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Divalent Lanthanide Hydride Complexes

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Molecular hydride complexes have attracted recent attention, and divalent lanthanides as central atoms in particular are very interesting. They open up possibilities of combining hydride reactivity and lanthanide reactivity. To date, only Yb(II), Eu(II) and Sm(II) as well as a mixed-valent Dy(II)/Dy(III) hydride complexes have been isolated and characterised but the known examples are still low in numbers. In this contribution the development of divalent lanthanide chemistry is summarised, and structural features, reactivity patterns in stoichiometric and catalytic reactions as well as spectroscopic details are outlined.

Introduction

The research in hydride complexes based on transition metals has been developed for decades.[1,2] Insight into the synthesis, structure and reactivity of these complexes has encouraged the interest in other non-transition metal hydride species. Especially f-element complexes came in focus.[3] The majority of these hydride complexes, include lanthanides in their typical oxidation state of +III. After their high reactivity and potential as catalysts was determined, they have been developed rapidly.[4,5] Due to the larger ionic radii and less common oxidation state of Ln^{2+} ions, their development emerged later.[6] The unsaturated coordination sphere of lanthanide ions in hydride complexes frequently leads to the formation of dimeric or higher aggregated structures.[7] The bonding situation between hydride and lanthanide ions regardless of their oxidation state is highly ionic as the metal cation shows Lewis acidity and the hydride ions are strongly basic.[8,9] The key to stabilising lanthanide hydride complexes is the choice of co-ligands, as there is a pronounced tendency for ligand exchange reactions with concomitant elimination of binary lanthanide hydrides which is frequently described as lanthanide Schlenk-type redistribution.[10]

Previous reviews by Ephritikhine, Okuda, Trifonov, Lu and Xu, or, most recently by Bell were centered on lanthanide hydrides in their most common oxidation state +III.[3,8,11–14] To highlight recent developments of divalent lanthanide hydrides, this concept aims to detail syntheses and properties of these complexes.

Neutral Lanthanide(II) Hydride Complexes

A prerequisite for the stabilisation of divalent lanthanide hydride complexes is the development of suitable ligand sets. One such ligand set is based on the hydrotris(pyrazolyl)borate ligand, a tridentate monoanionic scaffold.[15] The tertbutyl-substituted hydrotris(pyrazolyl)borate ($Tp^{tBu,Me}$) was employed by Takats to synthesise the ytterbium(II) alkyl complex $[(Tp^{tBu,Me})Yb(CH_2SiMe_3)(THF)]$ which then was exposed to elemental hydrogen to yield the dinuclear and bis-hydride bridged complex $[((Tp^{tBu,Me})Yb^{II}H)_2]$ (**1**, Figure 1).[16]

Single crystal X-ray diffraction exhibited **1** as dimeric complex with no characteristics to form higher oligomeric structures. Each Yb^{2+} centre is five-coordinate with one $Tp^{tBu,Me}$ ligand and symmetrically constrained with bridging μ-hydrido ligands. The Yb–Yb contact was found to be 3.650(1) Å with Yb–H distances detected at 2.26(3) Å. NMR spectroscopic investigations showed the resonance of the hydrido ligands as singlet accompanied by ^{171}Yb satellites of $J=369$ Hz at $\delta=10.5$ ppm. A corresponding ^{171}Yb NMR resonance was detected as triplet at $\delta=772$ ppm, corroborating that the Yb_2H_2 motif is retained in solution.[16] In solution, the hydrido complex **1** decomposes over several days. Dissolution of **1** in THF initiated complete ligand redistribution yielding $Yb(Tp^{tBu,Me})_2$. Reactivity studies revealed that **1** undergoes acid-base, σ-bond metathesis and insertion reactions (Figure 2).[17] Exposure of the Yb hydride complex with a CO atmosphere proceeded the insertion of CO into the Yb–H bond and therefore a formation of the ethenediolate complex **1 a**. The hydride complex **1** reacted with bis(trimethylsilyl)acetylene, under cleavage of a Si–C bond to quantitatively afford $[(Tp^{tBu,Me})YbC{\equiv}CSiMe_3]_2$ (**1 b**) and $HSiMe_3$. When $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ (**1 c**) or diphenylacetylene were employed, hydrometalation of the C≡C bond was observed. With proton donors such as cyclopentadiene, $HN(SiMe_3)_2$ and $HC{\equiv}CSiMe_3$, **1** reacted under elimination of H_2 (**1 d**). The attempt of hydride abstraction with $B(C_6F_5)_3$ led to the formation of the hydridoborate anion $[HB(C_6F_5)_3]^-$ which remained in the coordi-

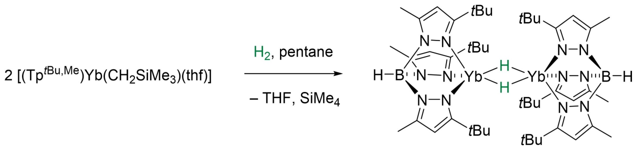

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Figure 1. Synthesis of the first divalent lanthanide hydride complex $[((Tp^{tBu,Me})YbH)_2]$ ($Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate, **1**) by Takats.[16]

