trans O–Re–O angles are 173.9 (2) and 170.6 (2)°, while the cis O–Re–O angles average 89.8°. Metal–oxygen bond lengths vary from 1.864 (4) to 1.879 (4) Å and Re–O–C_{ipso} angles fall in a narrow range between 138.1 (4) and 143.8 (4)°. In Figure 1, the Re atom is displaced 0.13 Å below the O_4 plane, while all of the C_{ipso} atoms are located above this plane (0.31 Å on average). The metal center is well protected from above and below the ReO_4 square plane by the *o*-isopropyl groups of the phenoxide ligands. This d^3 rhenium complex can be compared to the related d^2 complexes $W(DIPP)_4$ and $W(DMP)_4$, both of which are also square planar.[16] The observed geometry in $Re(DIPP)_4$ (like $W(OR)_4$) no doubt reflects an electronic effect, as the delocalization of oxygen π electrons over the entire ReO_4 core (possible in a square-planar conformation) may offer significant energetic advantages to the complex.[16] In the recently reported compound $Re(2\text{-}MeC_6H_4)_4$ where π interactions of this type are not possible, the compound assumes a tetrahedral geometry.[17]

An oxidation and a reduction couple are observed for both compounds **1** and **2** by cyclic voltammetry (Figure 2).[18] Redox couples for $Re(DIPP)_4$ feature cathodic/anodic peak separations between 120 and 155 mV (at 150 mV/s scan rate), and $i_{p,a}/i_{p,c}$ for the +0.49-V oxidation is not strictly 1.0, although plots of peak anodic current vs the square root of the sweep rate ($v^{1/2}$) are linear, *implying* electrochemical reversibility.[19] However, bulk electrolysis reveals that these processes transfer only 0.5 (±0.05) electron, which could reflect the stoichiometric reaction of $[Re(DIPP)_4]^+$ (or $[Re(DIPP)_4]^-$) with neutral $Re(DIPP)_4$ (an EC process).[20] The electrochemistry of $Re(DMP)_4$ parallels that of $Re(DIPP)_4$ except in one regard: the oxidation of $Re(DMP)_4$ is completely irreversible. The reactivity differences we observe between the neutral DMP and DIPP compounds (vide infra) are presumably sterically regulated and are likely to be augmented in reactive $[Re(OR)_4]^+$ cations, which could account for the EC process being fast on the CV time scale for the $Re(DMP)_4$ oxidation.

Preliminary reactivity studies of **1** and **2** have focused on their reactions with acetylenes.[21] No reaction was seen to occur between $Re(DIPP)_4$ (**1**) and an excess of 2-butyne or diphenylacetylene, a behavior which parallels that of the related $W(DIPP)_4$.[16] However, the reaction of $Re(DMP)_4$ with 1 equiv of $MeC{\equiv}CMe$ (Et_2O, −20 °C, 45 min) provides a dark red solid that we formulate as the acetylene adduct, $Re(MeC{\equiv}CMe)(DMP)_4$, (**3**, 59% yield).[22] The cyclic voltammogram of $Re(MeC{\equiv}CMe)(DMP)_4$ (**3**) reveals an irreversible[19] oxidation ($E_{p,a}$ = +0.80) and an apparently reversible (on the CV time scale) reduction ($E_{1/2}$ = −0.57 (120)) in dichloromethane. Both couples are shifted to more negative potentials relative to "base-free" $Re(DMP)_4$,[18] a result that is consistent with adduct formation, since, in general, one would expect the addition of an electron to be more difficult (and the removal of an electron to be more facile) in the adduct.

Because it is likely that some homogeneous rhenium metathesis systems involve $d^{n>0}$ complexes, and because π-donor ligation may be important in activating these species to catalysis, the alkoxide compounds reported here may provide a means by which to substantiate and understand the role of *midvalent* rhenium in metathesis chemistry.

