# Uranium−Ligand Multiple Bonding in Uranyl Analogues, [L═U═L]$^{n+}$, and the Inverse Trans Influence

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ABSTRACT: The societal importance of uranium complexes containing the uranyl moiety [O═U═O]$^{2+}$ continues to grow with the ongoing international nuclear enterprise and associated accumulating legacy waste. Further studies of the electronic structure of uranyl and its analogues are imperative for the development of crucial technologies, including lanthanide/actinide extractants and chemical and environmental remediation methodologies. Actinide oxo halides are a subset of the growing class of actinyl (uranyl) analogues. The

understanding of their electronic structures links the detailed spectroscopic studies of uranyl, indicating the role of the pseudocore 6p orbitals in U−O bonding, to hypotheses about the 6p orbitals' role in the chemical bonding of uranyl analogues. These actinide oxo halides are a very small class of actinide compounds that present the inverse trans influence (ITI). This class of complexes was, until recently, limited to two crystallographically characterized compounds, namely, [UCl$_5$O][PPh$_4$] and [PaCl$_5$O][NEt$_4$]$_2$. These complexes are important because they give a readily and clearly defined experimental observable: the difference between the M−X$_{trans}$ and M−X$_{cis}$ (here X = Cl) bond lengths in the solid state. This bond metric is a sensitive probe for the role of 6p, 6d, and 5f orbitals, as well as electrostatic interactions, in determining their electronic structure. This Viewpoint Article reviews the theoretical, experimental, and synthetic work on the ITI in actinide complexes and contextualizes it within broader studies on the electronic structure of uranyl and its analogues. Furthermore, our recent work on the ITI in high-valent uranium(V/VI) oxo and imido complexes is described as a whole. This work builds on the extant synthetic literature on the ITI and provides design parameters for the synthesis and characterization of high-valent uranium−ligand multiple bonds.
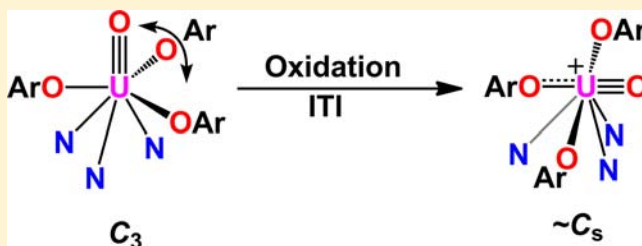
INTRODUCTION

Until quite recently, reliably structurally characterized actinide complexes presenting the inverse trans influence (ITI) were limited to two examples, namely, [UCl$_5$O][PPh$_4$][1−3] and [PaCl$_5$O][NEt$_4$]$_2$,[4] both of which were initially characterized 40 years ago. Strictly defined,[5] the ITI is a thermodynamic ground-state phenomenon, in which the M−X$_{trans}$ bond is shortened and strengthened in comparison to the M−X$_{cis}$ bond (X identifies identical anionic ligands under the closed-shell formalism). This phenomenon is so named because of its contrast with the well-known textbook[6] trans influence, which is typically seen in six-coordinate C_{4v} and four-coordinate square-planar transition-metal complexes, as best exemplified by [OsNCl$_5$]$^{2−}$.[7,8] In these transition-metal systems, the M−X$_{trans}$ bond is lengthened and weakened in comparison to the M−X$_{cis}$ bond.

This historical absence of definitive examples of the ITI in the literature is due to significant difficulties in the synthesis and characterization of these complexes. Lower-oxidation-state analogues of the uranium(V) oxo halides are prone to disproportionation,[9] and synthetic methods to install more electropositive multiply bonded ligands, such as imides or nitrides, remain unknown, despite the ready access to the heavy group VI analogues of molybdenum and tungsten (i.e., [MNCl$_5$]$^{2−}$).[10] Furthermore, the few neutral uranium oxo halide analogues that have been prepared [α-UOF$_4$ and

UOF$_2$(SbF$_6$)$_2$][11,12] suffer from significant disorder in the solid state, such that the U−O$_{ax}$ and U−F$_{ax}$ bond lengths cannot be definitely determined.

These complexes, however, are far from just an academic curiosity. Because they give a readily and clearly defined experimental observable (the difference between the M−X$_{trans}$ and M−X$_{cis}$ bond lengths in the solid state), they provide a sensitive probe for the role of 6p, 6d, and 5f orbitals, as well as electrostatic interactions, in determining the electronic structure of uranium(V/VI) complexes of uranyl and its analogues. A comprehensive understanding of the details of the bonding in these complexes is immediately applicable to and necessary for the continued development of the international nuclear enterprise in two ways. This knowledge (1) will aid in the design of lanthanide/actinide extractants and (2) may accelerate the development of uranyl sequestration and chemical remediation technologies. Technology to remove late actinides from spent nuclear fuel would facilitate its long-term storage. Given the importance of [UO$_2$]$^{2+}$ in such separation schemes, the recent finding that the uranyl analogue, [RN═U═NR]$^{2+}$ (R = ^{t}Bu or Ph), is more covalent than [UO$_2$]$^{2+}$, and thus a softer Lewis acid, is significant.[13,14] Because this electronic structure perturbation leads to changes
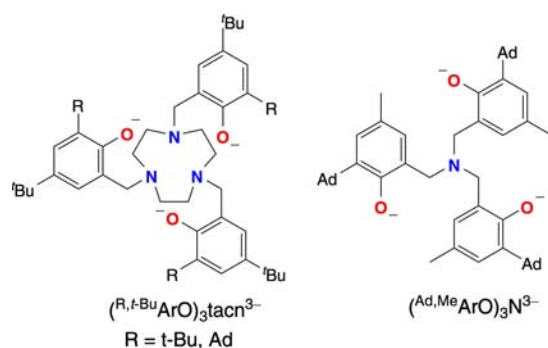
in the $U^{VI} \leftarrow L$ coordination (e.g., the binding of trialkylphosphines), detailing the basis of these electronic perturbations could lead to improved nuclear waste remediation technologies. It should be noted that significant progress on the development of uranyl sequestration and chemical remediation technologies has been made, most remarkably, the functionalization of the uranyl U−O bonds, which were previously thought to be chemically inert.[15−23]

Besides these immediate practical benefits, the detailed study of uranium−ligand multiple bonding extends the study of metal−ligand multiple bonding from the transition metals.[24,25] The insights garnered from these studies on transition metals have shed new light on a wide range of biologically and industrially relevant reactions.[26−28] Further study of uranium−ligand multiple bonding may afford similar benefits for the development of novel atom/group-transfer reactions.

In the Meyer lab, we have prepared a series of uranium(V/VI) monooxo and monoimido complexes supported by two different classes of chelating tris(aryloxide) ligands: the single nitrogen-anchored $(^{Ad}ArO)_3N^{3-}$ (trianion of tris(2-hydroxy-3-adamantyl-5-methylbenzyl)amine) and the tacn-anchored $(^{R}ArO)_3tacn^{3-}$ (trianion of 1,4,7-tris(3-R-5-tert-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane; R = tert-butyl (^{t}Bu) and 1-adamantyl (Ad)) (Figure 1).[29−34] Three of these compounds,

the uranium(VI) monoxides $[((^{t-Bu}ArO)_3tacn)U(O)_{eq}]SbF_6$ (1-**t-Bu**) and $[((^{t-Bu}ArO)_3tacn)U(O)_{eq}(OC(O)CF_3)_{ax}]$ (2-**t-Bu**) and the uranium(V) monoimide $[((^{Ad}ArO)_3N)U-(NMes)_{eq}(OEt_2)_{ax}]$ (3-**NMes**), unlike the other complexes in this series, distort from C_3 symmetry to pseudo-C_s symmetry in the solid state (Figure 2 and Table 1).[31,32] This connectivity places the imido nitrogen or oxido oxygen atom of the multiply bonded ligand in the equatorial plane defined by the oxygen atoms of the aryloxide ligands. Therefore, these three compounds meet the geometric and connectivity requirements in order to observe the ITI, namely, that the ligands disposed trans and cis to the uranium-ligand multiple bond are identical. In all three examples, the complexes present the ITI in their solid-state crystal structures. These new well-characterized examples of the ITI in uranium complexes greatly increase the experimental evidence for this phenomenon. These complexes, 1-**t-Bu**, 2-**t-Bu**, and 3-**NMes**, presenting the ITI, contrast strongly with the other members of this series of compounds, in which the uranium−ligand multiple bond prefers an axial orientation on the idealized C_3 axis. As a result, this series of complexes provides a unique opportunity to study the underlying electronic basis of the ITI.

