ELSEVIER

Journal of Alloys and Compounds 444–445 (2007) 477–482

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

sp^3 versus sp^2 C–H bond activation chemistry of 2-picoline by Th(IV) and U(IV) metallocene complexes

Jaqueline L. Kiplinger[a,*], Brian L. Scott[a], Eric J. Schelter[a], Jaime A. Pool Davis Tournear

[a] *Los Alamos National Laboratory, Mail Stop J514, Los Alamos, NM 87545, USA*

Received 13 April 2007; accepted 20 April 2007
Available online 4 May 2007

Abstract

The thorium alkyl complex $(C_5Me_5)_2Th(CH_3)_2$ and 2-picoline react to give preferential sp^3 C–H bond activation in the presence of a more reactive sp^2 C–H bond, while the analogous uranium complex, $(C_5Me_5)_2U(CH_3)_2$, reacts with only the *ortho* 2-picoline sp^2 C–H bond, as originally expected. Herein, we describe this competitive sp^3 versus sp^2 C–H bond activation chemistry with 2-picoline and $(C_5Me_5)_2An(CH_3)_2$ (An = Th, U) and provide experimental observations that suggest different mechanistic reaction pathways are operative for the uranium and thorium complexes. We also report the X-ray crystal structures for the thorium picolyl complex, $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}2\text{-}CH_2\text{-}NC_5H_3]$, and the η^2-pyridyl complexes $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}6\text{-}CH_3\text{-}NC_5H_3]$ and $(C_5Me_5)_2U(CH_3)[\eta^2\text{-}(N,C)\text{-}6\text{-}CH_3\text{-}NC_5H_3]$.

Keywords: Thorium; Uranium; sp^2 and sp^3 C–H bond activation; 2-Picoline; Organometallic

1. Introduction

The activation of C–H bonds and the subsequent functionalization of hydrocarbons is a field of considerable interest in organometallic chemistry. A diverse array of lanthanide, actinide, and transition-metal complexes have been found to activate hydrocarbon substrates such as alkanes and arenes by several different mechanisms [1]. It is generally accepted that metal complexes will preferentially cleave the stronger sp^2 C–H bonds (∼110 kcal/mol) in the presence of weaker sp^3 C–H bonds (∼95–105 kcal/mol). This trend is accounted for on both kinetic and thermodynamic grounds, such as prior π-coordination of an adjacent C=C bond to the metal and stability of the resulting M–C(sp^2) bond in the product [2].

In our ongoing studies on the synthesis, reactivity, and electronic structure of actinide complexes containing multiply bonded functional groups [3], we have discovered a remarkable selective hydrocarbon C–H bond activation reaction mediated by 5f-element metal centers. Contrary to expectations, the thorium dialkyl complex, $(C_5Me_5)_2Th(CH_3)_2$, and 2-picoline react to give preferential sp^3 C–H bond activation in the presence of a more reactive sp^2 C–H bond. Intriguingly, the analogous uranium complex, $(C_5Me_5)_2U(CH_3)_2$, reacts only with 2-picoline at the *ortho* sp^2 C–H bond as expected. Herein, we describe this competitive sp^3 versus sp^2 C–H bond activation chemistry with 2-picoline and $(C_5Me_5)_2An(CH_3)_2$ (An = Th, U) and provide experimental observations that suggest different mechanistic reaction pathways are operative for the isostructural uranium and thorium complexes.

2. Results and discussion

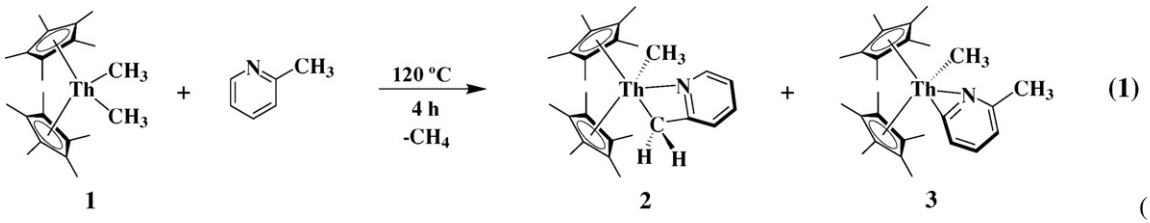
2.1. Reactivity of 2-picoline with thorium(IV) and uranium(IV) metallocenes

As depicted in Eq. (1), reaction of $(C_5Me_5)_2Th(CH_3)_2$ (**1**) with 2-picoline in toluene-d_8 at 120 °C for 4 h produced a 3:1 mixture of $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}2\text{-}CH_2\text{-}NC_5H_3]$ (**2**), as a result of sp^3 C–H bond activation at the 2-picoline methyl group, and $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}6\text{-}CH_3\text{-}NC_5H_3]$ (**3**), derived from sp^2 C–H bond activation at the *ortho* position. No reaction is observed between **1** and 2-picoline at room temperature. For characterization purposes, complexes

* Corresponding author. Tel.: +1 505 665 9553; fax: +1 505 667 9905.
E-mail address: kiplinger@lanl.gov (J.L. Kiplinger).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.04.272

2 and **3** were independently prepared from the reaction of $(C_5Me_5)_2Th(CH_3)Br$ and 2-picolyllithium or 2-lithio-6-methylpyridine, respectively.

