Progress in Nonaqueous Molecular Uranium Chemistry: Where to Next?

Stephen T. Liddle*

Read Online

ACCESS | 📊 Metrics & More | 📰 Article Recommendations

ABSTRACT: There is long-standing interest in nonaqueous uranium chemistry because of fundamental questions about uranium's variable chemical bonding and the similarities of this pseudo-Group 6 element to its congener d-block elements molybdenum and tungsten. To provide historical context, with reference to a conference presentation slide presented around 1988 that advanced a defining collection of top targets, and the challenge, for synthetic actinide chemistry to realize in isolable complexes under normal experimental conditions, this Viewpoint surveys progress against those targets, including (i) CO and related π-acid ligand complexes, (ii) alkylidenes, carbynes, and carbidos, (iii) imidos and terminal nitrides, (iv) homoleptic polyalkyls, -alkoxides, and -aryloxides, (v) uranium—uranium bonds, and (vi)

examples of topics that can be regarded as branching out in parallel from the leading targets. Having summarized advances from the past four decades, opportunities to build on that progress, and hence possible future directions for the field, are highlighted. The wealth and diversity of uranium chemistry that is described emphasizes the importance of ligand—metal complementarity in developing exciting new chemistry that builds our knowledge and understanding of elements in a relativistic regime.
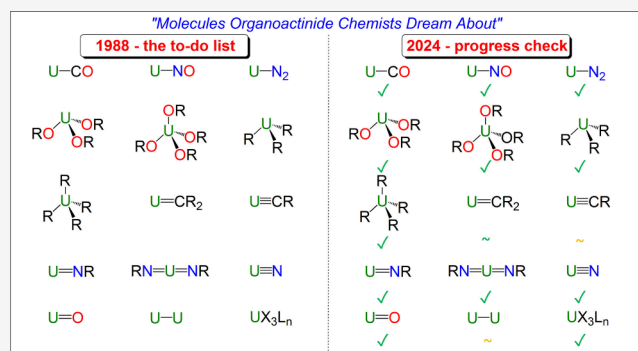
INTRODUCTION

Being subject to a rich interplay of relativistic, interelectronic repulsion, spin—orbit coupling, and crystal field effects, the chemistry of actinides is complex and fascinating, and there remains much to learn about these still somewhat enigmatic elements at a basic level.[1] From a molecular perspective, uranium, in depleted or natural forms, is one of the more intensively investigated actinides. This is not only because of its prominent role in nuclear technologies—with associated extraction, recycling, and cleanup legacy challenges—and relative ease to work with as a weak α-emitter but also because of fundamental questions over the nature of its chemical bonding. With variable oxidation states and a large range of valence orbitals available for hydridization with ligand frontier orbitals, uranium can behave like a covalent transition metal through to being rather ionic like trivalent lanthanides.[2] Indeed, the fact that uranium was originally classified as a Group 6 transition metal until its rightful place in the 5f actinide series was recognized underlines just how variable the chemical bonding of uranium can be.[1] Given the need for new knowledge and understanding in nuclear research, for many years the molecular chemistry of uranium was dominated by aqueous studies of the uranyl dication $(UO_2)^{2+}$.[1,2] However, seeking to answer the question of how transition-metal-like uranium can be and the role of 5f, 6p, 6d, 7s, and 7p orbitals in its chemical bonding, a debate sparked by the revolutionary molecule

uranocene $[U(\eta^8\text{-}C_8H_8)_2]$ (**1**; Figure 1) from Streitwieser and Raymond,[3,4] nonaqueous uranium chemistry has flourished over
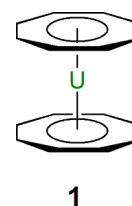

Figure 1. Revolutionary molecule uranocene **1**.[3,4]

the past four decades.[1,2] Underpinning all of the advances that have been made in nonaqueous uranium chemistry, and indeed more widely in aqueous studies, is the concept of ligand—metal complementarity because variation of the steric and electronic properties of ancillary ligands is key to enabling and developing
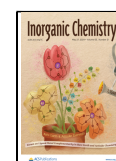
new uranium structural motifs, reactivity, and physicochemical properties.

Reflecting the aforementioned motivation to understand how transition-metal-like uranium is and given an appreciation of uranium's similarities to molybdenum and tungsten—and hence the likely ability of the former to engage in equivalent bonding motifs to the latter pair—around 1988 there was "that slide" on *Molecules Organoactinide Chemists Dream About*[5] presented by Sattelberger at the Third Chemical Congress of North America (including the 195th American Chemical Society National Meeting) in Toronto that year, an adapted version of which is illustrated in Figure 2.[6] The slide has since assumed a somewhat

Figure 2. Adapted version of "that slide" on *Molecules Organoactinide Chemists Dream About* from the Los Alamos National Laboratory archive.[5,6]

legendary status in actinide "folk lore" because it was presented in a conference talk rather than becoming fixed in a journal publication. However, it was an important call-to-arms to the synthetic actinide community to advance the nonaqueous chemistry of uranium in terms of structural linkages that could be isolated under normal experimental conditions. It is intended that, by providing some historical context, viz., Figure 2, and its role in inspiring the progress that followed, the journey and status of the field can be more fully appreciated than by simply presenting advances in isolation.

It is a widely held view that the chemistry of the early actinides lags behind that of the transition metals. However, the astonishing aspect of Figure 2 is just how much was still waiting to be realized ca. 1988 compared to the d block that had undergone major advances in the 1960−1980s. Much has been accomplished in the intervening decades, and so this Viewpoint aims to provide an overview of how the principal themes of Figure 2 developed, and indeed expanded, but will make the occasional detour into motifs or notable analogues with other f elements that assist in contextualizing the area. Hence, the

discussion will focus principally on advances directly related to Figure 2 and will then summarize other advances that developed in parallel. The interested reader is referred to several excellent recent reviews and books on the subject, and the cited references herein, for further detailed insight.[1,2,7−21]

■ CO AND RELATED π−ACID LIGAND COMPLEXES

There are numerous transition-metal carbonyls; indeed, this is a fundamental class of organometallic complex, so the absence of uranium analogues for many years stood in stark contrast. When Figure 2 was presented, a structurally authenticated uranium carbonyl remained elusive. However, uranium carbonyl had been identified in matrix isolation experiments in 1975 by Sheline and Slater,[22] and in 1986 spectroscopic evidence by Andersen showed that placing $[U(\eta^5\text{-}C_5H_4SiMe_3)_3]$ under an atmosphere of CO produced $[U(\eta^5\text{-}C_5H_4SiMe_3)_3(CO)]$ (**2**; Figure 3), but the CO coordination was reversible.[23] Never-

Figure 3. Molecular uranium carbonyl complexes **2−8**.[23−29]

theless, 1995 marked the first structurally authenticated uranium carbonyl, $[U(\eta^5\text{-}C_5Me_4H)_3(CO)]$ (**3**; Figure 3),[24] reported by Parry, Carmona, and Hursthouse. Since then, only a few uranium carbonyl complexes have been reported (Figure 3): $[U(\eta^5\text{-}C_5Me_5)_3(CO)]$ (**4**) by Evans in 2003;[25] $[\{U(\text{tacn-}[CH_2C_6H_2\text{-}2\text{-}O\text{-}3,5\text{-}{}^tBu_2]_3)\}_2(\mu\text{-}CO)]$ (**5**) by Meyer in 2005;[26] $[U\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(Si^iPr_3)_2\}(\eta^5\text{-}C_5Me_5)(CO)]$ (**6**) by Cloke in 2008;[27] $[U(\eta^5\text{-}C_5Me_5)(As_2Mes_2)(CO)]$ (**7**; Mes = 2,4,6-trimethylphenyl) by Walensky in 2021;[28] $[U(\eta^5\text{-}C_5Me_5)_2(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}Me\text{-}C_6H_2)(CO)]$ (**8**) by Walensky in 2023.[29] Evidently, U−CO bonds are not as strong as d-block metal−CO bonds and are hence more difficult to stabilize and isolate.

Interestingly, the IR spectra of **2−6** reveal that while the CO stretching frequencies are in the range 1880−1976 cm^{-1}, indicating back-bonding into the CO π^* orbitals, individual CO stretching frequencies do not correlate with their corresponding Cp−U distances but instead vary with the Cp substituents. In 2009, Eisenstein rationalized this on the basis of U−CO back-bonding from Cp−U bonding molecular orbitals of mainly Cp-ligand character.[30] Thus, in contrast to the conventional metal-to-ligand back-bonding model for transition-metal π-acid

complexes, the back-bonding in tris(cyclopentadienyl)uranium complexes has been classed as ligand-to-ligand back-bonding. Weak ligand-to-ligand back-bonding was also found by Evans and Furche for the cationic thorium complex $[Th(\eta^5\text{-}C_5Me_5)_3(CO)][BPh_4]$ reported in 2017,[31] which, formally, as a $5f^06d^0$ metal has no metal-based electrons with which to back-bond. Complex **7** was found to engage in Th−As σ to CO π^* back-bonding, and hence that system also engages in ligand-to-ligand back-bonding to stabilize the U−CO linkage.[28] However, quantum-chemical calculations on **8** suggested that the U−CO back-bonding is from a U 5f/6d hybrid orbital[29] and hence of metal-to-ligand back-bonding character. The exciting implication is that uranium can switch between ligand-to-ligand and metal-to-ligand back-bonding modes as a function of the ancillary ligands because the only difference between **4** and **8** is the replacement of one pentamethylcyclopentadienyl ligand with an aryloxide. This touches on the variable, responsive bonding nature of uranium, *vide supra*, exemplified by the parallel notion that uranium tends to π-bond to small ligands with mainly 5f character but often bonds to more expansive ligands through δ-bonding with increasing 6d character.[32]

Complexes **1−8** set the scene for reductive homologation of CO at uranium (Figure 4), which contrasts to the more
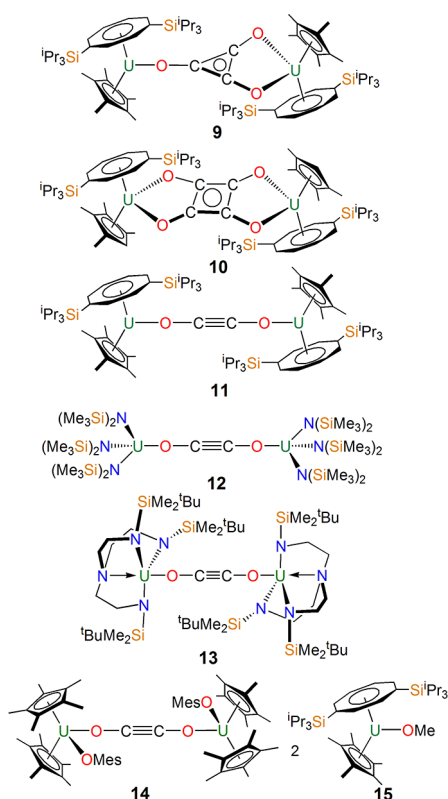
Figure 4. Reductively homologized CO complexes of uranium **9−15**.[29,33,35−38]

traditional 1,1-migratory insertion chemistry of CO at transition-metal centers. In 2006, Cloke reported the remarkable cyclotrimerization of CO using $[U\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(Si^iPr_3)_2\}(\eta^5\text{-}C_5Me_5)]$,[33] a structurally more sterically demanding analogue of $[U(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5Me_5)]$ reported in 1993 by Burns,[34] to produce the deltate complex $[U\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(Si^iPr_3)_2\}(\eta^5\text{-}C_5Me_5)]_2(\mu\text{-}\eta^1:\eta^2\text{-}C_3O_3)$ (**9**) and then through variation of the Cp substituents or reaction conditions could isolate the

cyclotetramerized squarate and dimerized ethynediolate forms of CO in $[U\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(Si^iPr_3)_2\}(\eta^5\text{-}C_5Me_4H)]_2(\mu\text{-}\eta^2:\eta^2\text{-}C_4O_4)$ (**10**)[35] and $[U\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(Si^iPr_3)_2\}(\eta^5\text{-}C_5Me_5)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C_2O_2)$ (**11**),[27] in 2006 and 2008, respectively. The formation of ethynediolate at uranium was also accomplished by P. Arnold in 2011 and Liddle in 2012 in $[U\{N\text{-}(SiMe_3)_2\}_3]_2(\mu\text{-}\eta^1:\eta^1\text{-}C_2O_2)$ (**12**)[36] and $[U(Tren^{DMBS})]_2(\mu\text{-}\eta^1:\eta^1\text{-}C_2O_2)$ (**13**; $Tren^{DMBS} = \{N(CH_2CH_2NSiMe_2^tBu)_3\}^{3-}$),[37] respectively. A synthetic cycle could be closed for the latter where a substituted furanone was liberated,[37] hinting at a possible catalytic process where uranium mediates the conversion of CO and silyl iodides into a functionalized furnanone. More recently, in 2023 Walensky demonstrated that $[U(\eta^5\text{-}C_5Me_5)_2(O\text{-}2,4,6\text{-}Me_3\text{-}4\text{-}Me\text{-}C_6H_2)]$ also reacts with CO to make the ethynediolate complex $[U(\eta^5\text{-}C_5Me_5)_2(O\text{-}2,4,6\text{-}Me_3\text{-}4\text{-}Me\text{-}C_6H_2)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C_2O_2)$ (**14**),[29] from which a range of complexes featuring further C−C bond-functionalized products could be accessed. A particularly notable result in this arena was the finding by Cloke in 2011 that the complex $[U\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(Si^iPr_3)_2\}(\eta^5\text{-}C_5Me_5)]$ reacts with CO and H_2 to form the methoxide complex $[U\{\eta^8\text{-}C_8H_6\text{-}1,4\text{-}(Si^iPr_3)_2\}(\eta^5\text{-}C_5Me_5)\text{-}(OCH_3)]$ (**15**).[38] The methoxide in **15** could be released as a methanol equivalent in Me_3SiOMe to, in principle, close a synthetic cycle, and this essentially corresponds to a selective molecular version of Fischer−Tropsch chemistry. Overall, complexes **9−15** demonstrate the highly reducing power of low-valent uranium, but thus far this has not gone beyond closed synthetic cycles to true catalysis. This likely reflects unbalanced cycles when factoring in returning uranium to the initial reactive trivalent state.

In parallel to uranium−CO chemistry has been the development of uranium−CO₂ chemistry. In contrast to the classical 1,2-migratory insertion chemistry of CO_2, uranium−CO₂ chemistry took a different turn when Meyer reported the synthesis of the terminal uranium−CO₂ radical-anion adduct $[U\{tacn(CH_2C_6H_2\text{-}2\text{-}O\text{-}3\text{-}Ad\text{-}5\text{-}^tBu)_3\}(\eta^1\text{-}OCO)]$ (**16**; Figure 5) in 2004.[39] No further reactivity has been reported for that
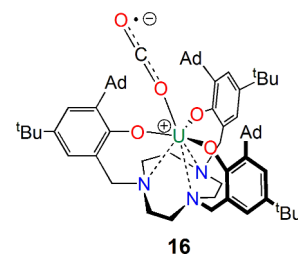

Figure 5. End-on bound uranium−CO₂ complex **16**.[39]

complex, likely because the very steric profile required to stabilize the U−CO₂ linkage inhibits subsequent reactivity. However, it presented a basis for subsequent studies by Meyer and Mazzanti reporting reductive CO₂-to-carbonate reactivities including closed synthetic cycles and heteroleptic heavy carbonate analogues.[40−42]

Closely related to CO is isoelectronic $(NO)^+$, which has an extensive array of coordination chemistry with transition metals. In 1989, Bursten predicted that a $[U(\eta^5\text{-}C_5H_5)_3(NO)]$ complex would curiously feature a linear U−N−O linkage that could be rationalized as a combination of uranium(IV) Cp_3U^+ and not $(NO)^+$ but $(NO)^-$ fragments, with a further notable prediction of that complex being diamagnetic.[43] However, experimental validation of those predictions would take 23 years to emerge. In

2012, Evans, Furche, and Long reported the synthesis of $[U(\eta^5\text{-}C_5Me_4H)_3(NO)]$ (**17**),[44] Figure 6, and it was found to have an
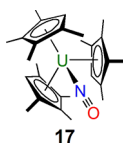

Figure 6. Uranium−NO complex **17**.[44]

essentially linear U−N−O bond angle. Furthermore, quantum-chemical calculations[44] revealed that the ground state is a diamagnetic singlet, which can be represented as $(C_5Me_4H)_3U\equiv N^+\text{−}O^-$, with a low-lying triplet state corresponding to the $U^{IV}/(NO)^-$ structure $(C_5Me_4H)_3U\text{−}N\equiv O$, which nicely accounted for the experimentally determined temperature-independent paramagnetism of **17**. Complex **17** remains the sole example of a uranium nitrosyl complex to date.

With U−CO and U−NO complexes structurally verified and predicted, respectively, by the mid-1990s, attention focused on the essential isoelectronic diatomic N_2. In 1998, 3 years after **3**, Scott reported the first actinide−N_2 complex $[U\text{-}(Tren^{DMBS})]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**18**; Figure 7).[45] The side-on bridging coordination of N_2 in that complex was reversible, which led to the initial belief that the uranium ions were trivalent, but it now recognized that N_2 is reduced to its dianionic form by back-bonding into a π^* orbital of N_2 but reversibly so.

