Inorganic Chemistry
Article
pubs.acs.org/IC

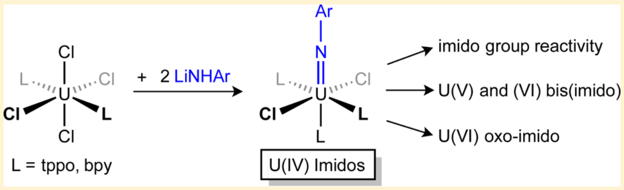
Preparation and Reactivity of the Versatile Uranium(IV) Imido Complexes $U(NAr)Cl_2(R_2bpy)_2$ (R = Me, ^{t}Bu) and $U(NAr)Cl_2(tppo)_3$

Robert E. Jilek, Neil C. Tomson, Ryan L. Shook, Brian L. Scott, and James M. Boncella*

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

Supporting Information

ABSTRACT: Uranium tetrachloride undergoes facile reactions with 4,4′-dialkyl-2,2′-bipyridine, resulting in the generation of $UCl_4(R_2bpy)_2$, R = Me, ^{t}Bu. These precursors, as well as the known $UCl_4(tppo)_2$ (tppo = triphenylphosphine oxide), react with 2 equiv of lithium 2,6-di-isopropylphenylamide to provide the versatile uranium(IV) imido complexes, $U(NDipp)Cl_2(L)_n$ (L = R_2bpy, n = 2; L = tppo, n = 3). Interestingly, $U(NDipp)Cl_2(R_2bpy)_2$ can be used to generate the uranium(V) and uranium(VI) bisimido compounds, $U(NDipp)_2X(R_2bpy)_2$, X = Cl, Br, I, and $U(NDipp)_2I_2(^tBu_2bpy)$, which establishes these uranium(IV) precursors as potential intermediates in the syntheses of high-valent bis(imido) complexes from UCl_4. The monoimido species also react with 4-methylmorpholine-N-oxide to yield uranium(VI) oxo-imido products, $U(NDipp)(O)Cl_2(L)_n$ (L = ^{t}Bu$_2$bpy, n = 1; L = tppo, n = 2). The aforementioned molecules have been characterized by a combination of NMR spectroscopy, X-ray crystallography, and elemental analysis. The chemical reactivity studies presented herein demonstrate that Lewis base adducts of uranium tetrachloride function as excellent sources of U(IV), U(V), and U(VI) imido species.



INTRODUCTION

Understanding the role of f-orbitals in uranium-element multiple bonding continues to be a focus for many actinide chemists. In particular, uranium imido complexes have received much attention over the past several years. Imido ligands offer both steric and electronic flexibility where their oxo analogues do not, making them attractive to researchers. A number of U(IV),[1−4] U(V),[5−13] and U(VI)[8,14−19] imido species have been prepared in recent years, most of which contain cyclopentadienide ligands or bulky amides. One such species, $U(N^tBu)_2I_2(THF)_2$, is prepared readily from uranium metal, iodine, and *tert*-butylamine and is isoelectronic with the uranyl ion.[18] This synthesis allowed, for the first time, a direct comparison of $U(NR)_2^{2+}$ to UO_2^{2+}. Unfortunately, arylimido analogues could only be obtained from $UI_3(THF)_4$, often requiring a more arduous workup to remove unwanted byproducts. For this reason, a facile route to $U(NR)_2^{2+}$, R = aryl, would be advantageous.

We recently reported the facile synthesis of uranium(IV) imido dihalides via metathesis reactions of UCl_4 and lithium anilides. This previously unknown class of compounds offers tremendous potential for chemical exploration. Still, numerous Lewis base adducts of UCl_4 remain which may serve as useful precursors to uranium(IV) imido species. For example, the bipyridine (bpy), phenanthroline, and triphenylphosphine oxide (tppo) adducts, $UCl_4(L)_2$, have been known for nearly 50 years,[20−22] with the Me_2bpy adduct being reported much later.[23] Surprisingly, the 4,4′-dialkylbipyridine (R_2bpy, R = Me, ^{t}Bu) adducts have yet to be characterized by NMR spectroscopy or single crystal X-ray crystallography, and very little is known about their chemical reactivity.

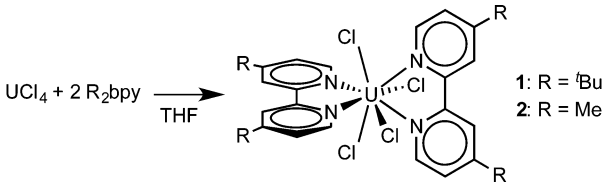
Herein, we report the syntheses of monoimido uranium(IV) complexes, $U(NDipp)Cl_2(L)_n$ (L = R_2bpy, n = 2, R = Me, ^{t}Bu; L = tppo, n = 3). These compounds are readily prepared from $UCl_4(L)_2$, (L = tppo, R_2bpy; R = Me, ^{t}Bu). The aforementioned imido complexes are extremely versatile starting materials for a range of U(IV), U(V), and U(VI) complexes; their reactivity is described in detail.

RESULTS AND DISCUSSION

Synthesis of $UCl_4(R_2bpy)_2$. The reaction of uranium tetrachloride with 2 equiv of R_2bpy in THF rapidly generates a pale green solution (R = ^{t}Bu) or a white precipitate (R = Me; Scheme 1). The former is crystallized from THF/hexane to provide $UCl_4(^tBu_2bpy)_2$ (**1**) in a nearly quantitative yield. The latter is isolated from THF and dried under vacuum to provide $UCl_4(Me_2bpy)_2$ (**2**), also in high yield.

Complex **1** is a pale green, crystalline solid, which is soluble in THF and CH_2Cl_2. The paramagnetic ^1H NMR spectrum contains three sharp resonances at −7.61, 3.38, and 15.03 ppm

Scheme 1



Received: June 16, 2014
Published: August 29, 2014

corresponding to the bpy aryl hydrogens. A fourth resonance at −2.52 ppm is attributed to the *tert*-butyl groups. In contrast, complex **2** is a white powder, which is insoluble in THF and CH_2Cl_2. It is soluble in pyridine, however, and a ^1H NMR spectrum acquired in pyridine-d_5 suggests that solvent molecules coordinate to the metal center, perhaps by replacing one of the Me_2bpy ligands. As such, pyridine has been avoided when conducting experiments with **1** and **2**.

Complex **1** has been characterized crystallographically. Pale green, nearly colorless plates were grown from a hexane layered THF solution at −40 °C. The compound exhibits approximate square antiprismatic geometry about uranium; the molecular structure is shown in Figure 1. The average U−Cl bond length of 2.634(2) Å compares favorably with other eight-coordinate adducts of UCl_4.[24−27] The average U−N bond length of 2.648(4) Å is much shorter than the corresponding U−N bond in $UCl_4(tmeda)_2$.[27] This is likely a result of bpy having a more rigid structure than tmeda.

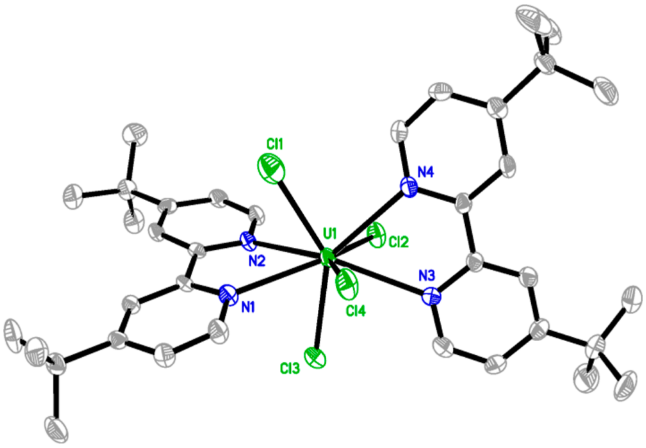
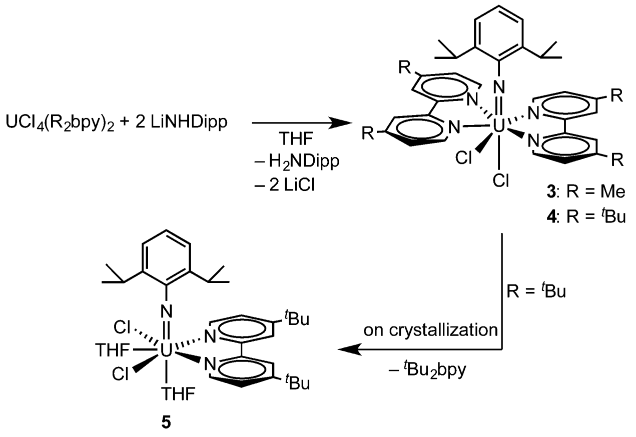


Figure 1. Solid state molecular structure of **1** with thermal ellipsoids set at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1−Cl1 2.622(2), U1−Cl2 2.635(1), U1−Cl3 2.639(1), U1−Cl4 2.641(1), U1−N1 2.617(3), U1−N2 2.646(3), U1−N3 2.674(3), U1−N4 2.654(3); N1−U1−N2 62.11(10), N3−U1−N4 61.59(10).