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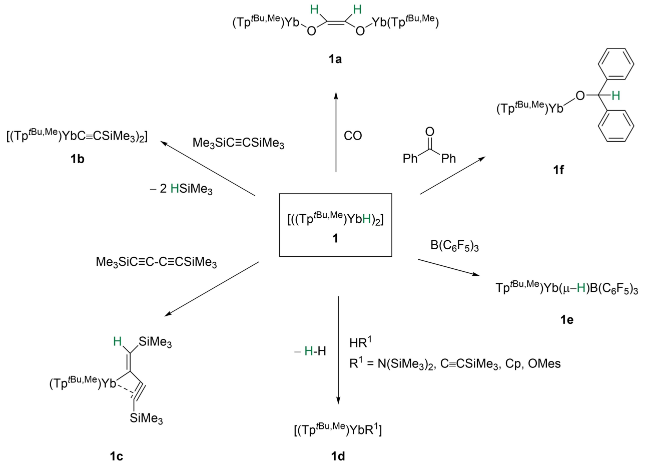
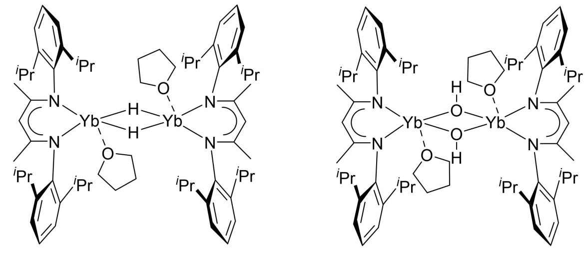


Figure 2. Reactivity studies on $[\{(\mathrm{Tp^{tBu,Me}})\mathrm{YbH}\}_2]$.[17]



$[(^{\mathrm{Dipp}}\mathrm{BDI})\mathrm{YbH(thf)}]_2$
2

$[(^{\mathrm{Dipp}}\mathrm{BDI})\mathrm{YbOH(thf)}]_2$
2a

Figure 3. $^{\mathrm{Dipp}}$BDI-stabilised $\mathrm{Yb^{II}}$ hydrido complex **2**, and the hydroxide derivative **2a**.[18]

nation sphere of Yb(II) but caused monomerisation (**1e**). The reaction of **1** with ketones, such as benzophenone, yielded the corresponding Yb alkoxide **1f**.

The second ytterbium(II) hydride complex was reported by the group of Harder in 2007.[18] As the sterically crowded $^{\mathrm{Dipp}}$BDI ligand ($^{\mathrm{Dipp}}\mathrm{BDI} = \mathrm{CH((CMe)(2,6\text{-}^{i}PrC_6H_3N))_2}$) was suitable for the stabilisation of a calcium hydride complex, the similarity of the ionic radii made the corresponding Yb(II) complex a desirable target.[19] Indeed, the hydride complex $[(^{\mathrm{Dipp}}\mathrm{BDI})\mathrm{Yb(THF)H}]_2$ could be obtained upon treatment of the amido precursor $[(^{\mathrm{Dipp}}\mathrm{BDI})\mathrm{YbN(SiMe_3)_2}]\cdot\mathrm{THF}$ with phenyl silane at 60 °C (Figure 3). In the dimeric complex both $\mathrm{Yb^{2+}}$ ions are symmetrically bridged with two hydrido ligands. The Yb–Yb distance of 3.5204(2) Å in **2** is considerably smaller than that in **1** which hints at smaller effective steric bulk provided by the BDI ligand.[18] The characteristic ^{1}H NMR resonance of the hydride anion was observed at 9.92 ppm with ^{171}Yb satellites of $J = 398$ Hz.

Compared to complex **1**, the $[(^{\mathrm{Dipp}}\mathrm{BDI})\mathrm{YbH(thf)}]_2$ is readily soluble in benzene, *n*-hexane and stable in benzene solution at room temperature. It decomposes to $(^{\mathrm{Dipp}}\mathrm{BDI})_2\mathrm{Yb}$ and $\mathrm{YbH_2}$ in about 2.5 hours when heating at 75 °C. The ytterbium hydride **2** was employed in the catalytic hydrosilylation of 1,1-diphenylethylene (DPE) with $\mathrm{PhSiH_3}$ and showed solvent-independent activity. Furthermore, a Yb(II) hydroxide complex **2a** (Figure 3) was synthesised, by adding a stoichiometric amount of $\mathrm{H_2O}$ to a THF solution of **2** at 60 °C. During this process, partial oxidation of $\mathrm{Yb^{II}}$ to $\mathrm{Yb^{III}}$ was observed, so several recrystallisations were required to obtain pure **2a** which showed $\mathrm{Yb^{II}}$-typical diamagnetic behaviour.

Later, Trifonov introduced another class of ligands, amidinates, for the stabilisation of Yb(II) hydride compounds. Utilising the amido precursor $[\{t\mathrm{BuC(NDipp)_2}\}\mathrm{Yb(THF)N(SiMe_3)_2}]$ in a σ-bond metathesis reaction with $\mathrm{PhSiH_3}$, the dimeric ytterbium hydride complex $[\{t\mathrm{BuC(NDipp)_2}\}\mathrm{YbH}]_2$ (**3**) was obtained in a yield of 88 % (Figure 4).

The ytterbium(II) hydride **3** features a dinuclear structure with two bridging hydrido ligands. Remarkably, the Yb–Yb distance of 3.3553(4) Å is even shorter than in either of the previously known Yb(II) hydride complexes, and the Yb–H bond lengths amount to 2.14(4) and 2.18(5) Å. Surprisingly, the coordination mode of the amidinato ligand changed from κ^2-*N,N'*- in the amide precursor to κ^1-amide and η^6-arene interactions in **3**. Compared to the previously described complexes, the hydrido ligands of $[\{t\mathrm{BuC(Dipp)_2}\}\mathrm{Yb(\mu\text{-}H)}]_2$ show an upfield-shifted signal in the ^{1}H NMR spectrum at $\delta = 7.74$ ppm ($J_{\mathrm{YbH}} = 460$ Hz) which could be caused by additional shielding by the aromatic π-system in close proximity.

