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Notes

Formation of a Dicationic Yttrium η^2-Pyridyl Complex from an Yttrium Methyl Dication by C−H Activation of Pyridine

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Summary: The activation of pyridine by the dicationic yttrium methyl complex $[YMe(THF)_6]^{2+}[BPh_4]^-{}_2$ *to give the structurally characterized cationic rare-earth metal* η^2*-pyridyl complex* $[Y\{\eta^2\text{-}(C,N)\text{-}C_5H_4N\}(C_5H_5N)_6]^{2+}[BPh_4]^-{}_2$ *is reported. The pyridyl complex adopts a pentagonal bipyramidal coordination geometry with the pyridyl ligand in the axial position; kinetic data demonstrate that this complex forms via the formation of the substitution product* $[YMe(C_5H_5N)_6]^{2+}[BPh_4]^-{}_2$*.*

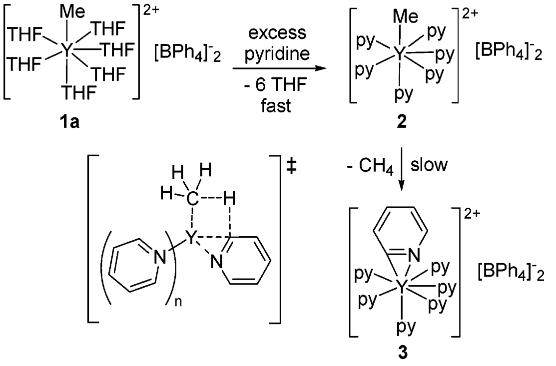
Introduction

C−H activation processes mediated by transition metals have been investigated in great depth.[1] In particular, Bercaw et al. have established that C−H bond activation reactions using metals with an f^xd^0 electron configuration proceed via σ-bond metathesis.[2] In the context of developing the chemistry of cationic organometallic rare-earth metal complexes,[3] we have recently reported cationic yttrium alkyl complexes $[YMe_{2-n}(solv)_x]^{n+1}$ ($n = 0, 1$) with borate anions $[B(C_6X_5)_4]^-$ (X = H, F).[4] Dicationic complexes with perfluorinated anions are precatalysts for ethylene[4a] and 1,3-diene[4b] polymerization. Furthermore, there is NMR spectroscopic evidence for the activation of pyridine-d_5 by the dicationic yttrium mono(alkyl) complex $[Y(CH_2SiMe_3)(12\text{-crown-4})(THF)_3]^{2+}[BPh_4]^-{}_2$.[5] We report here that the dicationic rare-earth metal methyl complexes $[LnMe(THF)_x]^{2+}[BPh_4]^-{}_2$ (Ln = Sc: $x = 5$; Ln = Lu, Y: $x = 6$; Ln = Nd: $x = 7$) react with pyridine via C−H activation to give, in the case of yttrium, the first structurally characterized cationic rare-earth metal pyridyl complex $[Y\{\eta^2\text{-}(C,N)\text{-}C_5H_4N\}(C_5H_5N)_6]^{2+}[BPh_4]^-{}_2$.

Results and Discussion

When the dicationic complex $[YMe(THF)_6]^{2+}[BPh_4]^-{}_2$ (**1a**) was dissolved in pyridine and immediately precipitated by the addition of excess pentane, ^{1}H NMR analysis in pyridine-d_5 confirmed that the THF ligands had been completely replaced by pyridine to give the THF-free colorless complex $[YMe(C_5H_5N)_6]^{2+}[BPh_4]^-{}_2$ (**2**, Scheme 1). Except for the absence of free THF, the ^{1}H NMR data for **2** in pyridine-d_5 are identical to those arising from **1a** in pyridine-d_5.[4] The greater affinity of rare-earth metal centers for pyridine with respect to Lewis bases with oxygen donors has already been noted for neutral cyclopentadienyl complexes.[6] Rapid exchange of neutral co-ligands in a polar medium is expected for a large, weakly polarizing metal ion with no appreciable crystal field stabilization such as lanthanides and is consistent with complexation−dissociation studies of lanthanide ions in water.[7]

Scheme 1



The dicationic pyridyl complex $[Y\{\eta^2\text{-}(C,N)\text{-}C_5H_4N\}(C_5H_5N)_6]^{2+}[BPh_4]^-{}_2$ (**3**) was isolated as a colorless crystalline solid in 35% yield when **1a** was dissolved in a 2:1 mixture of pyridine and pentane and left standing at room temperature for 5 days (Scheme 1). The solution gradually changed from colorless to deep red over this time.[8]