Synthesis of $U(NDipp)Cl_2(R_2bpy)_2$. The reaction of $UCl_4(Me_2bpy)_2$ with 2 equiv of LiNHDipp, Dipp = 2,6-diisopropylphenyl, in THF immediately generates a dark red solution. Recrystallization of the product from CH_2Cl_2/hexane provides $U(NDipp)Cl_2(Me_2bpy)_2$ (**3**) in a reasonable yield (Scheme 2). This species is a dark red, polycrystalline solid with limited solubility in THF and reasonable solubility in CH_2Cl_2. The ^1H NMR spectrum of **3** is paramagnetic but readily interpretable. Imido resonances at 11.36, 28.35, 53.19, and 64.27 ppm are narrow singlets that compare favorably with previously reported 2,6-di-isopropylphenyl imido uranium(IV) dichlorides.[4] Resonances at −66.25, −19.45, and −10.51 ppm are slightly more broad and have been assigned to the bpy aryl hydrogens. A peak at −9.92 ppm is attributed to the bpy methyl groups. Most importantly, the peak integrations are consistent with a Me_2bpy:imido ratio of 2:1. These data, in combination with bulk sample elemental analysis, are consistent with the formulation of **3** as the bis(bpy) species $U(NDipp)Cl_2(Me_2bpy)_2$.[28]

Under similar reaction conditions, the $^tBu_2bpy$ analogue $U(NDipp)Cl_2(^tBu_2bpy)_2$ (**4**) is not isolated. Instead, crystallization from THF/hexane yields $U(NDipp)Cl_2(^tBu_2bpy)(THF)_2$ (**5**) (Scheme 2). The isolation of this compound is not unprecedented, as evidenced by the previously reported complex, $U(N^tBu)I_2(^tBu_2bpy)(THF)_2$.[4]

Scheme 2



The terminal imido complex **5** has been characterized by single crystal X-ray crystallography. Dark red blocks were grown from a hexane layered THF solution at room temperature. The complex adopts approximate monocapped trigonal prismatic geometry about its uranium center (Figure 2). This is in contrast to the *tert*-butyl imido analogue, $U(N^tBu)I_2(^tBu_2bpy)(THF)_2$, which adopts a pentagonal bipyramidal geometry about uranium.[4] The geometric difference between these isoelectronic molecules is likely due to differences in the steric properties of the imido substituents. The U═N bond length of 1.981(2) Å compares favorably with previously reported terminal arylimido uranium(IV) species[1,2,29] but is ca. 0.05 Å longer than that in the *tert*-butyl analogue.

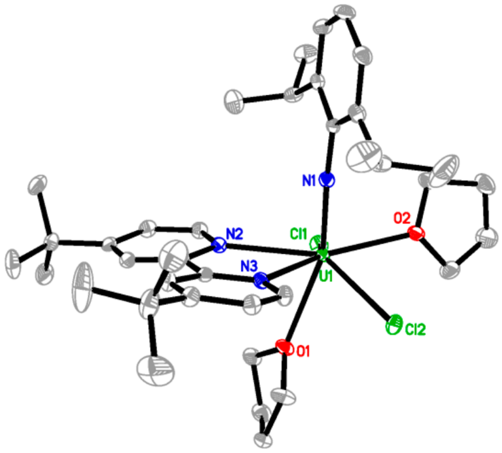


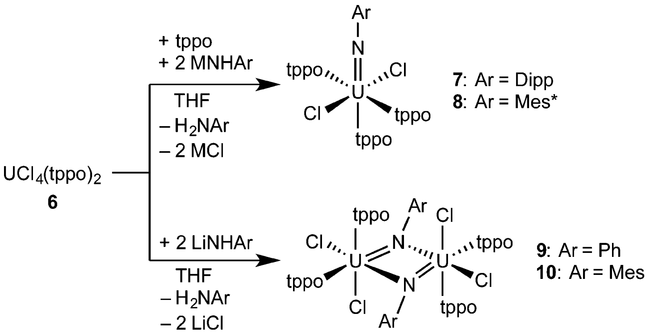
Figure 2. Solid state molecular structure of **5** with thermal ellipsoids set at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1−N1 1.981(2), U1−Cl1 2.7320(6), U1−Cl2 2.7231(5), U1−N2 2.626(2), U1−N3 2.607(2), U1−O1 2.590(2), U1−O2 2.544(2); N1−U1−N2 89.59(7), N2−U1−N3 62.36(6), Cl2−U1−O1 77.87(4), Cl1−U1−O2 73.11(4).

While we have not been able to crystallize the bis($^tBu_2bpy$) complex **4**, a comparison of the properties of **4** with those of **5** supports the notion that **4** is generated in situ. For example, **4** is extraordinarily soluble in CH_2Cl_2, while **5** is only sparingly soluble. This is consistent with the presence of additional *tert*-

butyl groups on **4**, which would serve to increase the molecule's solubility. Compound **4** is also a greasy semisolid, while **5** can be isolated as a crystalline material, again consistent with the presence of additional *tert*-butyl groups on **4**. Given both the limited chelation effect of R$_2$bpy on uranium[30] and the facile ligand displacement during functionalization (see below), it is conceivable that **4** and [**5** + ^{t}Bu$_2$bpy] exist in a non-negligible equilibrium in THF solutions. A crystal packing preference for **5** could then favor its isolation from solution, even though an equivalent of ^{t}Bu$_2$bpy is present during crystallization.

Synthesis of U(NAr)Cl$_2$(tppo)$_x$. Exchanging R$_2$bpy for triphenylphosphine oxide (tppo) as an auxiliary Lewis base provides similar reactivity. Treatment of UCl$_4$(tppo)$_2$ (**6**) with 2 equiv of either LiNHDipp or KNHMes* (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) in the presence of excess tppo generates U(NAr)Cl$_2$(tppo)$_3$ (**7**, Ar = Dipp; **8**, Ar = Mes*) in 62−72% yield (Scheme 3).

Scheme 3



To determine the scope of this synthetic methodology, we attempted analogous reactions with the sterically less-encumbering LiNHPh and LiNHMes. While these reactions failed to yield the desired terminal imido products, they provided the dimeric compounds [U(μ-NAr)Cl$_2$(tppo)$_2$]$_2$ (**9**, Ar = Ph; **10**, Ar = Mes) in 50−65% yield (Scheme 3).

^{1}H NMR spectra of the mononuclear complexes **7** and **8** are paramagnetic and complicated by the presence of two unique tppo environments. Fortunately, the imido resonances are much sharper than those of tppo, and for **8**, the imido group *tert*-butyl resonances appear at 4.0 and 8.9 ppm, while the aryl resonance appears at 26.8 ppm.[31] The ^{1}H NMR spectra of compounds **9** and **10** are more straightforward, with **9** exhibiting phenyl resonances at 2.21 and 13.9 ppm (with the third resonance obscured by tppo), while the mesityl resonances of **10** appear at −18.4, 15.5, and 18.4 ppm. The ^{31}P NMR spectra of compounds **7**−**10** should all contain two unique tppo environments. This is observed for **7**, which exhibits chemical shifts at −188.7 and 206.9 ppm, but the ^{31}P NMR spectrum of **8** contains only one observable resonance, and no resonances were observed for **9** and **10**.[32]

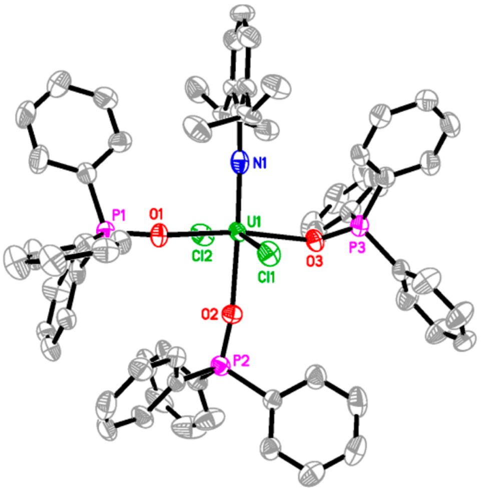


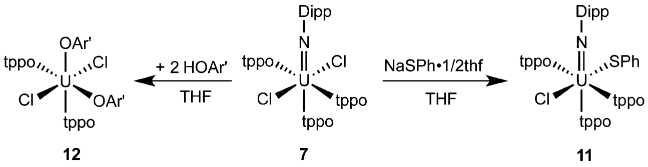
Figure 3. Solid state molecular structure of **7** with thermal ellipsoids set at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1−N1 1.995(5), U1−Cl1 2.722(2), U1−Cl2 2.703(2), U1−O1 2.352(4), U1−O2 2.373(4), U1−O3 2.375(4); N1−U1−O2 177.62(16), Cl1−U1−Cl2 165.01(5), O1−U1−O3 171.57(14).

