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f-Block hydride complexes – synthesis, structure and reactivity

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Complexes formed between the heaviest and lightest elements in the periodic table yield the f-block hydrides, a unique class of compounds with wide-ranging utility and interest, from catalysis to light-responsive materials and nuclear waste storage. Recent developments in syntheses and analytics, such as exploiting low-oxidation state metal ions and improvements in X-ray diffraction tools, have transformed our ability to understand, access and manipulate these important species. This perspective brings together insights from binary metal hydrides, with molecular solution phase studies on heteroleptic complexes and gas phase investigations. It aims to provide an overview of how the f-element influences hydride formation, structure and reactivity including the sometimes-surprising power of co-ligands to tune their behaviour towards a variety of applications.

Introduction

Although the reactivity of lanthanide and actinide metals towards hydrogen gas had been long observed, it was the Manhattan Project in the 1940s which first brought to light the utility and unique subtleties of hydride complexes of the f-elements.¹ Distinct from their substantially more numerous

main group and d-block counterparts, f-block hydrides are characterised by their predominantly ionic nature, high coordination numbers (which favour bridging hydride ligation) and relatively inaccessible redox activity. These properties, coupled with the inherent photophysical, magnetic and, for some, radioactive nature of the metal ions in these complexes, means that f-block hydrides still represent an important and accelerating field of inorganic chemistry.

Solubilised heteroleptic lanthanide hydrides are found to be the key catalytically active species in a range of hydroelementation transformations^{2,3} while binary lanthanide

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in the synthesis and stabilisation of highly-reactive compounds, as well as the development of novel tools and methodologies to aid in this pursuit.

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hydrides have also been investigated for applications in methanol synthesis,⁴ dinitrogen fixation⁵ and neodymium magnet recycling.⁶ Useful optical properties exhibited by lanthanide oxyhydrides allow them to be widely utilised in light-responsive materials, such as those now-frequently applied to corrective lenses.⁷ At the same time, actinide hydrides represent important potential by-products of radiolysis processes occurring during nuclear waste storage and remediation, which must be understood to facilitate safe nuclear waste handling.^{8–10} Superhydrides of both the lanthanides and actinides have demonstrated promise as potential room temperature superconductors and as hydrogen storage materials.^{11–13} Actinides have also been demonstrated to activate more challenging substrates, such as converting dinitrogen to ammonia;¹⁴ their reactivity is often unique within the periodic table, making them interesting potential reagents and catalysts in their own right.

Despite their importance, f-block hydrides are often overlooked. In catalysis, their presence is implicated in a wide range of processes; however, the utility of lanthanide alkyl precatalyst handling, for example, means the true nature of the hydride involved in these processes is opaque—with consequences for the development of these reactions.

In actinide chemistry, much work to date has focussed on the hydrogenation of actinide metals in the solid state to gain insights into nuclear waste remediation processes; however, bridging the gap between these studies and the well-defined academic curiosities, isolated using complex supporting co-ligands over the past few decades, has been challenging. Despite this, these heteroleptic actinide hydrides provided valuable contributions towards our understanding of the role of f-orbitals in actinide bonding more generally.¹⁵

In this perspective, we seek to put into context the chemistry of f-block hydrides, including the synthesis, structure and

reactivity of both lanthanide and actinide hydrides. We give an overview of the behaviour of binary hydrides (MH_x) of each period such that the structure and synthesis of heteroleptic molecular hydrides finds context. Within each section, we discuss synthetic strategies, solid-state structure and analytical data on the resulting hydrides and their further reactivity. This work follows on from an extensive early review of the field by Ephritikhine in 1997,¹⁶ drawing upon improvements in analytical data (notably X-ray diffraction), novel synthetic strategies and newly discovered reactivity profiles in the ensuing three decades to provide an overview of the now mature field.

Homoleptic lanthanide hydrides

Solid phase binary hydrides – structural insights

In the first step of hydrogen's reaction with bulk metallic lanthanides a solid solution is formed, whereby dihydrogen molecules occupy tetrahedral interstitial sites within the $Ln(0)$ crystal lattice. Specifically, one half of the sites (the second nearest neighbour sites), are occupied by dihydrogen (Fig. 1).¹⁷ This shifts to occupancy of all sites by a single hydride upon formation of LnH_2 (which has the CaF_2 structure; $La-H = 2.45 \text{ \AA}$). Recent work has demonstrated that Ln dihydrides ($Ln = La, Ce$) exist as electride materials with a $[Ln^{III}(H_0)_2(e^-)]$ formulation.¹⁸ Further hydrogens occupy octahedral sites but defects mean octahedral sites (H_0) can start filling before tetrahedral sites (H_t) are full. Transformation from LnH_2 to LnH_3 is accompanied by a transition from metal-like to insulating behaviour as the valence electrons are occupied in bonding, with the structure adopting a cubic BiF_3 or trigonal HoH_3 type lattice depending upon cation size ($La-H_t = 2.43 \text{ \AA}$; $La-H_o = 2.81 \text{ \AA}$). At the same time, a transition in optical properties

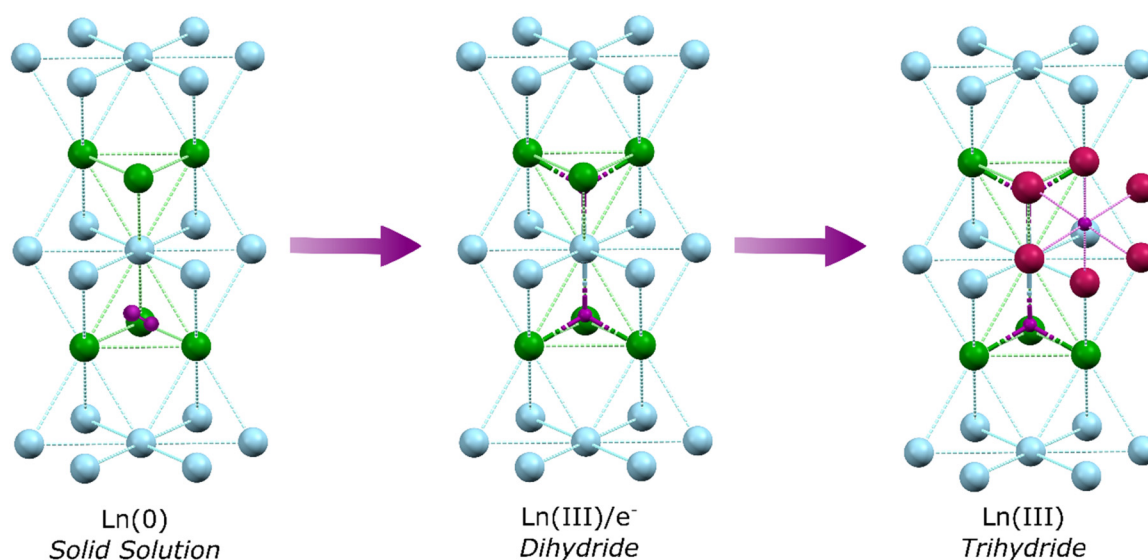


Fig. 1 The formation of binary lanthanide hydrides from $Ln(0)$ proceeds via a solid solution, with dihydrogen occupying nearest neighbour sites before oxidation first to lanthanide dihydride, with occupancy of tetrahedral vacancies, then $Ln(III)$, through occupancy of octahedral sites with hydride. Ln ions: Blue (general), Green (tetrahedral site) or Pink (octahedral site) spheres. Hydrogen/hydride atoms: Purple spheres.



from darkly coloured LnH_2 to metallic LnH_3 occurs.^{19,20} However, it should be noted that even at a >2.9 H:Ln ratio, conductivity can be high, with small defects in the lattice occupancy yielding superionic conductivity.²¹

Gas phase/molecular hydrides

Molecular binary lanthanide hydrides have been accessed using laser ablation of lanthanide metal atoms under H_2 within noble gas matrices. Andrews used this method to investigate the vibrational spectra across a range of LnH_x stoichiometries in the gas phase (*i.e.*, molecular examples), thereby finding evidence for a non-linear structure for LaH_2 in the gas phase, as well as the formation of the H_2 adduct $(\text{H}_2)\text{CeH}_2$.^{22,23} This was further investigated across the series, finding that stable adducts of dihydrogen may form with La, Ce, Pr and Nd.²⁴ Potential stability is more favourable with softer divalent lanthanides which bind molecular H_2 more strongly than harder trivalent ions, with hydrogen adduct formation occurring *via* transfer of a 6s electron to the H_2 molecule, and therefore representing the covalent extreme of lanthanide–hydrogen bonding. The trihydrides were also observed; later calculations determined that LnH_3 complexes exhibit a pyramidal geometry, due to 5d orbital contributions to the bonding.¹⁵ Thus, whilst bonding in these f-block hydrides is mostly ionic, subtle influences, such as interaction with 5f orbitals for the early actinides or with accessible 4f and 5d orbitals for the lanthanides, can have dramatic effects on structure and reactivity.

Lanthanide superhydrides

Higher stoichiometries, Ln_{4+x} , have been shown to be stable under elevated pressure and temperature regimes and are of interest as next-generation superconductors. This is because in these species hydrogen may exist as metallic $\text{H}(0)$.¹¹ The best-studied of these is LnH_{10} , which involves a clathrate-type arrangement of H atoms (32 H per Ln) encapsulating the lanthanide ion. These species can be synthesised above 10^6

bar pressure in a diamond anvil cell at high temperatures (1000 K). Raman spectroscopy shows no H–H bands, corresponding to bound diatomic hydrogen, despite the fact that LaH_{10} contains the shortest H–H distances other than molecular hydrogen.¹²

Heteroleptic lanthanide hydrides

Synthetic strategies

Hydrogenolysis. Hydrogenolysis of lanthanide alkyl, allyl or aryl complexes is one of the primary synthetic routes to heteroleptic lanthanide hydrides (Fig. 2a). This method has advantages in its simplicity and the generation of only volatile byproducts from the transformation; however, some hydrogenolysis reactions with larger lanthanides (Ce, Nd, Sm), have been shown to be reversible—even in the solid state—necessitating handling and storage of these species under a hydrogen atmosphere.²⁵

Okuda *et al.* report the synthesis of the lutetium complex $[(\text{Me}_4\text{TACD})\text{Lu}(\text{R})_2]^+$, which reacts with H_2 at 1 bar pressure in thf (Fig. 3). The dialkyl precursor yields a mixture of a ligand-metalated trihydrido dimer, $[(\text{L}^*)\text{Lu}(\mu^2\text{-H})_3\text{LuL}]^{2+}$ or $[(\kappa^3\text{-N,N,N,N,C-CH}_2\text{-Me}_3\text{TACD})\text{Lu}](\mu^2\text{-H})_3[\text{Lu}(\kappa^4\text{-N,N,N,N-Me}_4\text{TACD})]^{2+}$, and a hydrogenated tetrahydrido dimer, $[(\text{L})\text{Lu}_2(\mu^2\text{-H})_4]^{2+}$ or $[(\kappa^4\text{-N,N,N,N-Me}_4\text{TACD})\text{Lu}]_2(\mu^2\text{-H})_4]^{2+}$.²⁶ Based on this (as well as complementary reactions with silanes), the authors conclude that the metalate is an intermediate in the hydrogenation process. Many of the hydrides reported to date either arise directly from metalated complexes (*e.g.*, with substituted metallocene co-ligands) or utilise ligands which are able to undergo metalation.^{27–40} Importantly, a survey of the literature demonstrates that these examples allow for hydrogenation at low pressures of H_2 (1–4 bar). Lanthanide alkyl complexes of ligands which are not known to metalate (*e.g.*, Tp^{R}) have only been reported under significantly higher pressures for hydro-

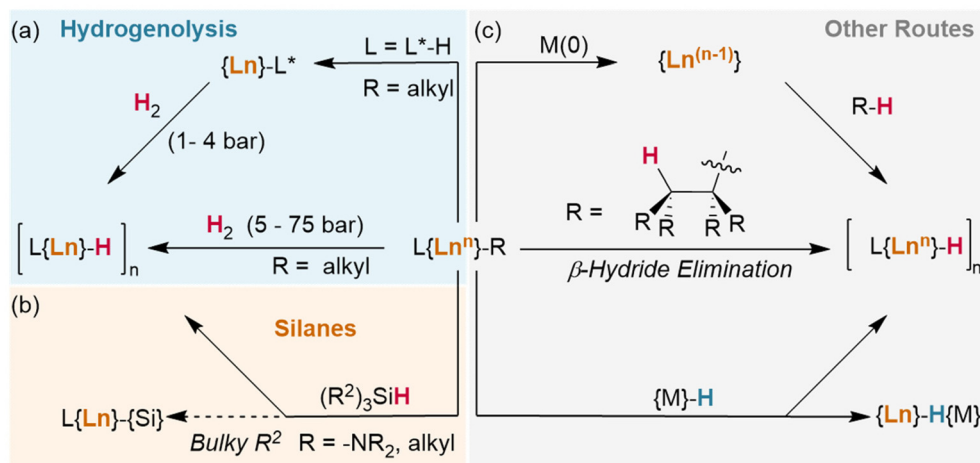


Fig. 2 Synthetic routes to lanthanide hydrides from $\text{L}(\text{Ln})\text{-R}$ complexes (a) *via* hydrogenolysis. L^* = metalated ligand, accessed *via* C–H activation/deprotonation. (b) Using silanes. (c) Other routes include reduction with alkali metals, β -hydride elimination and reactions with metal hydrides.



