Uranium Complexes

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The Renaissance of Non-Aqueous Uranium Chemistry

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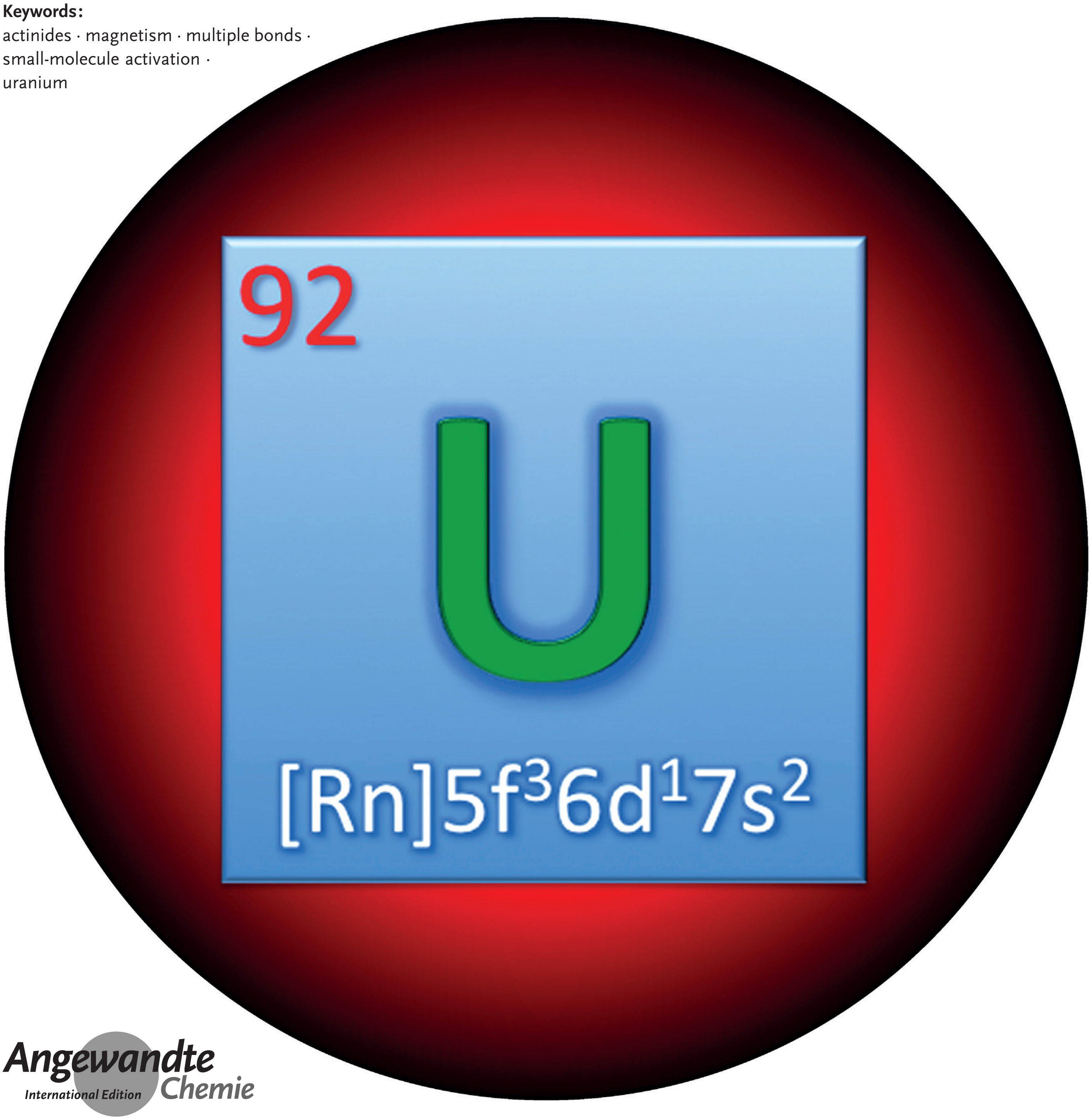

Prior to the year 2000, non-aqueous uranium chemistry mainly involved metallocene and classical alkyl, amide, or alkoxide compounds as well as established carbene, imido, and oxo derivatives. Since then, there has been a resurgence of the area, and dramatic developments of supporting ligands and multiply bonded ligand types, small-molecule activation, and magnetism have been reported. This Review 1) introduces the reader to some of the specialist theories of the area, 2) covers all-important starting materials, 3) surveys contemporary ligand classes installed at uranium, including alkyl, aryl, arene, carbene, amide, imide, nitride, alkoxide, aryloxide, and oxo compounds, 4) describes advances in the area of single-molecule magnetism, and 5) summarizes the coordination and activation of small molecules, including carbon monoxide, carbon dioxide, nitric oxide, dinitrogen, white phosphorus, and alkanes.

From the Contents

1. Introduction

Ever since the Manhattan Project, which sought to identify volatile compounds for the separation of fissionable isotopes for nuclear applications, there has been significant interest in actinide chemistry.[1] In a nuclear age, it is critical to understand the fundamental chemistry and speciation of actinides because of the potential scientific and societal implications for processing nuclear fuels and weapons and radioactive-waste clean-up.[2] Given its prominent role in these technologies and because it is one of the more amenable actinides to investigate, uranium is one of the most intensively researched actinide elements.[3] For many years, the majority of studies have involved aqueous systems of direct relevance to nuclear fuel processes. However, under these conditions, systems are operating at, or close to, thermodynamic sinks (e.g., uranyl) or can only be supported by water-compatible ligands. Under non-aqueous conditions, such restrictions are relaxed, giving opportunities to prepare uranium complexes that would not normally exist and thus gain glimpses of the "hidden" and "true" character of uranium.[4] Researching non-aqueous systems, which we define as complexes prepared in anhydrous organic solvents, permits the study of novel uranium–ligand bonds and their reactivity. This in turn enables us to address fundamental questions regarding the extent and nature (5f vs. 6d) of covalency in uranium chemical bonding and how it impacts reactivity and physicochemical properties. This knowledge could impact on waste remediation where a key approach to minimize the volume of radioactive waste, and recycle useful components, involves separation technologies; these aim to deploy ligands that exploit the different levels of covalency in the chemical bonding of the myriad of elements that are present in radioactive waste.[5]

Understanding the electronic structure of uranium complexes could impact on a number of areas aside from waste remediation. For example, the magnetism of uranium is complex and only partly understood, and novel phenomena, such as single-molecule magnetism, have been discovered. The rich redox chemistry of uranium gives unique opportunities for small-molecule activation. Also, the isolation of novel complexes provides opportunities to test theoretical models. Historically, the chemistry of the actinides was underdeveloped compared to the rest of the periodic table, as common d-block metal complexes, such as those featuring alkylidenes, carbynes, or terminal nitrides, are still, or until very recently were, unknown for uranium. Early work predominantly involved metallocene derivatives, and established the chemistry of uranium complexes with first-row-based multiply bonded ligands and their static magnetism. In recent years, the renaissance of the area has seen dramatic developments of supporting ligands and post-first-row complexes with multiply bonded ligands and in small-molecule activation and dynamic magnetism. Aside from the synthetic challenges in this area, the historical lag is due to a relatively low level of research activity because of the difficulty in sourcing suitable uranium starting materials, and real, or perceived, safety constraints. Furthermore, a significant factor has undoubtedly been the negative image of uranium from its association with nuclear weapons. However, as early as 1909, in the original Haber–Bosch patent, the chemical potential of uranium was revealed as it is a better promoter for ammonia formation than iron.[6] Therefore, from a chemical perspective, uranium is an exciting element to work with. There are certainly still entry barriers to working with this intriguing element, but a number of research groups now routinely work in this area, and with modern synthetic methods and ever better analytical techniques, the area has blossomed in recent years. This is evidenced by the fact that nearly half of all uranium entries in the Cambridge Structural Database have been added within the last decade.[7]

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On the topic of safety, ^{238}U, the principal uranium isotope in depleted uranium, is a relatively weak α-emitter, and with a half life of approximately 4.47×10^9 years, most research labs can be configured for this chemistry without needing the specialist equipment required for the more hazardous transuranics, which require national facilities. The use of depleted, as opposed to natural-abundance, uranium is particularly appealing because not only is the ^{235}U content reduced (0.2 % compared to 0.7 % in natural-abundance U), but its use in research finds utility for a "waste" by-product of uranium isotope enrichment. So long as diligent monitoring is established, material use logged, containment of materials ensured, disposal managed, and safety protocols and assessments are implemented, then non-aqueous uranium chemistry can be routinely conducted on multigram scales.

Reflecting the burgeoning nature of the area after progress in the 1960s and 1970s,[8,11] in the past three decades, a growing number of excellent review articles have been published.[12–32] Given that many areas (e.g., cyclopentadienyl, amide, alkoxide, and halide complexes, metal–ligand multiple bonding, metal–metal bonding, pentavalent uranium, uranyl, small-molecule activation, magnetism, catalysis) have already been described in comprehensive detail elsewhere, this Review adopts a different approach. Many readers may not be familiar with some of the specialist theories of uranium chemistry, so this Review describes pertinent aspects to provide a context for those new to the area before describing all-important starting materials. Some key ligand types of non-aqueous uranium chemistry are then described followed by aspects of single-molecule magnetism and small-molecule activation. In line with the criteria for review articles, a critical selection, rather than a complete literature survey, is presented, and discussions are limited to crystallographically authenticated compounds. The chemistry of uranium clusters, extended lattices in the solid state, and ionic liquids is beyond the scope of this Review.[33,34] An extended discussion of uranyl chemistry, which represents a class in its own right, is also beyond the remit of this Review.

The following abbreviations are used throughout: Ad = adamantyl, bipy = 2,2′-bipyridine, dbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene, COT = cyclooctatetrylene, Dipp = 2,6-diisopropylphenyl, Ditb = 2,6-di-*tert*-butylphenyl, dmap = 4-dimethylaminopyridine, DME = 1,2-dimethoxyethane, Mes = 2,4,6-trimethylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl, OTf = triflate, Py = pyridine, tacn = triazacyclononane, THF = tetrahydrofuran, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, SMM = single-molecule magnet, TMS = trimethylsilyl, Tol = *para*-tolyl, Xy = 3,5-dimethylphenyl, 12C4 = 12-crown-4 ether, 15C5 = 15-crown-5 ether, B15C5 = benzo-15-crown-5 ether, 18C6 = 18-crown-6 ether.

Stephen T. Liddle was born in Sunderland in the North East of England in 1974. He obtained his B.Sc. (Hons) in 1997 and his Ph.D. in 2000, both from Newcastle University, with Prof. Clegg. After postdoctoral fellowships at the Universities of Edinburgh, Newcastle, and Nottingham, he took up a Royal Society University Research Fellowship at Nottingham where he is currently a Professor of Inorganic Chemistry. His research interests include metal–ligand multiple bonding, metal–metal bonds, small-molecule activation, and single-molecule magnetism of the f block elements, with a particular focus on uranium.

2. Periodicity and Physicochemical Properties

Uranium was first isolated from pitchblende by Klaproth in 1789 and was named after the planet Uranus, which had been discovered by Herschel in 1781. As the first f element to be isolated, uranium was an anomaly for some time, especially considering that the structure of the periodic table was yet to be determined. Indeed, for some time, uranium was erroneously classified as a transition metal, owing to its pseudo-isovalence to Group 6 metals, until Seaborg recognized the existence of the 5f series, thus providing element 92 with its rightful place in the periodic table. However, it should be noted that uranium exhibits something of a "Dr. Jekyll and Mr. Hyde" character,[26c] not only in terms of the incongruous dichotomy of nuclear power and weapon applications, but also considering that in some scenarios, uranium behaves like transition metals but in others more like a lanthanide; therefore, it is not surprising that uranium was originally misclassified. The following Sections describe some of the fundamental aspects of uranium chemistry that should be appreciated when contextualizing later Sections.

2.1. Periodicity

With the principal quantum numbers $n = 5$, $l = 3$, $m_l = \pm 3$, ± 2, ± 1, and 0 (and for completeness $m_s = \pm {}^1\!/_2$), the seven 5f orbitals have a large angular momentum. The projection of these orbitals is not as straightforward as that of the standard d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz}, and d_{yz} orbitals for transition metals as there are the cubic (f_{z^3}, f_{y^3}, f_{x^3}, f_{xyz}, $f_{z(x^2-y^2)}$, $f_{y(z^2-x^2)}$, and $f_{x(y^2-z^2)}$) and general (f_{z^3}, f_{xz^2}, f_{yz^2}, f_{xyz}, $f_{z(x^2-y^2)}$, $f_{x(x^2-3y^2)}$, and $f_{y(3x^2-y^2)}$) representations. As cubic symmetry is not so common in molecular uranium chemistry, the general set is generally most appropriate (Figure 1). The notable difference to the 4f orbitals is the presence of an additional radial node owing to the *n*-*l*-1 rule (total number of angular and radial nodes = *n*-1); this affects the pull that the 5f orbitals "feel" from the effective nuclear charge, which becomes important in the context of oxidation states and covalency.

2.2. Relativistic Effects, Oxidation States, and Standard Potentials

At this point, a discussion of relativistic effects is warranted. In principle, relativistic effects affect all elements in the periodic table, but in practice, the effects are negligible for light elements. However, from around platinum onwards, relativistic effects begin to have tangible effects, such as the preference for linear coordination geometries in gold com-

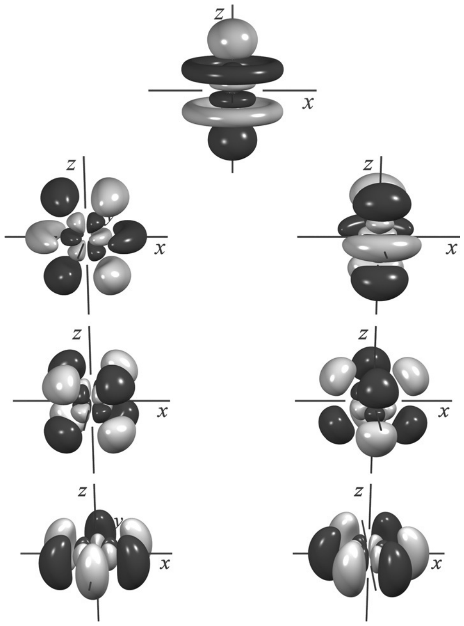


Figure 1. The seven 5f orbitals in the general setting. From top to bottom and left to right, they are: f_{z^3}, f_{xz^2}, f_{yz^2}, f_{xyz}, $f_{z(x^2-3y^2)}$, $f_{x(x^2-3y^2)}$, and $f_{y(3x^2-y^2)}$. Reproduced with kind permission of Prof. Mark Winter (University of Sheffield).

plexes. Einstein's special theory of relativity states that objects moving towards the speed of light gain mass because of the equivalence of kinetic energy and mass according to $E = mc^2$. Thus:

$$m = m_0 / \sqrt{(1 - (v/c)^2)}$$

where m_0 is the rest mass, v the velocity, and c the speed of light.

In atomic units, the average radial velocity $<v_{\mathrm{rad}}>$ of a 1s electron is approximately Z, so for uranium:

$$< v_{\mathrm{rad}} > /c = 92/137 = 0.67$$

where c is expressed in atomic units, hence the supposed limit of 137 for element atomic numbers.

Therefore, the mass increase amounts to:

$$m = m_{\mathrm{electron}} / \sqrt{(1 - (0.67)^2)} = 1.35\, m_{\mathrm{electron}}$$

Thus, because the electron is travelling at an appreciable fraction of the speed of light, the relativistic mass of the electron increases, and the 1s orbital contracts, as do all other s functions. A similar effect occurs for the p orbitals, and this phenomenon is known as the direct relativistic orbital contraction. A consequence of this is that the d and f orbitals are more greatly shielded from the effective nuclear charge than they would otherwise be, and so they undergo radial expansion; this is known as the indirect relativistic orbital expansion. The heavier the element, the greater the effect, such that by uranium, these effects are physically significant. Thus, the 5f orbitals extend out from the atomic core into the valence region, an effect that can be clearly seen in the radial distribution plots (Figure 2). This phenomenon lies behind the increased covalency of the 5f orbitals compared to the 4f orbitals, owing to a better overlap with ligand frontier orbitals; this underpins the ongoing debate over the levels of covalency (from electrostatic to covalent) that uranium exhibits compared to the lanthanides and transition metals.

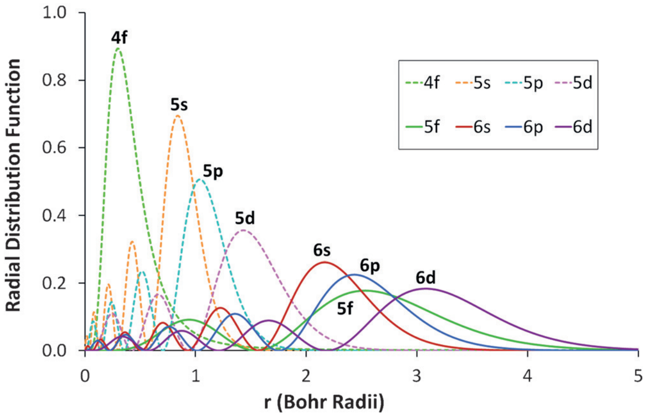
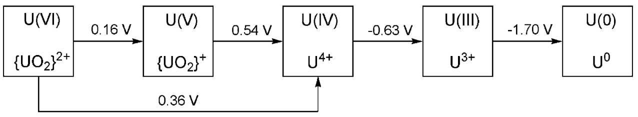


Figure 2. Illustrative radial distribution functions for 4f, 5s, 5p, 5d, 5f, 6s, 6p, and 6d atomic orbitals.

Relativistic effects, and the concomitant radial extension of the 5f orbitals, are also responsible for the range of easily accessible uranium oxidation states (+3 to +6); this behavior is typically characteristic of transition metals, whereas transuranics, with 5f orbitals that become increasingly "core-like" with increasing Z, increasingly favor the +3 oxidation state like the lanthanides. An illustration of the profound effect that relativistic effects have is that a non-relativistic calculation yields a binding energy of approximately 1665 kJ mol^{-1} for a 5f electron to uranium, but when relativistic effects are included, the binding energy is essentially halved to 869 kJ mol^{-1}.[4] Therefore, ionization, and a greater number of accessible oxidation states, is easier to achieve in a relativistic regime. It should be noted that some uranium oxidation states are more common than others. For example, uranium(III) may disproportionate into 0.75 equivalents of uranium(IV) and 0.25 equivalents of uranium(0). Uranium(III) is strongly reducing and can reduce substrates with low-lying π-systems to produce uranium(IV) complexes, whereas uranium(V) and (VI) can be very oxidizing. Uranium(V) is often unstable with respect to disproportionation to uranium(IV) and uranium(VI) and must be kinetically stabilized. Overall, uranium(IV) and uranium(VI) are the most common oxidation states, with the latter most prevalent in the uranyl dication $\{UO_2\}^{2+}$. This is all consistent with the 5f standard reduction potentials for uranium (Scheme 1).[35]

Thus far the discussion has focused on the 5f orbitals, but the 6d orbitals also merit consideration. At the start of the actinide series, the 5f orbitals are higher in energy than the 6d orbitals, but as the series is transversed, the 5f orbitals fall in energy and become increasingly core-like (see the small concentration of electron density close to the nucleus in



Scheme 1. Formal reduction potentials of uranium (in V vs. SHE in 1 M $HClO_4$ at 298 K).

Figure 2). At the same time, the 6d orbitals rise in energy. One consequence of the relativistic effects is that the valence orbitals of uranium are compressed into a tighter energetic range than they would otherwise be (Figure 3a).[36] As the 5f and 6d orbitals start in relatively close proximity (ca. 1.5 eV), and the former fall in energy and whereas the latter rise, at some point, they cross over. It so happens that the cross-over point occurs at uranium (Δ 5f/6d ≈ 300 cm^{-1}),[37] which is demonstrated by the calculated frontier orbitals of Cp_3An (An = Th, Pa, U, Np, Pu) shown in Figure 3b.[38] This provides uranium with a unique capacity to potentially hybridize 5f and 6d orbitals.

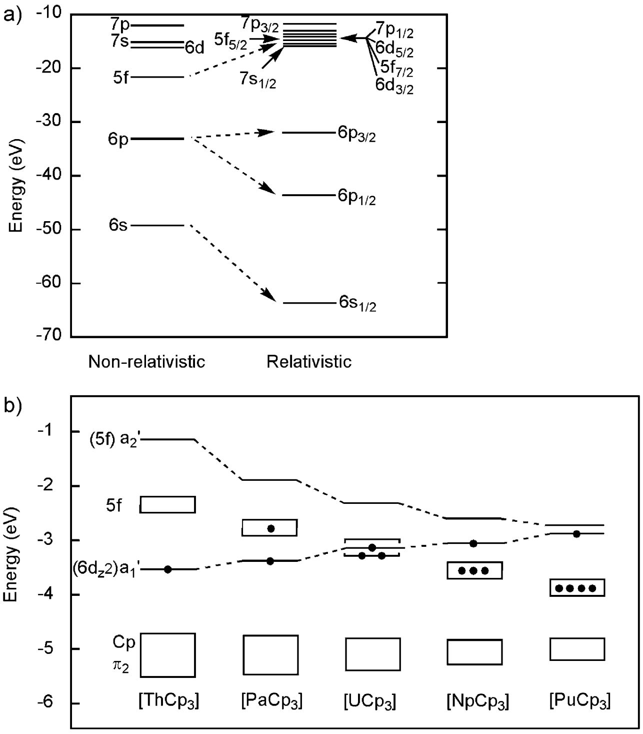
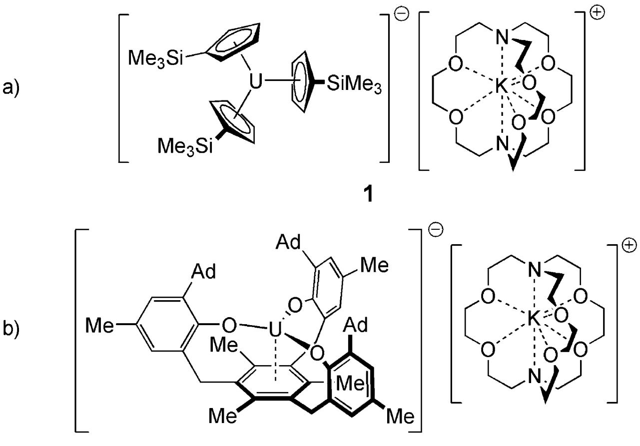


Figure 3. a) Variation of the uranium frontier orbital energies with and without relativistic effects; the latter incorporates spin–orbit coupling. Adapted from the *Handbook of Nuclear Chemistry*, *Vol. 2*, Dordrecht, **2003**. b) Variation of metal-based frontier orbital energies for the 5f^{n-1}6d^1 electron configurations of Cp_3An (An = Th, Pa, U, Np, Pu); the frontier electrons are shown as black dots. Adapted from Bursten et al., *J. Am. Chem. Soc.* **1989**, *111*, 2756.

It should be noted that the accessibility of oxidation states and the energetic separation of the 5f and 6d orbitals can be greatly affected by the ligand environment. For example, until recently there were no molecular examples of uranium(II). Starting with an electronic configuration of [Rn]5f^{3}6d^{1}7s^2, uranium would be expected to easily be ionized to form [Rn]5f^3 uranium(III) whereas [Rn]5f^{3}6d^1 uranium(II) would be expected to be difficult to achieve. However, recent experimental studies carried out at −45 °C yielded the uranium(II) complex [$U(\eta^5\text{-}C_5H_4SiMe_3)_3$][K(2,2,2-crypt)] (**1**; Figure 4a), and the characterization data are consistent with a [Rn]5f^{3}6d^1 ground state.[39] A demonstration that the ligand environment is key to the nature of the ground state was provided soon afterwards in another low-temperature study that yielded the uranium(II) complex [U{$\eta^6\text{-}C_6Me_3(CH_2C_6H_2$-3-Me-5-Ad-6-O$)_3$}][K(2,2,2-crypt)] (**2**), which is supported by δ-backbonding (Figure 4b).[40] Interestingly, for this complex, the characterization data are consistent with a [Rn]5f^4 ground state. These two landmark complexes demonstrate how ligand design is crucial to stabilizing novel structural motifs and controlling the electronic structure of uranium.



1

2

Figure 4. Landmark uranium(II) complexes. a) Structure of **1**. b) Structure of **2**.

2.3. Spin–Orbit, Russell–Saunders (LS), and j–j Coupling

Like relativistic effects, spin–orbit coupling affects all elements, but these effects are more pronounced for heavy elements. For the d block, spin–orbit coupling is relatively small (ca. 200 cm^{-1}), and crystal-field effects dominate instead ($\Delta_o \approx 15000\text{–}25000$ cm^{-1}). The orbital angular momentum (L) is thus often quenched, leaving the spin angular momentum (S). For the lanthanides, crystal-field effects are small (ca. 100 cm^{-1}), spin–orbit coupling is becoming significant (ca. 1000 cm^{-1}), but inter-electronic repulsions dominate. In contrast, for uranium, crystal-field effects are appreciable (ca. 1000 cm^{-1}) and inter-electronic repulsion is still greatest, but spin–orbit coupling is now also relatively large (ca. 2000 cm^{-1}). Therefore, for uranium, the coupling of S with L to give the quantum number J, the total atomic angular momentum, must be considered.