Compounds **7**−**10** have also been characterized crystallographically. Complexes **7** and **8** are mononuclear and adopt octahedral geometries about their respective uranium centers (Figure 3 and Supporting Information). The U═N bond lengths are 1.995(5) and 2.009(3) Å, which are longer than the U═N bonds in previously reported terminal imido dihalides of uranium(IV).[4] This is likely due to the combined steric bulk of the tppo ligands and aryl substituents. The steric difference between the Dipp and Mes* groups accounts for the difference in the Cl1−U−Cl2 angles, which are 165.01(5) and 148.53(3) degrees, respectively.

Complexes **9** and **10** are dimeric, adopting distorted octahedral geometries about their respective uranium centers (molecular structures of **9** and **10** are shown in the Supporting Information). Compound **9** is symmetric about its U$_2$N$_2$ core with *cis*-tppo and *cis*-chloride ligands. The U═N bond lengths are 2.182(5) and 2.252(5) Å (one-half molecule per asymmetric unit), which compare favorably to similar bridging imido species.[4] Surprisingly, the bonding in **10** is quite different, with one uranium center containing *cis*-tppo ligands and the other bound to *trans*-tppo ligands. Such a configuration is likely necessary to relieve strain caused by the bulkier mesityl imido bridges. The differences between **9** and **10** can also be seen in the U═N bond lengths. In complex **10**, these distances are shorter at one uranium center (2.196(9), 2.202(9) Å) than the other (2.252(10), 2.251(9) Å), while each uranium center in **9** contains one short and one long U═N bond.

Reactivity Studies − U(IV). The ability to substitute the chloride ligands on the monoimido U(IV) compounds would extend the utility of these materials. As an example, the reaction of **7** with NaSPh generates the monothiolate species, U(NDipp)Cl(SPh)(tppo)$_3$ (**11**, Scheme 4). The treatment of **7** with 2 equiv of NaSPh in THF resulted in an orange solution, from which **11** was isolated by crystallization from hexane/THF. A ^{1}H NMR spectrum of **11** reveals the presence of two isomers in solution, which display similar, paramagnetically shifted resonances for the Dipp group. The molecular structure of **11** was determined crystallographically and found to be pseudo-octahedral, with *mer*-disposed tppo ligands and a new S−U bond at 2.823(3) Å (see Supporting Information). The

Scheme 4



two isomers observed by NMR could result from *fac*/*mer* isomerization of the tppo ligands or from disorder within the *mer* arrangement of the PhS, Cl, and imido substituents.

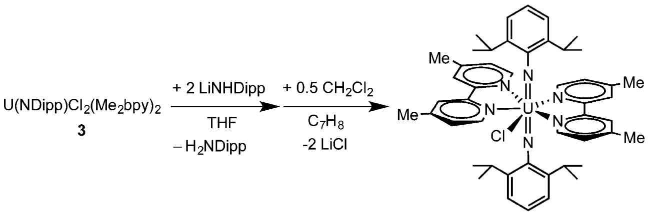
In addition to salt metathesis chemistry, reactivity of the imido group is also of interest. While a more thorough study of the nucleophilic character of the U(IV) imido groups in these compounds will be communicated elsewhere, initial studies have shown that protonolysis of the NDipp group in **7** can be effected by treatment with 2 equiv of HO(2,6-^{t}Bu$_2$-C$_6$H$_3$) (HOAr′) in THF, to provide the bis(aryloxide) complex U(OAr′)$_2$Cl$_2$(tppo)$_2$ (**12**, Scheme 4) as a green crystalline solid. Loss of one tppo ligand results in an overall pseudo-octahedral coordination environment, with two, *cis*-disposed phenoxide ligands replacing the imido group. The U−O/Cl distances are unremarkable, but distortion of the Ar′ rings is evident (see Supporting Information), likely resulting from the steric congestion about the metal center.

Only small amounts of **12** have been isolated, as reaction mixtures indicate the presence of multiple products, which appear to result from both incomplete protonolysis of the imido group and ligand redistribution reactivity. In particular, NMR spectroscopic data on a pale green powder that has been isolated in moderate yields suggest the presence of a C_{2v}-symmetric molecule containing one OAr′ ligand for every two tppo groups. This formulation would be consistent with U(OAr′)Cl$_3$(tppo)$_2$, as would result from disproportionation of **12**.

Reactivity Studies – Substitution and Oxidation to U(V) and U(VI). The reaction chemistry of **3** and **4** has been explored with respect to the formation of additional U═E multiple bonds.

Previous work had shown that a bis(imido) uranium(V) complex, U(NDipp)$_2$Cl(Me$_2$bpy)$_2$, could be formed directly from UCl$_4$ in high yield, by treating the uranium starting material with 2 equivs of Me$_2$bpy and 4 equiv of LiNHDipp, followed by in situ oxidation with CH$_2$Cl$_2$.[10] The treatment of compound **3** with 2 equiv of LiNHDipp and CH$_2$Cl$_2$ (Scheme 5) also led to the isolation of U(NDipp)$_2$Cl(Me$_2$bpy)$_2$ (**13**) in high yield, suggesting that **3** is either an intermediate in the previously reported reaction sequence or at least a viable starting material for the introduction of an additional imido group.

Scheme 5

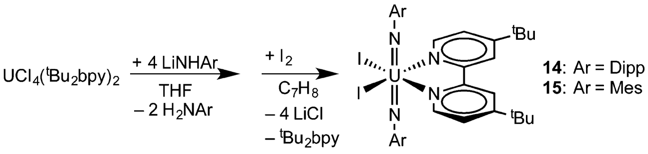


It is unknown at this point if the reaction of **3** with 2.0 LiNHDipp generates [U(NAr)(NHAr)$_2$] or [U(NAr)$_2$], but we were intrigued to test whether this species could also function as a precursor for U(VI) bis(imido) complexes. Previous routes to bis(arylimido) uranium(VI) involve complicated procedures for removing triethylammonium iodide—a byproduct of the reaction of UI$_3$(THF)$_4$ with aniline and triethylamine.[17,33] A preferred synthetic route would (i) allow for a large degree of variability in the imido substituent, (ii) generate easily removable byproducts, and (iii) avoid the use of UI$_3$(THF)$_4$, the synthesis of which can be problematic.[34]

The addition of 2.0 LiNHDipp to stirred solutions of **4** in THF resulted in a modest color change from red-brown to dark red. The subsequent addition of I$_2$ caused the solution to immediately turn dark green. The U(VI) product U(NDipp)$_2$I$_2$(^{t}Bu$_2$bpy) (**14**) was isolated from this mixture in reasonable yields following crystallization from hexane/toluene. As was observed for the synthesis of U(NDipp)$_2$Cl(Me$_2$bpy)$_2$ from UCl$_4$, reactions of **1** with 4 equiv of LiNHDipp, followed by oxidation with I$_2$ also provided reasonable yields of **14**, consistent with **4** serving as a functional intermediate during the synthesis of U(VI) bis(imido) complexes.

In order to test the versatility of this preparative method, we explored reactions of **1** with 4 equiv of LiNHMes (Mes = 2,4,6-trimethylphenyl) followed by oxidation with I$_2$. Indeed, this reaction produced U(NMes)$_2$I$_2$(^{t}Bu$_2$bpy) (**15**) in good yield (Scheme 6). Attempts to isolate a U(IV) mono(mesitylimido) species analogous to **4** were unsuccessful, but the isolation of **14** and **15** from **1** demonstrates the versatility of this reagent as a synthon for bis(arylimido) uranium(VI) species. It was further found that the use of 2 equiv of R$_2$bpy were not necessary for forming high valent derivatives of the U(IV) monoimido species. More convenient preparations of **14** and **15** were carried out by initially forming UCl$_4$(^{t}Bu$_2$bpy) adducts instead of UCl$_4$(^{t}Bu$_2$bpy)$_2$. So doing minimized resources with no loss in either yield or purity.

