Activation of C−H Bonds in Five-Membered Heterocycles by a Half-Sandwich Yttrium Alkyl Complex

Stefan Arndt,[a] Thomas P. Spaniol,[a] and Jun Okuda*[a]

Keywords: Yttrium / Chelates / C−H activation / Lewis acids / Heterocycles

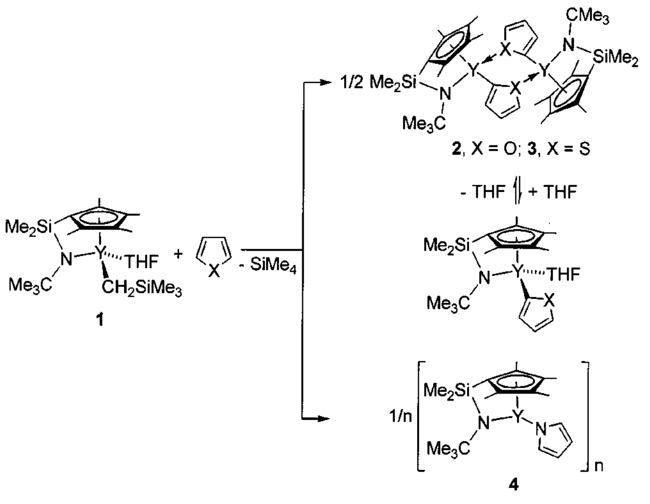
The highly labile half-sandwich alkyl complex [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] smoothly undergoes σ-bond metathesis with furan and thiophene in pentane to give tetramethylsilane and the sparingly soluble complexes [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(μ-2-C_4H_3X)]$_2$ (X = O, S). They dissolve in THF to give the THF adducts [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(2-C_4H_3X)(THF)$_n$]. Pyrrole reacts with [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] to give the Lewis base-free pyrrolide [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(NC_4H_4)]$_n$.

Introduction

Since the first report by Watson on intermolecular C−H bond activation involving lanthanocene alkyl complexes,[1] systematic studies by Bercaw et al. have established the σ-bond metathesis to be a general reaction type whenever metal complexes with an f^xd^0-electron configuration undergo C−H bond activation reactions.[2] In particular, the decamethyllanthanocenes [Ln(η^5-C_5Me_5)$_2$X]$_2$ (X = H, alkyl) were shown to undergo a variety of reactions with aromatic compounds[3] including furan and thiophene.[3e] The latter reaction recently allowed the development of an elegant method to synthesize 2-thienyl-functionalized polyethylenes by combining C−H bond activation with ethylene insertion chemistry.[4] While exploring the polymerization activity of lanthanide alkyls and hydrides supported by the sterically more accessible linked amido-cyclopentadienyl ligands [Ln(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)X],[5a,5b] we have noticed the absence of C−H bond activation processes, e.g. involving aromatic solvents or THF. We wish to report here that the highly labile yttrium alkyl [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] undergoes a C−H bond activation reaction with furan and thiophene.

Results and Discussion

When the labile half-sandwich alkyl complex [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] (**1**), most conveniently prepared in situ from $YCl_3(THF)_{3.5}$ and $LiCH_2SiMe_3$, followed by reaction with (C_5Me_4H)$SiMe_2NHCMe_3$,[5] is treated with an excess of furan or thiophene in pentane at ambient temperature, tetramethylsilane and sparingly soluble precipitates of the presumably dimeric complexes [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(μ-2-C_4H_3X)]$_2$ (X = O, **2**; S, **3**) are formed in good yield (Scheme 1). Elemental analysis indicates the absence of THF in these complexes. In analogy to the crystallographically characterized 2-thienyl permethylyttrocene complex [Y(η^5-C_5Me_5)$_2$(μ-2-C_4H_3S)]$_2$, recently reported by Hessen et al.,[4] the crystal structure determination of **2**[6] reveals a dimeric structure. The two "metallocene-like" Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$) fragments are connected by two bridging 2-furyl ligands. The $C_5Me_4SiMe_2NCMe_3$ ligands are arranged in a transoidal fashion. Due to severe disorder of the 2-furyl bridges, details of the structure determination will be published in due course. Both complexes dissolve in THF to give the corresponding monomeric THF complexes that can be fully characterized by ^1H and ^{13}C NMR spectroscopy. Most diagnostically, the yttrium-bound 2-carbon atoms in **2** and **3** give rise to doublets at δ = 204 and 176, with $^1J_{YC}$ = 59 and 55 Hz, respectively. The NMR spectra at room temperature in [D_8]THF indicate the presence of a mirror plane. Upon cooling a solution of **2** below −60 °C, the enantiotopic $SiMe_2$ and C_5Me_4 resonances decoalesce, indicating the slowing down of the THF dissociation process. The aromatic resonances do not change significantly suggesting free