This Viewpoint Article reviews the theoretical, experimental, and synthetic work on the ITI in actinide complexes and contextualizes it within broader studies on the electronic structure of uranyl and its analogues. A detailed review of the uranyl electronic structure and uranium−ligand multiple bonding broadly defined is beyond the scope of this article, but readers are referred to several excellent recent reviews.[35−39] Furthermore, our recent work on the ITI in high-valent uranium(V/VI) oxo and imido complexes will be described as a whole. This work strongly builds on the existing synthetic literature on the ITI and links the detailed spectroscopic studies of uranyl to the expanding class of uranyl analogues, thus providing design parameters for the synthesis and characterization of high-valent uranium−ligand multiple bonds.

Figure 1. Tris(aryloxide) ligands used for supporting high-valent uranium(V/VI) monooxo and monoimido complexes.
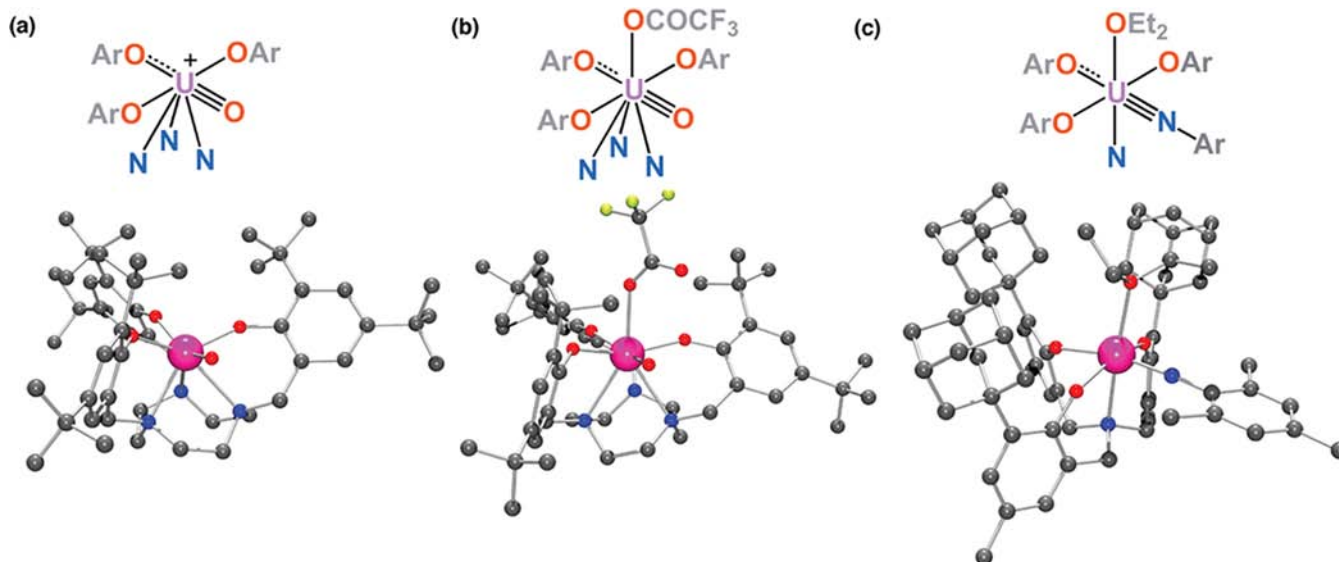
Figure 2. Solid-state structures of (a) **1-t-Bu⁺**, (b) **2-t-Bu**, and (c) **3-NMes** with respective schematic representations.

Table 1. Table of Selected Crystallographic Bond Lengths (Å) and Angles (deg)

	U$-$E$_{yl}$	U$-$O$_{cis}$	U$-$O$_{trans}$	O$_{trans}$$-U-E_{yl}$	ITI %[a]	ref
7-t-Bu; E = O	1.848(8)	2.203(5)	N/A	N/A	N/A	30
1-t-Bu; E = O	1.836(6)	2.154(5), 2.092(6)	2.063(5)	148.6(2)	95.8$-$98.6	31
2-t-Bu; E = O	1.811(2)	2.140(2), 2.161(2)	2.058(2)	159.67(6)	95.2$-$96.2	31
5-t-Bu; E = NTMS	1.985(5), 1.992(4)	2.161(4)$-$2.222(4)	N/A	N/A	N/A	29
4-t-Bu; E = NTMS	1.911(9), 1.917(9)	2.137(3), 2.134(4)	N/A	N/A	N/A	34
3-NMes; E = NMes	1.950(3)	2.173(2), 2.177(2)	2.145(2)	166.36(11)	98.5$-$98.7	32
3-NTMS; E = NTMS	1.943(3)	2.154 (av)	N/A	N/A	N/A	32

[a]ITI % is defined as $[r(M-X_{cis})/r(M-X_{trans})] \times 100$.

■ PROTACTINIUM AND URANIUM MONOOXO HALIDES: SYNTHETIC AND CRYSTALLOGRAPHIC EVIDENCE FOR THE ITI

The first evidence for the ITI phenomenon in actinide complexes was obtained through the crystallographic characterization of the C_{4v}-symmetric [PaCl$_5$O][NEt$_4$]$_2$ in 1972 by Brown and co-workers.[4] This complex was originally prepared by the same group in 1971 via hydrolysis of [PaCl$_4$(OEt)$_2$]-[NEt$_4$] in "wet" acetonitrile in the presence of excess [NEt$_4$]Cl.[40] Upon cooling of the reaction mixture, the product precipitates as bright-yellow crystals. Single-crystal X-ray analysis of the complex reveals a distorted octahedron. The low accuracy of the crystal structure is due to the small number of observed reflections, but the structure clearly shows a Pa$-$O bond of 1.74 Å and that the Pa$-$Cl$_{trans}$ bond (2.42 Å; trans to the terminal oxo ligand) is shorter than the Pa$-$Cl$_{cis}$ bond (2.59$-$2.72 Å; Table 2). The authors note that the IR spectrum

Table 2. Table of Crystallographic and DFT Bond Lengths (Å) of ITI Complexes

	M$-$O$_{yl}$	M$-$X$_{cis}$	M$-$X$_{trans}$	ITI %[a]
[UCl$_5$O]$^{-}$ ^{a}	1.76(1)	2.536(2)	2.433(4)	95.9
[PaCl$_5$O]$^{-}$ ^{b}	1.74	2.59$-$2.72	2.42	91.7
[UCl$_5$O]$^{-}$(DFT)^c	1.799	2.532	2.492	98.4
[UBr$_5$O]$^{-}$ (DFT)^c	1.794	2.694	2.659	98.7
UO(F$_4$)^d	1.760	2.047	1.966	96.0

^{a}Reference 3. ^{b}Reference 4. ^{c}Reference 63. ^{d}Reference 68.

presents two protactinium$-$chloride stretching vibrations: a strong one at 251 cm^{-1} and a weaker one at 289 cm^{-1} attributed to the short trans Pa$-$Cl bond.