Scheme 6



Complexes **14** and **15** are both dark red-green, crystalline solids, which are soluble in most organic solvents. Their ^{1}H NMR spectra exhibit, respectively, Dipp imido resonances at 0.89, 3.83, 5.43, and 6.83 ppm for **14** and mesityl imido resonances at 2.65, 2.77, and 6.52 ppm for **15**. The ^{t}Bu$_2$bpy chemical shifts for **14** and **15** are nearly identical.

The solid-state molecular structures of **14** and **15** have been determined by X-ray crystallography. Dark red-green blocks were grown from a hexane-layered solution in toluene or CH$_2$Cl$_2$ solution, respectively, at room temperature. Both species exhibit octahedral geometry about their uranium centers (Figure 4). The short U═N bond lengths of **14** (1.869(3) Å) and **15** (1.867(3) Å) are typical of UO$_2^{2+}$ and its analogues, where an inverse *trans*-influence results in very short uranium-element multiple bonds.[35,36] As expected, the U═N bond lengths are similar to those of previously reported U(VI) arylimido compounds, U(NPh)$_2$I$_2$(THF)$_3$ (1.863(3) Å) and U(NDipp)$_2$I$_2$(THF)$_3$ (1.887(3) Å).[17]

In addition to metathesis chemistry, we attempted the direct oxidation of compounds **3**, **4**, and **7**. In particular, we were interested in developing a facile, economical route to oxo-imido uranium(VI) species. The established route to this motif involves using the expensive water reagent H$_2$O·B(C$_6$F$_5$)$_3$.[16] As such, very little is known about the chemical reactivity of U(VI) oxo-imido compounds. We initially explored reactions of **3** with the oxygen-atom transfer reagent 4-methylmorpholine-N-oxide. The product was identified by NMR spectroscopy as being

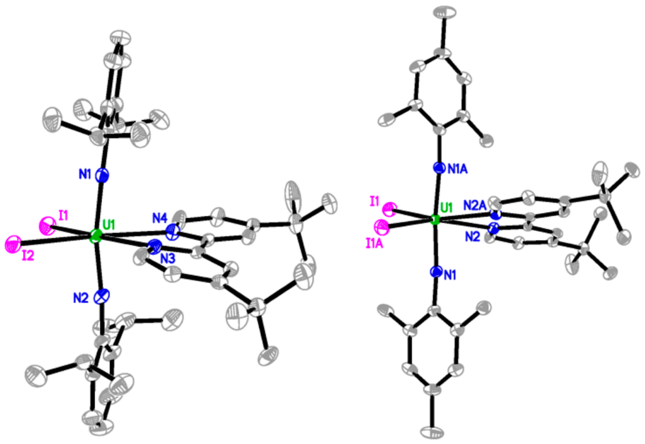
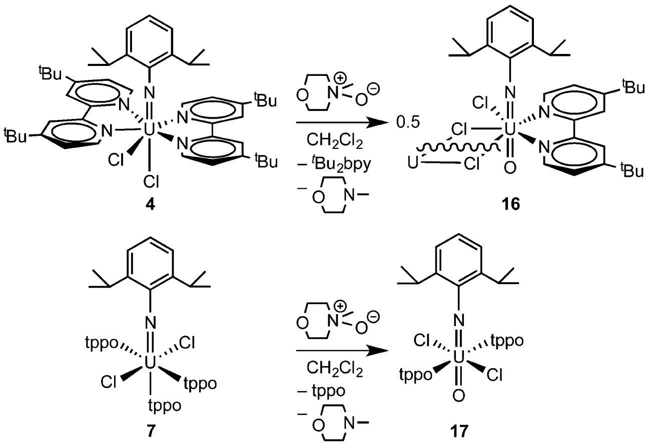


Figure 4. Solid state molecular structures of **14** (left) and **15** (right) with thermal ellipsoids set at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **14**: U1−N1 1.869(3), U1−N2 1.868(3), U1−N3 2.532(3), U1−N4 2.486(3), U1−I1 3.0243(4), U1−I2 2.9931(3); N1−U1−N2 168.40(14), N3−U1−N4 63.16(11), I1−U1−I2 95.36(1). Selected bond lengths (Å) and angles (deg) for **15**: U1−N1 1.867(3), U1−N2 2.505(3), U1−I1 3.0126(6); N1−U1−N1A 173.74(19), N2−U1−N2A 63.01(14), I1−U1−I1A 108.46(2).

diamagnetic, but we were unable to structurally characterize the compound. However, when analogous reactions were carried out with **4** and **7**, U(NDipp)(O)Cl_2(L)$_n$ (**16**, L = ^{t}Bu$_2$bpy, n = 1; **17**, L = tppo, n = 2) were generated in good yields (Scheme 7), and the products were readily separated from the neutral ligand (^{t}Bu$_2$bpy and tppo) byproducts via crystallization.

Scheme 7



Complex **16** is a green-black, crystalline solid with good solubility in most organic solvents. The ^{1}H NMR spectrum is diamagnetic with Dipp imido resonances appearing at 0.84, 4.10, 5.58, and 6.73 ppm. These chemical shifts resemble those of the closely related compound, U(NDipp)$_2$I$_2$(^{t}Bu$_2$bpy) (**14**), with coordinated bipyridine resonances appearing at 1.54, 7.86, 8.49, and 11.00 ppm. These values compare favorably with compounds **14** and **15**, but the bipyridine resonances of **16** are significantly broadened. Attempts to obtain crystallographic data on **16** resulted only in badly twinned structures, but the data were suitable for establishing connectivity, which clearly demonstrates that this species is a chloride-bridged dimer in the solid state. It is likely that the solution-state behavior involves rapid exchange between terminal and bridging chloride ligands, a factor that would account for the aforementioned broadening in the ^{1}H NMR spectrum of **16**.

The ^{1}H NMR spectrum of **17** is diamagnetic with characteristic 2,6-di-isopropylphenyl resonances at 0.82, 4.26, 5.72, and 6.81 ppm.[17] A single resonance is observed in the ^{31}P NMR spectrum at 46.34 ppm. Crystallographic data were obtained more readily in this case, revealing a pseudo-octahedral complex with extremely short U═N and U═O bonds of 1.847(3) and 1.778(2) Å, respectively (solid state molecular structure shown in the Supporting Information). These bond lengths compare favorably with those of previously reported U(N^{t}Bu)(O)I$_2$(tppo)$_2$ (1.821(7) and 1.764(5) Å).[16]

SUMMARY

In this paper, we have described the syntheses of the versatile uranium(IV) complexes, U(NDipp)Cl_2(L)$_n$ (L = R$_2$bpy, n = 1; L = tppo, n = 3). These species are made via salt metathesis on Lewis base adducts of UCl_4, leaving only easily separable salts and anilines as byproducts. Compounds **3**, **4**, and **7** are useful chemical synthons which can be used to prepare bis(imido) uranium(V), bis(imido) uranium(VI), and oxo-imido uranium(VI) products. The wide variety of chemistry reported herein demonstrates the synthetic utility of the mono(imido) U(IV) motif and further suggests that these compounds have may be useful as synthons for currently unknown uranium complexes. We anticipate that the development of this chemistry will provide a template for the preparation of analogous transuranic compounds, of which there are currently no known imido species. Synthetic efforts in this area are currently underway in our laboratories.

EXPERIMENTAL SECTION

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or an atmosphere of argon. Hexane, THF, diethyl ether, CH_2Cl_2, toluene, and benzonitrile were purchased anhydrous and stored over activated 4 Å molecular sieves for 24 h before use. NMR solvents C_7D_8, CD_2Cl_2, $CDCl_3$, and C_4D_8O were also dried over activated 4 Å molecular sieves prior to use. UCl_4 was synthesized by the published procedure.[37] LiNHAr (Ar = Ph, Mes, Dipp) were prepared from the appropriate aniline and ^{n}BuLi in hexane. KNHMes* was prepared from H$_2$NMes* and potassium bis(trimethylsilyl)amide in diethyl ether. 4,4′-dimethyl-2,2′-dipyridyl, 4,4′-di-*tert*-butyl-2,2′-dipyridyl, 4-methylmorpholine-*N*-oxide, and 2,6-di-*tert*-butylphenol were purchased from commercial suppliers and used as received. NMR experiments were performed on either a Bruker AVA300 or a Bruker Ascend 400 NMR spectrometer. ^{1}H NMR spectra are referenced to external SiMe$_4$ using the residual protio solvent peaks as internal standards. Elemental analyses were performed at Midwest Microlab, LLC.