Building on **18**[45] and recognizing the relevance of uranium−N_2 complexes to Haber−Bosch fixation of N_2,[46] in the intervening years to the present day, a range of uranium−N_2 complexes have been isolated, with most adopting side-on ($\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2$) binding modes that are not reversible.[47] However, a few of the more unusual end-on or labile side-on-bound derivatives have been reported (Figure 7), including the end-on bridging heterobimetallic complex $[\{R(R')N\}_3Mo(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)U\{N(^tBu)Xy\}_3]$ (**19**, R = ^{t}Bu, R′ = Ph; **20**, R = adamantyl, R′ = Xy, where Xy = $3,5\text{-}Me_2C_6H_3$) reported by Cummins in 1998,[48] $[\{U(\eta^8\text{-}C_8H_4[Si^iPr_3\text{-}1,4]_2)(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$

(**21**) by Cloke in 2002,[49] the terminal end-on N_2 complex $[U(\eta^5\text{-}C_5Me_5)_3(\eta^1\text{-}N_2)]$ (**22**) reported by Evans in 2003,[50] and the end-on bridging complex $[(BIPM^{TMS})U(NAd)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)Li(2.2.2\text{-crypt})]$ (**23**; $BIPM^{TMS} = \{C(PPh_2NSiMe_3)_2\}^{2-}$) reported by Liddle in 2019.[51] Complexes **21** and **22** are notable for the facile reversibility of N_2 coordination, whereas **23** features a high-oxidation-state complex that goes against traditional the donor−acceptor requirements of low-oxidation-state, electron-rich metals.

Other notable achievements in this area (Figure 7) include the splitting of N_2 into a bis(nitride) in the complex $[K(DME)_4][\{K(DME)(Et_8\text{-calix}[4]tetrapyrrole)U\}_2(\mu\text{-}NK)_2]$ (**24**) by Gambarotta in 2002,[52] hydrogenation to afford ammonia by $[\{U(OSi[O^tBu]_3)_3\}_2(\mu\text{-}N)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)K_3]$ (**25**) by Mazzanti in 2017,[53] and recently the formation of N_2^{3-} at uranium in $[K(L)_n][\{U(OC_6H_2\text{-}2,4,6\text{-}^tBu_3)_3\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**26**, L = 2.2.2-cryptand, n = 1; **27**, L = THF, n = 6) and subsequent N−N cleavage to afford polynitrides by Mazzanti in 2023.[54] Collectively, these advances highlight the ability of uranium to activate N_2, confirming the observation that uranium is a highly effective promoter for the formation of NH_3 from N_2 and H_2, as stated in the original Haber−Bosch patent from over a century ago.[46]

◼ ALKYLIDENES, CARBYNES, AND CARBIDOS

Because the M = CR_2 (R = H, alkyl, silyl) motif is a fundamental structural class in transition-metal chemistry, there has long been an interest in realizing uranium alkylidenes. However, outside of matrix isolation—where species such as $H_2C=U(X)(Y)$ (X, Y = F, Cl, Br, I), $H_2C=U(H)X$ (X = F, Cl, Br), and $H_2C=UH_2$ have been reported by Andrews and Li in the period 2006−2008[55−58]—it is a target that has remained elusive in "pure" M = CR_2 (R = H, alkyl, silyl) form outside of matrix isolation experiments and so is one of the targets in Figure 2 that remains unmet to this day in isolable molecules made under normal conditions.

In 1981, 7 years before Figure 2, Gilje reported the first U=C double bond in $[U(\eta^5\text{-}C_5H_5)_3(CHPMe_2Ph)]$ (**28**) by utilizing a phosphonioalkylidene ligand (Figure 8).[59] The complex

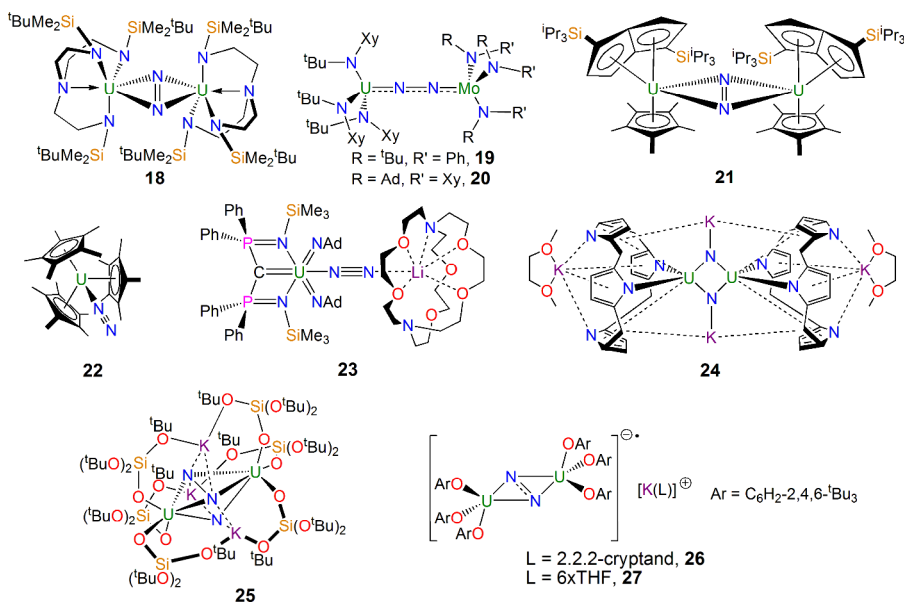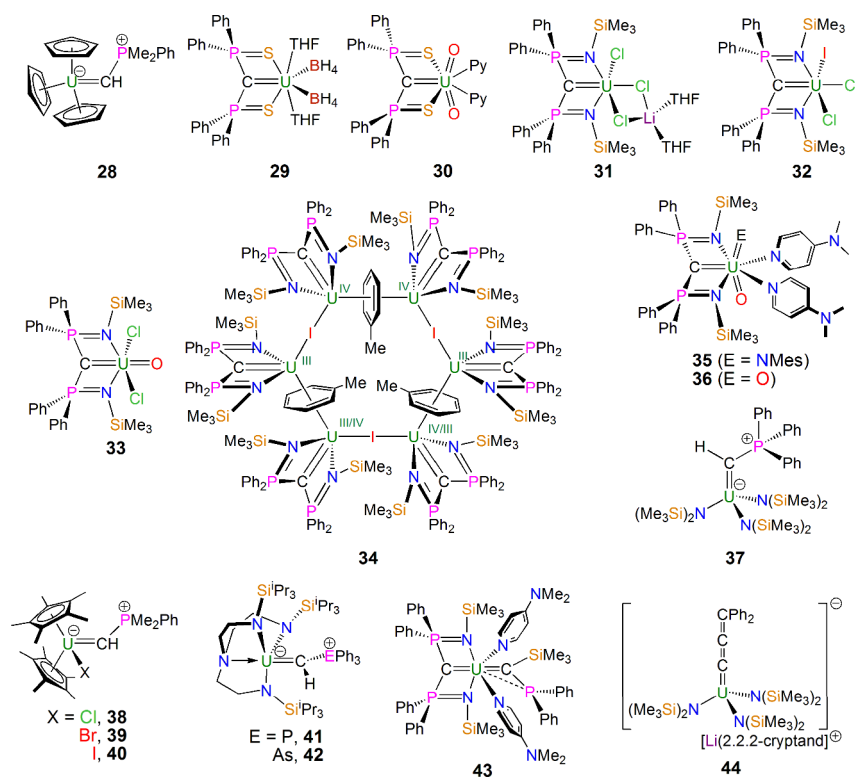**Figure 7.** Uranium−N_2 complexes **18**−**26**.[45,48−54]

Figure 8. U−C multiple bonds in complexes **28−44**.[59−69,71,72]

undoubtedly contains a U═C multiple bond, albeit polarized, but two competing resonance forms can be drawn [U−C(H)═PMe₃Ph and U⁻═C(H)-P⁺Me₂Ph] due to phosphonium-substituent stabilization, which renders the double bond not as clear-cut as that in a "pure" alkylidene. However, a range of reactivity studies were all consistent with UC double-bond character.[12]

The area then became dormant for the best part of three decades before Ephritikhine, Mézailles, and Le Floch revived it in 2009 with the synthesis of U═C double bonds using the diphosphoniomethanediide {C(PPh₂S)₂}²⁻ (Figure 8), as exemplified by the uranium(IV) complex [U{C(PPh₂S)₂}-(BH₄)₂(THF)₂] (**29**),[60] and then in 2011 the uranyl complex [U(O)₂{C(PPh₂S)₂}(py)₂] (**30**),[61] a rare example of a uranyl organometallic. In parallel, with the related diphosphoniome-thanediide BIPM^TMS (Figure 8), in 2011 and 2012 Liddle reported the uranium(IV), -(V), and -(VI) complexes [U-(BIPM^TMS)(Cl)₃Li(THF)₂] (**31**),[62,63] [U(BIPM^TMS)(Cl)₂(I)] (**32**),[63] and [U(BIPM^TMS)(O)(Cl)₂] (**33**),[64] respectively, allowing comparisons of the U═C bond over three oxidation states of uranium, with the majority of the ligand field conserved. This series was then completed by Liddle and Vlaisavljevich in 2018 with the synthesis of [{U(BIPM^TMS)}₆(μ-I)₃(μ-η⁶:η⁶-C₇H₈)₃] (**34**), which formally contains uranium(III) U═C double bonds[65] (Figure 8). In 2014, Liddle reported the uranium(VI) derivatives [U(BIPM^TMS)(O)(NMes)(dmap)₂] [**35**; dmap = 4-(dimethylamino)pyridine][66] and [U(BIPM^TMS)-(O)₂(dmap)₂] (**36**),[66] providing complexes with up to three different multiply bonded ligands at uranium and another rare example of an organouranyl complex (Figure 8). Further prominent examples from the period 2013−2020 of uranium phosphonioalkylidenes (Figure 8) include [U(CHPPh₃){N-(SiMe₃)₂}₃] (**37**) by Hayton and Walensky,[67] [U(CHPPh₃)(η⁵-C₅Me₅)₂(X)] (**38−40**; X = Cl, Br, I) by Walensky and Maron,[68]

and [U(CHPPh₃)(Tren^TIPS)] (**41**; Tren^TIPS = {N-(CH₂CH₂NSiⁱPr₃)₃}³⁻) by Liddle.[69] The latter provided impetus to prepare the arsonioalkylidene analogue [U-(CHAsPh₃)(Tren^TIPS)] (**42**),[69] which was the first arsonioalkylidene complex of any metal and which displays a more well-developed U═C double bond compared to the phosphonioal-kylidene analogue, consistent with diminished As versus P stabilization of the alkylidene center. The assertion of the presence of U═C double bonds in these complexes has proven controversial at times, but the weight of reactivity and computational analysis combined with a ¹³C NMR chemical shift anisotropy study in 2024 supporting the Ce═C double-bond formulations in related Ce(IV) complexes[70] all point to these complexes possessing polarized U═C double bonds.

The years 2018 and then 2021 marked two milestones in U═C double-bond chemistry (Figure 8) with reports of the phosphinosilylalkylidene complexes exemplified by [U{C-(PPh₂)SiMe₃}(BIPM^TMS)(dmap)₂] (**43**) by Liddle[71] and the allenylidene complex [Li(2.2.2-cryptand)][U(CCCPh₂){N-(SiMe₃)₂}₃] (**44**) by Hayton and Autschbach,[72] respectively. Both complexes are notable for exhibiting U═C double-bond interactions that depart from the use of pentavalent pnictonium alkylidene stabilization.

Compared to alkylidenes, the corresponding chemistry of uranium carbyne and carbido complexes is sparsely developed. Matrix isolation studies have led the way, with reports of fundamental, elegant species such as CUO, CUO⁻, UC, CUC, UCH, U(CC)₂, X₃U≡CH (X = F, Cl, Br), F₂ClU≡CH, and F₃U≡CF first being reported around the years 1999−2012 by Andrews, Bursten, and Li.[73−78] More recently, in recent years (2019−2023), work led by Chen has exploited the unique confinement effects of endohedral fullerenes to isolate a range of carbide compounds, including U(μ-η¹:η¹-C)U@C₈₀,[79] U(μ-η²:η²-C₂)U@C₇₈,[80] U(μ-η²:η²-C₂)U@C₈₀,[80] U(μ₃-η¹:η¹-

C)Sc$_2$@C$_{80}$,[81] U(μ-η^1:η^1-C)Ce@C$_{72}$,[82] and U(μ-η^1:η^1-C)Ce@C$_{80}$.[82] Akin to the eventually successful quest for terminal nitrides in isolable molecular species (see below), the prevalence of these species in confined trapping scenarios suggests that, with suitable ancillary ligands, isolable terminal molecular uranium alkylidenes, carbynes, and carbidos under normal experimental conditions should eventually be secured.

■ IMIDOS AND TERMINAL NITRIDE COMPLEXES

By the time the contents of Figure 2 emerged as a presentation slide, uranium mono(imido) complexes had already been realized, and some subsequent key complexes are illustrated in Figure 9.[15] Initially, in 1984 Gilje isolated the uranium(IV)
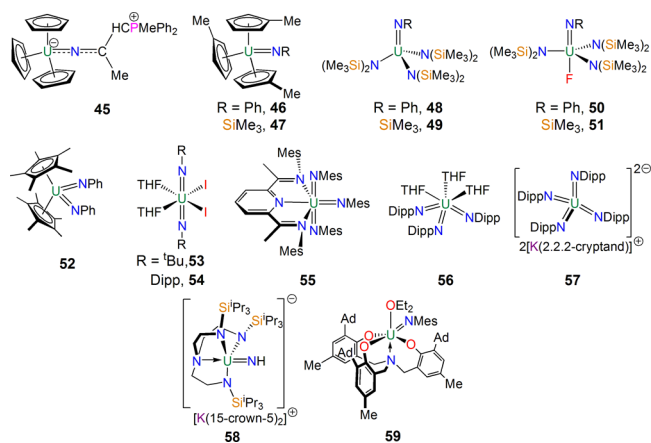
Figure 9. Uranium imido complexes **45**−**59**.[83−96]

imido complex [U(η^5-C$_5$H$_5$)$_3$\{NC(Me)C(H)PMePh$_2$\}] (**45**) from the insertion of CH$_3$CN into the U≡C bond of the PMePh$_2$ analogue of **28**, although this complex is not a "pure" imido linkage.[83] Soon after, in 1985 Andersen reported two-electron oxidation of [U(η^5-C$_5$H$_4$Me)$_3$(THF)] by azides to produce the first clear-cut uranium(V) imidos [U(η^5-C$_5$H$_4$Me)$_3$(NPh)] (**46**) and [U(η^5-C$_5$H$_4$Me)$_3$(NSiMe$_3$)] (**47**),[84] and the same approach with [U\{N(SiMe$_3$)$_2$\}$_3$] yielded [U\{N(SiMe$_3$)$_2$\}$_3$(NPh)] (**48**) and [U\{N(SiMe$_3$)$_2$\}$_3$(NSiMe$_3$)] (**49**) in 1988.[85] Apart from accessing imido functionalities, these were important reactions because they developed two-electron-oxidation chemistry, in contrast to the reputation that the f block has for one-electron-redox couples. In 1990 Sattelberger reported that **48** and **49** could be oxidized to produce uranium(VI) imido complexes [U\{N(SiMe$_3$)$_2$\}$_3$(NPh)(F)] (**50**) and [U\{N(SiMe$_3$)$_2$\}$_3$(NSiMe$_3$)(F)] (**51**),[86] which were the first uranium(VI) complexes to have multiple bonds to nitrogen.

With mono(imido) uranium complexes established, attention turned to polyimidos, and relatively quickly in 1992 Burns showed that the treatment of [U(η^5-C$_5$Me$_5$)$_2$(Cl)(Me)] with LiN(H)Ph and Me$_2$NCH$_2$CH$_2$NMe$_2$(tmeda) (tmeda = tetramethylethylenediamine) afforded [U(η^5-C$_5$Me$_5$)$_2$(μ-NPh)(μ-Cl)Li(tmeda)], which was oxidized by N$_3$Ph to afford the first uranium bis(imido) complex [U(η^5-C$_5$Me$_5$)$_2$(NPh)$_2$] (**52**),[87] which was also the first organouranium(VI) complex. Notably, due to the presence of the two Cp* rings, the N−U−N linkage is bent [98.7(4)°], raising interesting questions about its relationship to uranyl and, in particular, the still yet to be routinely isolated cis-uranyl. As an aside, noting that **52** was prepared by a two-electron oxidation, in 1993 Burns also found that the

oxidation of [U(η^5-C$_5$Me$_5$)$_2$(ODipp)] (Dipp = 2,6-diisopropylphenyl) and [U(η^5-C$_5$Me$_5$)$_2$(NDipp)] with pyridine N-oxide afforded the first uranium(V) and -(VI) complexes to contain mono(oxo) linkages, namely, [U(η^5-C$_5$Me$_5$)$_2$(O)(ODipp)] and [U(η^5-C$_5$Me$_5$)$_2$(O)(NDipp)].[88] Again, this demonstrated that the uranium(III/V) two-electron-redox couple is a powerful vehicle for installing multiply bonded ligands at uranium.

