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Hydrides of Lanthanides

A Double Addition of Ln–H to a Carbon–Carbon Triple Bond and Competitive Oxidation of Ytterbium(II) and Hydrido Centers[**]

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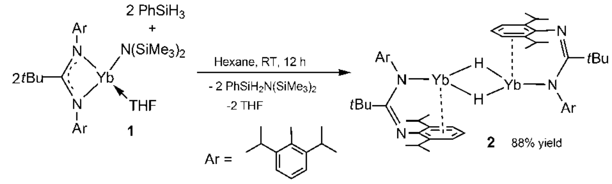
The unique reactivity and catalytic activity of organolanthanide hydrido complexes in various transformations of unsaturated substrates has given a powerful incentive to development this chemistry.[1] Although rare-earth hydrides have been known since the 1980s,[2] until very recently they were represented exclusively by Ln^{III} derivatives. The first structurally defined Ln^{II} hydrido complex supported by bulky hydrotris(pyrazolyl)borate ligand was published by Takats et al. in 1999.[3] The second example of a Yb^{II} hydride involves a complex coordinated by a DIPP-nacnac ligand.[4] Despite the fact that some classes of stoichiometric reactions of $[\{(Tp^{tBu,Me})Yb(\mu\text{-}H)\}_2]$[5] and the catalytic activity of $[\{(DIPP\text{-}nacnac)YbH(thf)\}_2]$ in 1,1-diphenylethylene hydrosilylation[4] have been described, the reactivity of Ln^{II} hydrido species still remains poorly investigated. Indeed, Ln^{II} hydrido complexes containing two reaction centers are of great interest for investigation of reactivity patterns. The presence of a low-valent Yb^{II} ion and hydrido ligand provides a basis for a rich redox chemistry of these complexes. The Yb–H bond can undergo insertions of multiple bonds and σ-bond metathesis reactions with reagents containing acidic X–H bonds. Moreover the Yb ion can coordinate Lewis bases, while the basic M–H bond can form complexes with Lewis acids. Formerly we synthesized new classes of rare-earth (III) hydrido and alkyl hydrido species containing guanidinate, amidopyridinate, amidomethylpyridinate, and linked amidinate ligands. These compounds demonstrated high catalytic activities in olefin polymerization and hydrosilylation.[6] Herein we present the synthesis and the structure of the novel Yb^{II} hydrido complex $[\{[tBuC(NC_6H_3\text{-}2,6\text{-}iPr_2)_2]Yb(\mu\text{-}H)\}_2]$, supported by a bulky amidinate ligand, and new types of reactions observed for hydrido species: oxidation reactions and double Ln–H addition to a C≡C bond.

Amido complex $[\{tBuC(NC_6H_3\text{-}2,6\text{-}iPr_2)_2\}YbN(SiMe_3)_2(thf)]$ (**1**)[7] was used as a precursor for the synthesis of related hydrido species (for the molecular structure of **1**, see the Supporting Information). The σ-bond metathesis reaction of **1** with $PhSiH_3$ in hexane (20 °C, 12 h) allowed the synthesis of the hydrido complex **2** in 88 % yield (Scheme 1). The reaction afforded $PhSiH_2N(SiMe_3)_2$ as a byproduct, which was isolated in 76 % yield. The blackish-violet crystals of **2** are highly air- and moisture-sensitive crystals that are poorly soluble in aliphatic and aromatic hydrocarbons.



Scheme 1. Synthesis of hydride complex **2**.

The X-ray diffraction study revealed that complex **2**, in a similar fashion to the previously reported $[\{(Tp^{tBu,Me})Yb(\mu\text{-}H)\}_2]$[3] and $[\{(DIPP\text{-}nacnac)\ YbH(thf)\}_2]$,[4] adopts a dimeric structure owing to the two hydrido ligands μ^2-bridging two Yb^{II} centers (Figure 1). The Yb–H bond lengths and Yb–Yb distance in **2** (2.14(4), 2.18(5), and 3.3553(4) Å, respectively) are close to the values previously reported for the dimeric Yb^{II} hydrido complexes.[3,4]

