JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

A Direct Route to Bis(imido)uranium(V) Halides via Metathesis of Uranium Tetrachloride

Robert E. Jilek,[†] Liam P. Spencer,[†] Richard A. Lewis,[‡] Brian L. Scott,[†] Trevor W. Hayton,[‡] and James M. Boncella*,[†]

[†]MPA Division, Los Alamos National Laboratory, MS J514, Los Alamos, New Mexico 87545, United States

[‡]Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States

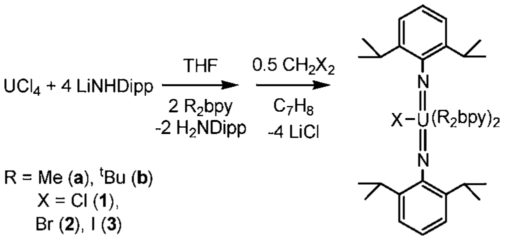
Supporting Information

ABSTRACT: Metathesis reactions between uranium tetrachloride and lithium 2,6-diisopropylphenylamide in the presence of 4,4′-dialkyl-2,2′-bipyridyl (R_2bpy; R = Me, ^{t}Bu) or triphenylphosphine oxide (tppo) appear to generate bis(imido)uranium(IV) in situ. These extremely reactive complexes abstract chloride from dichloromethane to generate $U(NDipp)_2Cl(R_2bpy)_2$ or $U(NDipp)_2Cl(tppo)_3$ (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$). The preparation of the bromide and iodide analogues $U(NDipp)_2X(R_2bpy)_2$ was achieved by addition of CH_2X_2 (X = Br, I) to the uranium(IV) solutions. The uranium(V) halides were characterized by X-ray crystallography and found to exhibit linear N−U−N units and short U−N bonds. Electrochemical measurements were made on the chloride bipyridine species, which reacts readily with iodine or ferrocenium to generate bis(imido)uranium(VI) cations.

It has been nearly 30 years since the first imidouranium complexes were discovered,[1] and recently, the chemistry of this functional unit has garnered much attention among actinide scientists. The primary reason for this interest is the opportunity to probe the fundamental differences in bonding and reactivity between the transition-metal series and actinide elements (i.e., whether the f orbitals significantly alter the M═NR reactivity). Much of the research in this area has focused on mono(imido)uranium(IV)[1a,2] and -uranium(V)[1b,3] compounds, with bis(imido) species almost exclusively limited to uranium(VI).[2c,4] The discovery of $U(NR)_2I_2(THF)_x$, which contains a $U(NR)_2^{2+}$ unit that is isostructural with UO_2^{2+}, allowed for direct comparisons of these isoelectronic molecules. The results demonstrated that the bonding in $U(NR)_2^{2+}$ is more covalent in nature than in uranyl.[4c] Pentavalent UO_2^+ species are much less common because of their propensity to disproportionate; however, there have been a number of recent reports concerning the synthesis of this important ion.[5] Unfortunately, there is only a single reported example of a bis(imido)uranium(V) compound, namely, $[U(\mu\text{-N}^t\text{Bu})(\text{N}^t\text{Bu})\text{I}(^t\text{Bu}_2\text{bpy})]_2$ (R_2bpy = 4,4′-dialkyl-2,2′-bipyridyl),[6] and because of the bridging nature of the imido ligand, the U═N bond is significantly lengthened. Thus, comparisons with monomeric UO_2^+ are not appropriate. We now report the syntheses of a series of monomeric bis(imido)uranium(V) complexes, $U(NDipp)_2X(R_2bpy)_2$ (X = Cl, Br, I; R = Me, ^{t}Bu; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$), which are readily prepared from uranium tetrachloride and may be generated via a bis(imido)uranium(IV) intermediate.

