

Enhancing the reactivity of uranium(vi) organoimido complexes with diazoalkanes†

Jaqueline L. Kiplinger,* David E. Morris, Brian L. Scott and Carol J. Burns*

Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: cjb@lanl.gov

Received (in Purdue, IN, USA) 16th October 2001, Accepted 8th November 2001

First published as an Advance Article on the web 3rd December 2001

Diphenyldiazomethane effects a two-electron oxidation of the uranium(IV) monoimido complex $(C_5Me_5)_2U(=N-2,4,6-t-Bu_3C_6H_2)$ to give the uranium(VI) mixed bis(imido) complex, $(C_5Me_5)_2U(=N-2,4,6-t-Bu_3C_6H_2)(=N-N=CPh_2)$, which undergoes a rare cyclometallation reaction upon mild thermolysis to afford a uranium(IV) bis(amide) complex that results from net addition of a C–H bond of an ortho *tert*-butyl group across the N=U=N core.

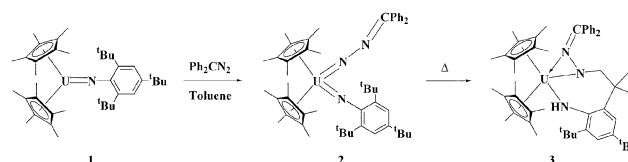
Arguably, one of the most exciting discoveries over the past 15 years in organometallic chemistry has been the observation that high-valent (d^0) early transition-metal imido complexes readily activate carbon–hydrogen bonds.¹ In addition, these compounds have been shown to display a rich chemistry^{1,2} that includes cycloadditions of unsaturated C–C and C–X bonds, addition of H_2 and alkylsilanes, hydroamination of alkynes to enamines, and recently, catalytic imine metathesis.³ High-valent (f^0) actinide imido complexes might be expected to display similar reactivity patterns to their early transition-metal counterparts; however, the most characteristic chemical property of uranium imido (U=N) bonds is their decided lack of reactivity. Presumably, this is a consequence of diminished polarity of the uranium–nitrogen bond due to higher bond order resulting from nitrogen 2p lone-pair donation to uranium, higher available coordination numbers for uranium, and the ability of uranium to access 5f-orbitals for multiple bonding.⁴

The reaction chemistry of uranium(VI) bis(imido) complexes is limited to reduction by H_2 ⁴ and arylsilanes⁵ to form the corresponding U(IV) bis(amide) complexes, catalytic disproportionation of 1,2-diphenylhydrazine to afford aniline and azobenzene,⁶ and a recent report involving the intramolecular activation of a pentamethylcyclopentadienyl methyl C–H bond across the two imido functional groups of a U(VI) bis(imido) complex to give the corresponding U(IV) bis(amide) ‘tuck-in’ complex.⁷ Importantly, most of these reactions were promoted under forcing conditions (elevated temperatures).

In our ongoing pursuit to develop synthetic entries towards uranium complexes containing multiply bonded functional groups, we discovered a method to access reactive uranium organoimido complexes. We now report that diazoalkanes can be used to prepare uranium(VI) bis(imido) complexes which are reactive toward sp^3 hybridized C–H bonds. This chemistry represents a new mode of intramolecular C–H activation for organoactinide complexes.⁸ The key feature of this work is that net 1,3 addition of a C–H bond across the N=U=N core of an uranium(VI) mixed-bis(imido) complex occurs under mild conditions to afford the corresponding bis(amide) complex.

As depicted in Scheme 1, treatment of a toluene solution of the uranium(IV) monoimido complex **1** with an equimolar amount of diphenyldiazomethane generates the uranium(VI) bis(imido) complex **2** as a brown crystalline solid in 97% yield.⁹

Complex **2** does *not* lose N_2 to give the uranium(VI) alkylidene complex. This in marked contrast with the chemistry



Scheme 1

observed for isoelectronic N_2O and organoazides (N_3R) which have been exploited as valuable two electron oxidative transfer agents to uranium(IV) imido precursors for the preparation of uranium(VI) oxo and uranium(VI) imido complexes, respectively.⁴ It is important to note that although the reaction between a transition metal complex and a substituted diazomethane to produce a complex that contains a metal–nitrogen multiple bond is a reaction type that has been known for the past 20 years,¹⁰ this work represents the first time that diazoalkanes have been utilized as two-electron oxidants at an actinide metal center.

