Intramolecular (sp^3-hybridized) C−H Activation: Yttrium Alkyls versus Transient Yttrium Hydrides

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*Summary: Intramolecular sp^3-hybridized C−H activation of novel yttrium alkyl and hydrido complexes supported by bulky aminopyridinato ligands derived from deprotonated 2,6-(diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amine (Ap′-H) is reported. Reaction of YCl_3 with a 2-fold molar excess of Ap′K in THF afforded complex [$Ap'_2YCl(thf)$] (**1**). Alkylation of **1** with an equimolar amount of $LiCH_2SiMe_3$ in hexane allowed isolation of the alkylyttrium derivative [$Ap'_2YCH_2SiMe_3(thf)$] (**2**) in 65% yield. Unexpectedly treatment of complex **2** with $PhSiH_3$ (toluene, 20 °C) afforded the product of intramolecular sp^3-hybridized C−H bond activation, Ap′(Ap'_{-H})Y(THF) (**3**). Most likely a hydrid species is formed in the course of this reaction, which undergoes rapid C−H activation since **3** is formed from **2** directly about 500 times slower than in the presence of 1 equiv of $PhSiH_3$. Molecular structures of complexes **2** and **3** have been confirmed by X-ray crystal structure analysis.*

Even after a lapse of twenty-five years since the pioneering works on the synthesis of the first molecular rare earth metal hydrido complexes,[1] these compounds still attract considerable attention[2] and remain one of the most promising classes of compounds for various catalytic applications.[3] Enhanced reactivity of hydrido complexes, which allows even C−F bond activation,[4] gives evidence of their high potential in stoichiometric reactions. Until very recently rare earth metal hydrides were represented exclusively by sandwich-[2] and half-sandwich-type ("constrained geometry")[5] complexes. Remarkable progress has been made in this field, and the formerly challenging monomeric[4] and dihydrido[6] species became a reality. The hydride supported by benzamidinate ligands {[PhC($NSiMe_3$)$_2$]$_2$Y(μ-H)}$_2$[7] synthesized by Teuben and co-workers in 1993 was the first and for a long time the sole example of a cyclopentadienyl-free rare earth metal hydrido complex. The recent advances in rare earth metal hydrido chemistry[8] are linked to application of novel types of coordination environments: bis(silylamido)biphenyl,[9a] calyx-tetrapyrrol,[9b,c] salicylaldimine,[9d,e] tris(pyrazolil)borate.[9f] However, to date, "post-metallocene" hydrides still remain a rarity. Recently we reported the synthesis of the series of hydrido lanthanide complexes supported by bulky tetrasubstituted guanidinate ligands, which have demonstrated high catalytic activity in olefin polymerization.[10] Sterically demanding aminopyridinato ligands[11] were also successfully used as a suitable coordination environment for stabilization of monomeric lanthanide species. Both guanidinate and aminopyridinate frameworks have a common feature: a chelating monoanionic planar NCN moiety. In order to investigate the influence of ancillary ligation on the reactivity of the Y−H and Y−C bonds, we decided to employ the aminopyridinate ligation system for synthesis of alkyl and hydrido complexes. Herein we report on the exiting outcomes of the attempts to synthesize alkyl and hydrido yttrium complexes supported by the bulky aminopyridinate ligand system.

Bulky 2,6-(diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amine (Ap′-H) (Scheme 1)[11a,b] was used as the ligand

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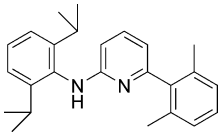
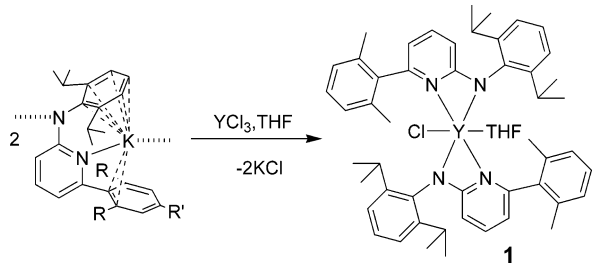
Scheme 1. Bulky Amidopyridinato Ligand (Ap′H)



Scheme 2. Synthesis of 1



precursor for preparation of the yttrium bis(aminopyridinato) chloride, alkyl, and hydride complexes.