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters, anisotropic thermal parameters, and bond distances and bond angles and figures showing ORTEP views of $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ (**1**) (6 pages). Ordering information is given on any current masthead page.

Carl S. Marvel Laboratories of Chemistry
Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Ian M. Gardiner
Michael A. Bruck
David E. Wigley*

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Lewis Base Adducts of Uranium Triiodide: A New Class of Synthetically Useful Precursors for Trivalent Uranium Chemistry

It is interesting, from a historical perspective, that, after some 50 years of synthetic actinide research, very little is known about the nonaqueous chemistry of trivalent uranium.[1] The paucity of molecular uranium(III) compounds is undoubtedly due to a lack of suitable starting materials.[2] The anhydrous uranium trihalides have all been prepared, but they are polymeric solids,[3,4] insoluble in common organic solvents, and quite unreactive.[5] Uranium tetrachloride, UCl_4, dissolved in tetrahydrofuran can be reduced (e.g., with NaH, $NaC_{10}H_8$, or Na/Hg) to give a sparingly soluble purple solid formulated as $UCl_3(THF)_x$.[6] The exact identity of the latter material is unknown, and its utility as a precursor to uranium(III) compounds is apparently limited.[6–11] We have encountered some difficulties using "$UCl_3(THF)_x$" as a starting material. For example, we find that the synthesis of $U[N(SiMe_3)_2]_3$ from $UCl_3(THF)_x$ (generated in situ) and sodium

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bis(trimethylsilyl)amide in THF (eq 1)[11] is often contaminated with $[(Me_3Si)_2N]_2\overline{UN(SiMe_3)(SiMe_2CH_2)}$,[12] a uranium(IV) complex that is difficult to separate from the desired product.

$$UCl_3(THF)_x + 3NaN(SiMe_3)_2 \xrightarrow{THF} U[N(SiMe_3)_2]_3 + 3NaCl \quad (1)$$

Recently, the first examples of trivalent uranium aryloxide complexes were reported from the reactions of 2,6-disubstituted phenols with $U[N(SiMe_3)_2]_3$ (eq 2).[13] Similar experiments em-

$$U[N(SiMe_3)_2]_3 + 3ArOH \xrightarrow{C_6H_{14}} U(OAr)_3 + 3HN(SiMe_3)_2 \quad (2)$$

ploying aliphatic alcohols give mixtures of uranium(IV) products.[14] Because these latter alcoholysis reactions effect oxidation of the uranium(III) center, a further elaboration of uranium(III) alkoxide chemistry will require ligand metathesis under reducing conditions. Unfortunately, as noted above, there are no well-defined soluble uranium trihalide starting materials for the metathetical procedures.

The thermodynamic stability of the binary uranium(IV) halides decreases in the order F > Cl > Br > I.[1,15,16] Uranium tetraiodide is thermally unstable at room temperature and decomposes slowly to uranium triiodide and iodine.[16-18] The fact that the trivalent oxidation state is *favored* by iodide ligands prompted a search for soluble forms of uranium triiodide. We have discovered a series of organic-solvent-soluble Lewis base adducts of uranium triiodide that are easy to prepare and serve as excellent precursors to a variety of new and known trivalent uranium compounds.

A slight excess of clean uranium turnings[19] reacts with freshly sublimed elemental iodine in THF solution at 0 °C to yield microcrystalline, dark purple $UI_3(THF)_4$ (**1**) in ca. 65% isolated yield after 24 h (eq 3).[20] Compound **1** is routinely prepared in