The uranium structural analogue of this system, [UCl$_5$O]-[PPh$_4$], was thoroughly structurally characterized in 1978 by de Wet and du Preez.[3] This complex, along with neutral uranium monooxo fluoride complexes (vide infra), is the first non-uranyl example of a molecular uranium complex with uranium$-$ligand multiple bonds. Originally described in 1973 by Bagnall and co-workers, the complex is prepared by the deoxygenation of hydrated UO$_2$Cl$_2$ in refluxing SOCl$_2$ with excess [PPh$_4$]Cl.[1,2] Upon cooling, the product precipitates from solution as dark-red crystals. The crystal structure presents the anion as a C_{4v}-symmetric pseudooctahedral anion. The U$-$O$_{yl}$ bond length is 1.76(1) Å, as is typically observed in complexes containing the [UO$_2$]$^{2+}$ moiety. The trans U$-$Cl bond (2.433(4) Å) is about 0.1 Å shorter than the cis U$-$Cl bond (2.536(2) Å). These structural features support the classification of the trans [Cl$-$U$\equiv$O$_{yl}$]$^{3+}$ core as a uranyl analogue. The uranium chloride vibrational spectra (Raman and IR) agree with crystallographic analysis. As in the IR studies of [PaCl$_5$O][NEt$_4$]$_2$, [UCl$_5$O]-[PPh$_4$] presents resonances at 300 and 331 cm^{-1}. The higher-

frequency stretch was assigned to the trans U$-$Cl bond via a comparison to the IR and Raman spectra of [UClBr$_4$O][PPh$_4$].

Recently, Minasian et al. considered whether the difference in the cis and trans bond lengths (0.103(3) Å) could be due to crystal-packing forces.[41] They estimated that it would require a force >1 kcal mol^{-1} to account for the observed difference in the U$-$Cl bond lengths, which, according to the authors, is unreasonably large for a crystal-packing force. The authors further conclude that this system is a rare example in actinide chemistry, in which small differences in the observed bond lengths can be used to make meaningful conclusions about the electronic structure.

[UCl$_5$O][PPh$_4$] undergoes halide exchange reactions with halo acids.[2] In neat HF, for instance, [UF$_5$O][PPh$_4$] is produced. However, passing HBr through a dichloromethane solution of [UCl$_5$O][PPh$_4$] yields the tetrabromide [UClBr$_4$O][PPh$_4$], in which the equatorial halides are exchanged selectively. Powder diffraction studies confirmed that this species is isostructural with [UCl$_5$O][PPh$_4$]. This reactivity contrasts with that of the tungsten analogue, [WCl$_5$O][PPh$_4$], which undergoes clean substitution of all chlorides under identical conditions. The thermodynamic stability of the trans chloride ligand highlights the increased bond strength of the uranyl-like core structure. The deep-blue uranium(V) analogue, [UCl$_5$O][NEt$_4$]$_2$, has also been prepared by two routes: (1) partial hydrolysis of [UCl$_6$][NEt$_4$] with excess [NEt$_4$]Cl[42] and (2) photolysis of UO$_2$Cl$_2$Py$_2$ in ethanol.[43] However, [UCl$_5$O][NEt$_4$]$_2$ is prone to disproportionation reactions and has not been crystallographically characterized. It is not reported whether or not [UCl$_5$O]-[NEt$_4$]$_2$ presents the ITI.

[UCl$_5$O][PPh$_4$] has also been used to build sulfiminato- and phosphiniminato-uranyl analogues, [UCl$_4$O(NSPh$_2$)][PPh$_4$] and [UCl$_4$O(NPPh$_3$)][PPh$_4$], via its reaction with the appropriate trimethylsilyl-protected precursor.[44$-$46] Both complexes have a linear uranyl-like core, [O$_{yl}$$\equiv$U$\equiv$N]$^{3+}$. Further reactivity of [UCl$_5$O][PPh$_4$] to construct other uranyl analogues has been hampered by its tendency to disproportionate. This limitation has led to the development of new methodologies for the construction of uranium(V/VI) alkyl/aryl trans-diimides from uranium metal or UI$_3$ and the appropriate primary amine or aniline in the presence of I$_2$ as the ultimate oxidant.[13,47$-$50] The emerging literature on the trans-diimides, [RN$\equiv$U$\equiv$NR]$^{2+ \text{ or } 1+}$ (R = ^{t}Bu or Ph), indicates that the bonding in these complexes is significantly more covalent than that in uranyl.[48,50,51] As a result, their reaction chemistry—ligand binding and deformation to cis-bisimide structures[14]—diverges dramatically from that of uranyl. The role of 6p and 5f orbitals in these systems (in comparison to uranyl) is key to this reactivity and is part of the

motivation for our synthetic studies on ITI complexes bearing an imido ligand (vide infra).

The neutral uranium oxo fluoride, α-UOF$_4$, has been structurally characterized by both single-crystal X-ray and neutron powder diffraction.[11,52] The heavier halide congeners are not known, but UOCl$_4$ is considered to be an intermediate in the chlorination of UO$_3$.[53] The original X-ray diffraction study of α-UOF$_4$ revealed a pentagonal-bipyramidal structure with positional disorder of the axial fluoride and oxo ligands. The observed axial U—X bond lengths are 1.77 and 1.79 Å, suggestive of a uranyl-like structure. The non-bridging equatorial U—F bonds are substantially longer at 1.98(3) Å and, thus, are similar to that observed for UF$_6$ (1.99 Å). The subsequent neutron powder diffraction study of α-UOF$_4$ confirmed the overall geometry but revised the disordered U—F and U—O axial bond lengths to 1.870(16) and 1.884(17) Å (due to a systematic absorption error in the original study). Additionally, α-UOF$_4$ reacts with SbF$_5$ in HF to give UOF$_4$·2SbF$_5$, which, in the solid state, has a pentagonal-bipyramidal structure like α-UOF$_4$.[12] Unfortunately, this structure also has positional disorder of the axial U—F and U—O bonds, leading to an observation of average distances (U—X(1) = 1.820(15) Å and U—X(2) = 1.825(15) Å). While these synthetic and structural studies of uranium oxo fluorides do not provide precise data for the evaluation of the ITI, the terminal (as opposed to bridging) oxo ligand and the trans disposition of a fluoride ligand are indicative of a uranyl-like electronic structure. As such, these studies have served as the basis of detailed density functional theory (DFT; vide infra) studies of the gas-phase structures of UOF$_4$, which clearly demonstrate the importance of a uranyl-like core structure and the resultant presence of the ITI.

■ ELECTRONIC BASIS OF THE ITI: THEORY AND SPECTROSCOPY

The known examples of actinide ITI represent a subclass of the growing group of actinyl (uranyl) analogues. Uranyl, [O=U=O]$^{2+}$, is defined by the linear trans arrangement of the oxo ligands. This functional group is the predominant feature of all crystallographically characterized uranium complexes[54] and sharply contrasts with the preferred cis geometry of transition-metal dioxo complexes. Uranyl analogue complexes are those that incorporate a linear trans arrangement between σ- and π-donating ligands that can engage in uranium—ligand multiple bonding, i.e., [L=U=L]$^{n+}$. Because the ITI actinide oxohalide complexes give a readily and clearly defined experimental observable (the difference between the M—X$_{trans}$ and M—X$_{cis}$ bond lengths in the solid state), they link the detailed spectroscopic studies of uranyl to hypotheses about the basis of the electronic structure of other uranyl analogues that lack directly observable indications of their electronic structures. It is in this context that these complexes have received significant theoretical attention.