UCl$_4$(^{t}Bu$_2$bpy)$_2$ (**1**). UCl_4 (250 mg, 0.658 mmol) was suspended in THF (3 mL) and solid ^{t}Bu$_2$bpy (353 mg, 1.316 mmol) was added. The resulting light green solution was stirred for 16 h, filtered through Celite, and layered with hexane (10 mL). After 2 days at −40 °C, solvent was decanted to reveal nearly colorless, light green crystals, which were dried *in vacuo* for 2h (597 mg, 99%). Anal. Calcd for $C_{36}H_{48}Cl_4N_4U$: C, 47.17; H, 5.28; N, 6.11. Found: C, 47.13; H, 5.29; N, 6.33. ^{1}H NMR (CD_2Cl_2, 25 °C, 300 MHz): δ −7.61 (s, 2H, ^{t}Bu$_2$*bpy*), −2.52 (s, 18H, ^{t}*Bu*$_2$bpy), 3.38 (s, 2H, ^{t}Bu$_2$*bpy*), 15.03 (s, 2H, ^{t}Bu$_2$*bpy*) ppm.

UCl$_4$(Me$_2$bpy)$_2$ (**2**). UCl_4 (250 mg, 0.658 mmol) was suspended in THF (5 mL) and solid Me$_2$bpy (243 mg, 1.319 mmol) was added. The resulting suspension was stirred for 16 h, and the product was isolated on a fritted glass filter and washed with THF (2 × 3 mL). The off-white powder was dried *in vacuo* for 2h (470 mg, 95%). Anal. Calcd for $C_{24}H_{24}Cl_4N_4U$: C, 38.52; H, 3.23; N, 7.49. Found: C, 38.46; H, 3.44;

N, 7.48. A procedure for the preparation of this compound in ethyl acetate has been previously reported.[23]

*U(NDipp)Cl$_2$(Me$_2$bpy)$_2$ (**3**).* UCl$_4$(Me$_2$bpy)$_2$ (121.5 mg, 0.161 mmol) and LiNHDipp (59 mg, 0.322 mmol) were combined in a 20 mL scintillation vial and THF was added (3 mL). The resulting red solution was stirred for 4 h and THF was removed *in vacuo*. Dichloromethane (3 mL) was added, and the contents were filtered, layered with hexane (3 mL), and left at −40 °C. After 2−3 days, solvent was decanted to reveal dark red needles, which were dried *in vacuo* for 1 h (70 mg, 51%). Anal. Calcd for $C_{36}H_{41}Cl_2N_5U$: C, 50.71; H, 4.85; N, 8.21. Found: C, 50.60; H, 4.78; N, 8.29. ^{1}H NMR (CD_2Cl_2, 25 °C, 300 MHz): δ −66.25 (v br, 4H, -bpy*H*), −19.45 (br, 4H, -bpy*H*), −10.51 (br, 4H, -bpy*H*), −9.92 (br, 12H, -*Me*$_2$bpy), 11.36 (s, 12H, −CH(C*H*$_3$)$_2$), 28.35 (s, 1H, -Dipp*H*$_{para}$), 53.19 (s, 2H, -Dipp*H*$_{meta}$), 64.27 (br, 2H, −C*H*(CH$_3$)$_2$) ppm.

*U(NDipp)Cl$_2$(^{t}Bu$_2$bpy)$_2$ (**4**).* This compound is synthesized as for **5** (see below). Removal of volatile materials from the CH_2Cl_2 solution provides a tacky brown semisolid that contains a mixture of the product and H_2NDipp. Because of the difficulty in handling this material, it is best generated and used in solution. Attempts to crystallize this complex resulted only in the isolation of compound **5**.

*U(NDipp)Cl$_2$(^{t}Bu$_2$bpy)(thf)$_2$ (**5**).* UCl$_4$ (150 mg, 0.395 mmol) and ^{t}Bu$_2$bpy (212 mg, 0.790 mmol) were combined in a vial, and ca. 3 mL of THF was added. The mixture was stirred at room temperature, quickly becoming a homogeneous green solution. Solid LiNHDipp (144.7 mg, 0.790 mmol) was added as a solid causing the color of the solution to immediately turn dark red. After stirring the mixture overnight, the volatile materials were removed under vacuum, and the residue was extracted with 2 mL of CH_2Cl_2. Filtering through Celite removed a white solid and provided a clear, dark red filtrate. The volatile materials were again removed under vacuum. The residue was dissolved in minimal THF and layered with hexane (1:5 THF:hexane), and then stored at −35 °C for several days. The product was collected by decanting the solvent and removing traces of volatile material under vacuum. Yield: 246 mg, 69%. ^{1}H NMR (pyr-*d*$_5$, 25 °C, 300 MHz): δ −18.39 (s, 2H, -bpy*H*), −14.03 (s, 2H, -bpy*H*), −6.77 (s, 18H, -^{t}*Bu*$_2$bpy), 13.18 (s, 12H, −CH(C*H*$_3$)$_2$), 29.60 (s, 1H, -Dipp*H*$_{para}$), 54.24 (s, 2H, -Dipp*H*$_{meta}$), 67.33 (br s, 2H, −C*H*(CH$_3$)$_2$) ppm. Coordinated ^{t}Bu$_2$bpy and THF are readily displaced in pyr-*d*$_5$ solutions to give what is presumably U(NDipp)Cl$_2$(pyr-*d*$_5$)$_4$. The ^{1}H NMR spectral data for this latter compound are as follows: ^{1}H NMR (pyr-*d*$_5$, 25 °C, 300 MHz): δ 13.60 (s, 12H, −CH(C*H*$_3$)$_2$), 29.73 (s, 1H, -Dipp*H*$_{para}$), 54.04 (s, 2H, -Dipp*H*$_{meta}$), 66.41 (br s, 2H, −C*H*(CH$_3$)$_2$) ppm. Resonances at δ 1.65 and 3.63 ppm are assigned to free THF, and they integrate to values corresponding to two molecules of THF per Dipp group.

*U(NDipp)Cl$_2$(tppo)$_3$ (**7**).* UCl$_4$ (200 mg, 0.527 mmol) and tppo (439.6 mg, 1.58 mmol) were combined in THF (3 mL) and stirred in a 20 mL scintillation vial. After 10 min, UCl$_4$(tppo)$_2$ had formed and solid LiNHDipp (192.9 mg, 1.05 mmol) was added. The resulting red reaction mixture was stirred for 16 h. At this time, an orange precipitate had formed, which was isolated on a frit and recrystallized from CH_2Cl_2/hexane to provide orange crystals. The product was dried open to the box atmosphere for 1 h (486 mg, 70%). As a finely divided orange powder, the product decomposes over 10−12 days (in the box atmosphere) to form U(NDipp)$_2$Cl$_2$(tppo)$_2$ and other, currently unidentified products. The isolated orange crystals are stable for months in the drybox atmosphere. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ −35.0 (br, tppo), −10.0 (v br, tppo), −9.0 (br, tppo), 11.5 (s, 12H, −CH(C*H*$_3$)$_2$), 16.9 (br, tppo), 24.5 (br, tppo), 29.9 (t, 1H, -Dipp*H*$_{para}$), 31.2 (br, tppo), 53.5 (d, 2H, -Dipp*H*$_{meta}$), 66.5 (br, 2H, −C*H*(CH$_3$)$_2$) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2, 25 °C) δ −188.7 (v br, 2 *cis*-tppo), 206.9 (br, *trans*-tppo) ppm. The ^{1}H NMR is extremely difficult to interpret outside of the Dipp resonances due to a combination of paramagnetism and two distinct tppo environments. Anal. Calcd for $C_{66}H_{62}Cl_2NO_3P_3U$: C, 60.10; H, 4.74; N, 1.06. Found: C, 59.06; H, 4.69; N, 1.28.

U(NMes)Cl$_2$(tppo)$_3$ (**8**).* UCl$_4$ (50 mg, 0.132 mmol) and tppo (91.6 mg, 0.329 mmol) were combined in THF (3 mL) and stirred in a 20 mL scintillation vial. After 10 min, UCl$_4$(tppo)$_2$ had formed and solid KNHMes* (78.8 mg, 0.263 mmol) was added. The resulting red slurry was stirred for 5 h. The reaction mixture was filtered through Celite, and the red filtrate was layered with hexane (5 mL). After 3−4 days at −40 °C, several red-orange crystals were isolated and dried in vacuo (115 mg, 62%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ −2.8 (v br, tppo), 4.0 (s, 18H, ^{t}Bu), 8.9 (s, 9H, ^{t}Bu), 12.9 (br, tppo), 14.0 (v br, tppo), 26.8 (s, 2H, -mes**H*) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2, 25 °C) δ 175.0 ppm. The second ^{31}P signal is not observed within our spectral window. Anal. Calcd for $C_{72}H_{74}Cl_2NO_3P_3U$: C, 61.63; H, 5.32; N, 1.00. Found: C, 61.82; H, 5.26; N, 1.05.

