Inorg. Chem. **2007**, *46*, 5320–5326

Inorganic Chemistry
Article

Syntheses and Structures of Ytterbium(II) Hydride and Hydroxide Complexes: Similarities and Differences with Their Calcium Analogues

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Received March 2, 2007

The Yb(II) hydride complex (DIPP-nacnac)YbH·THF (**3-Yb**, DIPP-nacnac = $CH\{(CMe)(2,6\text{-}i Pr_2C_6H_3N)\}_2$) was prepared by a mild metathesis reaction of (DIPP-nacnac)Yb[$N(SiMe_3)_2$]·THF with $PhSiH_3$. **3-Yb** crystallizes as a dimer with bridging hydride ions, and its geometry is similar to that of the analogue calcium hydride complex (**3-Ca**). **3-Yb** is well soluble in benzene and remarkably stable in solution at room temperature. Ligand exchange to the homoleptic Yb(II) complexes takes place at higher temperatures (**3-Yb** is less stable than the analogue **3-Ca**). The soluble hydride complexes **3-Ca** and **3-Yb** are catalysts for the hydrosilylation of 1,1-diphenylethylene, but differences in the product distributions are observed. Slow hydrolysis of (DIPP-nacnac)Yb[$N(SiMe_3)_2$]·THF gave reduction of water and unidentified Yb(III) complexes. Fast hydrolysis at low temperature, however, resulted in the first Yb(II) hydroxide complex, (DIPP-nacnac)Yb(OH)·THF (**4-Yb**, 20% yield), which is a dimer with bridging hydroxide ions in the solid state. The crystal structure is isomorphous to that of the calcium analogue **4-Ca**. **4-Yb** is well soluble in benzene and considerably more stable against ligand exchange and formation of homoleptic species than **3-Yb**.

Introduction

The organometallic chemistry of the lanthanides (Ln = lanthanide) has witnessed a rapid progress over the last decades.[1] This development is largely due to the enormous potential in catalysis[2] and new materials.[3] Although this is particularly true for the lanthanides in their most stable oxidation state III, the chemistry of Ln(II) complexes is much less developed. Despite extensive knowledge on cyclopentadienyl–Ln(II) chemistry,[1i–j] very few alkyl complexes have been published[4] and the first aryl[5] and benzyl[6] complexes were only reported recently. This backlog in Ln(II) chemistry is likely due to two factors: (i) Their much larger ionic radii make it hard to saturate the coordination spheres. (ii) Their much weaker and more ionic bonding of ligands results in lower stability and a more pronounced tendency toward ligand exchange (e.g., Schlenk equilibria).

The latter problems are very similar to those encountered in the chemistry of the heavier alkaline-earth metals, and consequently, parallels between these two research areas have been found: e.g., there is ample evidence for the striking similarity in the chemistry of Ca^{2+} and Yb^{2+}.[6,7] Despite similarities also remarkable differences have been found.[6]

We recently introduced synthetic pathways to and structures of two new functional groups in calcium chemistry:

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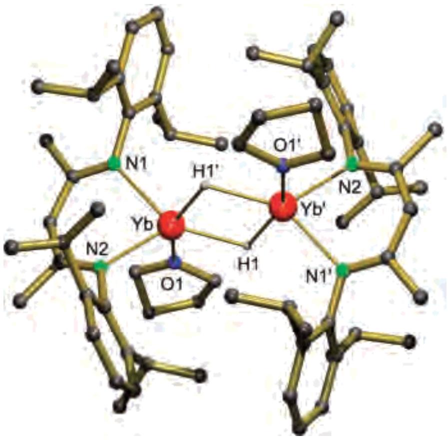
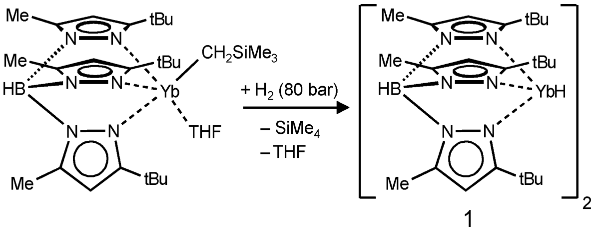


Figure 1. Crystal structure of **3-Yb**. All hydrogens, except the bridging hydride ions, have been omitted for clarity.

hydride[8] and hydroxide[9] complexes have been reported. In the course of our continuing interest in similarities and differences in the chemistry of Ca^{2+} and Yb^{2+}, we describe here the synthesis and structure of an ytterbium(II) hydride complex that is soluble in hydrocarbons and shows an unusual high stability toward ligand exchange. Moreover, we describe a synthetic route to the first Ln(II) hydroxide complex, a class of compounds which were not accessible yet. We specifically outline the differences with their calcium analogues.