Complexes showcasing the ITI phenomenon were initially viewed from the perspective of an ionic ligand—ligand repulsion model.[3] In other words, the absence of the expected normal trans influence was taken as an indication that the bonding was solely ionic, despite the fact that the M=O$_{yl}$ bond was exceptionally short, in the case of [UCl$_5$O][PPh$_4$], 1.76(1) Å. Under this analysis, the trans chloride ligand experiences the least electrostatic repulsion and, therefore, the trans U—Cl bond is shorter than the cis chlorides.

These curious structural phenomena did not receive further attention until the role of the 6p orbitals in the bonding of uranyl became clear from both theoretical and experimental perspectives.[55−60] In 1992, Denning suggested that the basis of the ITI (and the normal trans influence) is an electrostatic perturbation of the core electrons by an anionic ligand.[37] Hence, the resultant polarization of the core electrons generates a dipolar, a quadrupolar, or a higher multipolar moment. The dominant component of the polarization is dependent on the relative parity of the highest filled orbitals and the lowest-energy empty valence orbitals. If the parity is opposite, as in the transition metals (p core orbitals "gerade" vs d valence "ungerade"), then the moment is dipolar. In the case of actinyls, the opposite is true: the highest core and lowest valence orbitals have the same parity (p core and f valence orbitals are both "ungerade"), and the moment is quadrupolar.

This electrostatic model, in gross terms, explains the transition-metal dioxo preference for a cis geometry in that the trans-disposed negative charge forces the second oxo to the cis position. In analogy, in actinyl complexes, the trans partial positive charge in the quadrupole favors the location of the second oxo in a *mutually reinforcing* position in a trans linear relationship. However, this purely electrostatic approach is too simplified. In that this model depends on heavy, polarizable metals for the electrostatic interaction, the 3d and 4d transition metals are not likely to have dominant contributions from electrostatics to the ground-state geometry and electronic structure. Considerations of effective orbital overlap (covalency) certainly dominate the molecular orbital structure of these *cis*-dioxo transition-metal complexes. While some have suggested that the ITI underlies the stability of *trans*-dioxo transition-metal complexes,[61,62] such an argument ignores their divergent reactivity from the actinyls (ready dehydrohalogenation to monooxo complexes) and spectroscopic properties (i.e., the symmetric stretching frequency is lower than the asymmetric frequency in uranyl, which is the opposite of [OsO$_2$Cl$_4$]$^{2−}$ and even CO$_2$).[37] In the case of uranium oxo halides, in which the ITI is evident, the involvement of 6p orbitals in the bonding with the strongly bound oxo ligand leads to hybridization of and charge transfer to the 5f orbitals. This process produces a partial positive charge in the 6p orbital directed to the trans-coordinated halide, which, in turn, could increase the orbital overlap with the trans U—X entity. While this electrostatic model provides a rationale for the difference between transition-metal and actinide complexes and the dominance of either the normal trans influence or ITI, other factors, such as the similar energy of uranium 6p and oxygen 2p orbitals and the effective radial extent of uranium 6p orbitals in uranium(V) and (VI) complexes, certainly play a role as well.[37,39]

In order to understand the role of the 6p and 5f orbitals in the ITI, first O'Grady and Kaltsoyannis[63] and later Chermette et al.[64] and Pyykkö et al.[65] examined complexes of the type [MEX$_5$]$^{n−}$ (where M = Pa, U, Np, and Mo; E = O and S; X = F, Cl, and Br; and n = 0, 1, 2) using DFT. In general, these DFT studies have reproduced well the structural features observed for the two crystallographically characterized complexes, namely, the short M—O bond and the ITI. However, it should be noted that local density approximation (LDA) and hybrid generalized gradient approximation (GGA) methods more accurately predict the observed bond lengths than pure GGA methods,[63] which indicate qualitatively the importance of electrostatics in the bonding of actinide ITI complexes. LDA

methods have, in general, been noted to be more appropriate for the study of Werner-type complexes, in which electrostatics dominate the bonding picture.[66]

These DFT studies have also elucidated two key molecular orbitals in these C_{4v} complexes that contribute to the observation of the ITI (Figure 3).[63] First, orbital $6a_1$ is
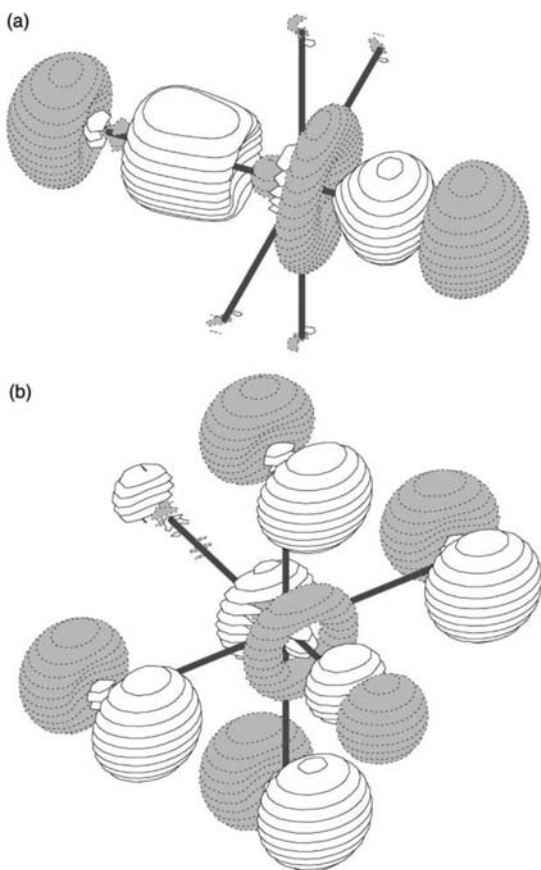
Figure 3. Molecular orbital plots of the (a) $6a_1$ and (b) $9a_1$ orbitals of $[UOBr_5]^-$. Reproduced with permission from ref 63. Copyright 2002 Royal Society of Chemistry.

antibonding with respect to the trans halide and, second, the metal contribution decreases and, hence, the antibonding to the trans halide decreases for the series bromine, chlorine, and fluorine. Furthermore, the orbital $9a_1$ is antibonding with respect to the cis halides and the metal contribution increases in the series bromine, chlorine, and fluorine. These synergistic trends lead to the predicted maximum observed ITI for $[UOF_5]^-$.[67]

For the actinide oxo complex series studied by O'Grady and Kaltsoyannis,[63] all of the complexes presented the ITI. The pseudocore 6p orbitals were confirmed to be a key component of the ITI. First of all, the $6p_z$ was found to mix with orbitals of a_1 symmetry and holes were observed in the 6p electron population. However, when the pseudocore 6p orbitals were "turned off", i.e., by placing them in the frozen core, which renders them unable to change energy during optimization, a small ITI was still observed. This observation suggests that while the 6p orbitals are important, they are not the only factor leading to the observation of the ITI.