Reaction of anhydrous YCl_3 with a 2-fold molar excess of Ap′K in THF at 50 °C afforded complex [Ap′$_2$YCl(thf)] (**1**), which was isolated after recrystallization from THF−hexane mixtures in 87% yield as yellow crystals (Scheme 2). No ate-complex formation was observed.

Complex **1** is well soluble in THF and toluene and sparingly soluble in hexane. Clear, yellow crystals of complex **1** suitable for X-ray crystal structure investigation were obtained by slow condensation of hexane into a THF solution at room temperature. The ^{1}H and ^{13}C{^{1}H} NMR data of complex **1** in C_6D_6 at 20 °C show the expected sets of resonances due to the aminopyridinate fragment and the coordinated THF molecule. The ^{1}H NMR signals of the THF methylene protons in **1** appear as broad singlets, reflecting labile coordination.

Alkylation of complex **1** with $LiCH_2SiMe_3$ was carried out in hexane at 20 °C and resulted in the formation of the alkylyttrium derivative [Ap′$_2$YCH$_2$SiMe$_3$(thf)] (**2**) (Scheme 2), which was isolated after recrystallization from hexane as yellow, moisture- and air-sensitive crystals in 65% yield.

In the ^{1}H NMR spectrum of complex **2** at 20 °C (C_6D_6) the hydrogen atoms of the methylene group attached to the yttrium atom appear as a multiplet ([AB system], $\delta = -0.39$ ppm) indicative of two diastereotopic CH_2 protons. In the ^{13}C{^{1}H} NMR spectrum the appropriate carbon gives rise to a doublet at 43.3 ppm ($^2J_{YC} = 43$ Hz). A singlet at 0.20 ppm in the ^{1}H NMR spectrum corresponds to the methyl protons of the $SiMe_3$ group. It is worthy of note that the signal sets corresponding to the aminopyridinate fragments in the ^{1}H NMR spectra of **1** and **2** are essentially different. Thus in the ^{1}H NMR spectrum of complex **1** the protons of the methyl substituents appear as a singlet at 2.20 ppm and the methyl protons of isopropyl groups appear as a doublet ($^3J_{H-H} = 7.0$ Hz) at 1.10 ppm. On the other hand, the same groups of protons in the ^{1}H NMR spectrum of **2** give rise to two singlets (1.57 and 2.24 ppm) and a complex multiplet in the region 0.97−1.37 ppm, respectively. Introduction of the sterically demanding CH_2SiMe_3 substituent into the coordination sphere of the yttrium results in slowing of ligand exchange processes and phenyl group rotation of the amidopyridinato ligands due to increased hindrance. The ^{1}H NMR signals of the THF methylene protons in **1** appear as broad singlets, reflecting labile coordination.

Crystallization of **2** by slow cooling of the concentrated toluene−hexane solution to −20 °C resulted in single crystals containing one molecule of toluene per one molecule of [Ap′$_2$-YCH$_2$SiMe$_3$(thf)]. The molecular structure of **2** is shown in

