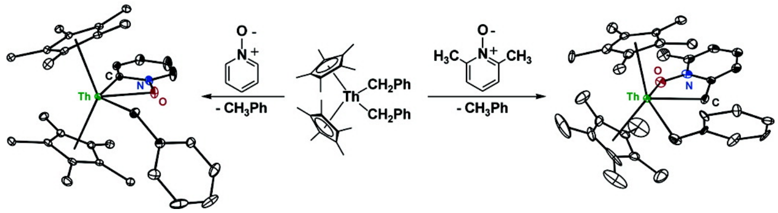
Communication

A New Mode of Reactivity for Pyridine *N*-Oxide: C–H Activation with Uranium(IV) and Thorium(IV) Bis(alkyl) Complexes

Jaime A. Pool, Brian L. Scott, and Jaqueline L. Kiplinger

J. Am. Chem. Soc., **2005**, 127 (5), 1338-1339• DOI: 10.1021/ja044153o • Publication Date (Web): 14 January 2005



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 17 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

A New Mode of Reactivity for Pyridine *N*-Oxide: C−H Activation with Uranium(IV) and Thorium(IV) Bis(alkyl) Complexes

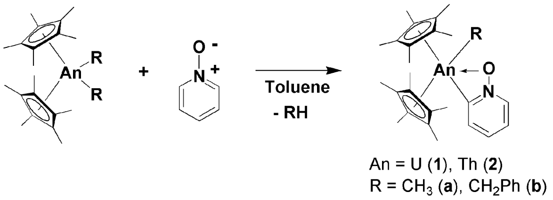
Jaime A. Pool, Brian L. Scott, and Jaqueline L. Kiplinger*

Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received September 26, 2004; E-mail: kiplinger@lanl.gov

Although transition-metal complexes possessing the terminal Schrock-type alkylidene and alkylidyne functionalities are well-known, related actinide complexes have remained elusive.[1] Recent reports have shown that oxidatively induced α-hydrogen abstraction may be used to prepare early transition-metal alkylidene complexes.[2] The propensity of uranium to exist in the hexavalent oxidation state coupled with the known oxophilicity of tetravalent uranium suggested to us that uranium(VI) alkylidene complexes of the type, $(C_5Me_5)_2U({=}O)({=}CHR)$, might be synthesized using oxidatively induced α-hydrogen abstraction chemistry between uranium(IV) bis(alkyl) complexes such as $(C_5Me_5)_2U(CH_2R)_2$ and an appropriate oxygen atom transfer agent.

Pyridine *N*-oxide is a prototypical oxygen atom transfer reagent that has been routinely used in the synthesis of high-valent transition-metal[1,3] and actinide[4] oxo complexes. However, addition of 1 equiv of pyridine *N*-oxide to a toluene solution of the uranium(IV) bis(alkyl) complexes $(C_5Me_5)_2UR_2$ ($R = CH_3, CH_2Ph$)[5] unexpectedly results in activation of an sp^2 hybridized C−H bond, with loss of alkane and formation of the novel cyclometalated pyridine *N*-oxide complexes $(C_5Me_5)_2U(R)[\eta^2\text{-}(O,C)\text{-}ONC_5H_4]$ ($R = CH_3$ (**1a**), CH_2Ph (**1b**)) in greater than 70% yield (eq 1).



(1)

To the best of our knowledge, this is a new mode of reactivity for pyridine *N*-oxide.[6] Importantly, this C−H activation chemistry also takes place with the analogous thorium bis(alkyl) derivatives $(C_5Me_5)_2ThR_2$ ($R = CH_3, CH_2Ph$)[5] to give the complexes $(C_5Me_5)_2Th(R)[\eta^2\text{-}(O,C)\text{-}ONC_5H_4]$ ($R = CH_3$ (**2a**), CH_2Ph (**2b**)). This observation obviates the need for involvement of an uranium(VI) intermediate along the pathway to the cyclometalated complexes **1a**,**b**.