Results and Discussion

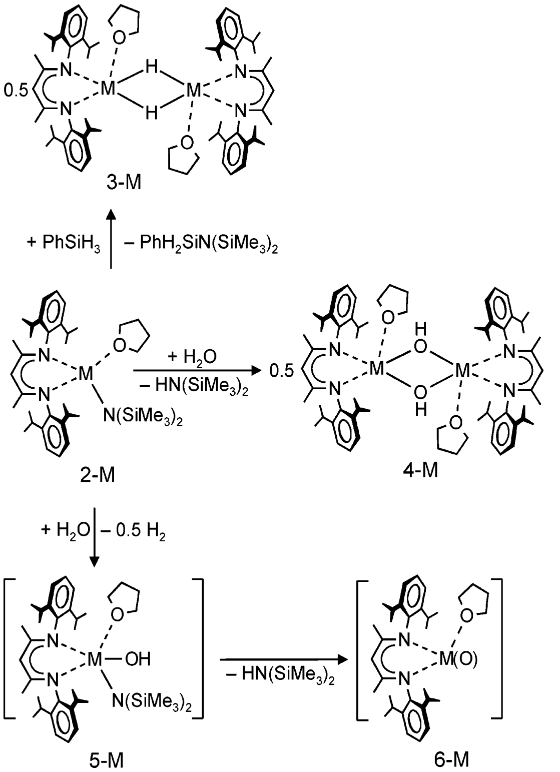
Recently, the first hydrocarbon-soluble ytterbium(II) hydride could be prepared by reaction of an alkyl precursor with pressurized dihydrogen (eq 1).[10] The extremely large tridentate scorpionate ligand ($Tp^{tBu,\ Me}$) in **1** provided sufficient steric bulk and thus supressed ligand exchange (which would result in formation of insoluble YbH_2). In solution at room-temperature complex **1** was stable for hours and decomposed gradually into unidentified products.



(1)

Interestingly, attempts to synthesize a calcium hydride complex with the very similar scorpionate ligand Tp^{tBu} gave formation of homoleptic $(Tp^{tBu})_2Ca$ in which one ligand is bonded to Ca in (κ^3-*N*,*N*′,*N*″)-fashion and the other with two pyrazole nitrogens and a B−H unit.[8] Synthesis of a stable calcium hydride complex **3-Ca** was accomplished by use of the sterically crowded DIPP-nacnac ligand system (Scheme 1; DIPP-nacnac = $CH\{(CMe)(2,6\text{-}i\text{Pr}_2C_6H_3N)\}_2$): reaction of the amide precursor **2-Ca** with $PhSiH_3$ gave good conversion to **3-Ca**. Therefore, following a similar route for an analogue ytterbium complex seemed promising.

Scheme 1



The heteroleptic precursor **2-Yb** could be prepared by the same convenient one-pot procedure that has been developed for **2-Ca**. Reaction of $KN(SiMe_3)_2$, YbI_2, and DIPP-nacnacH in a ratio of 2:1:1, respectively, gave **2-Yb** as dark-violet crystals in 54% yield. Subsequent reaction with $PhSiH_3$ gave the Yb(II) hydride complex **3-Yb** in the form of dark-violet crystals (27%).

The complex crystallized as a centrosymmetric dimer (Figure 1) with symmetrically bridging hydride ions that could be located and were isotropically refined as independent atoms. The Yb−H bond lengths range from 2.21(4) to 2.23(4) Å and are within the standard deviation similar to the average Yb−H bond of 2.26(3) Å in $[(Tp^{tBu,\ Me})YbH]_2$ (**1**). The Yb···Yb distance (3.650(1) Å) in **1** is significantly longer than that in **3-Yb** (3.5204(2) Å), which suggests that the steric bulk of the $Tp^{tBu,\ Me}$ ligand is larger than that of the DIPP-nacnac/THF combination.

Yb(II) complexes generally crystallize isomorphous to their Ca analogues. Complex **3-Ca** crystallized from hexane as a solvent-free crystal modification (Table 1, modification A)[8] and from benzene with a cocrystallized solvent molecule (modification B). Structurally these modifications differ in the orientation of the DIPP-nacnac ligands in respect to each other. Complex **3-Yb**, however, crystallized from hexane in a completely different modification again (Table 1). This might be due to the noticeable better solubility of **3-Yb** in hexane, which forced a crystallization at much lower temperature and led to cocrystallization of a hexane molecule.