The amidinate ligands in **2** chelate the Yb^{II} ions by κ^1-amide and η^6-arene interactions, leading to a coordination mode that is different from the κ^2-*N,N'*-chelating mode detected in the parent complex **1**. The κ^1-N,η^6-arene-chelating coordination mode was previously observed in the Yb^{II} complex with the bulky guanidinate ligand [{[Cy$_2$NC-

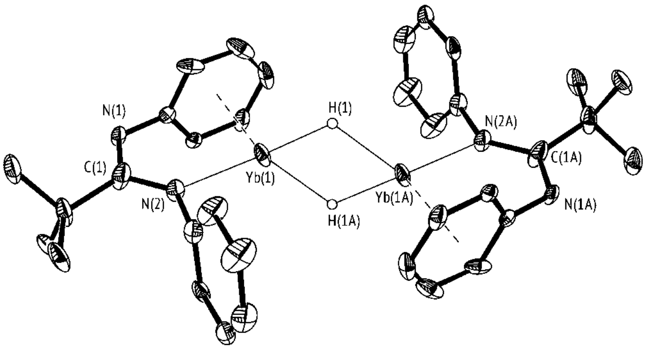


Figure 1. ORTEP of **2** with ellipsoids set at 30 % probability; non-hydride hydrogen atoms and *i*Pr substituents are omitted for clarity. Selected bond lengths [Å]: Yb1–H1 2.14(4), Yb1–H1a 2.18(5), Yb1–N2 2.329(3), Yb1–Ar$_{centroid}$ 2.410(5), Yb1–Yb1a 3.3553(4), N1–C1 1.330(5), N2–C1 1.370(5).

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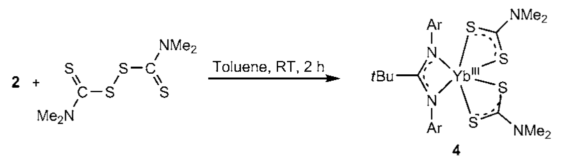
(NAr$_2$)]Yb(μ-I)}$_2$].[8] The Yb–N and Yb–Ar centroid distances in **2** (2.329(3), 2.420(4) Å) are close to the related values in [{[Cy$_2$NC(NAr$_2$)]Yb(μ-I)}$_2$] (2.360(3), 2.424(4) Å).[8] Despite the presence of THF in the reaction mixture and the highly oxophilic nature of the Yb ion, **2** crystallizes as THF-free species, whereas in [{[Cy$_2$NC(NAr$_2$)]Yb(μ-I)}$_2$][8] the Yb-η^6-arene interaction is labile and the arene ligand can be easily replaced by a THF molecule in the metal coordination sphere.

The chemical shift of the signal for the hydrido ligands for **2** (7.74 ppm) is shifted noticeably upfield compared to those for the related Yb^{II} derivatives in an *N,N*-coordination environment: [{(Tp^{tBu,Me})YbH}$_2$] (10.5 ppm)[3] and [{(DIPP-nacnac)YbH(thf)}$_2$] (9.92 ppm).[4] This can be explained by electron density donation from aromatic π system of the 2,6-diisopropylphenyl ring to the ytterbium atom. Unfortunately low solubility of **2** in C_6D_8 did not allow to record ^{13}C and ^{171}Yb spectra of **2**.

To evaluate the strength of the Yb–η^6-arene interaction by means of competitive coordination of arene and Lewis base to the metal center as well as to obtain monomeric hydrido species the reactions of **2** with various Lewis bases were carried out. No reaction was detected in the case of TMEDA, DPPE, or DPPM. Similar to [{(Tp^{tBu,Me})YbH}$_2$], addition of a ten-fold molar excess of THF to the solution of **2** in C_6D_6 gave no evidence for the dimer dissociation or THF coordination (ca. 24 h). However, unlike [{(Tp^{tBu,Me})YbH}$_2$] **2** is stable in THF solution for a short time (ca. 0.5 h) at ambient temperature. Dissolution of **2** in THF and subsequent recrystallization of the reaction product from toluene allowed **2** to be recovered in quantitative yield. However when **2** was kept in a THF–hexane mixture over several days, the bis(amidinate) Yb^{II} complex [{*t*BuC(NC$_6$H$_3$-2,6*i*Pr$_2$)$_2$}Yb] (**3**) was isolated from the reaction mixture.[7] If complex **3** is the result of the ligand redistribution reaction, [YbH$_2$(thf)$_n$][9] can be suggested as the second product, however it was not found in the reaction mixture. The results of the reactions of **2** with Lewis bases allow the conclusion that Yb–η^6-arene interaction is quite robust.