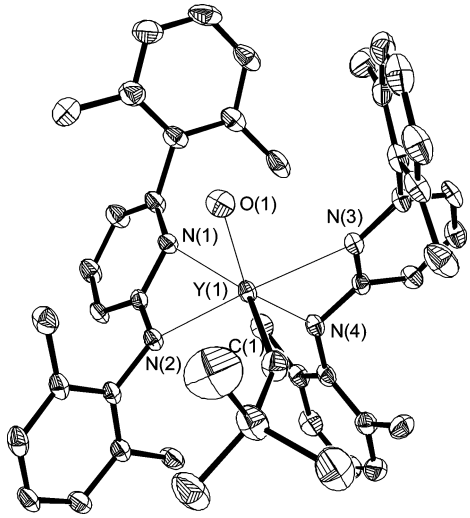


Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of [Ap′$_2$YCH$_2$SiMe$_3$(thf)] (**2**) [$a = 12.6840(6)$ Å, $b = 12.8250(8)$ Å, $c = 19.2775(11)$ Å, $\alpha = 105.398(5)°$, $\beta = 91.182(4)°$, $\gamma = 91.712(5)°$, $R_1 = 0.0706$, wR_2 (all data) $= 0.1522$] showing the numbering scheme. Hydrogen atoms and carbon atoms of THF and methyl radicals of isopropyl groups are omitted for clarity. Selected bond distances [Å] and angles [deg]: C(1)−Y(1) 2.342(5), N(1)−Y(1) 2.554(3), N(2)−Y(1) 2.301(3), N(3)−Y(1) 2.487(3), N(4)−Y(1) 2.344(3), O(1)−Y(1) 2.343(3), N(2)−Y(1)−C(1) 97.17(15), N(2)−Y(1)−N(4) 101.80(12), C(1)−Y(1)−N(4) 101.27(15), C(1)−Y(1)−O(1) 93.27(15), N(4)−Y(1)−O(1) 145.32(11), N(2)−Y(1)−N(3) 154.30(11), C(1)−Y(1)−N(3) 99.94(14), N(4)−Y(1)−N(3) 56.10(11), O(1)−Y(1)−N(3) 90.62(11), N(2)−Y(1)−N(1) 55.77-(11), C(1)−Y(1)−N(1) 150.88(14), N(4)−Y(1)−N(1) 95.40(11).

Figure 1. An X-ray diffraction study has revealed that complex **2** is monomeric. The coordination environment of the yttrium atom is set up by four nitrogen atoms of two chelating aminopyridinato ligands, one carbon atom of the alkyl group, and one oxygen atom of the THF molecule and can be considered as a strongly distorted octahedron. The yttrium atom coordination number in complex **2** is 6.

The Y−C bond length in complex **2** (2.342(5) Å) is comparable to the values reported for related compounds [[*t*-BuC$_6$H$_3$(CH=N)C$_6$H$_3$-*i*-Pr$_2$]$_2$YCH$_2$SiMe$_2$Ph] (2.384(2) Å),[13a] [(Me$_3$C$_6$H$_2$N=PPh(C$_6$H$_4$)(C$_6$H$_4$)NC$_6$H$_3$-*i*Pr$_2$)YCH$_2$SiMe$_3$(thf)] (2.418(5) Å),[13b] [Me$_2$Si(C$_5$H$_3$-*t*-Bu)$_2$YCH$_2$SiMe$_3$(thf)] (2.399-(2) Å),[13c] and [O{(CH$_2$)$_2$C$_9$H$_6$}$_2$YCH$_2$SiMe$_3$] (2.376(8), 2.35-(1) Å)[13d] taking into account the difference of yttrium ionic radii at different coordination numbers.[13e] The metric parameters within the Ap′$_2$Y fragment are indicative of a localization of the anionic function of the ligand at the amido N atom.

The most common synthetic route to hydrido complexes is σ-bond metathesis reaction of a parent alkyl on treatment with dihydrogen[3d,f] or phenylsilane.[14] In order to prepare a hydrido yttrium complex supported by amidopyridinato ligands, we have carried out reaction of equimolar amounts of complex **2** and $PhSiH_3$ in toluene at 20 °C.

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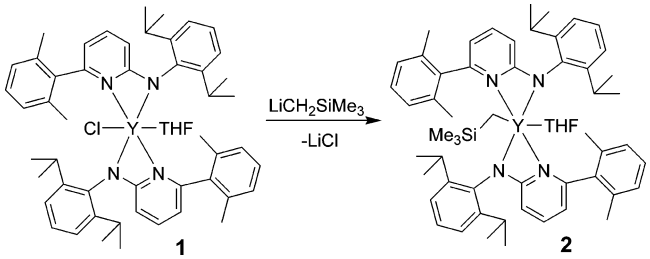
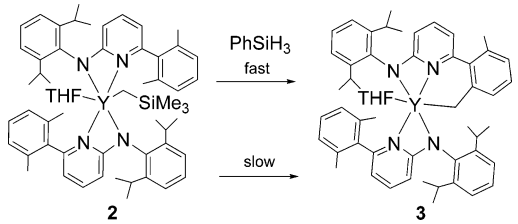
Scheme 3. Synthesis of 2