In THF solution complex **3** remained stable for 0.5 hours at ambient temperature and slowly reacted to the homoleptic bis(amidinate) $\mathrm{Yb^{II}}$ complex $[\{t\mathrm{BuC(Dipp)_2}\}_2\mathrm{Yb})]$ when kept in a THF/hexane mixture for several days.

The reactivity of the amidinato-stabilised Yb(II) hydride **3** was studied in several instances, and for the first time, double hydrometalation of diphenyl acetylene was possible, affording

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Emma Stapf studied chemistry at the Karlsruhe Institute of Technology. She obtained her Bachelor degree in reactivity studies on aluminum complexes at the group of Prof. Breher and then joined the group of Dr. Hinz to obtain a Master degree in the field of lanthanide chemistry. She started her doctoral studies in the beginning of 2024, continuing the investigation of lanthanide and alkaline earth metal chemistry.

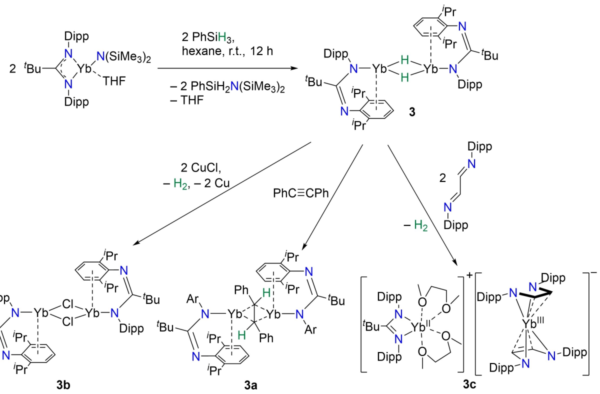


Figure 4. Synthesis and reactivity of [{tBuC(NDipp)$_2$}YbH]$_2$ (**3**).[20]

3 a (Figure 4).[20] However, no reaction was observed at the attempt to catalyse polymerisation of isoprene, ethene or propylene. Reactions with typical one-electron-oxidants such as I_2, $AgBPh_4$, $AgBF_4$ were not selective and lead to the oxidation of the Yb^{II} ion as well as the hydrido ligands. Nonetheless, copper(I) chloride showed selective activity as one-electron-oxidant affording the dimeric Yb^{II} chlorido complex **3 b** and forming H_2 (Figure 4).[21] Organic oxidants such as dibenzyldisulfide $(PhCH_2S)_2$ could be employed stoichiometrically enabling stepwise oxidation, initially affording [{tBuC(NDipp)$_2$}Yb^{II}(μ-SCH$_2$Ph)]$_2$ and eventually yielding the bis(benzyl sulfide) ytterbium(III) complex ([{tBuC(NDipp)$_2$}Yb^{III}(μ-SCH$_2$Ph)$_2$]$_2$). In contrast, the reaction of **3** with diazabutadiene (DippNCH)$_2$ lead to the formation of the mixed-valent ion pair complex **3 c**. This reaction is complex as both hydrido ligands and one Yb^{II} centre is oxidised and additionally, ligand redistribution occurred. The reaction of **3** with the weak Bronsted acid Ph_2PH exclusively afforded ([{tBuC(Dipp)$_2$}Yb(μ-H)(μ-PPh$_2$)Yb{tBuC(Dipp)$_2$}] (**3 d**)) even when an excess of the phosphine was employed. As both Yb moieties are linked by one μ-hydrido and one μ-diphenylphosphido ligand, this represents the first instance of a mixed-ligand bridged lanthanide(II) hydride complex.

In 2021 the groups of Anker and Maron reported on the BDI-stabilised Yb^{II} hydride complex [(^{Dipp}BDI)YbH]$_2$ (**4**) without co-ligands such as THF in Harder's study of **2**.[22] This complex was synthesised by treating the amido precursor [Yb(N(SiMe$_3$)$_2$)$_2$]$_2$ with ^{Dipp}BDI–H in toluene and subsequent σ-bond metathesis with $PhSiH_3$. X-Ray diffraction measurements corroborated its dimeric structure with two μ^2-hydride ligands. Each Yb^{2+} displays π-coordination the Dipp substituent of the secondary (^{Dipp}BDI)YbH unit (Figure 5). The ^{1}H NMR spectrum of **4** in benzene solution disclosed two different species in a 25 : 1 ratio. The major signal was observed at $\delta = 7.52$ ppm ($J_{YbH} = 398$ Hz), upfield-shifted compared to that of **2** but comparable to that of **3**, hinting at a structure of **4** in solution similar to its solid state structure. The minor species **4'** is characterised by a resonance at $\delta = 9.92$ ppm ($J_{YbH} = 302$ Hz) in good agreement with that of **2**, in an apparent isomer without π-coordination of arenes at Yb. EXSY NMR experiments demonstrated that both species are in equilibrium.