That the uranium metal center has been oxidized from U(IV) to U(VI) is clearly demonstrated by the 1H NMR and electronic absorption spectra of **2**. The room-temperature electronic absorption spectrum, recorded in toluene solution from 1600 to 300 nm, shows no $f \rightarrow f$ transitions in the near IR region, but does show a broad, intense, and featureless charge-transfer band in the visible region, which is consistent with the assignment of an f^0 U(VI) metal center.¹¹ Also, variable-temperature 1H NMR spectroscopy (-75 to $+60$ °C) reveals that the 1H NMR spectrum of **2** is temperature invariant and indicates that complex **2** behaves like a temperature-independent paramagnet (TIP), a characteristic property of U(VI) in related organometallic species.¹¹

The identity of complex **2** as a uranium(VI) bis(imido) complex was confirmed by a single-crystal X-ray diffraction study (Fig. 1(a)).[‡] The molecular structure of **2** reveals a typical bent metallocene framework with a pseudotetrahedral coordination environment about the uranium atom; the two imido ligands are terminally bound to the uranium metal center. The uranium–nitrogen bond lengths (U(1)–N(3) 1.987(5) Å and U(1)–N(1) 2.031(6) Å) and nearly linear U–N–C_{ipso} and U–N–N bond angles (U(1)–N(3)–C(34) 176.1(5)° and U(1)–N(1)–N(2) 157.1(5)°) are consistent with the assignment of the ligands as organoimido groups. The uranium–nitrogen bond distances lie at the high end of the range for other structurally characterized uranium(VI) complexes containing terminal imido groups (*e.g.* $(C_5Me_5)_2U(=NPh)_2$: U–N 1.952(7) Å;^{11b} $(C_5Me_5)_2U(=NAd)_2$: U–N 1.94(2), 1.96(2) Å;¹² $(C_5Me_5)_2U(=O)(=N-2,6-i-Pr_2C_6H_3)$: U–N 1.988(4) Å;^{11c} $[N(SiMe_3)_2]_3-U(F)(=NPh)$: U–N 1.979(8) Å).^{11a} The lengthening of the U=N bonds is most likely a manifestation of the immense steric demands dictated by the 2,4,6-*t*-Bu₃C₆H₂ group. Importantly, the metrical parameters associated with the fragment derived from the diazoalkane supports the formation of an uranium–imido linkage; the bound diazoalkane has been reduced as evidenced by the significant elongation of the N(1)–N(2) bond distance (1.308(8) Å) compared with that of uncomplexed diazoalkanes (1.12–1.13 Å).¹³

† Electronic supplementary information (ESI) available: experimental, including general procedures, materials and synthesis of complexes **2** and **3**. See <http://www.rsc.org/suppdata/cc/b1/b109455f/>