Complex **52** remained the only class of uranium bis(imido) complexes for 13 years (the N-adamantyl version of **52** was reported in 1998)[89] until 2005−2006 Boncella reported the synthesis of linear uranium bis(imido)uranyl analogues.[90,91] Oxidation of uranium metal or [U(I)$_3$(THF)$_4$] with I$_2$ in the presence of amines produced alkyl and arylbis(imido) complexes of the form [U(NR)$_2$(I)$_2$(THF)$_2$] (**53**, R = ^{t}Bu; **54**, R = Dipp) with the elimination of ammonium iodide salts. The linear formulation of these bis(imido) complexes suggests that an inverse trans influence operates as it does in isoelectronic uranyl. A tris(imido)uranium complex, isoelectronic to UO$_3$, was introduced by Bart in 2014.[92] The complex mer-[U\{C$_5$H$_3$N-2,6-(C[Me]NMes)$_2$\}(NMes)$_3$] (**55**) was obtained by the reaction of a highly reduced, i.e., noninnocent, pyridylbis(imino)uranium complex with MesN$_3$, where the U(NMe)$_3$ component is T-shaped. This was followed soon after in 2015 by another tris(imido) by Bart in a reaction that is elegant by virtue of its simplicity, where the reduction of [U(I)$_3$(THF)$_4$] by KC$_8$ in the presence of DippN$_3$ produced fac-[U(NDipp)$_3$(THF)$_3$] (**56**).[93]

Remarkably, in 2017 Bart reported that the polyimido motif could be extended to a range of tetrakis(imido)uranate(VI) complexes exemplified by [K(2.2.2-crypt)]$_2$[U(NDipp)$_4$] (**57**).[94] Quantum-chemical calculations showed that the significant amount of charge loading resulted in more activated U═NR bonds than in tris(imido) and bis(imido) analogues. It will be interesting to see if a pentakis(imido)uranium complex can be realized, given the range and number of vacant valence orbitals that uranium possesses.

There are now many uranium imido complexes, but two merit specific mention. The first is the parent imido complex [K(15-crown-5)$_2$][U(NH)(Tren^{TIPS})] (**58**) reported by Liddle in 2014.[95] Complex **58** is stable despite lacking any sterically demanding substituent protection at the imido, although the anion formulation of the imido component of **58** evidently plays a role because oxidation of **58** results in disproportionation. The imido complex [U\{N(CH$_2$C$_6$H$_2$-2-O-3-Ad-5-Me)$_3$\}NMes] (**59**) was reported by Meyer in 2012.[96] Notably, the imido resides trans to one of the aryloxides, where it would be more intuitive to predict the imido residing in the axial site trans to the tertiary amine. This implies the presence of an inverse trans influence in **59**.

The search for terminal uranium nitrides can trace its origins back to 1976, when Green and Reedy identified UN in a frozen argon matrix.[97] Then, in the period 1993−2016, fundamental species such as NUN, NUO, NUO$^+$, F$_3$UN, NUN-H, and U$_2$N$_2$ were variously reported or studied in matrix isolation or as spectroscopic transients by Andrews, Bursten, Gagliardi, Pyykkö, Roos, Schwarz, and Vlaisavljevich,[98−102] and UN was reported in the C$_{82}$ endohedral fullerene by Chen and Autschbach in 2022.[103] Nevertheless, when Figure 2 was making its debut in 1988, placing an emphasis on a molecular terminal uranium nitride as a key synthetic target and bonding benchmark, there were no molecular uranium nitrides at all.

Several polymetallic nitrides of uranium were reported in the 2000s[21,104] before (Figure 10) Cummins reported the borane-
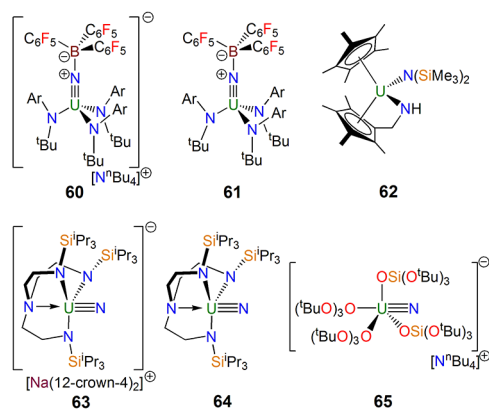
Figure 10. Notable uranium nitride complexes **60−65**.[105−108,111]

capped nitride complexes [NBu$^n_4$][U{NB(C$_6$F$_5$)$_3$}{N('Bu)-C$_6$H$_3$-3,5-Me$_2$}$_3$] (**60**) and [U{NB(C$_6$F$_5$)$_3$}{N('Bu)C$_6$H$_3$-3,5-Me$_2$}$_3$] (**61**) in 2009.[105] Complexes **60** and **61** can alternatively be formulated as imidoborates, but computational analysis reveals significant U≡N triple bonds. In 2010 Kiplinger provided evidence of a transient terminal uranium nitride through isolation of the C−H activated complex [U(η^5-C$_5$Me$_4$CH$_2$NH)(η^5-C$_5$Me$_5$){N(SiMe$_3$)$_2$}] (**62**) resulting from photolysis of the azide precursor [U(η^5-C$_5$Me$_5$)$_2$(N$_3$){N-(SiMe$_3$)$_2$}].[106]

The terminal uranium nitride was finally reported in 2012 by Liddle in the uranium(V) nitride complex [Na(12-crown-4)$_2$][U(N)(Tren^{TIPS})] (**63**),[107] Figure 10, prepared by [U-(Tren^{TIPS})]-mediated two-electron azide reduction and subsequent sodium sequestration with 12-crown-4 ether. Success hinged on Tren^{TIPS} providing exactly the right size and shape pocket for the nitride, combined with azide activation but stabilization by the sodium cation and then its gentle subsequent removal. In 2013, the uranium(VI) nitride [U(N)(Tren^{TIPS})] (**64**) was prepared by oxidation of **63**[108] (Figure 10), concluding the search for terminal uranium(VI) nitrides previously restricted to spectroscopic experiments as well as confirming the presence of intermediate nitrides in C−H activation such as **62−64**. A range of derivatives of **63** proved to be fertile ground for detailed electronic structure investigations.[109] Complex **64** was computationally predicted[108] and experimentally confirmed by ^{15}N NMR spectroscopy[110] to contain a highly covalent U≡N triple bond, and more so than Group 6 terminal nitrides, which is an astonishing result that goes to the heart of one of the original motivations behind Figure 2 to elucidate the bonding relationship of uranium to Group 6 elements like molybdenum and tungsten. Only one other class of terminal uranium nitride has since been reported, where photolysis of [NBu$^n_4$][U(N$_3$){OSi-(O'Bu)$_3$}$_4$] was reported to produce [NBu$^n_4$][U(N){OSi-(O'Bu)$_3$}$_4$] (**65**) by Mazzanti in 2020 (Figure 10).[111]

This area has now expanded to include many examples of astonishing small-molecule activations and structural motifs,[21,104] with notable examples including hydrogenation of **25** to produce ammonia by Mazzanti in 2017[53,112] and elegant preparations from UX$_5$ (X = Cl, Br) and NH$_3$ of bis(nitride) complexes containing the cations [(H$_3$N)$_8$UNUN(NH$_3$)$_5$U-(NH$_3$)$_8$]$^{8+}$, [(H$_3$N)$_8$UNUN(NH$_3$)$_4$(Br)U(NH$_3$)$_8$]$^{7+}$, and [(H$_3$N)$_8$UNUN(NH$_3$)$_3$(Cl)$_2$U(NH$_3$)$_8$]$^{6+}$ reported by Kraus in 2020.[113]

◼ HOMOLEPTIC POLYALKYL, -ALKOXIDES, AND -ARYLOXIDES

As a fundamental ligand type in organometallic chemistry, there has always been interest since the 1940s in uranium alkyl complexes particularly because at one stage volatile uranium alkyls were candidates for isotope enrichment work in the Manhattan Project.[114] In the 1980s, Marks pioneered the study of heteroleptic uranium bis(cyclopentadienyl)alkyls, having reported in 1974 that attempts to prepare tetrakis(alkyl) compounds resulted in decomposition.[115] Likewise, in 1982 Evans concluded that hydride species formed,[116] although in 1984 Andersen subsequently found that tetrakis(alkyl) complexes could be stabilized as heteroleptic derivatives by the addition of chelating diphosphine ligands to saturate the coordination sphere of uranium, for example, in [U-(CH$_2$Ph)$_3$(Me)(Me$_2$PCH$_2$CH$_2$PMe$_2$)] (**66**).[117] Thus, Figure 2 focused attention on homoleptic polyalkyl complexes of uranium.

As it turned out, a homoleptic polyalkyl was delivered rapidly (Figure 11), and in 1988 Sattelberger reported the first example
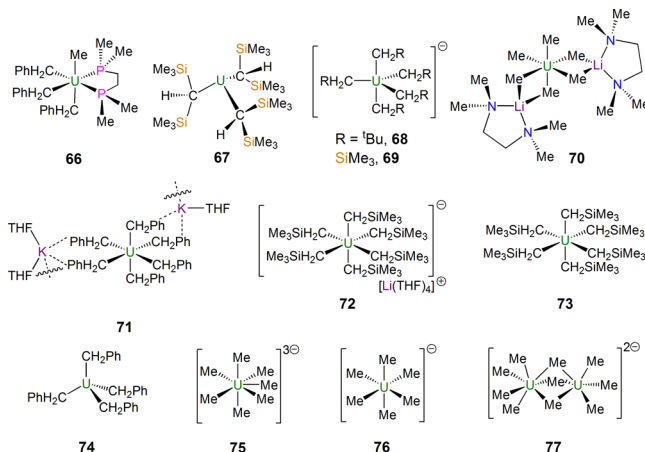

Figure 11. Homoleptic uranium alkyl complexes **66−77**. Only the anionic components of **68**, **69**, and **75−77** are shown for clarity.[117−123]

of a neutral homoleptic uranium alkyl with the synthesis of the tris(alkyl) complex [U{CH(SiMe$_3$)$_2$}$_3$] (**67**).[118] Like lanthanide analogues, **67** had to be prepared by the reaction of LiCH(SiMe$_3$)$_2$ with a uranium tris(aryloxide) because the more conventional route of reacting UCl$_3$(THF)$_n$ resulted in formation of the "ate" complex [U{CH(SiMe$_3$)$_2$}$_3$(Cl)Li-(THF)$_3$].[118] Complex **67** is isolable because of the sterically demanding alkyls, but it is not coordinatively saturated, so it decomposes in solution, underscoring the inherent reactivity of uranium alkyls.

The year 2009 marked a fresh impetus in the area (Figure 11) when Hayton reported the synthesis of several homoleptic uranium(IV) complexes, specifically separated ion-pair "ate" complexes of the anions [U(CH$_2$Bu^t)$_5$]$^−$ (**68**) and [U-(CH$_2$SiMe$_3$)$_5$]$^−$ (**69**) and contact ion triple assemblies of [U(Me)$_2$(μ-Me)$_4${μ-Li(tmeda)}$_2$] (**70**) and {[K(THF)][K-(THF)$_2$][U(CH$_2$Ph)$_6$]}$_∞$ (**71**).[119] Shortly after, in 2011 Hayton went on to report [Li(THF)$_4$][U(CH$_2$SiMe$_3$)$_6$] (**72**) and its oxidation to the remarkable hexakis(alkyl) [U-(CH$_2$SiMe$_3$)$_6$] (**73**),[120] although the latter was found to be thermally unstable and decompose above −25 °C. Soon after **72** and **73**, in 2012 Bart reported the synthesis and isolation of [U(η^2-CH$_2$Ph)$_4$] (**74**),[121] where the η^2-coordination mode of

the four benzyls evidently contributes to the stability of this tetrakis(alkyl) complex, and this led to a wide range of $[U(\eta^2\text{-}CH_2R)_4]$ (R = substituted aryls) complexes being reported by Bart in 2015.[122]

As mentioned above, homoleptic polyalkyl complexes of uranium often undergo facile decomposition and can be thermally unstable. This prompted Neidig to undertake low-temperature studies (Figure 11), where compounds were prepared and crystallized at −70 to −80 °C. The resulting range of compounds reported in 2020 underscored the complexity of uranium polyalkyl chemistry because $[Li(THF)_4][U(Me)_4(\mu\text{-}Me)_2\{\mu\text{-}Li(THF)_2\}]$, $[U(Me)(\mu\text{-}Me)_6\{\mu\text{-}Li(THF)_2\}\{\mu_3\text{-}Li(THF)\}(\mu_3\text{-}Li)]$ (**75**), $[Li(18\text{-}crown\text{-}6(THF)_2][U(Me)_6]$ (**76**), and $[Li(THF)_4]_2[Me_4U(\mu\text{-}Me)_3UMe_3]$ (**77**), built around hexakis- or septakis(methyl) motifs, could all be isolated under those conditions.[123]

The above activity in homoleptic polyalkyluranium chemistry has spurred renewed interest in related homoleptic polyaryluranium chemistry (Figure 12), with notable examples
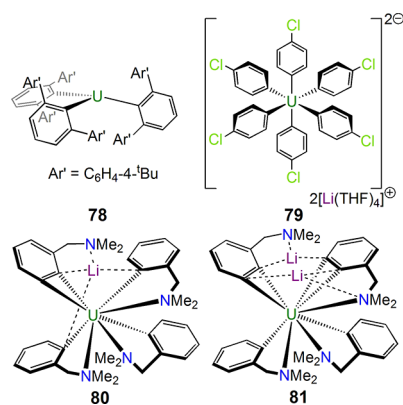
Figure 12. Uranium aryl and benzyne complexes **78−81**.[124−127]

including the uranium(III) tris(terphenyl) complex $[U\{C_6H_3\text{-}2,6\text{-}(C_6H_4\text{-}4\text{-}^tBu)_2\}_3]$ (**78**) by J. Arnold in 2016[124] and uranium(IV) hexakis(aryls) exemplified by $[Li(THF)_4][U(C_6H_5)_6Li(THF)]$ and $[Li(THF)_4]_2[U(C_6H_4\text{-}4\text{-}Cl)_6]$ (**79**) by Neidig in 2019;[125] like Neidig's alkyl work, the latter pair of aryls were synthesized and crystallized at low (−80 °C) temperature. Last, Hayton isolated exceedingly rare examples of uranium benzyne complexes, namely, $[U(\eta^2\text{-}C_6H_3\text{-}2\text{-}CH_2NMe_2)(C_6H_4\text{-}2\text{-}CH_2NMe_2)_3Li]$ (**80**) in 2013[126] and $[U(\eta^2\text{-}C_6H_3\text{-}2\text{-}CH_2NMe_2)_2(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2Li_2]$ (**81**) and the THF-solvate congener $[U(\eta^2\text{-}C_6H_3\text{-}2\text{-}CH_2NMe_2)_2(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2[Li(THF)_2](Li)]$ in 2016.[127]

Although uranium alkoxides had been known since the 1950s, rather than being straightforward homoleptic formulations, they were often polymetallic aggregates with "ate" character, mixed uranium oxidation states, or were constructed around oxide dianions (Figure 13). Prominent examples include $[U_2(\mu\text{-}O^tBu)_3(\mu_3\text{-}O^tBu)_2(O^tBu)_4K]$ (**82**), $[U_2(\mu\text{-}O^tBu)_3(O^tBu)_6]$ (**83**), and $[U_3(\mu_3\text{-}O)(\mu_3\text{-}O^tBu)(\mu\text{-}O^tBu)_3(O^tBu)_6]$ (**84**) reported in 1984 by Cotton,[128−130] and even the "pure" homoleptic $[U_2(\mu\text{-}O^tBu)_2(O^tBu)_8]$ (**85**) reported by Eller in 1983 is dimeric.[131] Furthermore, aryloxides were relatively scarce, and so Figure 2 sought to prompt an expansion of mononuclear homoleptic polyalkoxides and -aryloxides.

Some of the basic uranium alkoxide chemistry was reinvestigated in 2008 by Hayton,[132] who found that the tendency of alkoxides to form "ate" complexes could be
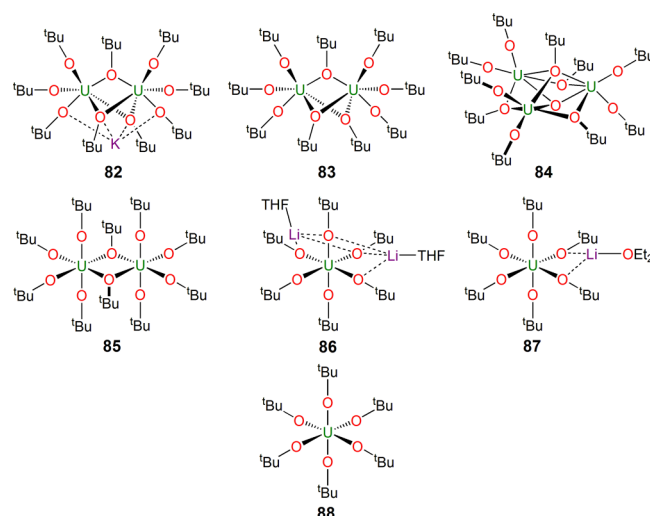

Figure 13. Uranium alkoxide complexes **82−88**.[128−132]

synthetically exploited. Hence, the preparation of $[U(O^tBu)_2(\mu\text{-}O^tBu)_4\{(\mu_3\text{-}Li(THF)\}_2]$ (**86**) was performed, and then stepwise oxidations with iodine first secured $[U(O^tBu)_4(\mu\text{-}O^tBu)_2\{\mu\text{-}Li(OEt_2)\}]$ (**87**) and then $[U(O^tBu)_6]$ (**86**); it is notable that this chemistry works when utilizing lithium to stabilize the aggregates rather than potassium, which tends to produce clusters such as **82**.[128] Electrochemical studies suggested significant stabilization of the uranium(VI) ion in **88** compared to the uranium(VI) hexakis(halide) series, which are generally considered to be quite oxidizing.