There are two principal ways of considering the construction of J. LS, or Russell–Saunders, coupling can be used in systems where spin–orbit coupling is relatively weak compared to inter-electronic repulsion. Two assumptions are then made. First, all electron spins couple amongst themselves to generate S; second, all electron orbital momenta couple amongst themselves to give L. S and L then couple together to give J. This gives rise to term symbols $^{(2S+1)}L_J$, which are $^5I_4$, $^4I_{9/2}$, $^3H_4$, $^2F_{5/2}$, and $^1S_0$ for uranium(II) (assuming [Rn]5f^4 not [Rn]5f^{3}6d^1), uranium(III) ([Rn]5f^3), uranium(IV) ([Rn]5f^2), uranium(V) ([Rn]5f^1), and uranium(VI) ([Rn]), respectively. This method assumes that the ground state is well separated from the excited states, that is, there is no mixing of J levels. The alternative method is j–j coupling. This method is applicable when the spin–orbit coupling is strong in relation to the inter-electronic repulsion. In this scheme, the spin angular and orbital angular momenta combine to give a total angular momentum for each individual electron, j. The individual j values are then coupled to give J. However, for uranium, it is not straightforward to use the LS or j–j coupling schemes because uranium sits in between the assumptions that underpin each approach. Furthermore, because of the diffuse nature of the 5f orbitals compared to that of the 4f orbitals and their increased sensitivity to the ligand field, neither method is entirely appropriate for uranium because, unlike in lanthanides, which have well separated J levels, the J levels mix in uranium; that is, J is no longer a reliable quantum number. However, it is useful to operate in a framework, and the LS coupling scheme provides a good first approximation on which to base uranium electronic structure and magnetism models.

2.4. Electronic Absorption Spectroscopy

Like for any other metal complex, the electronic absorption spectra of uranium complexes may in principle exhibit LMCT, MLCT, and π–π* transitions; however, the interpretation of uranium UV/Vis/NIR spectra in the context of f–f and f–d transitions is not always straightforward, and it is instructive to compare these spectra with transition-metal and lanthanide optical absorption spectra. The bonding of lanthanides is essentially ionic, and therefore, lanthanide ions experience a very small crystal field. Their optical spectra are thus reminiscent of the free ions and essentially independent of the ligand environment; f–f absorption bands are consequently very sharp (little vibronic character) and weak, because they are Laporte forbidden (this and subsequent statements will assume a centrosymmetric molecule, such as in O_h symmetry). The f–d transitions usually occur well into the UV region because of the large 4f–5d energy gaps, although this is of course oxidation-state-dependent. In contrast, transition-metal optical spectra are often broad, reflecting extensive vibronic coupling from strong crystal fields. The d–d transitions are also Laporte forbidden, but d orbital mixing with ligand frontier orbitals of opposite parity switches on transitions so that appreciable intensities are observed, although they are still not of the magnitude of π–π* and LMCT/MLCT transitions.

Uranium falls somewhere in between the above extremes, and its spectra are oxidation-state-dependent. Vibronic coupling is greater than for the lanthanides, but f–f transitions are still weak. However, greater covalency leads to modest line-broadening and enhanced mixing with ligand orbitals, which increases the absorption intensities. In some instances, the mixing is, by inference, so strong that significant intensities can be observed for f–f transitions, which is referred to as intensity stealing.[41] The 5f–6d energy gap is smaller than the corresponding 4f–5d gap, and thus, for uranium(III), Laporte allowed 5f–6d transitions are observed around 500–700 nm; for higher oxidation states, the 5f–6d gap increases, and those transitions usually shift into the UV region. The optical spectra of uranium(III) and uranium(IV) often exhibit weak ($\varepsilon \approx 5$–$100\,\text{M}^{-1}\text{cm}^{-1}$) and numerous f–f transitions because of multiple states and crystal-field sublevels. For example, setting 5f–6d transitions to one side, uranium(III) spectra contain 41 free-ion states (where inter-electronic repulsion and spin–orbit coupling have been accounted for) and 182 crystal-field sub-levels (each state is split into $(2J+1)/2$ levels). Uranium(V) is a special example of clarity, however;[10] as there is only one 5f electron, there is no inter-electronic repulsion, and the effects of spin–orbit coupling and the crystal field can be more straightforwardly treated. Assuming that spin–orbit coupling is larger than the crystal field, the former splits the ^2F term into the $^2F_{5/2}$ ground state and the $^2F_{7/2}$ excited state. Consideration of the crystal field splits each of the $^2F_{5/2}$ and $^2F_{7/2}$ states into $(2J+1)/2$ levels. As the spin, a half-integer term, and orbital, an integer term, angular momenta have been combined, double group theory needs to be used. This then generates the orbital manifold for uranium(V) (Figure 5). The labels change in different symmetries, and the exact energetic spacings will vary as a function of the magnitudes of spin–orbit coupling and the crystal field.[42] Uranium(V) thus usually exhibits a well-resolved manifold of f–f transitions ($\varepsilon < 500\,\text{M}^{-1}\text{cm}^{-1}$) whose intensity can be indicative of the site symmetry at uranium: O_h symmetry results in coupling to the A_{1g} mode, which reduces the absorptivities to approximately $50\,\text{M}^{-1}\text{cm}^{-1}$, but for low-symmetry systems, higher molar extinction coefficients have been reported.[43]

2.5. Magnetism

The static magnetism of uranium (dynamic magnetism is discussed in Section 5) can be crucial to determining formal oxidation states where this assignment is in doubt.[31c] For a d block ion, the magnetic moment μ_{eff} is given by $\mu_{\text{eff}} = \sqrt{[4S(S+1)+L(L+1)]}$. For many transition metals, the orbital component can be ignored because of the crystal field, and so the spin-only formula works well. For lanthanides, the orbital moment is not quenched, and as S and L weakly couple, J must be considered, which gives rise to the Landé formula:

$$\mu_{\text{eff}} = g_J\sqrt{J(J+1)}$$

where $g_J = 3/2 + ((S(S+1) - L(L+1))/2J(J+1))$.

The Landé formula does a good job of predicting the magnetic moments of the lanthanides in complexes, which are

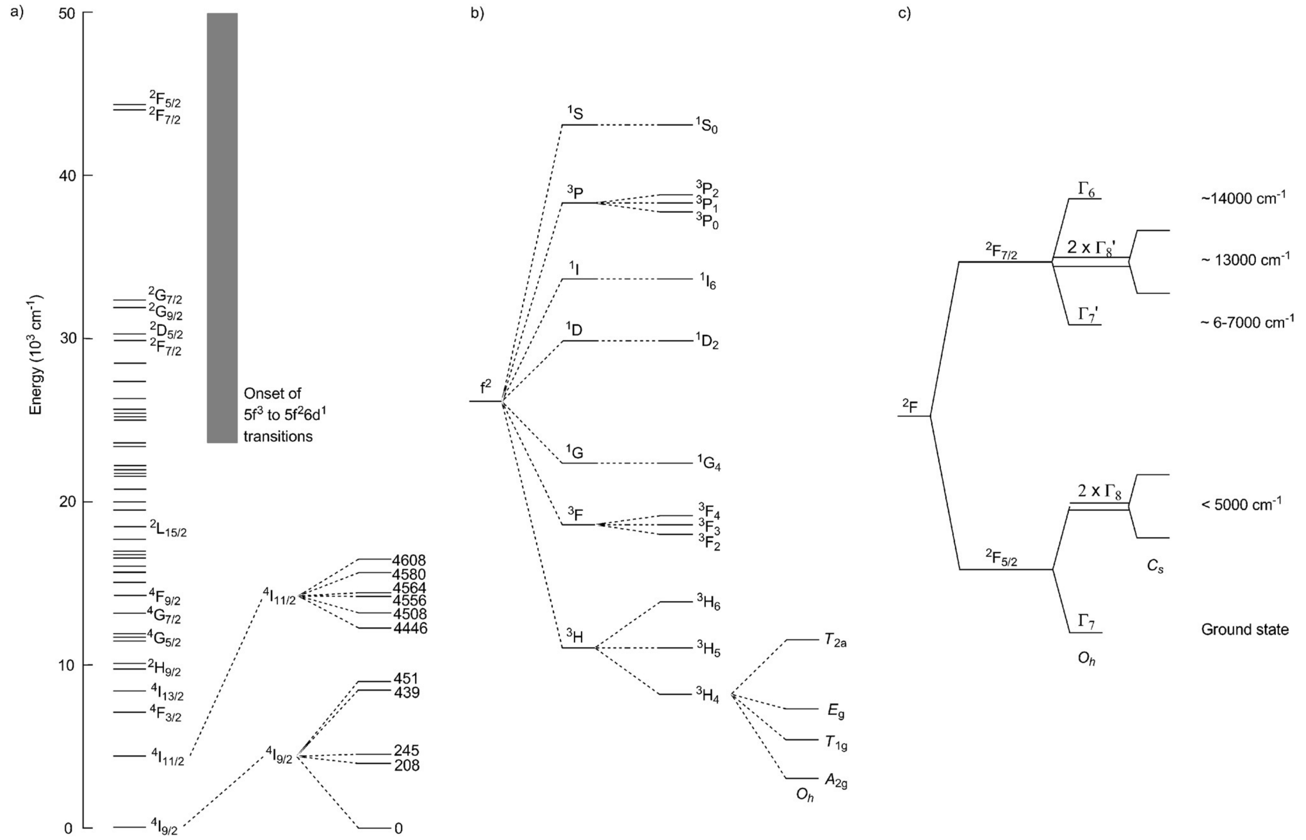


Figure 5. The effects of electrostatic repulsion, spin–orbit coupling, and the crystal field on the electronic configurations of ^{4}I uranium(III) (a), ^{3}H uranium(IV) (b), and ^{2}F uranium(V) (c).

similar to those of the free ions and by-and-large independent of the ligand environment; it fails only in two instances where the fundamental assumption of a good separation of the ground and first excited state is not obeyed (for Sm and Eu, low-lying paramagnetic states contribute to their magnetic moments).

In principle, the magnetism of uranium might not be expected to be well modelled by the Landé formula because, as established in Section 2.3, J is not a good quantum number. However, the Landé formula predicts the magnetic moments of uranium in various oxidation states rather well.[44] Representative plots of μ_{eff} (μ_B) against the temperature (K) for uranium(III), uranium(IV), and uranium(V) are shown in Figure 6. The theoretical magnetic moments of uranium(III) and uranium(IV) at room temperature are 3.62 and 3.58 μ_B, which is not a sufficient difference to assign a formal oxidation state if there is any ambiguity.[31c] However, the variable-temperature behaviors are distinct and revealing, and the exact shape of the magnetization response can be quite informative on crystal-field effects.[45] A typical uranium(III) magnetic moment will decrease only slowly until at low temperature, a drop in the moment occurs as low-lying states are depopulated and the uranium ion adopts an orbital doublet ground state. Notably, however, the magnetic moment is usually higher than what would be expected for the equivalent with one unpaired electron because some low-lying states are not completely depopulated, even at low temperature. In contrast, uranium(IV) usually presents a monotonous decrease in magnetic moment, and the curve tends to zero because at the low-temperature limit, uranium(IV) is an orbital singlet in O_h symmetry (Figure 5b), which most complexes approximate to. At 2 K, there is usually a residual magnetic moment of approximately 0.3–0.5 μ_B, which is due to temperature-independent paramagnetism. The magnetism of uranium(V) tends to present a flat line with little variation in the magnetic moment from room temperature (calculated moment of 2.54 μ_B) to approximately 50 K; below this temperature, there is a rapid drop-off of magnetic moment, which is due to the depopulation of low-lying states, but an appreciable moment (ca. 1.1 μ_B) tends to remain because uranium(V) is always an orbital doublet. However, the moment is smaller than for uranium(III) because there is less mixing with excited states. It should be noted that experimentally observed magnetic moments of uranium complexes frequently deviate below ideal behavior. In Figure 6, the magnetic moments at 298 K for uranium(III) and uranium(IV) are approximately 3 μ_B whereas for uranium(V), it is about 2 μ_B. It is tempting to attribute this to partial quenching of L by the crystal field, which invokes covalency, but numerous factors contribute to the observed magnetism in each case, and their inter-relationships are complex and non-linear so dogmatically invoking covalency is too simplistic.[26f]

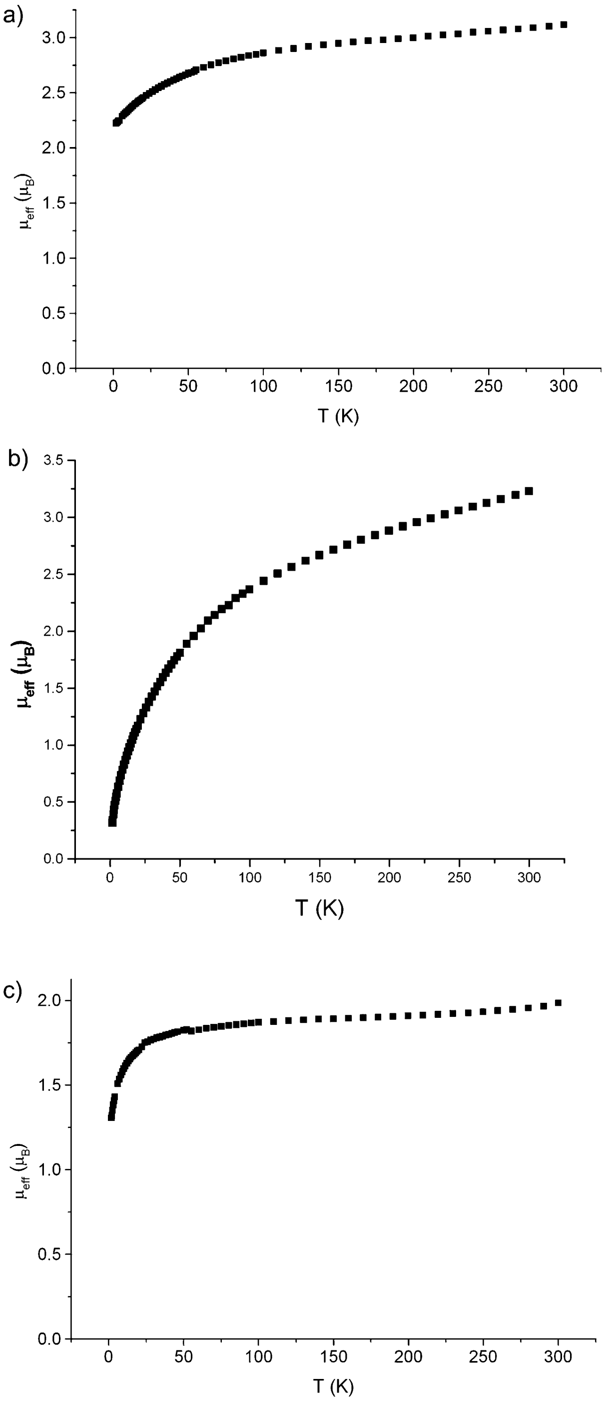


Figure 6. Typical μ_{eff} (μ_{B}) versus temperature (K) plots for a) uranium(III),[44a] b) uranium(IV),[44b] and c) uranium(V).[44a]

2.6. Bond Energetics and Chemical Bonding

Thermochemical studies have shown the uranium–carbon bond disruption enthalpies to be approximately 70–90 kcal mol^{-1}.[46] Therefore, it can be concluded that there is nothing thermodynamically unstable about uranium–ligand linkages. However, because of the predominantly electrostatic bonding, many of these linkages are labile for kinetic reasons.

The oxidation state of uranium profoundly affects the level of covalency in any uranium–ligand bond, and this will also be dependent on the type of ligand, but broadly speaking, it can be said that uranium(III) will be the most ionic and uranium(VI) the most covalent. Electrostatic interactions dominate the bonding, but there can be appreciable covalency, which is the source of much debate; although theoretical calculations are invaluable in providing models for the electronic manifolds of uranium complexes, there is a need to experimentally validate them, and this is an area that is beginning to show promise in terms of XANES studies.[47]

One consequence of the greater radial expansion of the 5f orbitals with respect to their 4f counterparts is the capability to engage in polarized covalent multiple bonding with terminal π-donor ligands[27a,30e] and to engage in back-bonding to π-acceptor ligands, such as carbon monoxide and arenes. This is a burgeoning area of non-aqueous uranium research, and contrasts to the more ionic lanthanides, which rarely engage in bonding to π-acceptor ligands or need constrained ligand frameworks to stabilize terminal multiply bonded ligands. Therefore, a great deal of attention needs to be given to ligand design in non-aqueous uranium chemistry to support novel and potentially reactive uranium–ligand linkages. If the uranium and ligand frontier orbitals are appropriately arranged with respect to each other, uranium can engage in σ, π, δ, and, unique to the actinides it would seem, φ bonding, although the latter tends to be limited to special cases, such as uranocene[48] and perhaps uranium–arene interactions.[40]

As the bonding is electrostatic, most ligand combinations with uranium arrange themselves to minimize steric hindrance. However, one structural motif that deserves special mention here is the rigorously *trans*-configured uranyl unit. In d block chemistry, especially in Group 6 dioxo complexes, the oxo groups would be anticipated to arrange themselves mutually *cis* to avoid these strong donors from competing with common d orbitals, which is a manifestation of the *trans* influence. The situation is clearly the opposite for uranyl. Specifically, when the parity of the highest occupied core orbitals (p, ungerade) is opposite to that of the lowest unoccupied metal orbitals (d, gerade), then dipolar polarization is observed and charge accumulation occurs in a *trans* position, thus destabilizing the *trans* bond so that a *cis* arrangement is favored. However, when the parities are the same (p and f, ungerade) then the polarization is quadrupolar and thus the *cis* positions are destabilized, and a *trans* arrangement is favoured. An alternative way of explaining this is that the semi-core 6p orbitals transfer electron density to vacant 5f orbitals leaving a 6p hole directed to the *trans* position, so that *trans*-bonded ligands reinforce each other ("pushing from below"). This is a complex and not fully understood phenomenon, which is referred to as the inverse *trans* influence (ITI).[30b,49] Interestingly, there is growing evidence for an ITI effect in certain uranium(V) complexes, which hints that this phenomenon may be more widespread than is currently appreciated.[50]

2.7. Principal Reaction Types

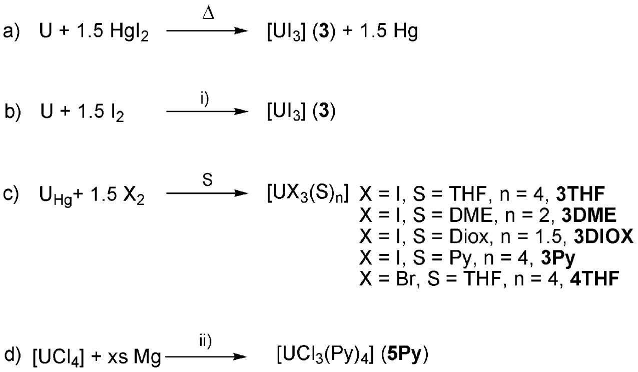
With predominantly ionic interactions, uranium–ligand linkages are often labile and therefore amenable to a range of reactions.[51] Salt, amine, and alkane elimination reactions are common, and migratory insertion reactions are also well known. β-Hydride elimination, as for early d-block metals, is an accessible decomposition pathway and needs to be avoided by using alkyl substituents that are void of β-hydrogen atoms or by steric blocking/saturation. Unlike for transition metals, classical single-metal two-electron oxidative addition is unknown, and the reverse reductive elimination is incredibly rare.[52] However, the redox chemistry of uranium tends to be dominated by one-electron redox events so bimetallic oxidative additions have extensive precedence.[53] Multi-electron reductions are known,[23f] but tend to involve metal redox processes coupled with non-innocent ligand reactivity. Two-electron oxidations are known but rare, for example, reactions with azides or oxygen-transfer reagents have been reported to make terminal imido or oxo complexes, respectively.[27a,30e] Low-valent uranium is very reducing, and accordingly, the reduction of substrates with low-lying π-systems to give coupled organic compounds is well known, whereas uranium(V) and uranium(VI) can be very oxidizing.

3. Commonly Used Uranium Halide Starting Materials

The starting points for essentially all molecular non-aqueous uranium chemistry are halide derivatives, and consequently, significant effort has been spent in producing reliable starting materials that can be made "in house" as there are very few commercial sources; the recent acceleration of the area can be correlated with contributions to improved starting materials. The following Sections describe key advances that have supported the renaissance of non-aqueous uranium chemistry.

3.1. Uranium(III)

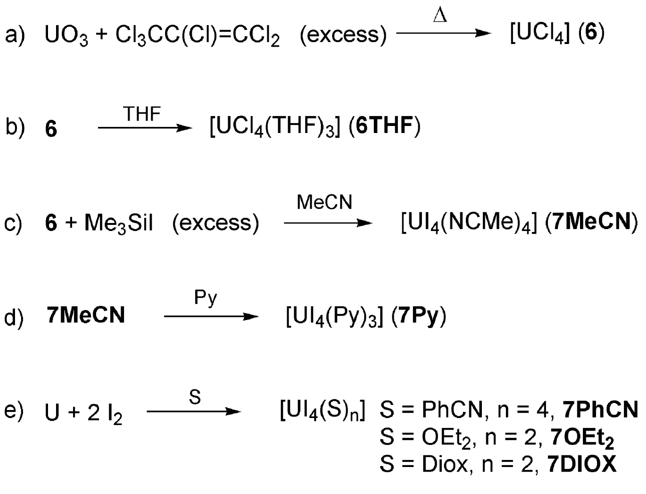
Several routes to uranium(III) halide starting materials are known (Scheme 2). Although the direct reaction of uranium and mercury diiodide is a proven method to prepare [UI_3] (**3**),[54] the synthesis involves harsh conditions and the use of specialist equipment and produces mercury as a by-product. The reaction of uranium with iodine has also been reported but involves heating the uranium to red heat.[55] A major advance, which opened up the area, was the 1989 report of a robust synthesis of [$UI_3(THF)_4$] (**3THF**) from uranium (ca. 5% mercury-amalgamated) and iodine in THF.[56] This method is quite flexible, and [$UI_3(DME)_2$] (**3DME**) and [$UI_3(Py)_4$] (**3Py**) could be prepared by changing the solvent to DME or Py, respectively,[56b] and iodine could be substituted by bromine to produce [$UBr_3(THF)_4$] (**4THF**).[56b] Compound **3THF** has proven to be the foundation of numerous experimental uranium studies in the last 25 years, but there are still occasions when solvent-free **3** is required. To avoid solid-state methods, a solution-based method was reported in 2008 where uranium is reacted with I_2 (1.5 equiv) in diethyl ether with occasional sonication.[57] Elemental analysis of the dark-purple powder prepared by this method shows minimal hydrocarbon inclusion (ca. 1% C, 0.5% H), and as this method avoids the need to prepare mercury-amalgamated uranium, as in the 1989 method,[56] soxhlet extraction using THF can be used to purify **3** to produce **3THF**, leaving behind a residual 2% impurity by weight, whose composition remains unknown. In 2011, an improved synthesis of solvated **3** was reported;[58] the reaction of uranium with I_2 (1.35 equiv) in 1,4-dioxane affords [$UI_3(1,4\text{-dioxane})_{1.5}$] (**3DIOX**) in excellent yield, and this complex exhibits a higher thermal stability than **3THF**. A uranium(III) trihalide that eluded unambiguous preparation for a number of years was [UCl_3] (**5**).[59] This was often prepared by an in situ reduction of [UCl_4] (**6**) with sodium naphthalenide but the resulting compound was ill-defined, and derivatives were often obtained in low yield, suggesting a complex reaction. However, it was not until as recently as 2014 that a robust synthesis of solvated complexes of **5** was reported.[60] Reduction of a 1,4-dioxane suspension of **6** with magnesium turnings at 100 °C for three days produces a blue powder, and after separation from excess magnesium and dissolution in pyridine and work-up, [$UCl_3(Py)_4]_2$ (**5Py**) is isolated in good yield as a purple/black crystalline solid.



Scheme 2. a–d) Synthesis of uranium(III) halides. Specific reagents and conditions: i) Solid state or diethyl ether; ii) dioxane, then hexane/pyridine.