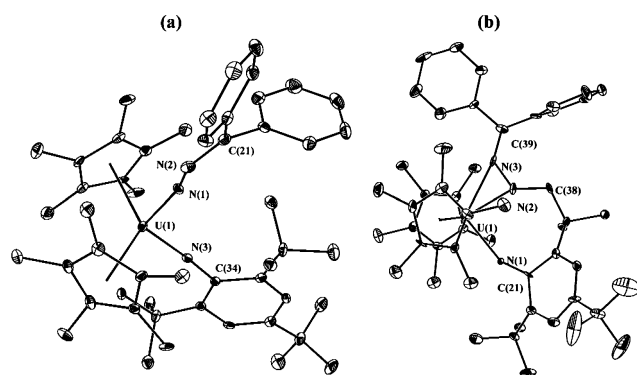


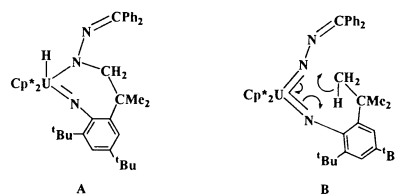
Fig. 1 (a) Molecular structure of **2** with thermal ellipsoids at the 20% probability level. Selected bond distances (Å) and angles (°): U(1)–N(1) 2.031(6), U(1)–N(3) 1.987(5), N(1)–N(2) 1.308(8), N(2)–C(21) 1.310(10); N(1)–U(1)–N(3) 104.9, U(1)–N(1)–N(2) 157.1(5), N(1)–N(2)–C(21) 130.3(7), U(1)–N(3)–C(34) 176.1(5). (b) Molecular structure of **3** with thermal ellipsoids at the 20% probability level. Selected bond distances (Å) and angles (°): U(1)–N(1) 2.315(9), U(1)–N(2) 2.228(10), U(1)–N(3) 2.496(12), N(2)–N(3) 1.364(13), N(1)–C(21) 1.404(14), N(2)–C(38) 1.461(14), N(3)–C(39) 1.325(16); N(1)–U(1)–N(2) 81.9(4), N(2)–U(1)–N(3) 32.9(3), U(1)–N(1)–C(21) 133.2(8), U(1)–N(2)–C(38) 150.2(9), U(1)–N(3)–C(39) 168.3(9).

Mild thermolysis of a toluene-*d*₈ solution of **2** (100 °C, 20 min) results in a marked color change from brown to dark cherry red and ¹H NMR spectroscopy signals the quantitative formation of the novel cyclometallated uranium(IV) bis(amide) complex **3** (Scheme 1); the NMR spectrum of the product is paramagnetically shifted, which indicates that the product is a reduced U(IV) species. Following work-up, the isolated yield for complex **3** is 73%.⁹

That the C–H bond of one of the ortho *tert*-butyl groups from the U=N–2,4,6-*t*-Bu₃C₆H₂ fragment has been activated is unambiguously ascertained by X-ray crystallography which clearly shows the net 1,3 addition of the C–H fragment across the N=U=N core (Fig. 1(b)).[‡] As with the bis(imido) complex **2**, complex **3** possesses the standard pseudotetrahedral geometry observed for bent metallocene uranium complexes. In the metallocene wedge lie three nitrogen atoms: two are associated with uranium–amide linkages (U(1)–N(1) 2.315(9) Å and U(1)–N(2) 2.228(10) Å) and one is an uranium–nitrogen dative interaction (U(1)–N(3) 2.496(12) Å). Notably, the U(1)–N(1)–C(21) bond angle is 133.2(8)° which deviates significantly from the nearly linear U–N–C_{ipso} angle (176.1(5)°) present in the bis(imido) complex **2**.

Perhaps the most striking aspect of the cyclometallation sequence is the net 1,3 addition of the C–H bond from one of the ortho *tert*-butyl groups across the N=U=N fragment; this reaction type has no equivalent in the transition metal series and represents a new mode of C–H activation available for imido ligands.^{7,8} The mechanism for this unusual transformation is not established yet. However, two mechanistic scenarios are proposed to rationalize the observed chemistry. One explanation invokes a stepwise process with initial addition of the C–H bond across one U=N fragment to generate the U(VI) hydride intermediate (A) which undergoes a 1,2-hydride shift to give the observed U(IV) bis(amide) complex (**3**). An alternative route is a thermally allowed (2π + 2π + 2σ) pericyclic reaction in which the C–H bond is transferred across the N=U=N fragment in a concerted fashion (B). The mechanism of this reaction is currently under investigation.

Clearly, the ability of the U=N–R functionality to activate C–H bonds is related to the nature of the R group. For the imido ligand derived from diphenyldiazomethane, R is N=CPh₂, which, owing to the nitrogen, might be expected to provide more electron density to the imido nitrogen relative to previously reported uranium(VI) imido complexes in which R = alkyl or aryl.^{4–7,11,12} Accordingly, the imido nitrogen would



experience enhanced basicity, which would translate into greater reactivity for the U=N moiety.

In summary, this work demonstrates that through judicious choice of diazoalkane it is possible to enhance the reactivity of the U=N linkage. Thus, diazoalkanes could serve as a versatile platform for the preparation of reactive uranium(VI) imido complexes. We are currently exploring the generality of this chemistry.