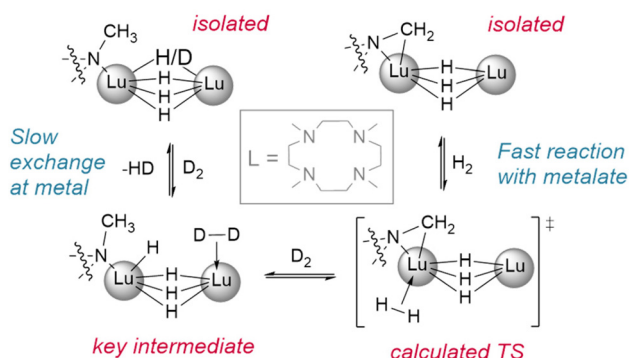


Fig. 3 Demonstration of the reactivity of metalated ligands in the activation of H_2 . Deuteration studies show metal based H/D exchange is slow with the tetrahydrido dimer while the metalated trihydrido complex reacts with H_2/D_2 quickly. $\text{L} = \text{Me}_4\text{-TACD}$.[†]

genolysis (5–75 bar), often with longer reaction times.^{41–47} This suggests that the ability of the ligand to metalate provides a significantly lower energy pathway for hydrogenolysis reactions. Kinetic isotope experiments and DFT calculations with these metalated TACD-lutetium hydrides indeed appear to suggest that ligand metalation favours the association of H_2 before cleaving the M–C bond.

The basicity of the alkyl is also shown to be a key factor for hydrogenolysis. Hou *et al.* demonstrate that hydrogenolysis of the tetrameric methanediide $\{(\text{Cp}')\text{Lu}\}_4(\mu^2\text{-CH}_2)_4$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$)[†] yields tetrahedral cluster $\{(\text{Cp}')\text{Lu}\}_4(\mu^2\text{-Me})_4(\mu^2\text{-H})_2(\mu^3\text{-H})(\mu^4\text{-H})$ through H_2 addition across the Lu– CH_2 bond.⁴⁸ Further hydrogenolysis of the remaining four methyl ligands does not occur in this example. Similarly, treatment of the trimeric cluster $\{(\text{Cp}')\text{Lu}\}_3(\mu^2\text{-Me})_6$ under the same conditions (1 bar H_2 , 70 °C) yielded the corresponding tetramer, $\{(\text{Cp}')\text{Lu}\}_4(\mu^2\text{-Me})_6(\mu^3\text{-Me})(\mu^4\text{-H})$, where only one of the eight possible methyl groups is protonated off (Fig. 4). This suggests a balance of donor properties, with strongly basic methane ligands competing with hydrides to stabilise the lanthanide complex. At the same time, this work suggests hydride structure persists in solution, at least to a degree sufficient to affect reactivity. These limits are important to understand when considering which lanthanide precatalysts to use in hydrogenation and hydroelementation reactions.

From silanes. The safety risks and technical challenges associated with the use of gaseous H_2 have led some authors to consider alternative hydride sources which are more straightforward

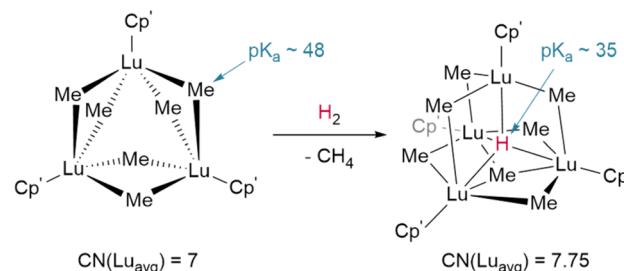


Fig. 4 Despite the higher pK_a of the methyl anion hydrogenolysis occurs with Hou's trimer due to the coordinative stabilisation provided by the μ^4 -hydride in the tetrameric product. CN = coordination number; $\text{Cp}' = (\text{C}_5\text{H}_4\text{SiMe}_3)$.[†]

to handle. Treatment with silanes (*e.g.*, PhSiH_3) is a facile and convenient route to lanthanide hydrides, enabling stoichiometric reactions (which can be challenging with H_2) but reacting similarly in most other ways (Fig. 2b).^{26,34,35,49–62}

In an advance on hydrogenolysis reactions, silanes have also been shown to add across $\text{Ln}-\{\text{N}(\text{SiMe}_3)_2\}$ bonds in addition to lanthanide alkyls,^{63,64} and have even been shown to supplant Cp^* ($\text{Cp}^* = \text{C}_5\text{Me}_5$)[†] as a ligand.⁶⁵ However, in rare circumstances, silanes have also been found to participate in other side reactions, including exchange with trimethylsilyl (TMS , Si')[†] groups on $\text{Ln}-\{\text{CH}_2\text{SiMe}_3\}$ ligands (Fig. 5a/b),⁶⁶ although this may be mitigated with ligand steric bulk.⁶⁷ In addition, the bulky silane $\text{H}_2\text{Si}(\text{Si}')_2$ was shown to undergo reversed σ -bond metathesis with $(\text{Cp}^*)_2\text{Sm}-\text{CH}(\text{Si}')_2$ yielding the $\text{Ln}-\text{Si}$ product rather than the hydride (Fig. 5c), likely due to steric hindrance preventing the formation of the expected four-centred transition state.^{68,69}

Investigating reactions with silanes has also allowed researchers to uncover differences across the lanthanide series, with early lanthanide $(\text{Me}_3\text{TACD})\text{Ln}(\text{allyl})_2$ complexes reacting to give octahydrido tetramer $\{(\text{Me}_3\text{TACD})\text{Ln}\}_4(\mu^2\text{-H})_8$ while the later lanthanides react with only one equivalent of silane to yield $\{(\text{Me}_3\text{TACD})\text{Ln}(\text{allyl})\}_2(\mu^2\text{-H})_8$.⁷⁰ This may be due to kinetic rather than thermodynamic factors since the reaction of $\{(\text{Cp}^*)_2\text{Ln}\}_2(\mu^2\text{-Me})_2$ with PhMeSiH_2 was found to follow a stepwise mechanism, with a fast initial transformation to $\{(\text{Cp}^*)_2\text{Ln}\}_2(\mu^2\text{-Me})(\mu^2\text{-H})$ followed by slower hydrogenolysis of the final methyl ligand. The rate of both of these processes decreased across the lanthanide series.⁷¹

Finally, even the siloxane reagent $\text{HSi}(\text{OEt})_3$ has been shown to hydrogenate lanthanide complexes (Fig. 6); however, this only occurs from the phenylacetylide bridged dimer $[\{\eta^5\text{-}\kappa^2\text{-N,N-(2,5-}\{\text{C}(\text{Ph})_2\text{pz}\}\text{-}\{\text{N}(\text{Me})\text{pz}\}\}\text{Yb}(\mu^2\text{-CCPh})\}_2]$ (pz = pyrazole). Reaction with the classical $\text{Ln}-\text{CH}_2\text{SiMe}_3$ precursor instead yields only the bridged ethoxide analogue $[\{\eta^5\text{-}\kappa^2\text{-N,N-(2,5-}\{\text{C}(\text{Ph})_2\text{pz}\}\text{-}\{\text{N}(\text{Me})\text{pz}\}\}\text{Yb}(\mu^2\text{-OEt})\}_2]$. The different bond dissociation energies of the $\text{Ln}-\text{C}_{\text{sp}}$ vs. $\text{Ln}-\text{C}_{\text{sp}^3}$ ligands and the ability of the dimer to act cooperatively likely promotes an alternate reaction pathway in the former case.⁷²

Hydride abstraction from alkyls. It is well-established that $\text{Ln}-(\text{tBu})$ complexes undergo β -hydride elimination reactions;

[†] The following abbreviations will be used throughout this work: $\text{Si}' = -\text{SiMe}_3$; $\text{N}'' = \text{N}(\text{SiMe}_3)_2$; $\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$; $\text{Cp}^{*+} = \text{C}_5(\text{Ph})_5$; $\text{Cp}^x = \text{C}_5(\text{CH}_3)_4\text{H}$; $\text{Cp}' = \text{C}_5\text{H}_4(\text{SiMe}_3)$; $\text{Cp}'' = 1,3\text{-}(\text{SiMe}_3)_2\text{C}_5\text{H}_3$; $\text{Cp}''' = 1,2,4\text{-}(\text{SiMe}_3)_3\text{C}_5\text{H}_2$; $\text{Cp}^{*+} = \text{C}_5(\text{CH}_3)_4(\text{SiMe}_3)$; $\text{Cp}^{*+} = \text{C}_5\text{Me}_4(\text{tBu})$; $\text{Cp}^{\dagger} = \text{C}_5\text{H}_4\text{tBu}$; $\text{Cp}^{\ddagger} = 1,3\text{-}(\text{tBu})_2\text{C}_5\text{H}_3$; $\text{Cp}^{\text{ttt}} = 1,2,4\text{-}(\text{tBu})_3\text{C}_5\text{H}_2$; $\text{Cp}^{\text{An}} = \{3\text{-}(\text{SiMe}_3)\text{C}_5\text{H}_4\}_2\text{SiMe}_2$; $\text{Tp}^* = \text{tris}(3,5\text{-dimethylpyrazolyl})$ borane; $\text{Tp}^{\text{Pr}} = \text{tris}((3\text{-isopropyl-5-methyl})\text{pyrazolyl})$ borane; $\text{Tp}^{\text{tBu,Me}} = \text{tris}((3\text{-tert-butyl-5-methylpyrazolyl})$ borane; $\text{Tp}^{\text{Ad,Me}} = \text{tris}((3\text{-adamantyl-5-methylpyrazolyl})$ borane; $\text{OSi}^{\text{Ot}} = -\text{OSi}(\text{O}^{\text{tBu}})_3$; $(\text{Ad,MeArO})_{\text{mes}} = 1,3,5\text{-tris}(\text{methylene}(3\text{-adamantyl-5-methylphen-2-ol})\text{mesitylene}$; $\text{Me}_4\text{TACD} = 1,4,7,10\text{-tetramethyl-azadodecane}$.

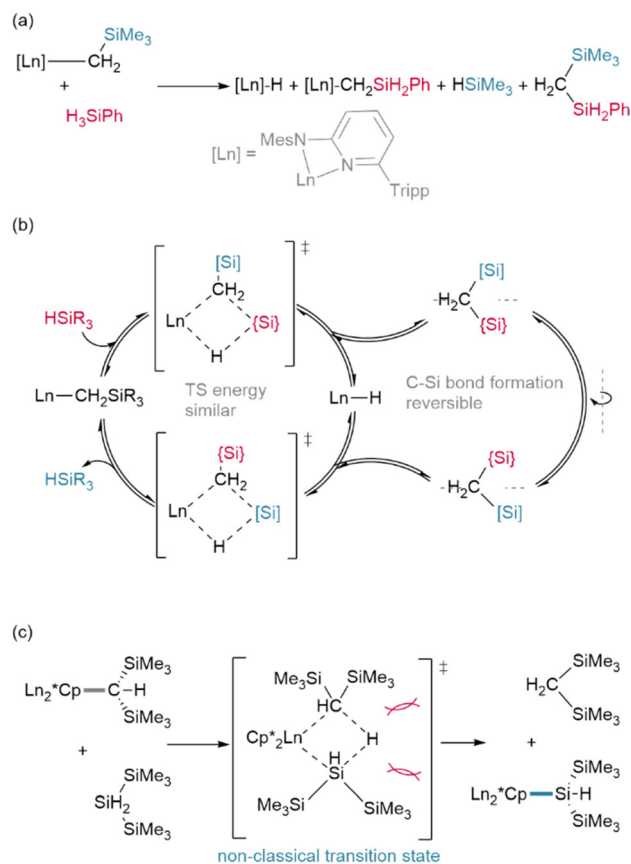


Fig. 5 Alternate non-classical reaction pathways for silanes with lanthanide organometallics: (a) Trifonov *et al.* found a mixture of silyl products from reaction of their $\text{Ln}-\text{CH}_2\text{SiMe}_3$ complexes with PhSiH_3 for $\text{Ln} = \text{Y}, \text{Yb}$ (but not Lu) when their ligand was not sufficiently bulky for classical reactivity to occur ($\text{Mes} = 1,3,5\text{-trimethylphenyl}$; $\text{Tripp} = 1,3,5\text{-triisopropylphenyl}$). (b) A mechanistic explanation for this different behaviour is based upon the reversibility of σ -bond metathesis in these complexes and the similar electronic properties of the $-\text{SiMe}_3$ (blue) and $-\text{SiH}_2\text{Ph}$ (red) groups. Re-attack of the disilylmethane by-product of the reaction in a different orientation can explain all of the products observed. (c) Tilley *et al.* found that bulky silanes reacting with bulky $\text{Ln}-\text{CH}(\text{SiMe}_3)_2$ ($\text{Ln} = \text{Sm}$) organometallics formed $\text{Ln}-\text{Si}$ bonds likely due to sterics preventing the formation of a classical 4-membered transition state. Instead the hydride likely occupies the position opposite the lanthanide in the TS for this transformation resulting in $\text{C}-\text{Si}$ bond formation.

