

Review

# Uranyl Analogue Complexes—Current Progress and Synthetic Challenges

Leonor Maria \*  and Joaquim Marçalo 

Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobadela LRS, Portugal

\* Correspondence: leonorm@ctn.tecnico.ulisboa.pt

**Abstract:** Uranyl ions,  $\{UO_2\}^{n+}$  ( $n = 1, 2$ ), display *trans*, strongly covalent, and chemically robust U-O multiple bonds, where 6d, 5f, and 6p orbitals play important roles. The synthesis of isoelectronic analogues of uranyl has been of interest for quite some time, mainly with the purpose of unveiling covalence and 5f-orbital participation in bonding. Significant advances have occurred in the last two decades, initially marked by the synthesis of uranium(VI) bis(imido) complexes, the first analogues with a  $\{RNUNR\}^{2+}$  core, later followed by the synthesis of unique *trans*- $\{EUO\}^{2+}$  ( $E = S, Se$ ) complexes, and recently highlighted by the synthesis of the first complexes featuring a linear  $\{NUN\}$  moiety. This review covers the synthesis, structure, bonding, and reactivity of uranium complexes containing a linear  $\{EUE\}^{n+}$  core ( $n = 0, 1, 2$ ), isoelectronic to uranyl ions,  $\{OUO\}^{n+}$  ( $n = 1, 2$ ), incorporating  $\sigma$ - and  $\pi$ -donating ligands that can engage in uranium–ligand multiple bonding, where oxygen may be replaced by heavier chalcogenido, imido, nitride, and carbene ligands, or by a transition metal. It focuses on synthetic methods of well-defined molecular uranium species in the condensed phase but also references gas-phase and low-temperature-matrix experiments, as well as computational studies that may lead to valuable insights.

**Keywords:** uranyl analogues; uranium–ligand multiple bonding; covalency; structural parameters; inverse *trans* influence



Citation: Maria, L.; Marçalo, J.

Uranyl Analogue

Complexes—Current Progress and Synthetic Challenges. *Inorganics* **2022**, *10*, 121. <https://doi.org/10.3390/inorganics10080121>

Academic Editor: Wolfgang Linert

Received: 18 July 2022

Accepted: 15 August 2022

Published: 18 August 2022

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## 1. Introduction

Actinide coordination chemistry remains a topic of interest due to unprecedented molecular structures and reactivity pathways [1–3]. Significant progress occurred in the last decade with the development of methods for generating multiple bonds between 5f and p-block elements [4–7]. From a fundamental point of view, the central drive behind this research has been to understand factors that govern the bonding in metals with diffuse and/or high energy valence orbitals, especially 5f and 6d orbitals, and the degree to which covalency may be invoked when describing actinide–ligand bonding.

On the other hand, the influence of nuclear power on the energy portfolio of a number of countries has also determined the evolution of this research. The initial focus was on the preparation of volatile compounds for uranium isotopic separation, a necessary step in the fabrication of materials for nuclear fuel and other applications. Later, and continuing to the present, studies concentrated on fuel reprocessing and waste management, and ultimately, on the elimination of waste from nuclear power plants and weapons dismantling, and related environmental issues.

Of all the actinides, uranium has been the most studied, particularly uranyl(VI),  $\{UO_2\}^{2+}$ , since it is the most stable form of uranium in the environment. The uranyl(VI) ion is characterized by a strictly linear OUO arrangement, short and strong uranium–oxygen bonds ( $\sim 1.78$  Å), formally triple bonds, resultant from one  $\sigma$ - and two  $\pi$ -bonds between 2p orbitals on the oxido ligands and 5f and 6d hybrid orbitals on uranium [8]. This results in thermodynamically stable and, generally, kinetically inert U-O bonds, with a gas-phase

average bond energy of  $618 \text{ kJ mol}^{-1}$  [9]. Ligands in the equatorial plane of  $\{\text{OUO}\}^{2+}$  complexes are bound to the uranium center through weaker bonds compared to the strong U-O ones.

The disproportionation of the unstable uranyl(V) cation,  $\{\text{UO}_2\}^+$ , to uranyl(VI) and uranium(IV) species is an important feature in uranium remediation by immobilization, and significant advances have been made in the isolation and study of reduced uranyl complexes [1,10–12]. Due to the lower stability of the +5 oxidation state, uranyl(V) species are less common; however,  $\{\text{UO}_2\}^+$  exhibits the same key characteristics of the hexavalent analogue, such as short U-O bonds and the *trans*- $\{\text{OUO}\}^+$  arrangement.

$\{\text{UO}_2\}^{n+}$  ( $n = 1, 2$ ) species are a particular case of uranium complexes containing multiply bonded ligands and have been the subject of many spectroscopic and theoretical studies [8,13,14]. The robust linear  $\{\text{OUO}\}^{n+}$  fragment is challenging to disrupt, with deviations from linearity found up to approximately  $20^\circ$ , generally in the presence of sterically demanding ancillary ligands [15] and contrasting with commonly encountered transition metal *cis*-dioxido species. Computational and spectroscopic investigations have suggested that two significant occurrences operate in the preference of *trans*-uranyl over *cis*-uranyl, namely, the involvement of the valence 5f orbitals, and of the “pseudo-core” U 6p orbitals in the U–O bonding framework, which result in an inverse *trans* influence (ITI) [8,14,16]. The ITI phenomenon was termed by Denning as opposite to the *trans* effect observed in transition metal complexes, where strongly bound anionic ligands weaken and lengthen the bonds with ligands *trans* to their own position [13].

A good example of the ITI phenomenon is the pseudo-octahedral complex  $[\text{UOCl}_5]^-$  [17], which exhibits a short axial U–O bond ( $1.76(1) \text{ \AA}$ ) as in the  $\{\text{UO}_2\}^{2+}$  fragment, and a U–Cl<sub>*trans*</sub> distance of  $2.433(4) \text{ \AA}$  that is approximately  $0.1 \text{ \AA}$  shorter than the average U–Cl<sub>*cis*</sub> bonds of  $2.536(2) \text{ \AA}$ . ITI also explains why two strongly bound oxido ligands are arranged mutually *trans*, as in the actinyl ions, with their inverse *trans* influence being cooperative.

The synthesis of uranyl,  $\{\text{UO}_2\}^{n+}$ , analogues, where one oxygen or both is replaced by a p-block element,  $\{\text{E=U=E}\}^{n+}$  ( $\text{E} = \text{O, S, Se, NR, N, PR, CR}_2$ ), and the nearly linear arrangement is maintained, has seen several advances lately, contributing to a comprehensive understanding of bonding and covalency in uranium compounds.

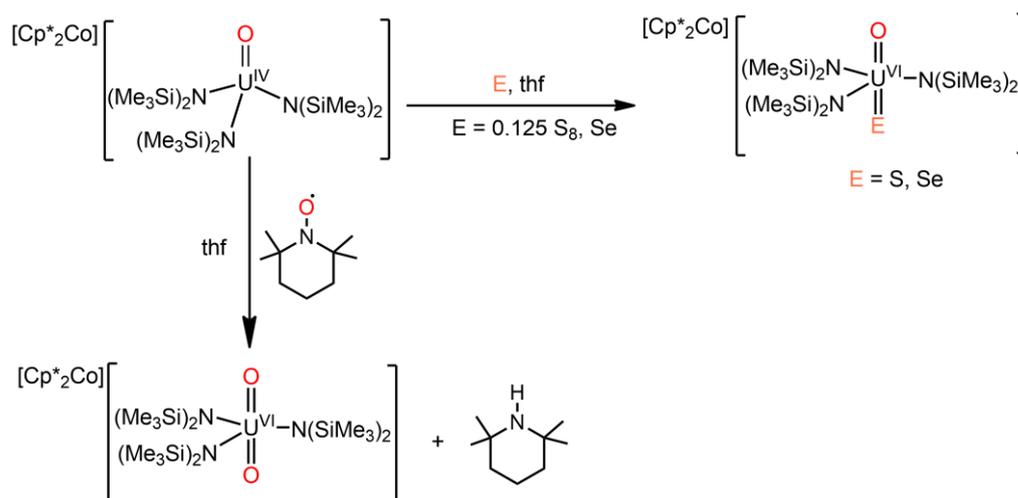
This review covers experimental and computational studies on uranyl analogue molecular compounds, including the identification of significant uranyl analogues in inert low-temperature matrices or the gas phase. We note that this topic has been partly discussed in several reviews of actinide-ligand multiple bond chemistry [4–6] and in more general uranium coordination chemistry reviews [2,3]. Several new, interesting compounds were reported afterwards, particularly the first complexes featuring a linear  $\{\text{N}\equiv\text{U}\equiv\text{N}\}$  core, iso-electronic to the uranyl(VI) cation [18], and, therefore, it seems timely to have an up-to-date examination of uranyl analogue complexes. This review provides an overview of synthetic methods that have been used to prepare uranyl-analogue molecular compounds. It only focuses on isoelectronic analogues of uranyl (V/VI); related complexes that may exhibit structural features of uranyl analogues due to ITI are not discussed.

The review is divided into four main sections: (a) Uranium-heavy chalcogenido complexes; (b) uranium pnictogenido complexes; (c) uranium carbene complexes; (d) uranium-transition metal complexes. The structures of uranyl analogue complexes are discussed with a specific focus on metric parameters for uranyl analogues  $\{\text{E=U=E}\}^{n+}$  ( $n = 1, 2$ ), combined, when possible, with data from computational studies. Reactivity studies of uranyl analogue complexes are also addressed, as are synthetic challenges not yet accomplished, such as those involving sulfido, phosphido, Schrock-carbene, or transition-metal ligands in complexes that can be considered to have uranyl analogue cores.

## 2. Heavy Chalcogenido Complexes

The synthesis of condensed-phase isoelectronic analogues of uranyl, where oxygen is replaced by another main-group element, is an ongoing subject of research. Despite the successes in this area, it is still striking to note the absence of experimentally characterized uranyl

analogues,  $\{UE_2\}^{2+}$ , with heavier elements of the oxygen group (E = S, Se, Te). The only reported analogous structurally characterized complexes are  $[Cp^*_2Co][U(O)(E)(NR_2)_3]$  [R = SiMe<sub>3</sub>; E = S, Se], which were produced by reacting  $[Cp^*_2Co][U(O)(NR_2)_3]$  with S<sub>8</sub> or elemental selenium in thf (Scheme 1) [19]. As expected for uranyl-like  $\{OUE\}^{2+}$  species, O–U–E bond angles (E = S: O–U–S 177.4(7)°; E = Se: O–U–Se = 177.3(4)°; E = O: O1–U–O2 = 178.8(3)°) are nearly linear and U–O bond lengths are shorter (E = S: U–O 1.74(2) Å; E = Se: U–O 1.739(8) Å) than those in the analogous uranyl  $[Cp^*_2Co][UO_2\{N(SiMe_3)_2\}_3]$  (1.811(5) Å and 1.788(5) Å), likely as a consequence of the observed disorder [19]. U–S and U–Se bond distances, 2.390(8) Å and 2.533(1) Å, respectively, are ~0.1 Å shorter than the U–E bond distances in terminal chalcogenido U(IV) complexes  $[U(E)(NR_2)_3]^-$  (E = S: 2.4805(5) Å; E = Se: 2.6463(7) Å). This reduction is larger than predicted based on the change in ionic radius from U<sup>4+</sup> to U<sup>6+</sup>, which may be evidence of the presence of an inverse *trans* influence in the  $\{OUE\}^{2+}$  complexes. The chalcogenido ligands seem to be stabilized by the presence of the strongly donating silylamido ligands and the negative charge of the complex, which stabilizes the 6+ charge on the uranium center and precludes auto-oxidation of the chalcogenido ligand. DFT calculations revealed considerable f-orbital contribution in the U–E interaction and suggested that U–E bonding becomes less covalent as group 16 is descended.



**Scheme 1.** Synthesis of *trans*- $\{OUE\}^{2+}$  (E = O, S, Se) complexes supported by silylamido ligands (adapted from ref. [19]).

In addition, the U(VI) *trans*-oxido-selenido complex,  $[U(O)(Se)(NR_2)_3]^-$ , was characterized by <sup>77</sup>Se NMR and the chemical shift was located at 4905 ppm, the highest <sup>77</sup>Se NMR shift yet reported [20]. <sup>77</sup>Se chemical shifts, in conjugation with natural bond analysis and QTAIM metrics, were identified as a probe of An–Se bond covalency within an isoelectronic series, and supported significant 5f-orbital participation in U–Se bonding for the uranium(VI) complex.

Based on the synthesis of  $\{O=U=S\}^{2+}$  and  $\{O=U=Se\}^{2+}$  complexes, it would seem possible to synthesize compounds containing the  $\{S=U=S\}^{2+}$  and  $\{Se=U=Se\}^{2+}$  moieties; however, this has not yet been the case and it remains a synthetic challenge concerning uranyl analogues.

Reactions of atomic uranium with different molecules in cryogenic matrices have provided evidence for elusive species and bonding, such as linear uranyl-like NUN, in advance of more conventional syntheses [21]. Typically, the characterization of novel uranium species was accomplished by infrared spectroscopy coupled with theoretical calculations. Different uranium sulfide molecules were prepared by this methodology, namely  $[US_3]$ ,  $[OUS_2]$ , and  $[U(O)(S)F_2]$  [22–24], from the reaction of laser-ablated U atoms with sulfur vapor, SO<sub>2</sub> or SOF<sub>2</sub>. These structures were identified on the basis of characteristic IR U–E

stretching modes in conjugation with DFT calculations. The  $\text{SUO}_2$  molecule displays a T-shaped geometry, retaining the *trans*-oxo configuration of uranyl, and a U-S bond length of 2.502 Å [23], while the  $\text{US}_3$  molecule exhibits a  $C_{2v}$  T-shaped geometry similar to its  $\text{UO}_3$  analogue, with bond lengths of 2.342 Å for the unique U-S bond and 2.333 Å for the other two equal U-S bonds, and with the larger S-U-S angle being 150.8° [22]. In  $[\text{U}(\text{O})(\text{S})\text{F}_2]$ , the  $\{\text{SUO}\}^{2+}$  moiety is stabilized by electron-withdrawing fluoride ligands. The optimized structure holds a slightly bent SUO moiety with a bond angle of 162.01°, close to the value of 168.01° for the OOU moiety in the  $\text{UO}_2\text{F}_2$  molecule computed at the same level of theory. Bonding analysis revealed the presence of one  $\sigma$  and two  $\pi$  bonding orbitals in the U-S bond of the S-U-O fragment [24]. A comparative computational study with  $[\text{U}(\text{O})(\text{S})(\text{NR}_2)_3]^-$  ( $\text{R} = \text{SiMe}_3$ ) [19], the only compound containing the  $\{\text{SUO}\}^{2+}$  moiety determined by X-ray diffraction, showed that the U-O and U-S bond lengths in  $[\text{U}(\text{O})(\text{S})\text{F}_2]$  are shorter and exhibit higher vibrational frequencies, indicative of stronger U-O and U-S bonds. QTAIM analysis indicated a decrease in covalency from U-O to U-S bonds in  $[\text{U}(\text{O})(\text{S})\text{F}_2]$  and that the U=E bonds in  $[\text{U}(\text{O})(\text{S})(\text{NR}_2)_3]^-$  should be less covalent than those in  $[\text{U}(\text{O})(\text{S})\text{F}_2]$  [24].

