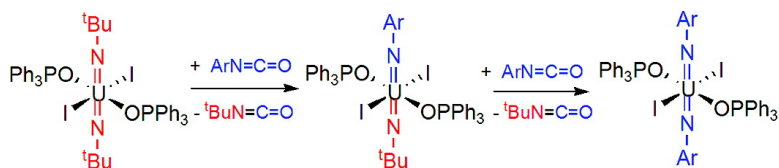## Communication

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Imido Exchange in Bis(imido) Uranium(VI) Complexes with Aryl Isocyanates

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For the past 150 years, studies of uranium(VI) have been generally directed toward understanding the chemical behavior and unique bonding in the uranyl ion (UO_2^{2+}). This ion possesses U−O bonds which have high thermodynamic stability and extreme kinetic inertness. As a result, the majority of UO_2^{2+} reaction chemistry involves substitution of equatorially coordinated ligands while leaving the U−O bond unaffected.[1] Recently, we have reported the syntheses of isoelectronic bis(imido) $[U(NR)_2]^{2+}$ and oxo-imido $[U(NR)(O)]^{2+}$ ions which possess many of the bonding features found in UO_2^{2+}.[2] Our recent isolation of these ions has stimulated us to investigate their reactivity to elucidate a more complete understanding of uranium(VI) chemistry.

In this communication, we report our investigations of the reactivity of the $[U(N^tBu)_2]^{2+}$ ion toward aryl isocyanates. Given the strength and stability of the U−O multiple bond, these reactions were anticipated to produce the oxo-imido framework. Instead, we observe an unexpected reaction that does not involve U=O bond formation but rather an imido exchange reaction in which aryl-imido for alkyl-imido substitution occurs.

Organic isocyanates have often been used in transition metal chemistry to effect transformations of M=N imido functional groups.[3] For instance, the reactions of R*NCO with M=NR imido compounds have been reported to produce either (1) carbodiimides (R*NCNR) and metal oxo complexes or (2) a new isocyanate (RNCO) and M=NR* metal imido compound. The latter transformation is unusual, although there are several reports in which high oxidation state titanium, vanadium, and molybdenum complexes can accomplish this conversion.[4−6] The isolation of *N,O-* or *N,N-*bound ureate complexes during these reactions suggests that the reaction proceeds by the formal [2 + 2] cycloaddition of either the C=O or C=N bond of the isocyanate across the M=N imido functional group.[7] Given the strength of U=O bonds, it was anticipated that the reaction of the bis(imido) complex U(N^{t}Bu)$_2$-(I)$_2$(OPPh$_3$)$_2$ (**1**) with aryl isocyanates would yield the oxo-imido complex **2** (Scheme 1) or possibly an *N,O-*bound ureate.

Stirring orange-red solutions of **1** with ArNCO (Ar=Ph, 2,4,6-Me$_3$C$_6$H$_2$) in CH$_2$Cl$_2$ generates dark red-brown solutions. In the reaction with PhNCO, the mixed bis(imido) complex, U(NPh)(N^t-Bu)(I)$_2$(OPPh$_3$)$_2$ (**3**), can be isolated from this reaction as a dark red powder in 74% yield. The ^{1}H NMR spectrum of **3** displays phenyl resonances at 5.35, 5.82, 6.92 ppm and a *tert*-butyl imido resonance at 0.19 ppm (Scheme 1).

Single crystals of **3** were grown from a mixture of CH$_2$Cl$_2$/hexanes and analyzed by X-ray crystallography. The solid-state molecular structure of **3** is shown in Figure 1. Complex **3** possesses a pseudo-octahedral geometry at the uranium center with *trans-*oriented bis(imido) ligands. The U−N(imido) bond lengths (U−N(alkyl) = 1.832 Å, U−N(Ph) = 1.841(8) Å) are comparable to bond lengths found in U(N^{t}Bu)$_2$(I)$_2$(OPPh$_3$)$_2$ (U−N avg = 1.840-
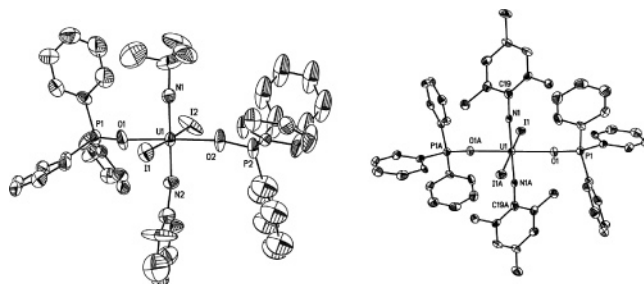
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‡ Theoretical Division.