X-ray data collected from **3** revealed that the pyridyl ligand coordinates in an η^2-fashion to the metal center and confirmed the coordination of six pyridine ligands. There are no close ion pair interactions in the solid state. The crystal contains one free molecule of pyridine in the lattice; the stoichiometry $\mathbf{3}\cdot C_5H_5N$

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indicated by the X-ray data was confirmed by elemental analysis. The seven-coordinate metal center adopts pentagonal bipyramidal coordination geometry with an axial pyridyl ligand in a manner very similar to the parent methyl dication **1a**.[4a] It was not possible to distinguish the pyridyl nitrogen and coordinated *ortho*-carbon atom crystallographically due to disorder at the pyridyl ligand. Thus C(1A)/N(1B) and C(1B)/N(1A) were refined to the same respective geometrical positions. This problem was also encountered with the crystal structure of $[Sc(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}(C,N)\text{-}C_5H_4N)]$.[2] The range of Y−N(pyridine) separations in **3** is reasonably large (2.458(3)−2.619(3) Å) and corresponds to those in $[Y(\{6,6'\text{-}Me_2\text{-}(C_6H_3)_2\}\{2,2'\text{-}NSiMe_2N^tBu\}_2)(\eta^1\text{-}C_5H_6N)(C_5H_5N)_2]$ (2.482(4), 2.486(4) Å)[9] and $[Y\{3,6\text{-}^tBu_2FluSiMe_2N^tBu\}(\eta^1\text{-}C_5H_6N)(C_5H_5N)_2]$ (2.5325(17), 2.5385(17) Å; flu = fluorenyl).[10] The shortest Y−N(pyridine) bond length in **3** was found for the axial ligand *trans* to the pyridyl group.

The $^{13}C\{^1H\}$ NMR data for the isolated sample of **3** show a characteristic doublet at δ 216.1 ppm ($^1J_{YC} = 26.8$ Hz) arising from the coordinated *ortho*-pyridyl carbon. These data are similar to those recorded for $[Y\{\eta^2\text{-}(C,N)\text{-}C_5D_4N\}(12\text{-crown-}4)(C_5D_5N)_n]^{2+}[BPh_4]^-_2$ (pyridine-d_5: δ 212.6 ppm, $^1J_{YC} = 28.9$ Hz),[5] $[Y(\eta^5\text{-}C_5Me_5)_2\{\eta^2\text{-}(C,N)\text{-}C_5H_4N\}$ (cyclohexane-d_{12}: δ 225.5 ppm, $^1J_{YC} = 33.2$ Hz),[11] and $[Y\{^tBuN(SiMe_2)O^tBu\}_2\text{-}\{\eta^2\text{-}(C,N)\text{-}C_5H_4N\}]$ (benzene-d_6: δ 226.0 ppm, $^1J_{YC} = 26.0$ Hz).[12]

Monitoring the reaction between **1a** and pyridine-d_5 by ^1H NMR spectroscopy at 25 °C, which gives the deuterated pyridyl derivative **3′**, revealed that **1a** was 24 ± 3% consumed after 14 h.[13] Coproduced CH_3D was observed in the ^1H NMR spectra. To determine the activation parameters for this reaction, **1a** was dissolved in an excess of pyridine-d_5 and four separate experiments were performed at 35, 45, 55, and 65 °C, respectively.[14] A pseudo-first-order rate of conversion was found, with the following half-lives at various temperatures: $\tau_{1/2}$ (35 °C) = 510 min, $\tau_{1/2}$ (45 °C) = 234 min, $\tau_{1/2}$ (55 °C) = 69 min, $\tau_{1/2}$ (65 °C) = 22 min. An Eyring plot gave the activation parameters, respectively $\Delta S^\ddagger = -46 \pm 3$ J K^{-1} mol^{-1} and $\Delta H^\ddagger = 89 \pm 1$ kJ mol^{-1} (Figure 2). The negative entropy of activation suggests a transition state depicted in Scheme 1. An analogous procedure using protio pyridine C_5H_5N (with a few drops of THF-d_8 to lock the spectrometer signal) gave a much faster rate of methyl group consumption at 55 °C. The kinetic isotope effect k_H/k_D of 8.4 supports a rapid pre-equilibrium exchange of Lewis bases, followed by a rate-determining C−H activation step. In a similar study using the neutral half-sandwich alkyl complex $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ to activate thiophene in THF-d_8, it was found that the complex $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(\mu\text{-}2\text{-}C_4H_3S)(THF)]$ formed with activation parameters in accordance with an associative process with a similar value for the kinetic isotope effect of $k_H/k_D = 6.4$ (25 °C).[15] In fact, when the ligand exchange reaction to convert **1a** to **2** was left standing for 30 min before addition of pentane, the integration arising from Y-Me at **2** was significantly lower than 3 H when the tetraphenylborate anion was used as an internal standard, due to partial formation of **3**.