O'Grady and Kaltsoyannis also examined the dependence of the ITI on the deformation angle between the cis halides and the oxo ligand from 90°. As the angle increases, the ITI

observed decreases and eventually produces a slight normal trans influence at 102°. Unlike in its transition-metal equivalent, $[OsNCl_5]^{2-}$,[8] this deformation is not favored even though it would reduce the antibonding interaction found in the $9a_1$ orbital. The preference of C_{4v}-symmetric monooxo actinyl complexes for a nearly 90° angle between the axial oxo and equatorial halide ligands stems from the fact that pyramidalization does not lead to an increase in the bond strength of the $M=O_{yl}$ bond in the actinide system and is principally due to the presence of the 5f orbitals in the actinides. Comparable DFT studies of transition-metal analogues indicate that the deformation is favored and that it strengthens the metal−ligand multiple bond. This phenomenon is related to the different ordering of the π-symmetry orbitals of the metal−ligand multiple bond in the actinide and transition-metal complexes. The observed dependence of the ITI on the local geometry at the metal is further supported by our synthetic studies of uranium monooxo complexes (vide infra). Chermette et al. have advanced Kaltsoyannis' DFT studies and have shown that the ITI observed in these actinide complexes disappears if the 5f orbitals are made energetically unavailable. This change is accomplished by arbitrarily raising them in energy by approximately 25 eV.

DFT has also been applied to the neutral uranium oxo halides. Kovács and Konings[68] studied the uranium(VI) oxo halides (I, Br, Cl, and F). In these systems, a linear uranyl structure, $[X—U=O]^{3+}$, is preferred, and for the lighter halides (Cl and F), these systems present an ITI: U=O, 1.760 Å; U−F_{ax}, 1.966 Å; U−F_{eq}, 2.047 Å (compare the α-UOF_4 studies described above). Furthermore, Chermette et al.'s work suggests that trans halides may experience an ITI,[64] which is an observation that recent experimental work has sought to address.[69] However, the uranium(VI) mixed-halide complexes remain difficult to characterize crystallographically because of disorder. Schreckenbach and co-workers similarly examined the uranium monooxo and dioxo fluorides.[70] These studies indicated that for the neutral uranium(VI) and (V) compounds a trans relationship exists between the oxo and fluorido ligands, indicating an electronic preference for a uranyl geometry.

While there are no definitive crystallographic studies of the uranium monooxo fluorides, in 1978, Bougon and co-workers reported solid-state ^{19}F NMR studies of $Cs[UOF_5]$.[71] Powder diffraction studies indicated that in the solid state the lattice parameters were nearly identical with $Cs[UF_6]$ and the oxygen and fluorine atoms were disordered. In the ^{19}F NMR spectra, at high field (76.1 MHz) and 300 K, two singlets at −285 and −405 ppm were observed in a 1:4 ratio. This downfield shift of the trans fluoride suggests that it is more covalently bonded than the cis fluorides, which is in agreement with analysis of the vibrational spectrum.

More recently, Kozimor and co-workers have extended this analysis to $PPh_4[UOCl_5]$ in a combined Cl K-edge X-ray absorption near-edge spectroscopy (XANES) and time-dependent DFT study of $(PPh_4)_2[UCl_6]$ and $NEt_4[UOCl_5]$.[72] In the model complex $[UCl_6]^{2-}$, the Cl 3p mixing with the U 6d orbitals is 12.2% per U−Cl bond (by calculation due to experimental limitation), while Cl 3p mixing with the U 5f orbitals is 5.7(3)% experimentally. However, the relative mixing with the Cl 3p orbitals, and hence the basis of covalency, is the opposite in $NEt_4[UOCl_5]$ where the 3p mixing with 6d orbitals is 7.0% per U−Cl bond (calcd; observation of a partial set of d transitions gives 7.3(4)%) and the 3p mixing with 5f orbitals is 26(1)% per U−Cl bond. The authors attribute the increased Cl

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Scheme 1. Synthesis of Uranium Monooxo and Monoimido Complexes Supported by $(^{R,t-Bu}ArO)_3tacn^{3-}$ (R = ^tBu and Ad)
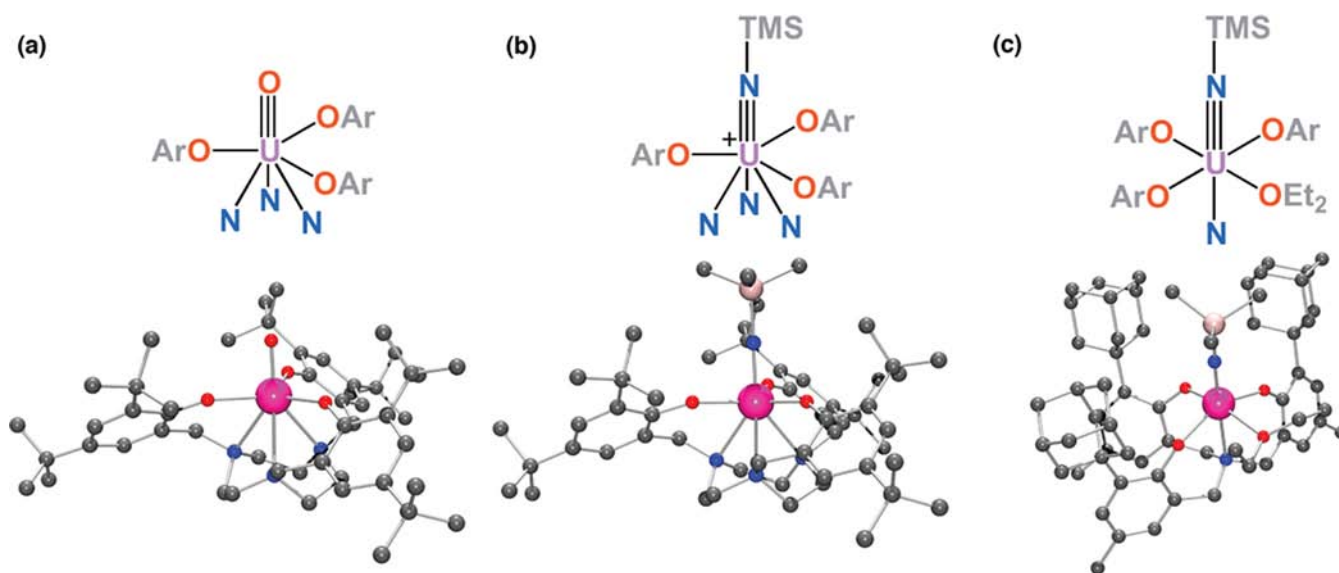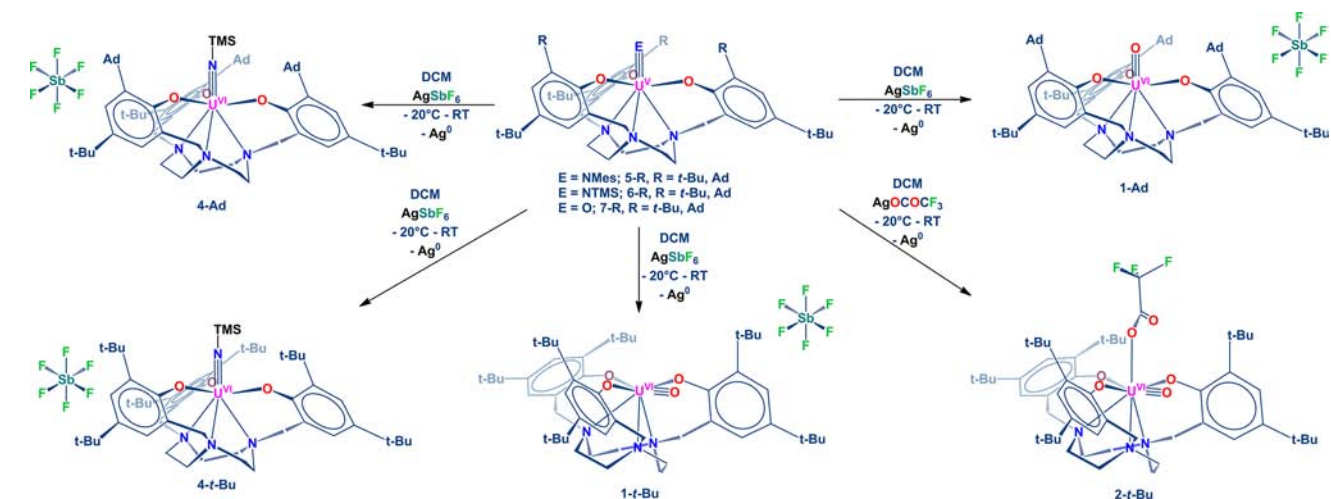
Figure 4. Solid-state structures of (a) **7-t-Bu**, (b) **4-t-Bu⁺**, and (c) **3-NTMS** with respective schematic representations.