*[U(NAr)Cl$_2$(tppo)$_2$]$_2$, Ar = Ph (**9**), Mes (**10**).* UCl$_4$ (50 mg, 0.132 mmol) and tppo (73.3 mg, 0.263 mmol) were combined in THF (3 mL) and stirred in a 20 mL scintillation vial. After 10 min, UCl$_4$(tppo)$_2$ had formed and solid LiNHAr (0.263 mmol) was added. The resulting dark red solution was stirred for 4 h and THF was removed *in vacuo*. Dichloromethane (2 mL) was added and the slurry was filtered through Celite to remove LiCl. The red filtrate was layered with hexane and after 2−3 days at −40 °C, orange-brown crystals were isolated and dried *in vacuo*. **9** (66 mg, 50%): ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 2.21 (br, 4H, Ph), 13.87 (br, 4H, Ph) ppm. The *para* proton is obscured by triphenylphosphine resonances; no ^{31}P NMR signal was observed. Anal. Calcd for $C_{85}H_{72}Cl_6N_2O_4P_4U_2$: C, 51.09; H, 3.63; N, 1.40. Found: C, 51.47; H, 3.78; N, 1.50. **10** (85 mg, 65%): ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ −18.36 (br, 6H, Me), 15.47 (br, 3H, Me), 18.42 (br, 2H, aryl*H*) ppm. ^{31}P signal not observed. Anal. Calcd for $C_{90}H_{82}Cl_4N_2O_4P_4U_2$: C, 54.12; H, 4.14; N, 1.40. Found: C, 53.80; H, 4.15; N, 1.30.

*U(NDipp)(SPh)Cl(tppo)$_3$ (**11**).* U(NDipp)Cl$_2$(tppo)$_3$ (100.0 mg, 0.076 mmol) was combined as a solid with NaSPh (20.0 mg, 0.152 mmol). The addition of THF (5 mL) resulted in an orange solution, which was stirred overnight at room temperature. Filtration, followed by concentrating to ca. 2 mL and slowly adding 10 mL of hexane, resulted in an orange powder, which was collected by filtration and dried under a vacuum. Yield: 0.83 g (78%). Material suitable for crystallographic analysis was obtained by layering a THF solution with hexane and storing at room temperature. ^{1}H NMR (CD_2Cl_2, 25 °C, 300 MHz): Isomer 1: δ 66.05 (br, 2H, −C*H*(CH$_3$)$_2$), 52.75 (d, 2H, -Dipp*H*$_{meta}$), 29.45 (t, 1H, -Dipp*H*$_{para}$), 11.73 (s, 12H, −CH(C*H*$_3$)$_2$) ppm; Isomer 2: δ 66.40 (br, 2H, −C*H*(CH$_3$)$_2$), 53.31 (d, 2H, -Dipp*H*$_{meta}$), 29.70 (t, 1H, -Dipp*H*$_{para}$), 11.36 (s, 12H, −CH(C*H*$_3$)$_2$) ppm. Anal. Calcd for $C_{72}H_{67}ClNO_3P_3SU$: C, 62.09; H, 4.85; N, 1.01. Found: C, 62.38; H, 5.02; N, 1.00.

*U(OAr′)$_2$Cl$_2$(tppo)$_2$ (**12**).* U(NDipp)Cl$_2$(tppo)$_3$ (100.0 mg, 0.076 mmol) was suspended in THF (4 mL). HOAr′ (31.3 mg, 0.152 mmol) was added as a solid, and the mixture was stirred for 48 h. The mixture formed a yellow, homogeneous solution over ca. 30 min, and then the color turned progressively more yellow-green over the course of the reaction. The volatile materials were removed under a vacuum, and then the residue was extracted with toluene, layered under an equal volume of hexane, and stored at ambient temperature. The dark green spikes that formed were found by crystallographic analysis to be **12**. Yield: 7 mg (7%). When the THF solution of the reaction mixture was filtered and layered with hexane, a pale green powder formed, which was tentatively identified by NMR spectroscopic analysis as U(OAr′)Cl$_3$(tppo)$_2$: ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 30.06 (d, 2H, -Ar′*H*$_{meta}$), 22.44 (t, 1H, -Ar′*H*$_{para}$), 12.23 (br s, 12H, tppo), 8.00 (s, 18H, tppo), 5.09 (s, 18H, ^{t}Bu) ppm.

*U(NDipp)$_2$Cl(Me$_2$bpy)$_2$ (**13**).* Solid LiNHDipp (30.1 mg, 0.164 mmol) was added to a slurry of **3** (70 mg, 0.082 mmol) in THF (2 mL). The resulting red solution was stirred for 4 h, and solvent was removed *in vacuo*. Toluene (2 mL) was added and the contents were filtered, layered with hexane, and left at RT. After 2 days, dark red blocks precipitated, which were isolated by decanting solvent and dried *in vacuo* (58 mg, 72%). Analytical data for this compound were identical to those reported previously.[10]

*U(NDipp)$_2$I$_2$(^{t}Bu$_2$bpy) (**14**).* UCl$_4$ (209.1 mg, 0.5505 mmol) and ^{t}Bu$_2$bpy (147.6 mg, 0.5499 mmol) were combined in THF (6 mL), and the resulting light green solution was stirred for 15 min. Solid LiNHDipp (403.4 mg, 2.202 mmol) was added, resulting in a dark red solution, and the reaction mixture was stirred for 4 h. Solid I$_2$ was

Table 1. X-ray Crystallographic Data for Complexes **1**·THF·hexane, **5**, **7**·$3CH_2Cl_2$, **8**, and **9**·$8CH_2Cl_2$

	1·THF·hexane	**5**	**7·3CH$_2$Cl$_2$**	**8**	**9·8CH$_2$Cl$_2$**
empirical formula	$C_{46}H_{70}Cl_4N_4OU$	$C_{38}H_{57}Cl_2N_3O_2U$	$C_{69}H_{68}Cl_8NO_3P_3U$	$C_{72}H_{74}Cl_2NO_3P_3U$	$C_{92}H_{86}Cl_{20}N_2O_4P_4U_2$
crystal habit, color	block, colorless	block, dark red	block, red-orange	block, red-orange	block, dark red
crystal size (mm)	0.20 × 0.12 × 0.10	0.24 × 0.14 × 0.10	0.20 × 0.12 × 0.04	0.38 × 0.26 × 0.10	0.18 × 0.12 × 0.08
crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
volume (Å^3)	4863.0(6)	1966.31(17)	3326.1(9)	3263.3(4)	4542.4(8)
a (Å)	16.542(1)	10.8616(5)	13.297(2)	13.511(1)	14.437(2)
b (Å)	11.554(1)	11.6484(6)	13.955(2)	13.697(1)	14.781(2)
c (Å)	25.530(2)	15.7897(8)	19.417(3)	18.199(2)	21.803(2)
α (deg)	90	99.832(1)	69.718(2)	102.956(1)	90
β (deg)	94.701(1)	91.493(1)	83.685(2)	90.359(1)	102.499(1)
γ (deg)	90	91.875(1)	80.296(2)	95.898(1)	90
Z, Z'	4, 1	2, 1	2, 1	2, 1	4, 0.5
formula weight (g/mol)	1074.92	896.8	1573.86	1403.16	2592.69
density (calc) (Mg/m^3)	1.350	1.515	1.317	1.428	1.399
absorption coefficient (mm^{-1})	3.588	4.298	2.634	2.689	3.792
F_{000}	1968	896	1320	1416	1864
total reflections ($I_o > 2\sigma I_o$)	9233	8008	12237	13248	8262
final R indices ($I_o > 2\sigma I_o$)[a]	$R_1 = 0.0319$, $wR_2 = 0.0696$	$R_1 = 0.0172$, $wR_2 = 0.0432$	$R_1 = 0.0476$, $wR_2 = 0.0988$	$R_1 = 0.0368$, $wR_2 = 0.0824$	$R_1 = 0.0456$, $wR_2 = 0.1056$
final R indices (all data)[a]	$R_1 = 0.047$, $wR_2 = 0.075$	$R_1 = 0.019$, $wR_2 = 0.044$	$R_1 = 0.0719$, $wR_2 = 0.1078$	$R_1 = 0.0466$, $wR_2 = 0.0869$	$R_1 = 0.0731$, $wR_2 = 0.1140$
largest diff peak/hole (e·Å^{-3})	1.028/−1.088	0.905/−0.376	1.488/−1.028	1.347/−1.174	1.864/−0.856