There is still no experimental evidence of a heavier chalcogenido analogue of the uranyl ion,  $\{\text{E}=\text{U}=\text{E}\}^{2+}$ . Indeed, the single report featuring the  $\{\text{US}_2\}^{2+}$  ion is from a gas-phase study, where  $\text{U}^{2+}$  ions produced by laser ionization of uranium metal reacted with COS to produce several mono- and dipositive uranium sulfide species in a FTICR mass spectrometer [25]. Sequential abstraction of two sulfur atoms from COS by  $\text{U}^{2+}$  resulted in a  $\{\text{US}_2\}^{2+}$  species; however, DFT calculations [25], later confirmed at the CASPT2 level [26], indicated that, in contrast to uranyl, linear thiouranyl is some 171  $\text{kJ mol}^{-1}$  higher in energy than the ground-state, side-on  $\eta^2\text{-S}_2$  triangular isomer [25,26].

It should be noted that the triangular  $\text{US}_2$  unit was also observed by Hayton and co-workers in the solid-state structure of the U(IV) complex  $[\text{K}(18\text{-crown-6})][\text{U}(\eta^2\text{-S}_2)(\text{NR}_2)_3]$  [27]. This complex was possibly the result of an attempt to introduce a second terminal sulfido ligand into the uranium(IV) monosulfido complex  $[\text{K}(18\text{-crown-6})][\text{U}(\text{S})(\text{NR}_2)_3]$ , by reacting it with  $\text{S}_8$ ; instead, a  $\{\text{S}_2\}^{2-}$  ligand was generated. An analogous complex,  $[\text{K}(18\text{-crown-6})][\text{U}(\eta^2\text{-SSe})(\text{NR}_2)_3]$ , was isolated when the reaction was performed with the U(IV) monosulfido and elemental selenium [27]. For the bare  $\{\text{SUO}\}^{2+}$  moiety, the DFT ground-state structure was concordant with a linear  $\{\text{OUS}\}^{2+}$  species [25], as observed by Hayton et al. in  $[\text{Cp}^*_2\text{Co}][\text{U}(\text{O})(\text{S})(\text{NR}_2)_3]$  [19].

A computational investigation of linear  $\{\text{E}=\text{U}=\text{E}\}^{2+}$  ( $\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ) complexes indicated an increased bond order and reduced charge separation on the descending group. Bending of the S-U-S angle in  $[\text{US}_2(\text{H}_2\text{O})_5]^{2+}$  was also examined, suggesting an increased stability of the *cis* structure [28]. The higher energy of the thiouranyl, linear isomer of  $\{\text{US}_2\}^{2+}$  is in agreement with Denning's prediction that the uranyl-type moiety would be limited to the first short period of elements, including only carbon, nitrogen, and oxygen [8]. The question remains: Is it possible to isolate isoelectronic  $\{\text{E}=\text{U}=\text{E}\}^{2+}$  uranyl analogues with heavier chalcogenides if the appropriate ancillary ligands and experimental conditions are chosen? Or can uranium bis(imido) complexes (see next section) be used as precursors, for instance, in reactions with favorable S-donor COS?

### 3. Uranium Pnictogenido Complexes

The synthesis and reactivity of uranium terminal imido complexes, with the oxidation state of the metal varying from +3 to +6, have been extensively studied for decades and summarized in several reviews [4,5,7]. The imido ligand  $\{\text{NR}\}^{2-}$  is isoelectronic with the oxido ligand  $\text{O}^{2-}$  and U-NR multiple bonds can serve as models for uranium-oxido multiple bonds, particularly uranyl compounds. The softer character of the ligand in conjunction with the alkyl or aryl substituents make imido  $\{\text{RN}=\text{U}=\text{E}\}^{2+}$  ( $\text{E} = \text{NR}, \text{O}$ ) analogues of uranyl more soluble in organic solvents, allowing the non-aqueous chemistry of these compounds to be developed and significantly increasing the number of uranyl analogue complexes (see below). Complexes with nitrido ligands,  $\text{N}^{3-}$ , in a *trans*- $\text{E}=\text{U}=\text{E}$  framework are rare.

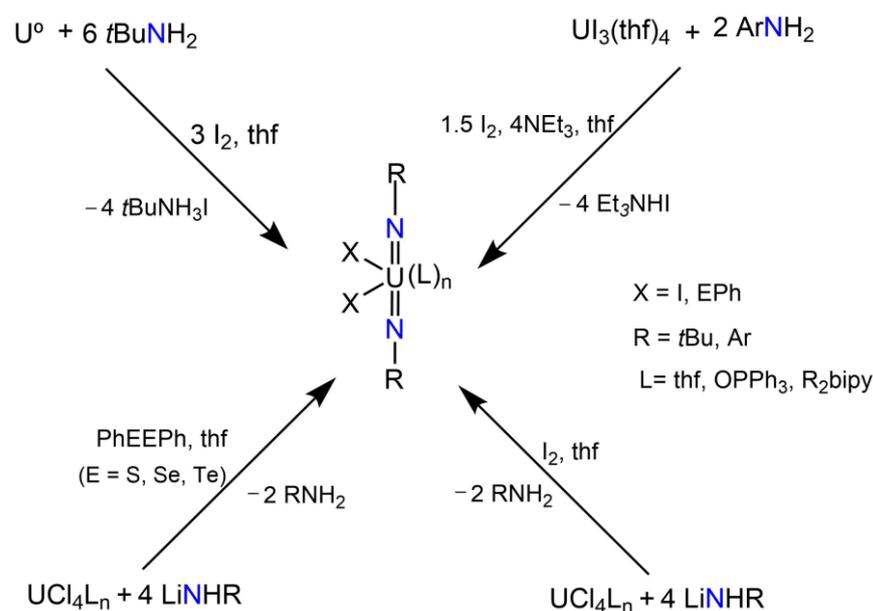
Uranium-ligand multiple-bond complexes with heavy pnictogen elements are less developed but they have emerged in the last 8 years, with the isolation of a few uranium(IV) phosphinidene  $\{\text{PR}\}^{2-}$ , phosphide  $\text{P}^{3-}$ , arsinidene  $\{\text{AsR}\}^{2-}$ , and arsenide  $\text{As}^{3-}$  compounds [6,29]. However, analogues with uranium in high oxidation states, including complexes with cores isoelectronic to uranyl, have not yet been isolated. An attempt to identify  $\text{P}=\text{U}=\text{P}$  in an argon matrix was inconclusive, and calculations on the identified U(IV) molecule suggested a triplet ground state with a short U–P bond length [30]. Similar to heavy chalcogenido complexes,  $\{\text{E}=\text{U}=\text{E}\}^{n+}$ , the heavy pnictogenido analogues of uranyl are attractive targets for studying the electronic structure and covalency of uranium bonding to soft donors, and due to the recent advances, it seems a plausible goal.

### 3.1. Uranium Bis(imido) Complexes

The first example of a uranium(VI) bis(imido) complex was described in 1992 by Burns and co-workers [31].  $[\text{Cp}^*_2\text{U}(\text{NPh})_2]$  was prepared as an analogue of the stable uranyl ion,  $\{\text{UO}_2\}^{2+}$ ; however, this molecular compound displayed a nonlinear geometry for the two organoimido groups (N–U–N  $98.7(4)^\circ$ ), likely due to steric constraints imposed by the  $\text{Cp}^*$  ligands. Since then, several uranium(VI) *cis*-bis(imido) complexes have been reported [7], but only in 2005 were the first examples of uranium(VI) bis(imido) complexes with a linear  $\{\text{RN}=\text{U}=\text{NR}\}^{2+}$  bonding mode reported [32]. Hayton et al. demonstrated that *trans*- $[\text{U}(\text{NR})_2\text{I}_2(\text{thf})_n]$  can be easily prepared by a one-step reaction from either uranium metal or  $[\text{UI}_3(\text{thf})_4]$  with iodine and alkyl- or arylamines (Scheme 2) [32,33]. Uranium(VI) bis(imido) complexes  $[\text{U}(\text{NR})_2\text{I}_2(\text{thf})_n]$  ( $n = 2, 3$ ) exhibit well-defined octahedral or pentagonal bipyramidal geometries about the uranium centers. Both geometries are common for uranyl-containing complexes. The U=N bonds are shorter (1.840(4)–1.89(1) Å) when compared to *cis*-bis(imido) uranium species (1.926(8)–1.975(3) Å) [6] and show an almost linear RN=U=NR arrangement. U–N–C angles are close to  $180^\circ$ , in agreement with a *sp* hybridization at nitrogen and the presence of a uranium–nitrogen triple bond. Largely, the geometry and metrical parameters of the  $\{\text{NUN}\}^{2+}$  fragment in the uranium *trans*-bis(imido) complexes resemble those of the uranyl ion. DFT calculations were used to analyze de U–N<sub>imido</sub> bond in these complexes, and in the case of  $[\text{U}(\text{NtBu})_2\text{I}_2(\text{thf})_2]$ , the compound  $[\text{U}(\text{NMe})_2\text{I}_2(\text{thf})_2]$  was used as the model [33]. Computations showed that six orbitals are involved in the uranium–nitrogen bonding, indicating the presence of two uranium–nitrogen triple bonds as in the  $\{\text{UO}_2\}^{2+}$  moiety. The most relevant uranium atomic orbitals involved in U–N bonding are  $5f_\sigma$ ,  $5f_\pi$ ,  $6d_\pi$ , and  $6d_\sigma$ , as in the case of the uranyl(VI) ion, with significant contribution of 5f orbitals. For instance, the two highest-energy U–N  $\pi$  bonding orbitals, HOMO-6 and HOMO-7, have 32% and 27% f character, respectively. Remarkably, the bonding in the RN=U=NR fragment is more covalent. The *cis* isomer of  $[\text{U}(\text{NMe})_2\text{I}_2(\text{thf})_2]$  was also calculated and revealed to be  $61.5 \text{ kJ mol}^{-1}$  higher in energy than the *trans* isomer. Structural parameters of reported uranium(VI) *trans*-bis(imido) complexes are summarized in Table 1.

The thf ligands in  $[\text{U}(\text{NR})_2\text{I}_2(\text{thf})_2]$  ( $\text{R} = \text{tBu}, \text{Ph}$ ) are easily displaced by a variety of neutral donors [33], including soft Lewis bases such as  $\text{Pme}_3$  and 1,2-bis(dimethylphosphano)ethane (dmpe) [33,36]. This contrasts with the  $\{\text{UO}_2\}^{2+}$  ion, which does not coordinate phosphane donor ligands, demonstrating that uranyl is a harder Lewis acid. Similar to their thf adduct parent compounds, the uranium(VI) bis(imido) complexes  $[\text{U}(\text{NR})\text{I}_2(\text{L})_n]$  ( $\text{R} = \text{tBu}, \text{Ph}$ ;  $n = 2, 1$ ;  $\text{L} = \text{PMe}_3, \text{py}, \text{OPPh}_3, \text{PhNH}_2, \text{dmpe}$ ) revealed nearly linear N–U–N angles and short U–N bond lengths (Table 1).

Later, Boncella and co-workers demonstrated that  $\text{UCl}_4$  is also a suitable precursor for generating U(VI) *trans*-bis(imido) complexes when treated with alkali metal amide salts and iodine or PhEPh ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ) in the presence of a neutral donor [37,44]. All of the routes to prepare the bis(imido) complexes of general formula  $[\text{U}(\text{NR})_2\text{X}_2(\text{L})_n]$  (Scheme 2) involved oxidation of in situ generated uranium amino/amido/imido complexes. Variations in the R substituent include the use of alkyl and aryl groups with different electron-donating/withdrawing abilities.



**Scheme 2.** Synthesis of  $\text{trans-}\{\text{RNUNR}\}^{2+}$  complexes.

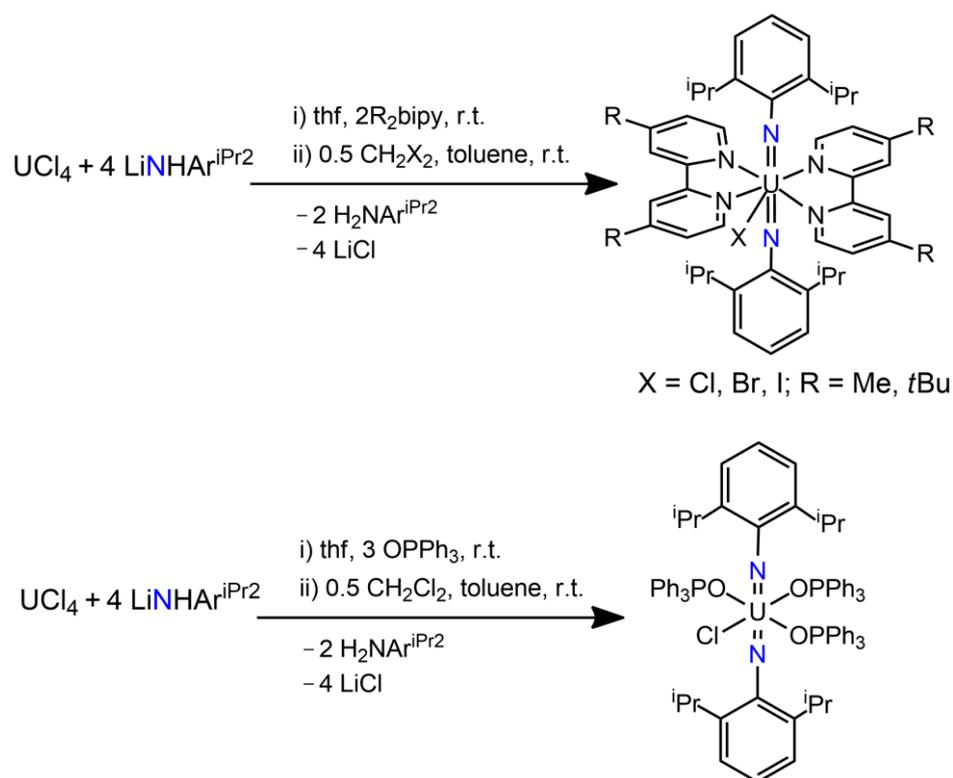
Boncella and co-workers also demonstrated that the iodide ligands in *trans*-bis(imido) complexes  $[\text{U}(\text{NR})\text{I}_2(\text{L})_n]$  can be efficiently replaced by anionic donors (OTf, Cp, Cp\*, pyrrolide, chalcogenates, dipyrrolylmethane), increasing the library of uranium(VI) bis(imido) complexes [33,36,38,41]. However, depending on stereochemical properties of the anionic ligand and the number of replaced iodides, the generated uranium(VI) species exhibit different N-U-N bending angles, varying from U(VI) *trans*-bis(imidos) to *cis*-bis(imidos) [41]. For example, the reaction of  $[\text{U}(\text{NtBu})_2\text{I}_2(\text{dmpe})]$  with 2 equiv. of NaCp generated the bis(imido)  $[\text{Cp}_2\text{U}(\text{NtBu})_2(\text{dmpe})]$  with a N-U-N angle of  $154.4(2)^\circ$ , somewhat away from linearity, which may reduce U-N orbital overlap and consequently cause longer U-N<sub>imido</sub> bonds as observed [41].