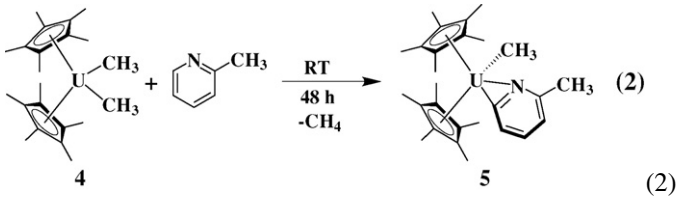


1 **2** **3**

Diagnostic ^1H NMR spectroscopic data clearly demonstrate the formation of a single isomer for the four-membered pyridylmethyl Th(IV) metallacycle (**2**) with resonances centered at δ 7.88, 6.77, 6.54, and 6.08 ppm for the four pyridyl protons, a singlet at δ 2.02 ppm for the two methylene protons, a singlet at δ 1.92 ppm for the C_5Me_5 ligands, and a singlet at δ 0.09 ppm for the thorium methyl group. The ^1H NMR spectrum for **3** is consistent with the η^2-pyridyl formulation and matches the spectral data previously reported for this complex [4]. Interestingly, the product ratio is dependent upon temperature, time, and concentration of 2-picoline; greater concentrations of 2-picoline, longer reaction times, or higher temperatures afforded greater yields of the sp^2 C–H bond activation product **3**. For example, reaction of complex **1** with 2-picoline in toluene-d_8 at 90 °C for 4 days produced an inverted 1:3 ratio of **2** to **3** as determined by ^1H NMR spectroscopy.

Furthermore, reaction of independently synthesized **3** with 1 equiv. 2-picoline in toluene-d_8 at 90 °C for 4 days did not yield complex **2**. However, reaction of the sp^3 C–H bond activation product **2** with substoichiometric (0.3 equiv.) 2-picoline in toluene-d_8 at 90 °C for 12 h resulted in quantitative conversion to the sp^2 C–H bond activation product **3**. In total, these observations establish that the selective activation of the sp^3 C–H bond at the 2-picoline methyl group occurs initially to give complex **2**, which is the kinetic product. Further reaction of **2** with another molecule of 2-picoline affords the η^2-pyridyl complex **3**, which is the thermodynamic product.

In marked contrast, the analogous uranium(IV) complex, $(C_5Me_5)_2U(CH_3)_2$ (**4**), reacts with 2-picoline at room temperature only at the sp^2 C–H bond at the *ortho* position of 2-picoline, to afford the known η^2-pyridyl $(C_5Me_5)_2U(CH_3)[\eta^2$-(*N*,*C*)-6-$CH_3$-$NC_5H_3]$ (**5**) (Eq. (2)) [4]:



4 **5** (2)

Differences in the chemical behavior of thorium and uranium complexes have been noted previously [5]. In a classic example, Marks and co-workers reported that for the benzene exchange reactions of $(C_5Me_5)_2An(C_6H_5)_2$ (An = U, Th) with C_6D_6, arene exchange proceeds at ambient temperature for the uranium complex but the thorium analogue requires a temperature of approximately 100 °C [5a]. More dramatic variations in chemical behavior have been recently noted for the reactivity of $(C_5Me_5)_2AnR_2$ (An = Th, U; R = CH_3, CH_2Ph) with 2,6-lutidine *N*-oxide. Whereas the thorium complexes react with the sp^3 C–H bond at room temperature to afford the corresponding cyclometallated complexes, $(C_5Me_5)_2Th(R)[\eta^2$-(*O*,*C*)-O-N-2-CH_2-5-CH_3-$C_5H_3]$, the uranium systems display no reactivity even at elevated temperatures [5b].

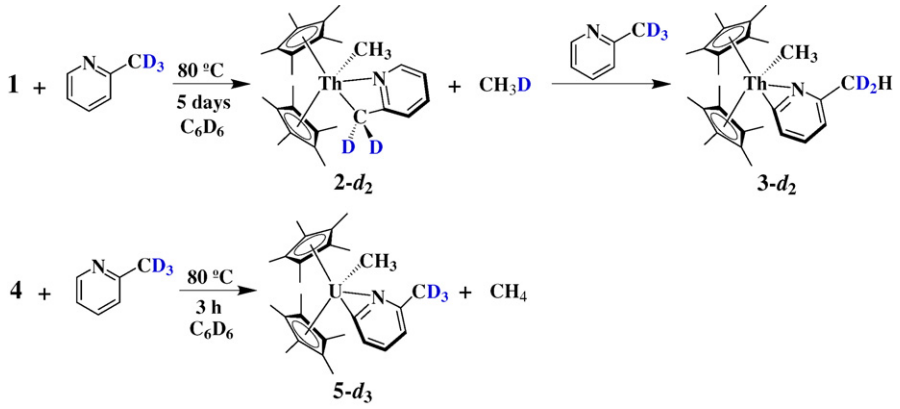
2.2. Mechanism of C–H activation chemistry