[a] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w F_o^4]^{1/2}$, $p = [F_o^2 + 2F_c^2]/3$. **1·THF·hexane**, $w = [\sigma^2 F_o^2 + (0.0319p)^2]^{-1}$. **5**, $w = [\sigma^2 F_o^2 + (0.0172p)^2]^{-1}$. **7·3CH$_2Cl_2$**, $w = [\sigma^2 F_o^2 + (0.0476p)^2]^{-1}$. **8**, $w = [\sigma^2 F_o^2 + (0.0368p)^2]^{-1}$. **9·3CH$_2Cl_2$**, $w = [\sigma^2 F_o^2 + (0.0456p)^2]^{-1}$.

added, which caused the solution to turn dark green immediately. The reaction mixture was stirred for 1 h, and THF was removed *in vacuo*. Toluene (15 mL) was added, the contents were filtered through Celite, separated into three vials and layered with hexane (10 mL each). After 2−3 days at RT, solvent was decanted to reveal dark green blocks, which were dried *in vacuo* (331.5 mg, 54%). Anal. Calcd for $C_{42}H_{58}N_4I_2U$: C, 45.41; H, 5.26; N, 5.04. Found: C, 46.51; H, 5.07; N, 4.30. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz) δ 0.89 (d, 24H, $-CH(CH_3)_2$), 1.61 (s, 18H, ^{t}Bu), 3.83 (sp, 4H, $-CH(CH_3)_2$), 5.43 (t, 2H, -DippH_{para}), 6.83 (d, 4H, -DippH_{meta}), 8.14 (d, 2H, -bpy$H$), 8.77 (s, 2H, -bpy$H$), 11.27 (d, 2H, -bpy$H$) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C, 100 MHz MHz) δ 25.82, 26.55, 30.47, 36.35, 118.63, 121.42, 124.10, 128.74, 149.10, 150.45, 151.89, 157.17, 166.43 ppm.

*U(NMes)$_2$I$_2$(^{t}Bu$_2$bpy) (**15**).* UCl_4 (219.7 mg, 0.5784 mmol) and ^{t}Bu$_2$bpy (155.2 mg, 0.5783 mmol) were combined in THF (6 mL), and the resulting light green solution was stirred for 15 min. Solid LiNHMes (425.5 mg, 2.306 mmol) was added, resulting in a dark brown solution, and the reaction mixture was stirred for 4 h. Solid I_2 was added, which caused the solution to turn dark green immediately. The reaction mixture was stirred for 1 h and THF was removed *in vacuo*. Dichloromethane (5 mL) was added, the contents were filtered through Celite and layered with hexane (10 mL). After 2−3 days at RT, solvent was decanted to reveal dark green blocks, which were dried *in vacuo* (348.3 mg, 59%). Anal. Calcd for $C_{36}H_{46}N_4I_2U$: C, 42.12; H, 4.52; N, 5.46. Found: C, 41.89; H, 4.41; N, 5.49. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz) δ 1.62 (s, 18H, ^{t}Bu), 2.65 (s, 12H, -Mes(CH_3)$_{ortho}$), 2.77 (s, 6H, -Mes(CH_3)$_{para}$), 6.52 (s, 4H, -Mes$H$), 8.13 (d, 2H, -bpy$H$), 8.71 (s, 2H, -bpy$H$), 11.26 (d, 2H, -bpy$H$) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C, 100 MHz) δ 18.42, 18.49, 30.51, 36.37, 121.73, 123.16, 123.98, 138.36, 139.53, 149.34, 153.28, 157.40, 166.72 ppm.

*[U(NDipp)(O)(μ-Cl)Cl(^{t}Bu$_2$bpy)]$_2$ (**16**).* UCl_4(^{t}Bu$_2$bpy)$_2$ (120 mg, 0.131 mmol) was dissolved in THF (3 mL), and solid LiNHDipp (48 mg, 0.262 mmol) was added. The resulting red solution was stirred for 4 h and THF was removed *in vacuo*. Dichloromethane (2 mL) was added, the contents were filtered, and solid 4-methylmorpholine-*N*-oxide (15.3 mg, 0.131 mmol) was added. Upon stirring for 16 h, the reaction mixture was filtered, layered with hexane (3 mL), and left at −40 °C. After 2−3 days, the solvent mixture was left at RT and within minutes, black blades began forming. Solvent was decanted and the crystals were dried *in vacuo* (60 mg, 59%). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 0.84 (d, 24H, $-CH(CH_3)_2$), 1.54 (s, 36H, ^{t}Bu), 4.10 (m, 4H, $-CH(CH_3)_2$), 5.58 (t, 2H, -DippH_{para}), 6.73 (d, 4H, -DippH_{meta}), 7.86 (br, 4H, -bpy$H$), 8.49 (br, 4H, -bpy$H$), 11.00 (br, 4H, -bpy$H$) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C, 100 MHz) δ 25.41, 26.92, 30.54, 36.05, 118.81, 120.74, 123.73, 128.58, 149.08, 149.47, 154.36, 157.79, 165.52 ppm.

*U(NDipp)(O)Cl$_2$(tppo)$_2$ (**17**).* U(NDipp)Cl_2(tppo)$_3$ (75 mg, 0.057 mmol) was dissolved in CH_2Cl_2 (3 mL) and solid 4-methylmorpholine-*N*-oxide (6.7 mg, 0.057 mmol) was added. After being stirred for 16 h, the dark reaction mixture was filtered and solvent was removed until ∼1 mL remained. Toluene (6−8 mL) was added and the contents were stirred for 16 h. The reaction mixture was filtered (to remove tppo), and the solvent was removed in vacuo. The product was dissolved in CH_2Cl_2 (2 mL), layered with hexane (2 mL), and left at −40 °C. After 2−3 days, black crystals formed which were isolated by decanting solvent and drying *in vacuo* (42 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.82 (d, 12H, $-CH(CH_3)_2$), 4.26 (m, 2H, $-CH(CH_3)_2$), 5.72 (t, 1H, -DippH_{para}), 6.81 (d, 2H, -DippH_{meta}), 7.47 (br, 12H, tppo), 7.60 (m, 6H, tppo), 8.10 (m, 12H, tppo) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C) δ 46.34 ppm. Anal. Calcd for $C_{48}H_{47}Cl_2NO_3P_2U$: C, 54.55; H, 4.48; N, 1.33. Found: C, 54.19; H, 4.81; N, 1.48.

X-ray Crystallography. The crystal structures of compounds **1·THF·hexane, 5, 7·3CH$_2$Cl$_2$, 8, 9·8CH$_2$Cl$_2$, 10·4CH$_2$Cl$_2$, 11, 12, 14, 15, and 17·C$_7$H$_8$** were determined as follows. The crystal was mounted in a nylon cryoloop from Paratone-N oil under argon gas flow. Data were collected on a Bruker X-ray diffractometer, with a D8 goniometer and an APEXII charge-coupled device (CCD) detector. The crystal was cooled with a KRYO-FLEX liquid nitrogen vapor cooling device to 141 K. The instrument was equipped with a graphite monochromatized Mo Kα X-ray source (λ = 0.71073 Å), with 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

Table 2. X-ray Crystallographic Data for Complexes $10{\cdot}4CH_2Cl_2$, 11, 12, 14, 15, and $17{\cdot}C_7H_8$