3.2. Uranium(IV)

Uranium(IV) is a common oxidation state for uranium, and hence there are a number of tetravalent halide precursors (Scheme 3). Uranium tetrachloride has been prepared by a number of methods over the years,[61] but perhaps the most popular method is to react UO_3 with hexachloropropene to produce [UCl_4] (**6**) as an emerald green solid in essentially quantitative yield; this compound can be easily converted into [$UCl_4(THF)_3$] (**6THF**) if solubility is an issue in subsequent processes.[62] The reaction requires a high temperature (ca. 200 °C), hexachloropropene is highly toxic, and the reaction initiates with a violent exotherm, so modifications, including

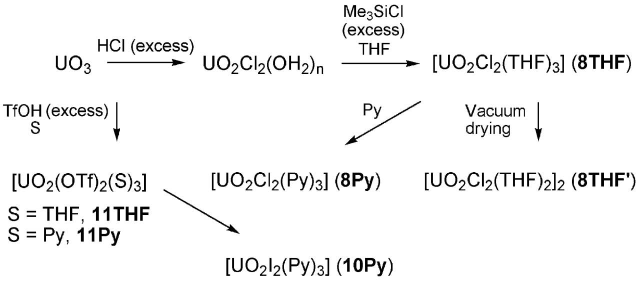


Scheme 3. a–e) Synthesis of uranium(IV) halide starting materials.

the slow addition of UO_3 to hot hexachloropropene, have been devised,[61d] but despite some drawbacks, UCl_4 represents the most commonly used uranium halide starting material apart from **3THF** and uranyl derivatives. Chloride is not always the optimal halide for salt elimination reactions and often, although a small number of UBr_4 derivatives are known,[63] the tetraiodides have received most attention as iodide is an excellent halide to eliminate, especially as KI. However, $[UI_4]$ (**7**) is known to be unstable at room temperature and decomposes to UI_3 and I_2.[64] Although pyridine or nitrile adducts, such as $[UI_4(S)_n]$ (S = Py, $n=3$, **7Py**; S = MeCN, $n=4$, **7MeCN**; S = PhCN, $n=4$, **7PhCN**), are known,[65] the latter are inevitably of limited utility because of the unsaturated nitrile linkage, but they have found application in the synthesis of nitride–azide clusters, for example.[66] However, in the same 2008 report of the synthesis of UI_3,[57] it was reported that when uranium is treated with I_2 (2 equiv) in diethyl ether with occasional sonication, $[UI_4(OEt_2)_2]$ (**7OEt$_2$**) is formed as a red powder in good yield. Complex **7OEt$_2$** is sensitive to loss of diethyl ether. In 2011, the synthesis of more robust uranium halides utilizing 1,4-dioxane was reported,[58] which seems to stabilize thermally robust adducts in spite of being a weak ligand and is resistant to ring-opening reactions that can plague THF complexes. Thus, reacting uranium with I_2 (2.05 equiv) in 1,4-dioxane affords $[UI_4(1,4\text{-dioxane})_2]$ (**7DIOX**), which can be converted into **7OEt$_2$** by treatment with diethyl ether or into $[UCl_4(1,4\text{-dioxane})]_2$ (**6DIOX**) by treatment with HCl/1,4-dioxane.

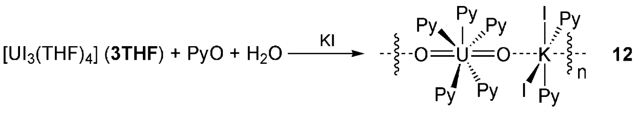
3.3. Uranium(V) and Uranium(VI)

The synthesis of uranium(V) chloride is known but it seems to be a rarely used starting material,[67] presumably because of disproportionation and/or reduction reactions when salt elimination reactions are attempted. Although hexahalides of uranium(VI) are known, they are very oxidizing and of limited synthetic utility. The most common uranium(VI) starting materials are uranyl derivatives (Scheme 4). Following aqueous HCl treatment of UO_3, $UO_2Cl_2(OH_2)_n$ is treated with a six-fold excess of Me_3SiCl in THF. After concentration and addition of hexane as an anti-solvent, $[UO_2Cl_2(THF)_3]$ (**8THF**) is isolated as a yellow powder.[68] Importantly, it should be noted that one THF molecule is labile, and drying under vacuum affords $[UO_2Cl_2(THF)_2]_2$ (**8THF′**). Although **8** is arguably the most important halide–coligand combination from an experimental perspective, a number of useful permutations have been prepared, including $[UO_2Cl_2(Py)_3]$ (**8Py**), $[UO_2Br_2(THF)_3]$ (**9THF**), and $[UO_2I_2(Py)_3]$ (**10Py**).[69] Uranyl triflates have also been prepared directly from UO_3 to give $[UO_2(OTf)_2(S)_3]$ (S = THF, **11Tf**; S = Py, **11Py**).[70]



Scheme 4. Synthesis of uranyl(VI) halides.

After initial studies in the 1960s,[10] pentavalent uranium chemistry has developed substantially in recent years.[26f] After a lull of around 40 years, great strides have in particular been made in pentavalent uranyl chemistry. Although $\{UO_2\}^+$ derivatives can be prepared from hexavalent precursors, the development of this area has largely been due to the availability of new uranyl(V) starting materials. For example, treatment of **3THF** with pyridine *N*-oxide and water affords a compound formulated as $[UO_2I(Py)_n]$, which can be treated with potassium iodide to produce the coordination polymer $[\{UO_2(Py)_5\}\{KI_2(Py)_2\}]_\infty$ (**12**; Scheme 5).[71] Compound **12** can also be prepared from UO_2I_2 and potassium pentamethylcyclopentadienyl; indeed, a range of pentavalent uranyl complexes of the general form $[\{UO_2(S)_5\}\{MX_2(S)_n\}]$ (S = Py, THF; M = Li, K; X = OTf, I) can be prepared from UO_2X_2 (X = I, OTf) and organolithium or -thallium reagents.[69c]



Scheme 5. Rational synthesis of the uranyl(V) halide precursor **12**.

4. Common Ligand Classes in Non-Aqueous Uranium Chemistry

The following Sections describe non-aqueous uranium complexes supported by a range of more commonly deployed ligands. The Sections are organized according to the donor atom type that is central to the ligand in question, moving from Group 14 to 16, and in a given group from top to bottom.

4.1. Ligands with Tetryl Donor Atoms

Organouranium chemistry was initiated in 1956 with the synthesis of $[U(\eta^5\text{-}C_5H_5)_3Cl]$ (**13**), which was structurally authenticated in 1965 (Figure 7).[72] In the intervening time, $[U(\eta^5\text{-}C_5H_5)_4]$ (**14**) was reported in 1962,[73] and in 1970, $[U(\eta^5\text{-}C_5H_5)_3(THF)]$ (**15**) was isolated.[74] It is important to realize that these complexes have no counterparts in transition-metal chemistry, which signaled the novelty of f block organometallic compounds. A landmark result for actinide chemistry was the report of uranocene, $[U(\eta^8\text{-}C_8H_8)_2]$ (**16**), in 1968 and its structural confirmation in 1969 because this complex instigated the debate on f electron participation in metal–ligand bonding, which continues to this day.[75] Uranium alkyl, cyclopentadienyl, and arene complexes have recently been reviewed in great detail,[30c,d,32b,c] and the following Section highlights key reports.

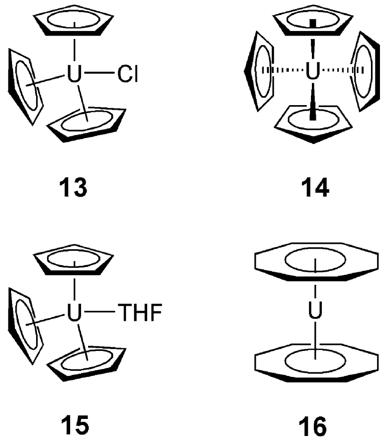


Figure 7. Progenitor organouranium complexes **13**–**16**.

The aforementioned complexes are all π-organometallic compounds; however, there had been prior interest in homoleptic uranium σ-alkyl compounds as volatile candidates for isotope separation,[30d] but early efforts to prepare such species were thwarted by decomposition. Indeed, the repeated failure to prepare homoleptic uranium alkyl compounds led to the perception that they could not be made.[1] This view was overturned in the 1970s, when it was shown that $[U(\eta^5\text{-}C_5H_5)_3R]$ (**17**, R = alkyl) complexes could be prepared (Figure 8),[76] and that steric saturation could impart stability to the U−R bond by blocking the vacant site required for facilitating β-hydride elimination. An example of this approach is the synthesis of $[U(Me)(CH_2Ph)_3(Me_2PCH_2CH_2PMe_2)]$ (**18**).[77] Thus, it is a matter of sterically taming the linkage,[78] and uranium mono- and dialkyl derivatives can be obtained with suitable ancillary ligands.[32b]

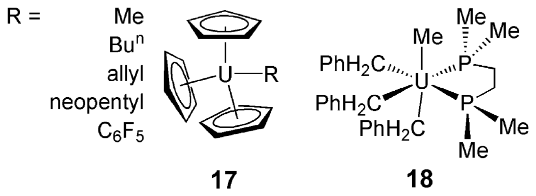
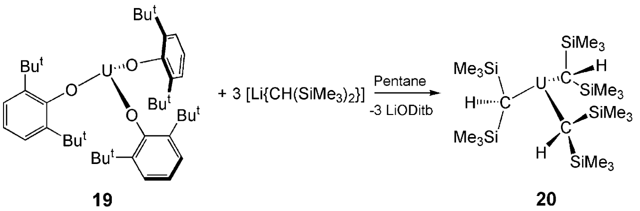


Figure 8. The stable uranium(IV) alkyl complexes **17** and **18**.

With the steric-saturation approach, homoleptic uranium alkyl complexes were finally prepared, for example, by utilizing the sterically demanding, β-hydrogen-free alkyl group $\{(Me_3Si)_2HC\}^-$. The reaction of $[U(ODitb)_3]$ (**19**) and $[Li\{CH(SiMe_3)_2\}]$ (3 equiv) to give the trigonal pyramidal uranium(III) complex $[U\{CH(SiMe_3)_2\}_3]$ (**20**) was reported in 1989 (Scheme 6).[79] Complex **20**, a nine-valence-electron, three-coordinate complex, is stabilized by agostic CH···U interactions and demonstrates the kinetic-stabilization effect of the $\{(Me_3Si)_2HC\}^-$ alkyl groups.



Scheme 6. Synthesis of the low-coordinate uranium(III) alkyl complex **20**.

More recently, the steric-saturation approach has been successfully applied to the preparation of higher-valent homoleptic uranium alkyl compounds with reports between 2009 and 2012 including $[U(CH_2Ph)_4]$ (**21**),[52b] $[U(CH_2Bu^t)_5][Li(THF)_4]$ (**22**), $[U(Me)_6\{Li(tmeda)\}_2]$ (**23**), $\{[U(CH_2Ph)_6][K(THF)][K(THF)_2]\}_\infty$ (**24**), $[U(CH_2SiMe_3)_6][Li(THF)_4]$ (**25**), and $[U(CH_2SiMe_3)_6]$ (**26**; Figure 9). The latter compound, despite being apparently sterically saturated, was reported to be only stable below −25 °C.[80] The highly reactive nature of uranium(VI) alkyl species, as evidenced by the sensitivity of **26**, is further highlighted by the chemistry of uranyl dialkyl compounds. In 1982, it was shown that the treatment of UO_2Cl_2 with an alkyl lithium reagent (2 equiv) resulted in transient uranyl dialkyl compounds that decompose, by a mixture of reductive elimination and homolytic scission/β-hydride elimination, to give UO_2 and organic compounds.[52a] However, again exploiting the steric-saturation approach, it was shown in 2013 that treating UO_2Cl_2 with $[Li(CH_2SiMe_3)]$ (4 equiv) at −25 °C gives $[UO_2(CH_2SiMe_3)_4\text{-}\{2\,Li(DME)_{2.5}\}]$ (**27**),[81] although like **26**, complex **27** is stable only at low temperatures and decomposes at room temperature in a few hours.

Like their alkyl counterparts, uranium aryl complexes are fairly rare and tend to be thermally unstable or require chelating stabilization as they are rather reactive. An example was reported in 2013, whereby the reaction of *ortho*-lithiated *N*,*N*-dimethylbenzylamine (5 equiv) with UCl_4 was found to produce the uranium benzyne complex $[U(C_6H_4\text{-}2\text{-}CH_2NMe_2)_3(C_6H_3\text{-}2\text{-}CH_2NMe_2)Li]$ (**28**; Scheme 7).[82] Complex **28** is the only example of an isolable f block benzyne complex, although uranium benzyne complexes have previ-

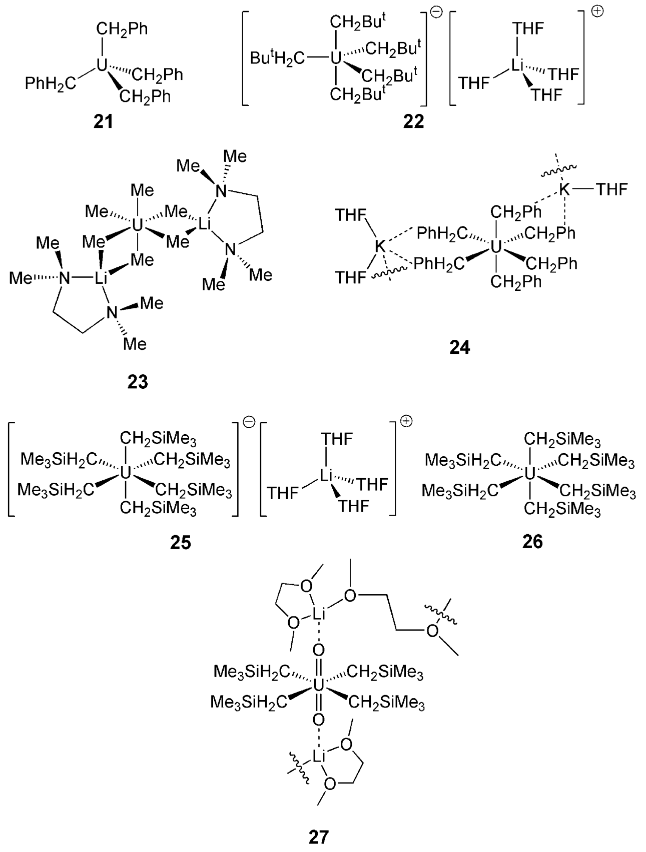
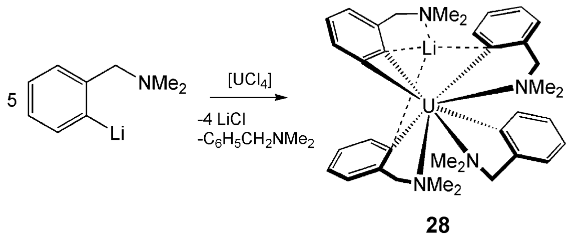


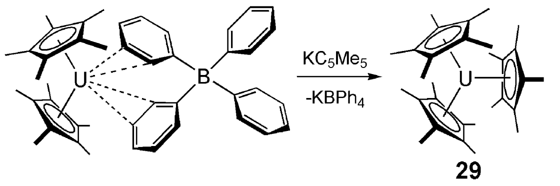
Figure 9. The uranium(IV), uranium(V), and uranium(VI) alkyl compounds **21**–**27**.



Scheme 7. Synthesis of uranium benzyne complex **28**.

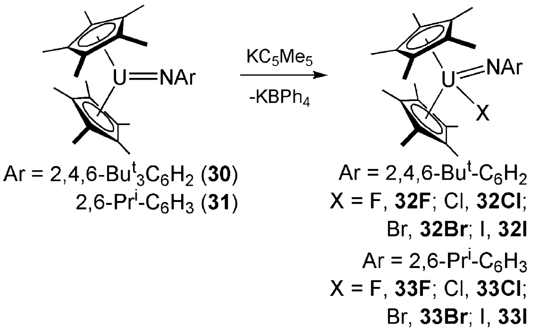
ously been invoked as reactive intermediates,[83] and a theoretical study concluded that the 5f orbitals play a significant role in stabilizing the uranium–benzyne interaction.

Returning to metallocenes, it was long thought that it was impossible to assemble three pentamethylcyclopentadienyl ligands at one metal center because the cone angle of this ligand exceeds 120°. However, in 1997 it was shown that by carefully choosing the strategy and reagents, $[U(\eta^5\text{-}C_5Me_5)_3]$ (**29**) can be prepared (Scheme 8).[84] Although small cylindrical molecules can coordinate to uranium in **29**[85] (Figures 12, 17, and 37), the complex is evidently sterically compressed as exemplified by a range of sterically induced reduction reactions that this molecule can undergo.[23f] This class of complexes also demonstrates that to ameliorate the cone angle issue, the uranium to cyclopentadienyl centroid distance is simply elongated, showing that distortions of such metrics are facile in the shallow potential-energy well that reflects the predominantly electrostatic uranium–ligand bonding.



Scheme 8. Synthesis of tris(pentamethylcyclopentadienyl) uranium(III) complex **29**.

Metallocenes have also proven to be an excellent platform from which to access the less common uranium(V) oxidation state. Complexes of the form $[U(\eta^5\text{-}C_5Me_5)_2NAr]$ (Ar = 2,4,6-Bu^t_3-C_6H_2, **30**; Ar = 2,6-Pr^i_2-C_6H_3, **31**) are amenable to one-electron oxidation by copper(I/II) halide reagents to afford $[U(\eta^5\text{-}C_5Me_5)_2(NAr)X]$ (X = F, Cl, Br, I, **32F**–**32I** or **33F**–**33I**, respectively; Scheme 9),[86] which could be converted into a range of $[U(\eta^5\text{-}C_5Me_5)_2(NAr)Y]$ (Y = OTf, SPh, CCPh) derivatives. These essentially isostructural complexes, except for the variation of the X or Y group, proved to be excellent tools to probe the ^2F electronic manifold of uranium(V), enabling the crystal-field effects of the X and Y groups to be probed.



Scheme 9. Synthesis of metallocene-type uranium(V) complexes.

A notable feature of most metallocene complexes that do not involve divalent d block metals is that they are bent unless very bulky substituents are installed on the cyclopentadienyl ligands. In a divergence from the overwhelming number of metallocene derivatives right across the periodic table, it was shown in 2006 and 2007 that donor ligands such as acetonitrile and cyanide can displace iodide and triflate ligands from $[U(\eta^5\text{-}C_5Me_5)_2X_2]$ complexes (X = I, OTf).[87] The resulting separated ion pair complexes contain a linear metallocene unit $[U(\eta^5\text{-}C_5Me_5)_2L_5]^n$ (L = MeCN, $n = +2$, **34**; L = CN, $n = -3$, **35**) with five nitrile or cyanide ligands around the equatorial girdle (Figure 10).

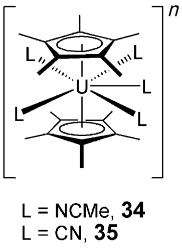
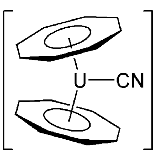


Figure 10. The linear metallocene anion portion of **34** and **35** (L = MeCN, $n = +2$ and CN^-, $n = -3$, respectively).

In contrast to the prevalence of bent metallocenes, molecules such as uranocene are always considered to be linear and fairly unreactive. This lack of reactivity arises from the fact that the uranium center in uranocene is well shielded from external ligands, but also because the adoption of a rigorously linear coordination geometry maximizes the symmetry-allowed overlap between the uranium and ligand frontier orbitals. Therefore, any deviation from this ideal geometry would be thermodynamically uphill, and indeed, uranocene often represents a thermodynamic sink where decomposition reactions of uranium COT complexes are concerned. However, in 2008, it was found that the coordination of cyanide to uranocene could be accomplished to generate a bent uranocene anion $[U(\eta^8\text{-}C_8H_8)_2(CN)]^-$ (**36**; Figure 11).[88] However, examples of bent uranocenes are scarce, whereas a significant number of bent thorocene derivatives are now known, which has been attributed to the more Lewis acidic nature of Th versus U, which may have its origins in the differences of the bonding covalency in thorocene and uranocene.[89]



36

Figure 11. Structure of the bent uranocene(IV) adduct **36**.

Carbon monoxide is a classical ligand in transition-metal chemistry, and there are hundreds of crystallographically characterized complexes thereof. The bonding model of CO is well understood, and electron-rich transition metals are well suited to partaking in the back-bonding model under ambient conditions. Under such conditions, there are no stable lanthanide carbonyl compounds because of the ionic bonding and core-like nature of the f orbitals that precludes back-bonding, which is the dominant part of the synergic metal–carbonyl bond.[90] With some covalency, uranium might be expected to be different, and indeed a handful of uranium CO complexes are known, but they remain very rare because the bonding of uranium is after all predominantly ionic (Figure 12). Uranium carbonyl has been spectroscopically observed in matrix-isolation experiments.[90] In an ambient molecular setting, the uranium carbonyl complex $[U(\eta^5\text{-}C_5H_4SiMe_3)_3(CO)]$ (**37**) was reported in 1986;[91] this complex was not structurally characterized, but exposure of $[U(\eta^5\text{-}C_5H_4SiMe_3)_3]$ to a CO atmosphere resulted in the green solution turning burgundy, and a υ_{CO} band at 1976 cm^{-1} was observed in the IR spectrum, which shifted to 1935 cm^{-1} when ^{13}CO was used. Structural evidence for a uranium carbonyl complex was obtained in 1995 by the synthesis of $[U(\eta^5\text{-}C_5Me_4H)_3(CO)]$ (**38**),[92] which exhibits a υ_{CO} band at 1880 cm^{-1} in the solid state. The rarity of uranium carbonyl complexes is underscored by the fact that the only other structurally characterized terminal uranium carbonyl complex, $[U(\eta^5\text{-}C_5Me_5)_3(CO)]$ (**39**),[93] was not reported until 2003. The IR spectrum of this complex exhibits a υ_{CO} band at 1922 cm^{-1}, which shifts to 1877 cm^{-1} for the ^{13}CO isotopomer. Only one other structurally authenticated CO adduct of uranium is known, which is a bridging radical in $[\{U(tacn[CH_2C_6H_2\text{-}2\text{-}O\text{-}3,5\text{-}Bu^t_2]_3)\}_2(CO)]$ (**40**) reported in 2005. This complex was prepared from CO that was derived from the reductive cleavage of CO_2.[94] The IR spectrum of **40** exhibits a υ_{CO} band at 2092 cm^{-1}, which is consistent with the bridging mode of CO. As complexes **37**–**40** exhibit υ_{CO} bands that are substantially below the value for free CO (2143 cm^{-1}), the π* orbital of CO is likely populated by electron density, which implies that back-bonding is operating in these complexes. However, theoretical calculations have shown that although back-bonding does occur, there is a crucial difference to the classical metal d orbital to π* back-bonding model of transition metals; for uranium carbonyl complexes that are supported by cyclopentadienyl ligands, the frontier orbital that is involved in the back-bonding has metal *and* ligand character.[95]

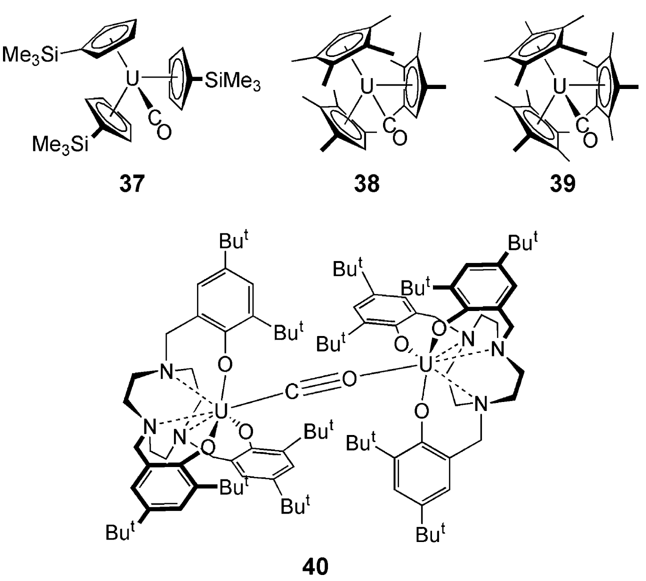


Figure 12. Terminal (**37**–**39**) and bridging (**40**) carbon monoxide complexes of uranium.

In 2001, the burgeoning field of N-heterocyclic carbenes (NHCs) was combined with uranium chemistry (Figure 13). Specifically, the bis-NHC uranyl complexes $[UO_2Cl_2\{C(NMesCX)_2\}]$ (X = H, **41H**; X = Cl, **41Cl**) were reported,[96] which represent the first examples of actinyl–carbon bonds. In 2004, this area was extended to encompass low-valent uranium(III) species, including $[U\{C(NMeCMe)_2\}\{N(SiMe_3)_2\}_3]$ (**42**) and $[U\{tacn(CH_2C_6H_2\text{-}2\text{-}O\text{-}3\text{-}Ad\text{-}5\text{-}Bu^t)_3\}\{C(NMeCMe)_2\}]$ (**43**).[97] The latter was investigated with theoretical calculations, which revealed a π-bond involving a singularly occupied f-type orbital and the vacant p orbital of the carbene carbon atom. From 2004 onwards, a range of increasingly sophisticated uranium NHC complexes have been reported for uranium(III), uranium(IV), and uranyl(VI), which utilize pincer or amide- or alkoxy-tethered NHCs, such as the alkoxy-NHC complex $[U\{OCH_2CMe_2C(NCHCHNPr^i)\}_4]$ (**44**),[23h,24b,98] where three NHCs are coordinated but one remains pendant.