Where aryloxides are concerned, there are still relatively few homoleptic variants (Figure 14), with reports by Sattelberger in 1988 of dimeric $[\{U(\mu\text{-}\eta^1:\eta^6\text{-}ODipp)(ODipp)_2\}_2]$ (**89**)[133] and the monomers $[U(O\text{-}C_6H_3\text{-}2,6\text{-}^tBu_2)_3]$ (**90**, suggested to be monomeric from IR data in the initial report[133] but only structurally confirmed as such in 2011 by P. Arnold[134]) and $[U(O\text{-}C_6H_3\text{-}2,6\text{-}^tBu_2)_4]$ (**91**).[135,136] The more sterically demanding $[U\{OC_6H_2[2,6\text{-}CHPh_2]_2\text{-}4\text{-}Me\}_3]$ (**92**) reported by
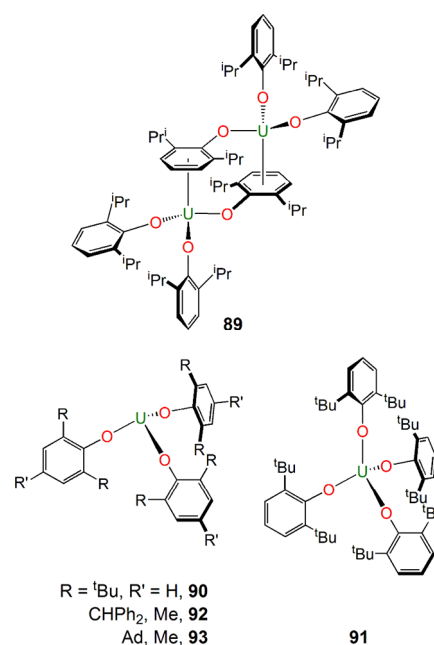

Figure 14. Uranium aryloxide complexes **89−93**.[133−136]

Meyer and Mindiola[137] and $[U(OC_6H_2\text{-}2,6\text{-}Ad_2\text{-}4\text{-}Me)_3]$ (**93**) disclosed by Meyer appeared in 2013 and 2016, respectively.[138] It is worth noting that some homoleptic uranium aryloxides exist but have not been structurally authenticated; however, they have been used to make N_2^{2-}, N_2^{3-}, and CO-coupled ethynediolate derivatives.[54,134]

U–U BONDS

Given the prevalence of Mo–Mo and W–W bonding in transition-metal chemistry, the absence of U–U bonds led to the latter being a natural target in Figure 2 in 1988. This was not for a lack of attempts to prepare U–U bonds by 1988, where one study by Cotton in 1984[130] investigating the possibility of accessing U–U bonding supported by alkoxides, given the tendency of alkoxides to support Mo–Mo and W–W bonding, stated that, "While we are not suggesting that on the basis of these two structural results all hope of observing U–U bonds is futile, we do feel that such hopes are rather dim." Indeed, in 2006 energy decomposition analysis calculations carried out on hypothetical U–U bonds in classical $[U_2X_8]^{2-}$ (X = Cl, Br) dianions by Kaltsoyannis[139] consistently found weak metal–metal bonds. Hence, this suggested that U–U bonds, at least in the $[U_2X_8]^{2-}$ formulation, would be unlikely to be formed or be isolable experimentally, in contrast to the large range of heterobimetallic uranium–metal bonds that have been reported.[20] However, like terminal uranium nitrides, the quest for isolable U–U bonds under normal experimental conditions has been stoked by advances in spectroscopic and trapped-species scenarios.

The U_2 and OUUO dimers were observed as spectroscopic transients as long ago as 1974 by Khodeev,[140] and in a theoretical study of actinide dimers by Roos in 2006, there is mention of U_2 and U_2^+ as spectroscopic transients from a private communication from Heaven,[141] but the nature of the bonding in U_2 has proven to be a challenge to definitively model due to the relativistic regime.[142,143] In 1996 and 1997, Andrews showed that HUUH and H_2UUH_2 form in cryogenic matrix isolation experiments.[144,145] It took until 2018 in a report by Chen, Feng, Echegoyen, and Poblet for U_2 to be formed and isolated in $U_2@C_{80}$,[146] although extensive disorder of the U_2 unit has made analysis of the U_2 unit challenging. Computational studies suggest a complicated bonding picture that is highly dependent on the U–U distance,[146–148] but the consensus appears to be that two uranium(III) ions are present with an overall septet spin state but with two ferromagnetic two-center one-electron bonds that correspond to a single bond. Unfortunately, it has not been possible to verify this experimentally due to the lack of magnetic data, which likely reflects the extremely challenging nature of the synthesis and which in itself underscores the achievement of preparing U_2 at all. The U–U bond in $U_2@C_{80}$ was described in 2015 by Straka and Foroutan-Nejad as attractive but "unwilling",[147] which was debated by Rodríguez-Fortea, Graaf, and Poblet,[148] but if correct would be in line with prior work suggesting the weak nature of 5f–5f bonding.[130,139]

Interestingly, more recently, in 2021 $Th_2@I_h(7)\text{-}C_{80}$ was reported by Chen and Poblet[149] and the trimer $[\{Th(\eta^8\text{-}C_8H_8)(\mu_3\text{-}Cl)_2\}_3\{K(THF)_2\}_2]_\infty$,[150] accessible under normal experimental conditions and on multigram scale, containing three-center two-electron σ-aromatic bonding,[151] was reported by Liddle and Kaltsoyannis, also in 2021. These advances in thorium chemistry, together with the matrix isolation and endohedral fullerene advances with uranium, suggest that U–U

bonding in a complex made under normal experimental conditions may eventually be realizable.

TOPICS THAT DEVELOPED IN PARALLEL TO "THAT SLIDE"

Figure 2 aimed to capture the spirit of high-value targets to primarily focus efforts on securing. However, of course, it could not envisage every subarea to target or predict what new lines of enquiry those primary endeavors might eventually branch out into, and indeed in many ways, that was also a motivation of Figure 2. This section will briefly summarize other key advances that have branched out in parallel.

One necessary spin-off has been the development of uranium halide starting materials, the importance of which can easily be overlooked when targeting high-value structural motifs, but, of course, the successful isolation of new compounds depends on having suitable starting materials to begin with. There are now many uranium halide starting materials, with UCl_4 playing a prominent role,[2,15] but perhaps the one that has had the most obvious sustained impact in terms of uplifting research outputs is that of $[U(I)_3(THF)_4]$, reported in publications in 1989 and 1994 by Clark, Sattelberger, and Zwick,[152,153] for example, already being mentioned above as a key starting point to accessing **53**–**57**.[90,93]

Many of the linkages in Figure 2 are organometallic, and, of course, organouranium chemistry has a rich heritage spanning back to the 1940s, but definitive compounds began emerging around 1956 and onward, with examples (Figure 15) including
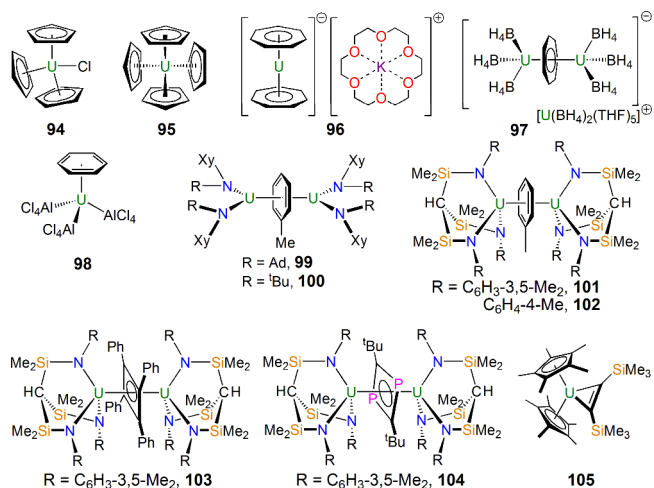

Figure 15. Uranium complexes **94**–**105** with C_n-type ligands (n = 2, 4–8).[154–159,161–163]

$[U(\eta^5\text{-}C_5H_5)_3Cl]$ (**94**) by Wilkinson in 1956,[154] $[U(\eta^5\text{-}C_5H_5)_4]$ (**95**) by Fischer in 1962[155] $[K(18\text{-}crown\text{-}6)][U(\eta^7\text{-}C_7H_7)_2]$ (**96**) in 1995 and $[U(BH_4)_2(THF)_5][\{U(BH_4)_3\}_2(\mu\text{-}\eta^7\text{:}\eta^7\text{-}C_7H_7)]$ (**97**) in 1994 by Ephritikhine,[156,157] and the aforementioned **1** in 1968/1969.[3,4] Arene complexes, for example, $[U(\eta^6\text{-}C_6H_6)(AlCl_4)_3]$ (**98**) reported by Marconi,[158] started appearing in the literature around 1971 and onward, although against the backdrop of Figure 2, a notable advance was the report of the inverse-sandwich complexes $[\{U(N[Xy]\text{-}R)_2\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_5Me)]$ (R = Ad; **99**, R = ^{t}Bu, **100**) in 2000 by Cummins.[159] There are now numerous inverse-sandwich complexes of uranium, most of which are best regarded as diuranium(III) with arene dianions,[160] although there are a few notable exceptions of diuranium(V) arene tetraanions, such as

[{U(Ts^R)}$_2$(μ-η^6:η^6C$_6$H$_5$Me)] [Ts^R = {HC(SiMe$_2$NR)$_3$}$^{3-}$; R = C$_6$H$_3$-3-5-Me$_2$ (Xy), **101**; R = C$_6$H$_4$-4-Me (Tol), **102**;[161] Figure 15], as unequivocally confirmed by spectroscopic and magnetic studies. The synthetic credentials of **101** and **102** were confirmed by their use as precursors to the first f-element diuranium cyclobutadienyl and diphosphacyclobutadienyl complexes [{U(Ts^{Xy})}$_2$(μ-η^5:η^5-C$_4$Ph$_4$)] (**103**) and [{U-(Ts^{Tol})}$_2$(μ-η^4:η^4-C$_2$P$_2$^{t}Bu$_2$)] (**104**) (Figure 15) reported by Liddle in 2013.[162] Continuing the small-ring theme, Walter, Ding, and Zi reported uranium metallacyclopropene complexes such as [U(η^5-C$_5$Me$_5$)$_2$(η^2-Me$_3$SiCCSiMe$_3$)] (**105**).[163] A recurring theme of **94−105** is significant 5f-orbital contributions to the bonding, including π- and δ-bonding motifs, again emphasizing once again how uranium, like transition metals, can engage in different bonding depending on the nature of the coordinated ligands.

Although not directly a result of inverse sandwich arene complexes, the oxidation state ambiguity of inverse sandwich arene complexes certainly prompted thoughts of uranium complexes with oxidation states below 3+. Thus, related to inverse sandwich uranium arene complexes, the chemistry of uranium in 2+ and 1+ oxidation states was developed (Figure 16). The first isolable uranium(II) complex was [K(2.2.2-
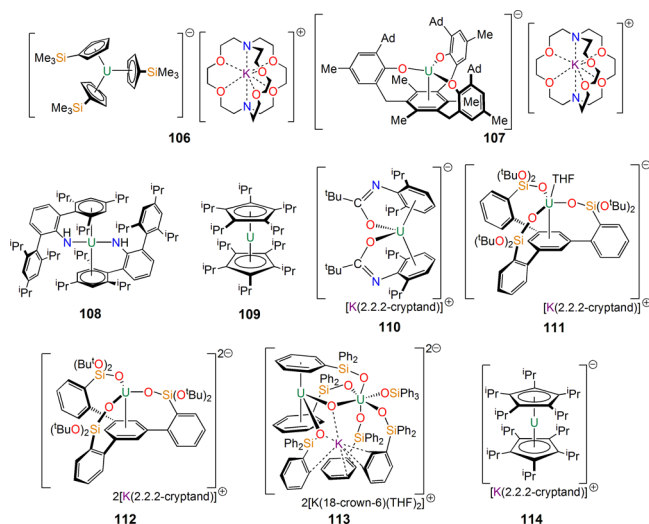

Figure 16. Reduced uranium(II) and (I) complexes **106−114**.[164−171]

cryptand)][U(η^5-C$_5$H$_4$SiMe$_3$)$_3$] (**106**) reported by Evans in 2013,[164] and then in 2014, Meyer reported [K(2.2.2-crypt)]-[U{η^6-C$_6$Me$_3$(CH$_2$C$_6$H$_2$-2-O-3-Ad-5-Me)$_3$}] (**107**).[165] These compounds were both important in terms of formally containing uranium(II) but also because the former was found to be 5f^{3}6d^1 and the latter 5f^{4}6d^0. That is a clear demonstration of how the ligand field at uranium can determine the electronic ground-state structure, which is very transition-metal-like behavior. This subarea has expanded significantly, with several ligand classes supporting uranium(II), including the terphenylamide [U{N-(H)C$_6$H$_3$-2,6-[C$_6$H$_2$-2,4,6-^{i}Pr$_3$]$_2$}$_2$] (**108**) by Odom Boncella, and Shores in 2018,[166] the parallel metallocene [U(η^5-C$_5$^{i}Pr$_5$)$_2$] (**109**) by Layfield in 2020,[167] the amidate [K(2.2.2-cryptand)]-[U{OC(^{t}Bu)N-η^6-Dipp}$_2$] (**110**) by J. Arnold in 2021,[168] and the arene-tris(siloxide) [K(2.2.2-cryptand)][U{C$_6$H$_3$-1,3,5-(C$_6$H$_4$Si[O^{t}Bu]$_2$O)$_3$}(THF)] (**111**) by Mazzanti in 2023.[169] Several uranium(I) synthons have now been isolated, including **110** by J. Arnold in 2021,[168] the arene-tris(siloxide) [K(2.2.2-

cryptand)]$_2$[U{C$_6$H$_3$-1,3,5-(C$_6$H$_4$Si[O^{t}Bu]$_2$O)$_3$}] (**112**) by Mazzanti in 2023,[169] and [K(THF)$_2$(18-crown-6)]$_2$[K-{(Ph$_3$SiO)U}(μ-O)(μ-κ^2:η^6-Ph,O-PhSiPh$_2$O)(μ-κ^2:η^4-Ph,O-PhSiPh$_2$O){U-(Ph$_3$SiO)$_3$}] (**113**) also by Mazzanti in 2023.[170] Uranium(I) has been identified in disordered [K(2.2.2-cryptand)][U(η^5-C$_5$^{i}Pr$_5$)$_2$] (**114**) by Layfield.[171] These results have paralleled advances isolating thorium(III) and, remarkably, thorium(II) in molecular tris(cyclopentadienyl) complexes.[172−174] This has even been extended to include neptunium(II)[175] and plutonium(II),[176] showing the impact that studying uranium can have on neighboring actinide elements.

As indicated above, there are now many amides,[15] imidos,[16] nitrides,[21,104] and oxos,[9−12,15] so attention naturally turned to developing to accessing multiply bonded heavier group 15 and 16 derivatives of uranium by way of phosphinidene, phosphido, diphosphorus, arsinidene, arsenido, sulfido, selenido, tellurido, and Zintl cluster complexes.[177−183] The result is that there is now a significant range of U=PR (R = H, aryl), U=P(R)K, U=P=U, U−P(H)−U, U(P$_2$)U, U(P$_3$)U, U=AsR, U=As(R)K, U=As=U, U≡AsK$_2$, U(As$_2$)U, U(As$_2$H$_2$)U, U=S, U=Se, and U=Te bonds reported with a range of supporting ligands. A selection of representative complexes reported by Burns, Liddle, Ephritikhine, Hayton, Mazzanti, Meyer, Kiplinger, and Walter can be found in Figure 17 (**115−134**), and the reader is directed to recent reviews[177,178] and subsequent publications.[179−184] Overall, the range of heavier Group 15 and 16 derivatives emphasizes how multiple bond linkages more often associated with the d block can be stabilized and isolated at uranium through appropriate synthetic approaches coupled to ligand−metal complementarity.

In addition to all of the above fascinating chemistry, the long-known uranyl dication has continued to produce new chemistry time and time again. Although the uranyl dication is often referred to as inert, Clark showed in 1999 that, under highly alkaline conditions, oxo−ligand exchange can occur in uranyl hydroxides.[185] In the years that followed, uranyl activation developed into two distinct but interrelated areas, that of pentavalent uranyl and its disproportionation chemistry, and functionalization of uranyl producing O-element bonds from the "yl" oxos, which often involved reduction and hence pentavalent uranyl-type intermediates.[186−193] Through a range of silylation and borane-silylation chemistry, activation of uranyl and reduction to uranium(IV) species is now well-established, which when taken together with the facile oxo exchange by Clark renders the classical textbook description of the inert nature of the uranyl dication, except for in acidic media, somewhat in need of revision. Another textbook description of uranyl is that it is rigorously linear, but several studies have now reported uranyl O−U−O angles of ~162−168°.[66,194,195] Furthermore, cis-uranyl was proposed by Meyer in 2023 as a credible reaction intermediate,[196] suggesting that with suitable trapping a cis-uranyl may be within reach, which would also contribute to a need to rewrite textbook descriptions of uranyl. Last, there is continued interest in the extraction of uranyl, with a recent highlight being redox-switchable carboranes for uranium capture and release reported by Ménard and Hayton in 2020.[197,198] Again, all of these advances rely on ligand−metal complementarity to be successful.

