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Synthesis and structure of trinuclear yttrium(III) dihydrido cluster stabilized by bulky amidinate ligand

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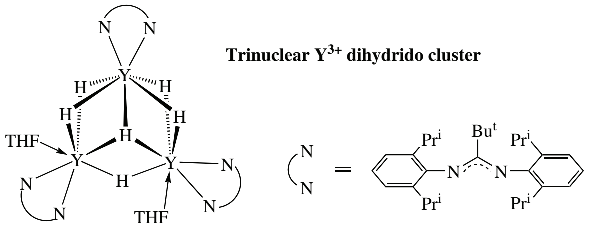
A new yttrium dihydride complex $[(\mathrm{Amd^{Bu^t}})\mathrm{Y}]_3(\mu\text{-H})_6(\mathrm{THF})_2$ ($\mathrm{Amd^{Bu^t}} = [\mathrm{Bu^tC(NC_6H_3Pr^i_2\text{-}2,6)_2}]^-$) was synthesized by the reaction of $(\mathrm{Amd^{Bu^t}})\mathrm{Y(CH_2SiMe_3)_2(THF)}$ with two molar equivalents of $\mathrm{PhSiH_3}$. This complex adopts a trinuclear structure both in the crystalline state and in the $\mathrm{C_6D_6}$ solution due to five μ^2- and one μ^3-bridging hydride ligands. The complex was found to be active in hydrosilylation of terminal alkenes with $\mathrm{PhSiH_3}$.



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Rare-earth metal hydride complexes present a unique class of compounds.[1–3] They exhibit high reactivity and are catalytically active in hydrogenation and hydrosilylation of alkenes and alkynes,[4–7] as well as in dehydro-cross-coupling of organohydrosilanes with arenes[8,9] or terminal alkynes.[10] Among the hydride complexes of rare-earth metals, the most studied to date are monohydrides of the general formula $[(\mathrm{L})_2\mathrm{MH}]_n$ or $[(\mathrm{L})(\mathrm{L'})\mathrm{MH}]_n$, stabilized by two monoanionic or one dianionic ancillary ligands.[11–15] On the contrary, dihydride derivatives of the $[\mathrm{LMH_2}]_n$ type have been much less explored,[16–24] due to their high reactivity and, as a consequence, low stability, as well as the difficulty of isolating them in the individual state. At the same time, dihydride complexes of rare-earth metals stabilized by monoanionic ligands are of interest for their use in catalytic and stoichiometric transformations, as well as for the study of their structural features and the identifying factors that determine the reactivity of Ln–H bonds.

Research over the past two decades has shown that the stability and reactivity of hydride complexes of rare-earth metals is greatly determined by the nature of the ancillary ligand environment, the variation of which allows one to significantly control the reactivity of Ln–H bonds. In this regard, the attention was directed precisely to the search for new ligand systems, primarily bulky polydentate N- and/or O-coordinating ligands capable of providing steric and coordination saturation of the sphere of the rare-earth metal ion, and, consequently, the kinetic stability of the metal complex.[25–27] Among such ligands, monoanionic chelating amidinate anions $[\mathrm{RC(NR')_2}]^-$ have found wide application. The main advantage of amidinate ligands is the possibility of modification of their steric and electronic properties by varying the substituents on the nitrogen and carbon atoms of the NCN fragment. Moreover, different coordination modes of these ligands allowed their complexation with metal ions of different nature and ionic radius.[28–30] Substituted amidinate anions turned out to be a suitable ligand platform for stabilization of highly reactive alkyl and hydride complexes of rare-earth metals,[31–34] including divalent lanthanides.[35–39]

Here, we report on the synthesis and structure of a novel trinuclear yttrium dihydride complex stabilized by a bulky amidinate ligand and its catalytic activity in the intermolecular hydrosilylation of terminal alkenes. The most common synthetic procedure towards rare-earth metal hydride complexes is the metathesis of the Ln–C σ-bond into bis(alkyl) derivatives $[(\mathrm{L})\mathrm{LnR_2}]$ under the action of molecular hydrogen $\mathrm{H_2}$ or phenylsilane $\mathrm{PhSiH_3}$.[40,41] As a starting compound, the bis(alkyl) complex $(\mathrm{Amd^{Bu^t}})\mathrm{Y(CH_2SiMe_3)_2(THF)}$ **1**, containing a bulky amidinato anion $[\mathrm{Bu^tC(NC_6H_3Pr^i_2\text{-}2,6)_2}]^-$, was used. The synthesis of **1** was described previously;[42] however, it was characterized only by solution NMR spectroscopy. In this work, the molecular structure of **1** was unambiguously confirmed by single crystal X-ray diffraction analysis (see Online Supplementary Materials).†