Scheme 4. Synthesis of the Intramolecular C−H Bond Activated Product 3 via Hydride Formation (above) and Directly from the Alkyl (below)



Unexpectedly, instead of the product of σ-bond metathesis reaction, the complex resulting from intramolecular C−H bond activation was isolated, [Ap′(Ap$_{-H}$′)Y(thf)] (**3**) (Scheme 4), in 72% yield. Complex **3** is also formed from **2** via standing in, for instance, a benzene solution (Scheme 4). This process needs a couple of weeks at room temperature. The yellow, crystalline compound **3** is highly moisture- and air-sensitive. Complex **3** is soluble in THF and toluene and sparingly soluble in aliphatic hydrocarbons. Transparent yellow crystals suitable for single-crystal X-ray diffraction study of **3** were obtained by slow cooling of a concentrated heptane solution to −20 °C. The molecular structure of **3** is depicted in Figure 2 and has revealed that complex **3** is monomeric, having the coordination number 6. The yttrium atom coordination environment can be classified as a strongly distorted octahedron. Unlike the parent alkyl compound **2**, one aminopyridinato ligand of complex **3** is tridentate due to metalation of the methyl group of one of the $Me_2C_6H_3$ fragments with formation of the new Y−C σ-bond.

The bond length between yttrium and the "benzylic" carbon atom in **3** (2.420(11) Å) is longer than that in parent alkyl complex **2** (2.342(5) Å), but shorter than the values previously reported for Y−C bonds in the benzylic complexes [$(C_5Me_5)_2$-YCH_2Ph(thf)] (2.484(6) Å)[15a] and [{PhC(NSiMe$_3$)N(CH$_2$)$_3$-NMe$_2$}$_2$YCH$_2$Ph] (2.487(6)) Å.[15b] The environment of the C(1) is slightly distorted; the value of the angle Y(1)−C(1)−C(2) is 112.2(7)°. The aminopyridinato ligands in complex **3** are coordinated to the yttrium atom in different ways. The type of coordination of the bidentate Ap′ ligand is similar to that observed in related complexes **2**: one short Y−N bond with the amido nitrogen atom (2.289(6) Å) and one long with the nitrogen atom of the pyridine fragment (2.430(7) Å). In the tridentate Ap$_{-H'}$ ligand, formation of the Y−C bond dramatically influences the bonding situation. The covalent bond between yttrium and the amido nitrogen atom (2.432(8) Å) becomes longer than the coordination bond between yttrium and the pyridine nitrogen atom (2.338(7) Å); hence a switch from the amidopyridine to the aminopyridinate form is observed.[16]