NHCs bind to metal centers datively through the carbene lone pair of electrons and may or may not engage in back-bonding depending on the requirements of the metal. However, covalently bound uranium carbenes, that is, U=C double bonds, have been known for over thirty years. In 1981, it was reported that treatment of **13** with $[Li\{(CH_2)_2PMePh\}]$

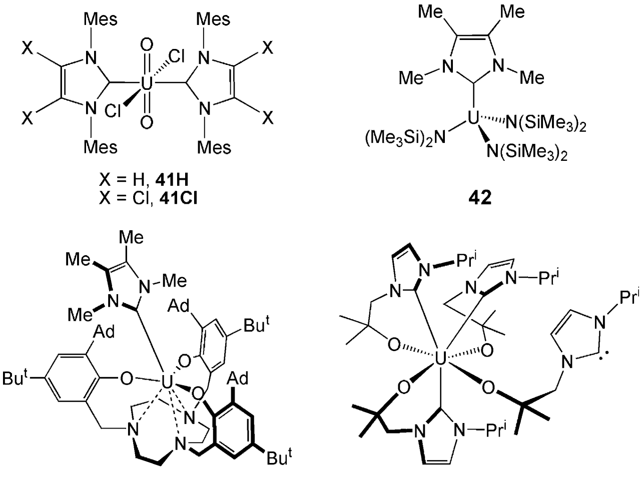
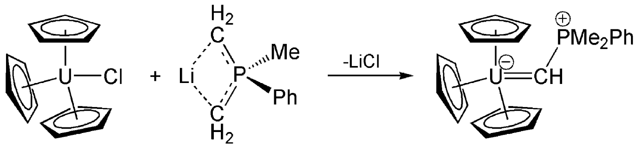


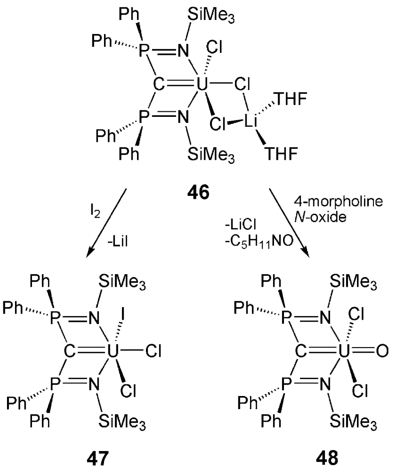
Figure 13. N-heterocyclic carbene complexes (**41**–**44**) of uranium(III) to uranium(VI).



Scheme 10. Synthesis of uranium(IV) carbene complex **45**.

afforded the uranium carbene complex $[U(\eta^5\text{-}C_5H_5)_3\{C(H)PMe_2Ph\}]$ (**45**, Scheme 10),[99] which exhibits a short U=C distance of 2.29(3) Å. The reactivity of complex **45** was examined with a wide range of substrates,[100] demonstrating bond-metathesis chemistry, and a notable product of one of these reactions was the first uranium imido complex (Scheme 18). The U=C bond is clearly more polarized than transition-metal analogues, and it is important to note that no true alkylidene $U{=}CR_2$ bond has been reported thus far; all examples of U=C bonds feature at least one phosphorus(V) substituent to stabilize the carbene, and there are still only few examples of U=C bonds. Indeed, after an initial flurry of activity, the area fell into a lull spanning nearly thirty years, and U=C bonds remained limited to uranium(IV) complexes for many years. However, much success has recently been achieved with $\{C(PPh_2NR)_2\}^{2-}$ (BIPM^R, R = SiMe$_3$, Mes, Dipp) and $\{C(PPh_2S)_2\}^{2-}$ (SCS) ligands in terms of expanding the range of complexes and securing U=C double bonds with different oxidation states of uranium.[30g]

In 2011, it was reported that the uranium(IV) carbene complex $[U(BIPM^{TMS})(Cl)_3Li(THF)_2]$ (**46**) can be straightforwardly prepared from UCl_4 and $[Li_2(BIPM^{TMS})]_2$, and that it is readily oxidized by I_2 to afford the uranium(V) carbene complex $[U(BIPM^{TMS})(Cl)_2(I)]$ (**47**, Scheme 11).[101] In related work in 2012, it was found that the oxidation of **46** with 4-morpholine *N*-oxide afforded uranium(VI) carbene $[U(BIPM^{TMS})(Cl)_2(O)]$ (**48**),[102] which features a *trans* $[R_2C{=}U{=}O]^{2+}$ linkage that is analogous to the uranyl



Scheme 11. Synthesis of the uranium(V) and uranium(VI) carbene complexes **47** and **48** from uranium(IV) carbene complex **46**.

$[O{=}U{=}O]^{2+}$ unit (Scheme 11). The progression of uranium(IV) to uranium(V) to uranium(VI) can be nicely seen in the complexes **46** to **48**, where the U=C bond is shortened from 2.310(4) to 2.268(10) to 2.184(3) Å; the latter value is the shortest U–C distance that has been reported thus far. This observation, along with computational studies, suggests that an ITI effect may be operating in the *trans* $[R_2C{=}U{=}O]^{2+}$ linkage, as in uranyl, and that their electronic structures are similar. A salient point to note is that the 5f orbital contributions to the U=C bond dominate over those of the 6d orbitals. The covalency in these U=C bonds can be inferred from their reactivity; they react, like cerium(IV)–carbon multiple bonds, with carbonyl compounds to give metallo-Wittig alkene products, $RC(H){=}C(PPh_2NSiMe_3)_2$ (R = phenyl, 9-anthracene), whereas ionic yttrium BIPM complexes activate C−H bonds.[103]

Over the past five years, uranium(IV) carbene complexes $[U(SCS)L_2S_n]$ (e.g., L = BH$_4$, S = THF, $n = 2$, **49**; L = C$_5$H$_5$, $n = 0$, **50**) have been prepared,[104] and a notable addition was the synthesis of uranyl(VI) carbene complex $[UO_2(SCS)(Py)_2]$ (**51**) from **11Py** and the parent methane $SCS(Li)_2$ in 2011 (Figure 14).[105] This result is notable because covalent uranyl organometallic compounds remain rare.[44b,102,106] Indeed, for example, for many years a curious omission from the literature was a cyclopentadienyl complex of uranyl, but in 2007, it was shown that the linear metallocene anion **35** could be converted into the uranyl complex $[UO_2(\eta^5\text{-}C_5H_5)(CN)_3]^{2-}$ (**52**) by careful treatment with pyridine *N*-oxide (Figure 14).[107] The U=C bond in **51** was found to be highly polar, almost of single-bond character, and long (2.430(6) Å), which reflects the strong bonding in the *trans* $[O{=}U{=}O]^{2+}$ linkage at the expense of the U=C bond. A similar effect was found in the mixed uranium(VI) carbene imido oxo complex $[U(BIPM^{TMS})(NMes)(O)(dmap)_2]$ (**53**),[108] which contains a *trans* $[MesN{=}U{=}O]^{2+}$ unit (Figure 14). The bonding is clearly strongest in this unit, which is at the expense of the U=C bond as reflected by calculated Nalewajski–Mrozek bond orders of 1.23, 2.34, and 2.68 for the U=C, U=N, and U=O bonds, respectively. Exactly

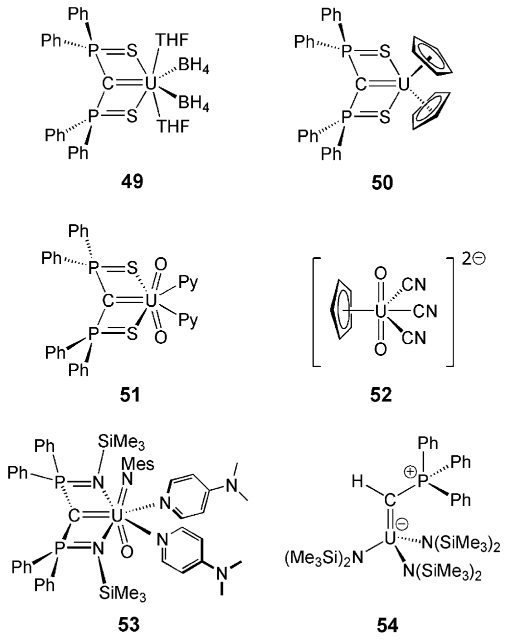


Figure 14. Uranium(IV) carbenes **49** and **50**, the uranyl(VI) carbene complex **51**, uranyl(VI) cyclopentadienyl complex **52**, uranium(VI) carbene imido oxo complex **53**, and uranium(IV) carbene complex **54**.

30 years after the first formation of a U=C bond, the closely related uranium(IV) carbene complex $[U\{N(SiMe_3)_2\}_3(CHPPh_3)]$ (**54**) was prepared (Figure 14).[109] When a solution of the trivalent ylide $[U\{N(SiMe_3)_2\}_3(CH_2PPh_3)]$ (**54H**) in diethyl ether is allowed to stand, **54** is formed along with $[U\{N(SiMe_3)_2\}_3(CH_3)]$ and PPh_3. Notably, the U=C bond in **54** is short at 2.278(8) Å and comparable to that in **45** and longer than that of **48**. Lastly, it should be noted that molecules such as UC, CUC, and CUO have been prepared in argon matrices at approximately 10 K, and the knowledge that such molecules can be prepared has helped to spur carbene chemistry forward.[110]

After the synthesis of arene complexes **13** (C_5) and **16** (C_8), the C_6 benzene derivatives were somewhat conspicuous by their absence until in 1971, the uranium(III) complex $[U(\eta^6\text{-}C_6H_6)(AlCl_4)_3]$ (**55**) was reported (Figure 15).[111] A number of complexes followed,[32c] which exploited either the electron richness of hexamethylbenzene or cationic formulations. However, in 2000, a new type of uranium arene was introduced.[112] Reduction of $[U(I)\{N(Xy)(R)\}_3]$ (R = Ad, **56Ad**; R = Bu^t, **56Bu**) by KC_8 resulted in the formation of the inverted sandwich complex $[\{U[N(Xy)(R)]_2\}_2(\mu{:}\eta^6\text{-}\eta^6\text{-}C_6H_5Me)]$ (R = Ad, **57Ad**; R = Bu^t, **57Bu**; Scheme 12). The C–C bond lengths of the bridging arene were modestly extended compared to those of free toluene and, together with theoretical calculations, suggested δ-back-bonding between uranium and the arene. The formulation of the oxidation state could either be uranium(II)/neutral arene, uranium(III)/dianionic arene, or uranium(IV)/tetraanionic arene. Spectroscopic and theoretical characterization favors the uranium(III)/dianionic arene formulation, but **57** reacts as a divalent synthon to cleave PhN=NPh or PhS–SPh, for example, to give dinuclear uranium(IV) μ-imido or μ-thiolate derivatives, respectively. Two years after the report of **57Ad/Bu**, the reduction of the uranium tris(ketimide) complex $[U(NCBu^tMes)_3(I)(DME)]$ (**58**) with sodium mirror or potassium graphite was reported to afford the inverted sandwich naphthalene complexes $[\{U(NCBu^tMes)_3\}_2(\mu{:}\eta^6\text{-}\eta^6\text{-}C_{10}H_8)(M)_2]$ (M = Na, **59Na**; M = K, **59K**), respectively (Scheme 12).[113] The synthesis of **59Na/K** is in contrast to that of **56Ad/Bu** as in the former compounds, all ketimide ligands are retained at uranium whereas in the latter, an amide ligand is lost during reduction. The μ:η⁶-η⁶ bridging mode of the naphthalene is notable as in lanthanide analogues, each six-membered ring bonds to a separate metal center on opposite sides of the naphthalene, which reflects the increased covalency in the uranium–naphthalene interactions. Complexes **59Na/K** spawned a range of arene-bridged diuranium complexes, which exhibit a rich redox chemistry towards a range of reducible substrates, for example, allowing access to the only example of a symmetrically bridging COT ligand in uranium chemistry to date, namely in $[\{U(NCBu^tMes)_3\}_2(\mu{:}\eta^8\text{-}\eta^8\text{-}C_8H_8)]$ (**60**; Scheme 12).

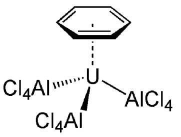


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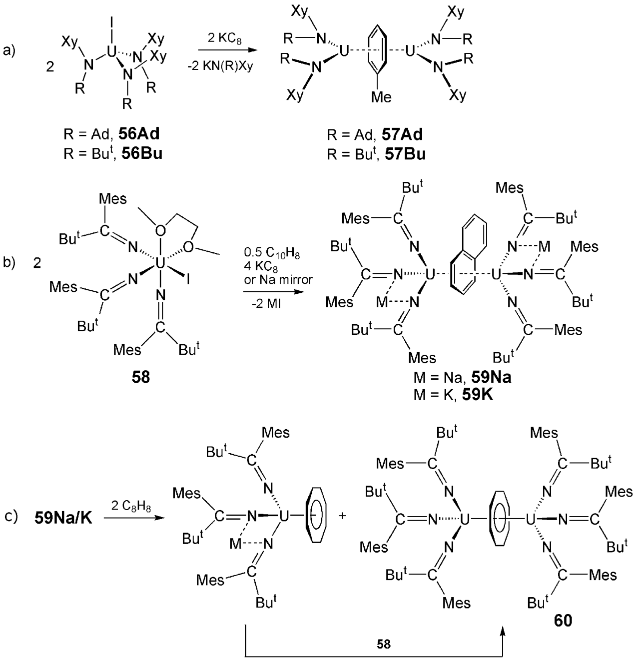
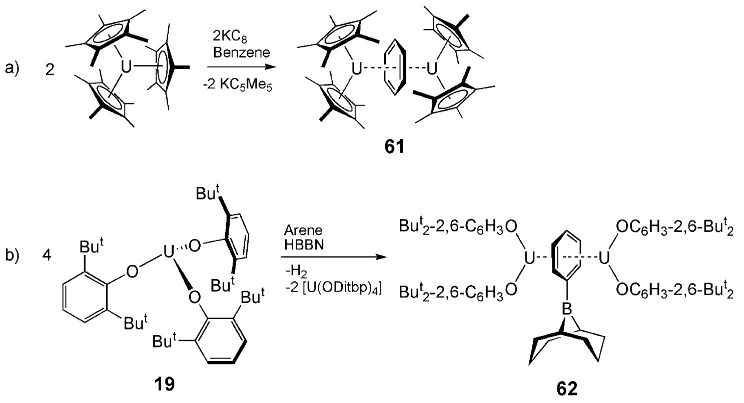
Figure 15. The benzene uranium(III) complex **55**.



Scheme 12. a–c) Synthesis of the inverted sandwich diuranium arene complexes **57Ad/Bu** and **59Na/K**, and conversion of the latter into the inverted cyclooctatetraenyl complex **60**.

In 2004, an inverted sandwich complex related to **57Ad/Bu** was reported that exploited the steric crowding in **29**. Treatment of **29** with KC_8 in the presence of benzene afforded $[\{U(\eta^5\text{-}C_5Me_5)_2\}_2(\mu{:}\eta^6\text{-}\eta^6\text{-}C_6H_6)]$ (**61**; Scheme 13).[114] It was determined that, like for **57Ad/Bu**, the most appropriate description of **61** invokes uranium(III) centers with an arene dianion. This implies that the best π-acceptor arenes should



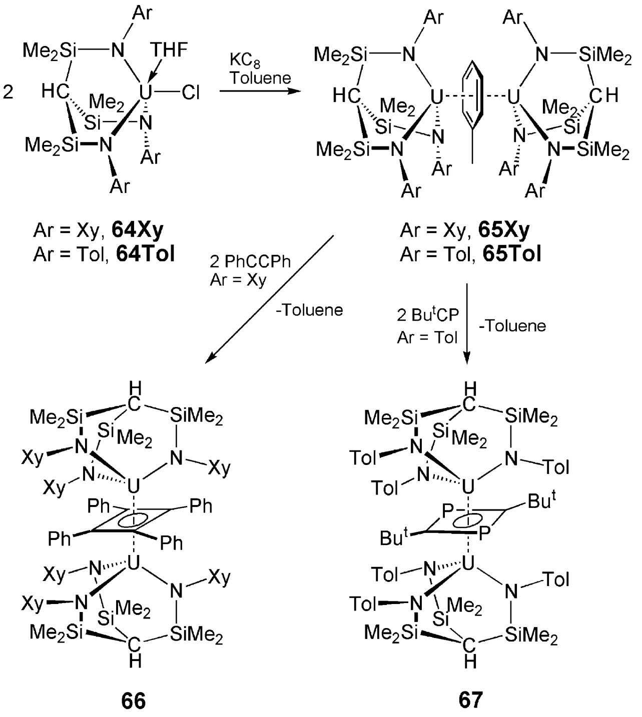
Scheme 13. a, b) Synthesis of the inverted sandwich diuranium(III) arene complexes **61** and **62**.

be the most suitable ligands, displacing poorer π-acceptor ligands. This hypothesis was confirmed experimentally as *para*-methyltoluene was displaced by benzene. In this regard, the bonding is distinctly different to that in transition-metal analogues where the arenes are principally acting as π-donors. Complex **61** was found to undergo multi-electron reductions with a range of substrates. Notable other examples in this area include a diuranium arene SMM (Section 5.1), and the reduction and C–H borylation of arenes mediated by uranium(III) disproportionation to afford $[\{U(ODitbp)\}_2(PhBBN)]$ (**62**) from **19** with sacrificial elimination of $[U(ODitbp)_4]$ (**63**).[115]

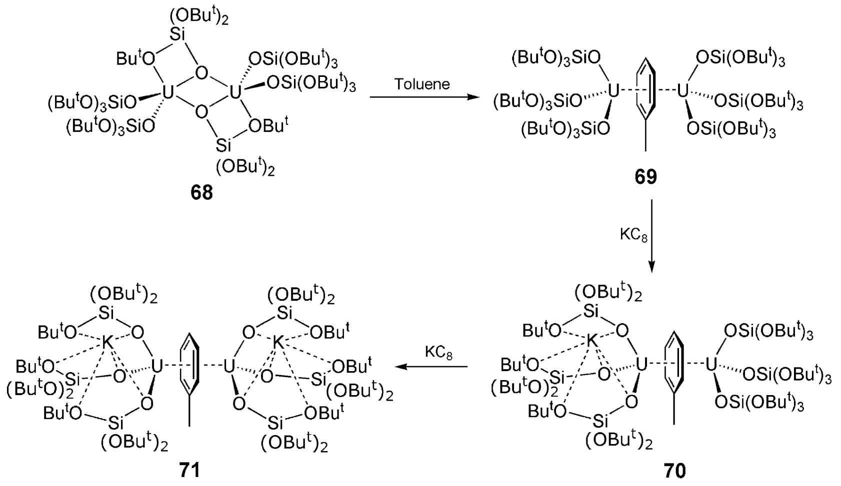
For the first eleven years of studying the chemistry of diuranium inverted sandwich arenes, all examples conformed to the uranium(III)/arene dianion description. However, in 2011, a new class of diuranium arene compounds emerged. Reduction of the uranium triamide chloride complexes $[U\{HC(SiMe_2NAr)_3\}(Cl)(THF)]$ (Ar = Xy, **64Xy**; Ar = Tol, **64Tol**) with KC_8 afforded $[\{U[HC(SiMe_2NAr)_3]\}_2(\mu{:}\eta^6\text{-}\eta^6\text{-}C_6H_5Me)]$ (**65Xy/Tol**; Scheme 14).[116] In contrast to **57Ad/Bu**, there are three amide donors in **65Xy/Tol**, but unlike in **59Na/K**, there are no alkali metal cations present. Surprisingly, of the three possible formulations, namely a neutral arene and uranium(III), an arene dianion and uranium(IV), or an arene tetraanion and uranium(V), the characterization data confirmed the latter combination, but the δ-bonding in these complexes renders this a formal description. Although the pairing of formal (and oxidizing) uranium(V) centers with an arene tetraanion may seem unlikely, δ-bonding will stabilize this interaction, and the toluene tetraanions in **65Xy/Tol** are 10π electron systems that satisfy Hückel's $(4n+2)\pi$ electron rule, giving stability. However, these molecules are very reactive and, for example, effect reductive [2+2] cycloadditions to assemble the first examples of f block cyclobutadienyl $[\{U[HC(SiMe_2NAr)_3]\}_2(\mu{:}\eta^5\text{-}\eta^5\text{-}C_4Ph_4)]$ (**66**, Ar = Xy)[117] and diphosphacyclobutadienyl $[\{U[HC(SiMe_2NAr)_3]\}_2(\mu{:}\eta^4\text{-}\eta^4\text{-}C_2P_2Bu^t{}_2)]$ (**67**, Ar = Tol) derivatives (Scheme 14).[118]

In 2012, another complex that was described as a diuranium(V) arene tetraanion was reported. The reaction of $[\{U(OSi[OBu^t]_3)_3\}_2]$ (**68**) with toluene afforded $[\{U(OSi[OBu^t]_3)_3\}_2(\mu{:}\eta^6\text{-}\eta^6\text{-}C_6H_5Me)]$ (**69**).[119] The uranium oxidation states were not assigned in the preliminary report, but a further study in 2013 found that **69** could be sequentially reduced to monoanionic $[\{U(OSi[OBu^t]_3)_3\}_2(\mu{:}\eta^6\text{-}\eta^6\text{-}C_6H_5Me)(K)]$ (**70**) and dianionic $[\{U(OSi[OBu^t]_3)_3\}_2(\mu{:}\eta^6\text{-}\eta^6\text{-}C_6H_5Me)(K)_2]$ (**71**), which are diuranium(IV/V) arene tetraanion and diuranium(IV/IV) arene tetraanion formulations, respectively (Scheme 15). The changes in the electronic structure could be observed by monitoring the change in the U–C bond distances from 2.689(3)–2.695(3) Å (**69**) to 2.602(9)–2.674(13) Å (**70**) to 2.589(4)–2.621(3) Å (**71**). DFT calculations revealed that as electrons are injected into the molecules, they occupy non-bonding f orbitals as the 10π-electron arene is already electronically saturated, and the remaining ψ_6 orbital is too high in energy to accept electrons.

Lastly, although there are a fairly large number of reports of transition-metal cycloheptatrienyl complexes,[120] the uranium analogues are exceptionally rare. Therefore, the only two known examples, which were reported in the mid-1990s, merit a mention. Aside from the sandwich complex $[U(\eta^7\text{-}C_7H_7)_2][K(C_{12}H_{24}O_6)]$ (**72**), which is a $5f^1$ analogue of uranocene, the only other example of a uranium cycloheptatrienyl complex is that of the inverse sandwich separated ion pair complex $[(H_4B)_3U(\mu{:}\eta^7\text{-}\eta^7\text{-}C_7H_7)U(BH_4)_3][U(BH_4)_2(THF)_5]$ (**73**; Figure 16).[121] Although no theoretical studies of **73** have been reported, it seems likely that δ-bonding will dominate the bonding in the inverse sandwich unit, as has been suggested for the bonding scheme of **72**,[122] which would



Scheme 14. Synthesis of the inverted sandwich diuranium(V) arene complexes **65Xy/Tol** and their conversion into diuranium(IV) cyclobutadienyl complex **66** and diphosphacyclobutadienyl complex **67**.



Scheme 15. Synthesis of the inverted sandwich diuranium(V/V), diuranium(V/VI), and diuranium(IV/IV) arene complexes **69**–**71** from **68**.

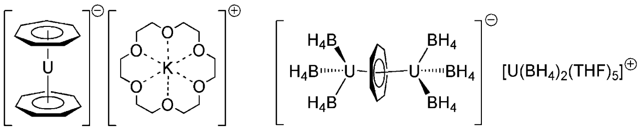


Figure 16. The cycloheptatrienyl complexes **72** and **73**.

be consistent with the planar C_7H_7 rings observed by X-ray diffraction. The formulations for **72** and **73** are consistent with uranium(V) and uranium(IV) centers, respectively, which suggests that the cycloheptatrienyl ligands bear charges of −3 in both complexes.

4.2. Ligands with Pnictide Donor Atoms

In analogy to the small number of uranium/carbon monoxide adducts, the isolation of a uranium nitrosyl complex is also of fundamental importance. The only known complex, namely [U(η^5-$C_5Me_4H)_3$(NO)] (**74**), was only reported in 2012, and prepared from trivalent **29** and NO gas (Figure 17).[123] Interestingly, the U–NO linkage is linear, which is typical for NO$^+$ when bonded to a d block metal. However, the U−N bond length is short (2.013(4) Å) and more in keeping with a U^{IV}−N distance rather than U^{III}, and the N−O distance is consistent with a NO$^-$ charge state (1.231(5) Å). The characterization data suggest that this complex is best formulated as a U^{IV} species with significant back-bonding between the uranium 5f and NO π* orbitals. Indeed, a linear binding of NO to uranium was theoretically predicted in 1989.[124]

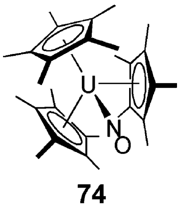


Figure 17. The uranium nitrosyl complex **74**.