Unexpectedly, iodide metathesis of  $[\text{U}(\text{NtBu})_2\text{I}_2(\text{tBu}_2\text{bpy})]$  with NaCp\* generated the reduced U(V) compound  $[\text{U}(\text{NtBu})_2\text{I}(\text{tBu}_2\text{bpy})]_2$ , the first example of a complex containing the *trans*- $\{\text{U}(\text{NR})_2\}^+$  ion [40]. The dimeric bis(imido) uranium(V) complex acts as a two-electron reducing agent with I<sub>2</sub>/AgX (X = Cl, Br), PhEPh (E = S, Se, Te), and chalcogen (O, S, Se) atom transfer reagents [39]. Adding I<sub>2</sub> and AgX was conducive to the formation of uranium(VI) dihalide complexes with general formula  $[\text{U}(\text{NtBu})_2(\text{I})(\text{X})(\text{tBu}_2\text{bpy})]$  (X = I, Cl, Br). The reductive cleavage of PhEPh (E = Se, Te) by the U(V) complex suggested that an equilibrium between the unsymmetrical complex  $[\text{U}(\text{NtBu})_2(\text{I})(\text{EPh})(\text{tBu}_2\text{bpy})]$  and symmetrical complexes  $[\text{U}(\text{NtBu})_2(\text{X})_2(\text{tBu}_2\text{bpy})]$  and  $[\text{U}(\text{NtBu})_2(\text{EPh})_2(\text{tBu}_2\text{bpy})]$  seems to exist in solution, indicating that both U-I and U-E bonds possess a labile nature in these uranium(VI) *trans*-bis(imido) complexes.

Boncella and co-workers demonstrated that uranium(V) *trans*-bis(imidos)  $[\text{U}(\text{NAr}^{\text{iPr}2})\text{X}(\text{L})_n]$  (X = Cl, Br, I, n = 2, L = Me<sub>2</sub>bipy, tBu<sub>2</sub>bipy; n = 3, L = OPPh<sub>3</sub>), analogues of the  $\{\text{UO}_2\}^+$  species, can be directly prepared via in situ generation of uranium(IV) bis(imido) compounds from UCl<sub>4</sub>, lithium anilide, and neutral Lewis bases, followed by halide abstraction from methylene halides with metal oxidation (Scheme 3) [52]. Complex  $[\text{U}(\text{NAr}^{\text{iPr}2})_2\text{Cl}(\text{Me}_2\text{bipy})_2]$  can be alternatively synthesized from the reaction of the uranium(IV) mono-imido  $[\text{U}(\text{NAr}^{\text{iPr}2})\text{Cl}_2(\text{Me}_2\text{bipy})_2]$  with two equivalents of lithium 2,6-diisopropylphenylamide and dichloromethane [37].

Table 1. Structural parameters of *trans*-[U(NR)<sub>2</sub>]<sup>2+</sup> complexes.

Compound	Average U-N Bond Lengths (Å)	N-U-N Angle (Deg)	Average U-N-C Angle (Deg)	Ref.
[U(N <i>t</i> Bu) <sub>2</sub> I <sub>2</sub> (thf) <sub>2</sub> ]	1.844(8)	175.4(2)	168.3(9)	[32,33]
[U(N <i>t</i> Bu) <sub>2</sub> I <sub>2</sub> (thf) <sub>3</sub> ]	1.855(2)	175.6(1)	166.3(2)	[33]
[U(N <i>t</i> Bu) <sub>2</sub> I <sub>2</sub> (py) <sub>2</sub> ]	1.835(2)	180	174.5(2)	[33]
[U(NPh) <sub>2</sub> I <sub>2</sub> (thf) <sub>3</sub> ]	1.862(4)	177.4(9)	177.0(9)	[32,33]
[U(Ar <sup>iPr2</sup> ) <sub>2</sub> I <sub>2</sub> (THF) <sub>3</sub> ]	1.887(4)	169.3(1)	175.6(16)	[33]
[U(Nar <sup>CF3</sup> ) <sub>2</sub> I <sub>2</sub> (thf) <sub>3</sub> ]	1.88(3)	176.8(4)	168.6(14)	[33]
[U(N <i>t</i> Bu) <sub>2</sub> I <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.840(4)	177.8(2)	170.9(8)	[33]
[U(N <i>t</i> Bu)(NPh)I <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.832(8)	177.4(4)	170.5(8)	[34]
	1.841(8)		172.9(9)	
[U(Nmes) <sub>2</sub> I <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.867(5)	180.0(5)	175.4(3)	[34]
[U(N <i>t</i> Bu) <sub>2</sub> Cl <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.848(4)	180.0(2)	170.0(4)	[35]
[U(N <i>t</i> Bu) <sub>2</sub> Br <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.828(9)	180.0(3)	167.0(8)	[35]
[U(N <i>t</i> Bu) <sub>2</sub> {N(Me)(SO <sub>2</sub> Ar') <sub>2</sub> (Me <sub>2</sub> bpy)}]	1.843(29)	167.0(3)	166.8(12)	[35]
[U(N <i>t</i> Bu) <sub>2</sub> (η <sup>1</sup> -Me <sub>2</sub> -C <sub>4</sub> H <sub>2</sub> N) <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.842(3)	171.4(2)	156.4(3)	[36]
[U(N <i>t</i> Bu) <sub>2</sub> (dpm)(thf) <sub>2</sub> ]	1.856(6)	172.8(3)	162(5)	[36]
[U(N <i>t</i> Bu) <sub>2</sub> (dpm <sup>Mes</sup> )(dmpe)]	1.856(18)	165.9(6)	170.0(85)	[36]
[U(N <i>t</i> Bu) <sub>2</sub> Br <sub>2</sub> (Me <sub>2</sub> bpy)]	1.838(5)	169.8(1)	171.6(36)	[35]
[U(N <i>t</i> Bu) <sub>2</sub> Cl(μ-Cl)(Me <sub>2</sub> bpy)] <sub>2</sub>	1.834(18)	172.3(3)	164.1(37)	[35]
[U(Nmes) <sub>2</sub> I <sub>2</sub> ( <i>t</i> Bu <sub>2</sub> bpy)]	1.867(3)	173.7(2)	171.7(3)	[37]
[U(Nar <sup>iPr2</sup> ) <sub>2</sub> I <sub>2</sub> ( <i>t</i> Bu <sub>2</sub> bpy)]	1.868(4)	168.4(1)	176.4(23)	[37]
[U(N <i>t</i> Bu) <sub>2</sub> (O-2- <sup>t</sup> BuC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.870(6)	180.0	180	[38]
[U(N <i>t</i> Bu) <sub>2</sub> (SPh) <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.840(7)	180	170.3(6)	[38]
[U(N <i>t</i> Bu) <sub>2</sub> (SePh) <sub>2</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]	1.861(6)	180	169.4(4)	[38]
[U(N <i>t</i> Bu) <sub>2</sub> I <sub>2</sub> (Me <sub>2</sub> bpy)]	1.816(17)	171.2(5)	173(2)	[38]
[U(N <i>t</i> Bu) <sub>2</sub> (SPh) <sub>2</sub> ( <i>t</i> Bu <sub>2</sub> bpy)]	1.840(8)	178.2(4)	172.25(21)	[38]
[U(N <i>t</i> Bu) <sub>2</sub> (SePh) <sub>2</sub> (Me <sub>2</sub> bpy)]	1.844(5)	175.9(2)	174.6(31)	[38]
[U(N <i>t</i> Bu) <sub>2</sub> (TePh) <sub>2</sub> ( <i>t</i> Bu <sub>2</sub> bpy)]	1.828(12)	177.4(3)	173(5)	[38]
[U(N <i>t</i> Bu) <sub>2</sub> (Cl)(I)( <i>t</i> Bu <sub>2</sub> bpy)]	1.822(6)	175.2(3)	171(7)	[39]
[U(N <i>t</i> Bu) <sub>2</sub> (SePh)(I)( <i>t</i> Bu <sub>2</sub> bpy)]	1.823(12)	174.7(4)	174.7(16)	[39]
[U(N <i>t</i> Bu) <sub>2</sub> (I)( <i>t</i> Bu <sub>2</sub> bpy)] <sub>2</sub> (μ-O)]	1.848(24)	165.6(6)	173(6)	[39,40]
[U(N <i>t</i> Bu) <sub>2</sub> (I)( <i>t</i> Bu <sub>2</sub> bpy)] <sub>2</sub> (μ-η <sup>2</sup> -η <sup>2</sup> -Se <sub>4</sub> )	1.833(8)	172.4(2)	173.9(43)	[39]
[Ucp <sub>2</sub> (N <i>t</i> Bu) <sub>2</sub> (dmpe)]	1.936(6)	154.4(2)	166.8(3)	[41]
[Ucp(N <i>t</i> Bu) <sub>2</sub> I(dmpe)]	1.886(8)	161.1(2)	166.1(26)	[41]
[Li(thf)] <sub>2</sub> [U(N <i>t</i> Bu) <sub>2</sub> (HN <i>t</i> Bu) <sub>4</sub> ]	1.915(5)	180	164.8(4)	[42]
[U(NR) <sub>2</sub> Cl <sub>4</sub> ][PPh <sub>4</sub> ] <sub>2</sub> (R = <i>t</i> Bu, Ph)	1.816(8)	180.0(5)	163.9(7)	[43]
	Ph: 1.842(8)	180.0(1)	158.7(7)	
[U(Nme) <sub>2</sub> Cl <sub>4</sub> ][Net <sub>4</sub> ] <sub>2</sub>	1.828(6)	180.0(5)	155.6(5)	[43]
[U(N <i>t</i> Bu) <sub>2</sub> Br <sub>4</sub> ][Net <sub>4</sub> ] <sub>2</sub>	1.825(4)	180.0	169.1(3)	[43]
[U(N <i>t</i> Bu) <sub>2</sub> (SPh) <sub>2</sub> (py) <sub>2</sub> ]	1.862(2)	180.0	172.9(1)	[43]
[U(Nar <sup>iPr2</sup> ) <sub>2</sub> (SePh) <sub>2</sub> (py) <sub>2</sub> ]	1.886(1)	180.0(1)	164.6(1)	[44]
[U(N <i>t</i> Bu) <sub>2</sub> (TePh) <sub>2</sub> (py) <sub>2</sub> ]	1.858(3)	180.0(1)	174.4(2)	[44]
[U <sub>2</sub> (Nad) <sub>4</sub> (OSi(O <i>t</i> Bu) <sub>3</sub> ) <sub>4</sub> ]	1.89(5) (U-N <sub>term.</sub> )	171.4(27)	167.5(8)	[45]
[U(Nad) <sub>2</sub> {CH <sub>2</sub> (Ph)N <sub>3</sub> (Ad)-κ <sup>2</sup> N <sup>1,3</sup> }]	1.907(14)	173.4(3)	162.6(8)	[46]
[U( <sup>Mes</sup> PDI)I(Nmes) <sub>3</sub> ]	1.992(5)	166.6(2)	170.8(3)	[47]
	2.024(5) (eq)		180.0(1)	
[Ucp*(Ntol) <sub>2</sub> ( <sup>Mes</sup> PDI <sup>Me</sup> )]	1.950(7)	155.9(3)	167.8(5)	[48]
[Ucp*(Ntol) <sub>2</sub> ( <sup>Mes</sup> PDI <sup>Me</sup> )] <sub>2</sub> [SbF <sub>6</sub> ]	1.927(5)	155.4(2)	173.1(14)	[48]
[Ucp*(Ntol) <sub>2</sub> ( <sup>tBu-Mes</sup> PDI <sup>Me</sup> )]	1.942(10)	155.5(3)	168.8(8)	[48]
[Ucp*(Ntol) <sub>2</sub> ( <sup>tBu-Mes</sup> PDI <sup>Me</sup> )] <sub>2</sub> [BPh <sub>4</sub> ]	1.950(10)	153.1(2)	169.6(18)	[48]
[U( <sup>tBu2</sup> ArO) <sub>2</sub> Me <sub>2</sub> -cyclam](NPh) <sub>2</sub> ]	1.901(8)	172.95(8)	154.9(2)	[49]
[U( <sup>tBu2</sup> ArO) <sub>2</sub> Me <sub>2</sub> -cyclam](NPh)(Ntol)]	1.909(6)	173.7(4)	152.9(7)	[50]
	1.911(7)		152.1(7)	
[K-(crypt)][U{N(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>3</sub> (NPh) <sub>2</sub> ]	1.932(11)	178.8(3)	163.8(1.8)	[51]



**Scheme 3.** Synthesis of U(V) *trans*-bis(imido) complexes [U(NAr)<sub>2</sub>X(L)<sub>n</sub>] (adapted from ref. [52]).

The uranium(V) bis(imido) complexes exhibit nearly linear N–U–N angles (166.02(16)–174.9(2)°) and the U–N<sub>imido</sub> bond lengths are 0.15 Å longer than those of their U(VI) analogues; however, larger than the ionic radius difference between U(VI) and U(V) (0.03 Å). Solution-phase redox studies of [U(NAr<sup>iPr2</sup>)<sub>2</sub>Cl(Me<sub>2</sub>bipy)<sub>2</sub>] revealed a quasi-reversible oxidation feature at –1.06 V, which was assigned to the U(V)/U(VI) couple. This value is much more negative than those observed for the uranyl ion {UO<sub>2</sub>}<sup>2+</sup>(aq.) (–0.35 V vs. Fc/Fc<sup>+</sup>), suggesting that the uranium bis(imido) complexes are more electron rich than their uranyl analogues, and confirming the strong π-donating character of the imido ligands in this system [52]. Structural parameters of reported uranium(V) *trans*-bis(imido) complexes are summarized in Table 2.

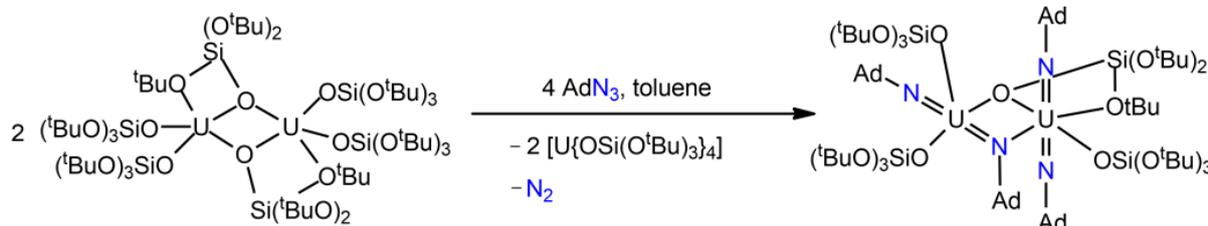
Surprisingly, Gaunt and co-workers reacted [NpCl<sub>4</sub>(dme)<sub>2</sub>] with only two equivalents of LiNHAr<sup>iPr2</sup> and 1 equiv of *t*Bu<sub>2</sub>bipy afforded the first Np(V) *trans*-bis(imido) complex [U(NAr<sup>iPr2</sup>)<sub>2</sub>(*t*Bu<sub>2</sub>bipy)<sub>2</sub>Cl], as determined by X-ray crystallography [55]. These reaction conditions and reagents stoichiometry only afford U(IV) mono(imido) products in uranium chemistry. The higher stability of Np(V) compared to U(V) could be a reason for this observation.

Boncella and co-workers also demonstrated that uranium bis(imido) tetrahalide anions [U(NR)<sub>2</sub>X<sub>4</sub>]<sup>2–</sup> (X = Cl, Br; R = *t*Bu, Ph) can be prepared from the reaction of [U(NR)<sub>2</sub>I<sub>2</sub>(thf)<sub>n</sub>] (n = 2 and R = *t*Bu, Ph; n = 3 and R = Me) with an excess of PPh<sub>4</sub>Cl, NEt<sub>4</sub>Cl, or NEt<sub>4</sub>Br [43]. Cl K-edge X-ray absorption spectroscopy (XAS) and both ground-state and time-dependent hybrid density functional theory (DFT and TDDFT) were used to probe U–Cl bonding interactions in [PPh<sub>4</sub>]<sub>2</sub>[U(N*t*Bu)<sub>2</sub>Cl<sub>4</sub>] and [PPh<sub>4</sub>]<sub>2</sub>[UO<sub>2</sub>Cl<sub>4</sub>]. The results indicated that the total amount of Cl 3p character mixed with the U 5f orbitals was approximately 7–10% per U–Cl bond for both compounds, showing that, moving from oxido to imido, the effect on orbital mixing is reduced. Compared with the mixing character found for the U–Cl bonds in [UOCl<sub>5</sub>]<sup>–</sup> (23.3%) [56], the value is smaller, which evidences that the oxido and imido ligands enhance bonding in the axial positions and limit uranium-ligand orbital mixing in the equatorial plane.