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† *Crystal data for* **1**. $\mathrm{C_{41}H_{73}N_2OSi_2Y}$, $F_\mathrm{w} = 755.10$, monoclinic, $a = 12.0119(2)$, $b = 13.3507(2)$ and $c = 27.6844(4)$ Å, $\beta = 93.4560(10)°$, $V = 4431.60(12)$ Å^3, space group $P2_1/c$, $Z = 4$, $d_\mathrm{calc} = 1.132$ g cm^{-3}, $F_{000} = 1632$, $\mu = 1.400$ mm^{-1}, colorless prism with a size of *ca.* 0.42×0.38×0.28 mm. Total of 79419 reflections (10562 unique, $R_\mathrm{int} = 0.0675$). The final residuals were $S(F^2) = 1.047$, $R_1 = 0.0526$ for 8213 reflections with $F^2 > 2\sigma(F^2)$ and $wR_2 = 0.1247$ for all data and 563 parameters with 700 restraints.

Crystal data for **2**. $\mathrm{C_{95}H_{151}N_6O_2Y_3 \cdot 2C_6H_{14}}$, $F_\mathrm{w} = 1848.28$, triclinic, $a = 12.83430(10)$, $b = 14.7902(2)$ and $c = 28.1490(3)$ Å, $\alpha = 97.2490(10)$, $\beta = 98.2320(10)$ and $\gamma = 91.0760(10)°$, $V = 5242.28(10)$ Å^3, space group $P\bar{1}$, $Z = 2$, $d_\mathrm{calc} = 1.171$ g cm^{-3}, $F_{000} = 1992$, $\mu = 1.695$ mm^{-1}, colorless prism with a size of *ca.* 0.21×0.18×0.12 mm. Total of 94408 reflections (24967 unique, $R_\mathrm{int} = 0.0805$). The final residuals were $S(F^2) = 1.027$, $R_1 = 0.0539$ for 17498 reflections with $F^2 > 2\sigma(F^2)$ and $wR_2 = 0.1130$ for all data and 1269 parameters with 1259 restraints.

The SC XRD data for **1** and **2** were collected with a Rigaku OD Xcalibur E diffractometer [Mo*K*α-radiation, ω-scans technique, $\lambda = 0.71073$ Å, $T = 100.0(2)$ K] using the CrysAlis$^\mathrm{Pro}$ software[53] package. The structures were solved *via* the intrinsic phasing algorithm and refined by full-matrix least squares against F^2 using SHELX.[54,55] Implemented

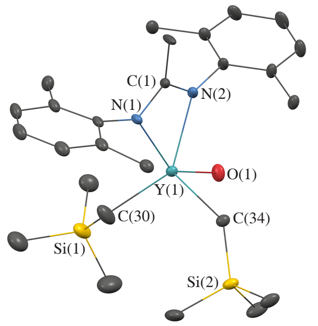


Figure 1 Molecular structure of complex **1**. Thermal ellipsoids are given with a 30% probability level. Hydrogen atoms, methyl fragments of Pr^i-substituents, and CH_2-groups of a coordinated THF molecule are omitted for clarity.

Complex **1** has a monomeric structure and contains a Y^{3+} ion coordinated by two nitrogen atoms of a bidentate amidinate ligand, two carbon atoms of covalently bonded alkyl groups, and one O atom of a coordinated THF molecule; formal coordination number of the cation in **1** is five (Figure 1). Complex **1** crystallizes in the monoclinic space group $P2_1/c$ and is isomorphous to the Yb^{III} analog.[38] The Y–C bond lengths in **1** are 2.379(4) and 2.381(3) Å, which is in a good agreement with the values in previously known five-coordinated yttrium mono-amidinato bis(alkyl) complexes [2.335(4)–2.404(4) Å].[43–45] The amidinate ligand in **1** is symmetrically bound to the metal center [Y–N 2.363(2), 2.364(2) Å] due to delocalization of the negative charge along the conjugated NCN system [C–N 1.347(4), 1.336(4) Å].

The reaction of **1** with an excess of $PhSiH_3$ (2.3 equiv. mol) in a THF/hexane mixture (1:4) at room temperature resulted in the formation of the yttrium dihydride complex $[(Amd^{Bu^t})Y(\mu\text{-}H)_2]_3(THF)_2$ **2** (Scheme 1), which was isolated in a 59% yield. Complex **2** is moderately soluble in aromatic solvents (benzene, toluene), and practically insoluble in hexane; it is extremely air- and moisture-sensitive; however, it can be stored in sealed tubes or under inert atmosphere (N_2 or Ar) both in a crystalline state and in solution at room temperature for several months without any signs of decomposition.