As a first step in understanding the observed reactivity and to determine if both the thorium and uranium systems were proceeding by the same mechanism, preliminary labeling studies were performed [6]. As shown in Scheme 1, treatment of $(C_5Me_5)_2Th(CH_3)_2$ (**1**) with 2-picoline-methyl-d_3 in benzene-d_6 at 80 °C for 5 days produced CH_3D as the sole methane isotopomer and a mixture of **2**-d_2 and **3**-d_2 as determined using ^1H NMR spectroscopy. In contrast, $(C_5Me_5)_2U(CH_3)_2$ (**4**) with 2-picoline-methyl-d_3 in benzene-d_6 at 80 °C for 3 h produced only CH_4 and **5**-d_3. The deuterium labeling studies suggest that a *different* mechanism is operative for the thorium and uranium complexes in their reaction chemistry with 2-picoline. Namely, the thorium complex **1** reacts selectively with the 2-picoline methyl group sp^3 C–H bond to initially give the kinetic product **2**, while the uranium complex **4** reacts selectively with the 2-picoline *ortho* sp^2 C–H bond to give **5**.

Transition-metal systems demonstrating this sort of unusual selectivity have been shown to involve intermediate alkylidene complexes [7]. However, no deuterium incorporation into the Th–CH_3 or U–CH_3 groups was observed in these studies, providing evidence that an actinide methylidene is not an intermediate in the C–H activation chemistry. Similarly, reaction of $(C_5Me_5)_2Th(CD_3)_2$ (**1**-d_6) and $(C_5Me_5)_2U(CD_3)_2$ (**4**-d_6) with 2-picoline-d_7 gave only CD_4 and the corresponding metallacycles with no deuterium incorporation into the methyl groups of the C_5Me_5 ligands, indicating that a "tuck-in" complex, *e.g.* $(C_5Me_5)(\eta^1,\eta^5$-$CH_2C_5Me_4)An(CH_3)$ (An = Th, U), is also not involved in the observed C–H activation chemistry [8]. In total, these observations are consistent with the C–H activation chemistry proceeding by a σ-bond metathesis pathway for both uranium and thorium.

2.3. Crystallographic characterization of complexes 2, 3, and 5

The molecular structures of the thorium complexes **2** and **3** are shown in Fig. 1 and that of the uranium system **5** is



Scheme 1. Labeling studies illustrating that thorium and uranium metallocene complexes proceed through different mechanistic reaction pathways with 2-picoline.

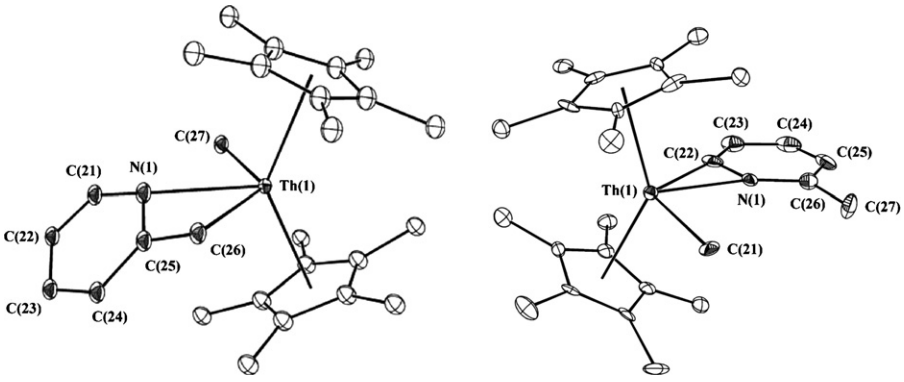


Fig. 1. Molecular structure of complexes **2** (left) and **3** (right) with thermal ellipsoids at the 25% probability level. Selected bond distances (Å) and angles (°) for complex **2**: Th(1)–C(27) 2.90(2), Th(1)–C(26) 2.642(10), Th(1)–N(1) 2.574(7), N(1)–C(25) 1.359(12), C(25)–C(26) 1.436(13), N(1)–Th(1)–C(26) 53.1(3), N(1)–Th(1)–C(27) 76.5(4), Th(1)–N(1)–C(25) 92.4(5), Th(1)–C(26)–C(25) 87.9(5), N(1)–C(25)–C(26) 113.1(8), $C_5Me_{5(cent)}$–Th(1) 2.618(4), 2.579(4), $C_5Me_{5(cent)}$–Th(1)–$C_5Me_{5(cent)}$ 137.5(2). For complex **3**: Th(1)–C(21) 2.5305(18), Th(1)–C(22) 2.4714(17), Th(1)–N(1) 2.4441(12), N(1)–C(22) 1.356(2), N(1)–Th(1)–C(22) 32.03(5), N(1)–Th(1)–C(21) 82.20(5), $C_5Me_{5(cent)}$–Th(1) 2.538(2), $C_5Me_{5(cent)}$–Th(1)–$C_5Me_{5(cent)}$ 140.1(2).

presented in Fig. 2. All three compounds display a typical bent-metallocene framework with the activated 2-picoline and alkyl ligands contained within the metallocene wedge. To the best of our knowledge, complex **3** is the first structurally characterized