however, this route has been shown to be inferior to hydrogenolysis⁷³ and, thus, is now a relatively uncommon pathway to hydrides (Fig. 2c). In a rare, recent example of similar behaviour, ethene elimination from the dysprosium methyl trimer $\{(\text{Cp}^*)\text{Dy}\}_3(\mu^2\text{-Me})_6$ yielded the μ^3 -hydride product $\{(\text{Cp}^*)\text{Dy}\}_3(\mu^2\text{-Me})_3(\mu^3\text{-CH}_2)(\mu^3\text{-H})$ (Fig. 7).⁷⁴ Cooperative reactivity with triisobutylaluminium reagents was also recently shown to neatly facilitate hydride formation *via* this mechanism.^{75,76}

Using low-valent lanthanides. Routes to lanthanide(II) complexes have increased dramatically in the past 25 years.⁷⁷ Divalent lanthanide precursor reagents, including $\text{YbI}_2(\text{thf})_2$ and $\text{EuI}_2(\text{thf})_2$, have been exploited to access hydride com-

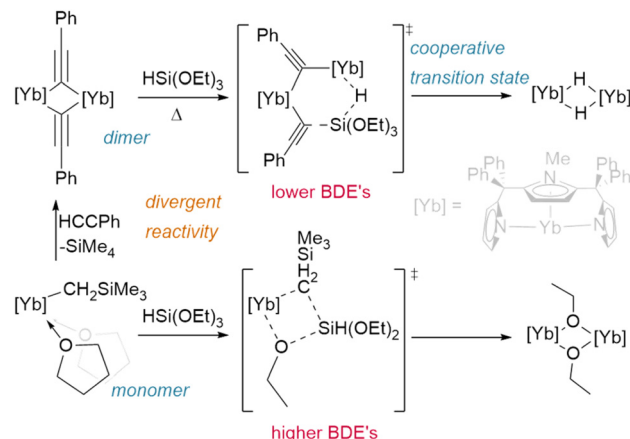


Fig. 6 Divergent reactivity was shown between the monomeric ytterbium alkyl and dimeric ytterbium phenylacetylide upon reaction with $\text{HSi}(\text{OEt})_3$, with the dimer proposed to react cooperatively to yield the hydride product.

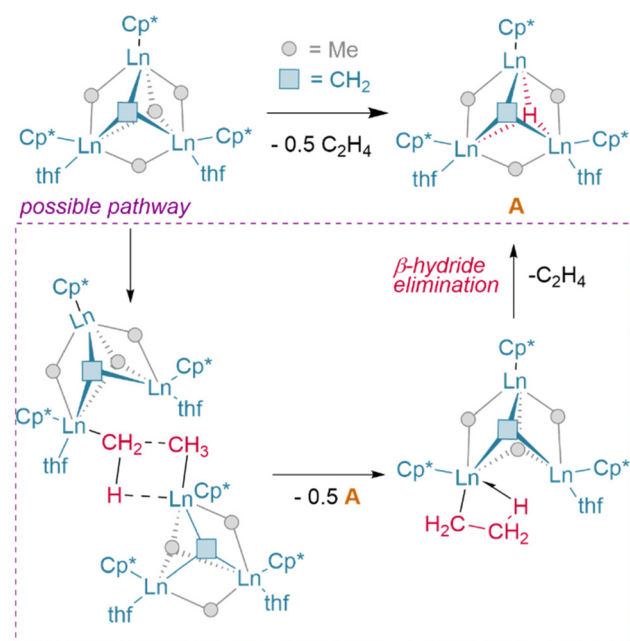


Fig. 7 Spontaneous $\text{C}=\text{C}$ bond formation from a lanthanide alkyl/alkylidene complex may proceed *via* β -hydride elimination to yield the μ^3 -hydride product (A).

plexes of these ions.^{41,55,78,79} Alternatively, reduction can also provide a route to lanthanide hydride formation from $\text{Ln}(\text{III})$ (Fig. 2c). Lappert *et al.* observed that treatment of $\text{Ce}(\text{Cp}^{\text{x}\dagger})_3$ or $\text{La}(\text{Cp}^{\text{x}\dagger})_3$ ($\text{Cp}^{\text{x}\dagger} = \text{C}_5\text{Me}_4(\text{tBu})^\dagger$) with K^0 in toluene in the presence of 18-crown-6 yielded $[\text{K}(18\text{-crown-6})][\{(\text{Cp}^{\text{x}\dagger})_3\text{Ln}\}_2(\mu^2\text{-H})]$, whilst with the bulkier Cp'' ligand ($\text{Cp}'' = \text{C}_5\text{H}_3(\text{SiMe}_3)_2$) one cyclopentadienyl is lost allowing a reduced toluene dianion to bridge the lanthanide centres.⁸⁰ Reduction of a holmium complex with the smaller Cp' ligand ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3^\dagger$) using lithium naphthalenide, $\text{Li}(\text{C}_{10}\text{H}_8)$, in Et_2O yielded a few crys-



tals of $[\text{Li}(2.2.2\text{-cryptand})][\{(\text{Cp}')_3\text{Ho}\}_2(\mu^2\text{-H})]$, while the larger terbium analogue gave crystals of the Cp' metalate instead (Fig. 8a).⁸¹ Notably, using the same conditions but with lithium metal as a reductant the Tb, Dy and Ho analogues were cleanly reduced to Ln(II) species, suggesting a key role for the reduced arene in hydride formation. Diaconescu's rationally-prepared $\{(\text{NN}^{\text{fc}})\text{Lu}(\text{thf})\}_2(\text{C}_{10}\text{H}_8)$ ($\text{NN}^{\text{fc}} = \kappa^2\text{-}N,N\text{-}[\eta^5\text{-}\{(\text{Me}_2\text{tBuSi})\text{N}\}\text{C}_5\text{H}_4\}_2\text{Fe}]$) was shown to undergo stoichiometric C–H bond activation upon heating, yielding a 1 : 1 molar ratio

of the corresponding lutetium(III) hydride and naphthalenide $\{(\text{NN}^{\text{fc}})\text{Lu}(\text{thf})\}_2(\text{C}_{10}\text{H}_7)$ (Fig. 8b).⁸² Differential C–H activation behaviour between the lanthanides was also observed with the reduction of lanthanides bound within Meyer's 1,3,5-tris(aryloxy)mesitylene ligand, $[(^{\text{Ad,Me}}\text{ArO})_3\text{mes}]^\dagger$. In this case, reduction with KC_8 in the presence of crypt in $\text{thf}/\text{C}_6\text{H}_6$ generated increasing relative yields of a terminal hydride product upon moving from larger to smaller lanthanides, Gd (35%) to Er (45%)—while no hydride was observed under similar conditions for neodymium (Fig. 8c).⁸³ Hydride formation was suggested to arise from activation at the benzylic position of the reduced central arene (*vide infra*). These data together suggest a key role for reduced arene functions in the formation of Ln–H bonds from Ln(II) complexes, rather than simply *via* abstraction from solvent.

Lanthanide dihydrogen complexes. Beyond the gas phase studies discussed above, there is limited, but intriguing, evidence of dihydrogen coordinating a lanthanide centre (as opposed to hydride formation). In 1989, $(\text{Cp}^*)_2\text{Eu}\{\eta^2\text{-(H}_2)\}$ was detected by Marks *et al.* using low-temperature NMR studies.⁸⁴ The low-valent $\text{Eu}^{\text{II}}(\text{Cp}^*)_2$ precursor provides an electron-rich centre to stabilise the dihydrogen ligand, with computational studies suggesting the diatom binds in a slightly asymmetric fashion, which can be represented as $\text{M}^{\delta+}\cdots(\text{H}^{\delta-}\text{--H}^{\delta+})$.⁸⁵

Lanthanide hydride structure. Trimers, tetramers, and hexamers of lanthanide hydrides have all been reported with cluster order increasing as lanthanide coordination number decreases or co-ligand sterics are reduced (Fig. 9). For example, dicationic metal fragments arising from $\{\text{LM}\}^{2+}$ ($\text{L} = \text{monoanionic ligand}; \text{M} = \text{Ln, An}$) precursors, such as $\{\text{CpLn}\}$, provide higher-order clusters than those arising from monocationic $\{\text{L}_2\text{M}\}^+$ moieties, such as $\{\text{Cp}_2\text{Ln}\}$ metallocene complexes.

With dicationic $\{\text{XM}\}^{2+}$ fragments, small co-ligands such as $\text{X} = \text{Cp}^*$ and Tp ($\text{Tp} = \text{tris}(\text{pyrazolyl})\text{borane}$)[†] can give rise to large hexamers. Few examples exist; however, treatment of Ln(III) complexes $(\text{Tp})\text{Yb}(\text{CH}_2\text{SiMe}_3)_2$ or $(\text{Tp})\text{Lu}(\text{CH}_2\text{SiMe}_3)_2$ with H_2 yields an octahedron of lanthanide ions as a $\{\text{Ln}_6\text{H}_{12}\}$ cluster with three μ^2 hydrides, eight face-bridging μ^3 hydrides, and a single, central μ^6 ligand—the highest hydride coordination number observed outside of lithium complexes.⁸⁶ In contrast, treatment of Sm(II) precursor $\text{K}[(\text{Cp}^*)_2\text{Sm}^{\text{II}}(\text{CH}_2\text{SiMe}_3)]$ with phenylsilane yields a trigonal prism of oxidised Sm(III) ions, containing a similar central bridging μ^6 hydride, which is tricapped with potassium ions, yielding a $\{\text{Sm}_6\text{H}_{15}\}$ core cluster (Fig. 9D).⁶⁵

The slightly larger Cp^* ligand ($\text{Cp}^* = \text{C}_5\text{Me}_4(\text{SiMe}_3)$)[†] yields tetramers³⁸ with μ^3 or μ^4 coordination modes which had been predicted by theory.⁸⁷ It should be noted that the μ^6 and μ^4 bridging modes of the hydride ligands within lanthanide clusters mirror the ionic binding of hydride in octahedral (H_6) and tetrahedral (H_4) sites, respectively, in the binary lanthanide hydrides (Fig. 1), with indistinguishable bond lengths in the latter case reinforcing the ionic nature of these bonds. In the tetramers, the lanthanides occupy the vertices of a tetrahedron, and the average coordination number of the eight hydrides increases concomitantly with lanthanide ionic

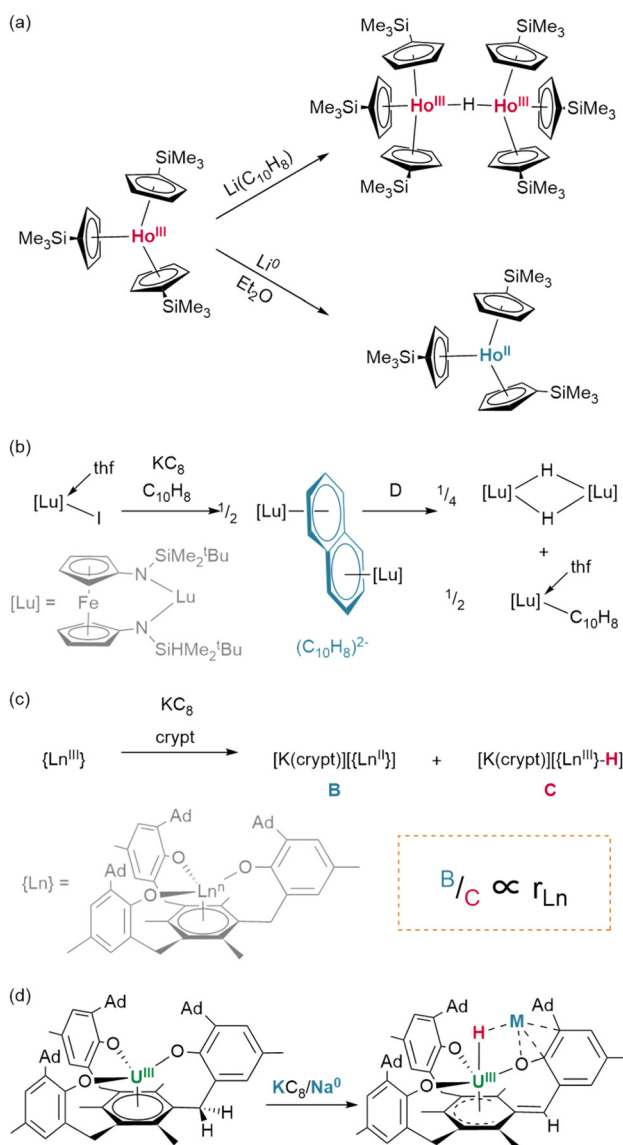


Fig. 8 Role of arenes in hydride formation under reducing conditions. (a) Hydride formation is observed *via* reduction with lithium naphthalenide but not lithium metal. (b) Diaconescu's rationally prepared lutetium naphthalenide yields the hydride and a lanthanide aryl cleanly upon heating. (c) Meyer demonstrated the importance of ion size with the ratio of Ln(II) product to lanthanide hydride found to be proportional to metal ionic radius. (d) Lanthanide behaviour can be compared to the uranium reactivity in which the ligand activated species was able to be trapped, demonstrating benzylic C–H activation within this scaffold. crypt = 2,2,2-cryptand.