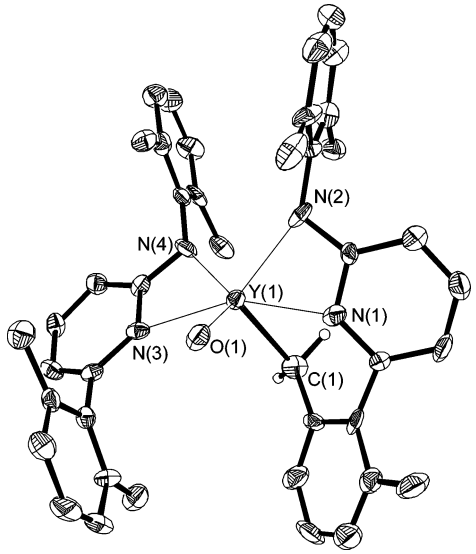


Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of [Ap′(Ap$_{-H}$′)Y(thf)] (**3**) [a = 13.2877(10) Å, b = 18.5068(12) Å, c = 20.1473(16) Å, β = 105.196(6)°, R_1 = 0.0646, wR_2 (all data) = 0.1219] showing the numbering scheme. Hydrogen atoms, carbon atoms of THF, and methyl radicals of isopropyl groups are omitted for clarity. Selected bond distances [Å] and angles [deg]: C(1)−Y(1) 2.420(11), N(1)−Y(1) 2.338(7), N(3)−Y(1) 2.430(7), N(2)−Y(1) 2.431(8), N(4)−Y(1) 2.289(6), O(1)−Y(1) 2.321(6), N(4)−Y(1)−N(1) 144.7(2), N(4)−Y(1)−N(3) 57.3(2), N(1)−Y(1)−N(3) 154.7(2), N(4)−Y(1)−N(2) 100.1(2), N(1)−Y(1)−N(2) 56.0(2), N(3)−Y(1)−N(2) 147.6(2), Y(1)−C(1)−C(2)−112.2(7).

Moreover Y−C bond formation influences mutual orientation of the 2,6-dimethylphenyl and pyridyl fragments. In the bidentate ligand the planes of these fragments adopt a near-orthogonal orientation (the value of the dihedral angle is 96.0°), while in the tridentate ligand the dihedral angle between these planes decreases to 47.4°.

Inter- and intramolecular activation of sp^2- and sp^3-hybridized C−H bonds by cyclopentadienyl[17,5b] and cyclopentadienyl-free[7a,9e,17f,18] lanthanide alkyl and hydride complexes is described. Intermolecular activation of C−H bonds of methyl groups of permethylated cyclopentadienyl rings was observed under thermolysis conditions, for instance, of the dimeric hydrido complex [$(C_5Me_5)_2$YH]$_2$.[19] The formation of complex **3** can result from three different reactions pathways: First, direct decomposition of complex **2** (Scheme 5, (I)) can occure. The second possible pathway is toluene C−H activation and

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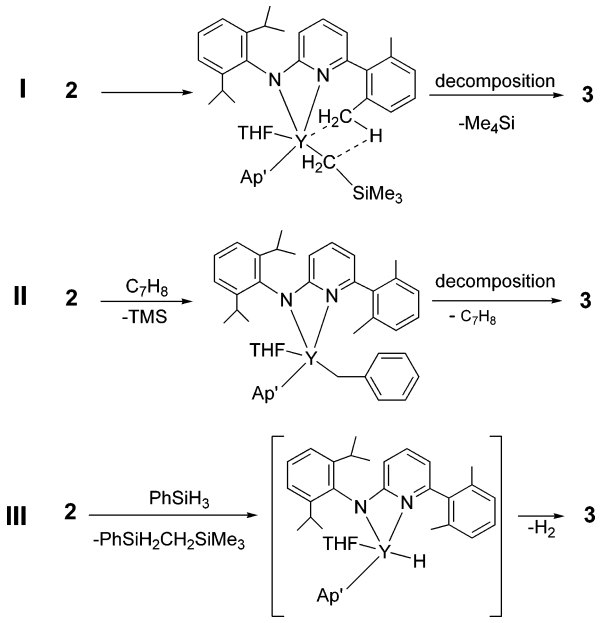
Scheme 5. Possible Pathways to Convert 2 into 3



subsequent decomposition of the yttrium benzyl complex (Scheme 5, (II)). Third such a process can include a σ-bond metathesis reaction on treatment of **2** with $PhSiH_3$, formation of highly reactive hydride species, followed by metalation of a methyl group (Scheme 5, (III)).

In order to understand which reaction is responsible for the formation of complex **3**, the decomposition of **2** and disappearance of complex **2** in the presence of $PhSiH_3$ were investigated by NMR spectroscopy. Both reactions were carried out in toluene-d_8 at 296 K. Complex **2** was rather thermally robust. Its decomposition was studied by monitoring the decrease of the integral intensity of the signal corresponding to the methyl protons of the silylalkyl group attached to the yttrium atom. The ^{1}H NMR-monitoring detected Me_4Si formation in the course of the reaction. The results are presented in Figure 3 (top.).

