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Reversible H_2 Activation

Reversible Dihydrogen Activation in Cationic Rare-Earth-Metal Polyhydride Complexes**

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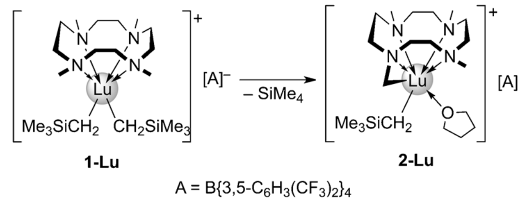
Dihydrogen activation by metal alkyl complexes via σ-bond metathesis is a facile non-redox reaction and a common method for the preparation of rare-earth[1] and early-transition-metal hydrido complexes.[2] The intramolecular C–H bond activation has been reported for metal alkyl or hydride complexes to give so-called "tucked-in" or "tucked-over" cyclometalated complexes with concomitant liberation of alkane or dihydrogen,[3] predominantly in metallocenes of early transition metals[2b,4] and f-block elements.[5] The metallocene hydrides of zirconium[6] and samarium[5d] and tris(amido) actinide hydrides[7] reversibly form the hydrido complex and the cyclometalated complexes by addition and removal of dihydrogen.

We have reported a bimetallic trivalent rare-earth-metal complex with two bridging hydrido ligands that adds dihydrogen across a metal–carbon bond and a metal–metal axis.[8] The reverse liberation of dihydrogen by C–H bond activation was not observed.[9] We have now obtained a rare-earth-metal hydrido complex capable of reversibly binding and releasing dihydrogen under mild conditions. No change in the oxidation state of the metals is involved, as addition and release occur by σ-bond metathesis involving a metal–carbon bond. Notably, hydrogenolysis in the solid state was also observed in a single-crystal to single-crystal transformation.

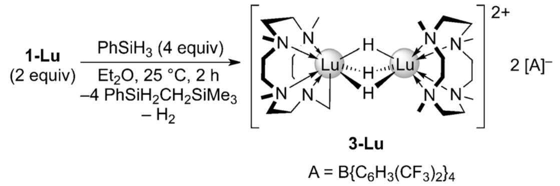
The cationic dialkyl lutetium complex $[Lu(CH_2SiMe_3)_2(thf)_3][A]$ ($A = B\{3,5\text{-}C_6H_3(CF_3)_2\}_4$)[10] was treated with the neutral NNNN-type macrocyclic ligand 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane ($Me_4TACD = Me_4[12]aneN_4$) to give the THF-free dialkyl complex $[(Me_4TACD)Lu(CH_2SiMe_3)_2][A]$ (**1-Lu**) in quantitative yield (Scheme 1).



Scheme 1. C–H bond activation in cationic bis(alkyl) complex **1-Lu** to give complex **2-Lu**.

By allowing the reaction mixture of **1-Lu** to stand for six days at 25 °C, the metalated monoalkyl complex **2-Lu** with a formally monoanionic NNNNC-type ligand was obtained in 97 % yield. This ligand was formed by C–H bond activation of one of the methyl substituents of the Me_4TACD ligand.

When **1-Lu** was reacted with phenylsilane in diethyl ether at 25 °C, the bimetallic trihydride $[(Me_3TACD\text{-}CH_2)Lu(\mu\text{-}H)_3Lu(Me_4TACD)][A]_2$ (**3-Lu**) was obtained in 92 % yield and was characterized by NMR spectroscopy and single-crystal XRD studies (Scheme 2). The coupling product of the σ-bond metathesis, $PhSiH_2CH_2SiMe_3$, was identified by an NMR-scale reaction in [D_8]THF. A characteristic singlet at $\delta = 8.92$ ppm in the ^1H NMR spectrum was found for the bridging hydride ligands, which is similar to that in the TREN-supported dilutetium trihydrido complex.[8] Another singlet at $\delta = 1.32$ ppm is ascribed to the methylene bridge protons of the metalated ligand $Me_3TACD\text{-}CH_2$. ^1H–^1H COSY and NOESY NMR studies revealed scalar and through-space coupling of the hydride ligands with the methyl protons of the ligands, respectively. A weak cross-peak between the hydrides and the methylene bridge of the metalated ligand was also observed in the NOESY, indicating a spatial proximity of these protons (Supporting Information, Figures S12 and S13).



