Synthesis and reactivity of \textit{bis}-tris(pyrazolyl)borate lanthanide-aluminium heterobimetallic trihydride complexes

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Abstract: Molecular heterobimetallic hydride complexes of lanthanides (Ln) and main group (MG) metals exhibit chemical properties unique from their monometallic counterparts and are highly reactive species, making their synthesis and isolation challenging. Herein, molecular Ln/Al heterobimetallic trihydrides [Ln(Tp)(µ-H2Al)(H)(N''')] \[^{2-Ln}\] (Ln = Y, Sm, Dy, Yb; Tp = hydrotris(1-pyrazolyl)borate; N''' = N(SiMe3)2) have been synthesised by facile insertion of aminonale [Me3N-AlH3] into the Ln–N amide bonds of [Ln(Tp)(N''')] \[^{1-Ln}\] Thus, providing a simple synthetic strategy to access a range of Ln/Al hydrides. Reactivity studies demonstrate that \[^{2-Ln}\] is a heterobimetallic hydride, for example it is able to reduce unsaturated substrates. Further evidence for the cooperative nature of \[^{2-Ln}\] is shown, as \[^{2-Ln}\] can catalytically dehydrocouple amine-borane under ambient conditions in contrast to its monometallic counterparts.

Heterobimetallic hydride complexes are desirable synthetic targets as they are highly reactive species and exhibit unique chemical activity properties distinct from their monometallic counterparts.\[^{[1]}\] However, their high reactivity makes the synthesis and isolation of heterobimetallic hydrides challenging. This is particularly true in the case of Ln aluminium hydrides, and as such require careful ligand design to stabilise the highly electrostatic Ln and aluminium cations which are bridged by small hydrides. In the bis substituted cyclopentadienyl (Cp\(^3\)) ligand environment heterobimetallic Ln/Al hydrides have been synthesised predominantly by salt metathesis for example by reacting \([\text{[Ln(Cp}^3\text{H}2\text{X})_2]\] (X = halide) with LiAlH\(^4\).\[^{[1]}\] The hydride and heterobimetallic Ln/Al hydride chemistry in Trofimenko’s scorpionate N-donor tris(pyrazolyl)borate (Tp\(^3\)) ligand environment is much less well established.\[^{[2]}\]

Homometallic lanthanide hydrides \([\text{[Ln(Tp}^3\text{H}2\text{)}(\text{H}2)]}\) supported by a mono (Tp\(^3\)) ligand, have been isolated in which both the size of the substituents in the 3,5-position of the Tp ligand dictates the nuclearity of the complex or cluster \((R = Pr, n = 3; R = Me, n = 4; R = H, n = 6)\).\[^{[26]}\] Notably only for \([\text{[Ln(Tp}^3\text{Me}3\text{)}(\text{H}2)_2]\] were Ln larger than Y stable, and when Tp\(^3\) = Tp\(^3\text{Bu,5-Me}\) was used no Ln(III) complexes were isolable. However, using Tp\(^3\text{Bu,5-Me}\) did enable the isolation of the first molecular Yb(II) hydride (\[^{[I]}\] in Figure 1). The Tp\(^3\) supported Ln hydrides are reactive, complex [I] undergoes facile activation chemistry at room temperature,\[^{[24]}\] whilst [II-Y] mediated hydrogenation and coupling of carbon monoxide (Figure 1).\[^{[26]}\]

