **2a-Lu**, **3-Lu**, **4-Lu**, and **4-Y**; variable-temperature ^{1}H NMR spectra of **3-Lu** in THF-d_8; tables of crystallographic data; data on computational studies; and X-ray crystallographic data, in CIF format, for **2a-Lu**, **3-Lu**, **4-Lu**, **4-Y**, and **6-Y**. This material is available free of charge via the Internet at http://pubs.acs.org.

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