Earlier, this Viewpoint touched on small-molecule activation and catalysis by uranium, mainly with CO, CO$_2$, and N$_2$, but uranium has a rich chemistry in this area with a range of small molecules and substrates,[8,12,19] even, in nonaqueous media,
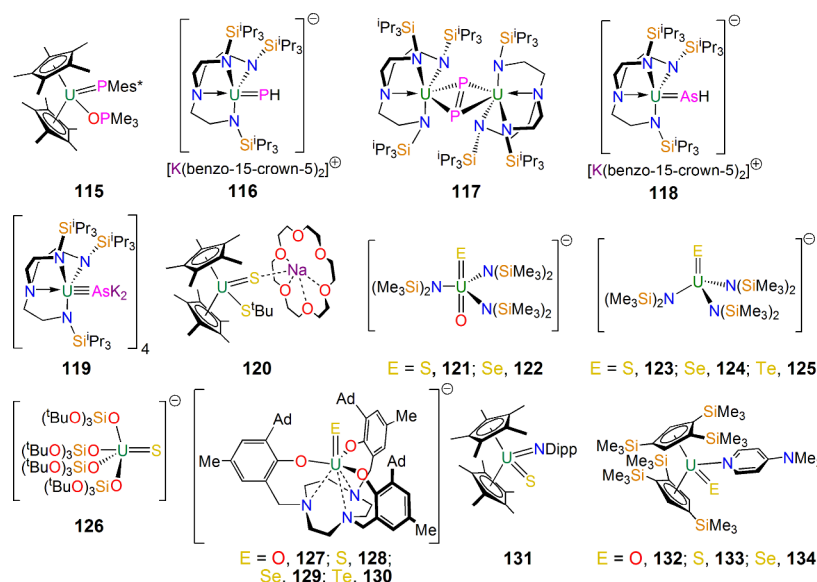
Figure 17. Selected examples of heavier Group 15 and 16 multiple bonds to uranium including **115−134**.[177−184] Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$. Dipp = 2,6-^{i}Pr$_2$C$_6$H$_2$. Cation components of **121−130** are omitted for clarity.

remarkably including water splitting reported by Meyer.[199,200] This is just one subarea of several novel physicochemical properties that uranium exhibits by virtue of its position in the Periodic Table, with others including studies encompassing single-molecule magnetism,[201] the inverse trans influence,[202] 6p-orbital pushing from below,[203] sterically induced reduction chemistry,[204] and even noble gas adducts under matrix isolation conditions.[205]

With such a rich range of new molecular complexes to study and with characterization techniques and methods becoming ever more capable and widely available, there has been growing interest in probing the covalency of uranium complexes; after all, this goes to the very heart of one of the prime motivations for pursuing molecular nonaqueous uranium chemistry, and methodological advances mean that studies that would have been unimaginable in 1988 are now verging on becoming relatively routine. From 2009 and onward, ligand K-edge X-ray absorption spectroscopy (XAS) has enabled uranium-ligand covalency to be probed from the perspective of the ligand,[206−212] and increasingly resonant inelastic X-ray spectroscopy (RIXS)[213−215] is providing a complementary perspective from the metal side. However, given that covalency can be understood and defined[216,217] as the spatial overlap of parent atomic orbitals or near-energy matching of parent atomic orbitals, or simply the net amalgamated result of both, precisely what XAS and RIXS data are reporting is an interesting debate.[218] Pulsed electron paramagnetic resonance spectroscopy has now been used to probe unpaired spin density,[219] although again how that relates exactly to describing covalency is an interesting question. Optical spectroscopy has been used to quantify 5f-orbital covalency and can be the basis of a quite detailed dissection of uranium bonding, but so far this has been limited to probing only the 5f-orbital contributions.[110,220−222] Last, NMR spectroscopy has emerged as a powerful way to probe the covalency of molecular actinide−ligand linkages, where a detailed interrogation of the shielding parameters can quantify the bonding. However, this approach is currently restricted to diamagnetic complexes and so has focused on uranium(VI) and thorium(IV) complexes.[111,223−231]

■ CONCLUSIONS AND OUTLOOK

Some 36 years after the vision of Figure 2 first emerged, this Viewpoint has sought to highlight the broad range of resulting advances that have directly, or in parallel, been delivered. An updated version of Figure 2 is presented in Figure 18, showing that most of the major targets have been secured or have close approximations. Many advances have resulted, and in particular an ever better understanding of chemical bonding in a relativistic
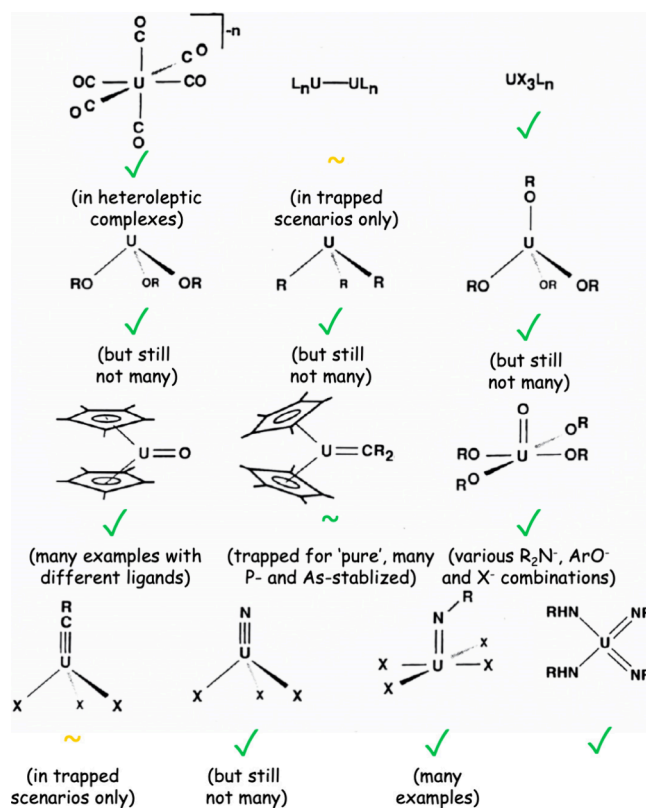

Figure 18. Updated version of Figure 2, the result of ~36 years of progress.

regime has been developed, and the redox chemistry of uranium has proven to be exploitable in numerous scenarios to secure new bonding motifs, reactivity, and physical properties. Perhaps one of the most important advances is the knowledge that even targets likely initially thought to be more aspirational than actually achievable were eventually secured—persistence is the victor.

What started as a presentation slide now requires this Viewpoint to barely scratch the surface of all of the advances that have occurred. That underscores just how much has been achieved in the intervening four decades, and those advances have undoubtedly prompted the community to reevaluate the nature of actinides. This naturally leads to the question, "Where to next?" While not claiming to be a definitive and exclusive list, the following emerge as obvious areas of focus:

- A "pure" alkylidene linkage of the form $M=CR_2$ (R = H, alkyl, silyl) is yet to be secured in an isolable molecular actinide complex under normal experimental conditions.

- Actinide carbyne and carbido complexes, in particular terminal variants, are yet to be secured in an isolable molecular actinide complex under normal experimental conditions.

- Heavier Group 14 and 15 element bonding to uranium requires further development.

- U—U bonding in an isolable molecular complex under normal experimental conditions is yet to be secured.

- A clear-cut *cis*-uranyl in an isolable molecular complex under normal experimental conditions is yet to be secured.

- The above all emphasize a need to develop the molecular chemistry of transuranium elements. Noting recent reports on a neptunium(V) bis(imido) in 2015,[232] a neptunium(V) mono(oxo) in 2022,[233] and neptunium-(III) and plutonium(III) diphosphonioalkylidenes in 2022 and 2024,[234,235] respectively, and early reports of alkyls and alkoxides that lack definitive structural authentication, many of the bonding motifs from Figure 2 that have been delivered with uranium demand realization in transuranium chemistry. This applies to thorium as well, although to a lesser extent given recent advances in its chemistry. It is also worth noting that protactinium chemistry is arguably the "sleeping beauty" of the actinides whose development is long overdue.

- All of the areas listed under parallel topics above would also certainly benefit from being translated to transuranium analogues in order to truly build a rigorous picture of actinide periodic trends.

The prior discussion above is not exhaustive by any means but aims to provide context, highlight what has been done and why, and perhaps provide inspiration to focus attention onto the possible opportunities and directions of future travel that researchers in the area might pursue. Finally, the above also serves as a powerful example of the importance of ligand—metal complementarity in developing exciting new chemistry to build our knowledge and understanding of the f elements, especially in a relativistic regime.

■ AUTHOR INFORMATION

Corresponding Author

Stephen T. Liddle − *Department of Chemistry and Centre for Radiochemistry Research, The University of Manchester, Manchester M13 9PL, U.K.;* ⊙ orcid.org/0000-0001-9911-8778; Email: steve.liddle@manchester.ac.uk

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.inorgchem.3c04533

Author Contributions

The manuscript was written by S.T.L., who has given approval for the final version of the manuscript.

Notes

The author declares no competing financial interest.

Biography

Steve Liddle is Professor and Head of Inorganic Chemistry and Co-Director of the Centre for Radiochemistry Research at The University of Manchester. His research interest spans experimental and computational investigations of metal—ligand multiple bonding, metal—metal bonding, small-molecule activation and catalysis, and magnetism, with a focus on early-transition and f-block metals but in particular the wonders of researching thorium, uranium, neptunium, and plutonium.

■ REFERENCES

(1) *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Katz, J. J., Eds.; Springer: Dordrecht, The Netherlands, 2006.

(2) *The Lanthanides and Actinides, Synthesis, Reactivity, Properties and Applications*; Liddle, S. T., Mills, D. P., Natrajan, L. S., Eds.; World Scientific: Covent Garden, London, 2022.

(3) Streitwieser, A., Jr.; Müller-Westerhoff, U. Bis-(cyclooctatetraenyl)uranium (uranocene). A new class of sandwich complexes that utilize atomic f orbitals. *J. Am. Chem. Soc.* **1968**, *90*, 7364−7364.

(4) Zalkin, A.; Raymond, K. N. The Structure of Di-π-cyclo-octatetraeneuranium (Uranocene). *J. Am. Chem. Soc.* **1969**, *91*, 5667−5668.

(5) Sattelberger, A. P. *Organo-f-Element Chemistry—Balancing Theory and Experiment*; Report LA-UR-88-0594; Los Alamos National Laboratory: Los Alamos, NM, 1988.

(6) Burns, C. J.; Smith, W. H.; Ryan, R. R.; Sattelberger, A. P. *High Valent Organouranium Complexes—Synthesis, Characterization and Reactivity*; Report LA-UR-88-0593, presented at the Third Chemical Congress of North America (including the 195th American Chemical Society National Meeting in Toronto); Los Alamos National Laboratory: Los Alamos, NM, 1988.

(7) Ephritikhine, M. The vitality of uranium molecular chemistry at the dawn of the XXIst century. *Dalton Trans.* **2006**, 2501−2516.

(8) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. Towards uranium catalysts. *Nature* **2008**, *455*, 341−349.

(9) Hayton, T. W. Metal-Ligand Multiple Bonding in Uranium: Structure and Reactivity. *Dalton Trans.* **2010**, *39*, 1145−1158.

(10) Jones, M. B.; Gaunt, A. J. Recent Developments in Synthesis and Structural Chemistry of Nonaqueous Actinide Complexes. *Chem. Rev.* **2013**, *113*, 1137−1198.

(11) Hayton, T. W. Recent Developments in Actinide-Ligand Multiple Bonding. *Chem. Commun.* **2013**, *49*, 2956−2973.

(12) La Pierre, H. S.; Meyer, K. Activation of Small Molecules by Molecular Uranium Complexes. *Prog. Inorg. Chem.* **2014**, *58*, 303−415.

(13) Gregson, M.; Wooles, A. J.; Cooper, O. J.; Liddle, S. T. Covalent uranium carbene chemistry. *Comments on Inorganic Chemistry* **2015**, *35*, 262−294.

(14) Johnson, S. A.; Bart, S. C. Achievements in uranium alkyl chemistry: celebrating sixty years of synthetic pursuits. *Dalton Trans.* **2015**, *44*, 7710−7726.

(15) Liddle, S. T. The Renaissance of Non-Aqueous Uranium Chemistry. *Angew. Chem., Int. Ed.* **2015**, *54*, 8604−8641.

(16) Schädle, D.; Anwander, R. Rare-Earth Metal and Actinide Organoimide Chemistry. *Chem. Soc. Rev.* **2019**, *48*, 5752−5805.

(17) Boronski, J. T.; Liddle, S. T. The emergence of actinide cyclobutadienyl chemistry. *Eur. J. Inorg. Chem.* **2020**, *2020*, 2851−2861.

(18) Boreen, M. A.; Arnold, J. The synthesis and versatile reducing power of low-valent uranium complexes. *Dalton Trans.* **2020**, *49*, 15124−15138.

(19) Hartline, D. R.; Meyer, K. From chemical curiosities and trophy molecules to uranium-based catalysis: developments for uranium catalysis as a new facet in molecular uranium chemistry. *JACS Au* **2021**, *1*, 698−709.

(20) Fang, W.; Maron, L.; Zhu, C. Chapter 327 - Recent advances in *f*-block metal-metal bonds. *Handbook on the Physics and Chemistry of Rare Earths* **2023**, *63*, 1−54.

(21) Keener, M.; Maria, L.; Mazzanti, M. Progress in the chemistry of molecular actinide-nitride compounds. *Chem. Sci.* **2023**, *14*, 6493−6521.

(22) Sheline, R. K.; Slater, J. L. Spectral evidence for lanthanoid and actinoid carbonyl compounds. *Angew. Chem., Int. Ed.* **1975**, *14*, 309−313.

(23) Brennan, J. G.; Andersen, R. A.; Robbins, J. L. Preparation of the first molecular carbon monoxide complex of uranium, $(Me_3SiC_5H_4)_3UCO$. *J. Am. Chem. Soc.* **1986**, *108*, 335−336.

(24) Parry, J.; Carmona, E.; Coles, S.; Hursthouse, M. Synthesis and single crystal X-ray diffraction study on the first isolable carbonyl complex of an actinide, $(C_5Me_4H)_3U(CO)$. *J. Am. Chem. Soc.* **1995**, *117*, 2649−2650.

(25) Evans, W. J.; Kozimor, S. A.; Nyce, G. W.; Ziller, J. W. Comparative Reactivity of Sterically Crowded nf³ $(C_5Me_5)_3Nd$ and $(C_5Me_5)_3U$ Complexes with CO: Formation of a Nonclassical Carbonium Ion versus an f Element Metal Carbonyl Complex. *J. Am. Chem. Soc.* **2003**, *125*, 13831−13835.

(26) Castro-Rodriguez, I.; Meyer, K. Carbon dioxide reduction and carbon monoxide activation employing a reactive uranium(III) complex. *J. Am. Chem. Soc.* **2005**, *127*, 11242−11243.

(27) Frey, A. S. P.; Cloke, F. G. N.; Hitchcock, P. B.; Day, I. J.; Green, J. C.; Aitken, G. Mechanistic Studies on the Reductive Cyclo-oligomerisation of CO by U(III) Mixed Sandwich Complexes; the Molecular Structure of $[(U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-}Cp^*)]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2O_2)]$. *J. Am. Chem. Soc.* **2008**, *130*, 13816−13817.

(28) Tarlton, M. L.; Yu, X.; Ward, R. J.; Kelley, S. P.; Autschbach, J.; Walensky, J. R. Backbonding in thorium(IV) and uranium(IV)

diarsenido complexes with *t*BuNC and CO. *Chem. Eur. J.* **2021**, *27*, 14396−14400.

(29) Ward, R. J.; Del Rosal, I.; Kelley, S. P.; Maron, L.; Walensky, J. R. isolation of C1 through C4 derivatives from CO using heteroleptic uranium(III) metallocene aryloxide complexes. *Chem. Sci.* **2023**, *14*, 2024−2032.

(30) Maron, L.; Eisenstein, O.; Andersen, R. A. The Bond between CO and Cp'_3U in $Cp'_3U(CO)$ Involves Back-bonding from the Cp'_3U Ligand-Based Orbitals of π-Symmetry, where Cp′ Represents a Substituted Cyclopentadienyl Ligand. *Organometallics* **2009**, *28*, 3629−3635.

(31) Langeslay, R. R.; Chen, G. P.; Windorff, C. J.; Chan, A. K.; Ziller, J. W.; Furche, F.; Evans, W. J. Synthesis, Structure, and Reactivity of the Sterically Crowded Th³⁺ Complex $(C_5Me_5)_3Th$ Including Formation of the Thorium Carbonyl, $[(C_5Me_5)_3Th(CO)][BPh4]$. *J. Am. Chem. Soc.* **2017**, *139*, 3387−3398.