The ^1H NMR spectra of the diamagnetic $6d^05f^0$ Th(IV) complexes **2a**,**b** revealed clean formation of one isomer of the corresponding cyclometalated product, $(C_5Me_5)_2Th(R)[\eta^2\text{-}(O,C)\text{-}ONC_5H_4]$, with four diagnostic downfield resonances attributed to the pyridine ring. The uranium derivatives **1a**,**b** exhibited relatively sharp, paramagnetically shifted resonances typical of $5f^2$ U(IV) species.[7]

Single-crystal X-ray diffraction studies confirmed that an sp^2 hybridized C−H bond had been activated to form the complexes **1b** and **2b**. The molecular structures of **1b** and **2b** are shown in Figure 1 and reveal a typical bent-metallocene framework with the activated pyridine *N*-oxide and alkyl ligand contained within the metallocene wedge. The complexes are isostructural; any significant deviation between the metal−ligand bond distances exhibited by the two complexes is readily attributable to the smaller ionic radius of U(IV) versus Th(IV).[8] For complex **1b**, the benzyl ligand interacts with the metal center in an η^1 fashion and the pyridine *N*-oxide is bound to the U(IV) metal center in an η^2-(O,C) fashion with the oxygen atom coordinated to the metal in the center of the metallocene wedge. The U(1)−O(1) bond length of 2.361(9) Å is shorter than other reported uranium−oxygen dative interactions.[7b,9] The O(1)−N(1) (1.377(13) Å) bond distance is comparable to the 1.330(9) Å reported for free pyridine *N*-oxide.[10] The U(1)−C(1) (2.561(13) Å) and U(1)−C(6) (2.505(14) Å) bond lengths fall within the range typically observed for an uranium−alkyl bond.[7b,c]

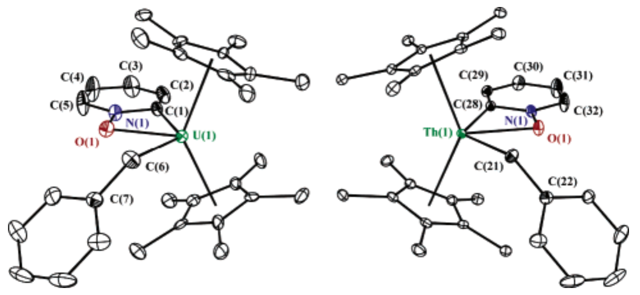


Figure 1. Molecular structures of complexes **1b** (left) and **2b** (right), with thermal ellipsoids at the 25% probability level.

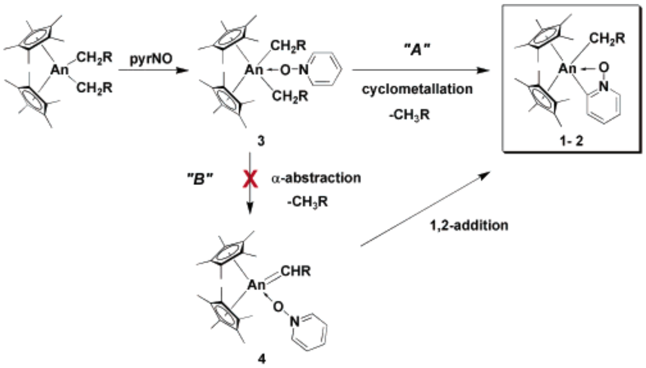
Two reasonable mechanisms for these transformations are illustrated in Scheme 1. In mechanism **A**, prior coordination of the *N*-oxide oxygen atom to the actinide metal center, leading to **3**, followed by direct activation of the sp^2 C−H bond on the pyridine *N*-oxide forms the cyclometalated product, $(C_5Me_5)_2An(R)[\eta^2\text{-}(O,C)\text{-}ONC_5H_4]$. Mechanism **B** also begins with *N*-oxide coordination, giving **3**, but is followed by formation of an actinide alkylidene complex (**4**) by α-abstraction and loss of alkane. Subsequent 1,2-addition of the sp^2 C−H bond across the alkylidene moiety yields the observed cyclometalated product.