Following the impressive number of uranium *trans*-bis(imido) complexes reported by Boncella and co-workers, other examples of U(VI) *trans*-bis(imido) complexes in different

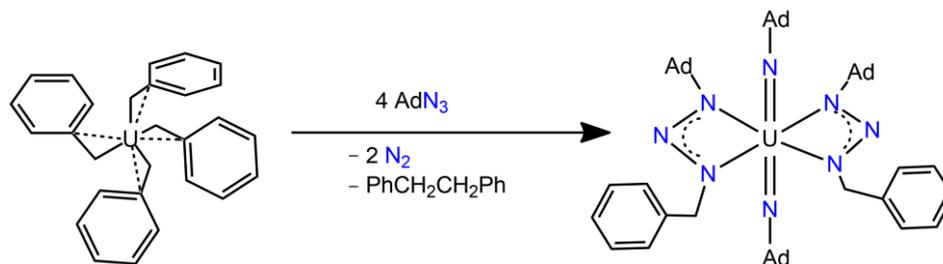
ligand environments have been prepared by other groups in the last 10 years, which involved, in most of the cases, the reduction of organic azides or diazenes.

Mazzanti and co-workers reported that treating the uranium(III) dimer  $[\text{U}\{\text{OSi}(\text{O}^t\text{Bu})_2\}_2\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_2]$  with the electron-donating adamantyl azide ( $\text{N}_3\text{Ad}$ ) generated, among other species, the dinuclear U(VI) bis(imido) complex  $[\text{U}_2(\text{NAd})_4\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4]$  (Scheme 4), which comprises nearly linear  $\{\text{U}(\text{NAd})_2\}^{2+}$  motifs ( $173.6(5)^\circ$  and  $169.2(5)^\circ$ ) with short U=N bond distances [45].



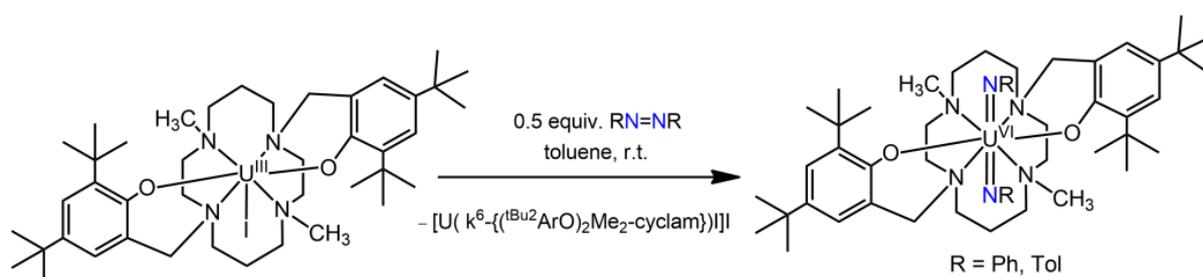
**Scheme 4.** Synthesis of U(VI) *trans*-bis(imido) complexes supported by siloxide ligands (adapted with permission from ref. [45]. Copyright 2022 American Chemical Society).

By reacting the uranium(IV) complex  $[\text{U}(\text{CH}_2\text{Ph})_4]$  with 4 equiv. of  $\text{N}_3\text{Ad}$ , Bart and co-workers obtained the U(VI) *trans*-bis(imido) complex  $[\text{U}(\text{NAd})_2\{\text{CH}_2(\text{Ph})\text{NNN}(\text{Ad})-\kappa^2\text{-N}^{1,3}\}_2(\text{thf})]$ , along with formation of bibenzyl and release of  $\text{N}_2$  (Scheme 5) [46]. When they performed the same reaction with 4 equiv. of mesityl azide ( $\text{N}_3\text{Mes}$ ), the result was the insertion product tetrakis(triazenido)uranium(IV) complex  $[\text{U}\{\text{CH}_2(\text{Ph})\text{NNN}(\text{Mes})-\kappa^2\text{-N}^{1,2}\}\{\text{CH}_2(\text{Ph})\text{NNN}(\text{Mes})-\kappa^2\text{-N}^{1,3}\}_3]$ .



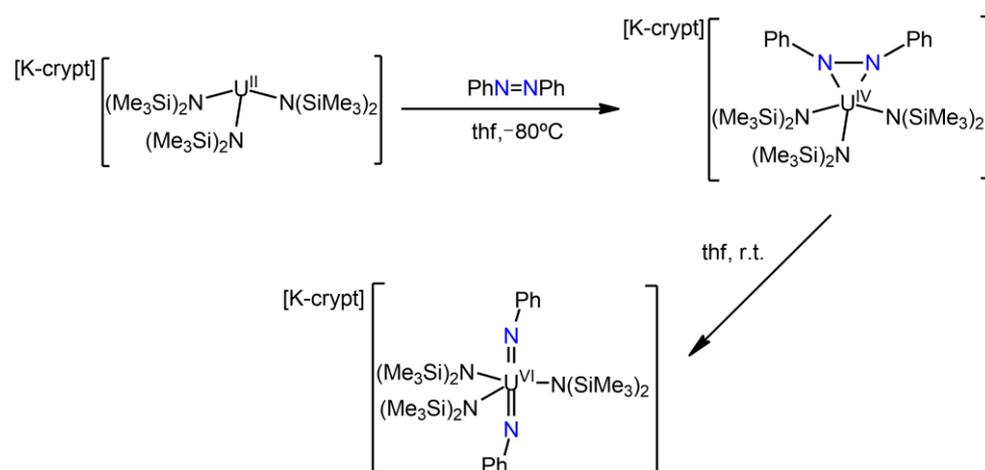
**Scheme 5.** Synthesis of a U(VI) *trans*-bis(imido) complex via reduction of organic azide by a U(IV) complex (adapted from ref. [46]).

In 2015, Maria and co-workers reported the first uranium(VI) *trans*-bis(imido) compound supported by a tetraazamacrocycle functionalized with two aryloxy arms [49]. The reaction of 2 equiv. of the uranium(III) complex  $[\text{U}(\kappa^6\text{-}\{\text{tBu}^2\text{ArO}\}_2\text{Me}_2\text{-cyclam})\text{I}]$  with azobenzene was conducive to the four-electron reduction of the  $\text{N}=\text{N}$  bonds, affording the U(VI) bis(imido) complex  $[\text{U}(\kappa^4\text{-}\{\text{tBu}^2\text{ArO}\}_2\text{Me}_2\text{-cyclam})\text{(NPh)}_2]$  and the U(IV) complex  $[\text{U}(\kappa^6\text{-}\{\text{tBu}^2\text{ArO}\}_2\text{Me}_2\text{-cyclam})\text{I}]$  (Scheme 6). The  $\{\text{tBu}^2\text{ArO}\}_2\text{Me}_2\text{-cyclam}\}^{2-}$  ligand flexibility and the weak interactions of the amines with the metal center allow the non-coordination of two nitrogen atoms and accommodation of the imido ligands in a *trans* configuration. The geometrical parameters of the  $\{\text{RN}=\text{U}=\text{NR}\}^{2+}$  moiety ( $\text{N-U-N}$   $173.0(1)^\circ$ ; Av.  $\text{U-N}_{\text{imido}}$   $1.901(8)$  Å) are close to those in the uranyl analogue complex  $[\text{U}(\text{NPh})_2\text{I}_2(\text{thf})_3]$  [33]. A similar reaction was made with 4-methylazobenzene ( $\text{ToI}(\text{NNPh})$ ), which led to the asymmetric *trans*-bis(imido)  $[\text{U}(\kappa^4\text{-}\{\text{tBu}^2\text{ArO}\}_2\text{Me}_2\text{-cyclam})\text{(NPh)}\text{(NTol)}]$ , with identical geometrical parameters [50].



**Scheme 6.** Synthesis of U(VI) trans-bis(imido) complexes supported by a bis(aryloxy) cyclam ligand (adapted from ref. [50] with permission from the Royal Society of Chemistry).

The four-electron reductive cleavage of azobenzene was first achieved by Burns and co-workers by using 2 equiv. of the U(III) complex  $[(Cp^*)_2UICl(NaCl)]$  to yield a mixture of the U(VI) cis-bis(imido)  $[(Cp^*)_2U(NPh)_2]$  and U(IV) species [57]. The proposed mechanism involves 2-electron transfer processes and the comproportionation of a U(V) intermediate, although the presence of a U(II) intermediate cannot be completely ruled out. In fact, in 2021, an experimental work combined with computational studies performed by Mazzanti and co-workers [51] showed that the U(II) complex  $[K(2.2.2\text{-cryptand})][U\{N(SiMe_3)_2\}_3]$ , previously reported by the Evans group [58], was conducive to the four-electron reduction of azobenzene, with the formation of a *trans*-bis(imido) anionic complex  $[K(2.2.2\text{-cryptand})][U(NPh)_2\{N(SiMe_3)_2\}_3]$  (Scheme 7) with an almost linear N-U-N angle  $178.8(3)^\circ$ . The U-N-C angles (av.  $163.8(23)^\circ$ ) deviate from linearity as found in other U(VI) bis(imido) complexes, suggesting partial localization of the  $\pi$  lone pair on the imido nitrogen, which was supported by bonding analysis. A similar reaction was performed with the masked U(II) complex  $[K(2.2.2\text{-cryptand})_2][U\{N(SiMe_3)_2\}_3(\mu-O)]$  [51] and azobenzene, which was conducive to the formation of the same U(VI) bis(imido) complex. In both reactions, it was possible to isolate the intermediate uranium(IV) hydrazido  $[K(2.2.2\text{-cryptand})][U(N_2Ph_2)\{N(SiMe_3)_2\}_3]$ , in agreement with the DFT calculated mechanism for the reactions [51].

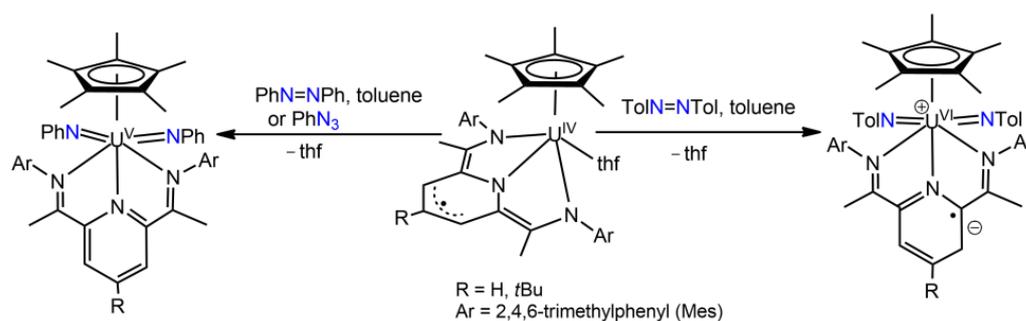


**Scheme 7.** Synthesis of a *trans*- $[U(NR)_2]^{2+}$  complex by single-metal 4-electron reduction of azobenzene by a U(II) complex (adapted from ref. [51] with permission from the Royal Society of Chemistry).

**Table 2.** Structural parameters of *trans*-[U(NR)<sub>2</sub>]<sup>+</sup> complexes.

Compound	Average U-N Bond Lengths (Å)	N-U-N Angle (Deg)	Average U-N-C Angle (Deg)	Ref.
[{U(μ-N <i>t</i> Bu)(N <i>t</i> Bu)I( <i>t</i> Bu <sub>2</sub> bpy)} <sub>2</sub> ]	1.898(5) 2.072(5)	170.1(2)	168(2) 130.2(4)	[40]
[U(NAr <sup>iPr2</sup> ) <sub>2</sub> Cl( <i>t</i> Bubpy) <sub>2</sub> ]	1.978(6)	166.0(2)	168(4)	[52]
[U(NAr <sup>iPr2</sup> ) <sub>2</sub> Br( <i>t</i> Bubpy) <sub>2</sub> ]	1.974(12)	165.9(2)	167(4)	[52]
[U(NAr <sup>iPr2</sup> ) <sub>2</sub> I( <i>t</i> Bubpy) <sub>2</sub> ]	1.958(22)	174.9(2) <sup>o</sup>	165.9(8)	[52]
[U(NAr <sup>iPr2</sup> ) <sub>2</sub> Cl(OPPh <sub>3</sub> ) <sub>3</sub> ]	1.972(8)	177.0(2)	178.2(8)	[52]
[U <sup>(Mes)PDI<sup>Me</sup></sup> ](NMe) <sub>2</sub> (thf)]	2.012(16)	167.0(4)	175(4)	[47]
[UCp <sup>*</sup> ( <sup>Mes</sup> PDI <sup>Me</sup> )(NPh) <sub>2</sub> ]	2.015(16)	154.2(2)	169.3(14)	[53]
[UCp <sup>*</sup> ( <sup>Mes</sup> PDI <sup>Me</sup> )](NPh)(NTol)]	2.012(8) 2.005(7)	154.8(3)	168.4(7) 175.4(6)	[54]

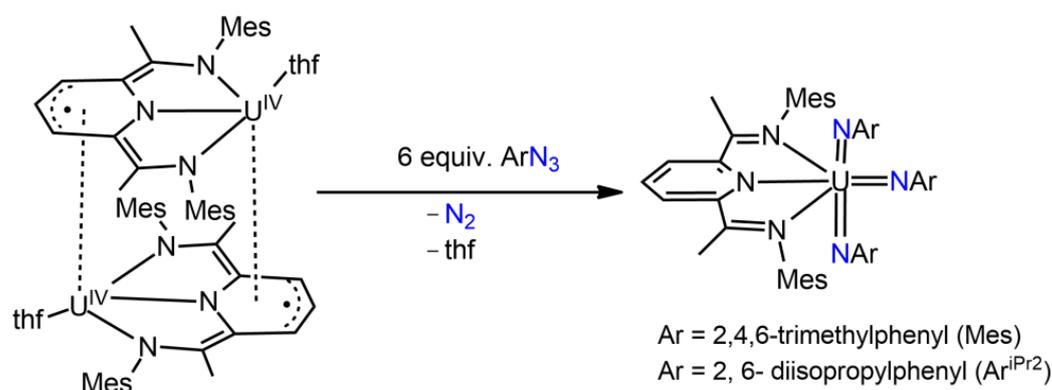
As seen above, most of the uranium bis(imido) complexes were obtained by redox processes involving the metal center and an oxidant. Bart and co-workers adopted the strategy of using a redox-active ligand with the ability to store and release electrons. The pyridine(diamine) ligand <sup>Mes</sup>PDI<sup>Me</sup> (2,6-(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>-N=CMe)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N) in the structure of [UCp<sup>\*</sup>(<sup>Mes</sup>PDI<sup>Me</sup>)(thf)] is consistent with a trianionic ligand {<sup>Mes</sup>PDI<sup>Me</sup>}<sup>3-</sup>, and when the U(IV) complex reacts with diazenes, the 4-electron reduction of the strong N=N bonds occurs, affording the uranium(V) *trans*-bis(imido) complexes [UCp<sup>\*</sup>(<sup>Mes</sup>PDI<sup>Me</sup>)(NPh)(NR)] (R = Ph, Tol) (Scheme 8) supported by a neutral {<sup>Mes</sup>PDI<sup>Me</sup>}<sup>0</sup> ligand [53,54]. The phenyl imido compound can also be obtained by the reduction of phenyl azide [48]. The N-U-N angles (av. 154.5(5)<sup>o</sup>) are highly deviated from linearity, most likely due to steric pressure imposed by the Cp<sup>\*</sup> ring. In contrast, when the U(IV) complex [UCp<sup>\*</sup>(<sup>Mes</sup>PDI<sup>Me</sup>)(thf)] was treated with TolN=NTol, the electronic structure changes and a U(VI) *trans*-bis(imido), [UCp<sup>\*</sup>(<sup>Mes</sup>PDI<sup>Me</sup>)(NTol)<sub>2</sub>], bearing a monoanionic pyridine(diimine) radical ligand {<sup>Mes</sup>PDI<sup>Me</sup>}<sup>•-</sup>, is generated [54]. A similar reaction with the *tert*butyl-substituted U(IV) analogue [UCp<sup>\*</sup>(<sup>t</sup>Bu-MesPDI<sup>Me</sup>)(thf)] also led to a U(VI) *trans*-bis(imido) (Scheme 8). These U(VI) bis(imido) complexes display average N-U-N angles of 155.7(5)<sup>o</sup>, which are smaller than the O-U-O angle observed in uranyl(VI) compounds [UCp<sup>\*</sup>O<sub>2</sub>(<sup>R-Mes</sup>PDI<sup>Me</sup>)] (R = H 168.3(2)<sup>o</sup>, *t*Bu 167.4(4)<sup>o</sup>) [59].