3p mixing with the U 5f orbitals in NEt₄[UOCl₅] to a more covalent axial U–Cl bond because of the ITI of the oxo ligand. This analysis is reasonable, considering the previously described theoretical work showing that mixing with 6p orbitals increases the covalent bonding interaction of the 5f orbitals with the trans Cl. However, in order to probe the role of the 6p orbitals directly in this interaction, the O K-edge XANES ought to be measured. An analogous experimental study has been performed on [UO₂Cl₄]²⁻, which clearly demonstrates the role of the 6p orbital in the bonding of uranyl.[59]

In summary, these theoretical and spectroscopic studies provide a framework for understanding the bonding in actinide ITI complexes and suggest that both covalent and electrostatic bonding underlie this phenomenon. It seems apparent that the synthesis and thorough characterization of further examples is necessary to understand how these factors influence the bonding in high-valent uranyl complexes as well as in complexes with other multiply bonded U=L systems, like imides and nitrides or alkylidenes and the (elusive) alkylidyne ligand.

## ■ TRIS(ARYLOXIDE) URANIUM(V/VI) MONOOXO AND MONOIMIDO COMPLEXES

Our interest in the ITI stems from our development of methods to synthesize uranium(V) and (VI) monooxo and monoimido complexes. In 2006 and 2008, our group reported a series of neutral uranium(V) monooxo and monoimido complexes supported by $(^{R}ArO)_3tacn^{3-}$ (R = *tert*-butyl (^tBu) and R = 1-adamantyl (Ad) (Figure 1 and Scheme 1).[29,30] The imido complexes were prepared by oxidation of the uranium-(III) precursors $(((^{R}ArO)_3tacn)U)$ (R = ^tBu and Ad) with mesityl azide or trimethylsilyl (TMS) azide, respectively. The mesitylimido complexes of both ligands and the (trimethylsilyl)imido complex of the adamantyl ligand system react with π acids because of steric pressure from the supporting ligand.[29,30] This pressure is clear from the slightly longer U–N bond lengths [cf. 2.1219(18) Å for **6-Ad** vs 1.989(5) Å for **6-t-Bu**] and their bent U–N–L linkages [L = Si and C$_{ipso}$; 162.55(12)° for **6-Ad** and 154.7(8)° for **5-t-Bu**]. The mesitylimido complexes (**5-t-Bu** and **5-Ad**), for instance, react with CO₂ to give terminal uranium(V) oxo complexes. At the time, these were among just a handful of crystallographically

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characterized uranium(V) terminal monooxo complexes (**7-*t*-Bu** and **7-Ad**), a class of complexes that has recently grown.[3,73−80] All of these complexes supported by (^{R}ArO)$_3$tacn^{3-} fit the expected ground-state geometry for the tacn-supported tris(aryloxide) ligands, in which the uranium-ligand multiple bond lies on the pseudo-C_3 axis. The metric parameters for these complexes are presented in Table 1, and the structure of [(($^{t\text{-}Bu}$ArO$_3$)tacnU)(V)O] (**7-*t*-Bu**) is depicted in Figure 4.

Cyclic voltammetry studies of the uranium(V) oxo complexes **7-*t*-Bu** and **7-Ad** (−0.13 and −0.19 V vs Fc$^+$/Fc) suggested that these complexes could be readily oxidized with silver salts.[31] In contrast with the cleanly reversible electrochemical oxidation, **7-*t*-Bu** undergoes a structural rearrangement during chemical oxidation. When AgSbF$_6$ is used to oxidize **7-*t*-Bu**, the product is a seven-coordinate uranium monooxo cation, **1-*t*-Bu**, charge-balanced by the noncoordinating [SbF$_6$]$^-$ anion (for structures, see Figure 2, and for the synthetic route, see Scheme 1). The solid-state structure reveals that the oxo ligand is displaced toward the equatorial plane (as defined by the equatorial aryloxide oxygen atoms). The bond length of the terminal uranium oxo ligand is reasonably short at 1.836(6) and 1.820(6) Å (**1-*t*-Bu**, two molecules in the asymmetric unit) compared to previously characterized uranium(VI) terminal oxo compounds and is slightly shortened compared to the bond length of the uranium(V) precursor, which is 1.848(8) Å (Tables 1 and 2). Despite the distortion from 3-fold symmetry, **1-*t*-Bu** does not present with a strong ITI. The *trans*-aryloxide U1−O2 bond length, 2.063(5) Å, is only slightly shorter than the *cis*-aryloxides: the U1−O1 and U1−O3 bond distances are 2.154(5) and 2.092(6) Å, respectively (trans, U2−O6, 2.066(5) Å; cis, U2−O7, 2.064(6) Å; U2−O5, 2.123(6) Å).

This diminished ITI can be anticipated by considering Kaltsoyannis's examination of the dependence of the observed ITI on the X$_{cis}$−U−O$_{yl}$ angle in his DFT studies of the actinide oxo halides (vide supra). Specifically, the O$_{oxo}$−U−O$_{trans\text{-}ArO}$ angle in **1-*t*-Bu** is relatively acute and very much non-linear (O4−U1−O2, 148.6(2)°; O8−U2−O6, 149.5(2)° in **1-*t*-Bu**, two independent molecules in the asymmetric unit). As a result, the uranium center in **1-*t*-Bu** lies significantly below the plane defined by the supporting aryloxide oxygen atoms of the ligand (U1, 0.735(4) Å; U2, 0.710(4) Å), which disfavors the requisite orbital overlap necessary for the ITI. This effect is also demonstrated by considering that the sum of the angles around U1 in the equatorial plane is 338.8° (sum of the angles around U2 in the equatorial plane = 339.7°).