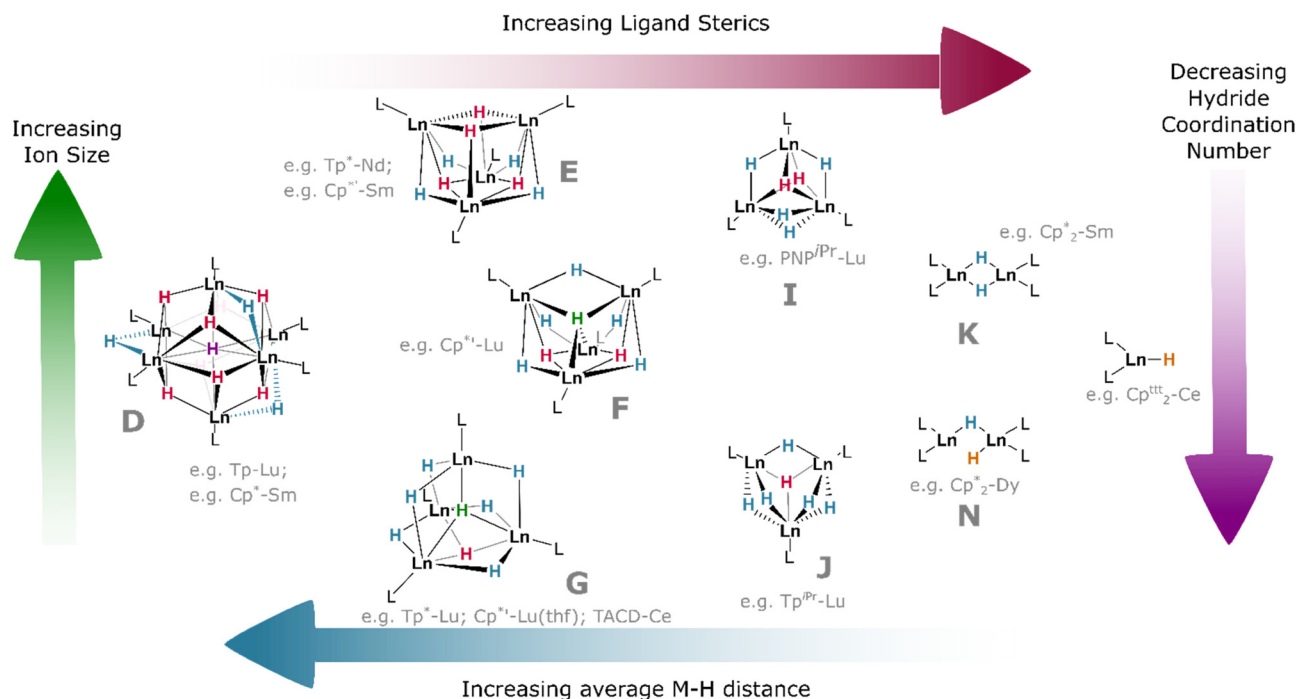


Fig. 9 Trends in structures of Ln hydride clusters with examples of L and Ln for each set. Ligand abbreviations: Cp* = C₅(CH₃)₅; Cp* = C₅(CH₃)₄(SiMe₃); Cp^{ttt} = C₅H₂(tBu)₃; Tp* = tris(3,5-dimethylpyrazolyl)borane; Tp^{IPr} = tris(3-isopropyl-5-methyl)pyrazolyl)borane; PNP^{IPr} = N(o-C₆H₄P(Pr)₂)₂; TACD = κ⁴-N,N,N,N-Me₄-1,4,7,10-tetraazadodecane.

radius; lutetium complexes, for example, have a greater tendency to include μ⁴ hydrides than the larger lanthanide analogues, with the small {(Cp*)Lu}₄(H)₈ complex comprising one μ⁴, two μ³, and five μ² hydrides in an overall C_{2v} symmetric central cluster (Fig. 9F).⁵⁸ Complexes of the larger metals yield clusters which have been crystallised as thf solvates: {(Cp*)Nd}₄(thf)₂(H)₈ (and earlier lanthanides) are found with four μ³ (2.18–2.34 Å) and four μ² (2.12–2.39 Å) hydrides, with overall C₂ cluster symmetry (Fig. 9E).³⁸ This trend is also reflected with different co-ligands: {(Tp*)Lu}₄(H)₈ (Tp* = tris(3,5-dimethylpyrazolyl)borane)[†] incorporates one μ⁴, one μ³, and six μ² hydrides, giving a C_{3v}-symmetric cluster (Fig. 9G); while the neodymium example {(Tp*)Nd}₄(H)₈ contains one μ⁴ and seven μ² hydrides in a cluster of C_{2v} symmetry (*cf.* Fig. 9F).⁴⁴ That smaller ions tend to construct higher-order bridging interactions is likely due to the contraction of the M–H bonds along the lanthanide series, which declines from 2.40(3) Å/2.26(5) Å (μ³/μ²) in {(Cp*)Pr}₄(thf)₂(H)₈ (Fig. 9E) to 2.13 Å/2.06 Å/2.16 Å (μ⁴/μ³/μ²) in {(Cp*)Lu}₄(thf)(H)₈ (Fig. 9G); indirectly, this is also observed in the concomitant increase in M–H stretching frequency (1307 to 1323 cm^{−1}) as the series is progressed. Additionally, the average M...M distance in these clusters spans the range 3.86–3.45 Å (La–Lu). The larger metal ions (La–Sm) retain two solvent molecules per cluster, falling to one at gadolinium, whilst the lutetium example has been characterised as existing without solvent incorporation.⁵⁸

As co-ligand size increases, lower-order clusters become more prevalent. Illustratively, with the Tp^{IPr} ligand (Tp^{IPr} = tris(3-isopropyl-5-methyl)pyrazolyl)borane)[†] on Lu(III), a trimer is

formed with one μ³ hydride and five μ² hydrides. Bulkier Tp^{tBu,Me} (Tp^{tBu,Me} = tris(3-*tert*-butyl-5-methylpyrazolyl)borane)[†] imposes a dimeric structure to its lower-valent Yb(II) monohydride complex,⁴⁵ while the even larger Tp^{Ad,Me} ligand (Tp^{Ad,Me} = tris(3-adamantyl-5-methylpyrazolyl)borane)[†] enforces a monomeric structure.⁴¹ The high symmetry of some of these clusters can lead to interesting magnetic properties.⁸⁸

Within the same ligand class, there are identifiable trends in M–H bonding due to clustering. With hexameric [(Tp)Lu(H)₂]₆, the average coordination number of the hydrides is 2.8, resulting in a longer M–H bond length of 2.25 Å (2.08–2.48 Å). For the tetrameric analogue with Tp*, the average hydride coordination number falls to 2.4, resulting in a mean M–H length of 2.11 Å (1.87–2.38 Å). Finally, for the trimer resulting from bulky Tp^{IPr}, the average hydride coordination number declines further to 2.2, which gives bond lengths of *ca.* 2.09 Å (1.99–2.25 Å).

In bis(cyclopentadienyl) ‘metallocene’ complexes, lower topology clusters are also favoured, in line with the lower M:H ratio (*vide supra*). Unsubstituted {(Cp)₂La₃(H)₃} exists as a distorted trimer with two μ² ligands and a single μ³ hydride as a result of the large ionic radius of this ion. Whereas Cp* complexes of Dy and Tb exist as trimers with three μ² hydrides, Cp*-ligated complexes of the same metals exist as dimers; [(Cp*)₂Dy(μ²-H)]₂ exhibits one bridging and one terminal hydride, whilst its Tb and Gd analogues exist as C₂-symmetric dimers with two μ² hydrides. With the very large Cp* ligand, monomeric complexes become isolable across the series: solvated Ce, Dy and Lu examples exhibit bond lengths ranging from 2.27–2.14 Å (Ce–Lu).^{25,37}



which appears at 1288 cm⁻¹. Therefore, reducing the steric bulk of the ligand appears to increase vibrational frequency as the M–H bond lengths shorten. At the same time, the coordination of donor co-ligands (such as solvent) lengthens the M–H bond. As one may expect, increasing cluster order from monomers with terminal bonds to dimers with bridging hydrides has a similar elongating effect, and this is in close concert with bond distances observed by X-ray crystallography.

Reactivity. The classical reactivity of Ln–R complexes, including R = H, involves two distinct but related mechanisms: σ -bond metathesis and 1,2-addition reactions (Fig. 10a). Utilizing these modes of reactivity, a wide range of catalytic processes have been developed which involve hydrides as key—but not necessarily isolated—intermediates (Fig. 10b). These reactions usually take advantage of *in situ* reactivity between Ln–R (R = alkyl, amide *etc.*) precatalysts and either silanes or boranes, which generates catalytically-active lanthanide hydrides analogously to stoichiometric processes (*vide infra*). For further insights into lanthanide catalysis from non-hydride precatalysts, we recommend works by Watson, Mindiola, Marks and Eisen,^{2,90–92}

σ -Bond metathesis. Stoichiometric σ -bond metathesis reactions are a staple of lanthanide chemistry, and lanthanide hydrides have been demonstrated to undergo σ -bond metathesis with a wide range of H-E reagents (E = C, N, S, O, P).^{16,97} The mechanism proceeds *via* a four-centred transition state, with loss of H₂ gas (Fig. 10).⁹⁸

Amines⁴⁵ ($E = NR_2$) readily react in this way—and so, too, does ammonia itself ($E = NH_3$). However, importantly, the latter was shown to react selectively with the tetrameric cluster $\{Cp^*Ln\}_4(H)_8$, yielding a heptaammine product which retains the same cluster topology, then undergoes a slower reaction (*ca.* 2 days) with the final, central, tetrahedral μ^4 -hydride; this seems to demonstrate that hydride structure—which may differ from that of a precatalyst—persists in solution, and that its impact on reactivity can be significant.⁹⁹ Ammonium salts ($E = NR_3$) have also been used similarly to generate cationic lanthanide fragments.⁴²

In another demonstrative case, σ -bond metathesis is mechanistically implicated in catalytic H/D exchange processes which occur between Ln-H centres and certain hydrocarbon substrates (preferentially, those possessed of hydrogens on sp^2 -hybridised carbons, or those with low steric hindrance).¹⁰⁰ Where alternative reaction pathways (insertion/addition; *vide infra*) are also possible, the strong driving force of H_2 loss is a significant factor in favouring σ -bond metathesis; terminal alkynes ($E = -C\equiv CR$) most often undergo H-C activation with loss of H_2 to yield Ln-CCR complexes, whereas less acidic alkenes undergo insertion across the Ln-H bond.⁵⁴ However, steric effects are also important in determining the reaction outcome: at a sterically-encumbered Yb centre, the disubstituted allene H_2CCCMe_2 preferentially reacts by σ -bond metathesis, whilst less bulky $H_2CCC(H)Cy$ undergoes 1,2-insertion.⁴¹

Metathesis of σ -bonds is also the primary process responsible for many ligand activation reactions at lanthanides. As

Subset	μ^2 -M-H (Å)	μ^3 -M-H (Å)	μ^4 -M-H (Å)
Dimer	2.17(15)	—	—
Trimer	2.20(20)	2.19(13)	—
Tetramer	2.22(18)	2.36(18)	2.20(12)
Lanthanum	2.38(11)	2.56(14)	2.43(4)
Lutetium	2.08(11)	2.20(14)	2.11(5)
All Lanthanides	2.20(17)	2.29(18)	2.20(12)
All Actinides	2.25(14)	2.35(15)	—

Compound	IR Band (cm ⁻¹)	Assignment	Ref.
Ln-H	1100-1300	M-H	16
[Cp* ₂ LaH] ₂	1120	M-H (bridging)	93
[Cp* ₂ LuH] ₂	1345	M-H (bridging)	93
[Cp ₂ YH(thf)] ₂	1315	M-H (bridging)	94
[Cp ^{Me} ₂ YH(thf)] ₂	1240	M-H (bridging)	94
Cp* ₂ YH(thf)	1295	M-H (terminal)	95
[Cp*YH] ₂	1272	M-H (bridging)	96
{Cp*Lu} ₄ (H) ₈	1304	M-H (bridging)	58
{Cp*Lu} ₄ (H) ₈ (thf)	1288	M-H (bridging)	58

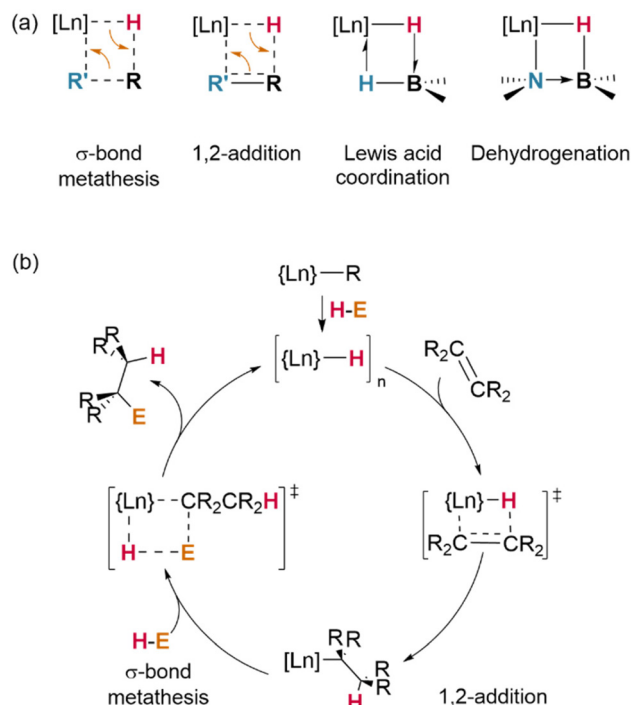


Fig. 10 Overview of primary mechanisms of reactivity of lanthanide hydrides. (a) Key transition states for primary reactions types. (b) General catalytic scheme for Lanthanide hydride catalysed hydroelementation processes.