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Table 1. Cell Parameters and Selected Bond Distances (Å) for Dimeric Calcium and Ytterbium Hydride Complexes **3-Ca** and **3-Yb**

param	**3-Ca** (modification A)[8]	**3-Ca** (modification B)	**3-Yb**
a (Å)	47.980(2)	19.7751(7)	13.2493(5)
b (Å)	12.5912(4)	19.7929(6)	14.5646(5)
c (Å)	22.2426(8)	18.2045(5)	18.9955(7)
α (deg)	90	90	90
β (deg)	103.069(2)	99.231(2)	93.654(2)
γ (deg)	90	90	90
V (Å^3)	13 089.2(8)	7033.1(4)	3658.1(2)
cryst system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$	$P2_1/n$
asym unit	1 dimer	2 half-dimers over *i*	2 half-dimers over *i*
cosolvent		2 half-C_6H_6 over *i*	1 *n*-hexane
M−H range	2.09(4)−2.21(3)	2.16(4)−2.22(4)	2.21(4)−2.23(4)
M−H av	2.15(3)	2.18(4)	2.22(4)
M−O	2.355(1)−2.391(1)	2.407(3)−2.415(3)	2.443(2)
M−N	2.372(1)−2.390(1)	2.365(3)−2.378(3)	2.376(2)−2.379(2)

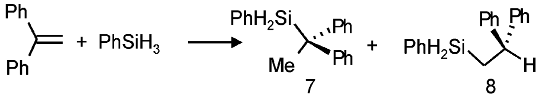
Comparison of the structure of **3-Yb** with both **3-Ca** modifications shows that the ligand−metal bonding in these compounds is similar (Table 1); bonds to Ca are slightly shorter on account of its somewhat smaller ionic radius (Ca^{2+}, 1.00 Å; Yb^{2+}, 1.02 Å).[11] The best agreement is observed between **3-Yb** and **3-Ca** (modification B), which are both centrosymmetric dimers with a similar orientation of the ligands.

The Yb(II)−hydride complex **3-Yb** dissolves well in benzene and is stable in solution at room temperature, however, slowly decomposes at 75 °C into homoleptic (DIPP-nacnac)$_2$Yb and presumably YbH_2. At 75 °C the half-lifetime of **3-Yb** in benzene is ca. 2.5 h. The analogue **3-Ca** is much more stable: whereas shortly heating a benzene solution of **3-Ca** to 75 °C did not result in noticeable decomposition, prolonged heating at 75 °C gave decomposition into (DIPP-nacnac)$_2$Ca and CaH_2 with a half-lifetime of ca. 24 h.

Recently, we observed unexpected close similarities in the ^{1}H NMR spectra of benzylcalcium and benzylytterbium(II) analogues.[6] This is remarkable, since it is known that the metal in benzyl complexes has a large influence on charge delocalization and thus on the chemical shift of the ring protons.[12] ^{1}H NMR spectra of **3-Yb** and **3-Ca** (Figure 2) are different: whereas the chemical shifts for most of the protons compare well, a huge discrepancy is observed for the hydride protons. The signal for the hydride hydrogen atom in **3-Ca** is a singlet at 4.45 ppm. The analogue resonance in **3-Yb** is found at 9.92 ppm, an unusually high chemical shift for a proton with considerable hydride character. This value is confirmed by two-dimensional NMR experiments and by the clearly visible ^{171}Yb satellites ($J_{Yb-H} = 398$ Hz). The rather high chemical shift as well as the ^{171}Yb−^{1}H coupling in **3-Yb** also compare well to the values obtained for [(Tp^{tBu,Me})YbH]$_2$ (**1**): $\delta(H^-) = 10.50$ ppm and $J_{Yb-H} = 369$ Hz.

The considerable differences in chemical shifts for the hydride protons in **3-Ca** and **3-Yb** should not be explained by differences in charge distributions in both complexes. Rather we attribute this extreme downfield shift to spin−orbit-induced heavy-atom effects. These effects, which have been well-described,[13] are very pronounced for atoms close to the heavy nuclei (r^{-3} dependence) and depend strongly on the involvement of valence s-orbitals.

Recently, we reported on the catalytic hydrosilylation of alkenes with early main-group metal complexes and proposed catalytic cycles that explain the influence of polar solvents on the regioselectivity of this reaction.[14] Since a metal hydride complex is considered the catalytical active species, we tested the soluble complexes **3-Ca** and **3-Yb** in the hydrosilylation of 1,1-diphenylethylene (DPE) with $PhSiH_3$ (eq 2).