Scheme 2. Preparation of dicationic trihydrido complex **3-Lu**.

The solid-state structure of **3-Lu** was refined in the non-centrosymmetric space group *P*1. Restraints for the C–C, C–N, and C–F distances had to be employed. Both lutetium centers are bridged by three hydrogen atoms in μ_2 fashion (Figure 1). Owing to the heavy Lu atoms in the structure, the hydrogen atom positions from X-ray diffraction are not

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Supporting information for this article, including detailed experimental conditions, synthetic procedures, and spectroscopic, kinetic, crystallographic, and computational analyses, is available on the WWW under http://dx.doi.org/10.1002/anie.201303958.

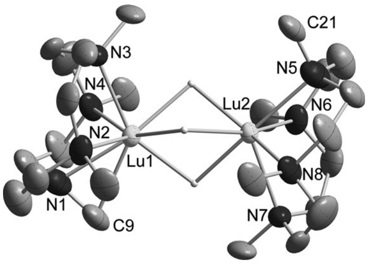
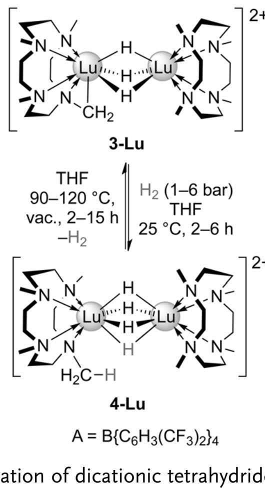


Figure 1. Molecular structure of the cationic part of **3-Lu** in the solid state. Hydrogen atoms except for bridging hydrides are omitted for clarity. Ellipsoids are set at 50% probability.

absolutely reliable but consistent with the ^{1}H NMR data and calculations (see below). One metal center (Lu2) is coordinated by four nitrogen atoms of the neutral Me_4TACD ligand and three hydrido ligands, adopting a capped trigonal prismatic geometry. A similar environment is found for the eight-coordinate Lu1, except for an additional capping metalated carbon atom C9. The Lu···Lu distance of 3.1747(5) Å is shorter than those found in similar complexes [(Me_5TRENCH$_2$)Lu(μ_2-H)$_3$Lu(Me_6TREN)][B{3,5-C_6H_3-(CF_3)$_2$}$_4$]$_2$ (3.2775(4) Å),[8] [(Me-PNPi^{Pr})$_2$Lu$_2$H$_3$(thf)$_2$][BPh$_4$] (3.2174(4) Å),[11] and [(NCN)LuH$_2$]$_2$(thf)$_3$ (3.2359(5) Å).[12]

In THF at 25 °C under 1 bar hydrogen pressure, **3-Lu** is fully converted into the bimetallic tetrahydrido complex [(Me_4TACD)Lu(μ-H)$_4$Lu(Me_4TACD)][A]$_2$ **4-Lu** (Scheme 3). This compound was directly obtained by treating **1-Lu** with dihydrogen (1 bar) in diethyl ether at 25 °C (Supporting Information).

The addition of dihydrogen is supposed to proceed by σ-bond metathesis involving the metalated methylene group in **3-Lu** or both alkyl ligands in **1-Lu**. Upon addition of dihydrogen to a solution of **1-Lu**, a colorless oil is formed and crystallization is observed after 2 h. At this stage, the analysis of the product mixture reveals both **4-Lu** and **3-Lu**. Apparently, **3-Lu** is an intermediate, and hydrogenolysis toward **4-Lu** continues in the solid state. To corroborate this hypothesis, isolated crystalline **3-Lu** was treated with H_2 (1 bar) at 25 °C overnight. The H_2 atmosphere was removed completely by evacuation and replaced by argon. The ^{1}H NMR spectrum in [D$_8$]THF showed that **3-Lu** was converted into **4-Lu** in the solid state. Crystalline **1-Lu** was also transformed into **4-Lu**.



Scheme 3. Preparation of dicationic tetrahydrido complex **4-Lu**.