demonstrated by Evans and Furche, in $[(\text{Cp}^*)_2\text{Ln}(\text{H})]_2$, the activation of Cp^* methyl substituents occurs preferentially in complexes of the early (larger) lanthanides—although, in their experiments, a mixture of species was observed in all cases.²⁸

Whilst dehalogenation of alkanes by lanthanide hydrides has long been known, Andersen and Maron have more recently demonstrated C–F bond metathesis using a bulky Ce(IV) hydride (Fig. 11).²⁹ Likewise, dehydrogenative coupling of terminal alkynes with silanes, mediated by a catalytically-active hydride species, is proposed to occur through σ -bond metathesis.⁷²

Addition reactions/insertion reactions. The primary alternative reactivity profile of these complexes is 1,2-addition, or insertion into the $\text{Ln}–\text{H}$ bond;¹⁰¹ this proceeds, mechanistically, through a similar four-centred transition state to σ -bond metathesis (Fig. 10).¹⁰² By this route, insertion of alkenes has been widely utilized for olefin polymerization catalysis,¹⁰³

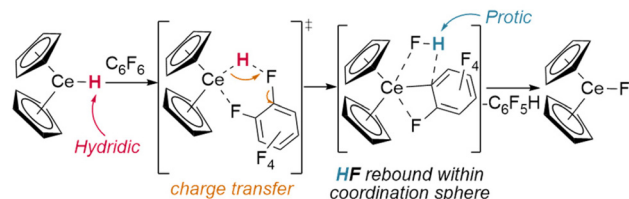


Fig. 11 Calculated mechanism of $\text{Cp}^{\text{ttt}}_2\text{CeH}$ reactions with C_6F_6 (shown as calculated with Cp (i.e. C_5H_5) for computational simplicity).

while insertion of CO_2 has been demonstrated to allow copolymerization with epoxides. In stoichiometric reactions, insertion across alkenes,⁵¹ alkynes,⁵⁰ ketones,⁴⁹ esters,¹⁰⁴ nitriles,⁵⁴ isocyanides,⁵⁴ and nitrogen heterocycles⁴⁹ have all been reported.

Lacking the driving force of H_2 elimination, the likelihood of alkynes undergoing insertion reactivity over σ -bond metathesis is subject to a fine balance of effects. It has been shown that bis(trimethylsilyl)acetylene undergoes Si–C bond metathesis with $[(\text{Tp}^{\text{tBu,Me}})\text{Yb}^{\text{II}}\text{H}]_2$, yielding the dimer $[(\text{Tp}^{\text{tBu,Me}})\text{Yb}^{\text{II}}(\mu^2-\eta^1:\eta^2-\text{CCSiMe}_3)_2]$ (Fig. 12)—but bis(trimethylsilyl)but-1,3-diyne instead undergoes an addition reaction to yield a monomeric, η^3 -bound product, $(\text{Tp}^{\text{tBu,Me}})\text{Yb}^{\text{II}}(\eta^3-\text{Me}_3\text{SiCC-CC}(\text{H})\text{SiMe}_3)$.⁴⁵

Hill and Anker demonstrated that, after olefin insertion into the hydride of $[(\text{NacNac}^{\text{iPr}})\text{Yb}^{\text{II}}\text{H}]_2$ ($\text{NacNac}^{\text{iPr}} = N,N'$ -bis(diisopropylphenyl)- β -pentanediimide), it is activation of the benzene- d_6 solvent which subsequently regenerates the hydride (deuteride) and affords the resultant hydroarylation product (Fig. 13).⁶³ This reactivity contrasts with classical $\text{Ln}(\text{III})$ alkyl activation of benzene, which results in the formation of lanthanide aryl species—and may proceed through a cooperative transition state similar to that proposed by Zhu.⁷²

Dehydrogenation. In 2013, the catalytic dehydrogenation of dimethylaminoborane was demonstrated to occur through a ligand-assisted process.¹⁰⁵ Initial protonolysis of the hydride yields an amide-tethered borane (Fig. 10a), which can subsequently react to couple $\text{H}_2\text{B}–\text{NMe}_2$ units. Thus, the resting state of the catalyst most likely relies on cooperative lanthanide-borohydride chemistry distinct from $\text{Ln}–\text{H}$ behaviour.

Redox reactions. In recent years, increasing work has been undertaken with low-valent lanthanide complexes with these ions adding a new facet of redox activity to lanthanide behaviour.

Reduction of the *ansa*-cyclopentadienyl ligated dimer $\{(\eta^5,1\eta^5-\text{Cp}^{\text{Am}})\text{Dy}^{\text{III}}(\text{thf})_2(\mu^2-\text{H})_2\}$ ($\text{Cp}^{\text{Am}} = (\text{Cp}')_2\text{SiMe}_2$) resulted

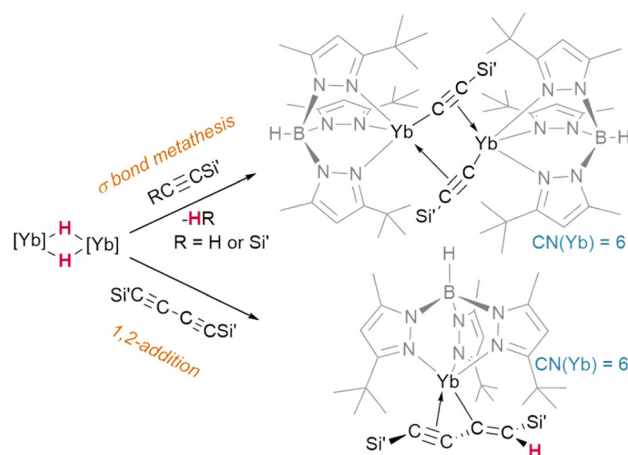
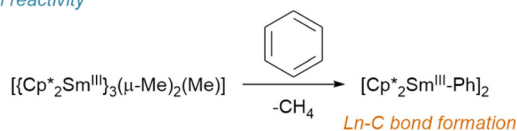


Fig. 12 Divergent pathways for reactions of ytterbium hydrides with silyl acetylenes ($[\text{Yb}] = \text{Tp}^{\text{tBu,Me}}\text{Yb}^{\text{II}}$) may be driven by maintaining a high coordination number at the metal.

Classical reactivity



Hydroarylation

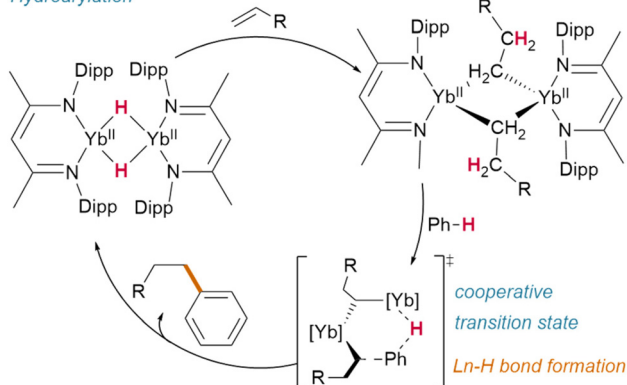


Fig. 13 Hydroarylation catalysed by an ytterbium(II) hydride complex contrasts with classical sigma bond metathesis reactivity observed for Sm(III).

in an unusual ligand rearrangement: in its new, desolvated form, $[K(18\text{-crown-6})][\{1\eta^5:2\eta^5\text{-Cp}^{\text{An}}\}_2\text{Dy}^{\text{III/II}}_2(\mu^2\text{-H})_2]$, the supporting ligands bridge between the two metal centres—although it retains the pre-existing $\{\text{Dy}_2\text{H}_2\}$ core (Fig. 14a).¹⁰⁶

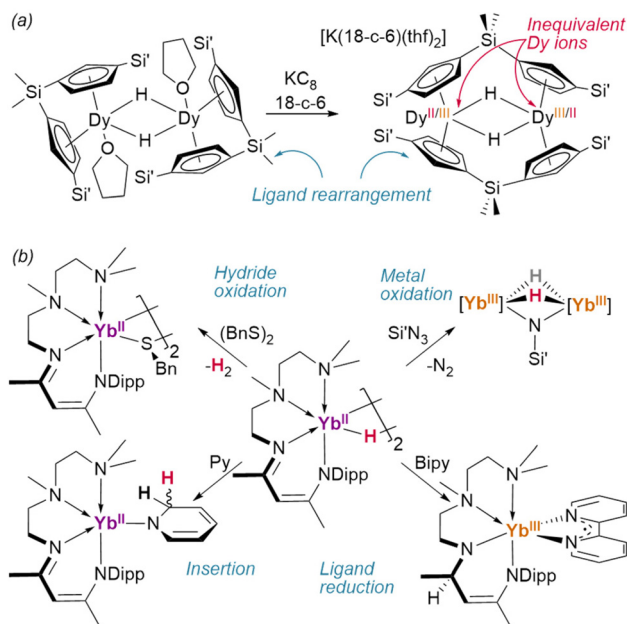


Fig. 14 Redox reactions of lanthanide hydrides. (a) Single electron reduction of the ansa-metalloocene ligated dysprosium hydride yields a ligand rearrangement product with unsymmetrical Dy charge density and a calculated Dy...Dy ground state interaction. $\text{Si}' = \text{SiMe}_3$; 18-c-6 = 18-crown-6. (b) Different redox reactivity of a Yb^{II} hydride complex. $[\text{Yb}] = \{\kappa^4\text{-TMEDA-NacNac}^{\text{Dipp}}\text{Yb}\}$; Dipp = 2,6-diisopropylphenyl; Bipy = 2,2'-bipyridine; Py = pyridine.

Intriguingly, low-valent $\text{Yb}(\text{II})$ dihydride $[\{\kappa^4\text{-TMEDA-NacNac}^{\text{Dipp}}\text{Yb}^{\text{II}}(\mu^2\text{-H})\}_2]$ has been shown to reduce azidotrimethylsilane without perturbing the hydrides, affording a dihydrido-imido $\text{Yb}(\text{III})$ complex (Fig. 14b).¹⁰⁷ In this case, further reaction with $\text{Se}(\text{0})$ dehydrogenated the complex entirely—while with $(\text{BnS})_2$ direct dehydrogenation of the hydride was observed to yield the $\text{Yb}(\text{III})$ product.⁵⁵ This complex was also shown to reduce 2,2-bipyridine, during which reaction hydride transfer to the NacNac backbone occurs. A $\text{Tp}^{\text{Ad, iPr}}$ complex of the same ion was also shown to reduce cyclooctatetraene to its dianion, yielding the inverse sandwich product $\{(\text{Tp}^{\text{Ad, iPr}})\text{Yb}^{\text{III}}\}_2(\text{COT})$ (COT = cyclooctatetraene).

Lewis acid coordination. Worth mentioning is a related mode of reactivity, demonstrated by Evans, in which a Lewis acid (e.g. borane) coordinates to the hydride ligand.¹⁰⁸ This method has also been used to great effect in the synthesis of lanthanide borohydrides and aluminohydrides.

Lewis acid coordinated lanthanide hydrides

In addition to homometallic clusters of lanthanide hydrides, a wealth of complexes of the form $\text{Ln}\cdots\text{H-E}$ or $\text{Ln}\cdots\text{H-M}$ have been reported, ranging from silane complexes containing β -agostic interactions^{109,110} (and potentially α -agostic interaction¹¹¹) to complexes of the BH_4 anion¹¹² and those of heavier main group and transition metals (Fig. 15).^{113,114}

Borohydrides¹⁰⁸

Complexes of lanthanides with tetrahydroborate ligands—both $\text{Ln}(\text{II})$ and $\text{Ln}(\text{III})$ —are myriad in the literature,¹¹² owing in part

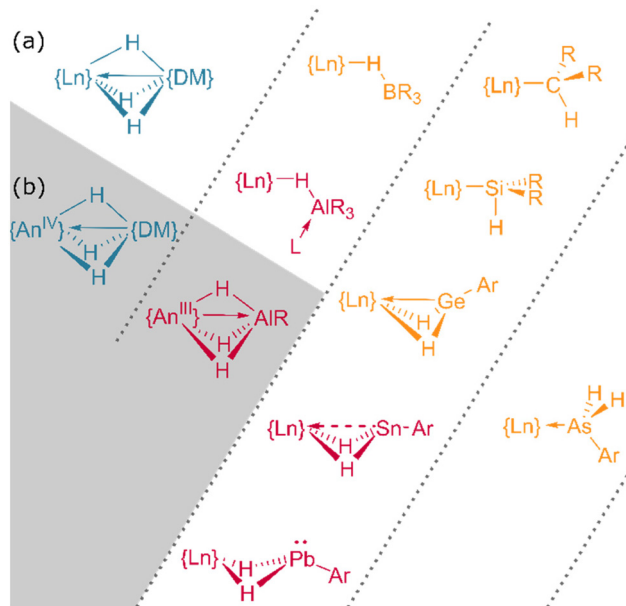


Fig. 15 The bonding interactions of heterobimetallic f-block hydrides. (a) Lanthanide complexes. (b) Actinide complexes. DM = d-block metal. Further examples can be found in ref. 109 and 123.