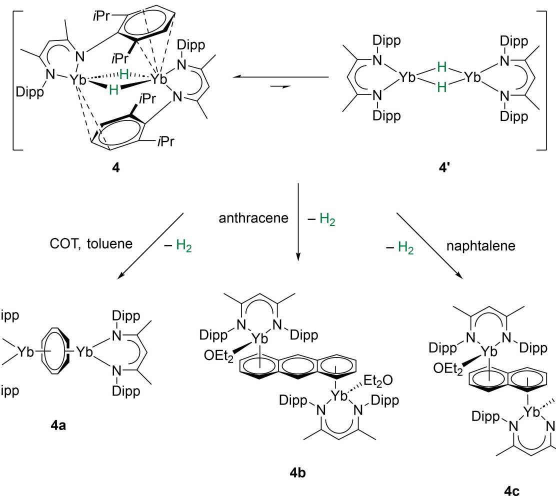


Figure 5. Equilibrium of complexes **4** and **4'** at room temperature and their reactivity.[22]

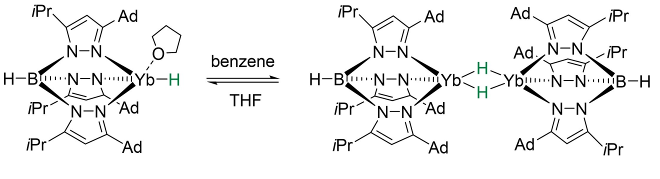
The reaction of [(^{Dipp}BDI)YbH]$_2$ (**4**) with ethene or propene yielded the corresponding dimeric Yb(II) ethyl or *n*-propyl derivatives due to hydrometalation of the double bonds. These alkyl complexes can react with benzene in a S$_N$2-type reaction to regenerate the Yb(II) hydride complex and form alkylated benzenes as corroborated by DFT calculations.[22] Thus, catalytic hydroarylation of alkenes became feasible and indeed, the hydroarylation of propene with **4**/**4'** as catalyst proceeded selectivly and yielded the *n*-propylbenzene as exclusive product. In contrast, hydroarylation of ethene was unselective, and ethene polymerization was observed as competing process.

Later, Anker and co-workers studied the reactivity of **4**/**4'** as multielectron reductant.[23] The addition of cyclooctatetraene (COT) to the Yb(II) hydride resulted in the formation of the aromatic COT^{2-} dianion in the inverted sandwich complex [(^{Dipp}BDI)Yb(μ-COT)Yb(^{Dipp}BDI)] (**4 a**, Figure 5). As DFT calculations implied the feasibility of a 1 : 1 reaction as well, the synthesis of the Yb(III) complex [(^{Dipp}BDI)Yb(COT)] was attempted as well and allowed its isolation as minor product. Furthermore, anthracene and naphthalene could be reduced to yield compounds **4 b** and **4 c**. In complex **4 b**, two [(^{Dipp}BDI)Yb] moieties interact in η^4-fashion with the terminal C$_6$-ring of the dianionic anthracene from opposing faces. The coordination sphere of each Yb centre is saturated by two bonds of the BDI ligand and one Et$_2$O molecule. **4 c** can be described similarly with one dianionic η^3-coordinating naphthalene moiety that is located between the Yb ions. Further insight into the mechanism of the reductions was given by DFT calculations of the reduction of polyunsaturated hydrocarbons with complex **4** which indicate stepwise hydrometalation and deprotonation with concomitant H_2 elimination. Further reactivity studies on **4** were conducted by adding different cyclopentadienes such as tetramethylcylcopentadiene, pentamethylcyclopentadiene, fluorene and indene.[24] Under extrusion of hydrogen gas, the corresponding Yb^{II} cyclopentadienide complexes were obtained as mononuclear species in solution and solid state.

Prior to 2021, all reported Yb(II) hydride complexes adopt a dinuclear structure. However, Cheng, Maron and co-workers reported the first example of a mononuclear divalent Yb hydride complex with a terminal hydrido ligand.[9] To this end, the modified tris(pyrazolyl)borate scorpionate ligand $Tp^{Ad,iPr}$ ligand was used ($Tp^{Ad,iPr}$ = hydrotris(3-adamantyl-5-isopropyl-pyrazolyl)borate, Figure 6) with isopropyl substituents instead of methyl groups and adamantyl substituents instead of tertbutyl groups compared to Takats' $Tp^{tBu,Me}$ ligand in **1**.

The mononuclear $[(Tp^{Ad,iPr})Yb^{II}(H)(THF)]$ (**5**) was synthesised by addition of $K(Tp^{Ad,iPr})$ and potassium benzyl to a solution of $YbI_2(THF)_2$ and subsequent hydrogenolysis with H_2. Further analysis via single crystal diffraction confirmed the mononuclear structure. The Yb^{II} centre is five-coordinate with one κ^3-$Tp^{Ad,iPr}$, one THF and one terminal hydrido ligand. The Yb–H distance of 2.49(4) Å is longer than in comparable dimeric complex **1**. NMR spectroscopy showed the resonance of the hydrido ligand at $\delta = 10.64$ ppm in the ^{1}H NMR spectrum with $J_{YbH} = 833$ Hz. In the ^{171}Yb NMR spectrum, a corresponding doublet was observed at 974.31 ppm, indicating that the Yb only possesses one hydride ligand. In solution, a monomer-dimer equilibrium of **5** was observed which showed a ratio of 1:2 when **5** was dissolved in C_6D_6. In the presence of 7 equivalents of THF, exclusively the monomeric ytterbium hydride was observed. In contrast, in C_6D_{12}, only the dimer was detected. Furthermore, it was possible to fully remove the THF molecule by dissolving **5** in benzene and subsequent removing the solvent for three times which then yielded the dimeric $[(Tp^{Ad,iPr})Yb^{II}(\mu\text{-}H)]_2$ (**5′**). In the ^{1}H NMR spectrum, the resonance of the hydride ligands of **5′** was detected at $\delta = 10.32$ ppm ($J_{YbH} = 378$ Hz). The monomeric hydride $[(Tp^{Ad,iPr})Yb(H)(THF)]$ was tested in different reactions such as insertion and dehydrogenation. Treating **5** with 1,1-diphenyl-ethylene (DPE) in hexane yielded the corresponding derivative $[(Tp^{Ad,iPr})Yb(CPh_2(Me))]$, while adding cyclohexylallene afforded the $[(Tp^{Ad,iPr})Yb(\eta^3\text{-}CH_2CHCH(Cy))]$. However, stochiometric reaction of **5** with 1,1-dimethylallene afforded the Yb allenyl complex $[(Tp^{Ad,iPr})Yb(\eta^1\text{-}CH{=}C{=}CMe_2)(THF)]$, instead of the hydrometalation product. COT reacted in a dehydrogenation reaction with **5** as well, by forming an inverse sandwich complex structurally comparable to complex **4a**. Moreover, activation of small molecules such as CO, CO_2 and CS_2 by **5** was investigated (Figure 7).[25]