We recently reported the synthesis of $[U(\mu\text{-NDipp})Cl_2(THF)_2]_2$ by metathesis of UCl_4 with 2 equiv of LiNHDipp.[2f] We have since attempted reactions of UCl_4 with 4 equiv of LiNHDipp and have been unable to identify the major products. This prompted us to explore analogous metathesis reactions with Lewis base adducts of UCl_4. Surprisingly, the reaction of $UCl_4(Me_2bpy)_2$ with 4 equiv of LiNHDipp does not yield a bis(imido)uranium(IV) species but rather provides single crystals of $U(NDipp)_2Cl(Me_2bpy)_2$ (**1a**), the first monomeric bis(imido)uranium(V) complex (Scheme 1).

Scheme 1



Initially, we believed that adventitious CH_2Cl_2 was the cause of this oxidation. To test this hypothesis, we developed a rational synthesis of a series of halide complexes wherein $UCl_4(Me_2bpy)_2$ is treated with 4 equiv of LiNHDipp in THF followed by addition of 0.5 equiv of CH_2X_2. This procedure generates $U(NDipp)_2X(Me_2bpy)_2$ [X = Cl (**1a**), Br (**2a**), I (**3a**)] in yields of 74−80% (Scheme 1). The imido ligands in **1a**−**3a** may be generated either intramolecularly via α-hydrogen abstraction or externally with a Lewis base serving as a proton shuttle between Dipp-amides. Given the reaction conditions under which these compounds are generated, either mechanism is possible. The formation of the bromide and iodide complexes **2** and **3** from UCl_4 suggests that halogen atom abstraction from dihalomethane by a U(IV) intermediate that does not contain Cl^- leads to the formation of the U(V) products. The identity of this intermediate, while unknown, is either a bis(imido)uranium(IV), imidobis(amido)uranium(IV),

Received: November 17, 2011
Published: June 6, 2012

dx.doi.org/10.1021/ja2108432 | *J. Am. Chem. Soc.* 2012, 134, 9876−9878

or tetrakis(amido)uranium(IV) complex, though the last of these is very unlikely since the mono(imido) complex, $[U(\mu\text{-NDipp})Cl_2(THF)_2]_2$, is formed in the reaction of UCl_4 with 2 equiv of LiNHDipp.[2f]

The proton NMR spectra of **1a**−**3a** are nearly identical and contain resonances that are significantly broadened, which is expected for paramagnetic uranium(V) compounds.[6,7] Chemical shifts at 5.6, 13.4, and 25.4 ppm are assigned to the Dipp imido ligands, while a broad region centered around −2.0 ppm arises from coordinated Me_2bpy.[8]

Compounds **1a**−**3a** were found to be isostructural by single-crystal X-ray crystallography, although the structures were badly disordered. For this reason, a similar procedure was used to prepare the $^tBu_2bpy$ analogues **1b**−**3b**, which provided higher-quality single crystals.[9] Complexes **1b**−**3b** are mononuclear with distorted pentagonal-bipyramidal geometries about uranium [the solid-state molecular structures are shown in Figure 1 and Figures S9 and S10 in the Supporting Information (SI)]. The coordinated bipyridine ligands contain C−C bond lengths consistent with neutral $^tBu_2bpy$ ligands rather than radical anions.[10] The imido ligands occupy the axial positions with nearly linear N−U−N angles of 166.02(16), 165.9(2), and 174.9(2)°, respectively. The $U{-}N_{imido}$ bond lengths are almost identical throughout the series, and for **1b**, the values are 1.977(4) and 1.980(4) Å. These bond lengths are longer than the terminal imido distances in $[U(\mu\text{-N}^tBu)(N^tBu)I(^tBu_2bpy)]_2$ [$U{=}N_{avg}$ = 1.898(7) Å].[6] They are also significantly longer than the U═O distances in $[UO_2(tppo)_4]OTf$ [1.819(6) Å][5b] and $UO_2(Ar_2nacnac)(Ph_2MePO)_2$ [1.819(6) Å],[5e] even considering the difference in atomic radii.[11] The bond lengths indicate stronger bonding in the UO_2^+ complexes, although the steric bulk of the Dipp groups almost certainly causes a lengthening of the U═N bonds in **1b**−**3b**.