Main group hydrides

5-coordinate Al(III)

'Masked' hydride

Rapid Exchange

Ln = Sm, Dy, Yb

Transition metal hydrides

Heterobimetallic complexes with transition metal hydrides have also attracted interest due to the excellent hydrogen storage properties of materials such as LaNi_5H_x . Complexes of lanthanide hydrides with Mo, W, Re, Ru, Os, and Ir are all known and these have been synthesised by a range of routes including alkane elimination,¹²⁴ salt elimination,¹²⁵ CH activation¹²⁶ and H_2 elimination.³⁷ Transition metals can lend the lanthanide clusters redox activity which would otherwise be inaccessible, enabling facile C–H bond activation in Cp, PPh_3 and PR_3 co-ligands.^{126–130} These oxidative addition-like C–H activation steps provide both bridging organometallic and hydride ligands, which buttress direct Ln–TM bonds.¹²⁸ In Ln/Mo clusters, H_2 addition was even observed by single-crystal X-ray diffraction.¹³¹

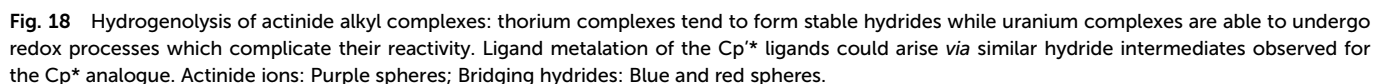
Homoleptic actinide hydrides

The use of the actinides in synthetic chemistry is distinguished from that of the lanthanides in two key respects. First and foremost, the radioactivity of many actinides—particularly the transuranic elements—makes necessary numerous additional precautions and, in the latter case, their handling remains unfeasible in all but the most specialist of laboratory environments; the natural consequence is that markedly less work has been conducted in this area. It is the second respect which makes the effort worthwhile: although their bonding interactions are predominantly electrostatic, the early actinides—especially uranium—are softer, more polarizable metals, for which the valence 5f and 6d orbitals possess sufficient radial extension to impart some degree of covalent character to An–E bonds. As a result, the chemistry of these elements diverges conspicuously from that of the lanthanides—moreover, exhibiting a unique combination of behaviours to which no other region of the periodic table can entirely attest.¹³²

Observations from gas phase and matrix isolation experiments

Early actinide hydrides, AnH_x ($\text{An} = \text{Th, U}; x = 1\text{--}4$), have, like their lanthanide analogues, been observed by pulsed laser ablation studies in argon. Under these conditions, where $x = 1\text{--}3$, IR spectroscopic measurements indicate that Th–H bonds are somewhat stronger than their uranium analogues—although those of UH_4 complexes are stronger still.^{133,134} Dimeric, hydride-bridged $\{\text{An}_2\text{H}_2\}$ species are also known for uranium, whereas isostructural thorium analogues have not been observed; calculations imply that a dithorium-bonded $\{\text{HTh}\equiv\text{ThH}\}$ formulation may be more favourable in this case.¹³⁵ Thorium(IV) dihydrogen complexes are also stabilised due to the highly ionic nature of the bonding in ThH_4 generating polarized H_2 complexes which exhibit Crabtree’s “dihydrogen bond”-type interactions. This stands in contrast to the uranium example, which has more 5f orbital involvement in bonding. Dihydrogen complexes have also been predicted by these methods and observed in the gas phase and recently in solution (*vide infra*).^{136,137}

Dalton Trans., 2024, **53**, 12814–12836 | 12825



With less accessible redox activity, preparations of thorium hydrides often more closely resemble those of lanthanide congeners; syntheses are somewhat more affected by steric and electronic differences in the coordination sphere of the alkyl precursor complex than the feasibility of ligand cyclometallation. The preparation of a range of thorium hydride clusters, $[(\text{Cp}^{\text{R}})\text{Th}(\mu^2\text{-H})_n]$ ($n = 5\text{--}13$, *vide infra*), from thorium monocyclopentadienyl trialkyl precursors, necessitates higher pressures of H_2 (10–60 bar), elevated temperatures (up to 60 °C), and extended reaction times (12–96 h).¹⁵¹ Likewise, thorium trialkyl complexes bearing a single, extremely hindered pentaaryl cyclopentadienyl ligand undergo a combined protonolysis and hydrogenolysis upon treatment with HCp^* or $\text{HCp}^\times$ ($\text{Cp}^\times = \text{C}_5\text{Me}_4\text{H}$) and H_2 , affording the corresponding $(\text{Cp}^{\text{Ar}})(\text{Cp}^{\text{R}})\text{Th}(\text{H})_2(\text{thf})$ ($\text{Cp}^{\text{Ar}} = \text{C}_5(3,5\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)_5$, $\text{Cp}^{\text{R}} = \text{Cp}^*$ or $\text{Cp}^\times$) species—although reactions are reported only at relatively high pressures of H_2 (10–20 bar).¹⁵² Only some preformed thorium bis(cyclopentadienyl) complexes are known to react under

Hydrogenation of nitrides – insights into reversibility. Whilst hydrogenation conditions need not be forcing, the effective stabilisation of discrete uranium hydrides is highly substrate-dependent. Illustratively, the Mazzanti group's recent bimetallic $\text{U}^{\text{III}}/\text{U}^{\text{IV}}$ hydride, $\{(\text{N}^{\text{II}})_2\text{U}(\text{thf})\}_2(\mu^2\text{-H})(\mu^2\text{-NH})$, and mixed-metal U^{IV} species $\text{Cs}\{[(\text{Si}^{\text{IV}}\text{O})_3\text{U}]_2(\mu^2\text{-H})(\mu^2\text{-NH})\}$, are readily prepared by hydrogenation (1 bar, -40°C) of the respective nitride precursors $\{(\text{N}^{\text{II}})_2\text{U}(\text{thf})\}_2(\mu^2\text{-N})$ or $\text{Cs}\{[(\text{Si}^{\text{IV}}\text{O})_3\text{U}]_2(\mu^2\text{-N})\}$.¹⁵³ However, the former reaction proceeds at -40°C only with concomitant formation of another cyclometalated complex, $\{(\text{N}^{\text{II}})_2\text{U}(\text{thf})\}(\mu^2\text{-NH})(\mu^2\text{-}\kappa^2\text{-C}, N\text{-CH}_2\text{SiMe}_2\text{N}^{\text{II}})\{\text{U}(\text{N}^{\text{II}})\}$, which is found present in equal measure with $\{(\text{N}^{\text{II}})_2\text{U}(\text{thf})\}_2(\mu^2\text{-H})(\mu^2\text{-NH})$. No reaction is observed at lower temperatures, precluding the arrestation of this further reactivity, and, in the absence of H_2 atmosphere, $\text{Cs}\{[(\text{Si}^{\text{IV}}\text{O})_3\text{U}]_2(\mu^2\text{-H})(\mu^2\text{-NH})\}$ gradually decomposes by loss of H_2 (*i.e.*, hydrogenation is reversible).¹⁵⁴ Conversely, structurally-related diuranium(IV) complex $[\text{NBu}_4]\{[(\text{Si}^{\text{IV}}\text{O})_3\text{U}]_2(\mu^2\text{-NH})(\mu^2\text{-H})\}$ forms from $[\text{NBu}_4]\{[(\text{Si}^{\text{IV}}\text{O})_3\text{U}]_2(\mu^2\text{-N})\}$ under yet milder conditions of hydrogenation (1 bar, r.t.) and persists even under vacuum.¹⁵⁵ Mazzanti posits that the coordinated alkali metal cation has a destabilising effect on the hydride product, an assertion which is lent weight by catalytic studies with other rare earth hydride

'ate' complexes.¹⁵⁶ It is also interesting to note that complexes of this type were shown to facilitate the reduction of dinitrogen to ammonia by hydrogenolysis.¹⁴

Hydride transfer from salts and silanes. One possible solution to the problem of challenging hydrogenation conditions is the use of alkali metal hydride-transfer reagents, which have been studied somewhat more extensively in actinide systems than in lanthanide congeners. By treatment with NaH, mononuclear $[\text{Na}(18\text{-crown-6})][(\text{Cp}')_3\text{U}(\text{H})]$, dinuclear $[\text{Na}(18\text{-crown-6})(\text{thf})_2][(\text{Cp}')_3\text{U}^{\text{III}}_2(\mu^2\text{-H})]$, and Na-bridged 'ate' complex $[\text{Na}(\text{thf})_2][(\text{Cp}')_3\text{U}^{\text{III}}_2(\mu^2\text{-H})]$ are respectively accessible from the corresponding $(\text{Cp}')_3\text{U}^{\text{IV}}(\text{Cl})$ or $(\text{Cp}')_3\text{U}^{\text{III}}(\text{thf})$ (Fig. 19a);^{157–159} comparably, in the presence of 2.2.2-cryptand, treatment of *in situ*-generated $(\text{Cp}')_3\text{U}^{\text{III}}$ with KH affords mononuclear $[\text{K}(2.2.2\text{-cryptand})][(\text{Cp}')_3\text{U}^{\text{III}}(\text{H})]$ (Fig. 19a),¹⁶⁰ whilst thorium(IV) tris(cyclopentadienyl) complex $(\text{Cp}^*)_3\text{Th}^{\text{IV}}(\text{Cl})$ ($\text{Cp}^* = 1,3\text{-}(\text{tBu})_2\text{C}_5\text{H}_3$) reacts with excess KH to yield the corresponding monomeric hydride.¹⁶¹

Alternatively, but in similar fashion to lanthanide examples, the exchange of An–C for An–H linkages is also achievable by actinide complexes through the σ -bond metathesis of silanes. Complementary to the original, hydrogenative preparations of $[(\text{Cp}^*)_2\text{An}(\text{H})_2]_2$ (An = U, Th), Kiplinger and colleagues report that treatment of $(\text{Cp}^*)_2\text{An}(\text{Me})_2$ with PhSiH_3 (toluene, 50 °C, 30 minutes) effects the near-quantitative conversion of these alkyl complexes to the respective hydrides.¹⁶² Reactions with $\text{K}(\text{HBET}_3)$ salts may also generate hydrides with concomitant loss of $\text{K}(\text{RBET}_3)$: treatment of tris(cyclopentadienyl) halide precursor $(\text{Cp}')_3\text{U}^{\text{IV}}\text{Cl}$ with $\text{K}(\text{HBET}_3)$ effects the abstraction and exchange of chloride for hydride, yielding $(\text{Cp}')_3\text{U}^{\text{IV}}(\text{H})$ (Fig. 19b).¹⁵⁷

Low valent actinides. Though a relatively new development, low-valent actinide complexes (*i.e.* $\text{U}(\text{II})$, $\text{Th}(\text{III})$, $\text{Th}(\text{II})$) also offer excellent opportunities to access hydrides. Treatment of divalent $[\text{K}(18\text{-crown-6})(\text{thf})_2][(\text{Cp}')_3\text{Th}^{\text{II}}]$ with $[\text{Et}_3\text{NH}][\text{BPh}_4]$ affords a mixture of trivalent $(\text{Cp}')_3\text{Th}^{\text{III}}$ and tetravalent $(\text{Cp}')_3\text{Th}^{\text{IV}}(\text{H})$. This same $\text{Th}(\text{II})$ 'ate' complex also reacts with H_2 (4 bar, r.t.) in the solid state and in thf solution (1 bar, 0 °C)—although the hydride-containing product is instead the trihydride-bridged dimer $[\text{K}(18\text{-crown-6})(\text{Et}_2\text{O})][(\text{Cp}')_2\text{Th}^{\text{III}}(\mu^2\text{-H})_3\{\text{Th}^{\text{IV}}(\text{H})(\text{Cp}')_2\}]$, which forms concomitantly with $(\text{Cp}')_3\text{Th}^{\text{III}}$ (Fig. 19c).¹⁶³ Likewise, the rare uranium(II) tris(cyclopentadienyl) complex, $[\text{K}(2.2.2\text{-cryptand})][(\text{Cp}')_3\text{U}^{\text{II}}]$, is readily converted to $[\text{K}(2.2.2\text{-cryptand})][(\text{Cp}')_3\text{U}(\text{H})]$ by direct hydrogenation (1 bar, 0 °C),¹⁶⁰ or by treatment with silane.¹⁶⁴

Structure, bonding insights & co-ligand effect. In comparison to that of the lanthanide hydrides, the extent to which actinide hydrides have been characterised is somewhat less complete, hampered by the small number of examples and inconsistency of analyses to which novel materials have been subjected.