The redox reactions of Yb^{II} hydrido complexes has to date remained unexplored. This prompted us to carry out a series of reactions with one-electron oxidants (I$_2$, AgBF$_4$, AgBPh$_4$, *N,N′*-dimethylthiuramdisulfide) with the aim of the selective oxidation of the metal ion and the synthesis of cationic or mixed ligand Yb^{III} hydrido species. This study was also directed towards an estimation of comparative reductive properties of hydrido and Yb^{II} ions. The reactions of **2** with I$_2$, AgBF$_4$, and AgBPh$_4$ turned out to be not selective; they resulted in hydrogen evolution (resulting from oxidation of the hydrido anion) and the formation of intractable mixtures of products containing both Yb^{II} and Yb^{III} species.[10] In contrast, the reaction with the milder oxidant *N,N′*-dimethylthiuramdisulfide occured without H$_2$ evolution, but regardless the reagents ratio the bis(dithiocarbamato) amidinato Yb^{III} complex [{*t*BuC(NC$_6$H$_3$-2,6*i*Pr$_2$)$_2$}Yb(S$_2$CNMe$_2$)$_2$] (**4**) was afforded in 36 % yield (Scheme 2, Figure 2). The value of the effective magnetic moment of **4** at 293 K is 4.30 μB and corresponds to Yb^{III}. The fact that no remaining **2** was found in the reaction mixture indicates that at the initial stage it reacts with *N,N′*-dimethylthiuramdisulfide in a 1:1 molar ratio. Obviously, formation of **4** is the result of the ligand redistribution reaction, and [{*t*BuC(NC$_6$H$_3$-2,6*i*Pr$_2$)$_2$}YbH$_2$]$_n$ could be suggested as the second reaction product. At present, isolation and identification of the reaction byproducts are in progress.



Scheme 2. Formation of bis(dithiocarbamato)amidinato ytterbium(III) complex **4**.

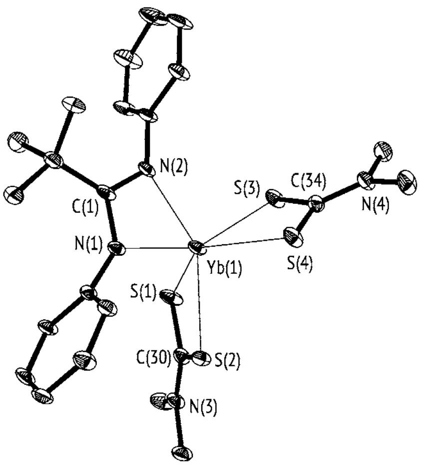
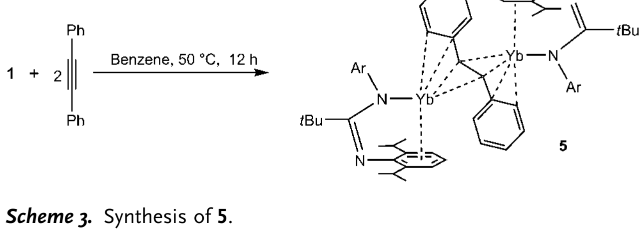


Figure 2. ORTEP of **4** with ellipsoids set at 30% probability; hydrogen atoms and *i*Pr substituents are omitted for clarity. Selected bond lengths [Å]: Yb1–N1 2.294(4), Yb1–N2 2.295(4), N1–C1 1.344(5), N2–C1 1.350(5), Yb1–S4 2.6946(12), Yb1–S2 2.6980(11), Yb1–S3 2.6989(10), Yb1–S1 2.7004(12).