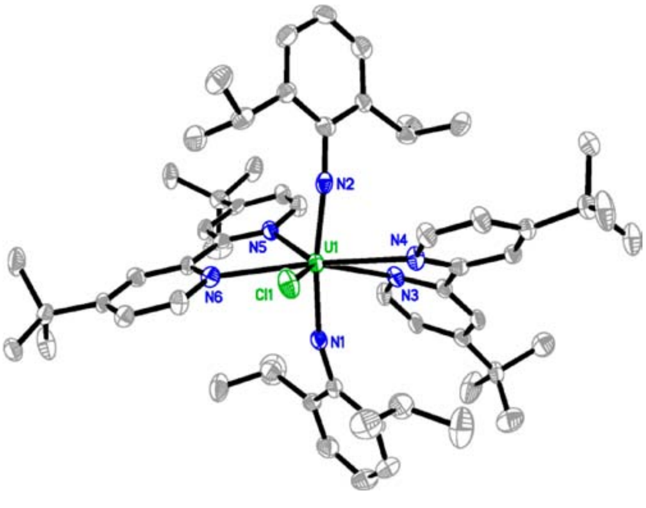


Figure 1. Solid-state molecular structure of **1b** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1−N1 = 1.977(4), U1−N2 = 1.980(4), U1−N3 = 2.683(4), U1−N4 = 2.594(4), U1−N5 = 2.595(4), U1−N6 = 2.659(4), U1−Cl1 = 2.729(2), N1−U1−N2 = 166.02(16), N1−U1−Cl1 = 94.93(12), N2−U1−Cl1 = 97.84(12).

The chemical oxidation of **1a** and **2a** was carried out with iodine or ferrocenium. Proton NMR spectroscopy confirmed that these reactions result in clean conversion to $[U(NDipp)_2X(Me_2bpy)_2]^+$ (X = Cl, Br). The triiodide salt, $[U(NDipp)_2Br(Me_2bpy)_2]I_3$ (**4**), was characterized by single-crystal X-ray crystallography (Figure 2). The cation in **4** is structurally similar to **2b**, but the $U{-}N_{imido}$ bond lengths of 1.869(7) and 1.856(8) Å are more than 0.1 Å shorter in the U(VI) compound. These U−N bond lengths are similar to those observed for other bis(imido)uranium(VI) complexes.[4c,14] Treatment of **4** with 3 equiv of decamethylcobaltacene in THF-d_8 results in rapid formation of **2a**, as observed by ^1H NMR spectroscopy, demonstrating the chemical reversibility of the U(V)/U(VI) redox couple.

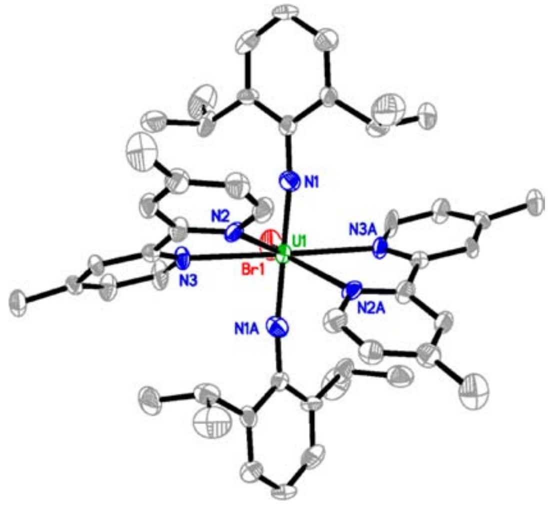


Figure 2. Solid-state molecular structure of **4** with thermal ellipsoids drawn at the 50% probability level; the I_3^- ion has been omitted for clarity. The molecule shown is one of two independent molecules in the asymmetric unit. Selected bond lengths (Å) and angles (deg): U1−N1 = 1.856(8), U1−Br1 = 2.787(2), N1−U1−N1A = 177.4(5).