Similar to complex **1**, **5** reacted with CO in an insertion reaction to form *cis*-ethenediolate $[(Tp^{Ad,iPr})Yb^{II}(cis\text{-}OC(H){=}C(H)O)]$ (**5a**). Exposure of **5** with one atmosphere of CO_2 yielded the corresponding Yb^{II} formate $[(Tp^{Ad,iPr})Yb(\kappa^2\text{-}O_2CH)(THF)]$ (**5c**).



5 **5`**

Figure 6. Equilibrium of mono- and dinuclear Yb(II) complex **5**/**5′** (Ad = adamantyl).[9]

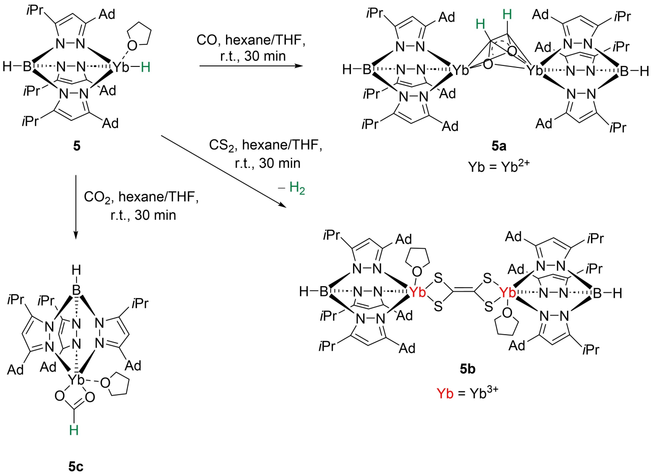


Figure 7. Small molecule activation studies on $[(Tp^{Ad,iPr})Yb^{II}(H)(THF)]$ (**5**).[25]

While activation of CO and CO_2 maintain the divalent Yb centres, the reaction of **5** with CS_2 caused reductive coupling and concomitant release of H_2, affording of the trivalent Yb complex $[(Tp^{Ad,iPr})Yb^{III}]_2(C_2S_4)$ (**5b**). X-Ray crystallographic studies showed a disorder of the C atoms in the C_2S_4 moiety indicating two distinct bonding modes. In one instance, there is a four-membered ring as shown in **5b** in Figure 7, while the other comprises a five-membered Yb-κ²-SCCS cycle.

Also in 2021, a new tetradentate β-diketiminato-based ligand was used by the groups of Xiang and Chen to prepare Yb(II) hydrido compounds. The BDI-ligand with a pendant diamino side chain was initially treated with Yb(II) dialkyls and subsequently transformed to the hydride **6** derivative with H_2 or phenyl silane (Figure 8).[26] The complex **6** displayed a dimeric

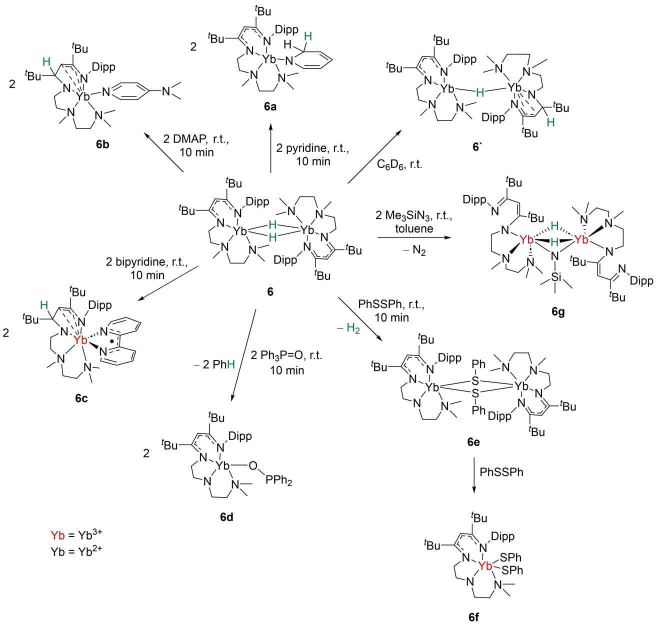


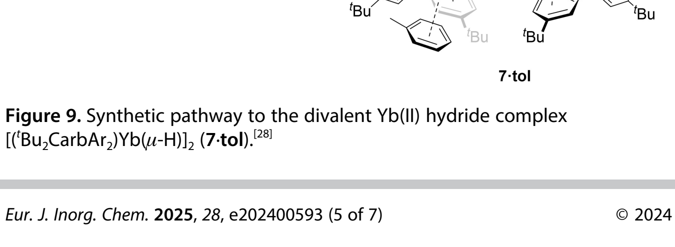
Figure 8. Reactivity studies on $[(^tBuC(NDipp)CHC(^tBu)NCH_2CH_2N(Me)\text{-}CH_2CH_2NMe_2)Yb(\mu\text{-}H)]_2$ (**6**).[26,27]