**Scheme 8.** Synthesis of U(V/VI) *trans*-bis(imidos) supported by the <sup>R-Mes</sup>PDI<sup>Me</sup> ligand framework (adapted with permission from ref. [48]. Copyright 2022 American Chemical Society).

Oxidation of the metal center in [UCp<sup>\*</sup>(<sup>Mes</sup>PDI<sup>Me</sup>)(NPh)<sub>2</sub>] and of the radical ligand in the U(VI) complex [UCp<sup>\*</sup>(<sup>R-Mes</sup>PDI<sup>Me</sup>)(NTol)<sub>2</sub>] (R = H, *t*Bu) with AgSbF<sub>6</sub> generated the cationic U(VI) bis(imido) complexes [UCp<sup>\*</sup>(<sup>Mes</sup>PDI<sup>Me</sup>)(NPh)<sub>2</sub>][SbF<sub>6</sub>]<sup>+</sup> and [UCp<sup>\*</sup>(<sup>R-Mes</sup>PDI<sup>Me</sup>)(NTol)<sub>2</sub>][SbF<sub>6</sub>]<sup>+</sup>, respectively [48].

In 2014, the Bart group reported the synthesis of the first uranium(VI) tris(imido) complexes also supported by the redox-active framework <sup>Mes</sup>PDI<sup>Me</sup> [47]. The imido complexes, [U(<sup>Mes</sup>PDI<sup>Me</sup>)(NMe)<sub>3</sub>] and [U(<sup>Mes</sup>PDI<sup>Me</sup>)(NAr<sup>iPr2</sup>)<sub>3</sub>], were prepared by treating the uranium(IV) dimer [U(<sup>Mes</sup>PDI<sup>Me</sup>)(thf)]<sub>2</sub>, supported by <sup>Mes</sup>PDI<sup>Me</sup> tetraanions, with 6 equiv. of N<sub>3</sub>Me or N<sub>3</sub>Ar<sup>iPr2</sup>, respectively (Scheme 9) [47,60]. During the electron transfer reactions, the eight electrons stored in both {<sup>Mes</sup>PDI<sup>Me</sup>}<sup>4-</sup> ligands and the four electrons stored in the

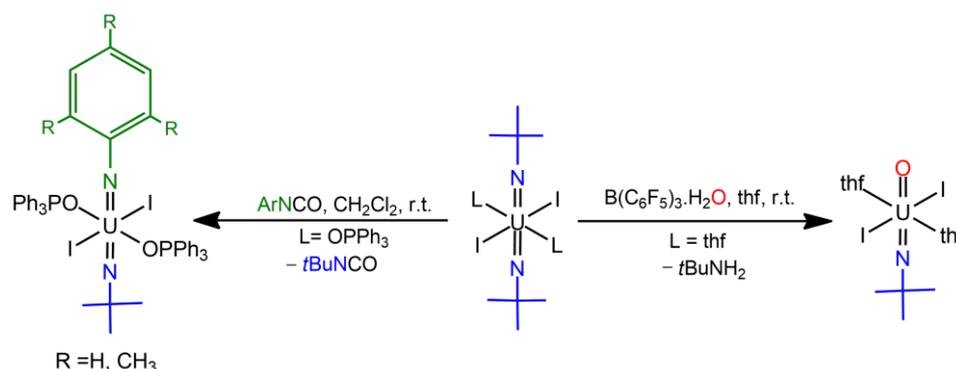
uranium(IV) act as potent reductants for the organic azides. From the reaction of the U(IV) dimer  $[U^{(Mes)PDI^{Me}}I]_2$  and 4 equiv. of  $N_3Mes$ , the U(V) bis(imido)  $[U^{(Mes)PDI^{Me}}I(NMes)_2]$  supported by a  $\{^{Mes}PDI^{Me}\}^0$  ligand was isolated [47]. The molecular structures of the U(VI) tris(imido) complexes exhibit equatorial U–N<sub>imido</sub> bond lengths slightly longer (av. 2.023(6) Å) than the axial U–N<sub>imido</sub> bonds (av. 1.975(20) Å). These observations were suggested by the authors to result from ITI, which was supported by theoretical calculations. The *trans* imidos have small N–U–N angles (167.0(4)°, 168.8(4)°) when compared with those in  $[U(NtBu)_2I_2(thf)_2]$  and  $[U(NPh)_2I_2(THF)_3]$  (Table 1), and the bond lengths are longer than those in the bis(imido) complexes, which can be explained by the equatorial imido ligand competing for uranium orbitals with neighboring axial imidos. DFT calculations and NBO analysis indicated a triple-bond character for the *trans*-U–N<sub>imido</sub> bond, composed of two covalent bonds of predominantly U 5f, U 6d, and N 2p orbitals. Computational studies were also performed to compare the uranium tris(imidos) electronic structures and bonding with the hypothetical tris(oxido) analogue  $[UO_3(^{Mes}PDI^{Me})]$ , revealing less covalent-bond character in the U–N multiple bonds than in the U–oxido bonds in  $UO_3$ , in contrast to that observed in  $\{UO_2\}^{2+}$  versus  $\{U(NR)_2\}^{2+}$  complexes.



**Scheme 9.** Synthesis of uranium(VI) tris(imido) complexes with a *trans*- $\{RNUNR\}^{2+}$  moiety (adapted from refs. [47,60]).

### 3.2. Uranium Oxido—Imido Complexes

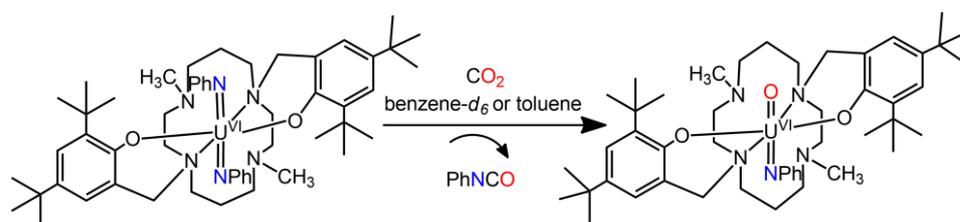
Considering the thermodynamic and kinetic stability of U–O multiple bonds, Spencer et al. expected that the reaction of the U(VI) *trans*-bis(imido)  $[U(NtBu)_2I_2(OPPh_3)_2]$  with aryl isocyanates could involve U=O bond formation and yield oxido imido species. Instead, an imido exchange reaction occurred between alkyl-imido and aryl-imido with the formation of mixed bis(imido) complexes  $[U(NtBu)(NAr)_2(OPPh_3)_2]$  ( $Ar = Ph, Mes$ ) (Scheme 10) [34]. A second equivalent of isocyanate led to the formation of  $[U(NtBu)(NAr)_2(OPPh_3)_2]$ . DFT calculations and  $^{15}N$ -labelling studies showed that the reaction involves  $[2 + 2]$  cycloaddition of the aryl isocyanate C=N bond across the U=N bond; for the formation of the oxido-imido species  $[U(NtBu)(O)_2(OPPh_3)_2]$ , the calculated  $[2 + 2]$  C=O cycloaddition involved the formation of a higher-energy N,O-bound ureate intermediate. Oxido-imido complex  $[U(NtBu)(O)_2(thf)_2]$  can be prepared by selective hydrolysis of one of the imido ligands in  $[U(NtBu)_2I_2(thf)_2]$  with an equimolar quantity of  $B(C_6F_5)_3 \cdot H_2O$  (Scheme 10) [61]. The triphenylphosphane oxide adduct  $[U(NtBu)(O)_2(OPPh_3)_2]$  was obtained by replacement of the thf ligand in toluene. X-ray diffraction analysis complemented with DFT calculations clearly showed that this complex is a uranyl analogue. The U–O<sub>oxido</sub> and U–N<sub>imido</sub> bond lengths are 1.781(4) Å and 1.823(4) Å, respectively, and the N<sub>imido</sub>–U–O<sub>oxido</sub> angle is 178.6(2)°.



**Scheme 10.** Reactivity of U-imido bonds of  $[U(NtBu)_2]^{2+}$  with group transfer reagents (adapted from refs. [34,61]).

Similar to U-O bonds in  $\{UO_2\}^{2+}$  ion and U-N bonds in the U(VI) bis(imido) complex  $[U(NMe)_2I_2(thf)_2]$ , DFT calculations were consistent with a total of four  $\pi$  bonds and two  $\sigma$  bonds in the *trans*- $\{U(NR)(O)\}^{2+}$  fragment [61]. In this complex, the uranium 6p orbital was found to participate in one  $\sigma$  bond with a contribution of 6.5%. The two  $\pi$  bonding orbitals involved in the U-O bond have a larger component of d character, while the U-N bond showed larger uranium f orbital participation. Mulliken population analysis was consistent with an effective total charge of +1.60 for uranium in  $[U(NtBu)(O)I_2(OPPh_3)_2]$ , which is greater than the one calculated for  $[U(NMe)_2I_2(thf)_2]$  (+1.50) [33], suggesting that the U-ligand multiple bonding in  $\{U(NR)(O)\}^{2+}$  is less covalent than in the U(VI) bis(imido).

Maria and co-workers demonstrated that one of the imido ligands of the uranium(VI) *trans*-bis(imido) complex  $[U(\kappa^4\text{-}((tBu)_2ArO)_2Me_2\text{-cylclam})(NPh)_2]$  reacts with excess  $CO_2$  to generate the uranium(VI) *trans*-oxido-imido complex  $[U(\kappa^4\text{-}((tBu)_2ArO)_2Me_2\text{-cylclam})(NPh)(O)]$ , with the release of phenyl isocyanate (Scheme 11) [50]. DFT studies indicated that the reaction proceeds via endergonic formation of a [2 + 2] cycloaddition intermediate, with subsequent exergonic extrusion of phenyl isocyanate and the formation of the U(VI) oxido-imido. Similarly, the reaction of  $[U(\kappa^4\text{-}(((tBu)_2ArO)_2Me_2\text{-cylclam})(NPh)(NTol))]$  with  $CO_2$  gave an equimolar mixture of oxido-imido complexes,  $[U(\kappa^4\text{-}((tBu)_2ArO)_2Me_2\text{-cylclam})(NPh)(O)]$  and  $[U(\kappa^4\text{-}((tBu)_2ArO)_2Me_2\text{-cylclam})(NTol)(O)]$ . These are rare examples of activation and cleavage of  $CO_2$  mediated by uranium(VI) imidos.



**Scheme 11.** Reactivity of  $[U(\kappa^4\text{-}((tBu)_2ArO)_2Me_2\text{-cylclam})(NPh)_2]$  with  $CO_2$  (adapted from ref. [50] with permission from the Royal Society of Chemistry).

This type of reaction was previously observed with U(V) and U(VI) mono-imido complexes to generate uranium(IV/V) mono-oxido complexes [62]. The molecular structure determined for  $[U(\kappa^4\text{-}((tBu)_2ArO)_2Me_2\text{-cylclam})(NPh)(O)]$  exhibits a nearly linear  $\{PhN=U=O\}^{2+}$  fragment ( $O_{oxido}\text{-U-N}_{imido}$  176.4(3) $^\circ$ ) [50], which is comparable with the  $O_{oxido}\text{-U-O}_{oxido}$  bond angle observed for the isoelectronic uranyl(VI) complex,  $[UO_2(\kappa^4\text{-}((tBu)_2ArO)_2Me_2\text{-cylclam})]$  (177.6(3) $^\circ$ ) [61] and slightly less bent than the NR-U-NR angle in  $[U(\kappa^4\text{-}((tBu)_2ArO)_2Me_2\text{-cylclam})(NPh)_2]$  (173.0(1) $^\circ$ ). The U(VI) oxido-imido complex displays a slightly shorter U-N<sub>imido</sub> bond distance (1.879(3) Å) than that of U(VI) *trans*-bis(imido) (av. 1.901(8) Å), and also the linearity of U-N-C<sub>ipso</sub> (154.3(3) $^\circ$ , 2: 156.9(3) $^\circ$ ) increased from the bis(imido) to the oxo-imido complex, likely resulting from a more pronounced ITI in the oxido-imido complex. The U-O<sub>oxido</sub> bond length in the bis(phenolate) cyclam oxido-imido metal complex distance

of 1.787(3) Å is 0.012 Å longer than the U–O<sub>oxido</sub> bonds in the analogous uranyl complex [U(κ<sup>4</sup>-{(tBu<sub>2</sub>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam})(O)<sub>2</sub>] [63].

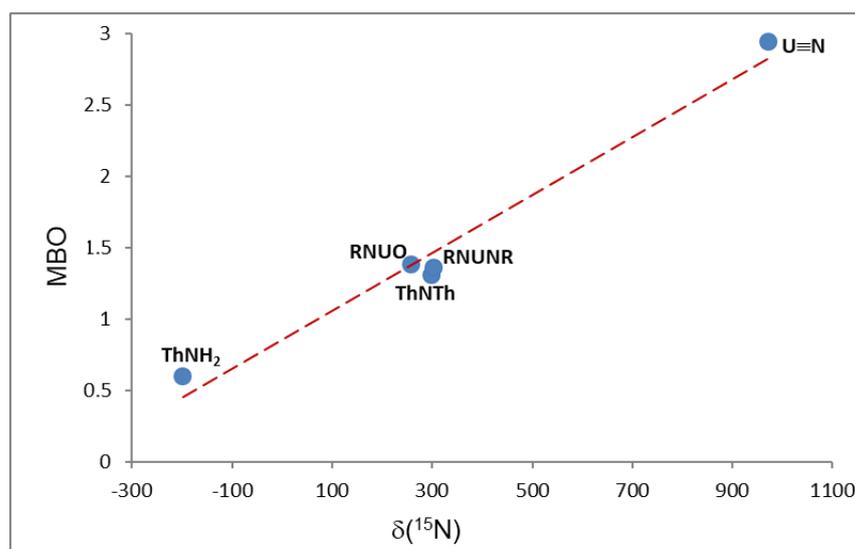
Natural bond orbital (NBO) analysis was used to evaluate covalency in {O=U=O}<sup>2+</sup> and {E=U=NR}<sup>2+</sup> (E = O and NR) fragments of the U(VI) bis(aryloxo) cyclam complexes, through the NBO coefficient λ, which is defined by the ratio of the energetic stabilization (H<sub>UX</sub><sup>2</sup>), which is directly proportional to the overlap integral, and the energy separation of the interacting natural hybrid orbitals (NHOs):

$$\lambda = \frac{H_{UX}^2}{\epsilon_U - \epsilon_X}$$

The mixing parameter λ values indicated greater orbital overlap for U–O<sub>oxido</sub> versus U–N<sub>imido</sub> bonds and more U=NR covalency in the *trans*-oxido-imido complex [U(κ<sup>4</sup>-{(tBu<sub>2</sub>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam})(O)(NPh)] versus *trans*-bis(imido) [U(κ<sup>4</sup>-{(tBu<sub>2</sub>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam})(NPh)<sub>2</sub>] [63]. However, the U–N<sub>imido</sub> covalency in the {PhN=U=O}<sup>2+</sup> complex seems to be driven primarily by quasi-degeneracy of the orbitals involved, whereas that in {PhN=U=NPh}<sup>2+</sup> reflects enhanced orbital overlap. The NBO analysis identified for each axial ligand one σ and two π interactions, suggesting a triple-bond character for the U–N<sub>imido</sub> and U–O<sub>oxido</sub> bonds. The σ NBO and π NBO compositions of the uranium–nitrogen bonds in terms of 5f and 6d contribution are almost identical in both U(VI) imido complexes. The most striking difference is that the U–N σ bonds in the {PhN=U=NPh}<sup>2+</sup> complex, composed of 20% uranium, have 6% more of a 5f orbital contribution than in the {PhN=U=O}<sup>2+</sup> complex.