To distinguish between these two possible mechanisms, deuterium labeling studies were performed. The reaction of $(C_5Me_5)_2U(CD_2C_6D_5)_2$ with pyridine *N*-oxide exclusively yielded $(C_5Me_5)_2U(CD_2C_6D_5)[\eta^2\text{-}(O,C)\text{-}ONC_5H_4]$ and $CHD_2C_6D_5$ as determined by integration using ^1H NMR spectroscopy. Similarly, the reaction of $(C_5Me_5)_2Th(CH_3)_2$ with pyridine *N*-oxide-d_5 afforded $(C_5Me_5)_2Th(CH_3)[\eta^2\text{-}(O,C)\text{-}ONC_5D_4]$ and CH_3D as the sole methane isotopomer (no CH_4 detected). The deuterium labeling studies clearly suggest that the same mechanism is operative for both the uranium and thorium complexes and that the C−H activation chemistry proceeds by mechanism **A**, or direct cyclometalation. Mechanism **B** is *not* operative since formation of an intermediate alkylidene complex (**4**) would be accompanied by the production of $CD_3C_6D_5$ and CH_4, respectively, for the uranium and thorium reactions examined.

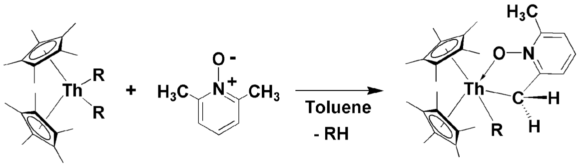
This chemistry is not limited to sp^2 hybridized C−H bonds. As depicted in eq 2, reaction of 1 equiv of 2,6-lutidine *N*-oxide with

10.1021/ja044153o CCC: $30.25

Scheme 1



the Th(IV) bis(alkyl) complexes $(C_5Me_5)_2ThR_2$ ($R = CH_3$, CH_2Ph) for 3 h at ambient temperature affords the cyclometalated complexes **5a**,**b** in 70−80% yield.



(2)

R = CH_3 (**5a**), CH_2Ph (**5b**)

Analysis of the crude reaction mixture by ^1H NMR spectroscopy revealed formation of only one isomer for each of the cyclometalated products, **5a**,**b**, which presented four resonances for the activated lutidine *N*-oxide fragment along with a doublet of doublets for the diastereotopic protons on the activated methyl group. In contrast, no reaction was observed between the analogous U(IV) bis(alkyl) derivatives $(C_5Me_5)_2UR_2$ ($R = CH_3$, CH_2Ph) and 2,6-lutidine *N*-oxide, even under elevated temperatures (60 °C) for 12 h. We do not understand the basis for this marked difference in reactivity between the thorium and uranium bis(alkyl) complexes with 2,6-lutidine *N*-oxide. Studies to gain insight into the steric and electronic factors governing this chemistry are currently underway. While it seems unlikely that steric factors significantly contribute to the observed difference in reactivity, they cannot be ruled out.[8]

Single-crystal X-ray diffraction studies confirmed that the methyl C−H bond of the 2,6-lutidine *N*-oxide in complexes **5a**,**b** had been activated. The molecular structures of **5a**,**b** are presented in Figure 2 and show that the activated lutidine *N*-oxide and alkyl ligands are located within the metallocene wedge. The cyclometalated 2,6-lutidine *N*-oxide in complexes **5a**,**b** is coordinated to the Th(IV) metal center in an η^2-(O,C) fashion, with the methylene carbon atom oriented and bound to the metal in the center of the metallocene wedge, which is in contrast to the pyridine *N*-oxide derivatives **1** and **2**. For complex **5a**, the Th(1)−O(1) bond distance of 2.424(3) Å is shorter than expected for a dative interaction,[11] and the O(1)−N(1) (1.359(5) Å) bond distance is slightly longer than the 1.347(4) Å reported for the pentachlorophenol adduct of 2,6-lutidine *N*-oxide.[12] Although Th(1)−C(28) (2.496(5) Å) is unexceptional, the Th(1)−C(27) (2.641(5) Å) bond length is considerably longer than those reported for other thorium−alkyl complexes and may be a manifestation of steric crowding in these molecules.[7c] Similar metrical parameters are observed for complex **5b**.