The Tp\(^3\text{Bu,5-Me}\) ligand environment can also support monomeric heterobimetallic Ln/Al dihydrides \([\text{[Ln(Tp}^3\text{Bu,5-Me})(\mu-H\text{AlMe}3)]}\) where \(\text{Ln} = \text{Y} \text{and Lu ([III] in Figure 1).}\[^{[20]}\] Complex [III] was synthesised by reaction of \([\text{[Ln(Tp}^3\text{Bu,5-Me)}(\text{Me}3)]\) with 2 equivalents of HAiMe\(_3\) and moreover was shown to deprotonate amines to access a rare inside-bridged Ln–Al hydride ([IV] in Figure 1).\[^{[2, 3]}\] The insertion of substituted alanes into Ln–Me σ-bonds has also been shown to be a viable route to heterobimetallic Ln/Al dihydrides in the bis-Cp* (Cp* = C\(_3\)Me\(_3\)) ligand environment. The reaction of HAi(Me\(_3\))\(_2\) with \([\text{[Cp}^*\text{Y}(\text{Me})\text{Al}(\text{Me})\text{Al}(\text{Me})\text{Al}(\text{Me})\text{Al}(\text{Me})\text{]}]\) yielded \([\text{[Cp}^*\text{Y}(\mu-H\text{Al}(\text{Me})\text{Al}(\text{Me})\text{)}(\text{Me})\text{]}]\) (IV) in Figure 1) and Al(Me\(_3\))\(_2\).\[^{[10]}\] Complex [V] was the first example of a Ln catalyst in the hydroalumination of 1-oxetane. Using Tp\(^2\) the Ln scope is limited to Y and Lu, and there are no bis-Tp stabilised heterobimetallic Ln/Al complexes, directly analogous to the isolable bis-Cp\(^3\) complexes. Recently, monomeric bis-Tp complexes \([\text{[Ln(Tp}^3\text{H}2\text{)}(\text{X})]\] (Ln = Y, Dy, Yb; X = triflate)\[^{[5]}\] have shown themselves to be a versatile tool for accessing new Ln-element bonds (E = O\(^{[34]}\), N\(^{[36]}\)) as the anion can be readily exchanged via metathesis or protonolysis. Here we show that aminonalane [Me3N-AlH\(_3\)] insertion into the Ln–N amide bond in \([\text{[Ln(Tp}^3\text{H}2\text{)}(\text{N}'')]\) \[^{1-Ln}\] is facile and applicable to a wide range of Ln, yielding the molecular Ln/Al heterobimetallic trihydrides \([\text{[Ln(Tp}^3\text{H}2\text{)}(\mu-H\text{Al}(\text{H})\text{Al}(\text{N}''))]\) \[^{2-Ln}\] (Ln = Y, Sm, Dy, Yb).

This study began by extending the scope of \([\text{[Ln(Tp}^3\text{H}2\text{)}(\text{X})]\) complexes to include Sm(III), allowing for a representative range of differing Ln(III) ions to be studied. Following the same method as previously reported,\[^{[5]}\] \(^{1-\text{Sm}}\) \([\text{[Sm(Tp}^3\text{H}2\text{)}(\text{N}'')]\) was obtained by

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**Figure 1.** Reactive Ln hydride and Ln/Al heterobimetallic hydride complexes supported by Tp\(^3\) and Cp\(^3\) ligands.

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metathesis between the heteroleptic Sm(III) triflates \( [\text{Sm(Tp)}_2(\text{OTf})] \) (\( \text{OTf} = \text{CF}_3\text{SO}_3 \)) with \( K\text{N}_{\text{Me}} \) in toluene. To target Ln-aluminium hydride species we opted to use the Lewis base stabilised parent alanes of the type \( L\text{AlH}_3 \) (\( L = \text{NMe}_3 \),  \( \text{N-Heterocyclic Carbene} (\text{NHC}) \)). As these should undergo insertion chemistry into the \( L\text{N}^- \) bond akin to formation of [III] and [V], with the latter providing additional steric and electronic stabilisation from the NHC ligand. Firstly, the reaction of IDippAlH\(_3\) (IDipp = 1.3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with 1·Ln (\( L = Y, \text{Dy}, \text{Yb} \)) was slow and resulted in a mixture of products. Major products were identified as [Ln(Tp)]\(_2\)[8] and \([\text{IDipp}]\text{Al}(\text{N}^-)(\text{H}_2)\) \( \text{Al-Dipp} \) [4]. The closest structural comparator of \( \text{Al-Dipp} \) is \( \text{V} \), which exhibits the same \( \mu^2 \) binding mode of the bridging hydrides. Notably, \( 2\text{-Dy} \) is the first crystallographically characterised example of the Dy–(\( \mu^2\text{H} \))–Al unit. The Ln–N(\( \mu^2\text{Tp} \)) bond distances in \( 2\text{-Ln} \) are consistent with 1·Ln and [Ln(Tp)]\(_2\)\(^+\) literature. The Al–N(\( \text{N}^- \)) bond distances of 1.8430(19):1.844(3) Å in \( 2\text{-Ln} \) are similar to those in \( \text{V} \) (1.837(2) Å), transition metal TM/Al heterobimetallic hydrides containing TM–(\( \mu^2\text{H} \))–Al(\( \text{N}^- \)),\(^[6] \) and the homoleptic complex \( \text{Al}(\text{N}^-) \)\(_3\) (1.813(3) Å).\(^[7] \)