Figure 1. Solid-state molecular structure of [U(NPh)(N^{t}Bu)(I)$_2$(OPPh$_3$)$_2$] (**1**) and [U(NMes)$_2$(I)$_2$(OPPh$_3$)$_2$] (**6**) (Mes = 2,4,6-Me$_3$C$_6$H$_2$). Selected bond lengths (Å) and angles (deg) for **1**: U1−N1 = 1.832(8), U1−N2 = 1.841-(8), U1−O1 = 2.320(7), U1−O2 = 2.306(7), U1−I1 = 3.0623(9), U1−I2 = 3.0486(9), O1−P1 = 1.493(7), O2−P2 = 1.497(7), N1−U1−N2 = 177.4(4), N1−U1−O1 = 92.6(4), O1−U1−O2 = 178.2(3). Selected bond lengths and angles for **6**: U1−N1 = 1.867(5), U1−O1 = 2.313(4), U1−I1 = 3.0618(5), O1−P1 = 1.513(5), N1−U1−N1A = 180.0(5), N1−U1−O1 = 89.9(2).

Scheme 1
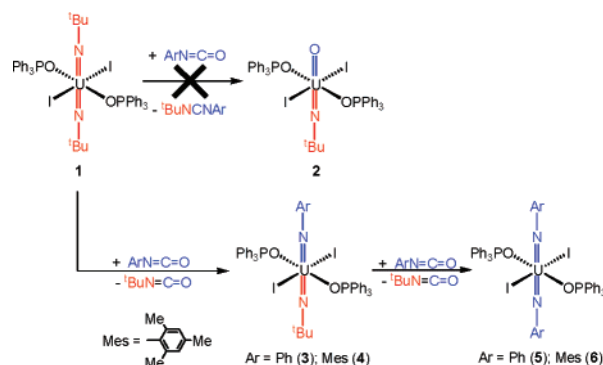
(3) Å) and U(NPh)$_2$(I)$_2$(THF)$_3$ (U−N avg = 1.863(2) Å) complexes as is the N1−U1−N2 bond angle (177.4(4)°).[2b] The U−I and U−O(phosphine oxide) bond lengths are also similar to those of other previously described uranium *trans-*bis(imido) complexes.

The reactions between **1** and 2 equiv of ArNCO (Ar = Ph, 2,4,6-Me$_3$C$_6$H$_2$) yield symmetric bis(imido) complexes **5** and **6** (Scheme 1). ^{31}P NMR spectroscopy confirms the formation of **6** as observed by a singlet at 48.5 ppm. The ^{1}H NMR spectrum indicates only one set of aryl-imido resonances, with two methyl groups located at 2.41 and 2.45 ppm. In the case of **5**, the ^{1}H NMR spectrum of the product matches the compound U(NPh)$_2$(I)$_2$(OPPh$_3$)$_3$ which has been previously described. Interestingly, there are no reverse reactions between *tert*-butyl isocyanate and aryl imido complexes **3**−**6** as indicated by ^{31}P NMR spectroscopy.

Single crystals of **6** suitable for an X-ray diffraction study were grown from CH$_2$Cl$_2$/hexanes, and the solid-state molecular structure is shown in Figure 1. Complex **6** was found to crystallize in the triclinic space group $P\bar{1}$, with an inversion center at the uranium metal atom. The molecule possesses short U−N bonds (U1−N1

Scheme 2 Relative Free Energies of the Products and Intermediates in the Potential Pathways for the Formation of **2** and **3**[a]
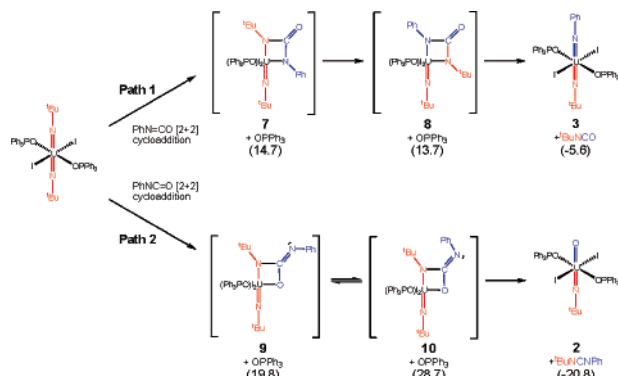
[a] Energies reported at the hybrid DFT level of theory relative to the energy of **1** are provided in parentheses in kcal mol⁻¹.