structure which exists in solution as mixture of two isomers with characteristic ^{1}H NMR resonances and $\delta = 8.95$ ppm and 9.04 ppm with J_{YbH} of 358 and 352 Hz, respectively. In C_6D_6 solutions of **6**, isomerisation to the mono-μ-hydrido complex **6′** was observed within 3 hours. This complex **6′** features a ^{1}H NMR resonance at 9.64 ppm with two distinct sets of satellites with $J_{YbH} = 371$ and $J_{Yb'H} = 505$ Hz.

Complex **6** reacts with pyridine by hydrometalation of a C=N bond (**6a**), while with the stronger donor DMAP, migration of the hydrido ligand to the BDI scaffold is induced (**6b**). When treating **6** with bipyridine, a redox reaction occurs and the Yb^{II} centre is oxidised, while the hydride ion migrates to the BDI backbone (**6c**). Furthermore, the hydride complex can cleave off phenyl groups of triphenylphosphine oxide ($Ph_3P{=}O$) or triphenylphosphine sulfide ($Ph_3P{=}S$) to yield the corresponding phosphite complex with concomitant formation of benzene (**6d**). Similar to Trifonov's observations with **3**, the ytterbium hydride complex **6** can be stepwise oxidised with diphenyl disulfide to yield **6e** and **6f**. Additional reactivity studies on complex **6** by Chen, Maron and co-workers showed that the synthesis of a hydrido- and imido-bridged dinuclear Yb(III) complex (**6g**) was possible by adding two equivalents of Me_3SiN_3 at room temperature.[27]

Recently, for the first time a monodentate carbazolide was successfully employed in the stabilisation of ytterbium(II) hydride complexes.[28] The synthetic route lead again via amido precursors that were treated with phenyl silane to yield dimeric bis-hydride bridged Yb complexes (**7·tol**, Figure 9).

In addition to the hydride and carbazolide ligands, there is a solvent molecule that is either THF or toluene coordinated to Yb in each instance (toluene **7·tol**, THF **7·THF**). Due to the insolubility of the compound, no NMR characteristics could be identified. Structurally, **7·tol**, THF **7·THF** feature Yb–Yb distances of 3.508(2) and 3.5085(4) Å, respectively. The shortest Yb–C contact in **7·tol** of 2.808(7) Å was observed towards the coordinated toluene molecule. The catalytic activity of the complexes was tested in the addition of hydrosilanes such as $PhSiH_3$ to pyridines. **7·tol** showed high activity in these reactions, enabling conversion up to 89%, while **7·THF** was not tested, due to the expected competition of THF and $PhSiH_3$ for the metal coordination site. In another study by our group, this carbazolide was used to stabilise the benzene adduct **7·C$_6$H$_6$** and characteristic vibrations of the Yb_2H_2 core could be identified.[29] Beyond that, the formation of ethenediolate upon treatment of the hydride with CO was observed.



7·tol

Figure 9. Synthetic pathway to the divalent Yb(II) hydride complex [(^{t}Bu$_2$CarbAr$_2$)Yb(μ-H)]$_2$ (**7·tol**).[28]

Only recently, the scope of divalent lanthanide hydride compounds was extended beyond Yb(II) as Jones, Anker and co-workers prepared Eu(II) hydride complexes such as **8** (Figure 10).[30] Supported by very bulky BDI-based ligands, the synthesis was conducted via salt metathesis to furnish [(BDI)EuI]$_2$ which was alkylated and then reacted with 1,4-cyclohexadiene (Figure 10). Three BDI ligands used in that study: A symmetric BDI bearing 2,6-dicyclohexylphenyl (DCHP) groups as N-substituents, and two unsymmetric ones, each with one Dipp substituent and either a 2,6-dicyclohexylphenyl or a 2,4,6-tricyclohexylphenyl group (TCHP). As [(^{DCHP}BDI)Eu^{II}(μ-H)]$_2$ (**8**) displayed poor solubility, complexes with the unsymmetric BDI ligands $^{Dipp/DCHP}$BDI and $^{Dipp/TCHP}$BDI were prepared in an analogous way and indeed, showed solubility in aromatic but not aliphatic hydrocarbons.

The molecular structures of **8** and its analogs display dimeric complexes with two bridging hydrido ligands with Eu–Eu distances ranging from 3.6044(3) to 3.681(2) Å. Each Eu(II) atom is coordinated in η^3-mode to an aryl moiety beyond the expected Eu–N contacts. The reactivity of the Eu(II) hydrides towards COT was investigated and resulted in the formation of inverted sandwich complexes such as [{(^{DHCP}BDI)Eu^{II}}$_2$(μ-COT)] (**7c**) in which the bridging COT ligand shows η^8-coordination to both metal atoms as observed for **4a**. It is noteworthy that the oxidation state of Eu remained at +II.