Scheme 1

---

[a] Institut für Anorganische Chemie und Analytische Chemie,
Johannes Gutenberg-Universität Mainz
Duesbergweg 10−14, 55099 Mainz, Germany
E-mail: okuda@mail.uni-mainz.de

1434−1948/01/0101−0073 $ 17.50+.50/0

rotation about the yttrium-2-carbon bond without a strong yttrium-heteroatom coordination.

A pseudo first-order rate law was found for the reaction of [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] (**1**) with a 32-fold excess of thiophene in [D_8]THF to give **2** (Figure 1). The activation parameters $\Delta H^\ddagger = 68 \pm 1$ kJ mol^{-1} and $\Delta S^\ddagger = -85 \pm 3$ J K^{-1} mol^{-1} were calculated from the temperature dependence of the rate constants (Figure 2). The negative entropy is in accordance with an associative process. A well-defined arrangement of the reactants in the transition state can be inferred. Although the THF in **1** was previously shown to be labile,[5b] examples for stable five-coordinate complexes of the type [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(X)(L)$_2$] (X = one-, L = two-electron ligand) were recently reported.[5b,5c]

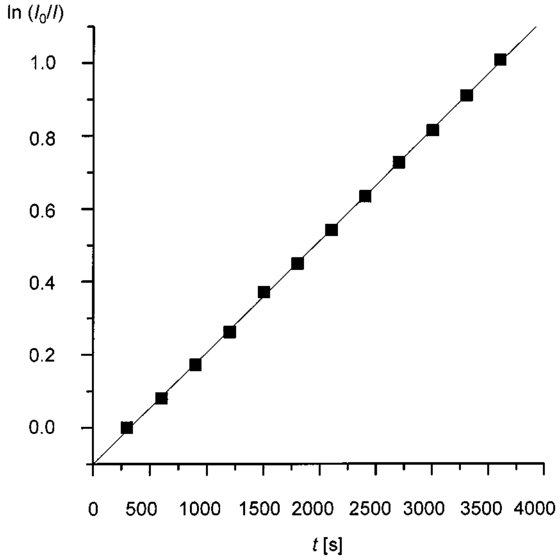


Figure 1. Reaction of [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] (**1**) with thiophene in [D_8]THF: plot of ln(I_0/I) vs. t at 25 °C

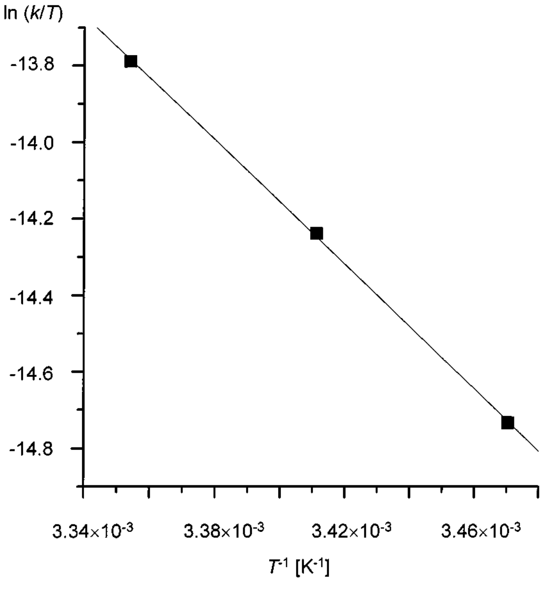


Figure 2. Reaction of [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] (**1**) with thiophene in [D_8]THF: Eyring plot