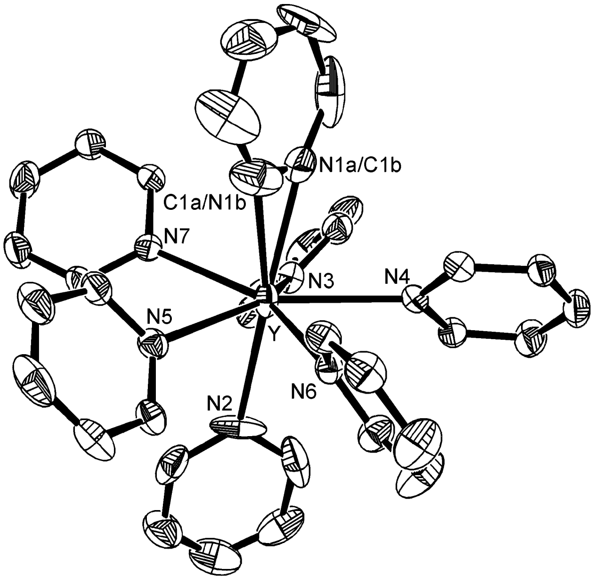

Figure 1. Molecular structure of **3** (ellipsoids drawn at the 50% probability level; hydrogen atoms, tetraphenylborate anions, and lattice pyridine omitted for clarity). Selected bond lengths (Å) and angles (deg): Y−N(2) 2.458(3), Y−N(3) 2.568(3), Y−N(4) 2.582(3), Y−N(5) 2.619(3), Y−N(6) 2.494(3), Y−N(7) 2.512(3); C(1A)−Y−N(1A) 28.69(13), C(1A)−Y−N(2) 161.70(15), N(1A)−Y−N(2) 167.08(13), N(5)−Y−N(7) 76.93(8), N(3)−Y−N(7) 71.43(8), N(3)−Y−N(4) 75.74(8), N(4)−Y−N(6) 69.72(8), N(5)−Y−N(6) 70.11(8).

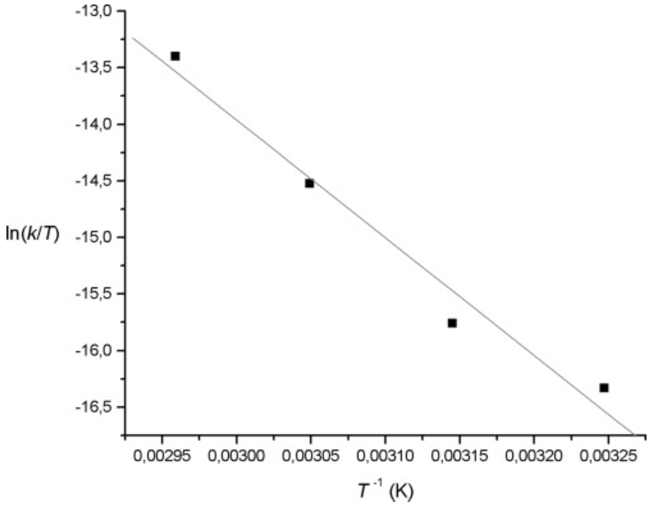

Figure 2. Eyring plot for the reaction of **1a** with pyridine-d_5.

The reactions between both $[LuMe(THF)_6]^{2+}[BPh_4]^-_2$ (**1b**) and $[ScMe(THF)_5]^{2+}[BPh_4]^-_2$ (**1c**) with pyridine-d_5 were also monitored by ^1H NMR spectroscopy at 25 °C. We found that the scandium complex **1c** reacts with pyridine-d_5 at a rate similar

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(8) We tentatively assign the deep red coloration of this reaction mixture and the relatively low concentration of other products that invoke radical coupling or ring-opening of pyridine units. Similar reactivity has previously been noted for rare-earth metal pyridyl and phenyl complexes, refs 11, 15b. The reaction of $[Y(CH_2SiMe_3)_2(THF)_4]^+[BPh_4]^-$ with pyridine gave a crystallographically characterized dicationic complex that contains a bipyridyl ligand, $[Y\{\eta^2\text{-}(C,N)\text{-}C_5H_4N\}(bpy)(py)\text{-}fac\text{-}(THF)_3]^{2+}[BPh_4]^-_2$: Nakajima, Y.; Spaniol, T. P.; Okuda, J., unpublished results.