Also in 2024, the group of Cheng succeeded in the synthesis of the first molecular samarium(II) hydride complex [(Cp^{Ar5})Sm^{II}(μ-H)(DABCO)]$_2$ (**9**).[31] To this end, a penta-arylated cyclopentadienyl ligand was utilised. Initially, (Cp^{Ar5})K(THF)$_2$ was treated with [Sm^{II}I$_2$(THF)$_5$] in THP (tetrahydropyran). After exchange of the THP ligand for DABCO, the complex was reacted with KCH(SiMe$_3$)$_2$ to form a samarium(II) alkyl that was subjected to hydrogenolysis to afford the targeted hydride complex [(Cp^{Ar5})Sm^{II}(μ-H)(DABCO)]$_2$ (**9**). The highly reactive complex is not stable in benzene which hampered NMR characterisation of the paramagnetic compound. Single-crystal X-ray diffraction revealed its dimeric structure with two bridging hydrido ligands and Sm–Sm distance of 3.7966(5) Å.

The reactivity of [(Cp^{Ar5})Sm^{II}(μ-H)(DABCO)]$_2$ was investigated towards the potential as four-electron reducing agent. Indeed, in the reaction with elemental selenium, the corresponding Sm^{3+} complex **9a** was obtained (Figure 11). When PhN=NPh was added to **9** the bis(diazene-diide)-bridged complex [(Cp^{Ar5})Sm^{III}(μ-PhN-NPh)(THF)]$_2$ was obtained. The samarium(II) hydride complex also showed reactivitiy towards CO$_2$ which resulted in the formation of a trivalent Sm mixed-bis-formate/carbonate complex (**9b**). In this reaction, two CO$_2$ molecules underwent two-electron reduction and disproportionation

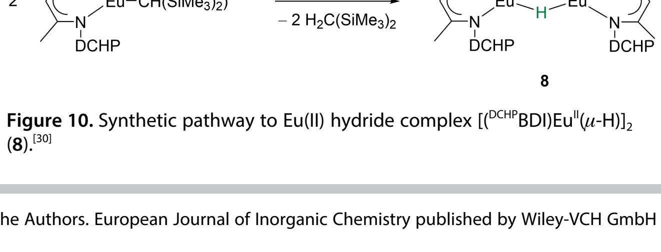


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Figure 10. Synthetic pathway to Eu(II) hydride complex [(^{DCHP}BDI)Eu^{II}(μ-H)]$_2$ (**8**).[30]

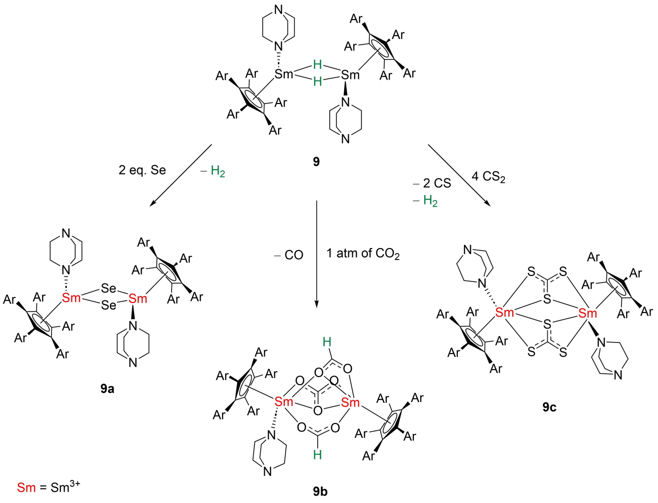

Figure 11. Reactivity studies on first Sm-based divalent hydride complex (Ar = 3,5-^{i}Pr-C_6H_3).[31]

(forming $[CO_3]^{2-}$) with concomitant release of CO, while two other CO_2 molecules inserted into the Sm–H bonds. In contrast, when **9** was treated with CS_2, oxidation of both the Sm^{II} centres and the hydrido ligands yielded the Sm^{3+} bis-thiocarbonate complex **9 c**.

A unique example of an anionic mixed-valent Dy hydride complex was reported by Evans in 2023.[32] Reduction of the Dy(III) hydride $[(Cp^{An})Dy(THF)(\mu\text{-}H)]_2$ (CpAn=$Me_2Si[C_5H_3(SiMe_3)\text{-}3]_2$) with KC_8 in the presence of 2.2.2-cryptand resulted the formation of $[K(18\text{-crown-}6)(THF)_2][(\mu\text{-}Cp^{An})Dy(\mu\text{-}H)]_2$ which features Dy(II) and Dy(III) bridged by hydride and CpAn ligands.