$$U + 1.5I_2 \xrightarrow[0\ °C]{THF} UI_3(THF)_4 \quad (3)$$

our laboratory on a 50-g scale.[21] This represents a synthetically

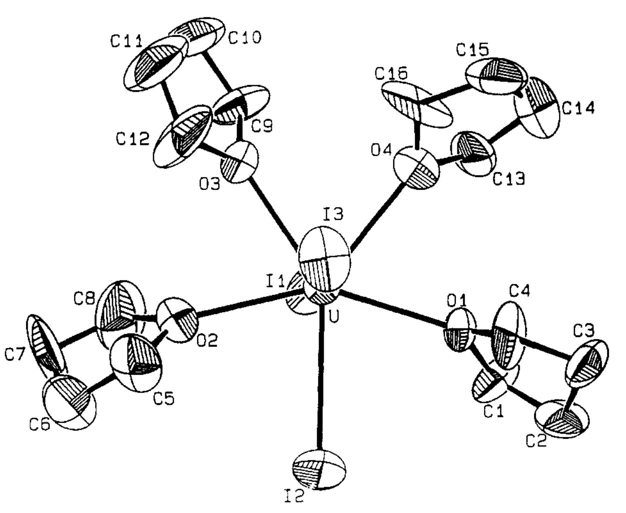

Figure 1. ORTEP drawing of the $UI_3(THF)_4$ molecule (**1**), emphasizing the pentagonal plane and giving the atom-numbering scheme. Selected bond distances and angles: U–I(1) = 3.103 (2) Å; U–I(2) = 3.167 (2) Å; U–I(3) = 3.119 (2) Å; U–O(1) = 2.48 (1) Å; U–O(2) = 2.51 (1) Å; U–O(3) = 2.54 (1) Å; U–O(4) = 2.56 (1) Å; I(1)–U–I(2) = 95.01 (5)°; I(1)–U–I(3) = 171.30 (5)°; O(1)–U–O(4) = 68.9 (4)°; O(3)–U–O(4) = 71.4 (5)°; O(3)–U–O(2) = 70.2 (4)°; I(2)–U–O(2) = 76.1 (3)°; I(2)–U–O(1) = 73.9 (3)°.

useful quantity, and the gentle solution reaction is a clear improvement over the high-temperature tube–furnace technique, which yields polymeric UI_3, a material of little synthetic value.[16]

The solution reaction of freshly cleaned uranium turnings with elemental iodine is not specific to THF alone. Indeed, a slight excess of uranium turnings reacts with iodine at 0 °C in 1,2-dimethoxyethane (dme) solution to give $UI_3(dme)_2$ (**2**) as a purple microcrystalline solid in 80% yield (eq 4). The reaction is,

$$U + 1.5I_2 \xrightarrow[0\ °C]{dme} UI_3(dme)_2 \quad (4)$$

$$U + 1.5I_2 \xrightarrow[0\ °C]{py} UI_3(py)_4 \quad (5)$$

however, slower than the one employing THF and requires 3 days for completion. In a similar fashion, with pyridine as solvent, we obtain black microcrystalline $UI_3(py)_4$ (**3**) in 80% yield (eq 5) after 2 days of stirring.

Compounds **1**–**3** are *exceedingly* air- and moisture-sensitive, and all are soluble in THF. Adducts **1** and **3** are also slightly soluble in benzene and toluene. Only one type of THF or pyridine ligand is observed in the ^1H NMR spectra of **1** and **3**, respectively, at room temperature.[22] The Nujol mull infrared spectra