According to single crystal X-ray diffraction (SC XRD) study, complex **2** adopts a trinuclear structure in which two fragments $(Amd^{Bu^t})Y(THF)$ and one fragment $(Amd^{Bu^t})Y$ are bonded by six bridging hydride ligands (Figure 2).† Five hydride ligands are μ^2-bridging; *i.e.*, four of them are located above or below the Y_3-plane with deviation of 0.78–1.23 Å, while the fifth μ^2-bridged hydride ligand lies in the plane. The sixth μ^3-bridged hydride ligand is bonded simultaneously to three yttrium atoms and is located above the Y_3-plane at 0.96 Å. It is important to note that the μ^3-bridged hydride ligand is disordered by two sites, one above the plane and the other below it. Previously,[46] identical arrangement of hydride ligands in rare-earth metal trinuclear polyhydrido clusters was observed in yttrium and lutetium dihydrides $[(Tp^{Pr^i_2})LnH_2]_3$ stabilized by a tris(pyrazolyl)-borate ligand.

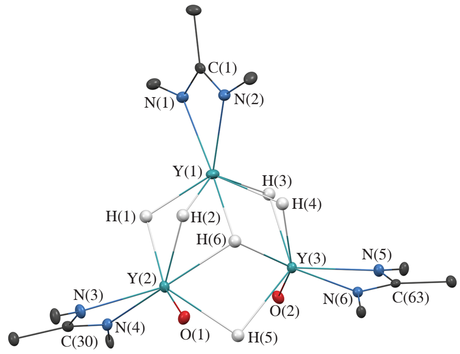
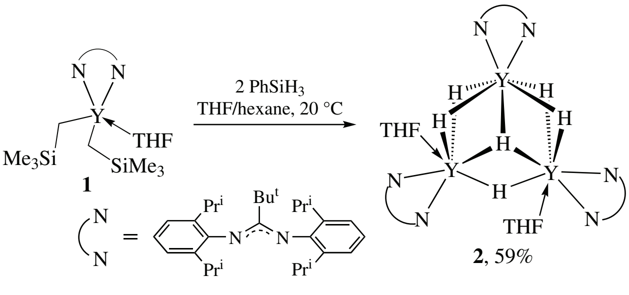


Figure 2 Molecular structure of complex **2**. Thermal ellipsoids are given with a 30% probability level. H atoms except of the hydride ligands, 2,6-diisopropyl substituents of amidinate ligands, methyl fragments of Pr^i-substituents, and CH_2-groups of coordinated THF molecules are omitted for clarity.



Scheme 1

It should be noted that hydrogenilysis of the Ln–C bond in related bis(alkyl)s $(Amd^{Ph})Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y, Lu), stabilized by a benzamidinate ligand (Amd^{Ph} = = $[PhC(NC_6H_3Pr^i_2\text{-}2,6)_2]^-$) with H_2 in THF led to the formation of the corresponding binuclear dihydrides $[(Amd^{Ph})Ln]_2(\mu\text{-}H)_3(\kappa\text{-}H)(THF)_3$,[40] in which two metal centers were linked by three μ^2-bridging hydride ligands, while the fourth one was terminal. On the other hand, treating the ytterbium analog $(Amd^{Bu^t})Yb(CH_2SiMe_3)_2(THF)$ with $PhSiH_3$, in which the metal center had stable oxidation states of +2, was accompanied by the spontaneous reduction of Yb^{III} to Yb^{II} yielding a dimeric monohydride of divalent ytterbium $[(Amd^{Bu^t})Yb^{II}(\mu\text{-}H)]_2$.[35]

The distances between the yttrium atoms of the $(Amd^{Bu^t})Y(THF)$ fragments and the solvate-free $(Amd^{Bu^t})Y$ are 3.3245(4), 3.3282(4) Å, while the distances between the yttrium atoms of the $(Amd^{Bu^t})Y(THF)$ fragments are somewhat longer [3.6449(4) Å]. Despite these differences, the Y···Y distances in **2** are comparable to those in previously known trinuclear polyhydride complexes [3.165(5)–3.684(3) Å].[18,22,46] The Y–H distances between μ^2-bridging hydride atoms located above and below the Y_3 plane are 2.11(2)–2.22(2) Å. For the μ^2-bridged hydride ligand located in the Y_3 plane between the solvated metal centers $(Amd^{Bu^t})Y(THF)$, the Y–H bond lengths are surprisingly longer [2.42(2) Å]. For a μ^3-bridging hydride ligand, the Y–H distances lie in the range 2.10(4)–2.27(4) Å. In general, these values fall within the range of Y–H distances found in previously known trinuclear polyhydride complexes [Y–(μ^2-H): 2.01–2.29 Å; Y–(μ^3-H): 2.11–2.43 Å],[18,22,46] as well as in dimeric yttrium dihydride $[(Amd^{Ph})Y]_2(\mu\text{-}H)_3(\kappa\text{-}H)(THF)_3$ with a benzamidinate ligand.[47]