In contrast to furan and thiophene, pyrrole reacts with the alkyl **1** in pentane in a stoichiometric ratio under protolysis to give the pyrrolide [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(NC_4H_4)] (**4**) in good yield. This compound is sparingly soluble, even in THF, but dissolving in [D_5]pyridine allowed the recording of NMR spectra, presumably as the pyridine adduct [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(NC_4H_4)([D_5]pyridine)$_n$]. The low solubility suggests a dimeric structure for **4**, although the related amido complexes of the type [Ln(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$){N($SiMe_3$)$_2$}] (Ln = Y, Nd, Sm, Lu) are all monomeric.[7] The crystallographically characterized monomeric lutetocene pyrrolide [Lu(η^5-C_5H_5)$_2$($NC_4H_2Me_2$-2,5)(THF)] (Ln = Y, Lu) was also reported to be insoluble.[8] The room temperature NMR spectroscopic data of the pyridine adduct of **4** [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(NC_4H_4)([D_5]pyridine)$_n$] are in agreement with the presence of a mirror plane, indicating a solution structure in which the pyridine ligand is rapidly exchanging its site at the chiral metal center.

In summary we have shown that the labile alkyl [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] smoothly undergoes σ-bond metathesis not only with dihydrogen[5a] and phenylsilane,[5b] but also with furan and thiophene to give metalated products. Further extension of this C−H bond activation chemistry is underway.

Experimental Section

General: All experiments were performed under argon by using standard Schlenk or glove-box techniques. Solvents were purified, dried and distilled under argon. − ^{1}H, ^{13}C, and ^{29}Si NMR: Bruker DRX 400; all spectra at 25 °C; ^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{29}Si: 79.5 MHz. − Elemental analyses: Microanalytical laboratory of this department.

[Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(μ-2-C_4H_3O)]$_2$ (2) and [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(2-C_4H_3O)([D_8]THF)$_n$]: A solution of furan (750 μL, 10.0 mmol) in hexane (3 mL) was layered on neat hexane (4.5 mL) which was already layered on top of [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] (**1**) (300 mg, 0.6 mmol) dissolved in toluene (3 mL). Colorless crystals (163 mg, 66%) formed upon standing over a period of 6 days at 5 °C. − ^{1}H NMR ([D_8]THF): δ = 0.39 [s, 6 H, Si(CH_3)$_2$], 1.26 [s, 9 H, C(CH_3)$_3$], 2.01, 2.02 [s, 2 × 3 H, C_5(CH_3)$_4$], 6.04 (m, 1 H, C_4H_3O-3), 6.22 (d, $^3J_{HH}$ = 2.9 Hz, 1 H, C_4H_3O-4), 7.46 (m, 1 H, C_4H_3O-5). − ^{1}H NMR ([D_8]THF, −100 °C): δ = 0.33, 0.36 [s, 2 × 3 H, Si(CH_3)$_2$], 1.26 [s, 9 H, C(CH_3)$_3$], 1.71, 1.84, 1.95, 2.01 [s, 4 × 3 H, C_5(CH_3)$_4$], 6.01 (br, 1 H, C_4H_3O-3), 6.17 (br, 1 H, C_4H_3O-4), 7.49 (m, 1 H, C_4H_3O-5). − ^{13}C{^{1}H} NMR ([D_8]THF): δ = 5.8 [Si(CH_3)$_2$], 8.6, 11.9 [C_5(CH_3)$_4$], 32.3 [C(CH_3)$_3$], 51.7 [s, C(CH_3)$_3$], 104.0 [C_5(CH_3)$_4$ at Si], 104.6, 116.4 (s, C_4H_3O), 118.7, 123.8 [C_5(CH_3)$_4$], 139.8 (s, C_4H_3O). 204.4 (d, $^1J_{YC}$ = 59 Hz, C_4H_3O-2). − ^{29}Si{^{1}H} NMR ([D_8]THF): δ = 28.8 (d, $^2J_{SiY}$ = 2 Hz). − $C_{38}H_{60}N_2O_2Si_2Y_2$ (810.9): calcd. C 56.29, H 7.46, N 3.45; found C 55.07, H 7.37, N 3.58.

[Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(μ-2-C_4H_3S)]$_2$ (3) and [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(2-C_4H_3S)([D_8]THF)$_n$]: A suspension of anhydrous YCl_3 (586 mg, 3.0 mmol) in THF (20 mL) was heated to 60 °C for 30 min. The solvent was then removed in vacuo and the residue taken up in pentane (24 mL). At −78 °C a solution of $LiCH_2SiMe_3$ (860 mg, 9.1 mmol) in pentane (24 mL) was added.

After stirring for 2 h at 0 °C the reaction mixture was filtered and the filtrate treated with neat $(C_5Me_4H)SiMe_2NHCMe_3$ (715 mg, 2.8 mmol). After stirring for 2 h at 0 °C and filtration, the filtrate containing the alkyl $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ was treated with thiophene (3.9 mL, 48.0 mmol) and stirred for 1.5 h at room temperature. The supernatant was decanted off from the colorless precipitate which was washed with pentane (2 × 10 mL) to give colorless microcrystals (711 mg, 56%) − ^1H NMR ($[D_8]THF$): $\delta = 0.43$ [s, 6 H, $Si(CH_3)_2$], 1.32 [s, 9 H, $C(CH_3)_3$], 1.98, 2.05 [s, 2 × 6 H, $C_5(CH_3)_4$], 6.97 (dd, $^3J_{HH} =$ 2.9 Hz and 4.4 Hz, 1 H, C_4H_3S-3), 7.09 (d, $^3J_{HH} = 2.9$ Hz, 1 H, C_4H_3S-4), 7.31 (d, $^3J_{HH} = 4.4$ Hz, 1 H, C_4H_3S-5). − $^{13}C\{^1H\}$ NMR ($[D_8]THF$): $\delta = 5.9$ [$Si(CH_3)_2$], 8.9, 11.8 [$C_5(CH_3)_4$], 32.5 [$C(CH_3)_3$], 52.1 [$C(CH_3)_3$], 104.1 [$C_5(CH_3)_4$ attached to Si], 119.3, 123.6 [$C_5(CH_3)_4$], 124.2, 124.3, 131.4 (C_4H_3S), 176.7 (d, $^1J_{YC} =$ 55 Hz, C_4H_3S-2). − $^{29}Si\{^1H\}$ NMR ($[D_8]THF$): $\delta = 23.5$. − $C_{38}H_{60}N_2S_2Si_2Y_2$ (843.0): calcd. C 54.14, H 7.17, N 3.32, S 7.61; found C 54.61, H 7.18, N 3.32, S 7.64.

Kinetics: Compound **1** (20 mg, 40 µmol) was dissolved in a mixture of $[D_8]THF$ (400 µL) and thiophene (100 µL, 1260 µmol) and ^1H NMR spectra (2 scans) were recorded every 5 min. over a period of 1 h at 15, 20 and 25 °C. The rate constants were obtained by a plot of $\ln(I_0/I)$ vs. t. Integrals of the β-CH_2 groups of THF were used as internal standard for calibrating the integrals I of the YCH_2 group; $I_0 = I(t = 0\ \mathrm{s})$. $k(T = 288\ \mathrm{K}) = (1.15 \pm 0.04) \times 10^{-4}\ \mathrm{s}^{-1}$, $k(T = 293\ \mathrm{K}) = (1.92 \pm 0.02) \times 10^{-4}\ \mathrm{s}^{-1}$, $k(T = 298\ \mathrm{K}) = (3.06 \pm 0.02) \times 10^{-4}\ \mathrm{s}^{-1}$. The kinetic isotope effect using $[D_4]$thiophene at 298 K was $k_H/k_D = 6.4$.