An X-ray study of complex **4** revealed the expected κ^2-N,N′chelating coordination mode of the amidinate ligand. The lengths of Yb-S and Yb–N bonds in **4** are indicative of the trivalent state of the ytterbium ion.[11]

C≡C bond insertions into a Yb–H bond were described for [{(Tp^{tBu,Me})Yb(μ-H)}$_2$].[5] The reaction of **2** with two moles of PhC≡CPh was carried out in benzene at 50 °C. Regardless the reagent ratio, the reaction affords a product involving the addition of two Yb–H bonds to a PhC≡CPh molecule, namely [{[*t*BuC(NC$_6$H$_3$-2,6*i*Pr$_2$)$_2$]Yb}$_2$(μ-η^4:η^4-PhCHCHPh)] (**5**; Scheme 3).

The X-ray study of **5** showed that the complex adopts a dimeric structure in which two Yb^{II} centers are linked by



Scheme 3. Synthesis of **5**.

a μ-bridging 1,2-dianionic PhCHCHPh fragment (Figure 3). Each Yb ion is bound to two benzylic carbon atoms (2.6218(16) and 2.6355(17) Å) and ipso (2.66242(16) Å) and ortho carbon atoms (2.8568(18) Å) of the phenyl ring, thus resulting in η^4-coordination.[12] The bond lengths between Yb atoms and benzylic carbon atoms (2.6218(16), 2.6355(17) Å) in **2** are slightly shorter than those in Yb^{II} benzylic derivatives [(Me$_3$SiC$_6$H$_4$NMe$_2$)$_2$Yb(thf)$_2$].[13] The length of the bond of the former alkyne carbon atoms (1.482(3) Å) is close to that of a single bond.[14]

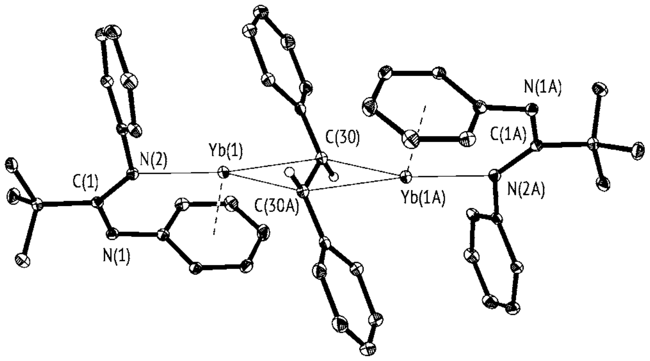


Figure 3. ORTEP of **5** with ellipsoids set at 30% probability; hydrogen atoms and *i*Pr substituents are omitted for clarity. Selected bond lengths [Å]: Yb1–N2 2.4075(14), N1–C1 1.316(2), N2–C1 1.359(2), Yb1–C30a 2.6218(16), Yb1–C30 2.6355(17), C30–C30a 1.482(3), Yb1–Ar$_{centroid}$ 2.416(5).

Magnetic measurements showed that **5** is diamagnetic, thus indicating a divalent state for the ytterbium atom. Complex **5** is stable in the crystalline state and can be kept at room temperature without decomposition; nevertheless, all our attempts to record the NMR spectra of **5** failed. Solubilization of brownish-black crystals of **5** in C$_6$D$_6$ or [D$_{12}$]cyclohexane results in immediate decoloration of the solution and formation of an off-white precipitate. The ^{1}H NMR spectrum of this solution clearly shows the presence of bibenzyl and NH protons of the parent amidine. The absence of deuterium in bibenzyl implies that the amidinate ligand can be the only source for hydrogen abstraction for its formation.

Surprisingly, **2** does not react with Me$_3$SiC≡CSiMe$_3$ and *t*BuC≡CH even when heated at 50 °C for 3 days, demonstrating pronounced difference of the reactivity of **2** and that of [{(Tp^{tBu,Me})Yb(μ-H)}$_2$].[5] Complex **2** is inert in the attempted catalysis of isoprene, ethylene, propylene (20 °C, 1 bar) polymerizations, but slowly polymerizes styrene (12 % conversion after 48 h).