(32) Lu, E.; Sajjad, S.; Berryman, V. E. J.; Wooles, A. J.; Kaltsoyannis, N.; Liddle, S. T. Emergence of the structure dictating role of f-orbital overlap-driven covalency. *Nat. Commun.* **2019**, *10*, 634.

(33) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. Reductive cyclotrimerization of carbon monoxide to the deltate dianion by an organometallic uranium complex. *Science* **2006**, *311*, 829−831.

(34) Schake, A. R.; Avens, L. R.; Burns, C. J.; Clark, D. L.; Sattelberger, A. P.; Smith, W. H. Synthesis of mixed-ring organoactinide complexes. 2. (Cyclooctatetraene)(pentamethylcyclopentadienyl)(THF)uranium $[(C_8H_8)(C_5Me_5)U(THF)]$ and its 4,4'-dimethyl-2,2'-bipyridine derivative. *Organometallics* **1993**, *12*, 1497−1498.

(35) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. Reductive Cyclotetramerization of CO to Squarate by a U(III) Complex: The X-ray Crystal Structure of $[(U(\eta\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta\text{-}C_5Me_4H)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_4O_4)]$. *J. Am. Chem. Soc.* **2006**, *128*, 9602−9603.

(36) Arnold, P. L.; Turner, Z. R.; Bellabarba, R. M.; Tooze, R. P. Carbon monoxide coupling and functionalisation at a simple uranium coordination complex. *Chem. Sci.* **2011**, *2*, 77−79.

(37) Gardner, B. M.; Stewart, J. C.; Davis, A. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. Homologation and Functionalization of Carbon Monoxide by a Recyclable Uranium Complex. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 9265−9270.

(38) Frey, A. S. P.; Cloke, F. G. N.; Coles, M. P.; Maron, L.; Davin, T. Facile conversion of CO/H_2 into methoxide at a uranium(III) center. *Angew. Chem., Int. Ed.* **2011**, *50*, 6881−6883.

(39) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. A linear, O-coordinated η^1-CO_2 bound to uranium. *Science* **2004**, *305*, 1757−1759.

(40) Schmidt, A.-C.; Nizovtsev, A. V.; Scheurer, A.; Heinemann, F. W.; Meyer, K. Uranium-mediated reductive conversion of CO_2 to CO and carbonate in a single-vessel, closed synthetic cycle. *Chem. Commun.* **2012**, *48*, 8634−8636.

(41) Cooper, O.; Camp, C.; Pécaut, J.; Kefalidis, C. E.; Maron, L.; Gambarelli, S.; Mazzanti, M. Multimetallic cooperativity in uranium-mediated CO_2 activation. *J. Am. Chem. Soc.* **2014**, *136*, 6716−6723.

(42) Lam, O. P.; Franke, S. M.; Heinemann, F.; Meyer, K. Reactivity of U-E-U (E = S, Se) Toward CO_2, CS_2, and COS: New Mixed-Carbonate Complexes of the Types U-CO_2E-U (E = S, Se), U-CS_2E-U (E = O, Se), and U-COSSe-U. *J. Am. Chem. Soc.* **2012**, *134*, 16877−16881.

(43) Bursten, B. E.; Rhodes, L. F.; Strittmatter, R. J. Bonding of tris(η^5-cyclopentadienyl)-actinide complexes. 3. Interaction of π-neutral, π-acidic, and π-basic ligands with $(\eta^5\text{-}C_5H_5)_3U$. *J. Am. Chem. Soc.* **1989**, *111*, 2758−2766.

(44) Siladke, N. A.; Meihaus, K. R.; Ziller, J. W.; Fang, M.; Furche, F.; Long, J. R.; Evans, W. J. Synthesis, Structure, and Magnetism of an f Element Nitrosyl Complex, $(C_5Me_4H)_3UNO$. *J. Am. Chem. Soc.* **2012**, *134*, 1243−1249.

(45) Roussel, P.; Scott, P. Complex of dinitrogen with trivalent uranium. *J. Am. Chem. Soc.* **1998**, *120*, 1070−1071.

(46) Haber, F. Verfahrenzur Herstellung von Ammoniak durch katalytische Vereinigung von Stickstoff und Wasserstoff, zweckmäßig unter hohem Druch. German Patent DE 229126, 1909.

(47) Mansell, S. M.; Farnaby, J. H.; Germeroth, A. I.; Arnold, P. L. Thermally stable uranium dinitrogen complex with siloxide supporting ligands. *Organometallics* 2013, 32, 4214−4222.

(48) Odom, A. L.; Arnold, P. L.; Cummins, C. C. Heterodinuclear uranium/molybdenum dinitrogen complexes. *J. Am. Chem. Soc.* 1998, 120, 5836−5837.

(49) Cloke, F. G. N.; Hitchcock, P. B. Reversible binding and reduction of dinitrogen by a uranium(III) pentalene complex. *J. Am. Chem. Soc.* 2002, 124, 9352−9353.

(50) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. A monometallic f element complex of dinitrogen: $(C_5Me_5)_3U(\eta^1-N_2)$. *J. Am. Chem. Soc.* 2003, 125, 14264−14265.

(51) Lu, E.; Atkinson, B. E.; Wooles, A. J.; Boronski, J. T.; Doyle, L. R.; Tuna, F.; Cryer, J. D.; Cobb, P. J.; Vitorica-Yrezabal, I. J.; Whitehead, G. F. S.; Kaltsoyannis, N.; Liddle, S. T. Back-bonding between an electron-poor, high-oxidation-state metal and poor π-acceptor ligand in a uranium(V)-dinitrogen complex. *Nat. Chem.* 2019, 11, 806−811.

(52) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. A highly reactive uranium complex supported by the calix[4]tetrapyrrole tetraanion affording dinitrogen cleavage, solvent deoxygenation, and polysilanol depolymerization. *Angew. Chem., Int. Ed.* 2002, 41, 3433−3436.

(53) Falcone, M.; Chatelain, L.; Scopelliti, R.; Živković, I.; Mazzanti, M. Nitrogen reduction and functionalization by a multimetallic uranium nitride complex. *Nature* 2017, 547, 332−335.

(54) Batov, M. S.; Del Rosal, I.; Scopelliti, R.; Fadaei-Tirani, F.; Živković, I.; Maron, L.; Mazzanti, M. Multimetallic uranium nitride cubane clusters from dinitrogen cleavage. *J. Am. Chem. Soc.* 2023, 145, 26435−26443.

(55) Lyon, J. T.; Andrews, L. Formation and characterization of the uranium methylidene complexes CH_2═UHX (X = F, Cl, Br). *Inorg. Chem.* 2006, 45, 1847−1852.

(56) Lyon, J. T.; Andrews, L.; Malmqvist, P. -Å.; Roos, B. O.; Yang, T.; Bursten, B. E. Infrared spectrum and bonding in uranium methylidene dihydride, CH_2=UH_2. *Inorg. Chem.* 2007, 46, 4917−4925.

(57) Li, J.; Hu, H.-S.; Lyon, J. T.; Andrews, L. Chirality, agostic interactions, and pyramidality in actinide methylidene complexes. *Angew. Chem., Int. Ed.* 2007, 46, 9045−9049.

(58) Lyon, J. T.; Andrews, L.; Hu, H.-S.; Li, J. Infrared spectra and electronic structures of agostic uranium methylidene molecules. *Inorg. Chem.* 2008, 47, 1435−1442.

(59) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. A uranium-carbon multiple bond. Crystal and molecular structure of $(\eta^5$-$C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$. *J. Am. Chem. Soc.* 1981, 103, 3589−3590.

(60) Cantat, T.; Arliguie, T.; Noël, A.; Thuéry, P.; Ephritikhine, M.; Le Floch, P.; Mézailles, N. The U═C double bond: synthesis and study of uranium nucleophilic carbene complexes. *J. Am. Chem. Soc.* 2009, 131, 963−972.

(61) Tourneux, J.-C.; Berthet, J.-C.; Cantat, T.; Thuéry, P.; Mézailles, N.; Ephritikhine, M. Exploring the uranyl organometallic chemistry: from single to double uranium-carbon bonds. *J. Am. Chem. Soc.* 2011, 133, 6162−6165.

(62) Mills, D. P.; Moro, F.; McMaster, J.; Van Slageren, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. A delocalized arene-bridged diuranium single molecule magnet. *Nat. Chem.* 2011, 3, 454−460.

(63) Cooper, O. J.; Mills, D. P.; McMaster, J.; Moro, F.; Davies, E. S.; Lewis, W.; Blake, A. J.; Liddle, S. T. Uranium-Carbon Multiple Bonding: Facile Access to the Pentavalent Uranium Carbene $[U\{C(PPh_2NSiMe_3)_2\}(Cl)_2(I)]$ and Comparison of U^V=C and U^{IV}=C Double Bonds. *Angew. Chem., Int. Ed.* 2011, 50, 2383−2386.

(64) Mills, D. P.; Cooper, O. J.; Tuna, F.; McInnes, E. J. L.; Davies, E. S.; McMaster, J.; Moro, F.; Lewis, W.; Blake, A. J.; Liddle, S. T. Synthesis of a Uranium(VI)-Carbene: Reductive Formation of Uranyl(V)-Methanides, Oxidative Preparation of a $[R_2C$ = U=$O]^{2+}$ Analogue of the $[O$ = U=$O]^{2+}$ Uranyl Ion (R = $Ph_2PNSiMe_3$), and

Comparison of the Nature of U^{IV}=C, U^V=C and U^{VI}=C Double Bonds. *J. Am. Chem. Soc.* 2012, 134, 10047−10054.

(65) Wooles, A. J.; Mills, D. P.; Tuna, F.; McInnes, E. J. L.; Law, G. T. W.; Fuller, A. J.; Kremer, F.; Ridgway, M.; Lewis, W.; Gagliardi, L.; Vlaisavljevich, B.; Liddle, S. T. Uranium(III)-Carbon Multiple Bonding Supported by Arene δ-Bonding in Mixed-Valence Hexauranium Nanometre-Scale Rings. *Nat. Commun.* 2018, 9, 2097.

(66) Lu, E.; Cooper, O. J.; McMaster, J.; Tuna, F.; McInnes, E. J. L.; Lewis, W.; Blake, A. J.; Liddle, S. T. Synthesis, Characterization, and Reactivity of a Uranium(VI) Carbene Imido Oxo Complex. *Angew. Chem., Int. Ed.* 2014, 53, 6696−6700.

(67) Fortier, S.; Walensky, J. R.; Wu, G.; Hayton, T. W. Synthesis of a Phosphorano-Stabilized U(IV)-Carbene via One-Electron Oxidation of a U(III)-Ylide Adduct. *J. Am. Chem. Soc.* 2011, 133, 6894−6897.

(68) Rungthanaphatsophon, P.; Bathelier, A.; Castro, L.; Behrle, A. C.; Barnes, C. L.; Maron, L.; Walensky, J. R. Formation of Methane versus Benzene in the Reactions of $(C_5Me_5)_2Th(CH_3)_2$ with $[CH_3PPh_3]X$ (X = Cl, Br, I) Yielding Thorium-Carbene or Thorium-Ylide Complexes. *Angew. Chem., Int. Ed.* 2017, 56, 12925−12929.

(69) Seed, J. A.; Sharpe, H. R.; Futcher, H. J.; Wooles, A. J.; Liddle, S. T. Nature of the Arsonium-Ylide Ph_3As = CH_2 and a Uranium(IV) Arsonium-Carbene Complex. *Angew. Chem., Int. Ed.* 2020, 59, 15870−15874.

(70) Baker, C. F.; Seed, J. A.; Adams, R. W.; Lee, D.; Liddle, S. T. $^{13}C_{carbene}$ nuclear magnetic resonance chemical shift analysis confirms $Ce^{IV}C$ double bonding in cerium(iv)-diphosphonioalkylidene complexes. *Chem. Sci.* 2024, 15, 238−249.

(71) Lu, E.; Boronski, J. T.; Gregson, M.; Wooles, A. J.; Liddle, S. T. Silyl-phosphino-carbene complexes of uranium(IV). *Angew. Chem., Int. Ed.* 2018, 57, 5506−5511.

(72) Kent, G. T.; Yu, X.; Wu, G.; Autschbach, J.; Hayton, T. W. Synthesis and electronic structure analysis of the actinide allenylidenes, $[\{(NR_2)_3\}An(CCCPh_2)]^-$ (An = U, Th; R = $SiMe_3$). *Chem. Sci.* 2021, 12, 14383−14388.

(73) Zhou, M.; Andrews, L.; Li, J.; Bursten, B. E. Reaction of Laser-Ablated Uranium Atoms with CO: Infrared Spectra of the CUO, CUO^-, OUCCO, $(\eta^2$-$C_2)UO_2$, and $U(CO)_x$ (x = 1−6) Molecules in Solid Neon. *J. Am. Chem. Soc.* 1999, 121, 9712−9721.

(74) Andrews, L.; Liang, B.; Li, J.; Bursten, B. E. Ground-state reversal by matrix interaction: electronic states and vibrational frequencies of CUO in solid argon and neon. *Angew. Chem., Int. Ed.* 2000, 39, 4565−4567.

(75) Lyon, J. T.; Hu, H.-S.; Andrews, L.; Li, J. Formation of unprecedented actinide≡carbon triple bonds in uranium methylidyne molecules. *Proc. Natl. Acad. Sci. U.S.A.* 2007, 104, 18919−18924.

(76) Wang, X.; Andrews, L.; Malmqvist, P. -Å.; Roos, B. O.; Gonçalves, A. P.; Pereira, C. C. L.; Marçalo, J.; Godart, C.; Villeroy, B. Infrared spectra and quantum chemical calculations of the uranium carbide molecules UC and CUC with triple bonds. *J. Am. Chem. Soc.* 2010, 132, 8484−8488.

(77) Wang, X.; Andrews, L.; Ma, D.; Gagliardi, L.; Gonçalves, A. P.; Pereira, C. C. L.; Marçalo, J.; Godart, C.; Villeroy, B. Infrared spectra and quantum chemical calculations on the uranium-carbon molecules UC, CUC, UCH, and $U(CC)_2$. *J. Chem. Phys.* 2011, 134, 244313.

(78) Hu, H.-S.; Qiu, Y.-H.; Xiong, X.-G.; Schwarz, W. H. E.; Li, J. On the maximum bond multiplicity of carbon: unusual C≡U quadruple bonding in molecular CUO. *Chem. Sci.* 2012, 3, 2786−2796.

(79) Zhang, X.; Li, W.; Feng, L.; Chen, X.; Hansen, A.; Grimme, S.; Fortier, S.; Sergentu, D.-C.; Duignan, T. J.; Autschbach, J.; Wang, S.; Wang, Y.; Velkos, G.; Popov, A. A.; Aghdassi, N.; Duhm, S.; Li, X.; Li, J.; Echegoyen, L.; Schwarz, W. H. E.; Chen, N. A diuranium carbide cluster stabilized inside a C_{80} fullerene cage. *Nat. Commun.* 2018, 9, 2753.

(80) Zhuang, J.; Abella, L.; Sergentu, D.-C.; Yao, Y.-R.; Jin, M.; Yang, W.; Zhang, X.; Li, X.; Zhang, D.; Zhao, Y.; Li, X.; Wang, S.; Echegoyen, L.; Autschbach, J.; Chen, N. Diuranium(IV) carbide cluster U_2C_2 stabilized inside fullerene cages. *J. Am. Chem. Soc.* 2019, 141, 20249−20260.

(81) Jiang, H.; Yu, X.; Guo, M.; Yao, Y.-R.; Meng, Q.; Echegoyen, L.; Autschbach, J.; Chen, N. USc$_2$C$_2$ and USc$_2$NC clusters with U-C triple bond character stabilized inside fullerene cages. *J. Am. Chem. Soc.* **2023**, *145*, 5645−5654.

(82) Yao, Y.-R.; Zhao, J.; Meng, Q.; Hu, H.-S.; Guo, M.; Yan, Y.; Zhuang, J.; Yang, S.; Fortier, S.; Echegoyen, L.; Schwarz, W. H. E.; Li, J.; Chen, N. Synthesis and characterization of U≡C triple bonds in fullerene compounds. *J. Am. Chem. Soc.* **2023**, *145*, 25440−25449.

(83) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. Uranium carbon multiple-bond chemistry. 3. Insertion of acetonitrile and the formation of a uranium nitrogen multiple bond. *J. Am. Chem. Soc.* **1984**, *106*, 1853−1854.

(84) Brennan, J. G.; Andersen, R. A. Electron-transfer reactions of trivalent uranium. Preparation and structure of the uranium metal-locene compounds (MeC$_5$H$_4$)$_3$U = NPh and [(MeC$_5$H$_4$)$_3$U]$_2$[μ-η^1,η^2-PhNCO]. *J. Am. Chem. Soc.* **1985**, *107*, 514−516.

(85) Zalkin, A.; Brennan, J. G.; Andersen, R. A. Tris[bis-(trimethylsilyl)amido](trimethylsilylimido)uranium(V). *Acta Cryst. C* **1988**, *44*, 1553−1554.

(86) Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. Uranium(VI) organoimido complexes. *J. Am. Chem. Soc.* **1990**, *112*, 3237−3239.