$[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(NC_4H_4)]_n$ (4) and $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(NC_4H_4)([D_5]\text{pyridine})_n]$: A suspension of **1** (200 mg, 0.4 mmol) in hexane (3 mL) was treated with neat pyrrole (28 µL, 0.4 mmol) at 25 °C and the reaction mixture stirred at 0 °C for 2 h. Colorless microcrystals (107 mg, 65%) were obtained by filtration. − ^1H NMR ($[D_5]$pyridine): $\delta = 0.81$ [s, 6 H, $Si(CH_3)_2$], 1.42 [s, 9 H, $C(CH_3)_3$], 1.74, 2.07 [s, 2 × 6 H, $C_5(CH_3)_4$], 6.69, 7.09 (br s, 2 × 2 H, NC_4H_4). − $^{13}C\{^1H\}$ NMR ($[D_5]$pyridine): $\delta = 9.0$ [$Si(CH_3)_2$], 11.3, 15.0 [$C_5(CH_3)_4$], 34.8 [$C(CH_3)_3$], 54.7 [$C(CH_3)_3$], 107.2 [$C_5(CH_3)_4$ attached to Si], 108.6, 124.7 (s, NC_4H_4), 127.2 [$C_5(CH_3)_4$]; one signal for the $C_5(CH_3)_4$ carbon is obscured by solvent signals. − $^{29}Si\{^1H\}$ NMR ($[D_5]$pyridine): $\delta = 28.1$ (d, $^2J_{SiY} =$ 2 Hz). − $C_{19}H_{31}N_2SiY$ (404.5): calcd. C 56.42, H 7.73, N 6.93; found C 56.51, H 7.62, N 7.25.

Acknowledgments

Generous financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

---

[1] [1a] P. L. Watson, *J. Am. Chem. Soc.* **1982**, *104*, 337−339. − [1b] P. L. Watson, *J. Am. Chem. Soc.* **1983**, *105*, 6491−6495. − [1c] P. L. Watson, G. W. Parshall, *Acc. Chem. Res.* **1985**, *18*, 51−56.

[2] M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203−219.

[3] [3a] P. L. Watson, *J. Chem. Soc., Chem. Commun.* **1983**, 276−277. − [3b] W. J. Evans, T. A. Ulibarri, J. W. Ziller, *Organometallics* **1991**, *10*, 134−142. − [3c] K. H. den Haan, Y. Wielstra, J. H. Teuben, *Organometallics* **1987**, *6*, 2053−2060. − [3d] M. Booij, A. Meetsma, J. H. Teuben, *Organometallics* **1991**, *10*, 3246−3252. − [3e] B. J. Deelman, M. Booij, A. Meetsma, J. H. Teuben, H. Kooijman, A. L. Spek, *Organometallics* **1995**, *14*, 2306−2317. − [3f] N. S. Radu, S. L. Buchwald, B. Scott, C. J. Burns, *Organometallics* **1996**, *15*, 3913−3915.

[4] [4a] S. N. Ringelberg, A. Meetsma, B. Hessen, J. H. Teuben, *J. Am. Chem. Soc.* **1999**, *121*, 6082−6083. − [4b] B. Hessen, S. N. Ringelberg, G.-J. Meppelder, J. H. Teuben, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41(1)*, 397−398.

[5] [5a] K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Angew. Chem.* **1999**, *111*, 163−165; *Angew. Chem. Int. Ed.* **1999**, *38*, 227−230. − [5b] K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228−243. − [5c] S. Arndt, P. Voth, T. P. Spaniol, J. Okuda, *Organometallics* in press.

[6] Yellow crystal, 0.37 × 0.44 × 0.90 mm, $C_{38}H_{60}N_2O_2Si_2Y_2$, $T =$ 293(2) K, $a = 14.89(1)$, $b = 23.845(2)$, $c = 11.5086(9)$ Å, $V =$ 4086.1(6) Å^3, orthorhombic space group *Cmca* (No. 66), $Z =$ 4, $D_{calcd.} = 1.318$ g cm^{-3}.

[7] [7a] Y. Mu, W. E. Piers, M.-A. MacDonald, M. J. Zaworotko, *Can. J. Chem.* **1995**, *73*, 2233−2238. − [7b] S. Tian, V. M. Arrendondo, C. L. Stern, T. J. Marks, *Organometallics* **1999**, *18*, 2568−2570.

[8] H. Schumann, P. R. Lee, A. Dietrich, *Chem. Ber.* **1990**, *123*, 1331−1334.

Received August 9, 2000
[I00310]