Colourless single crystals of 2·Ln suitable for single crystal X-ray diffraction (SCXRD) were grown from either saturated hexane solutions (\( L = Y, \text{Dy} \)) or saturated toluene solutions in the presence of hexane antisolvent (\( L = \text{Yb} \)) at -35 °C. Important structural metrics are tabulated in the ESI (data comparison S2, and crystallographic information S3). The structures of 2·Ln are all monomeric with an 8-coordinate Ln(III) ion bound to two \( \mu^2 \)-coordinated Tp ligands and two bridging hydrides, which are arranged around the Ln(III) ion in a distorted square antiprismatic geometry (see Figure 2 for 2-Dy and ESI Figures S110-112). In 2-Ln the bridging and terminal hydrides were found and refined freely, with Ln-H-Al bond distances comparable to previously reported Ln/Al heterobimetallic hydrides.\(^[14] \) The Ln–Al separation is similar across the 2-Ln series (2-Dy 3.1826(6), 2-Y 3.1822(5), 2-Yb 3.1439(9) Å). The close Ln-Al separation (approximately the sum of Ln and Al covalent radii) is therefore indicative of strong Ln-(\( \mu^2\text{H} \))–Al bonding, consistent with previous bridging hydride and 3c-2e bonds.\(^[8] \) The closest structural comparator of 2-Ln is \( \text{V} \), which exhibits the same \( \mu^2 \) binding mode of the bridging hydrides.\(^[10] \) Notably, 2-Dy is the first crystallographically characterised example of the Dy–(\( \mu^2\text{H} \))–Al unit. The Ln–N(\( \mu^2\text{Tp} \)) bond distances in 2-Ln are consistent with 1-Ln and [Ln(Tp)]\(_2\)\(^+\) literature.\(^[6] \) The Al–N(\( \text{N}^- \)) bond distances of 1.8430(19):1.844(3) Å in 2-Ln are similar to those in \( \text{V} \) (1.837(2) Å),\(^[11] \) transition metal TM/Al heterobimetallic hydrides containing TM–(\( \mu^2\text{H} \))–Al(\( \text{N}^- \)),\(^[6] \) and the homoleptic complex \( \text{Al}(\text{N}^-) \)\(_3\) (1.813(3) Å).\(^[7] \)

The reactivity scope of 2-Ln was investigated to understand the nature of the heterobimetallic hydride. In a similar manner to the initial synthetic attempts, reaction of 2-Ln with 1 eq. of IDipp again led to the formation of Al-Dipp and multiple products. Importantly, no discrete homometallic Ln hydrides, putative \([\text{Ln(Tp)}_2(\mu^2\text{H})_2]^-\) were observed spectroscopically (see ESI Section B2.2). Previously, the ion pair reaction chemistry of Ln(\( \text{L}^2\))\(_2\)(\( \mu^2\text{X} \))\(_2\) (\( L = \text{Ligand}, \text{X} = \text{monoanionic substituent}, \text{e.g.} \text{H}, \text{CH}_3 \)) has shown that these complexes should be considered

![Scheme 1. Synthesis of lanthanide-aluminium heterobimetallic trihydride complexes \([\text{Ln(Tp)}_2(\mu^2\text{H})\text{Al}(\text{N}^-)]\) 2-Ln (\( L = Y, \text{Sm}, \text{Dy}, \text{Yb}; \text{N}^- = \text{N(SiMe}_3\text{)}^\text{ii} \)) by reactions of [Ln(Tp)]\(_2\)\(^-\) 1-Ln with [Me\(_2\text{N}\)Al(\( \text{N}^- \))].](https://doi.org/10.26434/chemrxiv-2024-fx65b)

![Figure 2. Molecular structure of 2-Dy. Hydrogen atoms except for H, HA and HB are omitted for clarity and pyrazolyl carbon atoms of Tp displayed in wireframe. Displacement ellipsoids drawn at 50% probability. Displacement ellipsoids drawn at 50% probability.](https://doi.org/10.26434/chemrxiv-2024-fx65b)
as [Ln(L1)L2][AlX3]. These Ln/Al ion pair complexes undergo facile metathesis reactions for example, metathesis of Y(Cp)2[µ2-CH2=CH2]2Al(CH2)32 with KOAr (OAr = O2C-C6H4Me2) yielded Y[Cp2(µ-OAr)] and KAl(CH2)3.[10] With this in mind, we examined the potential ion pair character of 2-Ln. The reaction of 2-Ln with K(NH4) should yield the starting material 1-Ln, however, this resulted in complicated reaction mixtures containing 1-Ln, [Ln(Tp)2(µ-H)]2.[8] [K(µ-κ-N)2(µ-H)Al(H)2][Nh], H2 gas, and in addition for 2-Yb, reduction to [Yb(Tp)2][9] (see ESI Sections B2.3-B2.7). Complexes 2-Ln do not undergo facile ion exchange, indicating that the strong Ln-(µ-H)-Al interaction that is observed in the solid state persists in solution (also consistent with the VT NMR data). Thus, 2-Ln should be considered as bimetallic hydrides.