(2)

Both hydride complexes indeed were catalytically active in this reaction, but the product distributions (Table 2) differ substantially from each other and from that obtained with the homoleptic catalyst: (α-Me_3Si-*ortho*-Me_2N-benzyl)$_2$Ca• 2THF (**9**).[14] The calcium catalysts **9** gave regioselectively product **7** or **8**, depending on the polarity of the medium. Hydrosilylation with **3-Ca** and **3-Yb**, however, is independent of the polarity of the solvent and gave in all cases **7** as the major product. This difference is likely related to the heteroleptic nature of the catalytically active species in reactions with **3-Ca** and **3-Yb**.

The latter catalysts also resulted in formation of Ph_2CHMe as an unexpected byproduct, which is especially observed for runs with **3-Ca** under polar conditions. The mechanism for formation of Ph_2CHMe as well as the consequence of metal choice on the product distributions are hitherto unclear and encourage further investigation.

The ability of the DIPP-nacnac ligand in stabilizing complexes with low coordination numbers and unique functionalities allowed the synthesis of hydrocarbon-soluble hydride complexes of Ca^{2+} and Yb^{2+}. The unusual stability of these complexes is presumably due to the rather strongly bonded bidentate ligand and its bulky nature. This results in

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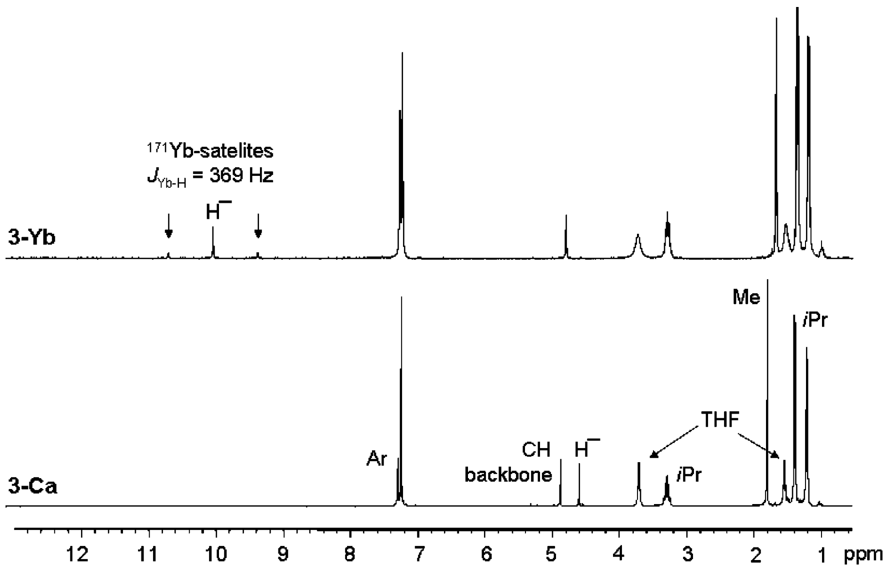

Figure 2. ^{1}H NMR spectra of the hydride complexes **3-Yb** and **3-Ca** in C_6D_6 at 20 °C.

Table 2. Product Distribution (%) in the Catalytic Hydrosilylation of 1,1-Diphenylethylene with Phenylsilane[a]

catalyst	solvent	t (h)[b]	**7**	**8**	Ph_2CHMe
9		16	100	0	0
9	THF	3	0	100	0
3-Ca		5	79	2	19
3-Ca	THF	4	53	5	42
3-Yb		4	99	0	1
3-Yb	THF	4	95	0	5

[a] Reactions at 50 °C; 2.5 mol % catalyst for **9** and 5 mol % catalyst for **3-Ca** and **3-Yb**. [b] Time indicating >98% conversion of one of the substrates (1,1-diphenylmethane or phenylsilane).

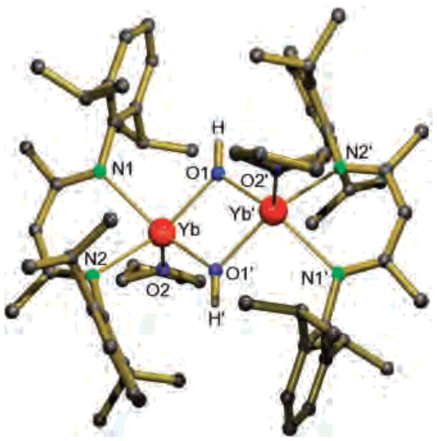

Figure 3. Crystal structure of **4-Yb**. All hydrogens, except those of the hydroxide ions, have been omitted for clarity.

a stable cage around the central $(MH)_2$ core and thus prevents ligand exchange reactions. The recent isolation of an isomorphous calcium hydroxide complex, [(DIPP-nacnac)-CaOH·THF]$_2$ (**4-Ca**, Scheme 1),[9] is proof of principle that this ligand system allows the isolation of calcium complexes with other small anionic functionalities. The same ligand environment could also enable the synthesis of the analogue ytterbium(II) hydroxide complex.