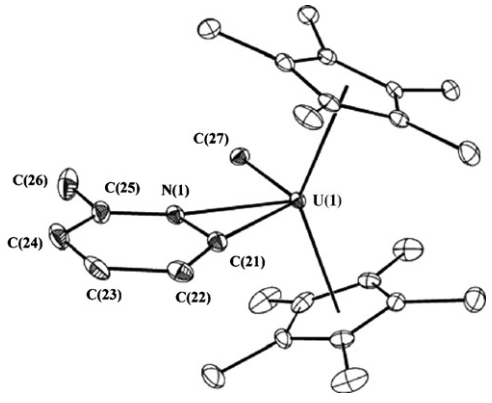


Fig. 2. Molecular structure of complex **5** with thermal ellipsoids at the 25% probability level. Selected bond distances (Å) and angles (°) for complex **5**: U(1)–C(27) 2.467(4), U(1)–C(21) 2.396(4), U(1)–N(1) 2.394(3), N(1)–C(21) 1.355(5), N(1)–U(1)–C(21) 32.85(12), N(1)–U(1)–C(27) 82.62(13), $C_5Me_{5(cent)}$–U(1) 2.476(4), 2.474(4), $C_5Me_{5(cent)}$–U(1)–$C_5Me_{5(cent)}$ 140.2(1).

example of a thorium η^2-pyridyl complex. The Th–C_{methyl} and U–C_{methyl} bond lengths for the η^2-pyridyl complexes **3** and **5** (**3**: Th(1)–C(21) = 2.5305(18) Å, **5**: U(1)–C(27) = 2.467(4) Å) fall within the range typically observed for thorium- and uranium-alkyl bonds, respectively [3a]. In both η^2-pyridyl complexes (**3** and **5**), the pyridyl ligand is bound to the actinide metal center in an η^2-(*N*,*C*) fashion with the nitrogen atom coordinated to the metal in the center of the metallocene wedge.

To date, η^2-pyridyl complexes of the transition metals, lanthanides and actinides are still quite uncommon: only three such complexes of zirconium, one of molybdenum, two of rhenium, one of ruthenium, one of scandium, one of lutetium, and three of uranium have been structurally characterized [4,9]. The pyridyl N–C bond distances for compound **3** (N(1)–C(22) = 1.356(2) Å) and compound **5** (N(1)–C(21) = 1.355(5) Å) fall within the range (1.24–1.47 Å) of the previously reported complexes [4,9]. The N–Th–C angle in complex **3** (N(1)–Th(1)–C(22) = 32.03(5)°) and the N–U–C angle in **5** (N(1)–U(1)–C(21) = 32.85(12)°) are comparable to those observed in the structurally analogous complexes, $(C_5Me_5)_2U(CH_3)[\eta^2$-(*N*,*C*)-$NC_5H_4]$ (N–U–C = 31.8(3)°) and $(C_5Me_5)_2U(CH_3)[\eta^2$-(*N*,*C*)-4-^{t}Bu–$NC_5H_3]$ (N–U–C = 32.69(10)°) [4]. Additionally, the uranium–nitrogen and uranium–carbon bond distances for the coordinated pyridyl

ligands in **5** (U(1)-N(1) = 2.394(3) Å, U(1)–C(21) = 2.396(4) Å) are in agreement with those reported for the structurally analogous, $(C_5Me_5)_2U(CH_3)[\eta^2\text{-}(N,C)\text{-}NC_5H_4]$ (U–N = 2.424(6) Å, U–C = 2.406(7) Å) and $(C_5Me_5)_2U(CH_3)[\eta^2\text{-}(N,C)\text{-}4\text{-}^tBu\text{–}NC_5H_3]$ (U–N = 2.402(3) Å, U–C = 2.386(3) Å) [4], and slightly shorter than those reported for $[N(CH_2CH_2NSiMe_2{}^tBu)_3]U[\eta^2\text{-}(N,C)\text{-}NC_5H_4]$ (U–N = 2.440(7) Å, U–C = 2.453(7) Å), which suffer from exchange disorder associated with the η^2-pyridyl ligand [9h]. Finally, the thorium–nitrogen and thorium–carbon bond distances for the coordinated pyridyl ligands in **3** (Th(1)–N(1) = 2.4441(12) Å, Th(1)–C(22) = 2.4714(17) Å) are within expected values. Any significant deviations in the Th–C and Th–N bond distances compared to those in the uranium η^2-pyridyl systems discussed above are readily attributable to the larger ionic radius of Th(IV) versus U(IV) [10].

The molecular structure of the kinetic product **2** clearly shows that the sp^3 C–H bond of the 2-picoline methyl group has been cleaved by the thorium(IV) metal center. The resulting four-membered (Th(1)–N(1)–C(25)–C(26)) ring is folded over an angle of 40.4(8)° along the N(1)–C(26) vector and the thorium atom is located 0.563(8) Å out of the pyridine plane. The metallacycle features long $Th\text{–}C_{methylene}$ (Th(1)–C(26) = 2.642(10) Å) and $Th\text{–}N_{pyridine}$ (Th(1)–N(1) = 2.574(7) Å) interactions when compared to those displayed in the η^2-pyridyl complex **3**. The $Th\text{–}C_{methyl}$ (Th(1)–C(27) = 2.90(2) Å) bond distance is unusually long; however useful comparison of this bond distance is prevented by the substitutional disorder with chloride observed at the $Th\text{–}C_{methyl}$ site. The source of this adventitious chloride group present in the structure of **2** is unknown.