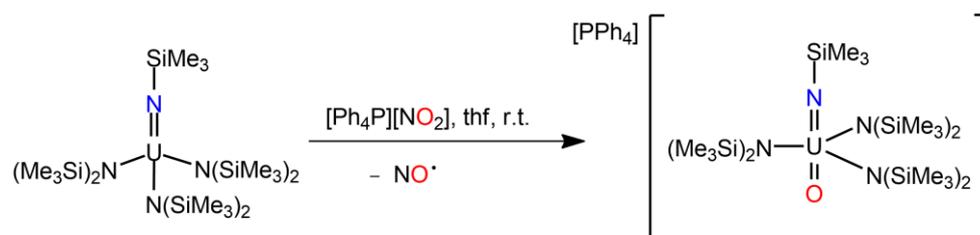
The synthesis of <sup>15</sup>N labeled U(VI) bis(imido) and oxido-imido complexes allowed researchers to, in addition, characterize [U(κ<sup>4</sup>-{(tBu<sub>2</sub>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam})(NPh)<sub>2</sub>] and [U(κ<sup>4</sup>-{(tBu<sub>2</sub>ArO)<sub>2</sub>Me<sub>2</sub>-cyclam})(NPh)(O)] by <sup>15</sup>N NMR spectroscopy [63]. The <sup>15</sup>N chemical shifts observed of 302.4 and 256.7 ppm (ref. CH<sub>3</sub>NO<sub>2</sub>) for the uranium bis(imido) and oxido-imido complex, respectively, are substantially shifted downfield. The calculated and experimental <sup>15</sup>N chemical shifts were in good agreement, displaying the same trend of δ<sub>N</sub> (δ<sub>N</sub> (<sup>15</sup>N-bis(imido)) > δ<sub>N</sub> (<sup>15</sup>N-oxido-imido)), which is consistent with the slightly higher participation of 5f orbitals and greater orbital overlap in the U(VI) bis(imido) complex. <sup>15</sup>N NMR spectroscopy was previously demonstrated by Hayton [64] and Liddle [65] to be a powerful experimental probe of chemical bonding and covalency in An–N bonds since the nitrogen nuclei was revealed to be highly sensitive to interactions with actinide ions. Hayton found a <sup>15</sup>N chemical shift of 298.8 ppm for the bridging thorium(IV) nitride [(NR<sub>2</sub>)<sub>3</sub>Th(μ-<sup>15</sup>N)Th(NR<sub>2</sub>)<sub>3</sub>]<sup>−</sup> (R = SiMe<sub>3</sub>) [64] and Liddle found the most downfield deshielded δ<sub>iso</sub> value to date, 972.6 ppm, for the uranium(VI)-nitride triple bond complex [U(<sup>15</sup>N)(Tren<sup>TIP5</sup>)] [65]. As expected, the nitrogen of the imido groups in the uranium bis(imido) and oxido-imido complexes are more shielded than the nitrogen in the U≡N triple bond of the terminal nitride complex. Combining DFT calculations and <sup>15</sup>N spectroscopy, Hayton correlated the magnitude of the downfield shift with the amount of 5f covalency within the Th–N bonding. As expected, and emphasizing the highly covalent nature, there is a higher dominance of 5f U and 2p N orbitals in the U≡N bonding of U(VI) nitrido complex.

Liddle and co-workers combined their results with already-reported data to confirm correlated linear relationships between <sup>15</sup>N δ<sub>iso</sub> and the M–N bond order. Plotting experimental <sup>15</sup>N NMR chemical shifts together with the actinide data of Hayton and Liddle and correlating with Mayer Bond Order (MBO) of U–N bonds, as proposed by Liddle [65], a fair linear relationship is obtained as depicted in Figure 1.



**Figure 1.** Correlation of experimental  $^{15}\text{N}$  NMR chemical shifts with computed Mayer bond orders. Linear regression:  $\text{MBO} = 0.002 \times \delta(^{15}\text{N}) + 0.8567$ ,  $R^2 = 0.98$ .

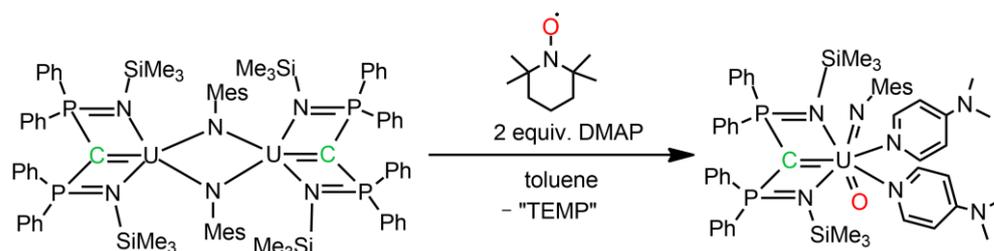
Reactions of lower valence uranium complexes with oxygen transfer reagents were also conducive to the formation of  $\{\text{OUNR}\}^{2+}$  molecular compounds. Schelter and co-workers synthesized the uranium(VI) *trans*-oxido-imido complex  $[\text{Ph}_4\text{P}][\text{U}(\text{O})(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]_3]$  directly by a one-electron reduction of nitrite with the uranium(V) mono-imido complex  $[\text{U}(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]_3]$  (Scheme 12) [66]. This reaction was proposed to proceed through a  $\kappa^1\text{-(ONO)}^-$  intermediate [67]. The oxido-imido complex exhibits short U-O and U-N<sub>imido</sub> lengths, 1.805(2) and 1.980(3) Å, respectively, and nearly linear O-U-N ( $179.8(1)^\circ$ ) and U-N-Si angles ( $176.2(2)^\circ$ ), consistent with an isoelectronic  $\{\text{UO}_2\}^{2+}$  analogue moiety. Voltammetry studies were in accordance with U(VI)/U(V) irreversible reduction at  $-2.34$  V (vs.  $\text{Fe}^+/\text{Fe}^\circ$ ), showing a strong stabilization of the +6 oxidation state, which is reminiscent of  $\{\text{UO}_2\}^{2+}$  complexes.



**Scheme 12.** Synthesis of a *trans*- $\{\text{OUNR}\}^{2+}$  complex supported by silylamido ligands (adapted from ref. [66]).

The authors performed a systematic computational study with the model complexes *cis/trans*  $[\text{UO}_n(\text{NSiMe}_3)_{2-n}[\text{N}(\text{SiH}_3)_2]_3]^-$  to probe the ability of the trimethylsilylimido ligand to stabilize the *trans*-axial geometry [66]. The *trans*- $\text{UO}_2$  geometry was calculated to be  $131.4$   $\text{kJ mol}^{-1}$  more stable than the *cis*- $\text{UO}_2$  configuration, while when one of the oxido ligands was replaced by an imido group, the *trans*- $\{\text{UO}(\text{NSiMe}_3)\}^{2+}$  structure was only  $75.3$   $\text{kJ mol}^{-1}$  more stable than the *cis*- $\{\text{UO}(\text{NSiMe}_3)\}^{2+}$  isomer. Expanding the analysis to  $[\text{UO}(\text{NR})\{\text{N}(\text{SiH}_3)_2\}_3]^-$  complexes ( $\text{R} = \text{SiMe}_3, \text{Ph}, \text{CF}_3$ ), the following trend,  $75.3$   $\text{kJ mol}^{-1}$ ,  $56.5$   $\text{kJ mol}^{-1}$ , and  $63.2$   $\text{kJ mol}^{-1}$ , was obtained for *trans/cis* isomerization, showing the strongest stabilization of the *trans* geometry with the trimethylsilylimido. The U(IV) mono-imido complexes  $[\text{U}(\text{NAr}^{\text{iPr}_2})\text{Cl}_2(\text{L})_n]$  ( $\text{L} = t\text{Bu}_2\text{bpy}$ ,  $n = 1$ ;  $\text{L} = \text{OPPh}_3$ ,  $n = 2$ ), when reacted with the oxygen atom transfer reagent methylmorpholine-N-oxide, led to the formation of U(VI) *trans*-oxido-imido complexes  $[\text{U}(\text{NAr}^{\text{iPr}_2})(\text{O})\text{Cl}_2(\text{L})_n]$  [37].

By treating the uranium(IV) carbene imido complex  $[\{U(\text{BIPM}^{\text{TMS}})(\mu\text{-NMes})\}_2]$  with tetramethylamine-N-oxide (TEMPO), Liddle and co-workers were able to effectively oxidize the U(IV) complex and afford the dimeric U(VI) carbene-imido-oxido complex  $[\{U(\text{BIPM}^{\text{TMS}})(\text{NMes})(\mu\text{-O})_2\}_2]$  [68]. The addition of dimethylamine pyridine (dmap) to this complex resulted in the monomeric carbene-imido-oxido complex  $[U(\text{BIPM}^{\text{TMS}})(\text{NMes})(\text{O})(\text{dmap})]$ . This complex can also be prepared by the one-pot reaction of the U(IV) precursor with TEMPO and dmap (Scheme 13). In the monomeric complex, the oxido and imido ligands adopt axial positions in a T-shaped motif with respect to the carbene. It is worth noting that the imido rather than the carbene is *trans* to the oxido ligand, which can be postulated as a result of an ITI, since the imido ligand can donate electron density most strongly and compensate for the 6p orbital hole [13,69]. The U-O and U-N<sub>imido</sub> bond lengths, 1.814(2) Å and 1.921(2) Å, respectively, are short but longer than the analogous distances in  $[U(\text{N}t\text{Bu})(\text{O})\text{I}_2(\text{OPPh}_3)_2]$  and  $[U(\text{NAr}^{\text{iPr}_2})(\text{O})\text{I}_2(\text{OPPh}_3)_2]$  [37,61]. The U-N-C<sub>ipso</sub> is nearly linear (174.2(2)°); however, the N-U-O angle is slightly distorted from linearity (167.14(9)°), possibly due to the constraints imposed by the pincer carbene ligand (U-C<sub>carbene</sub> 2.400(3) Å). DFT calculations were performed for this complex, suggesting that the uranium center mainly involves 5f rather than 6d orbitals in the multiple bonds to the carbene, imido, and oxido groups, as in other uranium–ligand multiple bond complexes. The frontier orbitals are extensively delocalized across the uranium–carbene, -imido, and -oxido interactions, excluding an assessment of ITI. This is in contrast to the calculations performed for the uranyl complex  $[U(\text{BIPM}^{\text{TMS}})(\text{O})_2(\text{dmap})_2]$  where the orbitals are more localized as discrete U=C or {O=U=O}<sup>2+</sup>, suggesting that the formulation of the U(VI) carbene *trans*-oxido-imido as a uranyl analogue is not adequate.

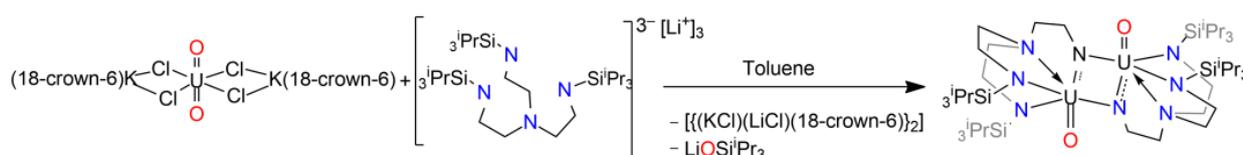


**Scheme 13.** Synthesis of a U(VI) carbene-imido-oxido complex with a *trans*-{OUNR}<sup>2+</sup> moiety (adapted from ref [68]).

In 2001, in an effort to prepare a *cis*-uranyl complex, Burns and co-workers reacted  $[\text{UO}_2(\mu\text{-Cl})_4\{\text{K}(18\text{-crown-6})\}_2]$  with  $\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{But})_3\}^{3-}$  (Tren<sup>DMBS</sup>) and verified that the loss of one *t*BuMe<sub>2</sub>Si and one oxido group per Tren/uranyl occurred, with the reduction and formation of the mixed-valent uranium(V/VI) oxido–imido dimer  $[\{\text{UO}(\mu\text{-NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{But})_2)\}_2][\text{K}(18\text{-crown-6})(\text{Oet}_2)]$  as major product [70]. This reaction involved the cleavage of a N–Si bond of the triamidoamine ligand and the activation of one of the usually robust U=O bonds of the uranyl(VI) fragment. One of the uranyl oxido groups is retained as a terminal ligand *trans* to the imido nitrogen, while the two amido ligands and the other imido donor occupy equatorial coordination positions of the trigonal bipyramid. The bond lengths U–O and U–N<sub>imido</sub> are 1.838(5) Å and 2.097(6) Å, respectively, and the axial O–U–N<sub>imido</sub> angle is significantly deviated from linearity (161.2(2)°).

More recently, Liddle and co-workers explored the same reaction with the related Tren<sup>TIPS</sup> ligand  $\{\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^{\text{iPr}_3})_3\}^{3-}$  (Tren<sup>TIPS</sup>) (Scheme 14), which is more sterically demanding than Tren<sup>DMBS</sup> [71]. The result was very similar to the previous reaction: The loss of a silyl and of oxido group with the generation of a dimeric uranium imido–oxido complex. We note that the uranium oxidation state remained +6, as did the starting material. The X-ray diffraction structure of the dimeric complex  $[\{\text{UO}(\mu\text{-NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^{\text{iPr}_3})_2)\}_2]$  exhibits shorter U–N bond distances (2.052(15)–2.057(14) Å) for the imido nitrogen *trans*

to a uranium–oxido bond, reflecting the presence of an ITI, albeit a weaker one than in uranyl(VI) complexes. The oxido-imido complex suggested a structure-dictating  $\text{RN}=\text{U}=\text{O}$  core as in the uranyl ion,  $\{\text{O}=\text{U}=\text{O}\}^{2+}$ , despite the  $\text{O}=\text{U}=\text{N}_{\text{imido}}$  bond angles (av.  $161.1(6)^\circ$ ) being significantly more bent than the linear geometry reported for other  $\{\text{RNUO}\}^{2+}$  compounds (Table 3). This can be attributed to the conformational constrain imposed by the Tren ligand. DFT calculations found a  $\sigma > \pi$  orbital energy ordering for the  $\text{U}=\text{N}$  and  $\text{U}=\text{O}$  bonds, which is uranyl-like in nature. Moreover, the oxido, imido, and amido ligands average charges ( $-0.77$ ,  $-1.83$ , and  $-1.55$ ) and the Mayer bond orders ( $\text{U}=\text{O}$  1.95,  $\text{U}=\text{N}$  1.21,  $\text{U}-\text{N}_{\text{imido}}$  0.57, and  $\text{U}-\text{N}_{\text{amido}}$  0.88) suggest that the terminal uranium–oxido bonds are likely more covalent in nature than the bridging imido to uranium bonds, consistent with the presence of a “ $\text{RN}=\text{U}=\text{O}$ ” core.