Lanthanide(II) hydroxide compounds are not easily accessible: homoleptic $Eu(OH)_2$ and $Sm(OH)_2$ were only recently isolated in an Ar matrix at 6 K[15] or could be detected as a precipitate on the electrode in electrochemical reduction of Ln(III) cations.[16] The lack of a well-defined heteroleptic Ln(II) hydroxide complex is inherent to the synthetic method for hydroxide complexes. Whereas the first well-defined group 3 hydroxide complex has been prepared by careful hydrolysis of Cp_3Y at −78 °C (eq 3),[17] controlled hydrolysis of Ln(II) complexes led to reduction of water and gave the Ln(III) hydroxide complexes in >80% yields (eq 4).[18] Interestingly, slow evaporation of water vapor into a THF solution of decamethylsamarocene gave a highly symmetric hexanuclear Sm(III) cluster in which water is not only oxidized to OH^- but partially further reacted to O^{2-} (eq 5).[19]

$$Cp_3Y(THF) \xrightarrow{H_2O} Cp_2Y{-}OH(THF) + CpH \tag{3}$$

$$Cp'_2Ln^{II} \xrightarrow{H_2O} Cp'_2Ln^{III-}OH + 0.5H_2 \tag{4}$$

$$Cp' = Me_3SiCp,\ Ln = Yb;\ Cp' = 1{,}3\text{-}(Me_3Si)_2Cp,\ Ln = Sm$$

$$Cp^*{}_2Sm^{II} \xrightarrow[THF]{H_2O(g)} (Cp^*Sm^{III})_6(O)_3(OH)_6 \tag{5}$$

The calcium hydroxide complex **4-Ca** could be obtained by two methods: (i) very slow diffusion of water vapor into a solution of **2-Ca** in hexane (the water phase was covered by a hexane layer in order to slow down diffusion), in which case it precipitated as well-defined crystals. (ii) By addition of water to a THF solution of **2-Ca** at −40 °C.[9] Very slow diffusion of water vapor into a solution of **2-Yb** resulted in

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Table 3. Cell Parameter and Selected Bond Distances (Å) for Dimeric Calcium and Ytterbium Hydroxide Complexes **4-Ca** and **4-Yb**

complex	**4-Ca** (modification A)[9]	**4-Ca** (modification B)[9]	**4-Yb**
a (Å)	48.190(5)	12.6659(9)	12.6955(15)
b (Å)	12.595(1)	12.7083(9)	12.7651(15)
c (Å)	22.291(2)	13.2977(10)	13.3877(14)
α (deg)	90	98.423(6)	97.950(7)
β (deg)	102.850(6)	113.730(5)	114.063(7)
γ (deg)	90	110.982(6)	111.239(7)
V (Å^3)	13191(2)	1720.6(2)	1739.1(3)
cryst system	monoclinic	triclinic	triclinic
space group	*C2/c*	$P\bar{1}$	$P\bar{1}$
asym unit	1 dimer	1 half-dimer over *i*	1 half-dimer over *i*
cosolvent		1 half-toluene over *i*	1 half-toluene over *i*
M−OH range	2.209(2)−2.228(2)	2.221(2)−2.230(4)	2.264(6)−2.265(5)
M−OH av	2.219(2)	2.226(3)	2.265(6)
M−O(THF)	2.372(1)−2.449(1)	2.414(3)	2.403(6)
M−N	2.414(2)−2.426(1)	2.419(3)−2.422(3)	2.433(5)−2.447(6)

a gradual discoloration of the intensely dark-purple solution and gave rise to a color gradient and formation of a white precipitate. We were not able to isolate well-defined products from the reaction mixture, but the drastic change in color and the paramagnetic behavior of products in NMR analysis suggested oxidation to Yb(III) species. We presume water acts in this reaction as oxidator and propose formation of intermediates **5-Yb** and **6-Yb** which might form a variety of products by ligand exchange (Scheme 1). The 0.32 V difference in reduction potentials for the reactions $Yb^{3+} + e^- \rightarrow Yb^{2+}$ (−1.15 V) and $H_2O + e^- \rightarrow OH^- + 0.5\ H_2$ (−0.83 V) indicates that the conversion of **2-Yb** to **5-Yb** is indeed thermodynamically allowed by ca. 15 kcal/mol. Similar redox problems are also encountered in the syntheses of Ln(II)−amine complexes, and Ln(III)−amide complexes resulted instead: $Ln^{II}X_2 + R_2NH \rightarrow (R_2N)Ln^{III}X_2 + 0.5\ H_2$.[20]

Addition of a stoechiometric amount of water to a THF solution of **2-Yb** at −60 °C, however, did not result in immediate discoloration, and we were able to crystallize an intensely dark-green compound from a toluene solution at low temperature. Although the intense color of the complex is characteristic for an Yb(II) species, the ^1H NMR signals of the product dissolved in benzene-d_6 were broadened considerably, which is indicative for the presence of Yb(III). Purification by repeated recrystallization resulted in a diamagnetic NMR sample.