The exo C(25)–C(26) bond length (1.436(13) Å) is intermediate to that of regular C–C and C=C bonds. Interestingly, the pyridyl N–C bond distance (N(1)–C(25) = 1.359(12) Å) is comparable to those displayed by complexes **3** and **5**. These combined data suggest considerable sp^2 hydridization of the methylene carbon C(26) and that the bonding of the α-picolyl fragment can be described as a distorted $\eta^2\text{-}(C,C',N)$-aza-allylic interaction. Although this is the first example of an actinide α-picolyl complex, this type of bonding is common in alkali metal and early transition α-picolyl complexes and is intermediate between an η^2-alkyl-amine and an η^1-amido-olefin [11].

3. Conclusion

We have provided preliminary experimental observations and deuterium labeling studies which demonstrate that the analogous thorium and uranium $(C_5Me_5)_2An(CH_3)_2$ complexes react with 2-picoline by different mechanistic reaction pathways. The thorium system selectively activates a sp^3 C–H bond on the 2-picoline methyl group to give kinetic α-picolyl product, $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}2\text{-}CH_2\text{–}NC_5H_3]$, which reacts with additional 2-picoline to afford the thermodynamic η^2-pyridyl product, $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}6\text{-}CH_3\text{-}NC_5H_3]$. This is in marked contrast with the uranium system which only reacts with a sp^2 C–H bond on the 2-picoline aromatic ring to give the η^2-pyridyl product $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}6\text{-}CH_3\text{-}NC_5H_3]$. Further experimental and theoretical studies are currently underway in our laboratory to elucidate the origin of these dramatic differences in the chemical behavior between thorium and uranium.

4. Experimental

4.1. Methods and materials

Reactions and manipulations were performed at 21 °C in a recirculating Vacuum Atmospheres Model HE-553-2 inert atmosphere (N_2 or He) drybox with a MO-40-2 Dri-Train, or using standard Schlenk and high vacuum line techniques. Glassware was dried overnight at 150 °C before use. NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility using a VG ProSpec (EI) mass spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility on a Perkin-Elmer Series II 2400 CHNS Analyzer.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. *Caution*: Depleted uranium (primary isotope ^{238}U) and natural thorium (^{232}Th) are both weak α-emitters (4.197 and 4.012 MeV, respectively) with half-lives of 4.47×10^9 and 1.41×10^{10} years, respectively. All of the manipulations and reactions involving these radioactive materials are carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

Solvents for air- and moisture-sensitive reactions were purchased from Aldrich (anhydrous) and passed through a column of activated alumina (A2, 12 × 32, Purifry) under nitrogen pressure and stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 and toluene-d_8 were obtained from Aldrich and dried over activated 4 Å molecular sieves prior to use. Celite (Aldrich) and alumina (Brockman I, Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. 2-Picoline (Aldrich), 2-picoline-d_7 (Aldrich) and 2-picoline-methyl-d_3 (Cambridge Isotope Laboratories) were degassed by three freeze–pump–thaw cycles, dried by passage through activated alumina and stored over activated 4 Å molecular sieves prior to use. $(C_5Me_5)_2Th(CH_3)_2$ (**1**) [5a], $(C_5Me_5)_2U(CH_3)_2$ (**4**) [5a], $(C_5Me_5)_2Th(CH_3)Br$ [5a], 2-picolyllithium [11e,12], and 2-lithio-6-methylpyridine [13] were prepared according to the literature procedures.

4.2. Preparation of $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}2\text{-}CH_2\text{-}NC_5H_3]$ (*2*)

A 125 mL side-arm flask equipped with a stir bar was charged with $(C_5Me_5)_2Th(CH_3)Br$ (0.246 g, 0.412 mmol) and toluene (30 mL). 2-Lithio-6-methylpyridine (0.053 g, 0.536 mmol) was added to this stirring solution. The resulting reaction mixture was stirred at room temperature for 4 h and then filtered through a Celite-padded frit, and the volatiles were removed from the filtrate under reduced pressure to afford a yellow solid. The solid was washed twice with diethyl ether (2× 20 mL) and dried under dynamic vacuum to afford analytically pure **2** as a yellow powder (0.228 g, 0.374 mmol, 91%). ^1H NMR (C_6D_6, 21 °C): δ 7.88 (d, ^1H, Ar-*H*), 6.77 (m, 1H, Ar-*H*), 6.54 (d, 1H, Ar-*H*), 6.08 (m, 1H, Ar-*H*), 2.02 (s, 2H, Th-C*H*$_2$), 1.92 (s, 30H, C_5Me_5), 0.091 (s, 3H, Th-C*H*$_3$).