However, when AgOC(O)CF$_3$ is used to oxidize **7-*t*-Bu**, a formally eight-coordinate, neutral uranium(VI) oxo (**2-*t*-Bu**) is isolated (Figure 2 and Scheme 1). In contrast to **1-*t*-Bu**, the oxo ligand [U−O$_{yl}$ = 1.811(2) Å] in **2-*t*-Bu** lies in the equatorial plane as defined by the aryloxide oxygen atoms. In this case, the observed ITI clearly is significant. Coordination of (F$_3$C(O)CO$^-$) linearizes the O$_{oxo}$−U−O$_{trans\text{-}ArO}$ angle (159.67(6)°) by pulling the uranium ion into the plane of the coordinating oxygen atoms (U1, 0.3802(8) Å, displacement below the plane defined by the three aryloxide oxygen atoms; Figure 5). Therefore, **2-*t*-Bu** has the correct geometry for the σ and π orbitals of the *trans*-aryloxide to mix with the valence 5f and core 6p orbitals to generate the observed ITI. The *trans*-aryloxide U1−O3 bond length, 2.058(2) Å, is about 0.1 Å shorter than the bond lengths of the *cis*-aryloxides: the U1−O1 and U1−O2 bond distances are 2.161(2) and 2.140(2) Å,
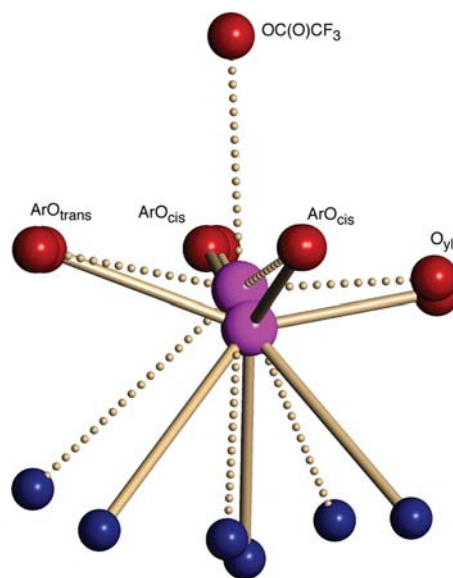
Figure 5. Overlay of the core geometries of **1-*t*-Bu**·3.5C$_6$H$_6$ (solid bonds) and **2-*t*-Bu**·DME (dotted bonds).

respectively. It should be noted that in complex **2-*t*-Bu** the U−O−C$_{ipso}$ angle of the trans aryloxide arm is significantly more linear than those of the cis aryloxides (**2-*t*-Bu**; U1−O3−C39, 157.7(2)°; U1−O2−C29, 147.9(2)°; U1−O1−C9, 130.0(2)°), which suggests π interactions, generated by the appropriate hybridization of the 6p$_x$ and 6p$_y$ with the valence 5f orbitals, may also be involved.

Remarkably, the use of the sterically encumbering adamantyl group at the ortho position of the supporting aryloxide ligand generates enough steric pressure to overcome the driving force for forming a uranyl-like core structure. The oxidation of [((^{Ad}ArO$_3$)tacn)U(V)O], **7-Ad**, with AgSbF$_6$ yields the "standard" C_3-symmetric complex (**1-Ad**) with a uranium(VI) oxo axially ligated on the 3-fold axis. While a high-quality X-ray crystal for **1-Ad** has not been obtained, the solution structure, as deduced from its ^{1}H NMR spectrum, clearly indicates 3-fold symmetry; all aryloxide arms are equivalent. These features contrast strongly with the pseudo-C_s solution structures of **1-*t*-Bu**, in which the appropriate resonances are split in an approximate 2:1 ratio, thus indicating that the arms are related by a mirror plane, and **2-*t*-Bu**, in which all three ligand arms have different chemical environments. This change in the ground-state geometry is reasonable considering that DFT studies of **1-*t*-Bu** suggest that axial and equatorial oxo isomers of the cation differ by about 6 kcal mol^{-1}.[31]
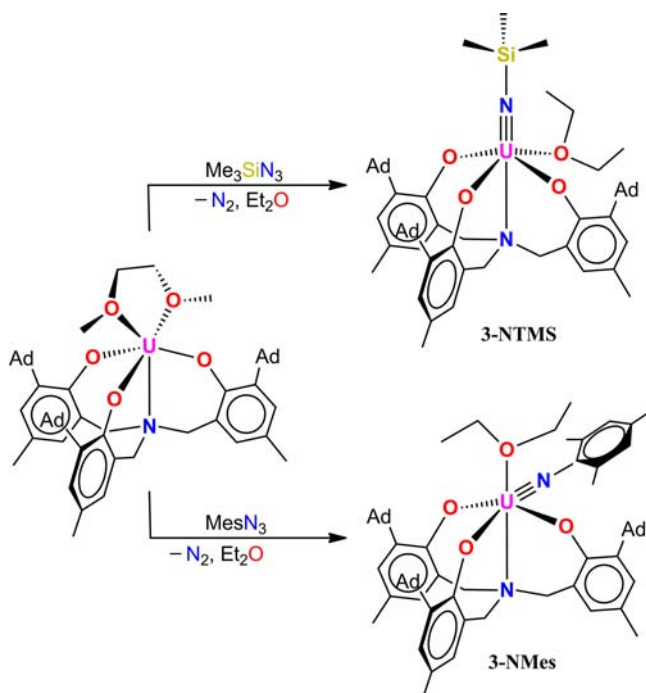
Oxidation of the uranium(V) (trimethylsilyl)imido complexes **5-*t*-Bu** and **5-Ad** with AgSbF$_6$ strikingly does not lead to a distortion to pseudo-C_s geometry. In both solution and the solid state, these complexes (**4-*t*-Bu** and **4-Ad**) have C_3 symmetry, and the imido is axially oriented and lies on the 3-fold axis.[34] The structures of the imido complexes **4-*t*-Bu** (Figure 4) and **4-Ad** are very similar. Their U−N$_{imido}$ bond distances are 1.911(9) and 1.917(9) Å in **4-*t*-Bu** (two independent molecules in the unit cell) and 1.921(4) Å in **4-Ad**. The uranium lies 0.195 and 0.189 Å below the plane of the three aryloxide oxygen atoms for **4-*t*-Bu**, while the out-of-plane shift of **4-Ad** is smaller at 0.139 Å.

The difference in the ground-state geometry (and electronic structures) of the analogous oxo and imido complexes **1-*t*-Bu** and **4-*t*-Bu** is quite unusual. Oxo and imido ligands are isolobal

and isoelectronic, and both are formally 1σ and 2π donors. The only significant difference between **1-*t*-Bu** and **4-*t*-Bu** (given that the sterics of the silylimido group seem to play a small role, as indicated by the similarity of **4-*t*-Bu** and **4-Ad**) is the electronegativity of the multiply bonded atom/group. This difference would reinforce Denning's proposal that the ITI, while participating in covalent bonding, is driven by electrostatics. Therefore, in the case of the actinides, the more electronegative the multiply bound ligand, the more strongly polarized the 6p orbitals are. As a result, they can mix to a greater degree with 5f orbitals and participate in a stronger covalent interaction in the linear, *trans*-$[L≡U≡L]^{n+}$ core. Such an analysis would further explain why the oxo ligands in the uranium(V) oxo complexes **7-*t*-Bu** and **7-Ad** do not distort to an equatorial position and express an ITI: as the uranium is less charged, the charge separation between the oxo oxygen atom and the uranium atom is less than that in **1-*t*-Bu**. Therefore, the 6p orbitals are less polarized and the thermodynamic driving force to achieve a uranyl-like core is insufficient to overcome the steric pressure of the bulky ligand.

In order to explore this idea further, we sought a less constrained ligand system that might support examples of the ITI with more electropositive multiply bonded groups and uranium in a lower oxidation state. To this end, we employed a more open and less hindered ligand and switched to a single N-anchored tris(aryloxide) ligand. The oxidation of $[(({}^{Ad}ArO)_3N)U(DME)]$ with mesityl azide and trimethylsilyl azide was pursued (Scheme 2).[32] Under appropriate conditions,

Scheme 2. Synthesis of Uranium(V) Monoimido Complexes Supported by $({}^{Ad}ArO)_3N)^{3-}$

the oxidation of $[(({}^{Ad}ArO)_3N)U(DME)]$ with trimethylsilyl azide afforded a uranium(V) (trimethylsilyl)imido complex, **3-NTMS**. The molecular structure of **3-NTMS** reveals a pseudooctahedral environment around uranium. The TMSN^{2-} ligand is in the axial position trans to the nitrogen anchor, and an ether molecule is bound in the equatorial position cis to the imide group (Figure 4).