**Scheme 14.** Synthesis of an uranium(VI) oxido-imido complex from activation of uranyl (adapted from ref. [71]).

**Table 3.** Structural parameters of *trans*- $[\text{U}(\text{O})(\text{NR})]^{2+}$  and of selected  $[\text{UO}_2]^{2+}$  complexes.

Compound.	U-N Bond Lengths (Å)	U-O Bond Lengths (Å)	E-U-E Angle (Deg)	U-N-C Angle (Deg)	Ref.
$[\text{U}(\text{N}^t\text{Bu})(\text{O})\text{I}_2(\text{OPPh}_3)_2]$	1.821(7)	1.764(5)	178.4(3)	172.3(7)	[61]
$[\text{U}(\text{N}^t\text{Bu})(\text{O})\text{I}_2(\text{thf})(\text{NH}_2\text{Ph})_2]$	1.823(4)	1.781(4)	178.6(2)	170.4(4)	[61]
$[\text{UO}_2\text{I}_2(\text{OPPh}_3)_3]$	-	1.760(4)	180	-	[72]
$[\text{U}(\text{N}^{\text{ar}^i\text{Pr}^2})(\text{O})\text{I}_2(\text{OPPh}_3)_2]$	1.847(3)	1.778(2)	178.9(1)	170.3(2)	[37]
$[\text{U}(\text{BIPM}^{\text{TMS}})(\text{Nmes})(\text{O})(\text{dmap})_2]$	1.921(2)	1.814(2)	167.1(1)	174.2(2)	[68]
$[\text{U}(\text{BIPM}^{\text{TMS}})(\text{O})_2(\text{dmap})_2]$	-	1.794(2)	167.2(1)	-	[68]
$[\text{U}(\kappa^4\text{-}\{(\text{t}^{\text{Bu}}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})(\text{NPh})(\text{O})]$	1.879(3)	1.787(3)	176.4(3)	156.9(3)	[50]
$[\text{U}(\kappa^4\text{-}\{(\text{t}^{\text{Bu}}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})(\text{O})_2]$	-	1.775(5)	177.6(3)	-	[63]
$[\{\text{UO}(\mu\text{-NCH}_2\text{CH}_2\text{N}\{\text{CH}_2\text{CH}_2\text{NsiPr}^t_3\}_2)_2]$	2.057(14)	1.805(13)	159.9(6)	-	[71]
	2.052(15)	1.811(14)	162.3(6)	-	

### 3.3. Uranium Nitrido Complexes

Until 2010, linear nitrido-substituted isoelectronic analogues of uranyl(V/IV),  $[\text{NUN}]$ ,  $[\text{NUO}]$ ,  $[\text{NUO}]^+$ , and  $[\text{NUNH}]$  had only been prepared in reactions of laser-ablated uranium metal with  $\text{N}_2$  or  $\text{NO}$  in argon or neon matrices and characterized by infrared spectroscopy coupled with computational studies [21,73–75].  $[\text{NUO}]^+$  was also detected in the gas phase by mass spectrometry, produced through sequential ion/molecule reactions starting from  $\text{U}^+$  and  $\text{N}_2\text{O}$ , followed by the reaction of the primary product  $\text{UN}^+$  with  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ , or  $\text{COS}$  [76]. Collision-induced dissociation (CID) experiments and ligand-exchange reactions conducted on the  $[\text{NUO}]^+$  species confirmed it to have N-U-O connectivity.

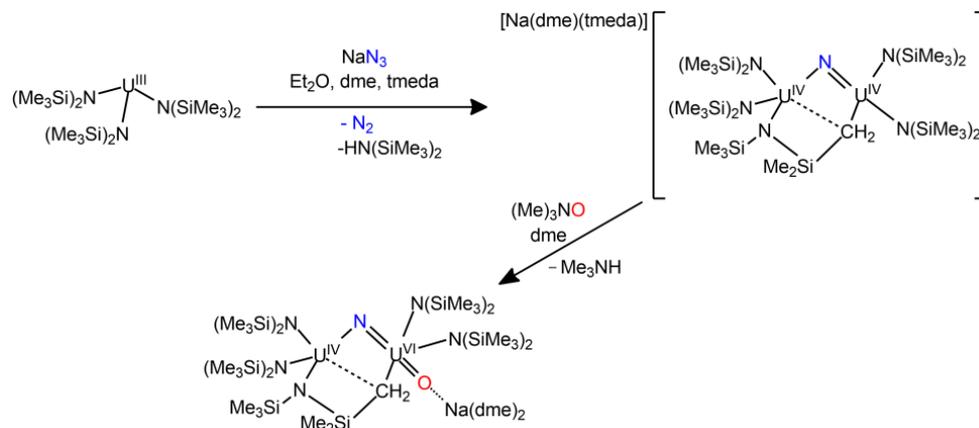
CID of the uranyl anionic complex  $[\text{UO}_2(\text{NCO})\text{Cl}_2]^-$  in a quadrupole ion trap mass spectrometer resulted in the  $[\text{NUOCl}_2]^-$  complex containing the  $\{\text{NUO}\}^{2+}$  fragment [77]. The formation of the nitrido-oxido complex resulted from an endothermic activation of one uranyl oxido bond with the elimination of  $\text{CO}_2$ . The reaction proved to be reversible as the addition of  $\text{CO}_2$  to isolated  $[\text{NUOCl}_2]^-$  led to the exothermic formation of the uranyl anion  $[\text{UO}_2(\text{NCO})\text{Cl}_2]^-$  [78].

Theoretical calculations performed by Schwarz [76] and co-workers and, previously, by Pyykkö [79], predicted similarities between linear  $\{\text{NUO}\}^+$  and the uranyl cation  $\{\text{OUO}\}^{2+}$  from the point of view of their electronic states and the relativistic effects on the U-O and U-N bond lengths. Kaltsoyannis conducted computational studies using quasi-relativistic gradient-corrected DFT in the naked  $[\text{NUN}]$  and  $[\text{NUO}]^+$  species, isoelectronic of the uranyl(VI) cation, inferring that the U-N bonding in  $[\text{NUN}]$  and  $[\text{NUO}]^+$  is significantly

more covalent than the U-O bonding exhibited in  $[\text{UO}_2]^{2+}$  and  $\{\text{NUO}\}^+$  moieties [80]. The author proposed that the greater covalency of the U-N bond may be responsible for the U-N bond distance (1.659 Å) being shorter than the U-O (1.751 Å) in the  $\{\text{NUO}\}^+$  species.

The structure and bonding of  $[\text{NUO}]^+$  was later discussed in other theoretical studies [81,82], and, in 2022, combined with a new gas-phase study [83]. In this work,  $[\text{NUO}]^+$  and its complexes with equatorial  $\text{N}_2$  ligands,  $[\text{NUO}(\text{N}_2)_n]^+$  ( $n = 1-7$ ), were synthesized and examined by mass-selected infrared photo-dissociation spectroscopy and quantum-chemical calculations. The results showed that the  $[\text{NUO}(\text{N}_2)_5]^+$  species is a sterically fully coordinated cation with  $\text{C}_{5v}$  structure, linear  $[\text{NUO}]^+$  core, and singlet ground state. The short N-U bond distances and high stretching modes, with slightly elongated U-O bond distances and lowered stretching modes, are rationalized as being due to cooperative covalent and dative  $[\text{N}\equiv\text{U}\equiv\text{O}]^+$  triple bonds.

In 2010, Hayton and co-workers synthesized the uranium(IV) bridged-nitrido complex  $[\text{Na}(\text{dme})_2(\text{tmeda})][(\text{NR}_2)_2\text{U}(\mu\text{-N})(\text{CH}_2\text{SiMe}_2\text{NR})\text{U}(\text{NR}_2)_2]$  ( $\text{R} = \text{SiMe}_3$ ) from the reaction of the uranium(III) complex  $[\text{U}\{\text{N}(\text{SiMe}_3)_2\}_3]$  with sodium azide [84]. The subsequent reaction with the oxygen transfer reagent trimethylamine N-oxide yielded the U(VI/IV) dimer complex  $[\text{Na}(\text{dme})_2][(\text{NR}_2)_2(\text{O})\text{U}(\mu\text{-N})(\text{CH}_2\text{SiMe}_2\text{NR})\text{U}(\text{NR}_2)_2]$  (Scheme 15), characterized in the solid state. The molecular structure of this U(VI/VI) complex comprises a sodium-capped oxido ligand bonded trans to the nitrido ligand ( $\text{O-U-N } 167.6(3)^\circ$ ), and short U-N<sub>nitrido</sub> (1.818(9) Å) and U-O<sub>oxido</sub> (1.797(7) Å) bond lengths, consistent with a  $\{\text{NUO}\}^+$  fragment, which comes close to the geometrical parameters of the uranyl(VI) ion.

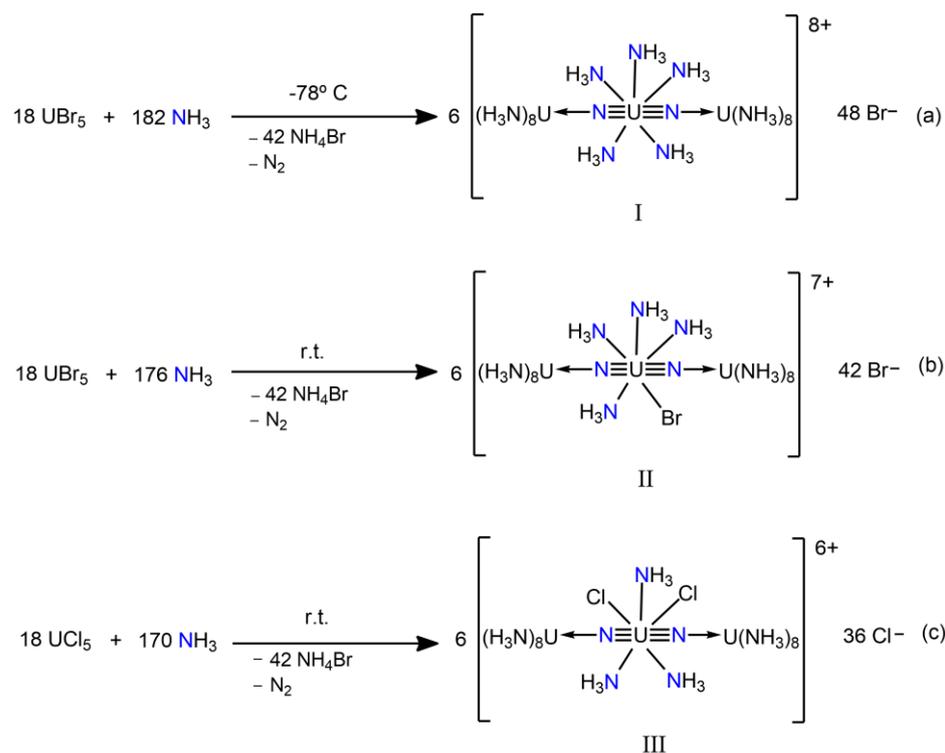


**Scheme 15.** Synthesis of a *trans*- $\{\text{OUN}\}^+$  complex supported by silylamido ligands (adapted with permission from ref. [84]. Copyright 2022 American Chemical Society).

Remarkably, in 2020, Rudel et al. prepared three molecular compounds containing linear  $[\text{N}\equiv\text{U}\equiv\text{N}]$  moieties (Scheme 16) from the reaction of uranium pentahalides,  $\text{UCl}_5$  or  $\text{UBr}_5$ , with anhydrous liquid ammonia. U(VI) nitrites are generated as metastable intermediates in the disproportionation and ammonolysis of the uranium pentahalides [18].

In the crystal structures, the linear  $\{\text{UN}_2\}$  fragments are contained in the center of trinuclear cations  $[\text{U}_3(\mu\text{-N})_2(\text{NH}_3)_{21}]^{8+}$  (I),  $[\text{U}_3\text{Br}(\mu\text{-N})_2(\text{NH}_3)_{20}]^{7+}$  (II), and  $[\text{U}_3\text{Cl}_2(\mu\text{-N})_2(\text{NH}_3)_{19}]^{6+}$  (III), and the central uranium atoms are additionally coordinated by five  $\text{NH}_3$  ligands, four  $\text{NH}_3$  ligands, and one bromide, or three  $\text{NH}_3$  ligands and two chlorides, respectively, resulting in pentagonal bipyramidal coordination geometries. In addition, in the three cations, the  $\{\text{N}\equiv\text{U}\equiv\text{N}\}$  moiety is coordinated through its lone pairs to two Lewis-acidic uranium(IV) amine cations,  $[\text{U}(\text{NH}_3)_8]^{4+}$ , forming nearly linear trinuclear cationic complexes. In cation I, the  $\text{U}_{\text{cent}}\text{-N}_{\text{nitrido}}$  bond lengths (1.853(3) and 1.854(3) Å) are longer than those calculated at the CASPT2 level for molecular  $[\text{N}\equiv\text{U}\equiv\text{N}]$  (1.73 Å) [85], but closer to the terminal  $\text{U}(\text{VI})\equiv\text{N}$  triple bond reported by Liddle and co-workers for  $[\text{U}(\text{N})(\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^i\text{-Pr}^3)_3)]$  (1.799(7) Å) [86]. The  $\text{U}_{\text{ter}}\text{-N}_{\text{nitrido}}$  bond lengths of 2.304(3) and 2.300(3) Å are longer than in single-bonded U(IV) nitrido complexes  $[(\text{Cp}^*\text{U}(\mu\text{-I})_2)_3(\text{N})]$

(2.138(3) to 2.157(3) Å) [87], consistent with less donation of the nitrido ligand to the terminal uranium atoms. The  $\text{N}=\text{U}_{\text{cent}}=\text{N}$  angle is nearly linear ( $179.1(1)^\circ$ ) and  $\text{U}_{\text{cen}}-\text{N}-\text{U}_{\text{ter}}$  angles are close to  $180^\circ$  ( $177.98(14)^\circ$  and  $178.44(17)^\circ$ ). The  $\text{U}_{\text{cen}}-\text{N}_{\text{nitrido}}$  bond distances of compounds II and III are comparable with those of I (II, av. 1.83(4); III, av. 1.84(1) Å), and the {NUN} fragments, as in cation I, are essentially linear with angles of  $178.8(5)^\circ$  and  $177.9(2)^\circ$ , while the  $\text{U}_{\text{ter}}-\text{N}-\text{U}_{\text{cent}}$  angles are slightly deviated from linearity, possibly due to the steric demand of Br and Cl. The Raman spectrum of the  $^{15}\text{N}$  labeled compound  $[\text{U}_3\text{Br}(\mu\text{-N})_2(\text{NH}_3)_{20}]^{7+}$  (II) allowed researchers to assign the band at  $906\text{ cm}^{-1}$  to the  $\text{U}=\text{N}$  stretch vibration of the {N=U=N} unit, which shifted to  $883\text{ cm}^{-1}$  upon  $^{15}\text{N}$  labelling.