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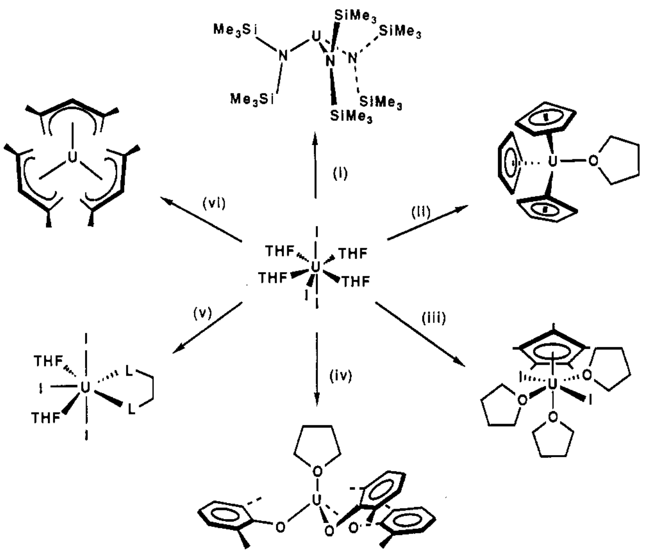
(19) A 30-g amount of ^{238}U metal turnings (99.99%) was obtained from the Los Alamos National Laboratory stock. The turnings were cut into 0.5-in. strips and washed (2×) with concentrated HNO_3. [*Caution! This reaction is very exothermic* and should be carried out in a well-ventilated fume hood.] After the second acid wash was decanted, the shiny turnings were washed with H_2O (3×), followed by acetone (3×), and then transferred to a 250-mL Schlenk vessel. The latter was evacuated to 10^{-3} Torr and refilled with UHP grade argon (3×). Under an argon purge, ca. 250 mg of HgI_2 was added and the evacuate/refill cycles were repeated. The Schlenk reaction vessel was removed to an inert-atmosphere glovebox, 100 mL of distilled (Na/K alloy) THF were added, and the mixture was shaken for 10 min to produce a dark blue solution of $UI_3(THF)_4$. The turnings were filtered out, washed with THF, and dried in vacuo. This procedure yields shiny, essentially oxide-free, metal. Attempts to store the turnings in the glovebox invariably results in the formation of a brown-black surface coating of UO_2 via scavenging of trace amounts of O_2 (our glovebox is routinely maintained at 0.5 ppm O_2).

(20) (a) This compound has been claimed recently from the reaction of uranium metal and mercuric iodide in THF.[20b] It was described as a "green-black solid" and characterized by elemental analyses and IR spectroscopy. In our hands, this synthesis gives a mixture of two compounds, one of which is $UI_3(THF)_4$ (53% yield) when clean U metal is employed. An oily green material (identity unknown) can be separated from $UI_3(THF)_4$ by washing the reaction solids with diethyl ether. (b) Deacon, G. B.; Tuong, T. D. *Polyhedron* **1988**, *7*, 249.

(21) Procedure: A 250-mL, one-neck standard Schlenk vessel was charged with 23.93 g (100.5 mmol) of U-turnings and a magnetic stir bar. A 200-mL portion of pure THF was introduced, and the mixture was cooled to −10 °C in an ice/salt bath. Under an argon purge, 35.0 g (137.9 mmol) of sublimed iodine was added, in one portion, to the mixture. The reaction vessel was removed from the ice bath and shaken vigorously by hand until the vessel became warm to the touch and then quickly immersed back into the ice bath to cool. This procedure was repeated four or five times or until enough metal was dissolved to permit magnetic stirring of the now dark red suspension. After 3 h at −10 °C, the suspension was warmed to room temperature and stirred for 10–12 h to produce a dark blue solution with much purple precipitate and some unreacted uranium turnings. The reaction vessel was removed to the glovebox, and the contents were stirred vigorously to suspend the $UI_3(THF)_4$ precipitate. The stirring was stopped, and the excess metal was allowed to settle to the bottom of the flask before the suspension was filtered onto a medium frit. The turnings were washed with fresh THF, and the washing was decanted from the metal and filtered. The microcrystalline purple solid was dried in vacuo to yield 42.9 g of $UI_3(THF)_4$. The blue-green filtrate was reduced in vacuo to ca. 30 mL and layered with 60 mL of distilled (Na/K alloy) Et_2O, and the suspension was cooled to −40 °C. After 12 h, 10.5 g of $UI_3(THF)_4$ was collected by filtration and washed with Et_2O. Combined yield: 53.4 g (64.0% based on I_2).