A crystal structure determination (Figure 3) confirmed the isolation of the ytterbium(II) hydroxide complex **4-Yb**. The compound crystallized as a centrosymmetric dimer in which the OH^- ions bridge the metal ions. The coordination geometry around Yb is a distorted square pyramid in which the oxygen atom of THF (O2) is at the apex and the nitrogen and hydroxide ligands form the square base.

Although the hydrogen atoms of the hydroxide functionalities could not be located unambiguously in this heavy-atom structure, we have ample evidence that the current complex indeed represents the first Ln(II) hydroxide and is not an Yb(III) oxide, e.g., dimeric **6-Yb**. (i) Its intense color and diamagnetic behavior are typical for a Yb(II) species. (ii) **4-Yb** crystalizes isomorphous to one of the two modifications previously found for its Ca analogue (Table 3): **4-Ca** and **4-Yb** both crystallize from toluene in a triclinic crystal system with similar cell parameters and one centrosymmetric dimer and a toluene molecule in the unit cell. Bond distances and angles are also strikingly similar (Table 3). (iii) The Yb−N bonds (average 2.445(6) Å) are much longer than those in similar β-diketiminate complexes of Yb(III) (range: 2.27−2.33 Å).[21] (iv) Complex **4-Yb** was fully characterized by two-dimensional ^1H NMR analysis. Nearly all chemical shifts are strikingly similar to those for **4-Ca**. Only the hydroxide group shows a resonance at −0.23 ppm which is somewhat downfield to that in **4-Ca** (−0.78 ppm) and exhibits characteristic ^{171}Yb satellites ($^2J_{Yb-H} = 10.5$ Hz).

A benzene solution of the Yb(II) hydroxide complex **4-Yb** is considerably more stable than the Yb(II) hydride complex **3-Yb**: 2 h at 75 °C did not result in noticeable decomposition. Prolonged heating resulted in line-broadening of the ^1H NMR signals. A possible decomposition route to Yb(III) species could be further reduction of of **4-Yb** according to the reaction **4-Yb** → 2 **6-Yb** + H_2. Isolation of well-defined reaction products from this decomposition reaction is in progress.

Conclusions

Hydrocarbon-soluble Yb(II) hydride complex **3-Yb** is easily accessible by reaction of an amide with phenylsilane under mild conditions, a procedure which was also used in the synthesis of the calcium analogue **3-Ca**. Although the crystal structures of **3-Yb** and **3-Ca** are not isomorphous, their geometries are very similar. The ^1H NMR spectrum of **3-Yb** differs from that of **3-Ca**: the signal for the hydride hydrogen in **3-Yb** is shifted 5.47 ppm downfield with respect to that in **3-Ca**, which is attributed to a spin−orbit-induced heavy-atom effect. The heteroleptic Yb(II) hydride complex is somewhat less stable to ligand exchange and formation of insoluble metal dihydride than its calcium analogue. This might be attributed to the slightly longer and weaker Yb−H bond.

The first Ln(II) hydroxide complex **4-Yb** could be obtained by a controlled low-temperature hydrolysis of **2-Yb**. Al-

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though partial oxidation of Yb(II) is observed, the product can be obtained Yb(III)-free by repeated crystallization.

Similar to its hydrocarbon-soluble calcium analogues, Yb(II) hydride and hydroxide complexes are well-soluble in nonpolar solvents and could find possible application as a molecular Yb(II) precursor in CVD or sol−gel syntheses of Yb(II) or Yb(III) salts.