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(13) **3′** was synthesized on the same scale as **3** with very similar yield. ^2H NMR (pyridine/THF-d_8, 25 °C): δ 8.69 (s, 2 D, py-2), 7.59 (s, 1 D, py-4), 7.21 (s, 2 D, py-3). The pyridyl resonances were not resolved separately from the pyridine resonances.

(14) The reaction proceeds too slowly at 25 °C to accurately determine the half-life by ^1H NMR spectroscopy.

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to that of **1a**, with 20 ± 3% methyl group loss measured over 14 h; complete loss of the Sc-Me resonance was observed after 8 days at room temperature. The lutetium complex **1b** is rather more stable, and over 50% of the methyl signal remained after 8 days at room temperature. These data are in stark contrast to the instantaneous reaction of $[NdMe(THF)_7]^{2+}[BPh_4]^-_2$ with pyridine-d_5.[16]

Conclusions

We have demonstrated that pyridine can be activated by the dicationic yttrium complex **1a**. This shows that despite the high cationic charge, the carbanionic metal−carbon bond character remains in **1a**. Thus the methyl group behaves in a manner similar to the alkyl group in neutral rare-earth metal complexes containing cyclopentadienyl-derived ligands.[17] Kinetic studies indicate that the reaction of **1a** with pyridine proceeds via a mechanism in which a rapid pre-equilibrium Lewis base exchange is followed by rate-determining pyridine activation. Although we assume that σ-bond metathesis is operating, we cannot rule out the involvement of radicals.[8] Product **3** contains an η^2-pyridyl ligand, a common coordination mode at early transition metal centers.

Experimental Section

General Procedures. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Pyridine was distilled from sodium. Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. $[YMe(THF)_6]^{2+}[BPh_4]^-_2$ was synthesized according to literature procedures.[4] NMR spectra were recorded on a Varian Unity 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125.6 MHz; ^{11}B, 160.3 MHz; ^{2}H, 61 MHz). Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{11}B NMR spectra were referenced externally to a 1 M solution of $NaBH_4$ in D_2O. Elemental analyses were performed by the Microanalytical Laboratory of the Johannes Gutenberg-University, Mainz, Germany. Metal analysis was performed by complexometric titration.[18] X-ray diffraction data were collected on a Bruker CCD platform diffractometer equipped with a CCD detector. The SMART program package was used to determine the unit-cell parameters and for data collection; the raw frame data were processed using SAINT and SADABS to yield the reflection data file.[19] Subsequent calculations were carried out using the SHELXS and SHELXL programs.[20] Analytical scattering factors for neutral atoms were used throughout the analysis.[21] The structure of **3** was solved by direct methods and Fourier difference analyses. Hydrogen atoms were included into calculated positions. C(1A)/N(1B) and C(1B)/N(1A) were refined to the same respective geometrical positions. Crystal data for **3** ($C_{83}H_{74}B_2N_7Y\cdot C_5H_5N$): $P2_12_12_1$ (No. 19), orthorhombic, $a = 13.9108(5)$ Å, $b = 22.5453(6)$ Å, $c = 23.4052(7)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 7340.4(4)$; $Z = 4$; $T = 110(2)$ K; $D_{calc} = 1.230$ Mg/m^3; $R(F_o^2)$, $R_w(F_o^2)$ $[I > 2\sigma(I)]$: 0.0537, 0.1204; $R(F_o^2)$, $R_w(F_o^2)$ (all data): 0.0858, 0.1339.

$[YMe(C_5H_5N)_6]^{2+}[BPh_4]^-_2$ (2). Complex **1a** (100 mg, 85 μmol) was dissolved in pyridine (2.0 mL) and stirred for 1 min. Pentane (10 mL) was added to the colorless solution to give an oily deposit. Further washings with pentane (2 × 10 mL) gave a white powder after drying in vacuo. ^{1}H NMR (pyridine-d_5, 25 °C): δ 0.68 (d, $^2J_{YH} = 1.95$ Hz, 3 H, YCH_3), 7.08 (t, $^3J_{HH} = 7.08$ Hz, 8 × 1 H, Ph-4), 7.16 − 7.28 (m, 8 × 2 H, Ph-3 and 6 × 2 H, py-3), 7.57 (m, 6 × 1 H, py-4), 8.03 (m, 8 × 2 H, Ph-2), 8.70 (m, 6 × 2 H, py-2). ^{13}C NMR (pyridine-d_5, 25 °C): δ 32.8 (dq, $^1J_{YC} = 53.6$ Hz, $^1J_{CH} = 105.5$ Hz, YCH_3), 124.2 (Ph-4), 128.0 (Ph-3), 139.0 (Ph-2), 166.8 (q, $^1J_{BC} = 49.2$ Hz, Ph-1). ^{11}B{^{1}H} NMR (pyridine-d_5, 25 °C): δ −4.7. Anal. Calc for $C_{79}H_{73}B_2N_6Y$: Y, 7.31. Found: Y, 6.95. Combustion analysis was not performed due to rapid decomposition.