(87) Arney, D. S.; Burns, C. J.; Smith, D. C. Synthesis and structure of the first uranium(VI) organometallic complex. *J. Am. Chem. Soc.* **1992**, *114*, 10068−10069.

(88) Arney, D. S.; Burns, C. J. Synthesis and structure of high-valent organouranium complexes containing terminal monooxo functional groups. *J. Am. Chem. Soc.* **1993**, *115*, 9840−9841.

(89) Warner, B. P.; Scott, B. L.; Burns, C. J. A simple preparative route to bis(imido)uranium(VI) complexes by the direct reductions of diazenes and azides. *Angew. Chem., Int. Ed.* **1998**, *37*, 959−960.

(90) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. Synthesis of imido analogs of the uranyl ion. *Science* **2005**, *310*, 1941−1943.

(91) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R.; Hay, P. J. Synthesis and reactivity of the imido analogues of the uranyl ion. *J. Am. Chem. Soc.* **2006**, *128*, 10549−10559.

(92) Anderson, N. H.; Odoh, S. O.; Yao, Y.; Williams, U. J.; Schaefer, B. A.; Kiernicki, J. J.; Lewis, A. J.; Goshert, M. D.; Fanwick, P. E.; Schelter, E. J.; Walensky, J. R.; Gagliardi, L.; Bart, S. C. Harnessing redox activity for the formation of uranium tris(imido) compounds. *Nat. Chem.* **2014**, *6*, 919−926.

(93) Anderson, N. H.; Yin, H.; Kiernicki, J. J.; Fanwick, P. E.; Schelter, E. J.; Bart, S. C. Investigation of uranium tris(imido) complexes: synthesis, characterization, and reduction chemistry of [U-(NDIPP)$_3$(thf)$_3$]. *Angew. Chem., Int. Ed.* **2015**, *54*, 9386−9389.

(94) Anderson, N. H.; Xie, J.; Ray, D.; Zeller, M.; Gagliardi, L.; Bart, S. C. Elucidating bonding preferences in tetrakis(imido)uranate(VI) dianions. *Nat. Chem.* **2017**, *9*, 850−855.

(95) King, D.; McMaster, J.; Tuna, F.; McInnes, E. J. L.; Lewis, W.; Blake, A. J.; Liddle, S. T. Synthesis and Characterization of an f-Block Terminal Parent Imido [U = NH] Complex: A Masked Uranium(IV)-Nitride. *J. Am. Chem. Soc.* **2014**, *136*, 5619−5622.

(96) Lam, O. P.; Franke, S. M.; Nakai, H.; Heinemann, F. W.; Hieringer, W.; Meyer, K. Observation of the Inverse Trans Influence (ITI) in a Uranium(V) Imide Coordination Complex: An Experimental Study and Theoretical Evaluation. *Inorg. Chem.* **2012**, *51*, 6190−6199.

(97) Green, D. W.; Reedy, G. T. The identification of UN in Ar matrices. *J. Chem. Phys.* **1976**, *65*, 2921−2922.

(98) Hunt, R. D.; Yustein, J. T.; Andrews, L. Matrix infrared spectra of NUN formed by the insertion of uranium atoms into molecular nitrogen. *J. Chem. Phys.* **1993**, *98*, 6070−6074.

(99) Zhou, M.; Andrews, L. Infrared spectra and pseudopotential calculations for NUO$^+$, NUO, and NThO in solid neon. *J. Chem. Phys.* **1999**, *111*, 11044−11049.

(100) Andrews, L.; Wang, X.; Lindh, R.; Roos, B. O.; Marsden, C. J. Simple N≡UF$_3$ and P≡UF$_3$ molecules with triple bonds to uranium. *Angew. Chem., Int. Ed.* **2008**, *47*, 5366−5370.

(101) Wang, X.; Andrews, L.; Vlaisavljevich, B.; Gagliardi, L. Combined triple and double bonds to uranium: the N≡U = N-H uranimine nitride molecule prepared in solid argon. *Inorg. Chem.* **2011**, *50*, 3826−3831.

(102) Vlaisavljevich, B.; Andrews, L.; Wang, X.; Gong, Y.; Kushto, G. P.; Bursten, B. E. Detection and electronic structure of naked actinide complexes: rhombic-ring (AnN)$_2$ molecules stabilized by delocalized π-bonding. *J. Am. Chem. Soc.* **2016**, *138*, 893−905.

(103) Meng, Q.; Abella, L.; Yao, Y.-R.; Sergentu, D.-C.; Yang, W.; Liu, X.; Zhuang, J.; Echegoyen, L.; Autschbach, J.; Chen, N. A charged diatomic triple-bonded U≡N species trapped in C$_{82}$ fullerene cages. *Nat. Commun.* **2022**, *13*, 7192.

(104) King, D. M.; Liddle, S. T. Progress in molecular uranium-nitride chemistry. *Coord. Chem. Rev.* **2014**, *266−267*, 2−15.

(105) Fox, A. R.; Cummins, C. C. Uranium-nitrogen multiple bonding: the case of a four-coordinate uranium(VI) nitridoborate complex. *J. Am. Chem. Soc.* **2009**, *131*, 5716−5717.

(106) Thomson, R. K.; Cantat, T.; Scott, B. L.; Morris, D. E.; Batista, E. R.; Kiplinger, J. L. Uranium azide photolysis results in C-H bond activation and provides evidence for a terminal uranium nitride. *Nat. Chem.* **2010**, *2*, 723−729.

(107) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. Synthesis and Structure of a Terminal Uranium Nitride Complex. *Science* **2012**, *337*, 717−720.

(108) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. Isolation and characterisation of a uranium(VI)-nitride triple bond. *Nat. Chem.* **2013**, *5*, 482−488.

(109) King, D. M.; Cleaves, P. A.; Wooles, A. J.; Gardner, B. M.; Chilton, N. F.; Tuna, F.; Lewis, W.; McInnes, E. J. L.; Liddle, S. T. Molecular and Electronic Structure of Terminal and Alkali Metal-Capped Uranium(V)-Nitride Complexes. *Nat. Commun.* **2016**, *7*, 13773.

(110) Du, J.; Seed, J. A.; Berryman, V. E. J.; Kaltsoyannis, N.; Adams, R. W.; Lee, D.; Liddle, S. T. Exceptional Uranium(VI)-Nitride Triple Bond Covalency from ^{15}N Nuclear Magnetic Resonance Spectroscopy and Quantum Chemical Analysis. *Nat. Commun.* **2021**, *12*, 5649.

(111) Barluzzi, L.; Scopelliti, R.; Mazzanti, M. Photochemical synthesis of a stable terminal uranium(VI) nitride. *J. Am. Chem. Soc.* **2020**, *142*, 19047−19051.

(112) Chatelain, L.; Louyriac, E.; Douair, I.; Lu, E.; Tuna, F.; Wooles, A. J.; Gardner, B. M.; Maron, L.; Liddle, S. T. Terminal Uranium(V)-Nitride Hydrogenations Involving Direct Addition or Frustrated Lewis Pair Mechanisms. *Nat. Commun.* **2020**, *11*, 337.

(113) Rudel, S. S.; Deubner, H. L.; Müller, M.; Karttunen, A. J.; Kraus, F. Complexes featuring a linear [N≡U≡N] core isoelectronic to the uranyl cation. *Nat. Chem.* **2020**, *12*, 962−967.

(114) Seaman, L. A.; Walensky, J. R.; Wu, G.; Hayton, T. W. In pursuit of homoleptic actinide alkyl complexes. *Inorg. Chem.* **2013**, *52*, 3556−3564.

(115) Marks, T. J.; Seyam, A. M. Observations on the thermal decomposition of some uranium(IV) tetraalkyls. *J. Organomet. Chem.* **1974**, *67*, 61−66.

(116) Evans, W. J.; Wink, D. J.; Stanley, D. R. Reinvestigation of the reaction of tert-butyllithium with uranium tetrachloride: formation of catalytically active uranium(III) hydride complexes. *Inorg. Chem.* **1982**, *21*, 2565−2573.

(117) Edwards, P. G.; Andersen, R. A.; Zalkin, A. Preparation of tetraalkyl phosphine complexes of the f-block metals. Crystal structure of Th(CH$_2$Ph)$_4$(Me$_2$PCH$_2$CH$_2$PMe$_2$) and U(CH$_2$Ph)$_3$Me-(Me$_2$PCH$_2$CH$_2$PMe$_2$). *Organometallics* **1984**, *3*, 293−398.

(118) Van der Sluys, W. G.; Burns, C. J.; Sattelberger, A. P. First example of a neutral homoleptic uranium alkyl. Synthesis, properties, and structure of U[CH(SiMe$_3$)$_2$]$_3$. *Organometallics* **1989**, *8*, 855−857.

(119) Fortier, S.; Melot, B. C.; Wu, G.; Hayton, T. W. Homoleptic uranium(IV) alkyl complexes: synthesis and characterization. *J. Am. Chem. Soc.* **2009**, *131*, 15512−15521.

(120) Fortier, S.; Walensky, J. R.; Wu, G.; Hayton, T. W. High-Valent Uranium Alkyls: Evidence for the Formation of U^{VI}(CH$_2$SiMe$_3$)$_6$. *J. Am. Chem. Soc.* **2011**, *133*, 11732−11743.

(121) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. Carbon-Carbon Reductive Elimination from Homoleptic Uranium(IV) Alkyls Induced by Redox-Active Ligands. *J. Am. Chem. Soc.* **2012**, *134*, 6160−6168.

(122) Johnson, S. A.; Kiernicki, J. J.; Fanwick, P. E.; Bart, S. C. New Benzylpotassium Reagents and Their Utility for the Synthesis of Homoleptic Uranium(IV) Benzyl Derivatives. *Organometallics* **2015**, *34*, 2889−2895.

(123) Sears, J. D.; Sergentu, D.-C.; Baker, T. M.; Brennessel, W. W.; Autschbach, J.; Neidig, M. L. The exceptional diversity of homoleptic uranium-methyl complexes. *Angew. Chem., Int. Ed.* **2020**, *59*, 13586−13590.

(124) Boreen, M. A.; Parker, B. F.; Lohrey, T. D.; Arnold, J. A homoleptic uranium(III) tris(aryl) complex. *J. Am. Chem. Soc.* **2016**, *138*, 15865−15868.

(125) Wolford, N. J.; Sergentu, D.-C.; Brennessel, W. W.; Autschbach, J.; Neidig, M. L. Homoleptic aryl complexes of uranium(IV). *Angew. Chem., Int. Ed.* **2019**, *58*, 10266−10270.

(126) Seaman, L. A.; Pedrick, E. A.; Tsuchiya, T.; Wu, G.; Jakubikova, E.; Hayton, T. W. Comparison of the Reactivity of 2-Li-C₆H₄CH₂NMe₂ with MCl₄ (M = Th, U): Isolation of a Thorium Aryl Complex or a Uranium Benzyne Complex. *Angew. Chem., Int. Ed.* **2013**, *52*, 10589−10592.

(127) Pedrick, E. A.; Seaman, L. A.; Scott, J. C.; Griego, L.; Wu, G.; Hayton, T. W. Synthesis and reactivity of a U(IV) dibenzyne complex. *Organometallics* **2016**, *35*, 494−502.

(128) Cotton, F. A.; Marler, D. O.; Schwotzer, W. Dinuclear uranium alkoxides. Preparation and structures of KU₂(OCMe₃)₉, U₂(OCMe₃)₉, and U₂(OCHMe₂)₁₀, containing [uranium(IV), uranium(IV)], [uranium(IV), uranium(V)], and [uranium(V), uranium(V)], respectively. *Inorg. Chem.* **1984**, *23*, 4211−4215.

(129) Cotton, F. A.; Marler, D. O.; Schwotzer, W. The structure of U₃(O)(OCMe₃)₁₀, an unusual trinuclear U(IV) oxo-alkoxide. *Inorg. Chim. Acta* **1984**, *95*, 207−209.

(130) Cotton, F. A.; Marler, D. O.; Schwotzer, W. Uranium-to-uranium bonds: do they exist? *Inorg. Chim. Acta* **1984**, *85*, L31−L32.

(131) Eller, P. G.; Vergamini, P. J. Nuclear magnetic resonance and chemical studies of uranium(V) alkoxides. *Inorg. Chem.* **1983**, *22*, 3184−3189.

(132) Fortier, S.; Wu, G.; Hayton, T. W. Synthesis and Characterization of Three Homoleptic Alkoxides of Uranium: [Li(THF)]₂[Uᴵⱽ(OᵗBu)₆], [Li(Et₂O)][Uⱽ(OᵗBu)₆], and Uⱽᴵ(OᵗBu)₆. *Inorg. Chem.* **2008**, *47*, 4752−4761.

(133) Van der Sluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger, A. P. Uranium alkoxide chemistry. 1. Synthesis and the novel dimeric structure of the first homoleptic uranium(III) aryloxide complex. *J. Am. Chem. Soc.* **1988**, *110*, 5924−5925.

(134) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. Small Molecule Activation by Uranium Tris(aryloxides): Experimental and Computational Studies of Binding of N₂, Coupling of CO, and Deoxygenation Insertion of CO₂ under Ambient Conditions. *J. Am. Chem. Soc.* **2011**, *133*, 9036−9051.

(135) Van der Sluys, W. G.; Sattelberger, A. P.; Streib, W. E.; Huffman, J. C. Tetrakis(2,6-di-t-butylphenoxy)uranium(IV): The first structurally characterized neutral homoleptic aryloxide complex of uranium-(IV). *Polyhedron* **1989**, *8*, 1247−1249.

(136) Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger, A. P.; Streib, W. E.; Van der Sluys, W. G.; Watkin, J. G. Early actinide alkoxide chemistry. Synthesis, characterization, and molecular structures of Th(IV) and U(IV) aryloxide complexes. *J. Am. Chem. Soc.* **1992**, *114*, 10811−10821.

(137) Franke, S. M.; Tran, B. L.; Heinemann, F. W.; Hieringer, W.; Mindiola, D. J.; Meyer, K. Uranium(III) Complexes with Bulky Aryloxide Ligands Featuring Metal-Arene Interactions and Their Reactivity Toward Nitrous Oxide. *Inorg. Chem.* **2013**, *52*, 10552−10558.

(138) Hoerger, C. J.; La Pierre, H. S.; Maron, L.; Scheurer, A.; Heinemann, F. W.; Meyer, K. Reductive disproportionation of nitric oxide mediated by low-valent uranium. *Chem. Commun.* **2016**, *52*, 10854−10857.

(139) Cavigliasso, G.; Kaltsoyannis, N. On the Paucity of Molecular Actinide Complexes with Unsupported Metal-Metal Bonds: A Comparative Investigation of the Electronic Structure and Metal-Metal Bonding in U₂X₆ (X = Cl, F, OH, NH₂, CH₃) Complexes and d-Block Analogues. *Inorg. Chem.* **2006**, *45*, 6828−6839.

(140) Gorokhov, L. N.; Emelyanov, A. M.; Khodeev, Y. S. Mass-spectroscopic investigation of stability of gaseous U₂O₂ and U₂. *High Temp.* **1974**, *12*, 1307−1309.

(141) Roos, B. O.; Malmqvist, P. -Å.; Gagliardi, L. Exploring the actinide-actinide bond: theoretical studies of the chemical bond in Ac₂, Th₂, Pa₂, and U₂. *J. Am. Chem. Soc.* **2006**, *128*, 17000−17006.

(142) Gagliardi, L.; Roos, B. O. Quantum chemical calculations show that the uranium molecule U₂ has a quintuple bond. *Nature* **2005**, *433*, 848−851.

(143) Knecht, S.; Jensen, H. J. A.; Saue, T. Relativistic quantum chemical calculations show that the uranium molecule U₂ has a quadruple bond. *Nat. Chem.* **2019**, *11*, 40−44.

(144) Souter, P. F.; Kushto, G. P.; Andrews, L. IR spectra of uranium hydride molecules isolated in solid argon. *Chem. Commun.* **1996**, 2401−2402.

(145) Souter, P. F.; Kushto, G. P.; Andrews, L.; Neurock, M. Experimental and Theoretical Evidence for the Formation of Several Uranium Hydride Molecules. *J. Am. Chem. Soc.* **1997**, *119*, 1682−1687.

(146) Zhang, X.; Wang, Y.; Morales-Martínez, R.; Zhong, J.; De Graaf, C.; Rodríguez-Fortea, A.; Poblet, J. M.; Echegoyen, L.; Feng, L.; Chen, N. U₂@Iₕ(7)-C₈₀: crystallographic characterization of a long-sought dimetallic actinide endohedral fullerene. *J. Am. Chem. Soc.* **2018**, *140*, 3907−3915.

(147) Foroutan-Nejad, C.; Vícha, J.; Marek, R.; Patzschke, M.; Straka, M. Unwilling U-U bonding in U₂@C₈₀: cage-driven metal-metal bonds in di-uranium fullerenes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 24182−24192.

(148) Moreno-Vicente, A.; Roselló, Y.; Chen, N.; Echegoyen, L.; Dunk, P. W.; Rodríguez-Fortea, A.; De Graaf, C.; Poblet, J. M. Are U−U bonds inside fullerenes really unwilling bonds? *J. Am. Chem. Soc.* **2023**, *145*, 6710−6718.