(22) ^1H NMR data (250 MHz, 22 °C) are as follows. **1** (toluene-d_8): δ 9.5 (s, THF), 5.4 (s, THF). **2** (THF-d_8): δ 3.4, 3.3 (s, CH_3), −84.5, −84.7 (s, CH_2). **3** (benzene-d_6): δ 17.8 (s, py), 15.4 (s, py), 12.0 (s, py).

Scheme I[a]



[a] Conditions: (i) 3 equiv of $Na[N(SiMe_3)_2]_3$ in THF at 23 °C for 24 h, >90%; (ii) 3 equiv of KC_5H_5 in THF at 23 °C for 24 h, 70%; (iii) 1 equiv of KC_5Me_5 in THF at 23 °C for 24 h, 80%; (iv) 3 equiv of K-[O-2,6-$Me_2C_6H_3$] in THF at 23 °C for 24 h, >90%; (v) excess $Me_2NCH_2CH_2NMe_2$(=L-L) in THF at 23 °C for 24 h, 70%; (vi) 3 equiv of Kpd (pd = 2,4-dimethylpentadienyl) in THF at 0 °C for 24 h, 70%.

(4000–400 cm^{-1}) of **1**–**3** only show absorption bands characteristic of the coordinated ligands. For example, infrared absorption bands at 1011, 853, and 833 cm^{-1} were observed for **1**, indicative of coordinated THF,[23] whereas **3** displayed the expected shift in the in-plane ring deformation of pyridine from 604 to 621 cm^{-1}, consistent with coordinated pyridine.[24] Satisfactory elemental analyses for **1**–**3** have been obtained.[25]

Single crystals of $UI_3(THF)_4$ were grown from a concentrated THF solution at -40 °C, and the structure was determined from X-ray diffraction data collected at 23 °C.[26] In the solid state, $UI_3(THF)_4$ is mononuclear with a pentagonal-bipyramidal coordination geometry about the uranium atom as shown in Figure 1.[27] Two iodide ligands occupy axial coordination sites with an average U–I distance of 3.111 (2) Å, while the third iodide ligand lies in the equatorial plane with U–I = 3.167 (2) Å. These bond lengths may be compared to the uranium–iodine distances of 3.165 (12), 3.244 (8), and 3.456 (11) Å found in polymeric UI_3, where uranium is located in a bicapped-trigonal-prismatic environment.[4] All four THF ligands lie in the equatorial plane with an average U–O distance of 2.52 (1) Å. The sum of the five angles within the equatorial plane is 360.5°, and the mean deviation is only ±0.08 Å from the plane. The I–U–I angles between equatorial and axial iodide ligands average 94.25 (5)°, forcing the axial iodide ligands to bend away from the equatorial iodide. The resulting I_{ax}–U–I_{ax} angle is 171.30 (5)°. Note that there are two types of THF ligands in the equatorial plane: those proximal to the unique iodide ligand and those distal to it. This result is consistent with the ^1H NMR spectrum, *provided* there is a rapid interconversion of seven-coordinate structures (e.g., pentagonal bipyramid ↔ capped trigonal prism) on the NMR time scale, which time-averages THF environments.[28]

Royal blue THF solutions of $UI_3(THF)_4$ react cleanly at, or below, room temperature with sodium or potassium salts to give, after appropriate workup, high yields of spectroscopically pure trivalent uranium products with concomitant loss of THF-insoluble NaI or KI (Scheme I).[29] Some of these compounds, i.e., $(C_5H_5)_3U(THF)$,[5,6,30,31] $U[N(SiMe_3)_2]_3$,[11] and $U(C_7H_{11})_3$,[9] have been reported previously, but the ready availability of large quantities of crystalline $UI_3(THF)_4$ greatly facilitates their syntheses. We anticipate that UI_3L_4 compounds will be excellent precursors to a host of other uranium(III) complexes. The development of this chemistry is currently under way in our laboratory.