Experimental Section

General Methods. Solvents were dried by standard methods and distilled prior to use. All moisture- and air-sensitive reactions were carried out under an inert argon atmosphere using standard Schlenk techniques. Samples prepared for spectral measurements as well as for reactions were manipulated in a glovebox. NMR spectra were recorded on Bruker DPX300 and Bruker DRX500 spectrometers. IR spectra were measured as nujol mull between KBr plates. Single crystals have been measured on a Siemens SMART CCD diffractometer. Structures have been solved and refined using the programs SHELXS-97 and SHELXL-97, respectively.[22] All geometry calculations and graphics have been performed with PLATON.[23]

Synthesis of 2-Yb. A 15 mL volume of THF was added to a mixture of DIPP-nacnac-H (2.30 g, 5.49 mmol) and $KN(SiMe_3)_2$ (2.19 g, 10.98 mmol). Subsequently, a slurry of YbI_2 (2.34 g, 5.49 mmol) in 10 mL of THF was added and the mixture was stirred overnight. After centrifugation, the volatile components were removed under vacuo (25 °C, 1 Torr, 30 min) and the resulting purple solid was recrystallized by cooling a concentrated pentane solution to −27 °C. The product crystallized in the form of large purple blocks (2.50 g, 54%). Anal. Calcd for $C_{39}H_{67}N_3OSi_2Yb$ (M_r = 823.18): C, 56.90; H, 8.20. Found: C, 56.64; H, 8.38. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 0.20$ (s, 18H; $SiMe_3$), 0.86 (m, 4H; THF), 1.24 (d, ^3J(H,H) = 6.6 Hz, 12H; *i*Pr), 1.36 (d, ^3J(H,H) = 6.6 Hz, 12H; *i*Pr), 1.62 (s, 6H; Me), 3.26−3.35 (m, 8H; *i*Pr, THF), 4.77 (s, 1H; H-backbone), 7.10−7.15 (m, 6H; aryl). ^{13}C NMR (75 MHz, C_6D_6, 20 °C): $\delta = 5.8$ (Me_3Si), 24.7 (*i*Pr−Me), 25.0 (THF), 25.4 (*i*Pr-H), 25.5 (*i*Pr-Me), 28.3 (backbone-Me), 69.3 (THF), 93.5 (backbone-CH), 124.0 (Ar), 124.6 (Ar), 141.3 (Ar), 147.0 (Ar), 165.4 (backbone-C). Mp: 150 °C (dec).

Synthesis of 3-Yb. Phenylsilane (129 mg, 1.19 mmol) was added to a solution of **2-Yb** (1.00 g, 1.19 mmol) in hexane (5.5 mL). The solution was stirred for 1 h at 60 °C and then concentrated to half of its original volume. Cooling to −27 °C gave **3-Yb** in the form of dark violett crystals (215 mg, 27%). Anal. Calcd for $C_{33}H_{50}YbN_2O$ (M_r = 663.80): C, 59.71; H, 7.59. Found: C, 59.43; H, 7.70. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 1.07$ (d, ^3J(H,H) = 6.9 Hz, 12H; *i*Pr), 1.24 (d, ^3J(H,H) = 6.9 Hz, 12H; *i*Pr), 1.41 (m, 4H; THF), 1.55 (s, 6H; Me), 3.17 (sept, ^3J(H,H) = 6.9 Hz, 4H; *i*Pr), 3.61 (m, 4H; THF), 4.68 (s, 1H, H-backbone), 7.05−7.15 (m, 6H, aryl), 9.92 ppm (s, satellites: $^1J(^{171}\text{Yb},^1\text{H}) = 398$ Hz, 1H, Yb−H). ^{13}C NMR (75 MHz, C_6D_6, 20 °C): δ =24.4 (*i*Pr-Me), 24.9 (Me-backbone), 25.4 (THF), 25.9 (*i*Pr-Me), 28.0 (*i*Pr-CH), 69.5 (THF), 94.2 (backbone), 123.6 (Ar), 123.9 (Ar), 141.9 (Ar), 145.8 (Ar), 163.8 ppm (backbone). Mp: 185 °C (dec).