4.3. Preparation of $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(N,C)\text{-}6\text{-}CH_3\text{-}NC_5H_3]$ (*3*)

Complex **3** was independently prepared according to the literature procedure [4]. ^1H NMR (C_6D_6, 21 °C): δ 7.60 (d, 1H, Ar-*H*), 7.13 (m, 1H, Ar-*H*), 6.44 (d, 1H, Ar-*H*), 2.39 (s, 3H, NC_5H_3-C*H*$_3$), 1.86 (s, 30H, C_5Me_5), 0.40 (s, 3H, Th-C*H*$_3$). ^{13}C NMR (C_6D_6, 21 °C): δ 155.60, 136.82, 123.85, 121.36, 110.82 (Ar-*C*) 120.85 (C_5Me_5), 53.21 (Th-C*H*$_3$), 22.39 (NC_5H_3-*C*H$_3$), 10.69 (C_5Me_5). Anal. Calcd. for $C_{27}H_{39}NTh$ (609.63 g/mol): C, 53.19; H, 6.45; N, 2.30. Found: C, 53.46; H, 6.50; N, 2.50.

4.4. Preparation of $(C_5Me_5)_2U(CH_3)[\eta^2$-(N,C)-6-$CH_3$-$NC_5H_3]$ (5)

Complex **5** was independently prepared according to the literature procedure [4]. ^{1}H NMR (C_6D_6, 21 °C): δ 139.20 (s, 3H, U-CH_3), 66.94 (d, 1H, Ar-*H*), 17.12 (m, 1H, Ar-*H*), 9.55 (d, 1H, Ar-*H*), −2.33 (s, 30H, C_5Me_5), −17.56 (s, 3H, NC_5H_3–CH_3). MS (EI, 70 eV): *m*/*z* 600 (M^+–Me). Anal. Calcd. for $C_{27}H_{39}NU$ (615.59 g/mol): C, 52.69; H, 6.39; N, 2.28. Found: C, 52.53; H, 6.45; N, 2.18.

4.5. NMR tube reaction of complexes 1 and 4 with 2-picoline-methyl-d_3 in C_6D_6

An NMR tube was charged with **1** (0.035 g, 0.066 mmol), 2-picoline-methyl-d_3 (0.015 g, 0.15 mmol), and approximately 0.5 mL of C_6D_6. The reaction mixture was placed in a 80 °C oil bath and monitored by ^{1}H NMR spectroscopy. $(C_5Me_5)_2Th(CH_3)[\eta^2$-(*N*,*C*)-2-$CD_2$-$NC_5H_3]$ (**2**-d_2), $(C_5Me_5)_2Th(CH_3)[\eta^2$-(*N*,*C*)-6-$CD_2H$-$NC_5H_3]$ (**3**-d_2) and CDH_3 were detected over the course of 5 days. A similar reaction was performed for complex **4** and 2-picoline-methyl-d_3 at 80 °C. and $(C_5Me_5)_2U(CH_3)[\eta^2$-(*N*,*C*)-6-$CD_3$-$NC_5H_3]$ (**5**-d_3) and CH_4 were detected over the course of 3 h [14].

4.6. NMR tube reaction of complexes 1-d_6 and 4-d_6 with 2-picoline-d_7 in C_6D_6

An NMR tube was charged with **1**-d_6 (0.023 g, 0.043 mmol), 2-picoline-d_7 (0.013 g, 0.13 mmol), and approximately 0.5 mL of C_6D_6. The reaction mixture was placed in a 85 °C oil bath and monitored by ^{1}H NMR spectroscopy. The corresponding thorium metallacycles (with no deuterium incorporation into the C_5Me_5 ligands) and CD_4 were detected over the course of 5 days. A similar reaction was performed with **4**-d_6 (0.040 g, 0.073 mmol), 2-picoline-d_7 (0.022 g, 0.22 mmol), and approximately 0.5 mL of C_6D_6. The corresponding uranium metallacycle (with no deuterium incorporation into the C_5Me_5 ligands) and CD_4 were detected over the course of 7 h.

4.7. Crystal structure determination

Crystal data for **2** ($C_{27}H_{38}NTh$): M = 608.62, orthorhombic, space group *Pnma*, a = 19.5905(8) Å, b = 14.6002(6) Å, c = 8.7051(4) Å, α = 90°, β = 90°, γ = 90°, V = 2489.88(18) Å^3, Z = 4, D_{calc} = 1.624 g cm^{-3}, T = 141(2) K, θ range 2.08–28.93°, μ(Mo Kα) = 6.001 mm^{-1}, 25617 reflections collected, 3176 reflections with $I > 2\sigma(I)$. R = 0.0325 (obs. data), wR_2 = 0.0875 (all data), GOF = 1.415 (F^2).

Crystal data for **3** ($C_{27}H_{39}NTh$): M = 609.63, monoclinic, space group $P2_1/c$, a = 18.4769(11) Å, b = 17.4651(10) Å, c = 17.3063(10) Å, α = 90°, β = 115.983(1)°, γ = 90°, V = 5020.3(5) Å^3, Z = 8, D_{calc} = 1.613 g cm^{-3}, T = 141(2) K, θ range 1.69–29.06°, μ(Mo Kα) = 5.953 mm^{-1}, 56090 reflections collected, 12420 reflections with $I > 2\sigma(I)$. R = 0.0272 (obs. data), wR_2 = 0.0421 (all data), GOF = 0.458 (F^2).