A linear decrease of $\ln(C/C_0)$ with time was observed, which is consistent with a rate law involving first-order dependence on **2** (Figure 3, top). The rate constant was found to be $k = 0.0038$ h^{-1}, and a half-time of reaction of about 181 h was observed. Moreover, complex [Ap′$_2$YCH$_2$Ph(thf)] (**4**), the expected intermediate of the solvent metalation route, was synthesized independently. Complex **4** turned out to be a stable alkyl compound since no decomposition was observed in benzene-d_6 solution at room temperature during 2 h. These studies indicate that the decomposition of complex **2** does not involve metalation of the solvent (alkyl toloyl exchange) due to the observed clear reaction order.

Reaction of complex **2** with an equimolar amount of $PhSiH_3$ was studied by monitoring the decrease of the integral intensity of the signal corresponding to the methyl protons of the silylalkyl group attached to the yttrium atom in the ^{1}H NMR spectrum of **2**. The results of these studies are presented in Figure 3 (bottom). The disappearance of **2** in the presence of $PhSiH_3$ is much faster than that in the case of decomposition of **2** at the same temperature without $PhSiH_3$. The data do not follow a clear reaction order, and the time for consumption of 50% of complex **2** is about 22 min. The ^{1}H NMR spectra did not indicate the presence of monomeric or dimeric yttrium hydride species in the reaction mixture. This may serve as evidence that the intermediate hydride species formed are highly reactive and rapidly undergo an intramolecular metalation, which leads to the formation of complex **3**. By comparing the half-time periods of the C−H activation reaction observed for the

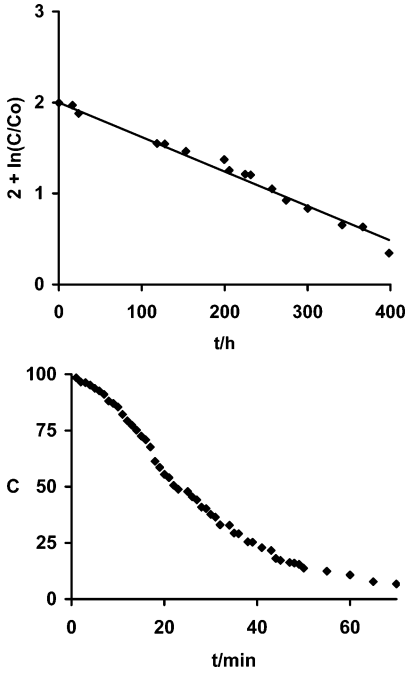


Figure 3. Top: First-order kinetic plot for the decomposition of **2** (296 K, toluene-d_8). Bottom: Plot of concentration of complex **2** versus t (h) in the presence of $PhSiH_3$ (296 K, toluene-d_8, $C(\mathbf{2})_0 = 0.062$ mol/L, $C(PhSiH_3)_0 = 0.062$ mol/L).

alkyl and for the transient hydride it can be roughly estimated that a C−H activation involving an Ln-hydride can be more than 500 times faster than for the corresponding Ln-alkyl reaction. It might be even faster since the monitoring studies did not indicate the presence of a hydride species, and thus the hydride formation seems to be the rate-limiting step, which means the C−H activation of the hydride is faster than derived from the half-time period comparison. It only appears as slow since the hydride formation is slow. Further work on this subject is being actively pursued as well as investigations of this C−H activation chemistry at other rare earth or group 3 metals in order to allow "interlanthanide" comparison.

Several conclusions can be drawn from this study. The bulky aminopyridinato ligand framework has been shown to be well-suited for the synthesis of isolable yttrium alkyl species. These alkyls undergo a very slow intramolecular C−H activation at a sp^3-hybridized carbon at room temperature. Corresponding hydrides, generated by the reaction of the alkyl with $PhSiH_3$, undergo an intramolecular metalation reaction very fast at room temperature. Intramolecular sp^3-hybridized C−H activation of a hydride can be more than 500 times faster than that of an alkyl.

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Supporting Information Available: Detailed information about the synthesis and characterization of the lanthanide complexes described here and crystallographic details of the structures determined by X-ray crystal structure analysis are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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