**Scheme 16.** Synthesis of uranium complexes featuring a linear {N≡U<sup>VI</sup>≡N} moiety (adapted from ref. [18]).

Hybrid DFT calculations of the uranium nitride cations using intrinsic bond orbitals (IBOs) was consistent with two  $\sigma$ - and four  $\pi$ -bonds for the  $\text{U}_{\text{cent}}-\text{N}_{\text{nitrido}}$ , which led the authors to consider the chemical bonds in the {NUN} fragment as  $\text{U}\equiv\text{N}$  triple bonds, as the  $\text{U}\equiv\text{O}$  bonds in the isoelectronic uranyl(VI) cation,  $\{\text{OUO}\}^{2+}$ . Chemical bonding analysis also demonstrated that the ionic character of the  $\text{U}\equiv\text{E}$  triple bonds ( $\text{E} = \text{N}, \text{O}$ ) increases from  $[\text{UN}_2(\text{NH}_3)_5]$  over cations I, II, and III to free  $\{\text{UO}_2\}^{2+}$  and  $[\text{UO}_2(\text{NH}_3)_5]^{2+}$ , as the contribution of the U atom to the  $\sigma$ - and  $\pi$ -orbitals decreases in this order [18]. The IBO analysis also indicated a  $\text{U}_{\text{ter}}-\text{N}_{\text{nitrido}}$  interaction, similar to the  $\text{U}-\text{NH}_3$  interaction.

The synthesis of the first uranium(VI) trans-bis(nitrido) complexes showed that the uranium-nitrido orbital interactions allow for the isolation of a trans-{NUN} core in molecular compounds, being an inspiration for the design and synthesis of new uranium bis(nitrido) complexes with other ligand environments.

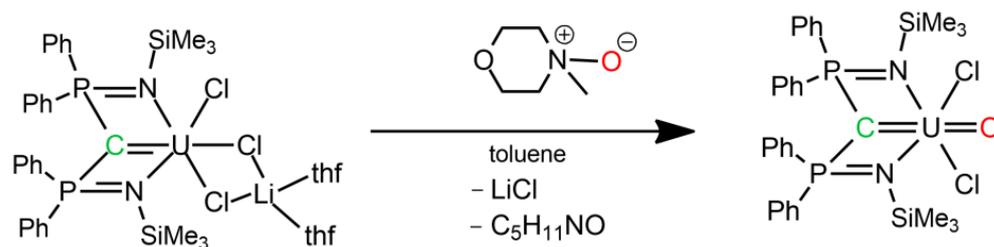
#### 4. Uranium Carbene Complexes

Transition metal carbene (Fischer carbene) and alkylidene (Schrock carbene) complexes are well established for d-transition metals [88–90], but in contrast, the only isolable carbene complexes of uranium are heteroatom stabilized [91], and the formation of uranium alkylidenes and alkylidyne, without the benefit of heteroatom stabilization, is limited to molecules identified in inert gas matrices at low temperatures, such as  $\text{X}_3\text{U}\equiv\text{CH}$  ( $\text{X} = \text{F}$ ,

Cl, Br) and  $\text{H}_2\text{U}=\text{CH}_2$  [92–94], or to the  $[\text{OUCH}]^+$  ion, produced in the gas phase in a linear ion trap mass spectrometer by two-stage CID of  $[\text{UO}_2(\text{O}_2\text{C}-\text{C}\equiv\text{CH})]^+$  yielding the decarboxylation and subsequent elimination of CO [95]. DFT calculations suggested that the generated  $[\text{OUCH}]^+$  complex is a linear uranium-methyldiyne species with a  $\text{U}\equiv\text{C}$  triple bond (1.801 Å), composed of one  $\sigma$ -bond with contributions from U 6d 5f and C sp hybrid orbitals, and two  $\pi$ -bonds with contributions from U 6d 5f and C p orbitals. The  $[\text{OUCH}]^+$  species is converted into  $[\text{UO}_2]^+$  by the reaction with both  $\text{H}_2\text{O}$  and  $\text{O}_2$  [96] and also reacts with  $\text{CH}_3\text{CN}$  and  $\text{CS}_2$  to form  $[\text{OUN}]^+$  and  $[\text{OUS}]^+$ , respectively [96,97].

The uranyl analogues CUO and CUC have also been observed in matrix isolation experiments [98,99]. CASPT2 calculations suggested  $\text{C}\equiv\text{U}\equiv\text{C}$  to have a triplet ground state with a linear geometry, U–C bond lengths of 1.84 Å, and molecular orbital occupancies for an effective bond order of 2.83 [99]. DFT calculations predicted that CUO is preferentially a linear singlet molecule with a U–C triple bond with significant U 5f character [98,100,101]. Though the terminal carbides CUC and CUO are both U(VI) molecules, the U–C in the neutral CUO molecule is slightly shorter (1.764 Å) [98]. This may result, in part, from the slightly higher positive charge on uranium in CUO than in CUC. The bonding in CUO was reexamined by other computational groups [102–104]. Hu et al. theoretical calculations suggested that the U–C bond in CUO has possibly some quadruple bond character, which results from two  $\sigma$  interactions and the expected two  $\pi$  bonds [104].

The shortest U–C distance in an isolated U(VI) complex was found in the uranium(VI)-carbene-oxido complex  $[\text{U}(\text{BIPM}^{\text{TMS}})(\text{O})(\text{Cl})_2]$  (2.184(3) Å) [105]. It was generated by two-electron oxidation of the uranium(IV)-carbene  $[\text{U}(\text{BIPM}^{\text{TMS}})\text{Cl}_3\text{Li}(\text{thf})_2]$  with 4-morpholine-N-oxide (Scheme 17).



**Scheme 17.** Synthesis of a  $\text{trans}\text{-}\{\text{R}_2\text{C}=\text{U}=\text{O}\}^{2+}$  molecular compound (adapted from ref. [105]).

The molecular structure contains a nearly linear CUO linkage ( $175.5(12)^\circ$ ) with the oxido group *trans* to the carbene and a U–O bond length of 1.841(4) Å, which is consistent with the presence of an ITI. These values, combined with a DFT study, confirmed that the uranium oxido-carbene moiety exhibits a uranyl-like electronic structure  $\{\text{R}_2\text{C}=\text{U}=\text{O}\}^{2+}$ . NBO analysis indicated that both the  $\sigma$ - and  $\pi$  components of the U=C double bond are well-defined, with the uranium contribution dominated by 5f character, while in the U–O triple bond, only the  $\pi$ -components are well-defined.

Preliminary reactivity studies of the U(VI) oxido-carbene with benzaldehyde resulted in  $[\text{UO}_2\text{Cl}_2]$  and  $(\text{Me}_3\text{SiNPPPh}_2)_2\text{C}=\text{CHPh}$ , via a formal double bond metathesis. Similar ‘metallo-Wittig’ reactivity has been observed for other uranium carbenes [106].

To date, the carbene analogue of uranyl,  $\text{trans}\text{-}\{\text{H}_2\text{CUCH}_2\}^{2+}$ , has synthetically not been achieved but a comparative analysis of electron densities calculated at the DFT and CASSCF levels of theory with bare  $\{\text{UO}_2\}^{2+}$  and  $\{\text{U}(\text{NH})\}^{2+}$  species, in order to evaluate the ITI, were performed by Fryer-Kanssen and Kerridge [107]. The study showed that the effect of ITI on the electronic structure is most pronounced in uranyl, as expected, consistent with the strong polarizing ability of the oxido ligands comparatively with imido and carbene ligands. The key role of the  $6p_\sigma$  interactions in the ITI previously suggested by Denning is supported by this study.

## 5. Uranium-Transition Metal Complexes

Gagliardi and Pyykkö predicted theoretically stable 5d metal-uranium-nitrido species,  $[\text{NUOs}]^-$ ,  $[\text{NUIr}]$ ,  $[\text{NUPt}]^+$ , and  $[\text{NUAu}]^{2+}$ , as well the oxido species  $[\text{IrUO}]^+$ , and considered them isoelectronic analogues to uranyl(VI) [108]. In accordance with the concept of “autogenic isolobality” [109,110], Au can behave as a pseudohalogen, Pt as a pseudo-chalcogen, and Ir as a pseudopnictogen. Considering this,  $[\text{IrUO}]^+$  can be formally represented as  $[\text{Ir}\equiv\text{U}=\text{O}]^+$ , which is nominally isoelectronic with  $[\text{N}\equiv\text{U}=\text{O}]^+$  and, therefore, isoelectronic of  $\{\text{O}=\text{U}=\text{O}\}^{2+}$ . Later, Marçalo, Gibson and co-workers were able to generate  $[\text{IrUO}]^+$  by direct laser ionization of a U/Ir alloy and oxidation of the formed  $\text{UIr}^+$  ions with  $\text{N}_2\text{O}$  or  $\text{C}_2\text{H}_4\text{O}$  [111].  $\text{UPt}^+$  ions obtained using the same method also reacted with  $\text{N}_2\text{O}$  to give  $[\text{OUPt}]^+$  that could be considered isoelectronic of  $\{\text{OUS}\}^+$  and an analogue of uranyl(V),  $\{\text{OUO}\}^+$ . In 2021, Peterson and co-workers computed Pt-actinide bond dissociation energies in  $\{\text{Pt-AnO}\}^{n+}$  ( $n = 1+, 2+$ ; An = U, Np, Pu) using a composite coupled cluster approach and determined a value of  $534.13 \text{ kJ mol}^{-1}$  for the  $[\text{PtUO}]^+$  species previously isolated in the gas phase [112].

In 2001, the cationic species  $[\text{OUFe}(\text{CO})_3]^+$  was generated in the gas phase in a FTICR mass spectrometer, by reacting the uranium oxide cation  $\text{UO}^+$  with  $\text{Fe}(\text{CO})_5$  [113]. Recently, Zhou and co-workers used a laser-vaporization supersonic ion source to produce the anions  $[\text{UFe}(\text{CO})_5]^-$  and  $[\text{OUFe}(\text{CO})_3]^-$  in the gas phase, characterized by infrared photo dissociation spectroscopy [114]. Quantum chemical studies were consistent with a uranium-iron triple bond, one covalent  $\sigma$  bond and two Fe-to-U dative  $\pi$  bonds, and a formal charge of 2- for iron. Based on these recent results, it is plausible that the  $[\text{OUFe}(\text{CO})_3]^+$  cation previously identified is formally “ $\{\text{O}=\text{U}=\text{Fe}(\text{CO})_3\}^+$ ”, an analogue of  $\{\text{UO}_2\}^+$ ; however, theoretical calculations on this species are needed for confirmation.

The preparation of U-metal bonds is not only important for improving the understanding of bonding between uranium and transition metal cations, but also for increasing the applications of uranium in catalysis using the synergetic effect of two metals [115]. The 5f orbitals have a suitable spatial extension but not yet a predictability of participation in bonding, making the d-f heterobimetallic bond a particularly attractive target to improve our understanding of the relative involvement of f- orbitals. Compared to uranium-oxygen, -nitrogen, and -carbon multiple bonds, the use of metal-based fragments as ligands under conventional experimental conditions is underdeveloped, and isolable uranyl analogues are yet to be prepared [115,116].

## 6. Conclusions and Outlook

Uranyl analogue complexes are a particular class of uranium-ligand multiple-bond molecular compounds and there has been significant progress in isolating and characterizing them. The majority of complexes reported containing a linear  $\{\text{E}=\text{U}=\text{E}\}^{n+}$  core isoelectronic to  $\{\text{OUO}\}^{n+}$  are those with imido ligands,  $\{\text{RN}\}^{2-}$ , in the axial positions. However, among many of the results described in this review are also the few but remarkable molecular compounds comprising *trans*- $\{\text{OUNR}\}^{2+}$ , *trans*- $\{\text{NUO}\}^+$ , *trans*- $\{\text{R}_2\text{CUO}\}^{2+}$  moieties, and the heavy chalcogenido-substituted analogues of uranyl, *trans*- $\{\text{OUE}\}^{2+}$  (E = S, Se). Another significant result is the isolation in 2020 of the first *trans*- $\{\text{NUN}\}$  nitrido compounds that had only been prepared in noble gas matrices.

A variety of supporting ligands have been used to stabilize the linear *trans*- $\{\text{E}=\text{U}=\text{E}\}^{n+}$  moiety; however, it should be noted that the classic, bulky silylamido ligand  $\{\text{N}(\text{SiMe}_3)_2\}^-$  is, to date, the one that allowed for isolating a uranyl complex and the diversity of its analogues, namely U(VI) oxido-imido, bis(imido), oxido-nitrido, and mono-chalcogenido-substituted analogues of uranyl. The reactions to access these compounds have mainly been electron-transfer reactions starting from low-valence uranium.

Diverse computational studies have been performed on many of these classes of compounds, with general findings being that uranium 5f and 6d orbitals participate highly in the  $\{\text{EUE}\}$  fragment bonding and that the U-E bonds have a triple-bond character but are rarely true triple bonds that could be implied by their structures. Moreover, as in

uranyl complexes, the inverse *trans* influence (ITI) is manifested in uranyl analogues, and theoretical calculations suggest that the pseudocore 6p shell plays a role in this effect and consequently in the preference for a *trans*-{EUE}<sup>n+</sup> conformation.

In light of the isolated complexes identified to date, it seems plausible that bis(chalcogenido) complexes in a *trans*-{E=U=E}<sup>n+</sup> framework may be isolable. The lack of these uranium derivatives can be traced to the sensitivity of these multiple-bond molecular compounds to steric effects imposed by the ligand environment at the metal atom, which makes the choice of supporting ligands fundamental. For instance, some uranium bis(imido) complexes mentioned in this review could be considered as candidate precursors for {S=U=S}<sup>2+</sup> molecular species in reactions with favorable S-donor COS.

Similar to heavy chalcogenido complexes, the heavy pnictogenido analogues of uranyl are attractive targets for studying uranium bonding to soft donors, and due to the recent advances in U-P multiple bonds, it also seems a plausible goal.

**Author Contributions:** Both authors contributed to the conceptualization, writing, and review. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors acknowledge the financial support from the Fundação para a Ciência e a Tecnologia (FCT—Portugal) through projects UIDB/00100/2020 (CQE) and LA/P/0056/2020 (IMS). L.M. thanks FCT for the contract IST-ID/091/2018.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

## Abbreviations

Ad.	adamantyl
Ar <sup>CF3</sup>	3,5-Bis(trifluoromethyl)phenyl
Ar <sup>iPr2</sup>	2,6-diisopropylphenyl
bpy	2,2'-bipyridine
{BIPM <sup>TMS</sup> } <sup>2-</sup>	bis-iminophosphoranomethanediide
dmap	4-dimethylaminopyridine
dme	1,2-dimethoxy-ethane
dmpe	1,2-Bis(dimethylphosphino)ethane
dpm	5,5'-dimethylpyrrolylmethane
dpm <sup>Mes</sup>	2,2'-bis(mesityl)-5,5-dimethyldipyrrolylmethane
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Me <sub>2</sub> -C <sub>4</sub> H <sub>2</sub> N	2,5-dimethylpyrrolyl
Me	methyl
Mes	2,4,6-trimethylphenyl
Me <sub>2</sub> bpy	4,4'-dimethyl-2,2'-bipyridine
py	pyridine
{N(Me)(SO <sub>2</sub> Ar')}	N,4-dimethylbenzenesulfonamido
OPPh <sub>3</sub>	triphenylphosphane oxide
<i>t</i> Bubpy	4,4'-di-tert-butyl-2,2'-bipyridine
TEMPO	tetramethylamine-N-oxide
thf	tetrahydrofuran

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