The ^{1}H NMR spectrum of **4-Lu** exhibits a singlet at $\delta = 8.99$ ppm for the hydrido ligands and one sharp singlet for all of the methyl groups at $\delta = 2.85$ ppm. The ethylene protons of the ligand coalesce to a broad signal ranging from $\delta = 2.0$ to 3.7 ppm at room temperature, indicating high fluxionality of the CH_2CH_2 bridges. Low-temperature NMR measurements show decoalesence of this signal into two triplets and two doublets owing to $^3J_{HH}$ coupling (Supporting Information, Figure S18). The hydride signal also splits at −40 °C, which is probably due to slowed interconversion between rotational isomers. COSY and NOESY experiments reveal that the hydride and methyl protons couple, and that they are spatially close to each other (Supporting Information, Figures S16 and S17).

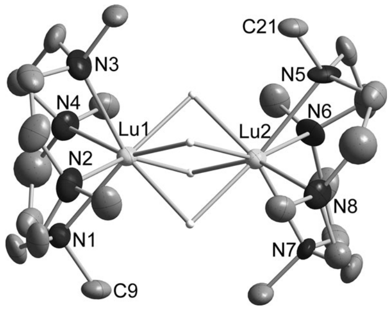


Figure 2. Molecular structure of the cationic part of **4-Lu** in the solid state. Hydrogen atoms except for bridging hydrides are omitted for clarity. Ellipsoids are set at 50% probability.

X-ray diffraction on a single crystal of **4-Lu** gave similar lattice parameters as for **3-Lu**. The structure could be solved by isotypic replacement using the coordinates of the latter structure. In the space group $P\bar{1}$, the positions of the CH_2 units lead to distortion from C_i symmetry and the structure was refined in the non-centrosymmetric space group $P1$. Both lutetium atoms are bridged by four hydrido ligands and supported by two neutral Me_4TACD ligands in an eclipsed arrangement (Figure 2). The coordination geometry around each metal center is roughly square-antiprismatic. The Lu···Lu distance of 2.9270(6) Å is the shortest known Lu···Lu distance, and is 0.248 Å shorter than that in **3-Lu**. The short intermetallic distance indicates the presence of the additional bridging hydrogen atom in **4-Lu**.[13] The Lu–Lu axis is almost perpendicular to the N_4 planes, with a distance between the lutetium center and the N_4 plane of 1.336(7) Å (Lu1–N1,2,3,4) and 1.344(7) Å (Lu2–N5,6,7,8). Binuclear dicationic complexes with four μ_2-bridging hydrides are unprecedented in rare-earth-metal chemistry.[13] Most neutral rare-earth-metal dihydride complexes featuring monoanionic ligands, such as cyclopentadienyls,[1c,14] amides,[11,12,15] or pyrazolylborates,[16] tend to form high nuclearity aggregates ([XLnH$_2$]$_n$ ($n = 3$–6)). The staggered conformation of the hydrides with respect to the opposing N-donor atoms was reported for d^0–d^5 systems to be the most stable.[17] It also appears in similarly bridged metal-hydride dimers of the composition $[L_4M{-}H_4{-}ML_4]$.[18]

As the crystal lattices of **3-Lu** and **4-Lu** are similar,[19] hydrogenolysis of a single crystal of **3-Lu** was performed to give **4-Lu** with retention of the crystal morphology (Supporting Information).

Complexes **3-Lu** and **4-Lu** can be stored as solids and as THF solutions under argon for several weeks at room temperature. Both **3-Lu** and **4-Lu** exhibit high thermal stability and melt under decomposition above 175 °C.

When a solution of **3-Lu** in $[D_8]$THF was exposed to H_2 (1.5 bar) and monitored by ^{1}H NMR spectroscopy, conversion into **4-Lu** proceeded by first-order kinetics with $k_{obs} = 4.58(6) \times 10^{-5}\ s^{-1}$, $t_{1/2} = 4.2$ h. By increasing the H_2 pressure to 5 bar, the decay of **3-Lu** was still pseudo first-order, but **4-Lu** was obtained much faster ($k_{obs} = 1.45(3) \times 10^{-4}\ s^{-1}$, $t_{1/2} = 1.4$ h). Increasing the pressure to 6.25 bar further accelerated the reaction ($k_{obs} = 1.81(4) \times 10^{-4}\ s^{-1}$, $t_{1/2} = 1.1$ h). A linear dependence of the rate on the dihydrogen pressure was found (Supporting Information, Figure S2).

