$[\eta^5{:}\eta^1\text{-}(3,6\text{-}t\mathrm{Bu_2Flu})\mathrm{SiMe_2N}t\mathrm{Bu}]\mathrm{Y}(\eta^1\text{-}\mathrm{NC_5H_6})(\mathrm{py})_2$: A 1,4-Hydride-Addition Product to Pyridine that Provides Evidence for the First Fluorenyl(hydrido)metal (Group 3) Complex

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Keywords: Fluorenyl / Hydrides / Insertion / Pyridine / Yttrium

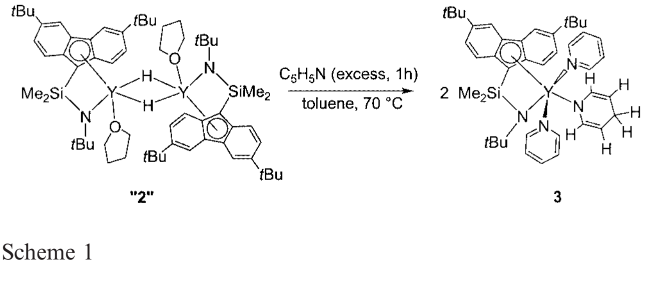
Reaction of pyridine with the "constrained geometry" fluorenyl(hydrido)yttrium complex $\{[(3,6\text{-}t\mathrm{Bu_2Flu})\mathrm{SiMe_2N}t\mathrm{Bu}]\mathrm{Y}(\mathrm{H})(\mathrm{THF})\}_2$ selectively gives the 1,4-addition product $[\eta^5{:}\eta^1\text{-}(3,6\text{-}t\mathrm{Bu_2Flu})\mathrm{SiMe_2N}t\mathrm{Bu}]\mathrm{Y}(\eta^1\text{-}\mathrm{NC_5H_6})(\mathrm{py})_2$, which was characterized by single-crystal X-ray diffraction and ^{1}H and ^{13}C NMR spectroscopy.

Introduction

Activation of C−H bonds by (hydrido)metal (group 3) complexes is well known for a wide variety of substrates, including aromatic heterocycles.[1] In particular, $[(\mathrm{C_5Me_5})_2\mathrm{Ln(H)}]_2$ (where Ln = Lu,[2] Sc,[3] Y[4]) and $[(\mathrm{C_5H_4R})_2\mathrm{Y(H)(THF)}]_2$ (where R = H, Me)[5] readily react with 1 equiv. of pyridine (py) leading to *ortho*-metalated pyridine complexes, $[(\mathrm{C_5R_5})_2\mathrm{Ln}(\eta^2\text{-}(C,N)\text{-}\mathrm{C_5H_4N})]$. In the presence of an excess of a strong Lewis base, such as THF or pyridine, the released dihydrogen may initiate the reductive transformation of the 2-pyridyl complexes to 1,2-hydride-addition products, eventually followed by isomerization to the 1,4-addition products upon heating.[4] Polar solvents promote direct addition of Ln−H to the pyridine ring.[5] Several yttrium hydrides bearing non-cyclopentadienyl ligands have been found to undergo such an insertion, giving directly both 1,2- and 1,4-addition products.[6] The structure of the 1,2-addition product, $\{[6,6'\text{-}\mathrm{Me_2}\text{-}(\mathrm{C_6H_3})_2]\text{-}(2,2'\text{-}\mathrm{NSiMe_2}t\mathrm{Bu})_2\}\mathrm{Y}(\eta\text{-}\mathrm{NC_5H_6})(\mathrm{py})_2$, was established by X-ray diffraction.[7] In this contribution, we report the first structurally characterized example of a 1,4-addition pyridine product, which provides indirect evidence for the formation of the first (hydrido)metal (group 3) complex supported by a fluorenyl ligand.