	$10{\cdot}4CH_2Cl_2$	11	12	14	15	$17{\cdot}C_7H_8$
empirical formula	$C_{94}H_{90}Cl_{12}N_2O_4P_4U_2$	$C_{72}H_{67}ClNO_3P_3SU$	$C_{64}H_{72}Cl_2O_4P_2U$	$C_{42}H_{82}I_2N_4U$	$C_{36}H_{46}I_2N_4U$	$C_{55}H_{55}Cl_2NO_3P_2U$
crystal habit, color	block, orange	block, orange	block, green	block, dark	block, dark red	block, brown-yellow
crystal size (mm)	0.22 × 0.16 × 0.08	0.16 × 0.12 × 0.08	0.18 × 0.10 × 0.10	0.12 × 0.10 × 0.10	0.24 × 0.16 × 0.08	0.22 × 0.14 × 0.08
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$
volume (Å^3)	4747(2)	6306.0(16)	17488(5)	4370.0(6)	3701.3(10)	5011.1(9)
a (Å)	13.633(4)	14.639(2)	36.310(6)	12.060(1)	21.198(3)	14.985(2)
b (Å)	14.664(4)	16.519(2)	18.368(3)	18.052(2)	11.818(2)	19.391(2)
c (Å)	26.722(7)	26.096(4)	26.281(4)	20.141(2)	17.977(4)	17.261(2)
α (deg)	104.440(3)	90	90	90	90	90
β (deg)	90.909(3)	92.194(2)	93.860(2)	94.730(1)	124.725(1)	92.402(1)
γ (deg)	112.380(3)	90	90	90	90	90
Z, Z'	2, 1	4, 1	12, 3	4, 1	4, 0.5	4, 1
formula weight (g/mol)	1997.32	1392.72	1276.09	1110.75	1026.60	1148.87
density (calc) (Mg/m^3)	1.397	1.467	1.454	1.688	1.842	1.523
absorption coefficient (mm^{-1})	3.632	2.774	2.977	5.159	6.082	3.453
F_{000}	2296	2800	7728	2144	1952	2288
total reflections ($I_o > 2\sigma I_o$)	17287	11535	35379	15966	10384	9464
final R indices ($I_o > 2\sigma I_o$)[a]	$R_1 = 0.0768$, $wR_2 = 0.1872$	$R_1 = 0.0631$, $wR_2 = 0.1285$	$R_1 = 0.0285$, $wR_2 = 0.0521$	$R_1 = 0.0333$, $wR_2 = 0.0782$	$R_1 = 0.0265$, $wR_2 = 0.0626$	$R_1 = 0.0264$, $wR_2 = 0.0533$
final R indices (all data)[a]	$R_1 = 0.1106$, $wR_2 = 0.2003$	$R_1 = 0.1472$, $wR_2 = 0.1625$	$R_1 = 0.0459$, $wR_2 = 0.0560$	$R_1 = 0.0457$, $wR_2 = 0.0835$	$R_1 = 0.0342$, $wR_2 = 0.0652$	$R_1 = 0.0421$, $wR_2 = 0.0577$
largest diff peak/hole (e·Å^{-3})	8.420/−3.320	1.243/−0.820	0.787/−0.692	1.810/−1.184	1.671/−1.441	0.587/−0.899

[a] $R_1 = \Sigma\,|(|F_o| - |F_c|)|/\Sigma\,|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma\, wF_o^4]^{1/2}$, $p = [F_o^2 + 2F_c^2]/3$. **$10{\cdot}4CH_2Cl_2$**, $w = [\sigma^2 F_o^2 + (0.0953p)^2]^{-1}$. **11**, $w = [\sigma^2 F_o^2 + (0.0703p)^2]^{-1}$. **12**, $w = [\sigma^2 F_o^2 + (0.0209p)^2]^{-1}$. **14**, $w = [\sigma^2 F_o^2 + (0.0364p)^2]^{-1}$. **15**, $w = [\sigma^2 F_o^2 + (0.0333p)^2]^{-1}$. **$17{\cdot}C_7H_8$**, $w = [\sigma^2 F_o^2 + (0.0264p)^2]^{-1}$.

collection and initial indexing and cell refinement were handled using APEXII software.[38] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[39] The data were S5 corrected for absorption using the SADABS program.[40] Decay of reflection intensity was monitored via analysis of redundant frames. The structures were solved using either Direct methods or a Patterson solution and difference Fourier techniques. All hydrogen atom positions were idealized and refined as riding on the atoms they were attached to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[41] Structures **1**, **7**, **9**, and **10** contained solvents of crystallization, which were removed with the function Squeeze in the program Platon. A summary of relevant crystallographic data is found in Tables 1 and 2, and full details are provided in the CIFs (see Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic details of **1·THF·hexane**, **5**, **7·3CH$_2$Cl$_2$**, **8**, **9·8CH$_2$Cl$_2$**, **10·4CH$_2$Cl$_2$**, **11**, **12**, **14**, **15**, **and 17·C$_7$H$_8$** are included in CIF format, as well as images and important bond lengths/angles for compounds **8**, **9**, **10**, **11**, **12**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: boncella@lanl.gov.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

R.E.J. and N.C.T. thank the G. T. Seaborg Institute at Los Alamos National Laboratory for fellowships in partial support of this research. This work was supported by the U.S. Department of Energy, Office of Science, under the Heavy Element Chemistry program. Los Alamos National Laboratory is managed and operated by Los Alamos National Security, LLC (LANS), under Contract Number DE-AC52-06NA25396 for the Department of Energy's National Nuclear Security Administration (NNSA).

■ REFERENCES

(1) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 9840.

(2) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448.

(3) Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2000**, *122*, 6108.

(4) Jilek, R. E.; Spencer, L. P.; Kuiper, D. L.; Scott, B. L.; Williams, U. J.; Kikkawa, J. M.; Boncella, J. M. *Inorg. Chem.* **2011**, *50*, 4235.

(5) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 12536.

(6) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514.

(7) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853.

(8) Evans, W. J.; Traina, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2009**, *131*, 17473.

(9) 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.

(10) Jilek, R. E.; Spencer, L. P.; Lewis, R. A.; Scott, B. L.; Hayton, T. W.; Boncella, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 9876.

(11) 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.

(12) Stewart, J. L.; Andersen, R. A. *New J. Chem.* **1995**, *19*, 587.

(13) Zalkin, A.; Brennan, J. G.; Andersen, R. A. *Acta Crystallogr. Sect. C* **1988**, *44*, 1553.

(14) Arney, D. S. J.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068.

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

(16) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R. *J. Am. Chem. Soc.* **2006**, *128*, 12622.

(17) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R.; Hay, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10549.

(18) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941.

(19) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 959.

(20) Gans, P.; Smith, B. C. *J. Chem. Soc.* **1964**, 4177.

(21) Gans, P.; Marriage, J. *J. Chem. Soc., Dalton Trans.* **1972**, 1738.

(22) Bombieri, G.; Brown, D.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1975**, 1873.

(23) Wassef, M. A.; Atya, L. *Egypt. J. Chem.* **1982**, *25*, 281.

(24) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Acta Crystallogr. Sect. C* **1984**, *40*, 1186.

(25) Schnaars, D. D.; Wu, G.; Hayton, T. W. *Dalton Trans.* **2008**, 6121.

(26) Van Den Bossche, G.; Rebizant, J.; Spirlet, M. R.; Goffart, J. *Acta Crystallogr. Sect. C* **1986**, *42*, 1478.

(27) Zalkin, A.; Edwards, P. G.; Zhang, D.; Andersen, R. A. *Acta Crystallogr. Sect. C* **1986**, *42*, 1480.

(28) Despite attempts to crystallize this compound from a variety of solvent systems, only polycrystalline materials have been obtained.

(29) Zi, G.; Jia, L.; Werkema, E. L.; Walter, M. D.; Gottfriedsen, J. P.; Andersen, R. A. *Organometallics* **2005**, *24*, 4251.

(30) Rivière, C.; Nierlich, M.; Ephritikhine, M.; Madic, C. *Inorg. Chem.* **2001**, *40*, 4428.

(31) The NDipp resonances of **1** compare favorably with those of the previously reported species, U(NDipp)I$_2$(THF)$_4$.[4]

(32) It is not uncommon for paramagnetic uranium complexes to exhibit no ^{31}P NMR resonances.

(33) The difficulty removing [Et$_3$N]I is not explicitly stated in ref 17, but our experience in this area has illustrated the need for repeated recrystallizations to remove reaction byproducts.

(34) Monreal, M. J.; Thomson, R. K.; Cantat, R.; Travia, N. E.; Scott, B. L.; Kiplinger, J. L. *Organometallics* **2011**, *30*, 2031.

(35) Denning, R. G. *Struct. Bonding (Berlin)* **1995**, *79*, 215.

(36) O'Grady, E.; Kaltsoyannis, N. *Dalton Trans.* **2002**, 1233.

(37) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 5978.

(38) *APEXII 1.08*; Bruker AXS, Inc.: Madison, WI, 2004.S15.

(39) *SAINT+ 7.06*; Bruker AXS, Inc.: Madison, WI, 2003.

(40) Sheldrick, G. M. *SADABS 2.03*; University of Gottingen, Gottingen, Germany, 2001.

(41) *SHELXTL 5.10*; Bruker AXS, Inc.: Madison, WI, 1997.