In summary, a novel Yb^{II} hydrido complex supported by bulky amidinate ligand has been synthesized. The first example of addition of two Ln−H bonds to a C≡C bond resulting in the formation of a 1,2-dianionic bibenzyl fragment is described. Preliminary studies on the oxidation of **2** revealed that both Yb^{II} and hydrido centers are oxidized under the reaction conditions. The Yb^{II}-η^6-arene interaction in **2** turned out to be surprisingly robust, as arene cannot be replaced from the metal coordination sphere when treated with Lewis bases. Obviously κ^1-*N*,η^6-arene coordination of amidinate and guanidinate ligands bearing bulky aryl groups by nitrogen atoms is characteristic for Yb^{II} derivatives, and the interconversion of κ^1-*N*,η^6-arene and κ^2-*N*,*N'* coordination modes can be influenced by modification of steric and coordination saturation of the metal. Work directed towards synthesis of Yb^{III} hydrido species coordinated by the bulky amidinate ligand is currently in progress.

Experimental Section

Synthesis of [{[*t*BuC(NC$_6$H$_3$-2,6-*i*Pr$_2$)$_2$]Yb(μ-H)}$_2$] (**2**): PhSiH$_3$ (0.125 g, 1.15 mmol) was added to a solution of **1** (0.953 g, 1.15 mmol) in hexane (20 mL) at room temperature and the reaction mixture was left overnight. The mother liquor was separated from blackish-violet crystals by decantation. The crystals of **2** were washed with hexane and dried for 20 min in vacuum. Compound **2** was isolated in 88 % yield (0.603 g). ^{1}H NMR (400 MHz, C$_6$D$_6$, 293 K): $\delta = 0.91$ (s, 18 H, C*H$_3$* *t*Bu), 1.22–1.37 (complex m, 48 H, C*H$_3$* *i*Pr), 3.24–3.55 (complex m, 8 H, C*H* *i*Pr), 6.93–7.10 (complex m, together 12 H, C*H* Ar), 7.74 ppm (s, 2 H, satellites ^{171}Yb, $^1J_{\mathrm{YbH}} = 460$ Hz). IR (KBr, Nujol): $\tilde{\nu} = 1660$ (w), 1620 (s), 1585 (m), 1565 (w), 1410 (m), 1320 (m), 1255 (m), 1230 (m), 1210 (m), 1160 (s), 1060 (s), 930 (s), 845 (m), 800 (m), 765 (s), 670 (w), 630 (w), 510 cm^{-1} (s); elemental analysis calcd (%) for C$_{58}$H$_{88}$N$_4$Yb$_2$ (1187.45 g mol^{-1}): C 58.67, H 7.47, Yb 29.15; found: C 58.95, H 7.69, Yb 29.04. The volatiles were removed from the mother liquor at room temperature in vacuum and the vacuum distillation of the resulted viscous liquid afforded PhSiH$_2$N(SiMe$_3$)$_2$ as colorless liquid (0.235 g, 76 %). ^{1}H NMR (400 MHz, C$_6$D$_6$, 293 K): $\delta = 0.27$ (s, 18 H, SiMe$_3$), 5.22 (s, 2 H, SiH$_2$, with ^{29}Si satellites, $^1J_{\mathrm{SiH}} = 205$ Hz), 7.16–7.25 (complex m, together 3 H, *o*-CH and *p*-CH Ph), 7.67 (d, $^3J_{\mathrm{HH}} = 5.0$ Hz, 2 H, *m*-CH Ph) ppm; ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, 293 K): $\delta = 3.4$ (SiMe$_3$), 128.1 (m-CH Ph), 129.7 (*ipso*-C Ph), 133.8 (o-CH Ph), 135.7 (p-CH Ph) ppm; ^{29}Si{^{1}H} NMR (79.5 MHz, C$_6$D$_6$, 293 K): $\delta = -36.2$ (SiH$_2$Ph), 5.8 (SiMe$_3$) ppm. Elemental analysis calcd (%) for C$_{12}$H$_{25}$NSi$_3$ (267.59 g mol^{-1}): C 53.86, H 9.42, N 5.23; found: C 53.70, H 9.48, N 4.99. MS (EI): $m/z = 267.1$ [M^+].

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