Results and Discussion

Recently we have reported on the synthesis and characterization of the first "constrained geometry" (alkyl)yttrium complex $[\eta^3{:}\eta^1\text{-}(3,6\text{-}t\mathrm{Bu_2Flu})\mathrm{SiMe_2N}t\mathrm{Bu}]\mathrm{Y}(\mathrm{CH_2SiMe_3})(\mathrm{THF})_2$ (**1**), stabilized by a fluorenyl-amido ligand.[8] In the course of these studies, we found that **1** reacts equally with $\mathrm{H_2}$ or $\mathrm{PhSiH_3}$ under ambient conditions (25 °C, 1 atm) to generate a yellow microcrystalline solid in high yield. Considering this reactivity and consistent with elemental analysis, the product was formulated as the putative hydride $\{[(3,6\text{-}t\mathrm{Bu_2Flu})\mathrm{SiMe_2}\text{-}\mathrm{N}t\mathrm{Bu}]\mathrm{Y(H)(THF)}\}_n$ (**2**). However, the surprising insolubility of the latter in common organic solvents (aromatic hydrocarbons, chlorinated solvents, THF), despite the presence of two *tert*-butyl substituents on the fluorenyl ligand, prevented its complete authentication. Complex **2** does not react with an equimolar amount of pyridine after one week at 25 °C but it completely dissolves in a toluene solution at 70 °C after 1 h in the presence of a 20-fold excess of $[\mathrm{H_5}]$pyridine (vs. Y) (see Scheme 1). After evaporation of the solution and extraction of the residue with pentane, the new "constrained geometry" (amido)yttrium complex, **3**, was isolated in 69 % yield as an orange-brown crystalline material.



Scheme 1

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^1H and ^{13}C NMR spectroscopic data establish that **3** is the sole product of the reductive 1,4-addition of pyridine to the hydrido complex **2**. The ^1H NMR spectrum of **3** ([D$_6$]benzene, 25 °C) displays one set of sharp resonances consistent with C_v-symmetry that include one singlet and two doublets from the three pairs of equivalent fluorenyl protons, one singlet from the SiMe$_2$ moiety, and one singlet from each of the *tert*-butyl(fluorenyl) and *tert*-butyl(amido) groups. The 1,4-dihydropyridyl fragment is characterized by a doublet for the 2,6-protons (δ = 6.35 ppm, $^3J_{H,H}$ = 6.9 Hz), a multiplet for the 3,5-protons (δ = 4.59 ppm) and a broad singlet for the 4-methylene group (δ = 3.61 ppm).[5] The signals from the coordinated-pyridine molecules are broad at room temperature, which illustrates their fluxional behavior and suggests that they dissociate in solution. On the other hand, there is no evidence for exchange of the coordinated-pyridine molecules with the 1,4-dihydropyridyl fragment, which indicates that the reaction is not reversible at this temperature on the NMR time-scale.

An X-ray-diffraction study confirmed the structure of complex **3** and the coordination of two pyridine molecules in the solid-state (see Figure 1). The formal 18-electron yttrium center is coordinated in a distorted square-pyramidal geometry to four nitrogen atoms and to the centroid of the five-membered ring of the fluorenyl moiety, which occupies the apical position. Complex **3** and the parent alkyl complex **1** have a very similar pseudo-five-coordinate geometry: the THF molecules and the alkyl group in **1** are replaced in **3** by pyridine molecules and by a 1,4-dihydropyridinyl group, respectively. However, the coordination modes of the fluorenyl ligands in the solid-state structures are quite different; that is, in the alkyl complex **1**, the fluorenyl moiety is coordinated in an unusual non-symmetric, exocyclic η^3-coordination mode that involves the bridgehead atom and a neighboring atom of the central five-membered cycle, and the adjacent carbon atom of a phenyl ring.[8] In contrast, the molecular structure of **3** features a symmetric η^5-coordination. This observation is rather surprising considering that pyridine is a stronger base than THF and, therefore, should favor reduced hapticity of the fluorenyl moiety. This difference evidences that the variety of flexible coordination modes of fluorenyl ligands that we recently observed in a series of group 3 metal and lanthanide complexes[8,9] is strikingly dependent on minute electronic and steric factors. The solid-state structure of **3** has a plane of symmetry (non-crystallographic) that embraces the Flu(centroid) and the C(9), N(12), Si(1) and Y(1) atoms as well as the plane of the 1,4-dihydropyridine cycle. The bite angle Flu$_{cent}$−Y(1)−N(12) is 97.36° and resembles the corresponding Cp$_{cent}$−Y−N angles (97.1−97.8°) observed in half-sandwich yttrium complexes supported by Cp-amido ligands.[10] The average Y−C (C9, C9a, C8a, C4a, C4b) distance in **3** [2.701(2) Å] is in the range of values 2.646−2.719 Å, observed for other yttrium complexes with silylene-substituted fluorenyl fragments.[11] Similarly, the Y(1)−N(12) bond length of 2.232(2) Å is in the range of 2.208−2.253 Å, found in related "constrained geometry" Cp(amido)yttrium complexes.[10,12] The Y(1)−N(21) bond length between the yttrium and the nitrogen atom of the 1,4-dihydropyridine fragment [2.302(2) Å] is in agreement with the values observed in other yttrium complexes bearing terminal amido groups.[7,13] The bonds in the dihydropyridine fragment (see b in Figure 1) indicate reduction of pyridine via 1,4-insertion,[14] that is, the bond lengths C(22)−C(23) [1.332(3) Å] and C(25)−C(26) [1.338(3) Å] are significantly shorter than the other two C−C bonds in the ring [C(23)−C(24) 1.510(4), C(24)−C(25) 1.484(4) Å]. Also, the angle C(23)−C(24)−C(25) of 108.2(2)° is indicative of the sp^3-hybridization of the C(24) carbon atom.