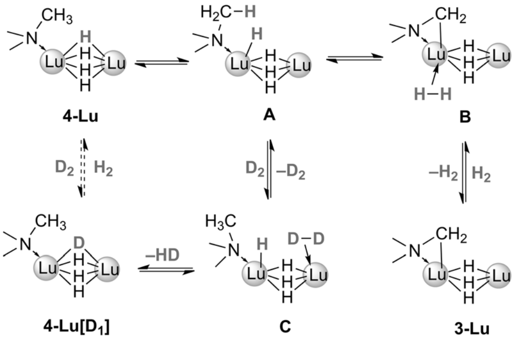
As the methyl groups of the ligand in **1-Lu** were easily metalated with concomitant elimination of $SiMe_4$, the transformation of tetrahydride **4-Lu** back to **3-Lu** or to a doubly metalated dihydrido complex by dehydrogenative C–H bond activation was investigated. By degassing a solution of **4-Lu** in $[D_8]$THF and heating to at least 50 °C, conversion of **4-Lu** into **3-Lu** was detected by ^{1}H NMR spectroscopy. The decay of tetrahydride **4-Lu** followed pseudo first-order kinetics (Table 1; Supporting Information, Figure S3).

Table 1: Rate constants and half-lifetimes for the conversion of **4-Lu** to **3-Lu** at various temperatures.

T [K]	k_{obs} [s^{-1}]	$t_{1/2}$ [h]
363	$2.51(10) \times 10^{-5}$	7.6(3)
373	$6.6(4) \times 10^{-5}$	2.7(2)
383	$1.66(6) \times 10^{-4}$	1.15(4)
393	$4.33(9) \times 10^{-4}$	0.44(2)

An Eyring plot of $\ln(k_{obs}T^{-1})$ against T^{-1} revealed an activation enthalpy of $\Delta H^{\neq} = 26.3(6)$ kcal mol^{-1}, a Gibbs free energy of $\Delta G^{\neq}(393\ K) = 29.3(8)$ kcal mol^{-1}, and an activation entropy of $\Delta S^{\neq} = -8(2)$ cal K^{-1} mol^{-1} (Supporting Information, Figure S5).

Remarkably, the tetradeuteride $[D_4]$**4-Lu** underwent faster C–H bond activation at $T = 393$ K ($k_{obs} = 7.0(3) \times 10^{-4}\ s^{-1}$, $t_{1/2} = 0.3$ h; Supporting Information, Figure S6). This inverse kinetic isotope effect (KIE) of $k_H/k_D = 0.62(2)$ presumably arises from an equilibrium isotope effect in a pre-equilibrium. This may involve either a terminal and bridging hydride/deuteride **A** or an H–H/H–D exchange reaction through an intermediate dihydrogen adduct **B** (Scheme 4). Species **B** is reminiscent of the calculated transition state (Figure 3). The formation of a C–H σ-complex prior to the C–H bond cleavage might also be responsible for an inverse KIE,[20] although this was not supported by theoretical calculations.



Scheme 4. Proposed mechanism for H/D exchange and C–H bond activation.

The isotope effect in the addition reaction was investigated by treating **3-Lu** and $[D_3]$**3-Lu** with H_2 versus D_2. **3-Lu** added H_2 twice as fast as $[D_3]$**3-Lu** (Table 2). D_2 was added more slowly by **3-Lu**, whereas no difference between H_2 and D_2 was measured with $[D_3]$**3-Lu**. In the reactions of **3-Lu** with D_2 and $[D_3]$**3-Lu** with H_2 and D_2, formation of significant amounts of HD was observed. H–D exchange, by reversible C–H bond activation with the ligand methyl groups or directly at the metal center (**C**), appears to be the critical pre-equilibrium step. This may be responsible for the inverse KIE observed for the C–H bond activation reaction.

Table 2: Rate constants for the conversions of **3-Lu** and $[D_3]$**3-Lu** with H_2 versus D_2 (1.5 bar, 25 °C).