To prove this hypothesis, we studied the insertion chemistry of 2-Ln towards unsaturated substrates. It is of note that the amides 1-Ln do not react with carbodiimides to yield the putative guanidinates [Ln(Tp)2(µ2-R)(N=N(N')(NR'))]. However, the bimetallic trihydride complexes 2-Ln exhibit carbodiimide insertion chemistry. Reaction of RN=CN-R (R = Pr or Cy) with 2-Ln in d8-benzene (Scheme 2(a)), resulted in the formation of the formamidinate complexes [Ln(Tp)2(µ2-R)(N=N(N')(NH))][3-Ln] and [Al(µ(κ-N)(N=N(N')(NH)))3][4-Al] (see ESI Sections B2.10-B2.13). The 1H NMR resonances of 3-Al were assigned compared to [Al(µ-κ-N)(N=N(N'))(X)] (X = hydride, halide) literature.[13] Following a scale up reaction with three equivalents of CyN=CN-Cy, the crude reaction mixture was washed with hexane to remove 3-Al, and the complexes 3-Ln were isolated in moderate yields (Y, 45%; Sm, 36%; Dy, 51%; Yb, 49%; Scheme 2(a)). The multinuclear NMR data for diamagnetic 3-Y and paramagnetic 3-Ln (Ln = Sm, Dy, Yb) confirms the transfer of the hydride to the carbodiimide. As the loss of the metal hydride signals at 1800-1810 cm-1 and 1730-1740 cm-1 are replaced with strong absorptions between 1556-1559 cm-1, which are assigned to the N-C-N linkage stretching frequencies (νNCN) in 3-Ln. The νNCN in 3-Ln is lower in wavenumbers compared to νNCN = 1650-1670 cm-1, observed for homoleptic [Ln(N,N,R2-formamidinate)]+[14] and heteroleptic [Ln(N,N,R2-formamidinate)(µ-X)] complexes, with X'-monoanions and aromatic R groups.[14]

Yellow crystals of [Ln(Tp)2(µ2-(Cy)(N=CN=Cy))][3-Ln] (Ln = Dy, Yb) suitable for SCXRD were grown from saturated toluene solutions in the presence of hexane anisolevent at -35 °C. Both 3-Yb (Figure 3) and 3-Dy (ESI Figure S113) structures are monomeric, containing an 8-coordinate Ln(III) ion bound to two µ2-coordinated Tp ligands and a µ2-coordinated bidentate (Cy)N=CN=Cy anion, arranged around the Ln(III) ion in a distorted square antiprismatic geometry. Reduction of the carbodiimide was confirmed by presence of H10 on the sp2 carbon (C10) in the now notably bent formamidinate fragment (N7-C10-N7 118.6(15)[*] (3-Dy) and 119.8(6) (3-Yb). Comparison of C-N bond lengths also confirms the reduced nature of the formamidinate fragment as C10–N7 falls between typical values for C-N single and double bonds (C10–N7 1.326(14) Å (3-Dy) and 1.315(5) Å (3-Yb) vs single (~1.47 Å and double (~1.15 Å) C-N bonds) consistent with delocalisation of the N-C-N fragment in 3-Ln.[15] The Ln-N(µ2-Tp) bond distances in 3-Ln are consistent with 1-Ln, 2-Ln, and [Ln(Tp2)(µ2-X)] literature.[15] The Ln–N7 bond distances in 3-Ln (Ln = Dy, 2.376(8) Å; Yb, 2.373(3) Å) are consistent with Ln–N bond distances in [Yb(µ2-(Dipp)N=CN=Dipp)(µ2-(THF))][16] (Dipp = C6H5Me2). With this in mind, we examined the insertion of carbodiimides and benzophenone, less than three equivalents of substrate when less than three equivalents of substrate was utilized, complete consumption of 2-Ln was not observed (see ESI Sections B2.14 and B2.15). Notably, 2-Ln behaves differently to the TM/Al heterobimetallic trihydride complex [Ti(Cp)2(µ2-H)Al(H)(C5SmMe3)],[19] with excess PrN=CN=NP r resulted in a single insertion product, the formamidinate-bridged Ti/Al complex [Ti(Cp)2(µ2-H)[µ2-(Pr)(N(CH)N(Pr))Al(H)(C5SmMe3)]][19].