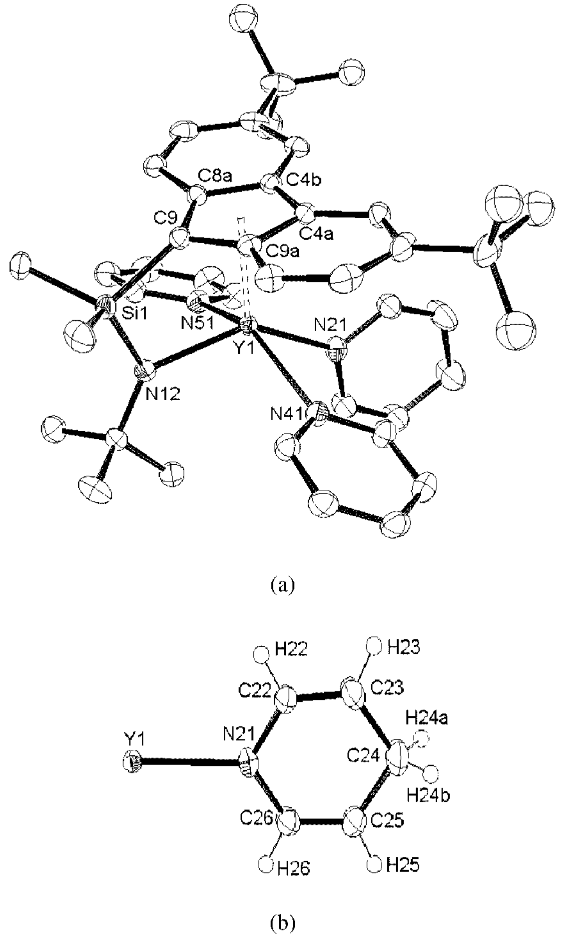

Figure 1. (a) ORTEP drawing of the molecular structure of **3**; thermal ellipsoids are drawn at the 50 % probability level; hydrogen and disordered carbon atoms from *tert*-butyl groups are omitted for the sake of clarity; selected bond lengths (Å) and angles (°) Y(1)−N(12) 2.2319(17), Y(1)−N(21) 2.3015(17), Y(1)−N(41) 2.5325(17), Y(1)−N(51) 2.5383(17), Y(1)−C(9) 2.6021(19), Y(1)−C(9A) 2.6883(18), Y(1)−C(8A) 2.6946(19), Y(1)−C(4B) 2.7588(19), Y(1)−C(4A) 2.7635(18), N(12)−Si(1)−C(9) 99.37(8), N(41)−Y(1)−N(51) 146.28(6), N(21)−Y(1)−N(41) 79.01(6), N(21)−Y(1)−N(51) 78.94(6), N(12)−Y(1)−N(21) 140.10(6); (b) view of the reduced pyridine fragment in **3**; selected bond lengths (Å) and angles (°) N(21)−C(22) 1.381(3), N(21)−C(26) 1.390(3), C(22)−C(23) 1.332(3), C(23)−C(24) 1.510(4), C(24)−C(25) 1.484(4), C(25)−C(26) 1.338(3), C(22)−C(23)−C(24) 123.3(2), C(23)−C(24)−C(25) 108.2(2), C(24)−C(25)−C(26) 123.3(2).

Two possibilities may account for the selective formation of the 1,4-hydride-addition product **3**: (i) although NMR monitoring showed no evidence for the formation of a transient 1,2-addition product during the reaction course, the latter may rapidly isomerize to **3** due to the enforced conditions, which are required for completion of the reaction;[5,15] (ii) the reaction may involve direct 1,4-addition: nucleophilic attack on both the 2- and 4-positions is well known for pyridine rings.[16]

In conclusion, the isolation of the 1,4-addition product **3** brings indirect evidence of the hydrido nature of the complex formed by hydrogenolysis of the "constrained geometry" (fluorenyl-amido)yttrium alkyl complex **1**. Although its molecular structure and the reasons for its insolubility remain to be determined, complex **1** is, to the best of our knowledge, the first example of a hydrido complex of a group 3 metal supported by a fluorenyl ligand. The scope of this insertion reaction is currently under investigation.