Similarly, the oxidation of $[(({}^{Ad}ArO)_3N)U(DME)]$ with mesityl azide also leads to the isolation of a uranium(V) imido complex, **3-NMes**. Most strikingly, and in stark contrast to the (trimethylsilyl)imido, the imido ligand in **3-NMes** is bound in the equatorial plane defined by the aryloxide oxygen atoms (Figure 2) and a diethyl ether molecule occupies the "axial" position. Besides distorting to a pseudo-C_s geometry and adopting uranyl-like geometry with aryloxide ligands disposed trans and cis to the imido group, the mesitylimido ligand exerts a slight ITI on the uranium−aryloxide bonds. The *trans* uranium−aryloxide bond, U−O3, is observed to be the shortest U−O$_{ArO}$ bond within the complex. The U−O3 bond distance is 2.145(2) Å, while the U−O1 and U−O2 bond distances are 2.177(2) and 2.173(2) Å, respectively.

The observed ITI in the molecular structure of **3-NMes** is small (the U−O bond length differences of 0.028 and 0.032 Å) and, as such, may well be influenced by crystal-packing forces. However, this observation contrasts strongly with the expectation in transition-metal chemistry that the imido ligand should exert a normal trans influence. Additionally, the thermodynamic preference to adopt a uranyl-like geometry overcomes significant steric crowding induced by the transition from a trigonal tris(aryloxide) ligand environment to a tetragonal tris(aryloxide) imido environment. As in the analysis of the oxo complexes, **1-*t*-Bu** and **4-*t*-Bu**, the change in the geometry between the imido complexes, **3-NTMS** and **3-NMes**, is essentially related to the electronegativity of the imido group. In the case of the more electronegative mesitylimide, the polarization of the 6p orbitals is sufficient to induce a change in the ground-state geometry.

■ CONCLUSIONS AND FUTURE DIRECTIONS

In summary, this Viewpoint Article has reviewed the synthetic, spectroscopic, and theoretical work on the actinide ITI. The collective body of work has demonstrated that electrostatic and covalent interactions are responsible for the ITI and that both the pseudocore 6p orbitals and the valence 5f orbitals are crucial for the ITI. Furthermore, while much work remains, analysis of the bonding in these ITI complexes suggests that the traditional conception of a *competition* between ionic (electrostatic) and covalent bonding is misleading. The basis of the ITI lies in the *synergistic interplay* between ionic and covalent bonding. In other words, the charge separation between uranium and the multiply bonded ligand leads to polarization of the 6p orbitals, which is necessary for their productive mixing of the 5f orbitals. While available spectroscopic techniques have for the most part been exhausted for these complexes (except for an O K-edge XANES investigation of $[UCl_5O][PPh_4]$), the synthesis of further examples of uranyl analogue complexes showing the ITI must be pursued and spectroscopically and theoretically studied in order to advance our understanding of this synergy between covalent and ionic bonding in high-valent actinide−ligand multiple bonds.

In our synthetic work on the ITI and terminal high-valent uranium−ligand multiple bonds, we have reported three new crystallographically characterized complexes displaying the ITI. This work has introduced a non-halide, monoanionic supporting aryloxide ligand as part of a chelating framework. These ligand systems allow for the direct comparison of a variety uranium−ligand multiple bonds and, in certain cases, a comparative analysis of the electronic and steric factors governing the ground-state geometry and electronic structure. Furthermore, by consideration of ligand sterics, this work has

provided the first crystallographically characterized example of the ITI in a uranium(V) compound and in an imido complex. In order to complete the comparative analysis of these systems, we are seeking the oxidation products of $[(({}^{R}ArO)_3tacn)U-(V)NMes]$, **6-t-Bu** and **6-Ad**, and **3-NTMS** and **3-NMes**. It is anticipated in the uranium(VI) mesitylimido complexes supported by the $({}^{R}ArO)_3tacn^{3-}$ framework that the increased charge separation in the uranium–ligand multiple bond may induce a distortion to C_s geometry. Similarly, in the oxidation of **3-NTMS** and **3-NMes**, it would be expected that the (trimethylsilyl)imide may prefer an equatorial orientation and the ITI observed in **3-NMes** would be amplified. Current work in the group has extended the observation of the ITI to uranium(V) oxo complexes supported by the tacn-achored ligand $({}^{R}ArO)_3tacn^{3-}$ (trianion of 1,4,7-tris(3-R-5-methyl-2-hydroxybenzyl)-1,4,7-triazacyclononane; R = neopentyl (Neo)).

The importance of electrostatics to the bonding of uranium–ligand multiple bonds and the extent of the covalent bonding in uranium–ligand bonds has begun to be understood more clearly in recent years.[76,81,82] In order to synthesize novel middle- and high-valent uranium–ligand multiple bonds, such as nitrides, alkylidenes, or alkylidynes, both steric, kinetic protection and electronic, thermodynamic stabilization must be pursued. The former approach has been successful in transition-metal chemistry and, recently, in the remarkable synthesis of a uranium(V) nitride complex.[83] The latter design criteria may be accomplished via the introduction of electronegative σ- and π-donating ligands trans to the desired uranium–ligand bond. This approach might require the further development of flexible but chelating ligand systems capable of placing electronegative σ- and π-donating ligands trans to the desired uranium–ligand multiple bond.

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Notes

The authors declare no competing financial interest.

Biographies

Karsten Meyer was born in North Rhine Westphalia, Germany, in 1968. In the summer of 1995, he received his diploma from the Ruhr-University Bochum and began his doctoral studies with Prof. Karl Wieghardt at the Max Planck Institute for Bioinorganic Chemistry in Mülheim/Ruhr. His doctoral degree was awarded with distinction (summa cum laude) in January 1998. He then received a DFG postdoctoral fellowship with Prof. Christopher C. Cummins at MIT.

In January 2001, he was appointed to the faculty at the University of California, San Diego, and was named an Alfred P. Sloan Fellow in summer 2004. In 2006, Karsten accepted the chair of inorganic and general chemistry at the University of Erlangen-Nuremberg. He is a lifetime honorary member of the Israel Chemistry Society and a Fellow of the Royal Society of Chemistry.

Henry S. La Pierre was born in St. Louis, Missouri, in 1983. He completed his bachelor's degree in Chemistry, magna cum laude, in 2006 under the direction of Prof. Jared T. Shaw at Harvard University. In the summer of 2005, he received the Herchel Smith Research Fellowship for studies with Prof. Masahiro Murakami at Kyoto University. Having recently completed his Ph.D. at the University of California, Berkeley, with Profs. John Arnold, Robert G. Bergman, and F. Dean Toste in the fall of 2011, he began his postdoctoral studies with Karsten at the University of Erlangen-Nuremberg.

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(5) The term inverse trans influence has been used loosely (in some cases to imply the preference in uranium compounds for metal–ligand multiple bonds to be coordinated in a trans relationship) and to describe a variety of phenomena. The paper focuses on this strict definition in order to understand phenomena unique to the actinides. The ITI described for cobaloximes is distinct from the ITI of the actinides. It describes "the observation that in cobaloximes both axial distances Co–X and Co–L lengthen when the electron-donating ability of X increase has been called inverse trans influence, in contrast with the regular trans influence, which occurs when the Co–X bond shortens and the Co–L bond lengthens." See: Randaccio, L.; Geremia, S.; Nardin, G.; Wuerges, J. *Coord. Chem. Rev.* **2006**, *250*, 1332 and references therein.

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