For financial support of this work, we acknowledge the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (C. J. B.) and the LANL LDRD Program (D. E. M.). J. L. K. is the recipient of a Frederick Reines fellowship at Los Alamos. Finally, we thank Professor Paul B. Duval (U Missouri, Columbia) for helpful discussions.

Notes and references

[‡] Crystal data for **2**: C₅₁H₆₉N₃U, *M* = 962.12, *a* = 12.407(4), *b* = 29.634(7), *c* = 12.836(4) Å, β = 103.484(5)°, *V* = 4590(2) Å³, monoclinic, space group *P*2₁/*m*, *Z* = 4, *T* = 203 K, *R*₁ (*I* > 2σ) = 0.0585, and *wR*₂ (*I* > 2σ) = 0.1092. Crystal data for **3**: C₅₄H₇₅N₃U, *M* = 1004.20, *a* = 10.778(3), *b* = 21.982(7), *c* = 22.876(9) Å, α = 104.703(9), β = 98.253(6), γ = 102.868(7)°, *V* = 4995(3) Å³, triclinic space group *P*1, *Z* = 4, *T* = 203 K, *R*₁ (*I* > 2σ) = 0.0951, and *wR*₂ (*I* > 2σ) = 0.1153. The reflection data were collected on a Bruker P4/CCD using φ scans. The structure was solved using standard direct methods techniques (SHELXS-97),¹⁴ and refined using full-matrix least-squares based on *F*² (SHELXL-97).¹⁴ Hydrogen atom positions were idealized, and rode on the atom they were attached to. All non-hydrogen atoms were refined anisotropically. CCDC reference numbers 172876 and 172877. See <http://www.rsc.org/suppdata/cc/b1/b109455f/> for crystallographic data in CIF or other electronic format.

- (a) P. J. Walsh, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 8729; (b) C. C. Cummins, S. M. Baxter and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1988, **110**, 8731.
- (a) W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123; (b) W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988; (c) D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239; (d) P. Mountford, *Chem. Commun.*, 1997, 2127; (e) J. L. Polse, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1998, **120**, 13405 and references therein.
- (a) G. K. Cantrell and T. Y. Meyer, *J. Am. Chem. Soc.*, 1998, **120**, 8035; (b) R. L. Zuckerman, S. W. Krska and R. G. Bergman, *J. Am. Chem. Soc.*, 2000, **122**, 751.
- D. S. J. Arney and C. J. Burns, *J. Am. Chem. Soc.*, 1995, **117**, 9448.
- R. C. Schnabel and C. J. Burns, unpublished results.
- R. G. Peters, B. P. Warner and C. J. Burns, *J. Am. Chem. Soc.*, 1999, **121**, 5585.
- R. G. Peters, B. P. Warner, B. L. Scott and C. J. Burns, *Organometallics*, 1999, **18**, 2587.
- J. A. Davies, P. L. Watson, J. F. Liebman and A. Greenberg, *Selective Hydrocarbon Activation: Principles and Progress*, VCH, New York, 1990.
- Experimental details are included as ESI[†].
- M. Dartiguenave, M. J. Menu, E. Deydier, Y. Dartiguenave and H. Siebald, *Coord. Chem. Rev.*, 1998, **178–180**, 623, and references therein.
- (a) C. J. Burns, W. H. Smith, J. C. Huffman and A. P. Sattelberger, *J. Am. Chem. Soc.*, 1990, **112**, 3237; (b) D. S. J. Arney, C. J. Burns and D. C. Smith, *J. Am. Chem. Soc.*, 1992, **114**, 10068; (c) D. S. J. Arney and C. J. Burns, *J. Am. Chem. Soc.*, 1993, **115**, 9840.
- B. P. Warner, B. L. Scott and C. J. Burns, *Angew. Chem., Int. Ed.*, 1998, **37**, 959.
- S. Patai, *The Chemistry of Diazonium and Diazo Groups, Parts 1 and 2*, Wiley, New York, 1978, and references therein.
- SHELXTL/NT Version 5.1, Bruker AXS, Inc., Madison, WI.