The reaction of **1a** with excess $CoCp^*_2$ [$E_{1/2}$ = −1.94 V vs Fc/Fc^+][15] was also performed to determine the possibility of isolating a more reduced species. In THF-d_8, a reaction occurred over 10−12 days wherein **1a** was slowly replaced by a new and as yet unidentified paramagnetic complex. The reaction rate was not consistent with a straightforward outer-sphere electron transfer, despite the large reduction potential difference between $CoCp^*_2$ and **1a** (*vide infra*), suggesting that this is a more complicated transformation. Experiments to elucidate the nature of this new species are ongoing.

We also investigated the solution-phase redox properties of complex **1a** by cyclic voltammetry (CV). In CH_2Cl_2, **1a** exhibits two quasi-reversible redox features at −1.06 and −1.22 V vs Fc/Fc^+ in its cyclic voltammogram (see the SI). We have assigned the feature at −1.06 V as a U(V)/U(VI) oxidation and tentatively assigned the feature at −1.22 V as a bipyridine-based reduction. Importantly, the CV data for **1a** represent the first electrochemical parameters determined for the bis(imido) series of complexes. The U(V)/U(VI) redox potential of **1a** is much more negative than that observed for the parent uranyl ion $UO_2^{2+}(aq)$ (−0.35 V vs Fc/Fc^+),[12] and even that for the mono(imido)uranium(V) complex $U({=}NSiMe_3)(N[SiMe_3]_2)_3$ (−0.41 V vs Fc/Fc^+),[13] but it is comparable to that observed for $[UO_2(OH)_4]^{2-}$ (−1.17 V vs Fc/Fc^+),[12] which contains four strongly electron-donating hydroxide ligands and a dianionic charge. Overall, these data demonstrate the electron-rich nature of the uranium center in **1a** and corroborate the strong π-donating character of the imido substituents in this system.[4c]

For further comparison, we attempted to prepare bis(imido)uranium(V) complexes containing redox-inactive ligands. Thus, the reaction of UCl_4 with 3 equiv of triphenylphosphine oxide (tppo) and 4 equiv of LiNHDipp in the presence of CH_2Cl_2 provided $U(NDipp)_2Cl(tppo)_3$ (**5**). The successful isolation of **5** from UCl_4 shows that the presence of a potentially redox-active ligand such as bpy is not necessary for the oxidation to U(V) and is consistent with the reaction occurring from a U(IV) intermediate. While **5** has been structurally characterized (Figure S12), we have been unable to separate this compound from the U(VI) byproduct $U(Ndipp)_2Cl_2(tppo)_2$, which forms regardless of the amount of dichloromethane present. Thus, it appears that further oxidation of the bis(imido)uranium(V) complex via halogen abstraction is a more facile reaction when tppo is coordinated. Qualitatively, this indicates that **5** is even more electron-rich than its bipyridine analogues **1−3**.[16]

We have presented facile syntheses of a series of bis(imido)uranium(V) complexes, $U(NDipp)_2X(R_2bpy)_2$ (X = Cl, Br, I; R = Me, ^{t}Bu) and $U(NDipp)_2Cl(tppo)_3$, from uranium tetrachloride and lithium 2,6-diisopropylphenylamide. These reactions proceed via salt metathesis and subsequent oxidation via halogen atom abstraction, resulting in the first monomeric bis(imido)uranium(V) species. Most notably, the products appear to be generated via extremely reactive intermediates. While these intermediates remain uncharacterized, their reactivity is consistent with bis(imido)uranium(IV) compounds, which present an intriguing target for future synthetic studies. We have reported the first electrochemical data on bis(imido)uranium complexes, which indicate highly electron-rich uranium(V) centers. Importantly, the ease with which these molecules are prepared from tetravalent precursors suggests that this methodology could be applied to transuranic compounds, which would greatly enhance our understanding of An═N multiple bonding.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete details of the preparation and characterization of **1−4**, including X-ray crystallographic details for **1b−3b**, **4**, and **5** (CIF), and electrochemical data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

boncella@lanl.gov

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

R.E.J. thanks the Seaborg Institute (Los Alamos National Laboratory) for fellowships to support his work. We also thank the LANL LDRD Program for funding portions of this work. T.W.H. thanks the Heavy Element Program of the DOE Office of Basic Energy Sciences (BES) for support of the electrochemical experiments. J.M.B. and R.E.J. also thank the DOE BES Heavy Element Progam at LANL for supporting the work on the chemical oxidation of the U(V) complexes.