Amides play a central role in coordination and organometallic chemistry, and the amide chemistry of uranium is no exception. Like for the alkyl derivatives, heteroleptic variants dominate, and there are relatively few homoleptic variants. One of the most utilized and perhaps iconic homoleptic amides is the uranium(III) complex [U{N(SiMe$_3$)$_2$}$_3$] (**75**), which was reported in 1981[125a,b] and can be easily prepared from **3THF** and sodium or potassium bis(trimethylsilyl)amide (3 equiv) and purified by sublimation or careful recrystallization (Figure 18). The low formal coordination number of 3 in **75** and substituted variants[125c] is potentially useful for reactivity studies, and this platform has supported the activation of a number of small molecules, the installation of novel ligand linkages, oxidation reactions to give uranium(V) derivatives,[126] and even SMM behavior (Section 5.1). Unlike most transition-metal analogues, which adopt trigonal planar geometries, **75** adopts a trigonal pyramidal geometry in the solid state, but this was recently shown to be surmountable by the use of larger silyl substituents in [U{N(SiMe$_2$Bu^t)$_2$}$_3$] (**76**).[127]

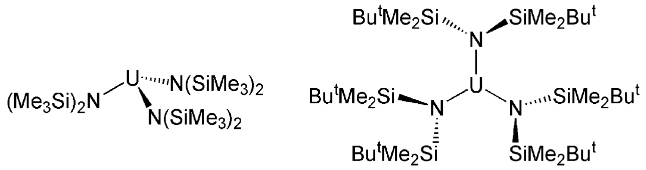
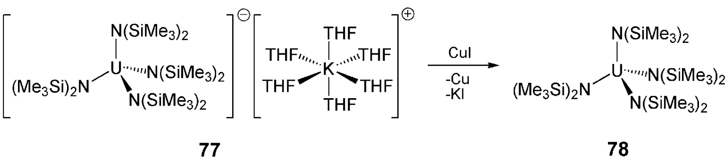


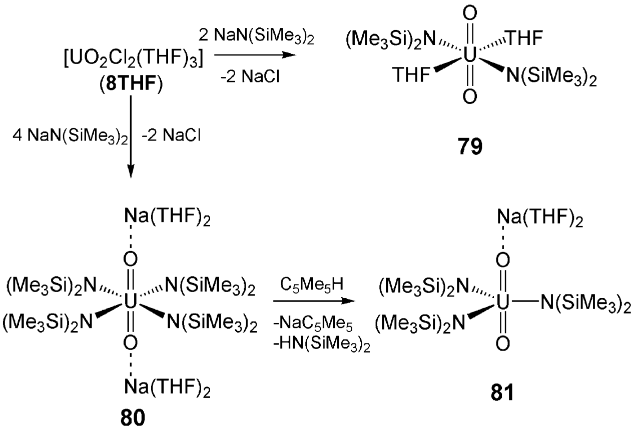
Figure 18. The trigonal-pyramidal and trigonal-planar uranium(III) amides **75** and **76**.

For many years, it was thought that the bis(trimethylsilyl)amide ligand was too sterically demanding to have four of them accommodated at one uranium(IV) center, although [U{N(SiMe$_3$)$_2$}$_4$][K(THF)$_6$] (**77**),[128] which contains a larger uranium(III) center, had been prepared from trivalent **3THF** and potassium bis(trimethylsilyl)amide (4 equiv). Treating **6** with alkali metal bis(trimethylsilyl)amides (4 equiv) produces the cyclometalated complex [U{N(SiMe$_3$)$_2$}$_2$(CH$_2$SiMe$_2$NSiMe$_3$)], which further reinforced the steric-overload notion.[129] However, in 2013, it was finally determined that oxidation of **77** with copper(I) iodide gives [U{N(SiMe$_3$)$_2$}$_4$] (**78**) in excellent yield (Scheme 16).[130] Although the synthesis of **78** is a recent development, given the extensive chemistry of **75**, it is likely that **78** will find interesting uses in the future.

The {(Me$_3$Si)$_2$N}$^-$ ligand finds utility over a wide range of uranium oxidation states. Aside from stabilizing uranium(III) and uranium(IV) species, it has been used for the preparation of uranyl(VI) derivatives (Scheme 17). For example, from 1979 it was known that treatment of **8THF** with sodium bis(trimethylsilyl)amide (2 equiv) produced [UO$_2$-



Scheme 16. Synthesis of uranium(IV) amide complex **78** from **77**.



Scheme 17. Synthesis of the $\{(Me_3Si)_2N\}^-$ uranyl(VI) derivatives **79**–**81**.

$\{N(SiMe_3)_2\}_2(THF)_2]$ (**79**),[131] which is an efficient reagent to introduce uranyl to pro-ligands by protonolysis. Alternatively, it was shown in 2000 that the treatment of **8THF** with sodium bis(trimethylsilyl)amide (4 equiv) produces $[UO_2\{N(SiMe_3)_2\}_4][Na(THF)_2]_2$ (**80**),[132] which when treated with C_5Me_5H eliminates $(Me_3Si)_2NH$ and $[Na(C_5Me_5)]$ to give $[UO_2\{N(SiMe_3)_2\}_3][Na(THF)_2]$ (**81**).[133]

Although **78** was reported only very recently, homoleptic uranium(IV) amides have been known for decades.[134] The dimeric diethylamide complex $[\{U(NEt_2)_4\}_2]$ (**82**) was reported in 1976 and was the first five-coordinate f block complex (Figure 19).[134b] The complex is straightforwardly prepared from **6** and lithium diethylamide, and so an excellent starting material in principle, but the compound must be carefully sublimed for purification as thermal decomposition is facile. Reported in 1977, $[U(NPh_2)_4]$ (**83**) illustrates the importance of steric effects in uranium chemistry[135] (Figure 19), inasmuch as making the amide more sterically demanding now enforces a monomeric four-coordinate formulation. In 2013, the synthesis of the homoleptic uranium(IV) complex $[U\{N(C_6F_5)_2\}_4]$ (**84**) was reported (Figure 19).[136] In contrast to **83**, which adopts a tetrahedral geometry, complex **84** notably adopts a pseudo-square-planar geometry, which is usually the preserve of d^8 Group 9 or 10 metals, underscoring the important effects of subtle and weak bonding interactions, in this case F···U, on the geometry of the complex.

In 2000, homoleptic uranium(V) and uranium(VI) hexa-amide complexes were reported (Figure 20).[137] The reaction of **3THF** with $[Li(dbabh)(OEt_2)]$, a potential nitride delivery reagent, afforded $[U(dbabh)_6]^-$ (**85**) as its lithium salt with elimination of lithium iodide and anthracene. This complex was crystallographically authenticated as its tetraphenylphosphonium salt. The uranium(V) center is well shielded by the six dbabh ligands, and therefore can be straightforwardly oxidized with AgOTf to afford $[U(dbabh)_6]$ (**86**). In 2011, a related pair of uranium(V) and uranium(VI) complexes were reported using the piperidide ligand (Figure 20).[138] Treatment of **6** with $[Li(NC_5H_{10})]$ (5 equiv) affords $[U(NC_5H_{10})_5Li(DME)]$ (**87**), which can be oxidized with iodine to form the uranium(V) amide $[U(NC_5H_{10})_5]$ (**88**). The structure of the latter was not reported, but addition of $[Li(NC_5H_{10})]$ (1 equiv) afforded the "ate" complex $[U(NC_5H_{10})_6][Li(DME)_3]$ (**89**), which could then be oxidized

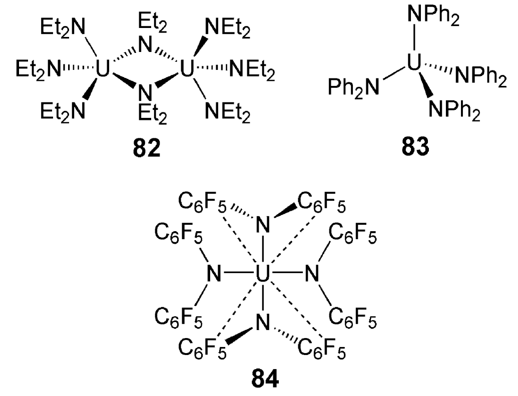


Figure 19. The uranium(IV) amide complexes **82**–**84**.

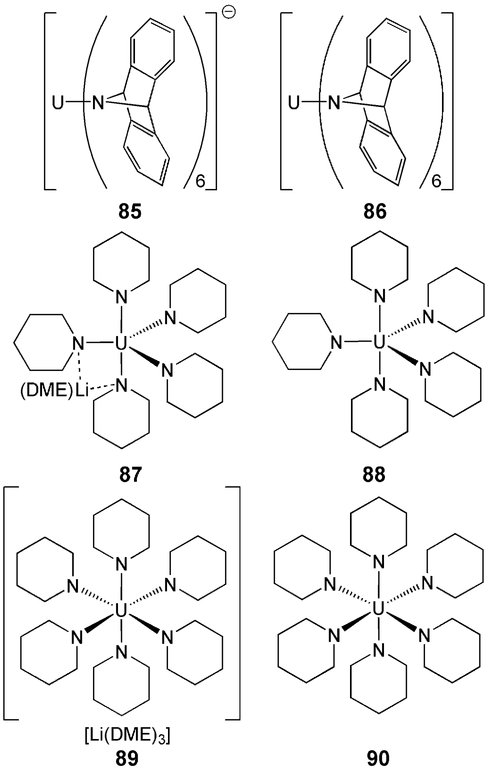
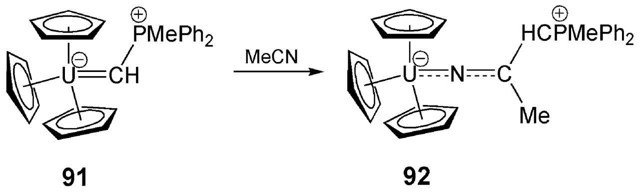


Figure 20. The homoleptic uranium(V) and uranium(VI) amides **85**–**90**.

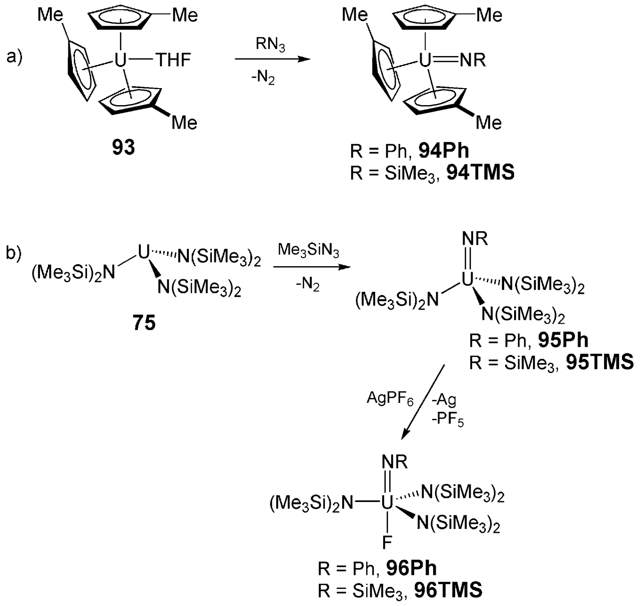
by iodine again to afford the uranium(VI) amide [U(NC$_5$H$_{10}$)$_6$] (**90**). In analogy to uranium alkyl and amide complexes, although uranium ketimides are known, most of them are heteroleptic, and only few homoleptic variants have been reported. Known homoleptic variants were synthesized following similar methods as for **85–90**.[139]

The first uranium imido complex was reported in 1984 (Scheme 18). Treatment of the uranium carbene complex [U(η^5-C$_5$H$_5$)$_3$\{C(H)P(Me)Ph$_2$\}] (**91**), a close analogue of **45**, with acetonitrile afforded the 1,2-migratory insertion product [U(η^5-C$_5$H$_5$)$_3$\{NC(Me)C(H)P(Me)Ph$_2$\}] (**92**).[140] The bond lengths within the UNC(Me)C(H)P fragment, as determined by X-ray crystallography, suggested some delocalization, but the short U–N distance of 2.06(1) Å is consistent with a U=N bond.



Scheme 18. Synthesis of uranium imido complex **92** from carbene complex **91**.

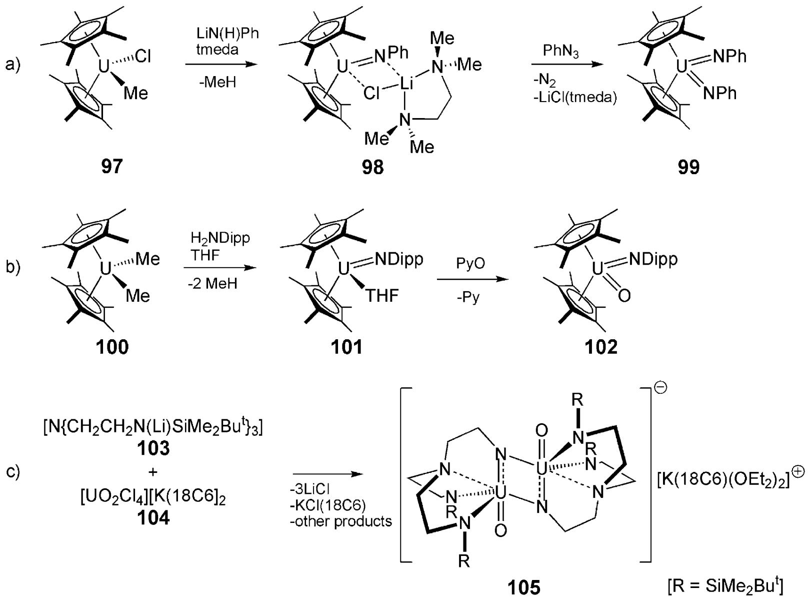
Complex **92** was prepared by insertion chemistry, and in 1985, a new two-electron oxidative route to an imido complex was reported (Scheme 19). Treatment of the uranium(III) complex [U(η^5-C$_5$H$_4$Me)$_3$(THF)] (**93**) with an organic azide (1 equiv) produced the uranium(V) complexes [U(η^5-C$_5$H$_4$Me)$_3$NR] (R = Ph, **94Ph**; R = SiMe$_3$, **94TMS**).[141] The phenyl derivative was crystallographically characterized, revealing a U=N bond length of 2.019(6) Å, which at that time was the shortest U–N distance ever reported. The generality of this route was confirmed in 1988 with the reaction of PhN$_3$ or Me$_3$SiN$_3$ with **75**, which afforded the uranium(V) imido complexes [U\{N(SiMe$_3$)$_2$\}$_3$NR] (R = Ph, **95Ph**; R = SiMe$_3$, **95TMS**; Scheme 19);[142] for the latter, an even shorter U=N distance (1.910(16) Å) than for **94Ph** was observed. Complex **95** provided a platform from which to prepare the first uranium(VI) imido complexes, which were reported in 1990. Treatment of **95Ph** or **95TMS** with AgPF$_6$ effected oxidation. Work-up of the reactions within 6–8 hours to avoid extensive by-product formation afforded the uranium(VI) imido complexes [U\{N(SiMe$_3$)$_2$\}$_3$(NR)(F)] (R = Ph, **96Ph**; R = SiMe$_3$, **96TMS**).[143] The solid-state structures revealed the fluoride to reside *trans* to the imido group in each case, and the U=N distances were found to be very short at 1.979(8) and 1.854(23) Å, the former distance corresponding to that of the phenyl imido group where delocalization into the aromatic ring might be expected.



Scheme 19. a, b) Synthesis of the uranium(V) and uranium(VI) imido complexes **94Ph/TMS** to **96Ph/TMS**.

An alternative route to uranium(IV) imido complexes was disclosed in 1992. Treatment of [U(η^5-C$_5$Me$_5$)$_2$(Me)(Cl)] (**97**) with lithium phenyl amide and tmeda afforded the LiCl occluded imido complex [U(η^5-C$_5$Me$_5$)$_2$(NPh)\{ClLi(tmeda)\}] (**98**), thus demonstrating that acid–base chemistry, driven by methane elimination, could construct U=N double bonds. Interestingly, **98** is quite reactive, and although uranium(IV) is in principle not very oxidizing, further reaction with phenyl azide afforded the first organometallic uranium(VI) complex [U(η^5-C$_5$Me$_5$)$_2$(NPh)$_2$] (**99**; Scheme 20).[144] Complex **99** is also notable for being the first example of a uranium bis(imido) complex, that is, an isoelectronic analogue of [O=U=O]$^{2+}$, and remained so for some time until a new route to these species was eventually discovered (Scheme 24). This chemistry also served to spur the synthesis of the first mixed imido–oxo complex, which was reported in 1993 (Scheme 20); conversion of **97** into [U(η^5-C$_5$Me$_5$)$_2$(Me)$_2$] (**100**) followed by treatment with DippNH$_2$ afforded the uranium(IV) imido complex [U(η^5-C$_5$Me$_5$)$_2$(NDipp)(THF)] (**101**; the Mes* variant is solvent-free),[144,145] which was subsequently oxidized by pyridine *N*-oxide to give [U(η^5-C$_5$Me$_5$)$_2$(NDipp)(O)] (**102**). Another example of a mixed oxo–imido dimer was reported in 2001 (Scheme 20); the reaction of [N\{CH$_2$CH$_2$N(Li)SiMe$_2$Bu^t\}$_3$] (**103**) with [UO$_2$Cl$_4$][K(18C6)]$_2$ (**104**) afforded the mixed-valent uranium(V/VI) oxo–imido dimer [\{U(O)[N(CH$_2$CH$_2$NSiMe$_2$Bu^t)$_2$(CH$_2$CH$_2$N)\}$_2$][K(18C6)(OEt$_2$)$_2$] (**105**).[146]

Like transition-metal imido compounds, uranium-imido complexes might be expected to engage in bond metathesis, and this expectation has indeed been met (Scheme 21).[147] In 2006, it was shown that the sterically encumbered uranium(III) complex [U\{tacn(CH$_2$C$_6$H$_2$-3-Bu^t-5-Ad-6-O)$_3$\}] (**106**) reacted with Me$_3$SiN$_3$, analogously to **75**, to give [U\{tacn(CH$_2$C$_6$H$_2$-3-Bu^t-5-Ad-6-O)$_3$\}NSiMe$_3$] (**107**). Because of the steric overload, the U=N distance is long at 2.1219(18) Å, which leads to facile reactivity with MeNC to liberate half an equivalent of Me$_6$Si$_2$ to give an isocyanate derivative [U\{tacn(CH$_2$C$_6$H$_2$-3-Bu^t-5-Ad-6-O)$_3$\}NCNMe] (**108**). Complex **108** reacts with dichloromethane to give [U\{tacn(CH$_2$C$_6$H$_2$-3-Bu^t-5-Ad-6-O)$_3$\}Cl] (**109**), which can be reductively converted into **106**, thus closing a cyclic reaction

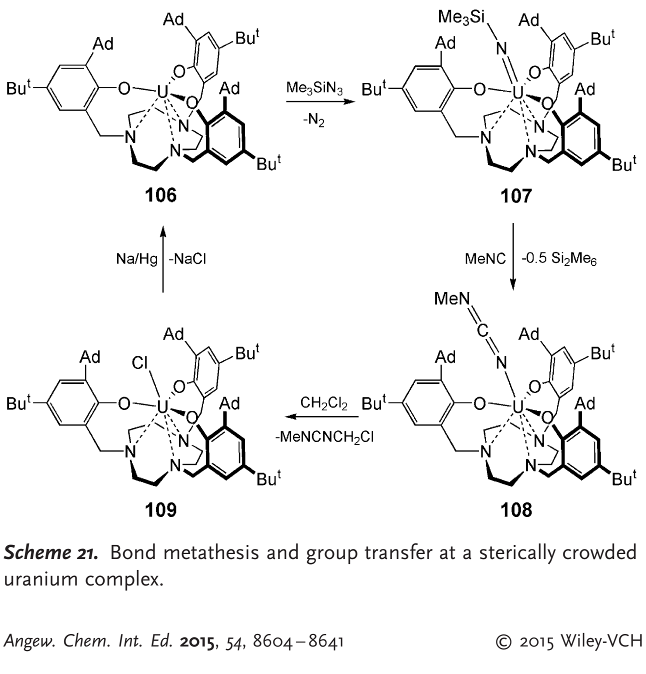


Scheme 20. a–c) Synthesis of the high-valent uranium imido complexes **99**, **102**, and **105**.

pathway. Interestingly, **107** also reacts with CO to afford the cyanate complex [U{tacn($CH_2C_6H_2$-3-Bu^t-5-Ad-6-O)$_3$}NCO].

For many years, terminal uranium imido complexes had been supported by a combination of fairly bulky ligands, but in 2011, it was shown that sterically demanding co-ligands are not necessarily a mandatory requirement, even for uranium(IV) (Scheme 22).[148] For example, treatment of **7** with KN(H)Dipp (2 equiv) affords [UI_2(NDipp)$(THF)_4$]. However, the synthesis of such species is evidently sensitive to the reagents and conditions as the analogous reaction between **6** and LiN(H)Dipp affords dimeric [{UCl_2(NDipp)$(THF)_2$}$_2$].

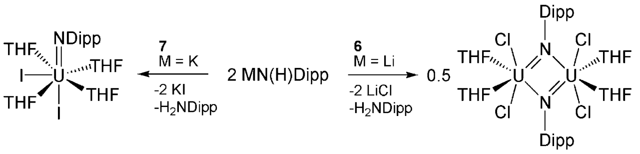
In 2012, the synthesis of the uranium(V) imido complex [U{N($CH_2C_6H_2$-3-Bu^t-5-Ad-6-O)$_3$}NMes] (**110**) from the trivalent precursor and $MesN_3$ was reported (Figure 21).[50a] Whereas the predicted structure would be a C_3-symmetric complex with the imido group *trans* to the amine, in fact the structure adopts a C_s structure with the imido group *trans* to an aryloxide oxo group. In contrast, the silyl imido congener adopts the anticipated C_3 geometry. The structure of **110** shows a relatively short U=N distance of 1.950(3) Å, and the *trans* oxo group displays the shortest of the three U−O distances at 2.145(2) Å (*cis* U−O on average 2.175(2) Å). This was taken as evidence of an ITI effect as for uranyl and represents the first observation of this effect with a uranium(V) center.



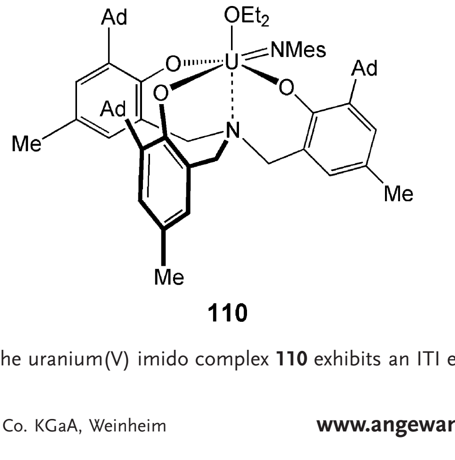
Scheme 21. Bond metathesis and group transfer at a sterically crowded uranium complex.

A notable feature of most metal imido complexes is the presence of a bulky *N*-R group, which stabilizes the U=N linkage. The stabilization of a U=N−R linkage with a small R group, especially R = H, would be expected to be challenging because of the large size of uranium. However, in 2014, the synthesis of the parent U=NH linkage was reported (Scheme 23).[149] Deprotonation of [U($Tren^{TIPS}$)NH_2] (**111**, $Tren^{TIPS}$ = N($CH_2CH_2NSiPr^i_3$)$_3$] with alkali-metal bases produces [{U($Tren^{TIPS}$)(NHM)}$_2$] (M = Li–Cs, **112Li**/**Na**/**K**/**Rb**/**Cs**), and for M = K, abstraction with two equivalents of 15C5 afforded [U($Tren^{TIPS}$)NH][K$(15C5)_2$] (**113**). The bulky $Tren^{TIPS}$ ligand and the anionic charge on the uranium component seem to stabilize the U=NH linkage; attempts to oxidize **113** resulted in disproportionation to give **111** and [U($Tren^{TIPS}$)N] (**114**),[50b] which most likely occurs by dimerization of the putative neutral intermediate "[U($Tren^{TIPS}$)NH]".