Cationic Lanthanide(II) Hydride Complexes

Beyond neutral Ln(II) hydride compounds, also cationic complexes of divalent lanthanide hydride complexes were discovered. Okuda published the first cationic Yb(II) hydride complex based on the tetradentate macrocyclic Me_4TACD ligand. Initially, this ligand was coordinated to a Yb silanide precursor which was then exposed to hydrogen to form the dimeric Yb^{II} trihydride complex $[(Me_4TACD)_2Yb_2(\mu\text{-}H)_3][SiPh_3]$ (**10**, Figure 12).[33]

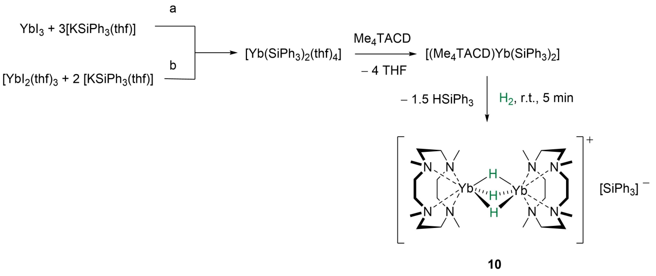

Figure 12. Synthetic pathway to cationic Yb^{II}-based hydride complex **10**; a) THF, r.t., 4 h, −3 KI, −0.5 Ph_6Si_2, 17 %; b) THF, r.t., 2 h, −2 KI, 70 %.[33]

Complex **10** is insoluble in aromatic or aliphatic solvents and was isolated from THF solution. It remains in solution for 6 h but slowly decomposes into the free Me_4TACD ligand and $[YbH_2(THF)_x]$.

^1H NMR measurements showed the chemical shift of the hydrido ligands at $\delta = 7.51$ ppm, with a corresponding ^{171}Yb NMR resonance at $\delta = 992$ ppm as quartet with $^1J_{YbH}$ of 300 Hz. Because the reactivity of **10** was impacted by the reducing character of the Ph_3Si^- counterion, ytterbium benzyl compounds were also investigated as precursors for cationic hydride complexes (Figure 13). This method allowed access to both the monocationic $[(Me_4TACD)_2Yb_2(\mu_2\text{-}H)_3][BAr_4]$ (**11**) and the dicationic $[(Me_4TACD)_2Yb_2(\mu_2\text{-}H)_2(THF)][BAr_4]_2$ (**12**).[33] The monocationic complex **11** can also be treated with a proton source such as $[NEt_3H][BAr_4]$ to remove one of the bridging hydride ligands to form the bis-hydride bridged **12**. In the ^1H NMR spectrum **11** shows the same resonance as **10** as only the bulky counteranion is changed. However, **12** shows a more downfield-shifted resonance at $\delta = 8.98$ ppm with ytterbium satellites of $^1J_{YbH} = 364$ Hz, YbH). Only one set of Yb satellites is observable despite the unsymmetric structure of the complex in the solid state because the NMR was recorded in THF. The monocationic complex **11** was subsequently employed as catalyst for the hydrogenation and hydrosilylation of 1-hexene.

Summary and Outlook

Recent developments have reinvigorated the investigation of divalent lanthanide hydride complexes. Commonly employed synthetic strategies involve either σ-bond metathesis of amido or alkyl precursors with phenyl silane or hydrogenolysis of alkyl complexes. Various ligand scaffolds have been proven suitable for the task of stabilising dinuclear hydride complexes, spanning neutral tetradentate amino ligands, tridentate tris(pyrazolyl)borates, bidentate or tetradentate β-diketiminates, bidentate amidinates and most recently, also monodentate carbazolides. Secondary interactions with the π-scaffold of ligand aryl groups or additional neutral donor molecules such

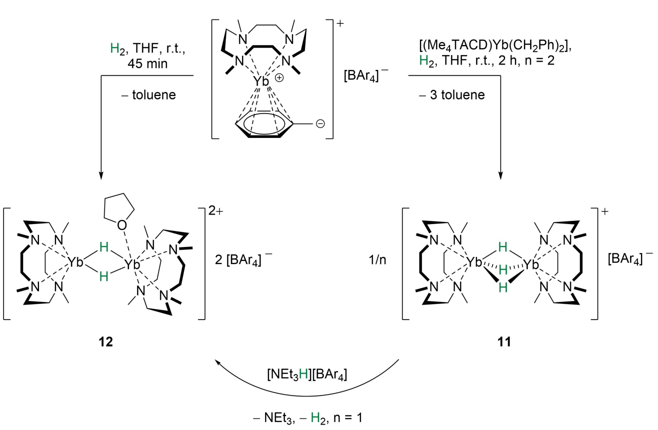

Figure 13. Synthetic pathway to cationic Yb^{II} hydride complexes $[(Me_4TACD)_2Yb_2(\mu_2\text{-}H)_2(THF)][BAr_4]$ (**12**) and $[(Me_4TACD)_2Yb_2(\mu_2\text{-}H)_3][BAr_4]$ (**11**).[33]

as THF contribute to the saturation of the coordination sphere. This even allowed the isolation of the monomeric Yb(II) hydride complex **5**. The extension of the synthetic capabilities towards Eu(II) and Sm(II) hydride complexes was successful. These complexes show a finely diffentiated reactivity, combining properties of the hydride with the strong reducing power of Sm(II), the weak reducing power of Yb(II) or the negligible reducing power of Eu(II). A variety of substrates were already studied in stoichiometric reactions. The Yb(II) hydrides were already used as catalyst in hydrogenation and hydrosilylation reactions.

Extrapolating from these instances of achievement, the next milestones are clearly laid out. Among the divalent lanthanides, Yb(II) hydrides are best understood as NMR spectroscopy can be readily employed for characterisation and reaction monitoring. The reactivity of these complexes might be investigated towards other substrates. Of particular interest are more reducing Sm(II) hydride complexes which may reveal new reactivity patterns. The incorporation of other lanthanides poses intriguing questions. Can hydride complexes of Tm(II), Dy(II) or Nd(II) be isolated as well? What requirements need to be met with respect to the ligand set to stabilise such complexes? Active research in this field of chemistry can be expected in the near future.

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Conflict of Interests

The authors declare no conflict of interest.

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