Morphology and connectivity. At the time of Ephritikhine's 1997 review of the field,¹⁶ very few species yet possessed complete X-ray crystallographic data. Such characterisation of actinide–hydride linkages is necessarily limited by the poor resolution of electron density associated with the hydride

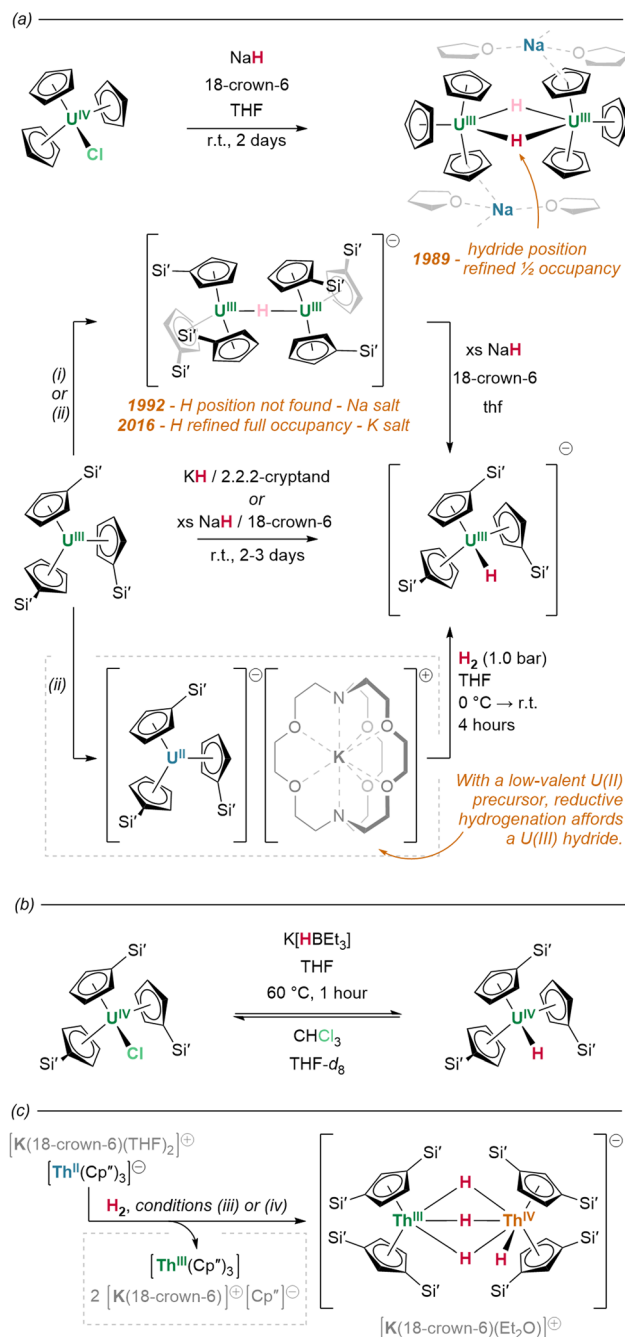


Fig. 19 Synthesis of hydrides *via* reactions with hydride transfer agents or *via* low-valent actinide species show similarities in their behaviour. (a) In 1989, salt metathesis of Cp_3UCl with NaH yielded a mono-hydride bridged dimer which was originally assigned as a crystallographically disordered species with bent hydride bridges exhibiting M–H–M angles around 160°. In 1992, treatment of $\text{U}^{\text{III}}\text{Cp}_3$ with NaH yielded a dimer with a proposed linear M–H–M angle; however, no hydride was found. In 2016, Evans *et al.* reported the K analogue and were able to refine the H position in the linear bound site. (i) NaH, 18-crown-6, thf, 2 days; (ii) $\text{K}(\text{Cp}^*)_3$ 18-crown-6, Et_2O , –35 °C (iii) H_2 (4.1 bar), 18 h, solvent free; (iv) H_2 (1 bar), 20 min, thf, 0 °C – r.t.

Spectroscopic insights. Whilst a number of uranium hydrides have been characterised by NMR spectroscopy, the paramagnetic nature of uranium oxidation states III–V precludes any useful discussion thereof.¹⁸⁰ In principle, the diamagnetism of thorium(IV) complexes enables more considered commentary, although hydride shifts are more indicative of ligand electronics than cluster size. For example, whilst the hydrides of $[(\text{Cp}^{\text{tt}})\text{Th}^{\text{IV}}(\mu^2\text{-H})_3]_5$ give rise to a resonance at

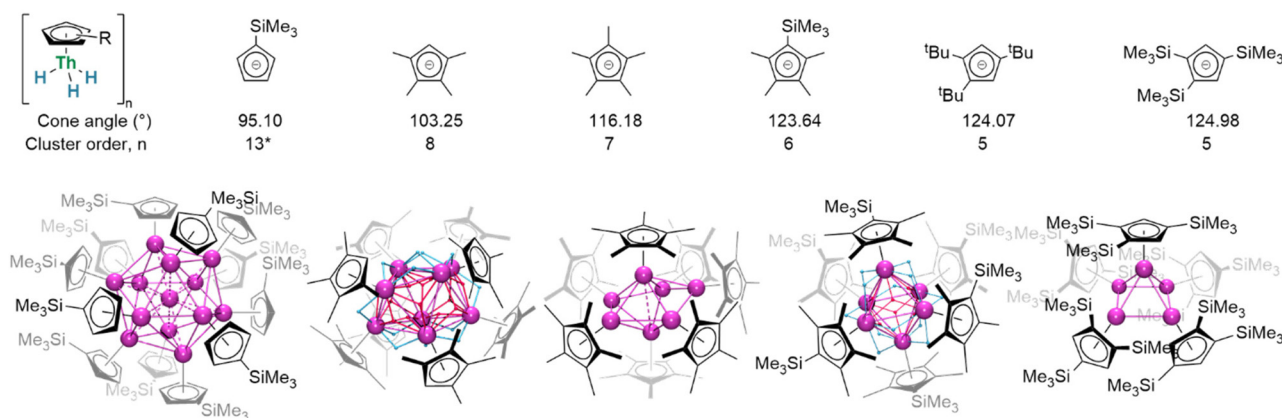


Fig. 20 Cluster order decreases with increasing with cyclopentadienyl ligand cone angle, measured from solid state structures. * The Cp* ligand results in a complex cluster of the form $\{(\text{Cp}^*\text{Th})_3(\text{H})_{10}\}_4\text{Th}$ in which the position of the hydrides is unknown. Despite its non-standard nature it is clear that this ligand can, and does, facilitate for formation of higher-order clusters than its smaller analogues. This cluster is also reminiscent of the structure of binary hydride Th_4H_{15} .

16.46 ppm in C_6D_6 , the replacement of *tert*-butyl substituents with more electropositive trimethylsilyl groups in $[(\text{Cp}^*)\text{Th}^{\text{IV}}(\mu^2\text{-H})_3]_5$ leads its analogous resonance to appear somewhat further upfield, at 15.78 ppm. A much more subtle effect is observed when ligand sterics, rather than electronics, are modulated: the hydrides of heptameric $[(\text{Cp}^*)\text{Th}(\mu^2\text{-H})_3]_7$ and octameric $[(\text{Cp}^*)\text{Th}(\mu^2\text{-H})_3]_8$ give rise to resonances at 16.68 ppm and 16.44 ppm—virtually indistinguishable from those of $[(\text{Cp}^*)\text{Th}(\mu^2\text{-H})_3]_5$.

IR spectroscopy can provide complementary insights where other techniques are limited. In general, An–H vibrations appear at slightly higher frequencies (1200 to 1500 cm^{-1}) than those of their lanthanide congeners, and there are also discernible differences in vibrational energies between the hydrides of isostructural thorium and uranium complexes, such as $(\text{N}^*)_3\text{An}(\text{H})$ (An = Th, $\nu_{\text{Th-H}} = 1480 \text{ cm}^{-1}$; An = U, $\nu_{\text{U-H}} = 1430 \text{ cm}^{-1}$). This discernibility is also retained upon deuteration, whereupon bands are instead observed at 1060 and 1020 cm^{-1} respectively.^{181,182} Unfortunately, the availability and assignment of IR spectral data in the literature has been somewhat limited to date; its inclusion in future publications is likely to offer new insights.

Redox behaviour and reactivity towards substrates. Among the greatest opportunities for future research, however, may yet be found in the reactivity of actinide hydrides. In some respects, this conforms to trends established elsewhere in the periodic table: the characteristic reactivity of hydride species towards haloalkanes makes treatment with CCl_4 a common chemical test for transition metal hydrides; this is also found to be effective in a number of actinide cases.^{163,175,179} Actinide hydrides may also participate in some of the same catalytic hydroelementation processes as lanthanides.^{183,184} Additionally, bimetallic $[(\text{Cp}^*)_2\text{Th}(\mu^2\text{-H})_2]_2$ is conventionally reducible in the presence of KC_8 and 18-crown-6, although the resulting trivalent complex is challenging to isolate.¹⁶³

In other respects, their chemistry can differ dramatically. Whilst the potentiality of these f-block species has not yet

been fully-established by comprehensive studies, in individual cases, detailed investigations have begun to illustrate the divergence and potential utility of their reactivity. A case worth considering in this context is that of Meyer and colleagues' trivalent scaffold complex, $\{(\text{Ad}^{\text{Me}}\text{ArO})_3\text{mes}\}\text{U}^{\text{III}}$, which undergoes an isomerization process upon reduction with KC_8 or Na^0 wherein $\text{H}^{\cdot}$, abstracted from the benzylic methylene linker of one arm of the supporting ligand, migrates to the metal centre (Fig. 8d); here, it bridges between the uranium centre and an alkali metal centre, which is itself η^4 -coordinated to the most proximate aryloxy moiety of the ligand. However, abstraction of the respective alkali metal centres by treatment with an appropriate encapsulation agent (18-crown-6, 15-crown-5) also induces the insertion of hydride into the central arene ring, disrupting its aromaticity.¹⁷⁵ Such an actinide-mediated rearrangement is at least suggestive of a novel dearomatisation strategy. Of course, as is true in this case, not all such reactivity is welcome; the aforementioned decomposition of suitably-ligated hydride species, eliminating H_2 to yield cyclometalated 'tuck-in' complexes, is indicative of the precarious balance of factors which keep these complexes stable. When reactions are reversible—as in the case of $(\text{COT}^{\text{TIPS}2})(\text{Cp}^*)\text{U}(\text{H})$, which exists in an equilibrium balanced by its 'tuck-in' analogue and H_2 —this can somewhat complicate the interpretation of complex reactivity.¹⁷⁶

Of some further interest is the potential for hydrides to exhibit redox activity, even in the absence of a typically redox-active metal (e.g. thorium, for which the tetravalent oxidation state overwhelmingly predominates): $[(\text{Cp}^*)_2\text{Th}^{\text{IV}}(\mu^2\text{-H})(\text{H})]_2$, generated *in situ*, reacts with S_8 to form $(\text{Cp}^*)_2\text{Th}^{\text{IV}}(\text{S}_5)$ (Fig. 21); its uranium(IV) analogue reacts with 2,2'-bipyridine to yield $(\text{Cp}^*)_2\text{U}^{\text{IV}}(\text{bipy})$, wherein the reduction of the 2,2'-bipyridyl ligand is achieved without any ultimate change in the metal oxidation state.¹⁶²

Alternatively, reactions of actinide hydrides with small molecules demonstrate the surprising potential for actinide hydride-mediated functionalization of organic fragments.



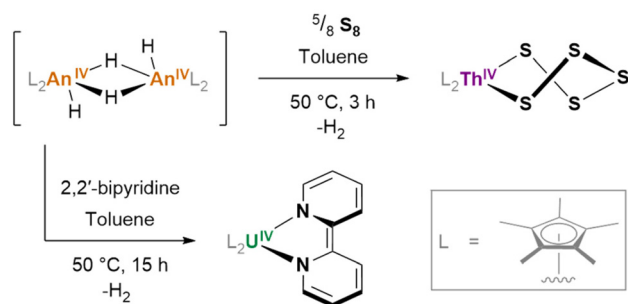


Fig. 21 Actinide hydride reduction behaviour towards substrates. $\{\text{Cp}^*\text{Th}\}_2(\text{H})_4$ generated *in situ* reacts with elemental sulfur to yield form a S_5^{2-} coordinated product. The analogous uranium hydride, $\{\text{Cp}^*\text{U}\}_2(\text{H})_4$, reacts with 2,2'-bipyridine to coordinate the reduced bipyridyl dianion (bipy^{2-}).