Returning to bis(imido) uranium chemistry, for 13 years, **99** had represented the only example of a bis(imido) uranium complex, until a general synthesis of bis(imido) uranyl

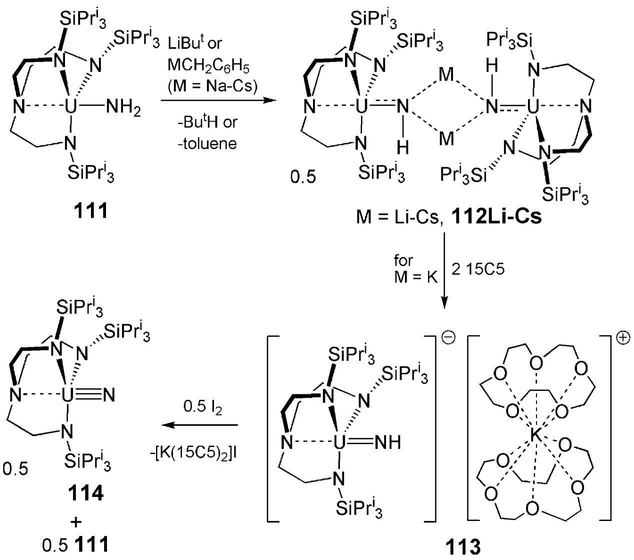


Scheme 22. Divergent outcomes in the preparation of uranium(IV) imido complexes.



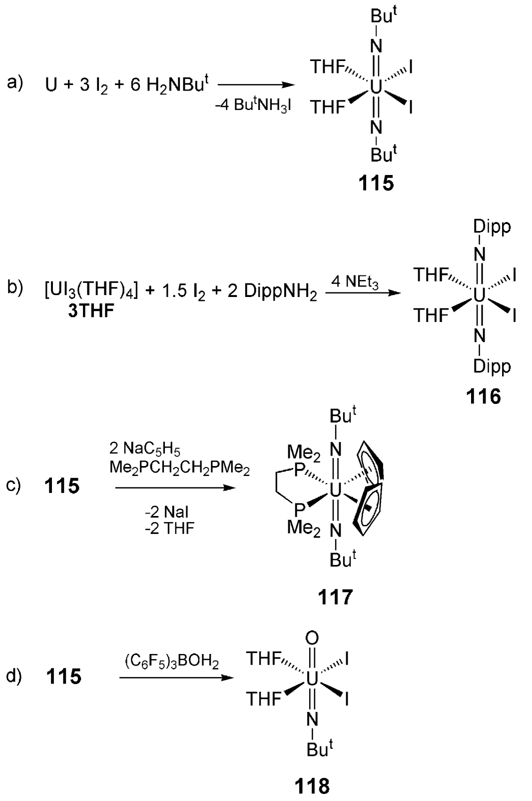
110

Figure 21. The uranium(V) imido complex **110** exhibits an ITI effect.



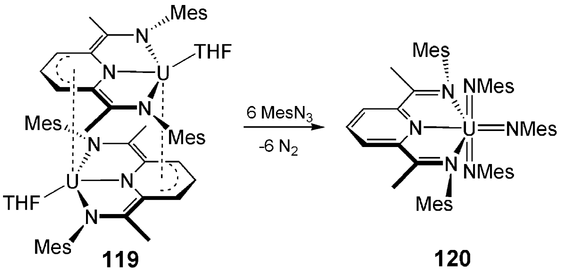
Scheme 23. Synthesis of bridging and terminal parent uranium(IV) imido complexes **112Li/Na/K/Rb/Cs** and **113**.

analogues was reported in 2005. Treatment of uranium metal with iodine and *tert*-butyl amine produced $[UI_2(NBu^t)_2(THF)_2]$ (**115**) in good yield (Scheme 24).[150] This chemistry could be extended to aryl imido compounds by reacting **3THF** with iodine, an aryl amine, and the auxiliary base triethylamine to form, for example, $[UI_2(NDipp)_2(THF)_3]$ (**116**). The $[RN{=}U{=}NR]^{2+}$ unit is isoelectronic to uranyl and, like uranyl, adopts a linear *trans* structure. This method has wide utility, and a large range of bis(imido) complexes have now been prepared. Theoretical studies of these bis(imido) complexes reveal a frontier orbital manifold with similarities to uranyl, but the bonding appears to be more covalent for the bis(imido) derivatives. Perhaps an indication of this is the fact that with suitable co-ligands, $[U(\eta^5\text{-}C_5H_5)_2(NBu^t)_2(Me_2PCH_2CH_2PMe_2)]$ (**117**) could be prepared by salt elimination whereas such reactions with uranyl would lead to reduction (see the necessity to prepare **52** by oxidation of a linear metallocene).[151] Complexes such as **115** were also shown to undergo oxo for imido group metathesis by hydrolysis to give a rare example of an OUNR linkage in $[UI_2(NBu^t)(O)(THF)_2]$ (**118**), which was computationally shown to maintain many of the bonding characteristics of uranyl.[152]



Scheme 24. a–d) Preparation and reactivity of uranium(VI) bis(imido) complexes **115**–**118**.

Having established that the bis(imido) uranium motif is generally available, the question was raised as to whether a tris(imido) complex of uranium could be prepared as this would be isoelectronic to UO_3. In 2014, the reducing power of uranium was combined with ligand non-innocence to prepare a uranium tris(imido) complex (Scheme 25).[153] Treatment of $[U\{C_5H_3N\text{-}2,6\text{-}(CMeNMes)_2\}(THF)]_2$ (**119**), which can be viewed either as a uranium(III)/ligand trianion or a uranium(IV)/ligand tetraanion combination, with $MesN_3$ (6 equiv) afforded $[U\{C_5H_3N\text{-}2,6\text{-}(CMeNMes)_2\}(NMes)_3]$ (**120**), which features a T-shaped $[U(NMes)_3]$ unit. A perhaps surprising conclusion from a theoretical assessment of **120** is that the $[U(NMes)_3]$ unit exhibits less covalency in the U−N bonds than the U−O bonds in the hypothetical model where the $[U(NMes)_3]$ unit is replaced by $[UO_3]$.

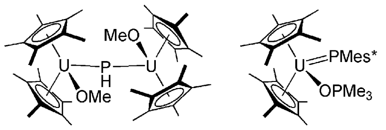


Scheme 25. Multi-electron reduction of **119** to afford the tris(imido) uranium(VI) complex **120**.

With the concept that uranium can support multiple bonding to nitrogen well-established, and single (amide) and double (imido, in a formal sense, in reality a triple-bonding interaction is often manifested) uranium–nitrogen bonds characterized, the search was on for a terminal uranium nitride complex with a covalent triple bond. The synthetic actinide community was given additional impetus to secure this target because molecules such as $[F_3U{\equiv}N]$, $[U{\equiv}N]$, and $[N{\equiv}U{\equiv}N]$, which date back to the 1970s, had been prepared and characterized in argon matrices at approximately 10 K,[154] whereas terminal uranium nitride complexes would remain elusive on a bulk preparative scale for four decades. Many elegant attempts resulted in nitrides that 1) bridge multiple metal centers, 2) are protected by a covalently bonded borane capping group that is impervious to removal, or 3) are generated photolytically, but activate ligand C−H bonds.[155] Finally, in 2012, the synthesis and characterization of a terminal uranium nitride was achieved on a bulk scale under ambient conditions (Scheme 26). Reaction of NaN_3 with trivalent [U(Tren^{TIPS})] (**121**) afforded the uranium(V) nitride [{U(Tren^{TIPS})(NNa)}$_2$] (**122**),[44a] which exhibits a U≡N bond length of 1.883(4) Å in the solid state. The observed ^{14}N/^{15}N isotopomer shift for the U≡N IR band from 955 to 930 cm^{-1} (calculated shift 925 cm^{-1}) supports the nitride formulation. Abstraction of the sodium cations by 12C4 from **122** yielded the terminal uranium(V) nitride complex [U(Tren^{TIPS})(N)][Na(12C4)$_2$] (**123**).[44a] An X-ray diffraction study revealed a U≡N bond length of 1.825(15) Å, which is approximately 0.06 Å shorter than in the bridging species. IR isotopic labelling studies (UN: 936 cm^{-1}, U^{15}N: 900 cm^{-1}) and other characterization data support the formulation. Theoretical calculations reveal one σ and two π components in the U≡N triple bond and a calculated Mayer bond order of 2.91. Interestingly, the σ bond is higher in energy than the two quasi-degenerate π bonds as is the case in uranyl. This is ascribed to an antibonding interaction between the nitride σ-bonding p orbital and the toroidal lobes of the uranium f and/or d orbitals that results from the short U≡N bond distance.

Although oxidation of **122** results in the loss of the nitride linkage, it was reported in 2013 that oxidation of **123** affords the neutral uranium(VI) nitride [U(Tren^{TIPS})(N)] (**114**) with a U≡N bond length of 1.799(7) Å (Scheme 26).[50b] The U−N$_{amine}$ distance is very short at 2.465(5) Å, which suggests the presence of an ITI effect as uranium–amine distances in Tren complexes tend to be approximately 2.6 Å irrespective of the oxidation state of uranium. Complex **114** is found to be photolytically unstable and decomposes to [U{N(CH$_2$CH$_2$NSiPr$^i_3$)$_2$(CH$_2$CH$_2$NS*i*Pr$^i_2$CMe$_2$NH}] (**124**), which is the same product as that obtained from the photolysis of [U(Tren^{TIPS})(N$_3$)] (**125**); this finding suggests that photolysis of this azide proceeds via a nitride as proposed by uranium metallocene azide photolysis chemistry.[155h] A theoretical study of nitrides **123** and **114** suggested that there is appreciable covalency in the U≡N bond, and surprisingly, for uranium(VI) at least, as much covalency as in analogous Group 6 terminal nitrides. Interesting reactivity of the U≡N bond is beginning to emerge, including reductive homologation by CO to produce cyanate, which provides a N_3^- to N^{3-} to OCN^- synthetic cycle and a rare example of complete nitride N-atom transfer to a substrate.[156]

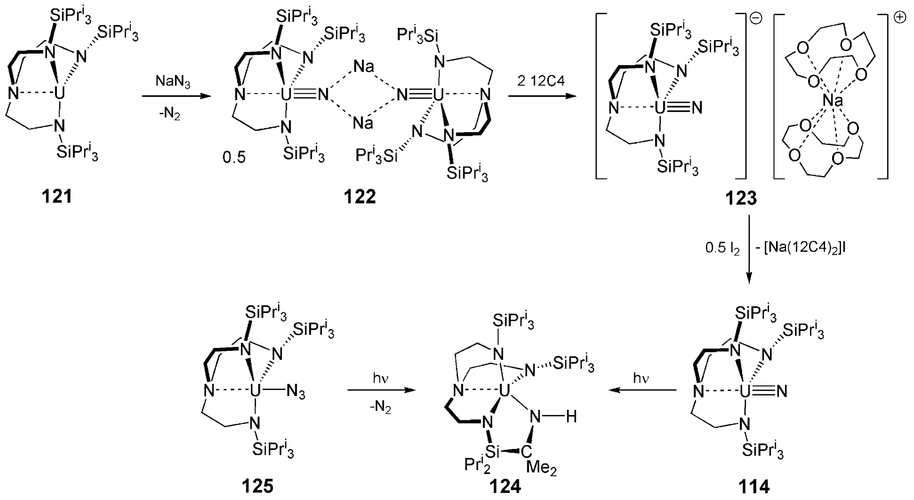
The majority of reported uranium pnictide chemistry involves nitrogen derivatives, and there are considerably fewer heavier-pnictide complexes reported in terms of covalent U−P bonds. A small number of phospholide complexes are known,[157] and only two phosphide complexes have been reported, namely [U(η^5-C$_5$Me$_5$)$_2$(Cl){P(SiMe$_3$)$_2$}] and [U(η^5-C$_5$Me$_5$)$_2$(CH$_2$SiMe$_2$PSiMe$_3$)].[158] Only two terminal phosphinidenes and two bridging phosphinidiides are known. The first bridging phosphinidiide was reported in 1984, where reaction of trimethylphosphite with [U(η^5-C$_5$Me$_5$)$_2$(H)$_2$] induces dealkoxylation to form [{U(η^5-C$_5$Me$_5$)$_2$(OMe)}$_2$(μ-PH)] (**126**),[159] with [U(η^5-C$_5$Me$_5$)$_2$(OMe)$_2$] concomitantly formed as a by-product (Figure 22). In 1996, the first terminal uranium phosphinidene was reported from the reaction of [U(η^5-C$_5$Me$_5$)$_2$(Me)(Cl)] with KP(H)Mes*; in the presence of trimethylphosphine oxide, methane and KCl are eliminated to produce the uranium(IV) complex [U(η^5-C$_5$Me$_5$)$_2$(PMes*)(OPMe$_3$)] (**127**; Figure 22).[160] The U=P distance was found to be 2.562(3) Å by X-ray crystallography, and the U-P-C$_{ipso}$ angle of 143.7(3)° is as expected for a combination of metal and phosphinidene triplet fragments.



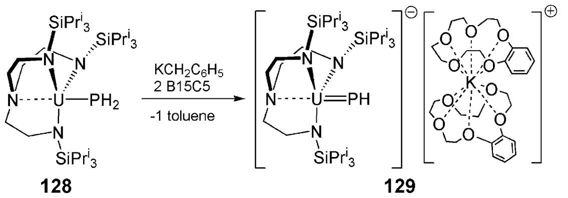
126 **127**

Figure 22. Uranium phosphinidiide and phosphinidene complexes **126** and **127**.

Simultaneously to the report of the parent terminal imido complex **113**,[149] the preparation of a parent terminal phosphinidene complex of uranium was also reported in 2014 (Scheme 27). In analogy to the preparation of **113**, treatment of [U(Tren^{TIPS})(PH$_2$)] (**128**) with benzyl potassium and B15C5 (2 equiv) afforded [U-



Scheme 26. Synthesis and reactivity of the terminal uranium nitrides **123** and **114**.

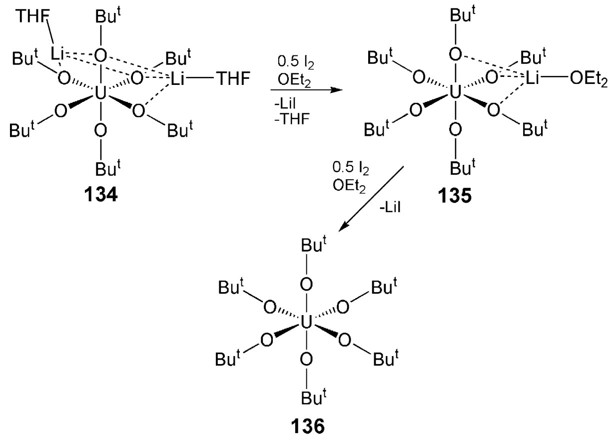


Scheme 27. Synthesis of the terminal parent uranium phosphinidene complex **129** from **128**.

(Tren$^{\mathrm{TIPS}}$)(PH)][K(B15C5)$_2$] (**129**).[161] The U=P distance in **129** was determined to be 2.613(2) Å by X-ray crystallography, and unlike the U=N–H linkage in **113**, which is essentially linear, the U=P–H linkage is bent with an angle of 118.8(9)°, as expected. The report of **129** demonstrates the ability of uranium to stabilize highly reactive parent main-group fragments, and, like **113**, that bulky stabilizing *E*-R ($E = \mathrm{N, P}$) groups are not always required.

4.3. Ligands with Chalcogenide Donor Atoms

A significant amount of effort was expended on investigations of uranium alkoxides owing to their possible applications in uranium isotope enrichment. This is due to their potential volatility and the fact that alkoxides are, aside from the oxo, imido, and halide ligands, one of the few ligand sets that can stabilize the hexavalent state of uranium. However, although extensive investigations of homoleptic [U(OR)$_6$] complexes (R = Me, Et, Pr^i, Bu^t) were carried out in the 1950s and 1960s, they were only partially characterized by modern-day standards.[162]



Scheme 28. Synthesis of the homoleptic uranium *tert*-butoxide **136** from **134** via **135**.

A common feature of electropositive metal alkoxide chemistry is that it is frequently more complicated than anticipated. For example, studies reported in the 1980s showed that attempts to prepare [U(OBu^t)$_4$] probably resulted in the formation of [U$_2$(OBu^t)$_9$K] (**130**), and it has been shown that **130** can be converted into the mixed-valence complex [U$_2$(OBu^t)$_9$] (**131**) or an oxo-capped trinuclear structure [U$_3$(O)(OBu^t)$_{10}$] (**132**) depending on the reaction conditions (Figure 23).[163] Pentavalent alkoxides are also known, but again often adopt dimeric structures such as [U$_2$(OBu^t)$_{10}$] (**133**; Figure 23).[164] Some of these reactions were revisited in 2008 (Scheme 28);[165] treatment of UCl$_4$ with LiOBu^t (6 equiv) results in the formation of [U(OBu^t)$_6$Li$_2$(THF)$_2$] (**134**), and this complex can be oxidized with iodine (0.5 or 1 equiv) to produce [U(OBu^t)$_6$Li(OEt$_2$)] (**135**) or [U(OBu^t)$_6$] (**136**), respectively. Notably, the U$^{\mathrm{VI}}$/U$^{\mathrm{V}}$ redox potential of −1.12 V for **136** (vs. Fc/Fc$^+$) contrasts to that of UF$_6$ (2.31 V vs. Ag/Ag$^+$); the latter is known to be a strong oxidizing agent, and these observations probably reflect the stronger π-donating capacity of alkoxides with respect to halides, which is an effect that has also been observed in Group 6 chemistry.

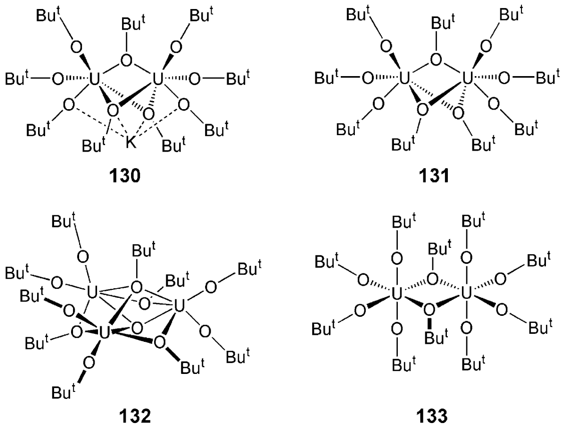


Figure 23. Uranium *tert*-butoxide complexes **130**–**133**.

Like alkoxides, aryloxides have also found utility in uranium chemistry. The majority of examples include heteroleptic systems where the aryloxide fragment is either one of several co-ligands or is part of a more complicated ligand, for example, in tacn-trisaryloxides. However, there are only few homoleptic examples. The first homoleptic uranium(III) aryloxide was reported in 1988 and utilized a bulky ODipp group. Treatment of **75** with DippOH (3 equiv) afforded [{U(ODipp)$_3$}$_2$] (**137**) as a dimer in the solid state, which is held together by U⋯η^6-arene interactions (Figure 24).[166] The

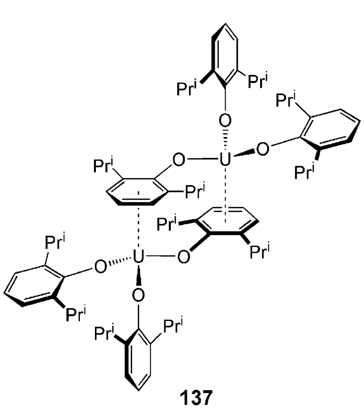


Figure 24. The homoleptic uranium(III) aryloxide complex **137**.

related complex [U(ODitb)$_3$] (**19**, see Scheme 6) was reported at the same time, and although a solid-state structure was not known then, analysis of the IR spectra suggested it to be monomeric, which was confirmed by a solid-state structural determination in 2011.[115] Complex **19** is clearly not totally sterically saturated because the tetravalent analogue [U(ODitb)$_4$] (**63**, see Scheme 13) can be prepared and is also monomeric.[167]

In recent years, there has been a focus on multiply bonded uranium–chalcogen bonds. The field of uranyl coordination chemistry is huge and constitutes nearly half of all structurally characterized uranium complexes in the Cambridge Structural Database. Uranyl chemistry has been extensively reviewed in recent years, both in terms of uranyl(VI) and uranyl(V) chemistry, the latter of which includes clusters that exhibit U–U magnetic coupling,[168] and creative routes to activate and silylate the yl-oxo unit[32e] and in some cases even functionalize or cleave the oxo ligand have been reported.[169] An extended discussion of uranyl chemistry is beyond the scope of this Review,[26g,27c] and therefore, this Section focuses principally on complexes with only one chalcogen donor atom.

In addition to the uranium mono-oxo complexes **48**, **53**, **102**, and **105** (Figure 14 and Schemes 11 and 20), the synthesis of uranium mono-oxo complexes, such as [OUCl$_5$]$^{2-}$ (**138**), [OUCl$_5$]$^-$ (**139**), and [OUF$_4$] (**140**), can be traced back to the 1970s (Figure 25).[170] In 2003, it was shown that bond metathesis of imido complexes [U(tacn[CH$_2$C$_6$H$_2$-2-O-3-R-5-Bu^t]$_3$(NMes)] (R = Bu^t, **141**; R = Ad, **142**) with carbon dioxide produced the terminal mono-oxo uranium complexes [U(tacn[CH$_2$C$_6$H$_2$-2-O-3-R-5-Bu^t]$_3$(O)] (R = Bu^t, **143**; R = Ad, **144**) with elimination of MesNCO isocyanate as the by-product (Scheme 29).[171]

Most mono-oxo complexes of uranium involve uranium(V) or uranium(VI). A notable exception is the base-free uranium(IV) terminal oxo species [U{HB(N$_2$C$_3$H-3,5-Me$_2$}$_2$(O)] (**145**), which was reported in 2010 (Figure 26).[172] Complex **145** was prepared by oxidation of the bipyridine complex [U{HB(N$_2$C$_3$H-3,5-Me$_2$}$_2$(bipy)] with pyridine *N*-oxide. Theoretical studies revealed a $\sigma^2\pi^4$ triple bonding interaction between uranium and oxygen and a U=O distance of 1.863(4) Å (ca. 0.1 Å longer than in uranyl derivatives).

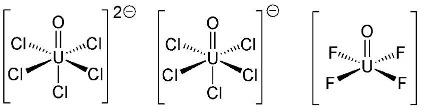
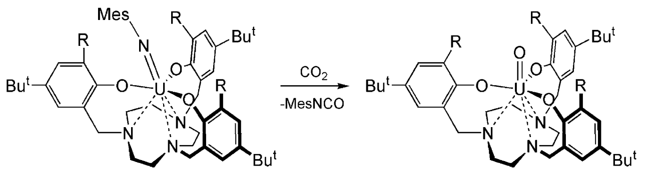

138 **139** **140**

Figure 25. Structures of the uranium mono-oxo complexes **138**–**140**.


R = Bu^t, **141**
R = Ad, **142**

R = Bu^t, **143**
R = Ad, **144**

Scheme 29. Bond metathesis of uranium(V) imido complexes to give the terminal uranium(V) mono-oxo complexes **143** and **144**.

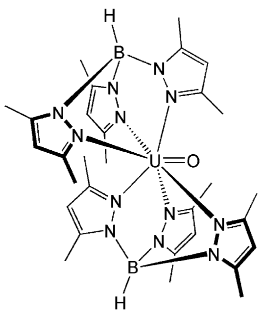
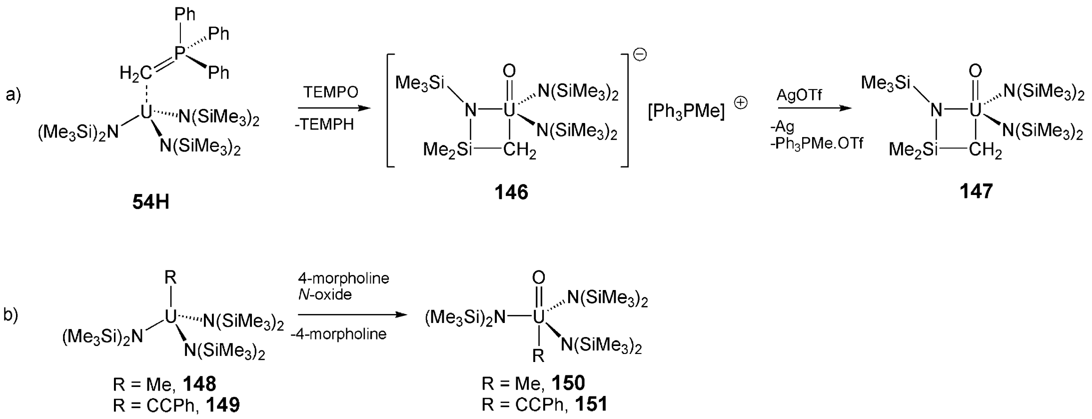

145

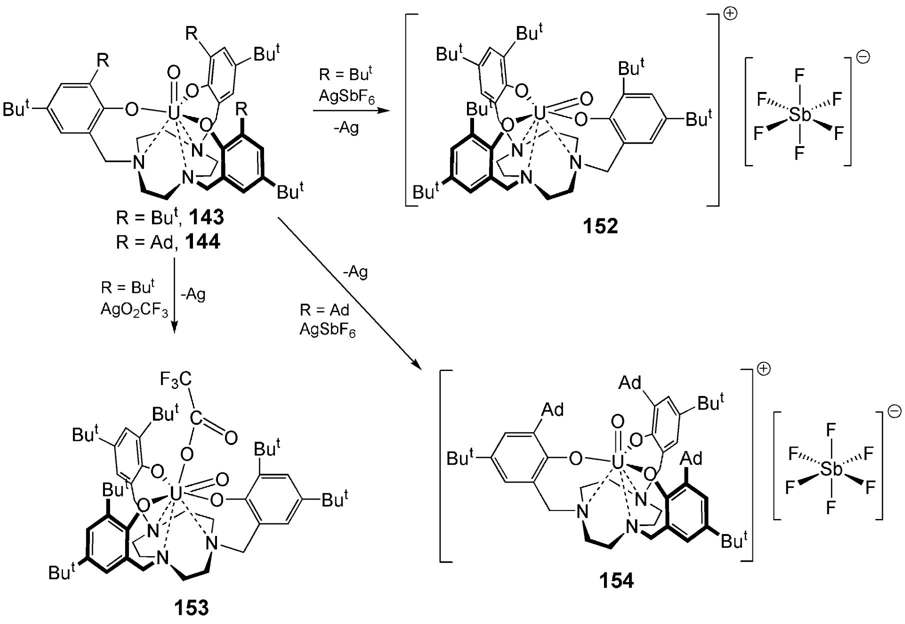
Figure 26. The terminal uranium(IV) mono-oxo complex **145**.