Crystal data for **5** ($C_{27}H_{39}NU$): M = 615.62, monoclinic, space group $P2_1/c$, a = 9.6595(7) Å, b = 15.9087(12) Å, c = 16.5975(12) Å, β = 102.363(1)°, V = 2491.4(3) Å^3, Z = 4, D_{calc} = 1.641 g cm^{-3}, T = 141(2) K, θ range 1.79–28.68°, μ(Mo Kα) = 6.527 mm^{-1}, 26606 reflections collected, 6033 reflections with $I > 2\sigma(I)$. R = 0.0294 (obs. data), wR_2 = 0.0773 (all data), GOF = 1.200 (F^2).

The crystal structures of compounds **2**, **3**, and **5** were determined as follows, with exceptions noted: single crystals of **2** (0.32 mm × 0.28 mm × 0.28 mm), **3** (0.12 mm × 0.10 mm × 0.08 mm), and **5** (0.32 mm × 0.14 mm × 0.10 mm) were mounted in a nylon cryoloop from Paratone-N oil under argon gas flow. The data were collected on a Bruker SMART APEX II charge-coupled-device (CCD) diffractometer, with KRYO-FLEX liquid nitrogen vapor cooling device. The instrument was equipped with a graphite monochromatized Mo Kα X-ray source (λ = 0.71073 Å) and MonoCap X-ray source optics. A hemisphere of data was collected using ω scans, with 5-s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software [15]. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software [16]. The data were corrected for absorption using the SADABS program [17]. Decay of reflection intensity was monitored by analysis of redundant frames. All three structures were solved using direct methods and difference Fourier techniques. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELX-TL [18].

For compound **2**, the methyl C(27) site was substitutionally disordered, with a 50% chloride occupation. The two sites were refined, with their site-occupancy-factors fixed at 0.5. The methyl carbon atom position was refined anisotropically, while the chloride site was refined isotropically. The crystal also contained a small twin that could not be successfully integrated as a second component, and was treated by the omission of 112 reflections (of 25 617 reflections collected, 3176 with $I > 2\sigma(I)$).

For compound **3**, two independent molecules per asymmetric unit were refined. One of the molecules was also found to consist of substitutionally disordered components comprised of sp^2 and sp^3 activated forms of the 2-picoline ligand, while the other independent molecule exhibited only the sp^2 activated form. The site-occupancy-factors of the two contributions were tied to 1.0, and refined to 0.637(1) and 0.363(1), respectively.

Acknowledgements

For financial support, we acknowledge LANL (Director's Postdoctoral Fellowships to E.J.S. & J.A.P.D.T., and Frederick Reines Postdoctoral Fellowship to E.J.S.), the LANL G.T. Seaborg Institute for Transactinium Science (Postdoctoral fellowship to E.J.S.), the Division of Chemical Sciences, Office of Basic Energy Sciences, Heavy Element Chemistry program, and the LANL Laboratory Directed Research & Development program. J.L.K. thanks Drs. Rebecca M. Chamberlin, David L. Clark, Jeffery T. Golden, Christopher R. Graves, P. Jeffrey Hay, and David E. Morris (all LANL) for helpful discussions.

Appendix A. Supplementary information

CCDC-643591, CCDC-643592, and CCDC-643593 contain the supplementary crystallographic data for complexes **2**, **3**, and **5**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Database Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

[1] This field has been extensively reviewed. See, for example:
(a) J.A. Davies, P.L. Watson, J.F. Liebman, A. Greenberg (Eds.), Selective Hydrocarbon Activation: Principles and Progress, VCH Publishers, New York, 1990;
(b) B.A. Arndtsen, R.G. Bergman, T.A. Mobley, T.H. Peterson, Acc. Chem. Res. 28 (1995) 154–162;
(c) A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer, Boston, 2000;
(d) R.H. Crabtree, J. Chem. Soc., Dalton Trans. (2001) 2437–2450;
(e) J.A. Labinger, J.E. Bercaw, Nature 417 (2002) 507–514;
(f) K.I. Goldberg, A.S. Goldman (Eds.), ACS Symposium Series 885, American Chemical Society, Washington, DC, 2004.
[2] (a) W.D. Jones, F.J. Feher, Acc. Chem. Res. 22 (1989) 91–100;
(b) W.D. Jones, F.J. Feher, J. Am. Chem. Soc. 107 (1985) 620–631.