Experimental Section

Crystallographic Data for 3: $C_{42}H_{55}N_4SiY$, $M = 732.90$, monoclinic, $T = 100$ K, space group $C2/c$, $a = 23.3709(2)$, $b = 13.03550(10)$, $c = 26.4358(2)$ Å, $\alpha = 90$, $\beta = 104.75$, $\gamma = 90°$, $V = 7788.33(11)$ Å^3, $Z = 8$, $D_c = 1.250$ g·cm^{-3}, μ(Mo-K_α) = 1.562 mm^{-1}; 65290 reflections collected, 12419 unique ($R_{\mathrm{int}} = 0.0504$), full-matrix least-squares on F^2 refinement, $R_1 = 0.0442$ [$I > 2\sigma(I)$], $wR_2 = 0.1094$ (all data). An orange crystal of dimensions 0.32 × 0.30 × 0.13 mm was coated in oil, mounted on a fibre and X-ray-diffraction data were collected using a Nonius−KappaCCD diffractometer employing CCD scans to cover reciprocal space up to 31.03° with 99.7 % completeness. Integration of raw data yielded a total of 65290 reflections, merged into 12412 unique reflections with $R_{\mathrm{int}} = 0.0504$ after applying Lorentz, polarization and absorption correction. The structure was solved by Patterson methods using SHELXS-97.[17] Atomic positions and displacement parameters, on the anisotropic level for all non-hydrogen atoms, were refined using full-matrix least-squares based on F^2 using SHELXL-97.[17] Refinement of 446 parameters using all reflections converged at $R_1 = 0.0442$, $wR_2 = 0.1094$, with the highest residual electron-density peak of 1.2 Å^3. CCDC-219360 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of 3: A solution of pyridine (0.668 g, 8.45 mmol, 20 equiv. vs. Y) in toluene (2 mL) was added to a suspension of **2** (0.240 g, 0.211 mmol of the dimer) in toluene (10 mL). The reaction mixture was stirred at 70 °C until complete dissolution of **2** was achieved (ca. 60 min). The resulting orange solution was evaporated under vacuum to give a brown residue, which was extracted with pentane (3 × 10 mL) to yield complex **3** as brown-orange crystals (0.210 g, 69 %) from combined pentane extracts. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): $\delta = 8.36$ (br. m, 4 H, 2,6-H, py), 8.08 (s, 2 H, 4,5-H, Flu), 7.93 (d, $^3J_{\mathrm{H,H}} = 8.4$ Hz, 2 H, 1,8-H, Flu), 6.88 (d, $^3J_{\mathrm{H,H}} = 8.3$ Hz, 2 H, 2,7-H, Flu), 6.78 (br. m, 2 H, 4-H, py), 6.51 (br. m, 4 H, 3,5-H, py), 6.35 (d, $^3J_{\mathrm{H,H}} = 6.9$ Hz, 2 H, NCHCHCH$_2$), 4.59 (m, 2 H, NCHCHCH$_2$), 3.61 (s, 2 H, NCHCHCH_2), 1.35 (s, 9 H, NCCH_3), 1.31 [s, 18 H, CCH_3(Flu)], 1.15 (s, 6 H, SiCH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C): $\delta = 150.8$ (C-2,6, py), 140.8 (C-3,6, Flu), 137.4 (C-4, py), 135.9 (NCHCHCH$_2$), 126.3 (C-10,13, Flu), 123.5 (C-3,5, py), 123.4 (C-2,7, Flu), 123.1 (C-11,12, Flu), 121.8 (C-1,8, Flu), 116.8 (C-4,5, Flu), 94.7 (NCHCHCH$_2$), 82.8 (C-9, Flu), 54.3 (NCCH$_3$), 35.3 (NCCH$_3$), 33.7 (Flu-CCH$_3$), 31.9 (Flu-CCH$_3$), 24.9 (NCHCHCH$_2$), 7.4 (SiCH$_3$) ppm. $C_{42}H_{55}N_4SiY$ (732.92): calcd. C 68.83, H 7.56, N 7.64; found C 67.92, H 7.00, N 7.32.

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