	$k_{obs}(H_2)$ [s^{-1}]	$k_{obs}(D_2)$ [s^{-1}]
3-Lu	$4.58(6) \times 10^{-5}$	$3.66(15) \times 10^{-5}$
$[D_3]$**3-Lu**	$2.34(14) \times 10^{-5}$	$2.42(9) \times 10^{-5}$

Exposure of **4-Lu** to D_2 resulted in a slow but steady decrease of the hydride signal, whereas the N-methyl signal remained almost unchanged, indicative of a direct H–D exchange at the metal center. A significant decrease of the methyl signal intensity for **4-Lu** was only observed after three weeks; this was accompanied by the appearance of decomposition products (Supporting Information, Figure S20). Of note, a stepwise deuteration of **4-Lu** could be observed by the gradually shifted hydride resonances of four different isotopomers in the range of $\delta = 8.99$ to 8.94 ppm (Supporting Information, Figure S21).

To gain more insight into the hydrogenation of **3-Lu** to **4-Lu**, a theoretical investigation at the DFT level (B3PW91) was carried out. The computed activation barrier at room temperature of 24.0 kcal mol^{-1} is in good agreement with the experimental value. The formation of **4-Lu** is exergonic by 9.2 kcal mol^{-1} (Figure 3). The transition state (TS) is reminiscent of that for σ-bond metathesis with an almost linear arrangement for the two hydrogen atoms of H_2 and CH_2 (H-H-C angle of 162°). The H–H bond is activated, as bond elongation indicates (0.95 versus 0.78 Å in free H_2).

In conclusion, the neutral macrocyclic NNNN-type ligand Me_4TACD has been shown to stabilize cationic alkyl and hydride complexes of the rare-earth metals. One of the

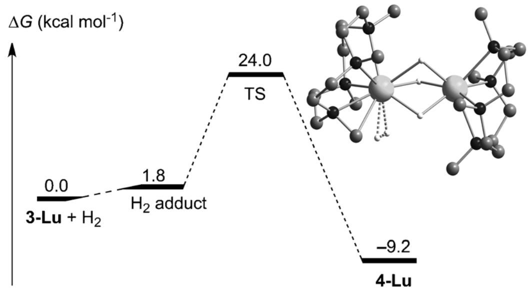


Figure 3. Calculated energy profile for the hydrogenolysis of **3-Lu** to give **4-Lu**.

methyl substituents on the Me$_4$TACD ligand was found to undergo C–H bond activation. Bimetallic trihydride **3-Lu** featuring a cyclometalated ligand underwent addition of dihydrogen to give the tetrahydrido complex **4-Lu**, containing a stable quadruply hydride bridged structure.[13] As was reported for a related bimetallic dihydrido lutetium complex,[8] dihydrogen addition is thermodynamically favored. As indicated by deuterium labeling experiments, the dihydrogen release mechanism seems to involve several steps including labile dihydrogen adducts.[21] In summary, the non-redox dihydrogen addition and release becomes possible for d^0f^x metal centers within a suitable ancillary ligand sphere.

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[13] a) The yttrium homologue of **4-Lu** was obtained, but failed to give a metalated species similar to **3-Lu** by heating under reduced pressure and dihydrogen loss. Bimetallic yttrium trihydride could not be obtained by hydrogenolysis of an alkyl precursor with $PhSiH_3$. b) For a dizirconium dication, see: $[(Me_3TACD)Zr(\mu\text{-}H)_4Zr(Me_3TACD)][A]_2$: H. Kulinna, T. P. Spaniol, L. Maron, J. Okuda, *Inorg. Chem.* **2012**, *51*, 12462–12472.

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[19] Crystal structure data of **3-Lu**: space group $P1$, $a=12.6786(14)$ Å, $b=13.8345(15)$ Å, $c=14.3063(15)$ Å, $\alpha=96.48(2)°$, $\beta=103.025(2)°$, $\gamma=92.127(2)°$, $V=2423.2(5)$ Å^3, $Z=1$; **4-Lu**: space group $P1$, $a=12.7156(13)$ Å, $b=13.7727(14)$ Å, $c=14.3122(15)$ Å, $\alpha=96.530(2)°$, $\beta=103.3104(18)°$, $\gamma=91.3757(19)°$, $V=2420.0(4)$ Å^3, $Z=1$.

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