In 2011, it was shown that the oxidation of the trivalent ylide complex **54H** with TEMPO affords the uranium(V) mono-oxo alkyl complex [U{N(SiMe$_3$)$_2$}$_2$(CH$_2$SiMe$_2$NSiMe$_3$)(O)][Ph$_3$PMe] (**146**; Scheme 30).[173] Complex **146** can be further oxidized with AgOTf to afford [U{N(SiMe$_3$)$_2$}$_2$(CH$_2$SiMe$_2$NSiMe$_3$)(O)] (**147**).[173] Both complexes represent rare examples of high-valent uranium alkyl species. Following a similar strategy, it was shown in 2013 that tetravalent [U{N(SiMe$_3$)$_2$}$_3$(R)] (R = Me, **148**; R = CCPh, **149**) could be oxidized by 4-morpholine *N*-oxide to afford [U{N(SiMe$_3$)$_2$}$_3$(R)(O)] (R = Me, **150**; CCPh, **151**), which are unusually stable for uranium(VI) alkyl compounds (Scheme 30).[174] Theoretical analyses revealed that an ITI effect was operating, and for a range of derivatives where the alkyl group was replaced with halides, and theoretically with other co-ligands, it was possible to construct a ligand stability series in which σ-effects dominate: $CN^- < I^- \approx Br^- < Cl^- \approx SPh^- < PhCC^- \approx F^- < MeO^- < Me_2N^- < Me^- < H^-$.

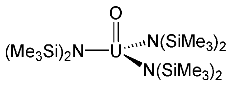
Some unusual uranium(VI) mono-oxo complexes that exhibit molecular structure driven by the ITI effect were reported in 2012 (Scheme 31).[175] When the uranium(V) complex [U{tacn(CH$_2$C$_6$H$_2$-2-O-3,5-Bu$^t_2$)$_3$}(O)] (**143**) is oxidized with AgSbF$_6$ or AgO$_2$CCF$_3$, the uranium(VI) complexes [U{tacn(CH$_2$C$_6$H$_2$-2-O-3,5-Bu$^t_2$)$_3$}(O)][SbF$_6$] (**152**) and [U{tacn(CH$_2$C$_6$H$_2$-2-O-3,5-Bu$^t_2$)$_3$}(O)(O$_2$CCF$_3$)] (**153**) are isolated. In both cases, rather than the oxo group residing in an axial position and the complexes adopting C_3 geometries, distorted C_S geometries are adopted, and the oxo groups reside *trans* to an aryloxide. In **153**, the acetate is coordinated in the axial position whereas in **152**, the axial position is vacant. The observation that in both complexes, the oxo groups adopt equatorial positions shows that the axial site plays no role in driving the geometry. Instead, noting that the *trans*-oxo group exhibits the shortest U–O distance, like in the ITI imido complex **110** (Figure 21), it is concluded that it is an ITI effect that drives the geometry. The energetics of this process have been qualitatively bracketed at approximately 6 kcal mol^{-1} from theoretical calculations, which is consistent with the fact that such complexes can be forced to adopt geometries with the oxo group in the axial position using sterically demanding aryloxide substituents that sterically disfavor equatorial binding, as found, for example, in the



Scheme 30. a, b) Synthesis of the mono-oxo uranium alkyl species **146**, **147**, **150**, and **151**.



Scheme 31. Synthesis of the uranium(VI) mono-oxo complexes **152**–**154**.



155

Figure 27. The uranium(V) oxo complex **155**.

closely related complex [U{tacn($CH_2C_6H_2$-2-O-3-Ad-5-Bu^t)$_3$}(O)][SbF_6] (**154**).

In 2012, it was reported that the oxidation of **75** with TEMPO affords the uranium(V) oxo complex [U{N($SiMe_3$)$_2$}$_3$(O)] (**155**), which adopts an unusual trigonal-pyramidal, rather than a tetrahedral, geometry (Figure 27).[176] Theoretical calculations suggest that this geometry is orbital-driven whereas a second-order Jahn–Teller effect is not discernable.

It was once thought that owing to the hard–soft mismatch, soft S-donor ligands were unsuitable for use with hard actinides. However, over the past two decades, this view has been invalidated, and a range of uranium thiolate complexes, such as [U(SMes*)$_3$] (**156**)[177] and [U(SMes*)$_4$] (**157**),[177] and dithiolenes, such as [U(COT){($SCSCH_2$)$_2$}]$^{2-}$ (**158**),[178] are now known (Figure 28), which once again demonstrates that with suitable ancillary ligands, linkages that were thought to be disfavored can be prepared, enabling the isolation of compounds that were thought to be unstable.

Going further still, it has recently been demonstrated that "naked" chalcogens can be assembled and stabilized at uranium (Figure 29).[179] For example, in the past four years, complexes with U-E-U (**159**–**162**), UE_2U (**163**), U(E_2) (E = S, Se, Te, **164**–**168**), and U(S_3) (**169**) fragments were prepared by reactions of the elemental chalcogens with uranium(III) precursors (for representative examples, see Figure 29). Some of these complexes have formed the basis for "stitching together" chalcogens to form E_2 and E_4 units (e.g., in **170**). Also, it was recently disclosed that EH_2 (E = S, Se, Te) reacted with [U{N($CH_2C_6H_2$-3-Me-5-Ad-6-O)$_3$}(DME)] to afford [U{N($CH_2C_6H_2$-3-Me-5-Ad-6-O)$_3$}(EH)(DME)] (**171**; Figure 30), which contains terminal EH units and is thus analogous to the parent imido and phosphinidene complexes **113** and **129** (see Schemes 23 and 27).

Heavier chalcogens have also been shown to be capable of forming multiple bonds to uranium, even though there are few examples. In 1999, it was found that treatment of [U(η^5-C_5Me_5)$_2$(SBu^t)$_2$] (**172**) with sodium–mercury amalgam resulted in C–S bond homolysis to give [U(η^5-C_5Me_5)$_2$(SBu^t)(S)][Na(18C6)] (**173**) after recrystallization in the presence of 18C6 (Scheme 32).[180] In the solid-state structure, the U=S unit is weakly coordinated to the Na center, but the U=S bond length of 2.477(2) Å is considerably shorter than the U–S bond distance of 2.744(2) Å, which supports a U=S multiple bond. Complex **173** was perhaps ahead of its time because the area fell dormant for over a decade until in 2012,

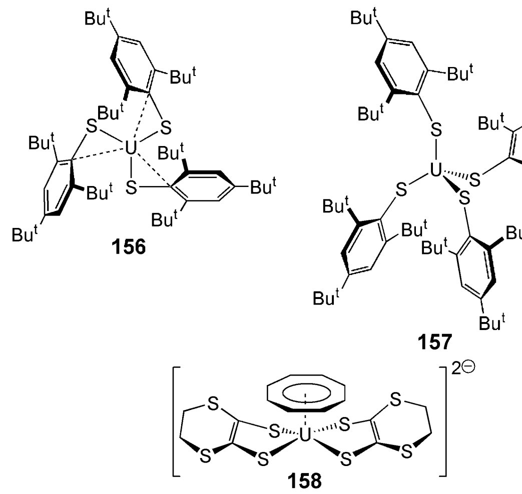


Figure 28. The uranium chalcogenide complexes **156**–**158**.

a series of uranium(IV) chalcogen complexes [U{N(SiMe$_3$)$_2$}$_3$(E)][Ph$_3$PMe] (E = S, **174**; E = Se, **175**; S = Te, **176**) were prepared (Scheme 32).[181] Proving its utility again, ylide complex **54H** was straightforwardly oxidized by elemental chalcogens to give complexes **174**–**176**. To complete the series, complex **155** was reduced with decamethyl cobaltocene to give [U{N(SiMe$_3$)$_2$}$_3$(O)][Co(η^5-C$_5$Me$_5$)$_2$] (**177**).

Multiple bonds with heavier chalcogens have also been extended to uranium(VI) to generate heavy uranyl(VI) analogues. Using **177** as a starting point, oxidation with S or Se afforded the heavy uranyl analogues [U{N(SiMe$_3$)$_2$}$_3$(O)(S)][Co(η^5-C$_5$Me$_5$)$_2$] (**178**) and [U{N(SiMe$_3$)$_2$}$_3$(O)(Se)][Co(η^5-C$_5$Me$_5$)$_2$] (**179**; see Scheme 33).[182] The tellurium analogue was not accessible by this method, presumably because Te is not sufficiently oxidizing. For completeness, the uranyl(VI) analogue, [UO$_2${N(SiMe$_3$)$_2$}$_3$][Co(η^5-C$_5$Me$_5$)$_2$] (**180**) was prepared, and this complex is analogous to **81** (Scheme 17). Theoretical calculations reveal uranyl-type bonding, but as E becomes heavier, the bonding of the U–E unit becomes increasingly localized on E, and thus delocalization across the [O=U=E]$^{2+}$ unit deconvolutes with less mixing as O is replaced by S and then Se.

5. Molecular Magnetism

The basic principles of static uranium magnetism are reasonably well understood (Section 2.5). However, the area continues to be fascinating because of novel phenomena that are frequently observed, such as magnetic coupling and

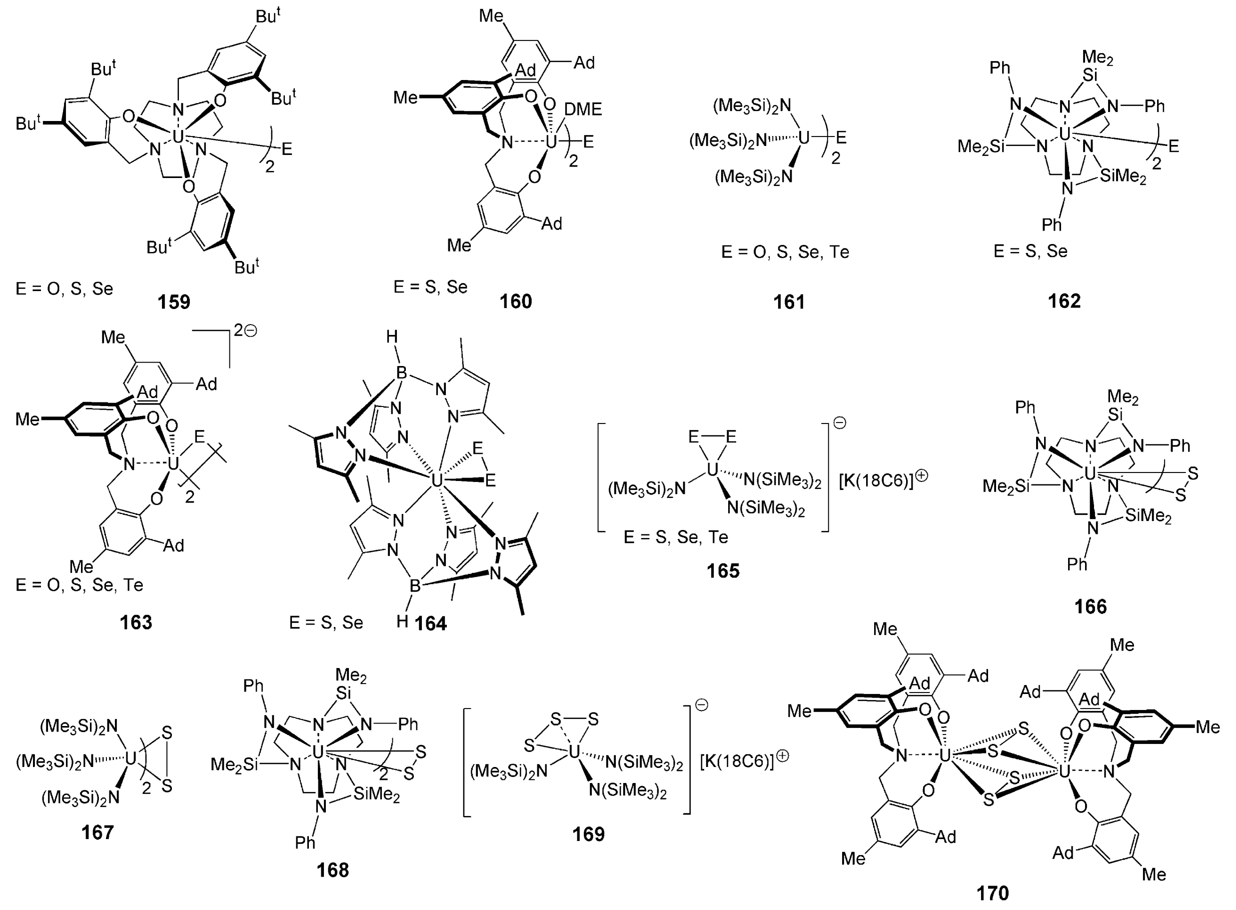


Figure 29. Selected uranium chalcogenide complexes **159**–**170**.

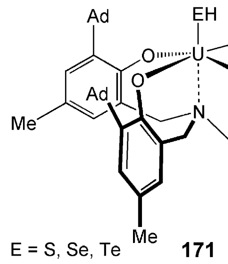
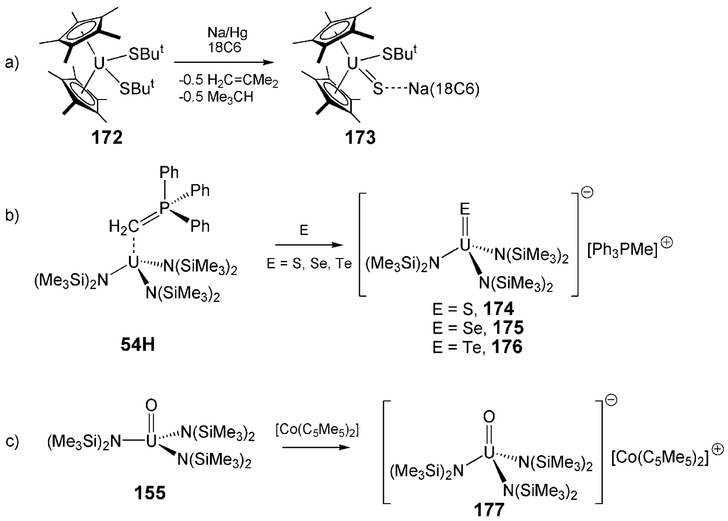


Figure 30. Terminal EH (E = S, Se, Te) moieties at uranium in complex **171**.

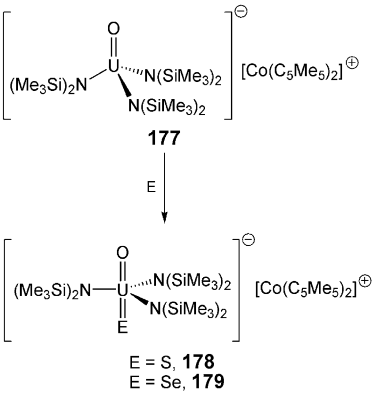


Scheme 32. a–c): Multiple bonds between heavier chalcogens and uranium in compounds **173**–**177**.

single-molecule magnetism.[183] Molecular antiferromagnetic coupling was first observed between uranium(V) centers in $[\{U(\eta^5\text{-}C_5H_4Me)_3\}_2(1,4\text{-}NC_6H_4N)]$ (**181**; Figure 31) in 1990 and rationalized on the basis of superexchange.[184] Further examples of unusual and notable uranium(V)–uranium(V) coupling involve a pentavalent bis(imido) uranium dimer,[185] diuranium(V) dioxo diamond cores,[186] which can exhibit Neél temperatures of up to 70 K, which are surpassed only by a Neél temperature of 110 K for the diuranium(III) arene dianion complex **57**, and pentavalent uranyl–uranyl coupling.[168] As expected for the more ionic uranium(IV) species, reports of uranium(IV)–uranium(IV) couplings are far fewer, and are limited to two examples,[179a,187] both of which are mediated by chalcogen bridges. However, examples of uranium(IV)–copper(II) and uranium(IV)–nickel(II) couplings have been reported.[188]

5.1. Single-Molecule Magnetism of Uranium(III)

In the arena of dynamic magnetism, it was first shown in 2009 that uranium(III) can exhibit SMM behavior.[189] The complex $[U\{Ph_2B(N_2C_3H_3)_2\}_3]$ (**182**; Figure 32) exhibits frequency-dependent maxima in the out-of-phase (χ''_{M}) ac susceptibility, which is indicative of slow magnetic relaxation. In the thermally activated regime, an energy barrier of $U_{\mathrm{eff}} = 20\ \mathrm{cm}^{-1}$ (29 K) was extracted, but at low temperature, quantum tunneling occurs, which bypasses the thermal barrier to relaxation. Since 2009, a number of uranium(III) SMMs have been reported,[127,190] which are mainly supported by pyrazolylborate ligands. Interestingly, **3THF**, **75**, **76**, and $[U(BIPM^{TMS}H)(I)_2(THF)]$ (**183**; Figure 32) have shown SMM behavior, and despite the fact that their symmetries at uranium are different, they present remarkably similar U_{eff} values of 12.9 (18.6 K), 21.5 (31 K), 21.4 (31 K), and 16.3 (23.4 K) cm^{-1}.[191] As stated above, one inverted sandwich diuranium(III) arene dianion complex uniquely exhibits SMM behavior. Specifically, $[\{U(BIPM^{TMS}H)(I)\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_5Me)]$ (**184**) was first described in 2011 (Figure 32),[192] and this complex exhibits slow relaxation as evidenced by frequency-dependent maxima in the χ''_{M} plots. Complex **184** exhibits hysteresis that collapses at zero-field to give a butterfly-shaped curve, which is a common phenomenon for uranium(III) SMMs, that is, uranium SMMs are often field-induced. Unfortunately, an energy barrier to the reversal of the magnetization could not be obtained, but this compound suggests promise for constructing polyuranium complexes with improved SMM characteristics. Quantum tunneling allows complexes to relax with much lower energy barriers than a purely thermal regime would suggest. One way to potentially avoid this is to force the m_J levels of opposite sign away from degeneracy by using a small external local magnetic field. One way to do this is with a neighboring spin, and this effect, called exchange bias, could be effected in a number of ways, but introducing an open-shell



Scheme 33. Synthesis of the heavy uranyl analogues **178** and **179**.

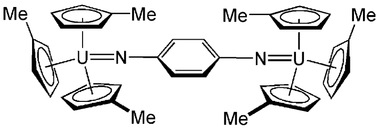


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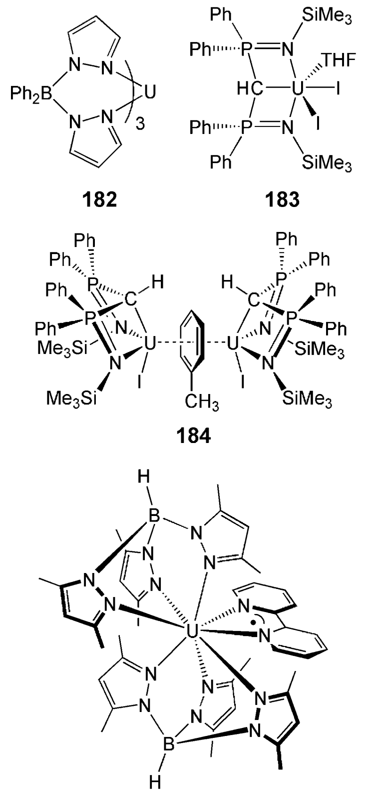
Figure 31. The diuranium(V) imido complex **181**, which exhibits antiferromagnetic U–U coupling.



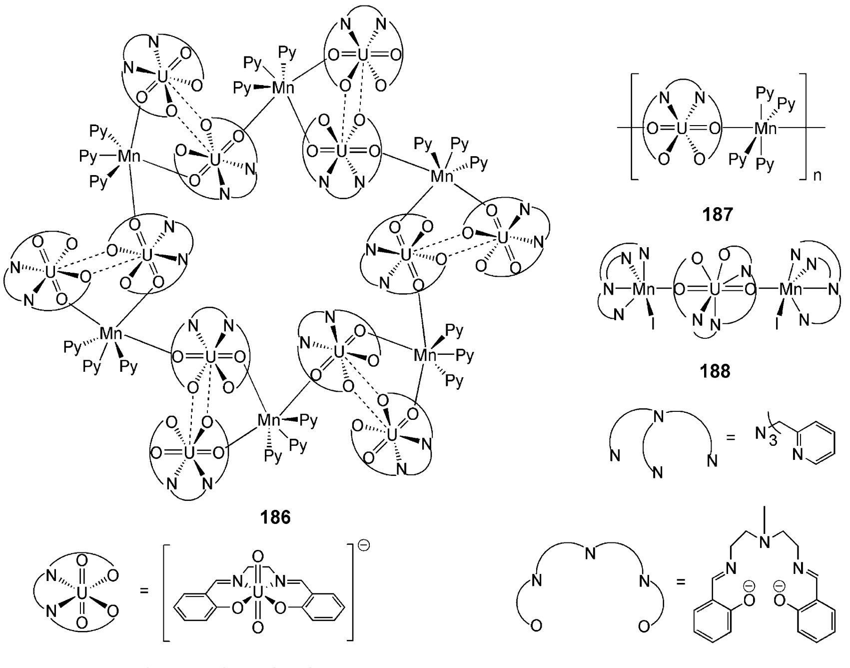
182 **183** **184** **185**

Figure 32. Selected uranium(III) single-molecule magnets **182**–**185**.

ligand radical is an attractive approach that was recently reported. Complex **185**[193] (Figure 32) shows clear signs of antiferromagnetic coupling at low temperature, but even in the zero-field, SMM behavior is exhibited suggesting that quantum tunneling has been suppressed by the ligand radical, which holds promise for the design of uranium(III) SMMs with higher blocking temperatures in the future.

5.2. Single-Molecule Magnetism of Uranium(V)

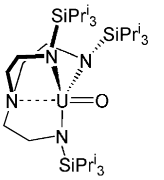
At first, all examples of uranium SMMs contained formally trivalent uranium ions. This changed in 2012 with the report of an aesthetically pleasing nanometer-scale wheel-shaped complex $[\{(UO_2[(CH_2NCHC_6H_4\text{-}2\text{-}O)_2])_2(Mn[Py]_3)\}_6]$ (**186**), which contains twelve uranyl(V) and six manganese(II) centers (Figure 33).[194] In complex **186**, uranyl/salen anion fragments dimerize via bridging aryloxide units, and each dimer coordinates via the yl-oxo groups to a Mn center, which in turn binds to one yl-oxo of the next unit. The dc susceptibility measurements are indicative of significant magnetic interactions between the uranyl(V) and manganese(II) ions. In the thermally activated regime of magnetic relaxation, an energy barrier of 98.7 cm^{-1} (142 K) was determined. As the manganese(II) centers might not have a sizeable anisotropy of their own, the uranyl(V) ions may play a significant role in the magnetization dynamics, but their relationship is not fully resolved as a variant with a non-magnetic metal(II) ion to isolate the uranyl(V) contribution is currently not available. This complex exhibits coercivity at 2.25 K with a coercive field of approximately 1.5 T. Quantum tunneling could be observed in hysteresis loops as step-like features. The strength of the mixed uranyl/3d approach was underlined by reports in 2014 of a uranyl(V)/manganese(II) single-chain magnet (**187**) with an energy barrier of 93 cm^{-1} (134 K), and a uranyl(V)/bis(manganese(II)) complex (**188**) with a relaxation barrier of 56.3 cm^{-1} (81 K).[195] The latter barrier is the largest for any discrete single-uranium-ion SMM, and in both systems, the hysteresis loops remain open at zero-field. In these latter two systems, the effective energy barrier depends on the magnetic coupling strengths as well as on the single-ion anisotropies.



186 **187** **188**

Figure 33. Uranyl(V) single-molecule magnets **186**–**188**.