In the ^1H NMR spectrum of **2** (room temperature, toluene-d_8), the hydride ligands appear as a quadruplet at 5.92 ppm ($^1J_{YH}$ = 16.5 Hz). The presence of one quadruplet arising due to the splitting of six hydride atoms on three ^{89}Y nuclei (I = 1/2, 100%) indicates their equivalence in solution at room

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in CrysAlis^{Pro}, scaling algorithms were used to perform absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and refined anisotropically. Hydride ligands in **2** were also found from Fourier syntheses of electron density but refined isotropically with geometrical restrictions (SADI instructions) and $U(H)_{iso} = 1.5\,U_{eq}$. All other hydrogen atoms in **1** and **2** were placed in calculated positions and refined isotropically in the ‘riding’ model with $U(H)_{iso} = 1.2\,U_{eq}$ of their parent atoms [$U(H)_{iso} = 1.5\,U_{eq}$ for methyl groups].

CCDC 2365616 (**1**) and 2365617 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

temperature. Lowering the temperature is accompanied by broadening of this signal; however, no decoalescence into several individual signals is observed even at 233 K.

The chemical shift of the hydride ligands in **2** is slightly lower than that for the related dimeric hydride $[(\mathrm{Amd}^{\mathrm{Ph}})\mathrm{Y(THF)}_2(\mu\text{-H})_3\mathrm{Y}(\mathrm{Amd}^{\mathrm{Ph}})(\mathrm{H})(\mathrm{THF})]$ (6.34 ppm), while the spin-coupling constant $^1J_{\mathrm{YH}}$ in **2** decreases significantly (16.5 Hz for **2** *vs.* 25.2 Hz). This tendency consisting in a decrease of $^{89}\mathrm{Y}$–$^1\mathrm{H}$ spin–spin coupling constant values with increasing nuclearity of the hydrido clusters is typical for yttrium complexes. For example, in the series of amidinate hydride derivatives the highest value of the $^1J_{\mathrm{YH}}$ constant (73.4 Hz) was found in the mononuclear cationic complex $[(\mathrm{Amd}^{\mathrm{Ph}})\mathrm{YH(THF)}_3][\mathrm{BPh}_4]$[33] containing a terminal hydride ligand, while in the case of its binuclear dicationic complex $[(\mathrm{Amd}^{\mathrm{Ph}})\mathrm{Y}(\mu^2\text{-H})(\mathrm{THF})_2]_2[\mathrm{BPh}_4]_2$ the $^1J_{\mathrm{YH}}$ constant decreases by more twice (29.0 Hz).[33] Similar patterns were observed for trinuclear $[(\mathrm{Tp}^{\mathrm{R,R'}})\mathrm{Y}(\mu\text{-H})_2]_3(\mathrm{THF})_n$ and tetranuclear $[(\mathrm{Tp}^{\mathrm{R,R'}})\mathrm{Y}(\mu\text{-H})_2]_4(\mathrm{THF})_n$ dihydride clusters with tris(pyrazolyl)borate ligands, for which the values of $^1J_{\mathrm{YH}}$ were 15.6 and 12.1 Hz, respectively.[19,20,46]

It is known that hydride complexes of rare-earth elements are effective catalysts for the hydrosilylation of multiple C–C bonds.[4–7,48,49] In this regard, the catalytic activity of dihydride **2** in intermolecular hydrosilylation of alkenes with $\mathrm{PhSiH_3}$ was studied. Complex **2** showed high activity in the addition of $\mathrm{PhSiH_3}$ to the terminal alkenes (non-1-ene and styrene), but was inactive in the case of cyclohexene or *cis*- and *trans*-stilbenes containing internal C=C double bonds. For styrene and non-1-ene, complex **2** at room temperature allowed one to achieve high conversions (>95%) of substrates in 4 and 6.5 h, respectively. Moreover, in the case of non-1-ene, complex **2** demonstrated 100% regioselectivity giving only the linear product $\mathrm{Me(CH_2)_8SiH_2Ph}$. In the case of styrene, regioselectivity was reversed and the branched product $\mathrm{PhCH(Me)SiH_2Ph}$ was predominantly formed with selectivity up to 88%. This difference in the regioselectivity of Si–H addition to multiple C=C bonds of alk-1-enes and styrenes is typical for complexes of rare-earth metals[50,51] and is due to the structure of the intermediate formed during the catalytic cycle.[52]

In conclusion, the metathesis of Y–C σ-bonds in the monoamidinate bis(alkyl) complex under action of phenylsilane occurs with the formation of a trinuclear dihydride complex. According to X-ray diffraction analysis, the binding of yttrium atoms into a trinuclear cluster is realized by five μ^2- and one μ^3-bridging hydride atoms. The yttrium dihydride can be used as a catalyst for intermolecular hydrosilylation reactions of terminal alkenes (non-1-ene and styrene) demonstrating high activity and regioselectivity.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7565.

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