![Scheme 2. Substrate insertion reactivity of [Ln(Tp)2(µ2-AI)](N')(NH)] 2-Ln (Ln = Y, Sm, Dy, Yb) with (a) carbodiimides and (b) benzophenone.](https://orcid.org/0000-0001-5643-9256) Content not peer-reviewed by ChemRxiv. License: CC BY 4.0
Colourless crystals of 4-Al suitable for SCXRD were grown from saturated hexane solutions at -35 °C. Complex 4-Al (Figure 4) is dimeric, containing two tetrahedral Al(III) ions each bound to a terminal hydride, a terminal monodentate N" anion and a bridging \( \mu^2 \)-benzophenoxido anion. Reduction of the carboxyl unit is confirmed by the elongation of C-O bond (C1--O1 1.454(3) Å vs Ph3CO 1.214(2) Å) and the now tetrahedral C1 centre.[20] The bridging Al--O(OCHPh) bond distances of Al1--O1 1.8631(14) and Al1--O1' 1.8576(14) Å in 4-Al are similar to those observed in the \( \mu^2 \)-benzophenoxide bridged complex [(Al2[2.2.6.6-tetramethylpiperidinato](OCHPh)3][\( \mu^2 \)-O(OCHPh)]2].[21] and the literature of aluminium dimers bridged by aryloxides (OCH3R and OCRR').[22]

Following stoichiometric reactivity, and inspired by the Ln/Al heterobimetallic hydride hydroalumination catalyst [V] (Figure 1),[9] the applicability of 2-Ln in catalysis was examined to further investigate the cooperative reactivity between the two metal centres. Recently the catalytic dehydrocoupling of [Me2HN+BH3] has attracted significant interest, owing to the utility of amine boranes in hydrogen storage and as precursors to boron-nitride materials.[23] Ln hydrides and aluminium hydrides have both been reported to catalyse the dehydrocoupling of [Me2HN+BH3] at elevated temperatures, thus providing a basic idea for this preliminary study.[16, 24] The dehydrocoupling of [Me2HN+BH3] by 10 mol% 2-Ln (Ln = Y, Sm, Dy, Yb) proceeds at room temperature to yield [Me2N+BH22] as the major product (Table 1, see ESI for further details). Notable differences were found across the 2-Ln series, with consumption of amine-borane occurring most efficiently in the following order Yb > Y ~ Dy > Sm in line with the relative Lewis acidity of the Ln(III) ion. Although the slow turnover of 2-Sm is additionally due to the poor solubility of the pre-catalyst in the reaction solvent. It is important to note that 1-Y and [Me2N+AlH3] do not catalyse this reaction under these conditions, therefore cooperativity between the two metal centres enables this transformation to occur at room temperature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Relative amount of [Me2N+BH22] (%)</th>
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</thead>
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<tr>
<td>2-Y</td>
<td>48</td>
<td>90</td>
<td>61</td>
</tr>
<tr>
<td>2-Sm</td>
<td>172</td>
<td>85</td>
<td>78</td>
</tr>
<tr>
<td>2-Dy</td>
<td>60</td>
<td>91</td>
<td>69</td>
</tr>
<tr>
<td>2-Yb</td>
<td>24</td>
<td>93</td>
<td>66</td>
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In conclusion, the facile synthesis and characterisation of lanthanide-aluminium heterobimetallic trihydride complexes [Ln(Tp)(\( \mu^2 \)-H2)Al(H)(N")] 2-Ln (Ln = Y, Sm, Dy, Yb) are reported. The reactivity of 2-Ln was investigated to understand the cooperative nature of the two different metal centres. Attempts to break apart 2-Ln by addition of Lewis bases or ion exchange chemistry resulted in multiple products. However, on reaction with unsaturated organic substrates clean conversion to discrete Ln(III) and Al(III) hydride insertion products were obtained. This reveals that 2-Ln is best described as a bimetallic hydride with a strong Ln(\( \mu^2 \)-H)-Al interaction. Preliminary catalytic investigations of 2-Ln also showed heterobimetallic cooperatively enabling the dehydrocoupling of [Me2HN+BH3] at room temperature. The trend in catalytic activity of 2-Ln follows Lewis acidity of the Ln(III), with 2-Yb being the most efficient. Exploration of the reactivity and catalytic activity of these Ln/Al heterobimetallic trihydrides is ongoing to fully understand and utilise the synergistic metal-metal interaction.

**Supporting Information**

The data that support the findings of this study are available in the supplementary material of this article and available from the University of Strathclyde KnowledgeBase at https://doi.org/10.15129/6aa42810-48e2-400e-81c2-465639e81845. Deposition numbers 2313687-2313695 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

The authors have cited additional references within the Supporting Information.[25]

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