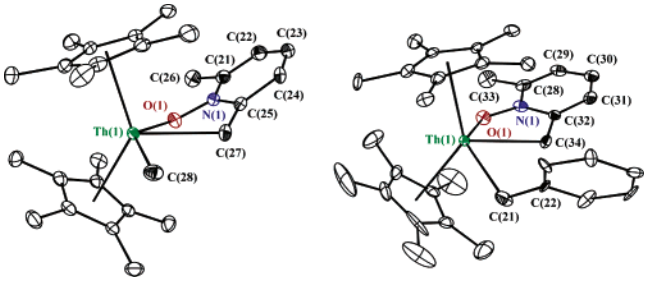


Figure 2. Molecular structures of complex **5a** (left) and **5b** (right), with thermal ellipsoids at the 25% probability level.

In summary, we have demonstrated that U(IV) and Th(IV) bis(alkyl) complexes readily activate both sp^2 and sp^3 hybridized C−H bonds in pyridine *N*-oxides, providing rare examples of C−H activation chemistry mediated by actinide metal centers.[7a,13] This is in contrast to the known oxygen atom transfer reactivity patterns of pyridine *N*-oxides with oxophilic metal complexes and constitutes a new mode of reactivity for pyridine *N*-oxides.

Acknowledgment. For financial support, we acknowledge LANL (Director's Postdoctoral Fellowship to J.A.P.), the Division of Chemical Sciences, Office of Basic Energy Sciences, and the LANL LDRD Program. J.L.K. thanks Dr. Carol J. Burns (LANL) for helpful discussions.

Supporting Information Available: Full experimental and spectroscopic details for all compounds and crystallographic data for complexes **1b**, **2b**, **5a**, and **5b** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145−179 and references therein.
(2) Basuli, F.; Bailey, B. C.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6052−6053.
(3) For example, see: (a) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448−1457. (b) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6952−6963. (c) Sung, K. M.; Holm, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 1931−1943.
(4) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448−9460.
(5) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650−6667.
(6) A benzamidinate Ta methylidene complex that reacts with pyridine *N*-oxides to give a Ta oxo complex and methylpyridines has been reported. See: Mullins, S. M.; Bergman, R. G.; Arnold, J. *Organometallics* **1999**, *18*, 4465−4467.
(7) (a) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Chem. Commun.* **2002**, 30−31. (b) Kiplinger, J. L.; John, K. D.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 4306−4308. (c) Jantunen, K. C.; Burns, C. J.; Castro-Rodriguez, I.; Da Re, R. E.; Golden, J. T.; Morris, D. E.; Scott, B. L.; Taw, F. L.; Kiplinger, J. L. *Organometallics* **2004**, *23*, 4682−4692.
(8) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751−767.
(9) (a) Wasserman, H. J.; Zozulin, A. J.; Moody, D. C.; Ryan, R. R.; Salazar, K. V. *J. Organomet. Chem.* **1983**, *254*, 305−311. (b) Berthet, J. C.; Lance, M.; Nierlich, M. *J. Organomet. Chem.* **1997**, *533*, 7−11.
(10) Marsh, R. E.; Kapon, M.; Hu, S.; Herbstein, F. H. *Acta Crystallogr., Sect. B* **2002**, *B58*, 62−77.
(11) (a) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3773−3775. (b) Edelman, M. A.; Hitchcock, P. B.; Hu, J.; Lappert, M. F. *New J. Chem.* **1995**, *19*, 481−489.
(12) Dega-Szafran, D.; Kosturkiewicz, Z.; Tykarska, E.; Szafran, M.; Lemański, D.; Nogaj, B. *J. Mol. Struct.* **1997**, *404*, 25−32.
(13) (a) Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. *Selective Hydrocarbon Activation: Principles and Progress*; VCH: New York, 1990, and references therein. (b) Clark, D. L.; Grumbine, S. K.; Scott, B. L.; Watkin, J. G. *Organometallics* **1996**, *15*, 949−957 and references therein. (c) Boaretto, R.; Roussel, P.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Alcock, N. W.; Scott, P. *Chem. Comm.* **1999**, 1701−1702.

JA044153O