■ REFERENCES

(1) (a) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853−1854. (b) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514−516.

(2) (a) Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237−3239. (b) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 9840−9841. (c) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448−9460. (d) Stewart, J. L.; Andersen, R. A. *New J. Chem.* **1995**, *19*, 587−595. (e) Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2000**, *122*, 6108−6109. (f) Jilek, R. E.; Spencer, L. P.; Kuiper, D. L.; Scott, B. L.; Williams, U. J.; Kikkawa, J. M.; Schelter, E. J.; Boncella, J. M. *Inorg. Chem.* **2011**, *50*, 4235−4237.

(3) (a) Zalkin, A.; Brennan, J. G.; Andersen, R. A. *Acta Crystallogr., Sect. C* **1988**, *44*, 1553−1554. (b) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 12536−12546. (c) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272−5285.

(4) (a) Arney, D. S. J.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068−10069. (b) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 959−960. (c) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941−1943.

(5) (a) Arnold, P. L.; Patel, D.; Wilson, C.; Love, J. B. *Nature* **2008**, *451*, 315−318. (b) Berthet, J.; Nierlich, M.; Ephritikhine, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1952−1954. (c) Berthet, J.; Siffredi, G.; Thuery, P.; Ephritikhine, M. *Dalton Trans.* **2009**, 3478−3494. (d) Mougel, V.; Horeglad, P.; Nocton, G.; Pecaut, J.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 8477−8480. (e) Hayton, T. W.; Wu, G. *J. Am. Chem. Soc.* **2008**, *130*, 2005−2014. (f) Arnold, P. L.; Hollis, E.; White, F. J.; Magnani, N.; Caciuffo, R.; Love, J. B. *Angew. Chem., Int. Ed.* **2011**, *50*, 887−890. (g) Graves, C. R.; Kiplinger, J. L. *Chem. Commun.* **2009**, 3831−3853. (h) Arnold, P. L.; Love, J. B.; Patel, D. *Coord. Chem. Rev.* **2009**, *253*, 1973−1978.

(6) Spencer, L. P.; Schelter, E. J.; Yang, P.; Gdula, R. L.; Scott, B. L.; Thompson, J. D.; Kiplinger, J. L.; Batista, E. R.; Boncella, J. M. *Angew. Chem.* **2009**, *121*, 3853−3856.

(7) Eller, P. G.; Vergamini, P. J. *Inorg. Chem.* **1983**, *22*, 3184−3189.

(8) Regardless of the Lewis base, the chemical shifts at 5.6, 13.4, and 25.4 ppm remained constant for $U(NDipp)_2X(L)_y$ compounds. Our assignments are based on this fact as well as on NMR integrations.

(9) Compounds **1a−3a** are quite soluble in most organic solvents, and for this reason they are difficult to isolate in appreciable yields.

(10) (a) Wiley, R. O.; Von Dreele, R. B.; Brown, T. M. *Inorg. Chem.* **1980**, *19*, 3351−3356. (b) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. *Inorg. Chem.* **2010**, *49*, 1103−1110. The average $C-C_{bridge}$ distance is 1.486(9) Å, which is statistically identical to the corresponding distance in free 2,2′-bpy [1.490(3) Å]. This distance is much shorter in complexes containing coordinated bpy radical anions.

(11) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: Oxford, U.K., 1998.

(12) Morris, D. E. *Inorg. Chem.* **2002**, *41*, 3542−3547.

(13) Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237−3239.

(14) (a) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R.; Hay, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10549−10559. (b) Spencer, L. P.; Yang, P.; Batista, E. R.; Scott, B. L.; Boncella, J. M. *Inorg. Chem.* **2009**, *48*, 11615−11623.

(15) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

(16) We observed no formation of U(VI) during the preparation of compounds **1−3**, even in the presence of excess dihalomethane.