In 2013, the synthesis of a terminal uranium(V) mono-oxo complex supported by a Tren ligand was reported (Figure 34).[196] Specifically, oxidation of **121** with Me$_3$NO afforded [U(Tren$^{\mathrm{TIPS}}$)(O)] (**189**). This complex is notable for three reasons. First, there appears to be an ITI effect in this molecule, as in the uranium(VI) nitride analogue **114** (Scheme 26) where the amine *trans* to the oxo bonds to uranium is located at an unusually close distance of 2.482(6) Å. Second, **189** is the first example of a monometallic f^1 SMM. Third, **189** unambiguously demonstrates the important principle that in a strong axial crystal field, uranium(V)



189

Figure 34. The single-ion uranium(V) single-molecule magnet **189**.

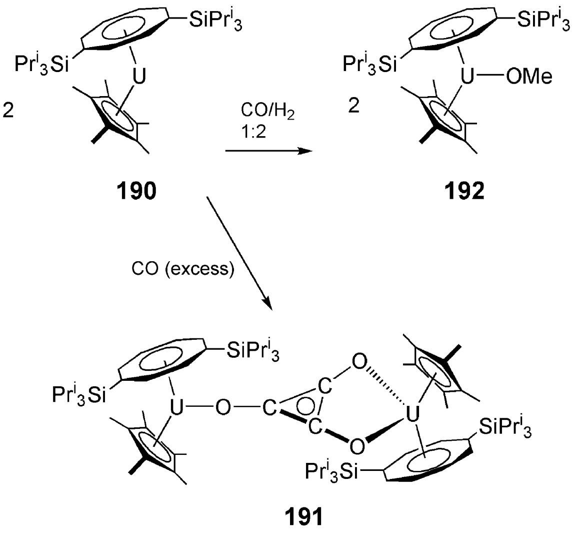
can exhibit SMM behavior. Complex **189** possesses a strong axial ligand field from the amine and oxo groups, and whilst the energy barrier of this complex to relaxation of the magnetization breaks no records at 15.3 cm^{-1} (22 K), it does exhibit slow relaxation up to a blocking temperature of 3.5 K and at scanning frequencies as low as 10 Hz.

6. Small-Molecule Activation

The binding and activation of small molecules at uranium has received intense interest over the past 15 years, and the area has been comprehensively reviewed recently.[25a,e,f,30j,31b] Therefore, and as various examples have been covered above, the following Section describes some of the more notable advances to provide a flavor of the novel small-molecule activation processes that uranium is capable of effecting. These examples usually have no counterparts in the d or p blocks.

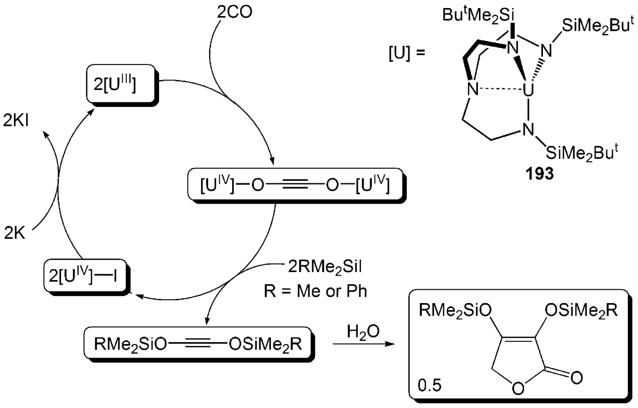
6.1. Carbon Monoxide

A major step forward in the reductive homologation of CO was reported in 2006.[197] Reaction of CO with the solvent-free organouranium(III) complex $[U\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(SiPr^i_3)_2\}(\eta^5\text{-}C_5Me_5)]$ (**190**) affords the cyclotrimerized product $[\{U(\eta^8\text{-}C_8H_6\text{-}1,4\text{-}[SiPr^i_3]_2)(\eta^5\text{-}C_5Me_5)\}_2(\kappa^1{:}\kappa^2\text{-}C_3O_3)]$ (**191**; Scheme 34). Subsequent studies have shown that a terminal CO adduct is first formed, which then couples in a "zig-zag" complex in a process that is promoted by the reduction. It was also found that varying the steric demand of the cyclopentadienyl ligand modulates the oligomerization of CO to produce squarate $(C_4O_4)^{2-}$ or ethyne diolate $(C_2O_2)^{2-}$.[198] When this reaction is carried out in the presence of two equivalents of hydrogen, a remarkable hydrogenation reaction occurs to give the methoxide complex $[\{U(\eta^8\text{-}C_8H_6\text{-}1,4\text{-}[SiPr^i_3]_2)(\eta^5\text{-}C_5Me_5)\}_2(OMe)]$ (**192**; Scheme 34). The methoxide can be extricated as its silyl ether, and the resulting uranium triflate can be reduced back to **190** to close the reaction cycle.[199]



Scheme 34. Reactivity of an organouranium(III) complex with CO and CO/H_2 to produce **191** and **192**.

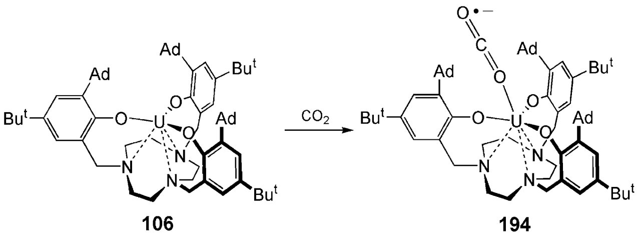
With the exception of **192**, reductive CO homologation usually resists further steps beyond the initial coupling because of the formation of strong U–O bonds. However, for example, it was shown in 2011 that $(C_2O_2)^{2-}$ can be formed when coupled by **75** and functionalized by activation of a ligand C–H bond.[200] In 2012, it was demonstrated that with certain reagents, $(C_2O_2)^{2-}$ can be liberated as its silyl ether to give closed synthetic cycles when the chemistry is supported by $[U(Tren^{DMBS})]$ (**193**, $Tren^{DMBS} = N(CH_2CH_2NSiMe_2Bu^t)_3$; Scheme 35).[187]



Scheme 35. Reductive homologation of CO to give a furanone in a synthetic cycle promoted by **193**.

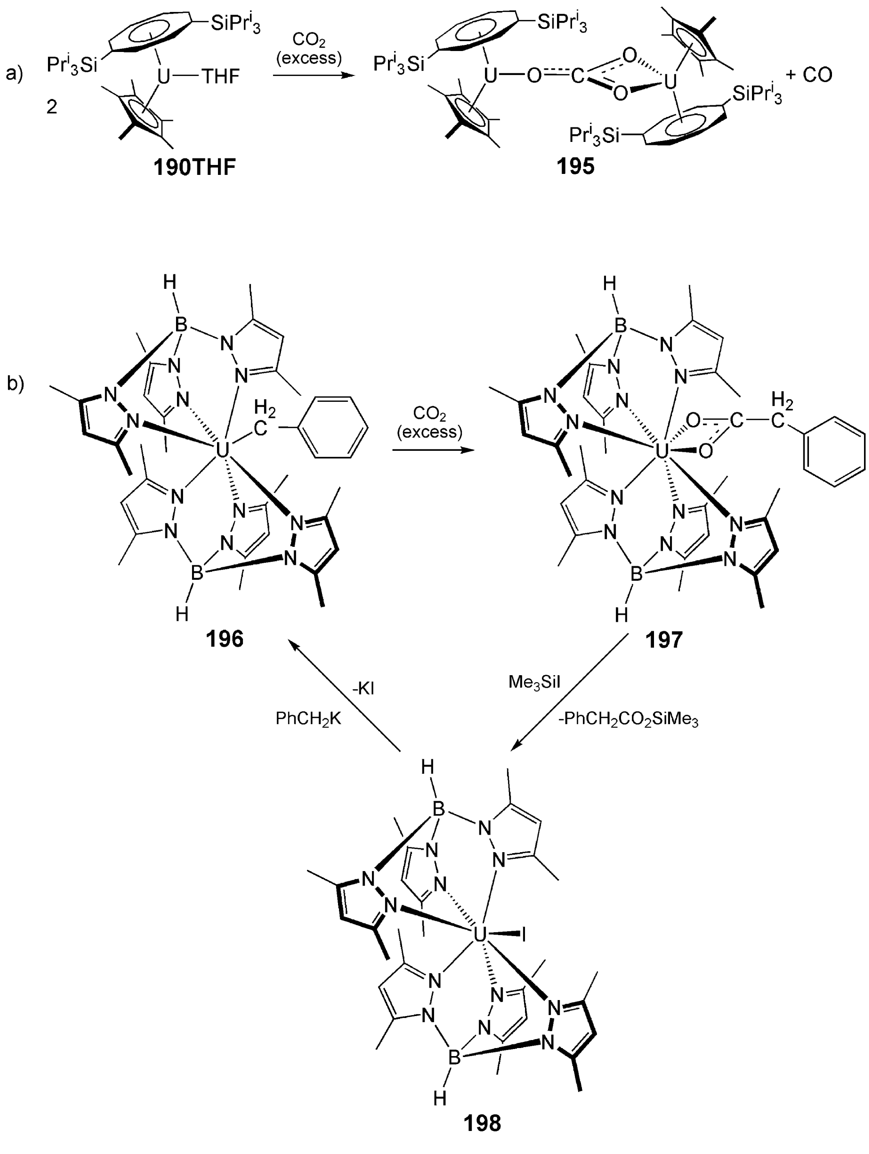
6.2. Carbon Dioxide

The potential for uranium(III) to reductively activate CO_2 was demonstrated in 2004. Addition of CO_2 to **106** afforded the end-on coordination complex $[U\{tacn(CH_2C_6H_2\text{-}2\text{-}O\text{-}3\text{-}Ad\text{-}5\text{-}Bu^t)_3\}\{OCO\}]$ (**194**; Scheme 36).[201] The coordination mode of CO_2 was unprecedented and results from the cylindrical cavity to uranium formed by the three adamantyl groups. Although characterization data are consistent with a reduced radical anion/uranium(IV) formulation, further reactivity has not been reported, perhaps because the steric requirements for stabilizing this novel linkage may suppress subsequent reactivity.



Scheme 36. Reaction of **106** with CO_2 to give the radical anion complex **194**.

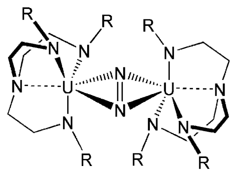
Where sterically less demanding complexes are employed, a rich redox chemistry with CO_2 has been uncovered, usually involving reductive disproportionation to give carbonate derivatives. For example, the THF adduct of **190** (**190THF**) reacts with CO_2 to give the carbonate **195** and CO (Scheme 37). A number of uranium(III) complexes are now known to promote this reaction, and studies have shown that in some cases, a bridging oxo group is formed, which reacts with CO_2 to give carbonate.[119a,203] The insertion reactivity of CO_2 into polar uranium–ligand bonds is also known in a wider context.[204] For example, insertion of CO_2 into the uranium–benzyl bond of **196** gives **197** (Scheme 37). Treatment of **197** with Me_3SiI produces the silyl ether $PhCH_2C(O)OSiMe_3$ along with the uranium iodide **198**, which is a precursor to **196**. A synthetic cycle for the production of silyl ethers could be continued over three [re]cycles.[205]



Scheme 37. a) Reductive disproportionation of CO_2 by uranium(III) to give **195**. b) Insertion of CO_2 into a uranium–benzyl bond to give **197**.

6.3. Dinitrogen

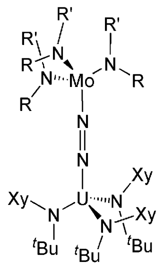
The activation of dinitrogen is of considerable interest and importance, and uranium has shown promise in this field (see the utility of uranium in the Haber–Bosch patent, Section 1). Nevertheless, compared to the extensive dinitrogen chemistry of transition metals, that of uranium is underdeveloped. The first dinitrogen complex of uranium was published in 1998. Exposure of a pentane solution of **193** to an atmosphere of dinitrogen gave $[\{U(Tren^{DMBS})\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ (**199**) in which the dinitrogen is bound in a side-on manner (Figure 35).[206] The N–N bond length of 1.109(7) Å is essentially unchanged compared to that of free N_2 (1.0975 Å). A full understanding of the bonding in the $U(N_2)U$ unit of **199** had to wait until theoretical methods were sufficiently advanced, but over a decade later, the weight of opinion, after initial analyses suggested that a π_p σ-type bond might be more favorable than a σ_p orbital, is now that uranium engages in back-bonding to the π^* orbital of N_2.[207] The original bonding model was based on the knowledge that **199** is easily converted back into **193** and free N_2, but it seems now that this reflects the weak nature of the back-bonding, and that the apparently small lengthening of the N–N bond is most likely due to an underestimation by the X-ray diffraction experiment, which locates electron density and not atomic positions.



199
R = $SiMe_2Bu^t$

Figure 35. The uranium complex **199** with a side-on-bound bridging dinitrogen.

Shortly after the report of side-on bound dinitrogen, two end-on variants were reported. Mixing the uranium(III) complex $[U\{N(Bu^t)(Xy)\}_3(THF)]$ (**200**), prepared from a Na/Hg reduction of $[U\{N(Bu^t)(Xy)\}_3(I)]$ (**56Bu**), with the Mo^{III} tris(amide) complexes $[Mo\{N(R)(R')\}_3]$ ($R = Bu^t$, $R' = Ph$; $R = Xy$, $R' = Ad$) was reported to afford $[U\{Ar(Bu^t)N\}_3(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)Mo\{N(R)R'\}_3]$ ($R = Bu^t$, $R' = Ph$, **201**; $R = Ad$, $R' = Xy$, **202**; Figure 36).[208] X-ray diffraction studies revealed evidence for the reduction of N_2, indicated by an N–N bond length of 1.232(11) Å in **201** (0.13 Å longer than that in free N_2) and U–N distances that are characteristic of uranium(IV). It was noted that the putative Mo dinitro-

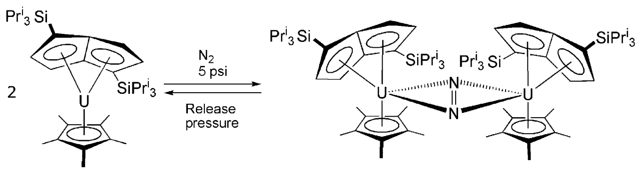


R = Bu^t, R' = Ph, **201**
R = Ad, R' = Xy, **202**

Figure 36. The heterobimetallic uranium molybdenum complexes **201** and **202** with an end-on-bound bridging dinitrogen.

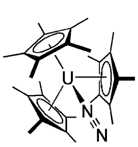
gen complex [Mo{N(R)(R′)}$_3$(N$_2$)] is more efficiently trapped by [U{N(Bu^t)(Xy)}$_3$] than by [Mo{N(R)(R′)}$_3$], leading to the observed product, which is a consequence of the strong Lewis acidity of U ions. The formal oxidation state of +4 was assigned for both metal centers, with molybdenum acting as the more effective π-donor to the complexed diazenide ligand.

In 2002, the mixed-sandwich uranium(III) complex [U(η^5-C$_5$Me$_5$){η^8-1,4-(SiPr$^i_3$)$_2$C$_8$H$_4$}] (**203**) was reported to reversibly bind and reduce dinitrogen to afford a dinuclear uranium(IV) complex [{U(η^5-C$_5$Me$_5$)[η^8-1,4-(SiPr$^i_3$)$_2$C$_8$H$_4$]}$_2$(μ-η^2:η^2-N$_2$)] (**204**),[209] which contains a bridging, sideways-bound N$_2^{2-}$ ligand (Scheme 38). An overpressure of dinitrogen (5 psi) was required to keep the dinitrogen bound to uranium, despite its formal reduction. X-ray diffraction analysis of **204** revealed an N–N bond length of 1.232(10) Å, which is consistent with an N=N double bond.



203 **204**

Scheme 38. Formation of uranium complex **204** with a side-on-bound bridging dinitrogen from **203**.



205

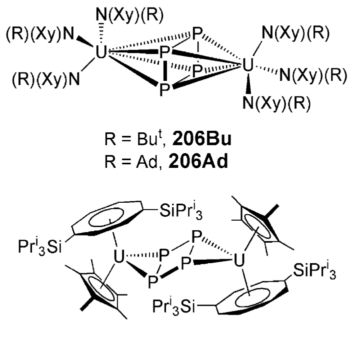
Figure 37. Uranium complex **205** with an end-on-bound terminal dinitrogen.

In 2003, it was shown that [U(η^5-C$_5$Me$_5$)$_3$(η^1-N$_2$)] (**205**; Figure 37) could be prepared from **29**, and the former exhibits a remarkable η^1-coordinated dinitrogen ligand.[210] However, a pressure of 80 psi N$_2$ was required to stabilize the complex, and when the overpressure was released, solutions of **205** released N$_2$, regenerating **29**. The dinitrogen binding to uranium in **205** is thus reversible and weak as emphasized by an X-ray diffraction study showing virtually no change in the [U(η^5-C$_5$Me$_5$)$_3$] fragment upon complexation of dinitrogen. The N–N distance in **205** is indistinguishable from that of free dinitrogen, but as stated above, X-ray crystallography may not be the best method to probe this metric.

6.4. P$_4$

Alongside the activation of dinitrogen, there has been considerable interest in the activation of white phosphorus to directly access organophosphorus species and avoid the intermediate chlorination step.[211] The highly strained P$_4$ tetrahedron is primed for rupture and reduction, and a significant amount of activity regarding the transition-metal- and main-group-mediated activation of P$_4$ has emerged in recent years.[211] However, examples of P$_4$ activation by uranium remain rare.

In 2004, it was reported in an MIT Thesis that treatment of the trivalent, halide-free analogues of **56Bu/Ad** with P$_4$ resulted in the isolation of an orange-brown solid. Recrystallization and determination of the structures by X-ray diffraction revealed the compounds to be [{U(N[Xy]R)$_3$}$_2$(μ-η^4:η^4-P$_4$)] (R = Bu^t, **206Bu**; R = Ad, **206Ad**) where two edges of the P$_4$ tetrahedron have been cleaved to produce a planar [P$_4$]$^{2-}$ square (Figure 38).[212] A similar activation of P$_4$ in an organometallic context was reported in 2011. Treatment of **190THF** with P$_4$ resulted in cleavage of two P–P bonds to give a square-planar [P$_4$]$^{2-}$ fragment in [{U(η^5-C$_5$Me$_5$)[η^8-1,4-(SiPr$^i_3$)$_2$C$_8$H$_4$]}$_2$(μ-η^2:η^2-P$_4$)] (**207**; Figure 38).[213] However, the [P$_4$]$^{2-}$ square in **207** is not bonded to each uranium in an η^4 coordination mode, instead, the [P$_4$]$^{2-}$ unit "slips" to bind to each uranium in η^2 fashion. Theoretical calculations suggest that by adopting an η^2 coordination mode to each uranium ion, the [P$_4$]$^{2-}$ square can engage in σ and π bonding. However, it is likely that this "slipped" coordination mode results from the best steric fit into the wedge shape of the [U(η^5-C$_5$Me$_5$){η^8-1,4-(SiPr$^i_3$)$_2$C$_8$H$_4$}] unit.

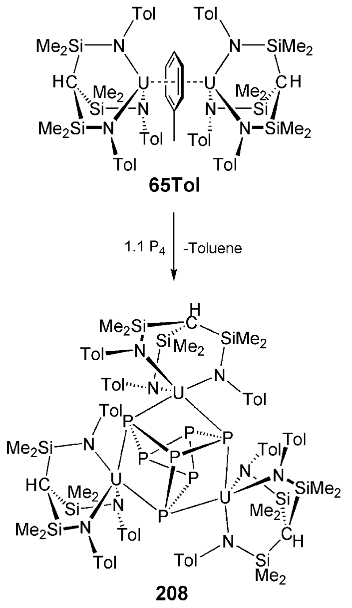


R = Bu^t, **206Bu**
R = Ad, **206Ad**

207

Figure 38. The [P$_4$]$^{2-}$ complexes **206Bu/Ad** and **207**.

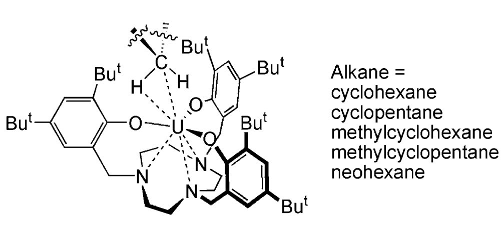
In the two examples described above, cleavage of two P–P bonds of P$_4$ occurs along with two-electron reduction. However, in 2013, the activation of P$_4$ by **65Tol** to give the first actinide Zintl [P$_7$]$^{3-}$ cluster [{U(HC[SiMe$_2$NAr]$_3$)}$_3$(μ$_3$-η^2:η^2:η^2-P$_7$)] (**208**, Ar = Tol) was reported (Scheme 39).[118] This example is unusual as a wholesale reorganization of P$_4$ occurs with catenation to generate the [P$_7$]$^{3-}$ ion, which in a wider context is a generally rare occurrence, and binary uranium phosphides do not form. It was shown that **208** could be treated with electrophiles to liberate [P$_7$R$_3$] [R = SiMe$_3$, Me, Ph, Li(tmeda)], and so a synthetic cycle is closed that could be operated over two turn-overs in preliminary experiments.



Scheme 39. Reaction of **65Tol** with white phosphorus to produce Zintl complex **208**.

6.5. Alkanes

There is intense interest in the study of σ-alkane complexes of transition metals because of the implications for C–H activation reactions. Perhaps reflecting the limited capacity for orbital involvement in agostic-type bonding to one of the poorest donor ligand types, it is perhaps of no surprise to note that examples of genuine, unsupported σ-alkane complexes of uranium are almost unheard of.[32e,214] However, in 2003, σ-alkane complexes of uranium were reported. Utilizing a sterically demanding tris(aryloxide)tacn ligand, it was possible to engender a pocket of just the right size to kinetically stabilize an η^2-bound alkane, as determined by X-ray diffraction, at uranium(III) in [U{tacn($CH_2C_6H_2$-2-O-3,5-$Bu^t{}_2$)$_3$}(alkane)] (**209**, alkane = cyclohexane, cyclopentane, methylcyclohexane, methylcyclopentane, neohexane; Figure 39).[215] A DFT study also suggested an η^2-bound alkane with a σ-type U–R interaction involving a uranium f_{z^3} orbital.



209

Figure 39. The uranium σ-alkane complex **209**.

7. Summary and Outlook

With recent advances in techniques, methods, and analytical equipment, the pace of advances has certainly quickened in recent years. Many new examples of complexes with the major uranium ligand classes, namely alkyl, aryl, arene, carbene, amide, imido, alkoxide, aryloxide, and oxo complexes, have been described, and several novel uranium–ligand linkages, including terminal nitrides and heavier chalcogenides, have now been achieved. Small-molecule activation studies have revealed a diverse and truly unique array of novel reactivity, and many new molecules are exhibiting fascinating magnetic phenomena, including single-molecule magnetism. Given that sufficient numbers of well characterized compounds have now become available for further study, advances in spectroscopic and computational techniques are providing unprecedented opportunities to fully understand the complex electronic structure of non-aqueous uranium complexes. Considering the unique combination of frontier orbitals that uranium has at its disposal, many exciting advances are almost certainly just around the corner.

Looking to the future, the area is hardly begging for "grand challenges". Despite major advances in multiply bonded uranium pnictide and chalcogenide derivatives, uranium alkylidenes and carbynes are targets still prominent by their absence under ambient conditions.[216] Given the increasing recognition that an ITI might be beneficial to stabilizing multiply bonded linkages at uranium, perhaps such linkages can be realized by exploiting this effect. The recent experimental reports of terminal uranium–nitride triple bonds suggest that with suitable supporting ligands, terminal U≡E bonds (E = P, As, Sb, Bi) could be accessible. With two examples of uranium(II) now reported, and even thorium(II) now known,[217] it is tempting to speculate that molecular uranium(I) and uranium(0) complexes might be isolable. Whereas uranium–metal bonds have not been discussed in this Review,[26e,h,29a,e] and only a few examples are known,[218] a uranium–uranium bond is unknown under "normal" conditions, but would be of significant interest given the prevalence of Group 6/Group 6 metal–metal bonds.[219] The isolation of a monomeric *cis*-uranyl and/or heavier chalcogen analogues would be of major interest in terms of assessing the magnitude of the ITI effect as well as for comparison with the *cis*-dioxo complexes of Group 6 metals. Much of the impressive small-molecule activation reactions of uranium hinge on the fact that uranium is highly reducing when low-valent; however, the "sting in the tail" becomes evident when trying to return uranium to this state after activating a substrate to close reactivity cycles—high reactivity can be a double-edged sword. A challenge here would be to better balance reactivity cycles to make them catalytic. In this regard, no genuine single-metal two-electron oxidative addition has yet been reported, reductive elimination remains incredibly rare, and the two have not been coupled together with uranium. Lastly, perhaps the biggest challenge is to combine the synthesis and electronic structure characterization of non-aqueous uranium complexes in a complete framework to realize routine, experimentally calibrated determinations of the nature and extent of covalency in the chemical bonding of uranium, and to relate this directly to reactivity and magnetism in an accurate and predictive capacity.

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