Acknowledgment. We wish to thank Professor R. D. Ernst (University of Utah), Dr. W. G. Van Der Sluys, and Dr. C. J. Burns for helpful discussions. D.L.C. is the recipient of a J. Robert Oppenheimer Fellowship at Los Alamos. This work was performed under the auspices of the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy. Los Alamos National Laboratory is operated by the University of California for the U.S. Department of Energy under Contract W-7405-ENG-36.

Supplementary Material Available: For **1**, Tables S1–S4, listing crystal data, atomic positional and equivalent isotropic thermal parameters, anisotropic thermal parameters, and selected distances and angles (4 pages); Table S5, listing structure factors (22 pages). Ordering information is given on any current masthead page.

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(25) Anal. Calcd for $UI_3O_4C_{16}H_{32}$ (**1**): C, 21.18; H, 3.56; I, 41.97. Found: C, 20.68; H, 3.38; I, 41.20. Calcd for $UI_3O_4C_8H_{20}$ (**2**): C, 12.03; H, 2.52; I, 47.65. Found: C, 11.91; H, 2.46; I, 47.55. Calcd for $UI_3N_4C_{20}H_{20}$ (**3**): C, 25.69; H, 2.16; N, 5.99; I, 40.70. Found: C, 25.81; H, 2.25; N, 5.89; I, 40.68.

(26) **1** crystallizes in the monoclinic space group $P2_1/c$, with $a = 8.750$ (3) Å, $b = 16.706$ (6) Å, $c = 17.697$ (7) Å, $\beta = 93.64$ (3)°, $V = 2582$ Å^3, $d_{calc} = 2.33$ g cm^{-3}, and $Z = 4$. A crystal measuring 0.08 × 0.11 × 0.18 mm was mounted in a Lindemann tube and placed on the goniometer head of an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Final cell parameters were determined from the least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 accurately centered reflections. Data were collected by θ–2θ scans. The intensities were corrected for Lorentz and polarization effects, an 11% decay, and absorption (transmission coefficients from 0.36 to 1.00). The structure was solved by routine Patterson and Fourier methods. After location of all non-hydrogen atoms, refinement with isotropic thermal parameters converged at $R = 0.095$. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms, which were constrained to "ride" upon the appropriate carbon atoms with $B(H) = 1.2B_{eq}(C)$, final refinement using 1816 unique observed ($I > 3\sigma(I)$) reflections converged at $R = 0.043$ and $R_w = 0.047$ (where $w = 1/\sigma(F)^2$). All calculations were performed by using the TEXRAY suite of computer programs (Molecular Structure Corp., 1987).

(27) The structure is very similar to that reported for $NdCl_3(THF)_4$. See: Wenqi, C.; Zongsheng, J.; Yan, X.; Yuguo, F.; Guandgdi, Y. *Inorg. Chim. Acta* **1987**, *130*, 125.

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(29) The three new compounds in Scheme I gave satisfactory elemental analyses. ^1H NMR data (250 MHz, 22 °C) are as follows. $(C_5Me_5)UI_2(THF)_3$ (toluene-d_8): δ −5.99 (s, 8 H, THF), 1.09 (s, 4 H, THF), 1.79 (s, 15 H, C_5Me_5), 2.60 (s, 8 H, THF), 8.03 (s, 4 H, THF). U(O-2,6-$Me_2C_6H_3)_3$(THF) (benzene-d_6): δ 13.98 (s, 9 H, meta), 12.13 (s, 3 H, para), 8.48 (s, 18 H, Me), −19.54 (s, 4 H, THF), −38.88 (s, 4 H, THF). $UI_3(THF)_2(Me_2NCH_2CH_2NMe_2)$ (benzene-d_6): δ 11.96 (s, 8 H, THF), 2.07 (s, 4 H, CH_2), 1.94 (s, 6 H, Me), −4.63 (s, 8 H, THF).

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Inorganic and Structural Chemistry
Group (INC-4)
Isotope and Nuclear Chemistry
Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

David L. Clark
Alfred P. Sattelberger*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Simon G. Bott
Raymond N. Vrtis

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