= 1.867(5) Å) and a linear N–U–N bond angle. The U–O(OPPh₃) bond lengths in **6** (U1–O1 = 2.313(4) Å) are comparable with those in **3** and the uranyl analogue UO₂I₂(OPPh₃)₂.[2b,8]

Density functional theory (DFT) calculations were performed to elucidate the relative energies of the intermediates and products of this reaction.[9] There are two reaction pathways which could generate the bis(imido) product **3** and the oxo-imido species **2** from U(N^{t}Bu)₂(I)₂(OPPh₃)₂ (Paths 1 and 2, Scheme 2). The first pathway involves the [2 + 2] cycloaddition of the C=N bond of the aryl isocyanate to form an *N,N*-bound ureato intermediate (**7**), which can isomerize to form species **8** with the −NPh group *trans* to the *tert*-butyl imido moiety. Compound **8** can then eliminate ^{t}BuNCO to generate the unsymmetrical bis(imido) complex **3** (Path 1). Alternatively, *N,O*-bound carbamate intermediates **9** and **10** could form which result from the [2 + 2] cycloaddition of the C=O bond of the aryl isocyanate across the U=N imido bond. Elimination of a substituted carbodiimide would generate the oxo-imido complex **2** (Path 2).

The computational results suggest the lowest energy pathway involves the [2 + 2] cycloaddition of the C=N bond of phenyl isocyanate to form the *N,N*-bound ureato intermediate **7** (Path 1, Scheme 2). In the calculations performed, it is assumed that OPPh₃ dissociation occurs in order to generate intermediates **7** and **8**. Experimentally, the reactions between **1** and PhNCO proceed much more slowly in the presence of excess OPPh₃ as is consistent with this assumption. Overall the transformation of U(N^{t}Bu)₂(I)₂(OPPh₃)₂ (**1**) to U(NPh)(N^{t}Bu)(I)₂(OPPh₃)₂ (**3**) is exergonic, with the free energy of the bis(*tert*-butyl)imido uranium complex (**1**) + PhNCO higher than the mixed imido species **3** + ^{t}BuNCO by 6.2 kcal mol⁻¹.

In contrast to this mechanism, the calculated [2 + 2] C=O cycloaddition bond pathway (Path 2) involves the formation of the higher energy *N,O*-bound ureato intermediates **9** (19.8 kcal mol⁻¹) and **10** (28.7 kcal mol⁻¹). Complex **9** can then eliminate the mixed carbodiimide ^{t}BuN=C=NPh and form the oxo-imido species **2**. As was anticipated, the relative energy of **2** is substantially lower in energy than the unsymmetrical imido species **3** (15.2 kcal mol⁻¹). This energy difference between U=O and U=N bond formation has also been observed in cyclopentadienyl-substituted uranium-(IV) complexes.[10]

The reaction between 1 and 2 equiv of Ph¹⁵NCO and **1** produces U(N^{t}Bu)(¹⁵NPh)(I)₂(OPPh₃)₂ (**¹⁵N-3**) and U(¹⁵NPh)₂(I)₂(OPPh₃)₂

(**¹⁵N-5**), respectively. **¹⁵N-3** and **¹⁵N-5** display single ¹⁵N resonances at 390.5 and 393.3 ppm in the ¹⁵N{¹H} NMR spectra, respectively. While the ¹⁵N{¹H} NMR chemical shifts of U(VI) imido compounds have yet to be reported, the resonances exhibited for **¹⁵N-3** and **¹⁵N-5** are similar to those of previously characterized ¹⁵N-labeled tungsten(VI) imido complexes.[11]

Given the evidence from DFT calculations and the results from ¹⁵N-labeling studies, it appears the mechanism for the formation of **3** involves the [2 + 2] cycloaddition of the aryl isocyanate C=N bond across the U=N imido moiety. These results are quite surprising given the thermodynamic and kinetic stability of U=O bonds. We are currently investigating the relative energies of the transition states in Paths 1 and 2 to determine if the selectivity for the formation of the mixed imido species **3** over the oxo-imido complex **2** is kinetic in origin. Preliminary experiments show that, at higher temperatures (50 °C), the initially formed mixed imido complex, **3**, reacts further with the ^{t}BuNCO that is produced to give the mixed oxo-imido complex **2** which is consistent with the relative energies determined by DFT calculations. While alkyl substituted carbodiimides do not react with **1** at room temperature or at 50 °C for 15 h, we are actively investigating the reactions of these and other unsaturated electrophiles to determine the generality of this unexpected imido reactivity.

Supporting Information Available: Complete details of the preparation and characterization of **3**−**6**, including X-ray crystallographic details (as CIF files) of **3** and **6**. Geometries of the calculated structures of **2**, **3**, and **7**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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