Synthesis of 4-Yb. Degassed water (32 μL, 1.78 mmol) was added to a cooled (−60 °C) solution of **2-Yb** (1.48 g, 1.79 mmol) in 10 mL of THF. The mixture was allowed to warm to room temperature, stirred for further 30 min, and then dried in vacuo (25 °C, 1 Torr, 30 min). The resulting green solid was washed with hexane (2 × 5 mL) and again dried in vacuo (25 °C, 1 Torr, 30 min). Yield: 480 mg, 40%. Crystals suitable for X-ray structural analysis could be obtained by slow cooling of a hot toluene solution to −27 °C (the final yield is ca. 20%). Anal. Calcd for $C_{33}H_{50}N_2O_2Yb$ (M_r = 679.80): C, 58.30; H, 7.41. Found: C, 57.98; H, 7.57. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): $\delta = -0.23$ (s, 1H; Yb−OH), 1.06 (d, ^3J(H,H) = 6.5 Hz, 12H; *i*Pr), 1.21 (d, ^3J(H,H) = 6.5 Hz, 12H; *i*Pr), 1.23−1.60 (m, 10H; Me, THF), 3.19 (sept, ^3J(H,H) = 6.5 Hz, 4H; *i*Pr), 3.48 (m, 4H; THF), 4.70 (s, 1H; H-backbone), 7.02−7.12 (m, 6H; aryl). ^{13}C NMR (75 MHz, C_6D_6, 20 °C): δ = 24.2 (*i*Pr-Me), 24.5 (*i*Pr-CH), 24.8 (*i*Pr-Me), 25.2 (THF), 27.6 (backbone-Me), 68.4 (THF), 94.2 (backbone-CH), 123.3 (Ar), 123.4 (Ar), 141.3 (Ar), 146.8 (Ar), 162.7 (backbone-C). IR (nujol): $\tilde{\nu}$ 1509, 1462, 1403, 1377, 1313, 1261, 1225, 1168, 1098, 1017, 923, 880, 784, 722 cm^{-1}. Mp: 198 °C (dec). Despite numerous attempts, we do not observe a resonance for the O−H vibration. In some cases we found a rather broad signal at 3423 cm^{-1} which we attribute to water impurities rather than to the OH^- stretching frequency. IR spectra of **2-Ca** showed a very weak but sharp resonance at 3697 cm^{-1}. A signal for the O−H stretching vibration in the IR spectrum of matrix-isolated $Sm(OH)_2$ was also absent. This has been attributed to the weakness of such signals as predicted by calculation.[15]

General Procedure for the Catalytic Alkene Hydrosilylation. A typical hydrosilylation experiment was carried out as follows: A dry Schlenk-tube was charged with 1,1-diphenylethylene (2.0 mmol, dried by destillation from CaH_2) and phenylsilane (2.0 mmol, used as received). After addition of the catalyst (2.5 mol % for **9** and 5 mol % for **3-Ca** and **3-Yb**), the solution was heated to 50 °C. For experiments in THF ca. 1 mL of the solvent was added before addition of the catalyst. The conversion was followed by taking samples at regular time intervals and analysis by ^{1}H NMR and GC-MS. All hydrosilylation products and initiation products have been isolated as pure compounds and have been completely characterized by ^{1}H, ^{13}C, and 2D-NMR methods as well as by GC-MS.

Crystal data for 3-Yb: measurement at −90 °C, Mo Kα, $2\theta_{max}$ = 57.2°, 9354 independent reflections (R_{int} = 0.068), 7743 reflections observed with $I > 2\sigma(I)$, monoclinic, space group $P2_1/n$, cell parameters in Table 1, formula $C_{66}H_{100}Yb_2N_4O_2$, $Z = 2$, R = 0.0282, wR2 = 0.0705, GOF = 1.08, $\rho_{max} = +0.66$ e Å^{-3}, $\rho_{min} = -0.73$ e Å^3. The bridging hydride atoms could be located and have been refined. The rest of the hydrogen atoms were placed on calculated positions and were refined in a riding mode. A cocrystallized hexane molecule was found in the difference Fourier but could not be refined satisfactorily due to disorder. The disorder was treated with the SQUEEZE procedure incorporated in PLATON.[23]

Crystal data for 4-Yb: measurement at −90 °C, Mo Kα, $2\theta_{max}$ = 53.0°, 8802 independent reflections (R_{int} = 0.056), 8116 reflections observed with $I > 2\sigma(I)$, triclinic, space group $P\bar{1}$, cell parameters in Table 3, formula $(C_{66}H_{100}Yb_2N_4O_4)(C_7H_8)$, $Z = 1$, R = 0.0475, wR2 = 0.1455, GOF = 1.11, $\rho_{max} = +1.74$ e Å^{-3}, $\rho_{min} = -1.74$ e Å^3. The crystal has been measured and refined as a nonmerohedral rotational twin with twin law (1 0 0 0.85 $\bar{1}$ 0 0.88 0 $\bar{1}$). The BASF value refined to 0.25. The cocrystallized toluene molecule is placed over a center of inversion and is consequently refined in a 50/50 disorder model. All hydrogen atoms, including the hydroxide hydrogen atoms, have been placed on calculated positions and were refined in a riding mode.

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Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 638591 (**3-Yb**) or 631498 (**4-Yb**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+44)1223-336-033. e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. We are grateful to the DFG for supporting our research within the priority program SPP1166. Prof. Dr. R. Boese and Dr. M. Kirchner are kindly acknowledged for collection of the X-ray data.

Supporting Information Available: Crystallographic data for **3-Yb** and **4-Yb** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700403D