Treatment of $[(\text{Cp}^*)_2\text{U}(\mu^2\text{-H})_2]$ with MeCN (6 equiv.) induces the condensation of three MeCN units to $(\text{C}_6\text{N}_3\text{H}_7)^{2-}$, which binds in a $\kappa^2\text{-N,N'}$ fashion, bridging the two uranium(IV) centres (Fig. 22, top left). Of further significance is that dithorium(IV) tetrahydride complex $[(\text{Cp}^*)_2\text{Th}(\mu^2\text{-H})(\text{H})_2]$ may be considered to possess similar reactivity to U(III) containing $[(\text{Cp}^*)_2\text{U}(\text{H})_2]$. It, likewise, undergoes reaction with MeCN to generate $(\text{C}_6\text{N}_3\text{H}_7)^{2-}$ (Fig. 22, top right).¹⁶⁸ Previously-mentioned $\text{Cs}[\{(\text{Si}^{\text{O}^+}\text{O})_3\text{U}\}_2(\mu^2\text{-H})(\mu^2\text{-NH})]$ also undergoes reaction with MeCN to give $\text{Cs}[\{(\text{Si}^{\text{O}^+}\text{O})_3\text{U}\}_2(\mu^3\text{-NH})(\mu^2\text{-NCHCH}_3)]$

(Fig. 22, middle), in which the μ^3 -imido ligand also coordinates Cs^+ . In the presence of CO_2 (2 equiv.), insertion into both the U–H and U–NH linkages of $\text{Cs}[\{(\text{Si}^{\text{O}^+}\text{O})_3\text{U}\}_2(\mu^2\text{-H})(\mu^2\text{-NH})]$ yields $\text{Cs}[\{(\text{Si}^{\text{O}^+}\text{O})_3\text{U}\}_2(\mu^2\text{-HCOO})(\mu^2\text{-NHCOO})]$.¹⁵³ In a further expansion on this concept, sequential reactions of related $\text{K}_2[\{(\text{Si}^{\text{O}^+}\text{O})_3\text{U}\}_2(\mu^2\text{-O})(\mu^2\text{-H})_2]$ with a range of small molecules demonstrate the efficacy of transfer hydrogenation at actinide centres, enabling the assembly of entire organic fragments (Fig. 22, bottom). By a two-electron process, the complex reductively couples MeCN to form $(\text{NC}(\text{CH}_3)\text{NCH}_2\text{CH}_2)^{2-}$, a dianionic fragment which may be isolated in a $\mu^2\text{:}\kappa^2$ bridging mode between its two uranium centres alongside its pre-existing μ^2 -oxo. Alternatively, treatment with CO results in the formation of an $(\text{OCH}_2)^{2-}$ fragment, whereafter further treatment with H_2 (1 bar, r.t.) affords $(\text{OCH}_3)^-$ and reintroduces a hydride ligand. From either the $(\text{OCH}_2)^{2-}$ bridged complex, or after further reaction of the $(\text{OCH}_3)^-$ bridged complex with CO_2 , separable organic compounds CH_2DOD —or, in the latter case, a mixture of formate, bicarbonate, and methanol—may be identified by NMR spectroscopy after treatment of the complex with D_2O .¹⁵⁰

Related insights: a dihydrogen complex. As a final note: albeit not a study of conventional hydride complexes, significant insights into the nature of actinide–hydrogen linkages may also be gleaned from related dihydrogen complexes. Only very recently has the first evidence for the formation of such an actinide complex been reported: by utilising the pseudocon-

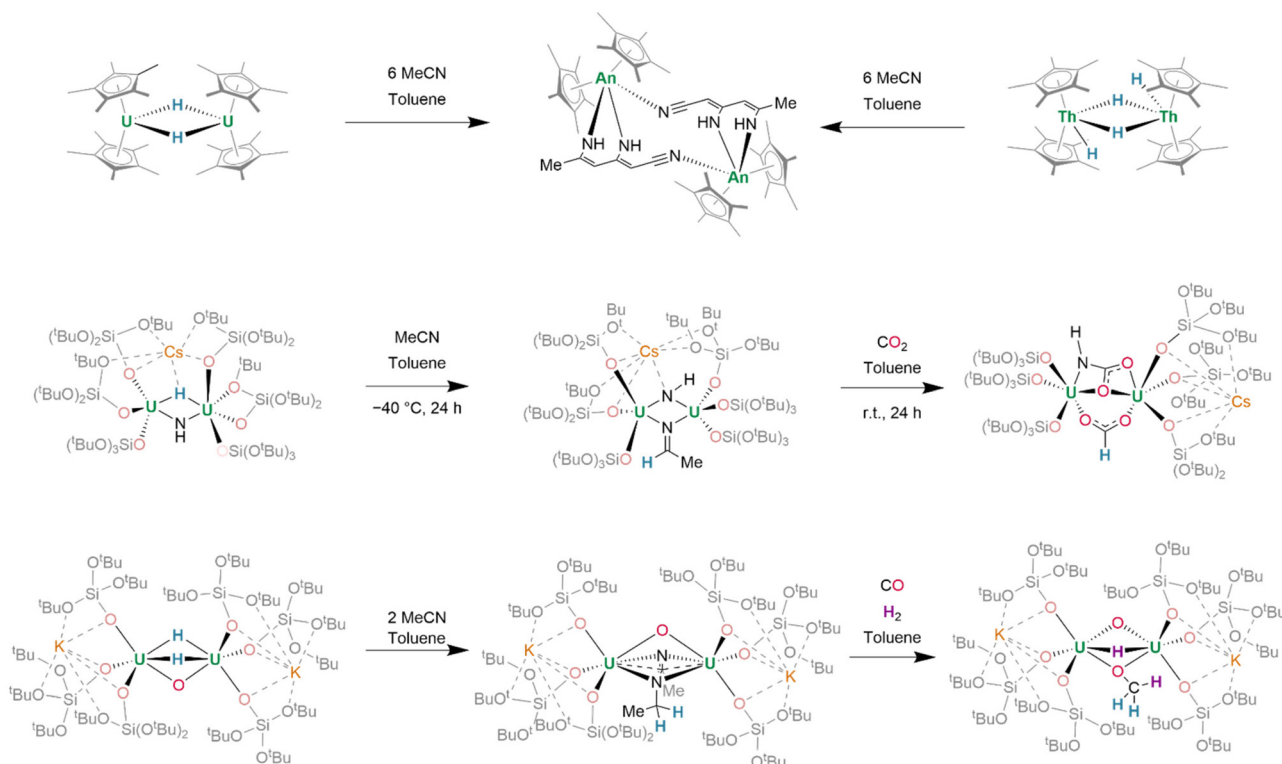


Fig. 22 Reactivity of actinide hydrides towards unsaturated small molecules. (a) Actinide metallocene hydrides facilitate β -coupling of nitriles. (b) and (c) U(IV) mono and dihydrides can facilitate hydride transfer to nitriles with C–N coupling in the latter case. In both cases further transfer of the hydrides to other unsaturated small molecules is possible.



Bridging and Lewis acid coordinated actinide hydrides

Such divergent reactivity suggests a structural cause. Coordination of group XIII metal hydrides to actinide centres characteristically involves $\text{An}\cdots\text{H-M}$ bridging interactions, wherein the hydrides span the metal centres in a 3c–2e bonding configuration. Sharing either two or three hydrides between actinide and group XIII metal centres, both μ^2 - and μ^3 -bridging modes are observed crystallographically in the iso-morphous, homoleptic, tetravalent borohydrides, $[\text{U}(\text{BH}_4)_4]$ and $[\text{Th}(\text{BH}_4)_4]$.^{193,194} That there is a degree of covalency in these linkages is supported by their volatility: $[\text{U}(\text{BH}_4)_4]$ sub-limes at temperatures as low as 30 °C, and the volatility of its transuranic analogues is reportedly even greater; these materials exist as pyrophoric liquids which decompose readily at room temperature.^{195,196} Conspicuously, sublimation of its thorium congener requires temperatures at least 100 degrees higher.¹⁹⁶ Furthermore, in an intriguingly straightforward procedure, it has been demonstrated by Daly and colleagues that $\text{U}(\text{BH}_4)_4$ is reducible to uranium(III) merely by heating the tetra-valent borohydride to 100 °C under argon, offering facile access to this low oxidation state.¹⁹⁷

offer complexes a degree of flexibility in their coordination spheres which cannot be achieved using comparable halides. The magnitude of U...H interactions have been quantified spectroscopically in hydrobis(mercaptoimidazolyl)borate (tim^{Me}) complex U{B(H)(R)(tim^{Me})₂}(thf)₂ (R = H, Ph), wherein a trivalent uranium centre is stabilised by tridentate ligands capable of enforcing a single U...H-B interaction per ligand (Fig. 23a). Straightforward IR spectroscopic observation of a shift in B-H stretching frequencies between the free (2446 cm⁻¹) and coordinated (2376 cm⁻¹) ligand is suggestive of a κ^3 -H,S,S-binding mode—although U-H distances are significantly elongated (R = H, 2.31(9) Å; R = Ph, 2.54(9) Å) relative to direct actinide hydrides.¹⁹⁸ In a further illustrative case, Bart and colleagues have observed a sterically-induced change in the coordination mode of a tris(pyrazolyl)borate ligand, which occurs upon introduction of imide ligands bearing substituents of differing steric size. Whereas the supporting ligands of (Tp*)₂U^{IV}(NR) (R = mes, Ph) both adopt typical κ^3 -N, N,N coordination modes to the uranium(IV) centre, the more substantial adamantyl substituent in (Tp*)₂U^{IV}(Nad) enforces a change to an unsymmetrical configuration, wherein one ligand instead binds in a κ^3 -N,N,H fashion with one of the pyrazolyl arms of the ligand in the apical position Fig. 23b.¹⁹⁹

Dalton Trans., 2024, 53, 12814-12836 | 12831

well as compared to their uranium(III) analogue, $(\text{Cp}^*)_2\text{U}\{\text{H}_3\text{Al}(\text{Si}')_3\}$. Of key interest in the latter two examples is the possibility, supported by DFT calculations, that $\text{An}^{\text{III}}\cdots\text{H}-\text{Al}$ interactions stabilise the first reported example of a dative $\text{An} \rightarrow \text{M}$ interaction (Fig. 15b). Curiously, there is described a greater degree of $\text{An} \rightarrow \text{Al}$ charge transfer character in the thorium(III) case than for either its uranium(III) or titanium(III) analogues.²⁰⁰

There are few examples of heterobimetallic actinide complexes incorporating transition metal hydrides; however, recent work by the Arnold and Camp groups has also characterised hydride-supported $\text{An} \rightarrow \text{M}$ interactions with iridium. The isolated complexes, $\{(\text{Cp}^*)\text{Ir}(\text{H})_3\}_4\text{U}^{\text{IV}}$ and $\{(\text{Cp}^*)\text{Ir}(\text{H})_3\}_4\text{Th}^{\text{IV}}$, wherein the respective actinide centres are twelve- and ten-coordinate, are calculated to possess notably high Wiberg $\text{An}-\text{M}$ bond indices ($\text{U} \rightarrow \text{Ir} = 0.97$; $\text{Th} \rightarrow \text{Ir} = 0.65$).²⁰¹

Conclusions

In this perspective, we have illustrated the key synthetic pathways for the synthesis of lanthanide and actinide hydrides, with hydrogenolysis and σ -bond metathesis reactions from metal alkyls being the most widely utilised. Our analysis suggests that sequential hydrogenolysis of metal alkyls is slower as the number of alkyl groups increases on a metal due to the formation of highly bridged hydride intermediates. In addition, hydrogenolysis appears to be facilitated greatly by metalated ligand intermediates which contain ring-strained metallacycles. Only a few examples of hydrides formed from, or with, low-oxidation state f-block metals are known; however, what has been reported to date suggests a key role for reduced arene ligands in their formation by this pathway.

In terms of structure, the order of clusters is shown to grow as co-ligand stoichiometry and sterics decrease, in order to retain high coordination numbers on the metals. The structure of these clusters also changes with metal ion size with smaller lanthanides, in particular, able to invoke μ^4 and even μ^6 coordination modes for the hydride, mirroring the ionic bonding in binary hydrides. At the opposite end of the covalency spectrum, evidence has now been presented for the formation of both lanthanide and actinide dihydrogen complexes, though current evidence suggests bonding is very different between the two periods.

The reactivity of lanthanide hydrides comprises primarily σ -bond metathesis and 1,2-addition reactions due to their limited access to redox reactivity; however, these two powerful mechanisms have been exploited to great effect in catalytic polymerisation, hydrogenation and hydroelementation.

In this work, we have outlined how cluster structure and nuclearity can influence reactivity, with highly bridged hydrides reacting more slowly with some substrates. This should inform choice of co-ligand for lanthanide pre-catalysts which invoke hydrides in the catalytic cycle. For actinides, different pathways may operate, allowing for coupling of nitrile ligands for example, rather than simple 1,2-addition; transfer

hydrogenation of small molecules; and redox-like reactivity for thorium(IV) hydrides.

Bridging hydrides are also shown to stabilise a wide range of complexes of the form $\text{Ln}\cdots\text{H}-\text{E}/\text{Ln}\cdots\text{H}-\text{M}$ with varying $\text{Ln}-\text{E}/\text{Ln}-\text{M}$ interactions from the extreme of $\text{Ln}-\text{E}$ bonds with agostic interactions to $\text{An} \rightarrow \text{M}$ species where a low-valent actinide is able to act as a Lewis base toward an electron-deficient metal centre.

Together, this survey presents an emerging picture of the field of f-block hydrides which is beginning to understand how to employ fine electronic and structural control to exploit the distinctive characteristics of complexes which span the full length and breadth of the periodic table.

Author contributions

This manuscript was conceived by Dr Bell and written together by both Dr Bell and Dr Drummond Turnbull, including preparation of all figures.

Conflicts of interest

There are no conflicts to declare.

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