[3] (a) K.C. Jantunen, C.J. Burns, I. Castro-Rodriguez, R.E. Da Re, J.T. Golden, D.E. Morris, B.L. Scott, F.L. Taw, J.L. Kiplinger, Organometallics 23 (2004) 4682–4692;
(b) D.E. Morris, R.E. Da Re, K.C. Jantunen, I. Castro-Rodriguez, J.L. Kiplinger, Organometallics 23 (2004) 5142–5153;
(c) R.E. Da Re, K.C. Jantunen, J.T. Golden, J.L. Kiplinger, D.E. Morris, J. Am. Chem. Soc. 127 (2005) 682–689;
(d) A.E. Clark, R.L. Martin, P.J. Hay, J.C. Green, K.C. Jantunen, J.L. Kiplinger, J. Phys. Chem. A 109 (2005) 5481–5491;
(e) E.J. Schelter, D.E. Morris, B.L. Scott, J.L. Kiplinger, Chem. Commun. (2007) 1029–1031;
(f) E.J. Schelter, P. Yang, B.L. Scott, R.E. Da Re, K.C. Jantunen, R.L. Martin, P.J. Hay, D.E. Morris, J.L. Kiplinger, J. Am. Chem. Soc. 129 (2007) 5139–5152.

[4] J.A. Pool, B.L. Scott, J.L. Kiplinger, J. Alloys Compd. 418 (2006) 178–183.

[5] (a) P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam, T.J. Marks, J. Am. Chem. Soc. 103 (1981) 6650–6667;
(b) J.A. Pool, B.L. Scott, J.L. Kiplinger, J. Am. Chem. Soc. 127 (2005) 1338–1339.

[6] Systematic studies of the thermochemistry of these systems are also being carried out using density functional theory (DFT) in order to gain an explanation for this behavior: P. Yang, I. Warnke, R.L. Martin, P.J. Hay, manuscript in preparation.

[7] (a) C.S. Adams, P. Legzdins, W.S. McNeil, Organometallics 20 (2001) 4939–4955;
(b) C.S. Adams, P. Legzdins, E. Tam, Organometallics 21 (2002) 1474–1486.

[8] (a) P.L. Watson, in: J.A. Davies, P.L. Watson, J.F. Liebman, A. Greenberg (Eds.), Selective Hydrocarbon Activation, VCH Publishers, New York, 1990;
(b) J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.J. Schultz, J.M. Williams, J. Am. Chem. Soc. 108 (1986) 40–56;
(c) R.G. Peters, B.P. Warner, C.J. Burns, Organometallics 18 (1999) 2587–2589.

[9] (a) Zr: R.F. Jordan, D.F. Taylor, N.C. Baenziger, Organometallics 9 (1990) 154–157;
(b) Zr: C.A. Bradley, E. Lobkovsky, P.J. Chirik, J. Am. Chem. Soc. 125 (2003) 8110–8111;
(c) Mo: G. Zhu, J.M. Tanski, D.G. Churchill, K.E. Janak, G. Parkin, J. Am. Chem. Soc. 124 (2002) 13658–13659;
(d) Rh: O.V. Ozerov, M. Pink, L.A. Watson, K.G. Caulton, J. Am. Chem. Soc. 126 (2004) 2105–2113;
(e) Ru: J.L. Kersten, R.R. Kucharczyk, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, Chem. Eur. J. 3 (1997) 1668–1674;
(f) Sc: M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santasiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203–219;
(g) Lu: K.C. Jantunen, B.L. Scott, J.C. Gordon, J.L. Kiplinger, Organometallics 26 (2007) 2777–2781;
(h) U: R. Boaretto, P. Roussel, N.W. Alcock, A.J. Kingsley, I.J. Munslow, C.J. Sanders, P. Scott, J. Organomet. Chem. 591 (1999) 174–184.

[10] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751–767.

[11] (a) M.H. Chisholm, K. Folting, J.C. Huffman, I.P. Rothwell, Inorg. Chem. 20 (1981) 1496–1500;
(b) S.I. Bailey, D. Colgan, L.M. Engelhardt, W.P. Leung, P.I. Papasergio, C.L. Raston, A.H. White, J. Chem. Soc., Dalton Trans. (1986) 603–613;
(c) S.M. Beshouri, D.E. Chebi, P.E. Fanwick, I.P. Rothwell, Organometallics 9 (1990) 2375–2385;
(d) R.F. Jordan, A.S. Guram, Organometallics 9 (1990) 2116–2123;
(e) R. Duchateau, E.A.C. Brussee, A. Meetsma, J.H. Teuben, Organometallics 16 (1997) 5506–5516;
(f) R.A. Corbin, B.E. Dusick, K. Phomphrai, P.E. Fanwick, I.P. Rothwell, Chem. Commun. (2005) 1194–1196.

[12] O.F. Beumel Jr., W.N. Smith, B. Rybalka, Synthesis (1974) 43–45.

[13] I. Kim, S.M. Kim, C.S. Ha, D.W. Park, Macromol. Rapid Commun. 25 (2004) 888–893.

[14] J.A. Pool, "Unexpected reactivity between aromatic nitrogenous molecules and uranium(IV) and thorium(IV) Complexes" Oral Presentation, G.T. Seaborg Institute Seminar Series, Los Alamos National Laboratory, March 31, 2005.

[15] APEX II, Version 1.08, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2004.

[16] SAINT+, Version 7.06, Data Collection Software, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2003.

[17] G. Sheldrick, SADABS 2.03, Empirical Absorption Correction Program, Version 2.03, University of Göttingen, Germany, 2001.

[18] SHELXTL, SHELTXTL, Version 5.10, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 1997.