$[Y(\eta^2\text{-}(C,N)\text{-}C_5H_4N)(C_5H_5N)_6]^{2+}[BPh_4]^-_2$ (3). Complex **1a** (99 mg, 84 μmol) was dissolved in pyridine (2.0 mL). Pentane (1.0 mL) was added and the sample was briefly shaken. After 5 days, the solution had become deep red and colorless crystals of the pyridine solvate had been deposited, which were collected and dried in vacuo (39 mg, 30 μmol, 36%). ^{1}H NMR (pyridine-d_5, 25 °C): δ 7.09 (t, $^3J_{HH} = 6.87$ Hz, 8 × 1 H, Ph-4), 7.20 (m, 6 × 2 H, py-3), 7.25 (m, 8 × 2 H, Ph-3), 7.46 (m, 1 H, py-5), 7.57 (m, 6 × 1 H, py-4), 7.81 (t, $^3J_{HH} = 7.33$ Hz, 1 H, py-4), 8.05 (s (br), 8 × 2 H, Ph-2), 8.10 (dd, $^3J_{HH} = 7.33$ Hz, $^3J_{YH} = 0.91$ Hz, 1 H, py-3), 8.71 (m, 6 × 2 H, py-2), 8.89 (d, $^3J_{HH} = 5.49$ Hz, 1 H, py-6). ^{13}C{^{1}H} NMR (pyridine-d_5, 25 °C): δ 122.4 (Ph-4), 123.8 (py-3), 124.0 (py-5), 126.2 (Ph-3), 129.5 (py-3), 136.0 (py-4), 136.1 (py-4), 137.1 (Ph-2), 143.9 (py-6), 150.2 (py-2), 165.0 (q, $^1J_{BC} = 49.4$ Hz, Ph-1), 216.1 (d, $^1J_{YC} = 26.8$ Hz, py-2). ^{11}B{^{1}H} NMR (pyridine-d_5, 25 °C): δ −5.8. Anal. Calc for $C_{83}H_{74}B_2N_7Y\cdot C_5H_5N$: C, 77.76; H, 5.86; N, 8.24; Y, 6.54. Found: C, 77.78; H, 5.89; N, 7.86; Y, 6.32.

Kinetic Measurements. Complex **1a** (25 mg, 22.7 μmol) was dissolved in pyridine-d_5 (0.5 mL). In four separate experiments, the sample was heated in the NMR spectrometer to respectively 35, 45, 55, and 65 °C. ^{1}H NMR spectra were measured at regular intervals (35 °C: every 30 min for 8 h; 45 °C: every 60 min for 14 h; 55 °C: every 30 min for 4 h; 65 °C: every 15 min for 2 h) using short delay ($d_1 = 0.2$ s) and acquisition (nt = 2) times. The rate constants were determined by plotting $\ln(I_0/I)$ against t (I = integration of Y-CH_3 group). The Ph-2 group of the tetraphenylborate anion was used as an internal standard for the integration by which the extent of conversion from **1a** to **3′** was calculated.

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Supporting Information Available: Time-conversion and Arrhenius plots for the formation of **3′**, time-conversion plot for the formation of **3** at 55 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] $[NdMe(THF)_7]^{2+}[BPh_4]^-_2$ reacts spontaneously with pyridine-d_5 such that only CH_3D and not the parent methyl dication could be observed in the ^{1}H NMR spectrum. Furthermore, the protonation of $[Nd\{(\mu\text{-Me})_2(AlMe_2)\}_3]$ with 1 equiv of $[NEt_3H]^+[BPh_4]^-$ gave the dicationic substance $[Nd\{O(CH_2)_4Me\}(THF)_6]^{2+}[BPh_4]^-_2$, which contains an *n*-pentoxide group derived from the ring-opening of THF rather than the expected Nd methyl monocation (see ref 4b).

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