(149) Zhuang, J.; Morales-Martínez, R.; Zhang, J.; Wang, Y.; Yao, Y.-R.; Pei, C.; Rodríguez-Fortea, A.; Wang, S.; Echegoyen, L.; De Graaf, C.; Poblet, J. M.; Chen, N. Characterization of a strong covalent Th³⁺-Th³⁺ bond inside an Iₕ(7)-C₈₀ fullerene cage. *Nat. Commun.* **2021**, *12*, 2372.

(150) Boronski, J. T.; Seed, J. A.; Hunger, D.; Woodward, A. W.; Van Slageren, J.; Wooles, A. J.; Natrajan, L. S.; Kaltsoyannis, N.; Liddle, S. T. A crystalline tri-thorium cluster with σ-aromatic metal-metal bonding. *Nature* **2021**, *598*, 72−75.

(151) Tomeček, J.; Liddle, S. T.; Kaltsoyannis, N. Actinide-Actinide Bonding: Electron Delocalisation and σ-Aromaticity in the Tri-Thorium Cluster [{Th(η⁸-C₈H₈)(μ-Cl)₂}₃K₂]. *ChemPhysChem* **2023**, *24*, No. e202300366.

(152) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. Lewis base adducts of uranium triiodide: a new class of synthetically useful precursors for trivalent uranium chemistry. *Inorg. Chem.* **1989**, *28*, 1771−1773.

(153) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. A convenient entry into trivalent actinide chemistry: synthesis and characterization of AnI₃(THF)₄ and An[N-(SiMe₃)₂]₃ (An = U, Np, Pu). *Inorg. Chem.* **1994**, *33*, 2248−2256.

(154) Reynolds, L. T.; Wilkinson, G. π-Cylopentadienyl compounds of uranium-IV and thorium-IV. *J. Inorg. Nucl. Chem.* **1956**, *2*, 246−253.

(155) Fischer, E. O.; Hristidu, Y. Uber aromatenkomplexe von metallen. 57. Uran-tetracyclopentadienyl. *Z. Naturforsch.* **1962**, *17*, 275−275.

(156) Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. Synthesis and crystal structure of [K(C₁₂H₂₄O₆)][U(η-C₇H₇)₂], the first cycloheptatrienyl sandwich compound. *J. Chem. Soc. Chem. Commun.* **1995**, 183−184.

(157) Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. Inverse cycloheptatrienyl sandwich complexes. Crystal structure of

$[U(BH_4)_2(OC_4H_8)_5][(BH_4)_3U(\mu-\eta^7,\eta^7-C_7H_7)U(BH_4)_3]$. *J. Chem. Soc. Chem. Commun.* **1994**, 847−848.

(158) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. Synthesis and structure of a π-arene complex of uranium(III) - aluminum chloride. *Inorg. Chim. Acta* **1971**, *5*, 439−444.

(159) Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. Arene-Bridged Diuranium Complexes: Inverted Sandwiches Supported by δ Backbonding. *J. Am. Chem. Soc.* **2000**, *122*, 6108−6109.

(160) Cryer, J. D.; Liddle, S. T. Arene complexes of the actinides. In *Comprehensive Organometallic Chemistry IV*; Parkin, G.; Meyer, K.; O'Hare, D., Eds.; Elsevier, 2022; Vol. *4*, pp 460−501.

(161) Patel, D.; Moro, F.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. A Formal High Oxidation State Inverse-Sandwich Diuranium Complex: A New Route to f-Block-Metal Bonds. *Angew. Chem., Int. Ed.* **2011**, *50*, 10388−10392.

(162) Patel, D.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. Reductive assembly of cyclobutadienyl and diphosphacyclobutadienyl rings at uranium. *Nat. Commun.* **2013**, *4*, 2323.

(163) Zhang, L.; Hou, G.; Zi, G.; Ding, W.; Walter, M. D. Influence of the 5f orbitals on the bonding and reactivity in organoactinides: experimental and computational studies on a uranium metal-lacyclopropene. *J. Am. Chem. Soc.* **2016**, *138*, 5130−5142.

(164) MacDonald, M. R.; Fieser, M. E.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Identification of the + 2 Oxidation State for Uranium in a Crystalline Molecular Complex, $[K(2.2.2-Cryptand)]-[(C_5H_4SiMe_3)_3U]$. *J. Am. Chem. Soc.* **2013**, *135*, 13310−133113.

(165) La Pierre, H. S.; Scheurer, A.; Heinemann, F. W.; Hieringer, W.; Meyer, K. Synthesis and Characterization of a Uranium(II) Monoarene Complex Supported by δ Backbonding. *Angew. Chem., Int. Ed.* **2014**, *53*, 7158−7162.

(166) Billow, B. S.; Livesay, B. N.; Mokhtarzadeh, C. C.; McCracken, J.; Shores, M. P.; Boncella, J. M.; Odom, A. L. Synthesis and characterization of a neutral U(II) arene sandwich complex. *J. Am. Chem. Soc.* **2018**, *140*, 17369−17373.

(167) Guo, F.-S.; Tsoureas, N.; Huang, G.-Z.; Tong, M.-L.; Mansikkamäki, A.; Layfield, R. A. Isolation of a perfectly linear uranium(II) metallocene. *Angew. Chem., Int. Ed.* **2020**, *59*, 2299−2303.

(168) Straub, M. D.; Ouellette, E. T.; Boreen, M. A.; Britt, R. D.; Chakarawet, K.; Douair, I.; Gould, C. A.; Maron, L.; Del Rosal, I.; Villarreal, D.; Minasian, S. G.; Arnold, J. A Uranium(II) Arene Complex That Acts as a Uranium(I) Synthon. *J. Am. Chem. Soc.* **2021**, *143*, 19748−19760.

(169) Keener, M.; Shivaraam, R. A.; Rajeshkumar, T.; Tricoire, M.; Scopelliti, R.; Živković, I.; Chauvin, A.-S.; Maron, L.; Mazzanti, M. Multielectron Redox Chemistry of Uranium by Accessing the + II Oxidation State and Enabling Reduction to a U(I) Synthon. *J. Am. Chem. Soc.* **2023**, *145*, 16271−16283.

(170) Shivaraam, R. A. K.; Keener, M.; Modder, D. K.; Rajeshkumar, T.; Živković, I.; Scopelliti, R.; Maron, L.; Mazzanti, M. A Route to Stabilize Uranium(II) and Uranium(I) Synthons in Multimetallic Complexes. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202304051.

(171) Barluzzi, L.; Giblin, S. R.; Mansikkamäki, A.; Layfield, R. A. Identification of oxidation state + 1 in a molecular uranium complex. *J. Am. Chem. Soc.* **2022**, *144*, 18229−18233.

(172) Langeslay, R. R.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Synthesis, structure, and reactivity of crystalline molecular complexes of the $\{[C_5H_3(SiMe_3)_2]_3Th\}^{1-}$ anion containing thorium in the formal + 2 oxidation state. *Chem. Sci.* **2015**, *6*, 517−521.

(173) Ortu, F.; Formanuik, A.; Innes, J. R.; Mills, D. P. New vistas in the molecular chemistry of thorium. *Dalton Trans.* **2016**, *45*, 7537−7549.

(174) Huh, D. N.; Roy, S.; Ziller, J. W.; Furche, F.; Evans, W. J. Isolation of a Square-Planar Th(III) Complex: Synthesis and Structure of $[Th(OC_6H_2{}^tBu_2-2,6-Me-4)_4]^{1-}$. *J. Am. Chem. Soc.* **2019**, *141*, 12458−12463.

(175) Su, J.; Windorff, C. J.; Batista, E. R.; Evans, W. J.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L.; Woen, D. H.; Yang, P. Identification of the Formal + 2 Oxidation State of Neptunium:

Synthesis and Structural Characterization of $\{Np^{II}[C_5H_3(SiMe_3)_2]_3\}^{1-}$. *J. Am. Chem. Soc.* **2018**, *140*, 7425−7428.

(176) Windorff, C. J.; Chen, G. P.; Cross, J. N.; Evans, W. J.; Furche, F.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L. Identification of the Formal + 2 Oxidation State of Plutonium: Synthesis and Characterization of $\{Pu^{II}[C_5H_3(SiMe_3)_2]_3\}^-$. *J. Am. Chem. Soc.* **2017**, *139*, 3970−3973.

(177) Du, J.; Cobb, P. J.; Ding, J.; Mills, D. P.; Liddle, S. T. f-Element heavy pnictogen chemistry. *Chem. Sci.* **2023**, *15*, 13−45.

(178) Ephritikhine, M. Molecular actinide compounds with soft chalcogen ligands. *Coord. Chem. Rev.* **2016**, *319*, 35−62.

(179) Kelly, R. P.; Falcone, M.; Lamsfus, C. A.; Scopelliti, R.; Maron, L.; Meyer, K.; Mazzanti, M. Metathesis of a U^V imido complex: a route to a terminal U^V sulfide. *Chem. Sci.* **2017**, *8*, 5319−5328.

(180) Andrez, J.; Pécaut, J.; Scopelliti, R.; Kefalidis, C. E.; Maron, L.; Rosenzweig, M. W.; Meyer, K.; Mazzanti, M. Synthesis and reactivity of a terminal uranium(IV) sulfide supported by siloxide ligands. *Chem. Sci.* **2016**, *7*, 5846−5856.

(181) Rosenzweig, M. W.; Scheurer, A.; Lamsfus, C. A.; Heinemann, F. W.; Maron, L.; Andrez, J.; Mazzanti, M.; Meyer, K. Uranium(IV) terminal hydrosulfido and sulfido complexes: insights into the nature of the uranium-sulfur bond. *Chem. Sci.* **2016**, *7*, 5857−5866.

(182) Pagano, J. K.; Arney, D. S. J.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L.; Burns, C. J. A sulphur and uranium fiesta! Synthesis, structure, and characterization of neutral terminal uranium(VI) monosulphide, uranium(VI) η^2-disulphide, and uranium(IV) phosphine sulphide complexes. *Dalton Trans.* **2019**, *48*, 50−57.

(183) Rosenzweig, M. W.; Hümmer, J.; Scheurer, A.; Lamsfus, C. A.; Heinemann, F. W.; Maron, L.; Mazzanti, M.; Meyer, K. A complete series of uranium(IV) complexes with terminal hydrochalcogenido (EH) and chalcogenido (E) ligands E = O, S, Se, Te. *Dalton Trans.* **2019**, *48*, 10853−10864.

(184) Li, T.; Wang, D.; Heng, Y.; Hou, G.; Zi, G.; Ding, W.; Walter, M. D. A Comprehensive Study Concerning the Synthesis, Structure, and Reactivity of Terminal Uranium Oxido, Sulfido, and Selenido Metallocenes. *J. Am. Chem. Soc.* **2023**, *145*, 14839−14855.

(185) Clark, D. L.; Conradson, S. D.; Donohoe, R. J.; Keogh, D. W.; Morris, D. E.; Palmer, P. D.; Rogers, R. D.; Tait, C. D. Chemical Speciation of the Uranyl Ion under Highly Alkaline Conditions. Synthesis, Structures, and Oxo Ligand Exchange Dynamics. *Inorg. Chem.* **1999**, *38*, 1456−1466.

(186) Graves, C. R.; Kiplinger, J. L. Pentavalent uranium chemistry - synthetic pursuit of a rare oxidation state. *Chem. Commun.* **2009**, 3831−3853.

(187) Arnold, P. L.; Love, J. B.; Patel, D. Pentavalent uranyl complexes. *Coord. Chem. Rev.* **2009**, *253*, 1973−1978.

(188) Fortier, S.; Hayton, T. W. Oxo ligand functionalization in the uranyl ion $(UO_2{}^{2+})$. *Coord. Chem. Rev.* **2010**, *254*, 197−214.

(189) Pedrick, E. A.; Wu, G.; Kaltsoyannis, N.; Hayton, T. W. Reductive silylation of a uranyl dibenzoylmethanate complex: an example of controlled uranyl oxo ligand cleavage. *Chem. Sci.* **2014**, *5*, 3204−3213.

(190) Pankhurst, J. R.; Bell, N. L.; Zegke, M.; Platts, L. N.; Lamfsus, C. A.; Maron, L.; Natrajan, L. S.; Sproules, S.; Arnold, P. L.; Love, J. B. Inner-sphere vs. outer-sphere reduction of uranyl supported by a redox-active, donor-expanded dipyrrin. *Chem. Sci.* **2017**, *8*, 108−116.

(191) Coughlin, E. J.; Qiao, Y.; Lapsheva, E.; Zeller, M.; Schelter, E. J.; Bart, S. C. Uranyl Functionalization Mediated by Redox-Active Ligands: Generation of O-C Bonds via Acylation. *J. Am. Chem. Soc.* **2019**, *141*, 1016−1026.

(192) Assefa, M. K.; Wu, G.; Hayton, T. W. Uranyl oxo silylation promoted by silsesquioxane coordination. *J. Am. Chem. Soc.* **2020**, *142*, 8738−8747.

(193) Faizova, R.; Fadaei-Tirani, F.; Chauvin, A.-S.; Mazzanti, M. Synthesis and characterization of water stable uranyl(V) complexes. *Angew. Chem., Int. Ed.* **2021**, *60*, 8227−8235.

(194) Hayton, T. W. Understanding the origins of O_{yl}-U-O_{yl} bending in the uranyl $(UO_2{}^{2+})$ ion. *Dalton Trans.* **2018**, *47*, 1003−1009.

(195) Kent, G. T.; Murillo, J.; Wu, G.; Fortier, S.; Hayton, T. W. Coordination of uranyl to the redox-active calix[4]pyrrole ligand. *Inorg. Chem.* **2020**, *59*, 8629−8634.

(196) Hartline, D. R.; Löffler, S. T.; Fehn, D.; Kasper, J. M.; Heinemann, F. W.; Yang, P.; Batista, E. R.; Meyer, K. Uranium-Mediated Peroxide Activation and a Precursor toward an Elusive Uranium cis-Dioxo Fleeting Intermediate. *J. Am. Chem. Soc.* **2023**, *145*, 8927−8938.

(197) Keener, M.; Hunt, C.; Carroll, T. G.; Kampel, V.; Dobrovetsky, R.; Hayton, T. W.; Ménard, G. Redox-switchable carboranes for uranium capture and release. *Nature* **2020**, *577*, 652−655.

(198) Keener, M.; Mattejat, M.; Zheng, S.-L.; Wu, G.; Hayton, T. W.; Ménard, G. Selective electrochemical capture and release of uranyl from aqueous alkali, lanthanide, and actinide mixtures using redox-switchable carboranes. *Chem. Sci.* **2022**, *13*, 3369−3374.

(199) Halter, D. P.; Heinemann, F. W.; Bachmann, J.; Meyer, K. Uranium-mediated electrocatalytic dihydrogen production from water. *Nature* **2016**, *530*, 317−321.

(200) Halter, D. P.; Heinemann, F. W.; Maron, L.; Meyer, K. The role of uranium-arene bonding in H$_2$O reduction catalysis. *Nat. Chem.* **2018**, *10*, 259−267.

(201) Magnani, N.; Caciuffo, R. Future directions for transuranic single molecule magnets. *Inorganics* **2018**, *6*, 26.

(202) La Pierre, H. S.; Meyer, K. Uranium-Ligand Multiple Bonding in Uranyl Analogues, [L = U=L]$^{n+}$, and the Inverse Trans Influence. *Inorg. Chem.* **2013**, *52*, 529−539.

(203) Motta, L. C.; Autschbach, J. Actinide inverse trans influence versus cooperative pushing from below and multi-center bonding. *Nat. Commun.* **2023**, *14*, 4307.

(204) Evans, W. J. Advances in f element reductive reactivity as a paradigm for expanding lanthanide and actinide science and technology. *J. Alloys Compd.* **2009**, *488*, 493−510.

(205) Li, J.; Bursten, B. E.; Liang, B.; Andrews, L. Noble gas-actinide compounds: complexation of the CUO molecule by Ar, Kr, and Xe atoms in Noble gas matrices. *Science* **2002**, *295*, 2242−2245.

(206) Kozimor, S. A.; Yang, P.; Batista, E. R.; Boland, K. S.; Burns, C. J.; Clark, D. L.; Conradson, S. D.; Martin, R. L.; Wilkerson, M. P.; Wolfsberg, L. E. Trends in Covalency for d- and f-Element Metallocene Dichlorides Identified Using Chlorine K-Edge X-ray Absorption Spectroscopy and Time-Dependent Density Functional Theory. *J. Am. Chem. Soc.* **2009**, *131*, 12125−12136.

(207) Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Clark, D. L.; Conradson, S. D.; Kozimor, S. A.; Martin, R. L.; Schwarz, D. E.; Shuh, D. K.; Wagner, G. L.; Wilkerson, M. P.; Wolfsberg, L. E.; Yang, P. Determining Relative f and d Orbital Contributions to M-Cl Covalency in MCl$_6^{2-}$ (M = Ti, Zr, Hf, U) and UOCl$_5^-$ Using Cl K-Edge X-ray Absorption Spectroscopy and Time-Dependent Density Functional Theory. *J. Am. Chem. Soc.* **2012**, *134*, 5586−5597.

(208) Spencer, L. P.; Yang, P.; Minasian, S. G.; Jilek, R. E.; Batista, E. R.; Boland, K. S.; Boncella, J. M.; Conradson, S. D.; Clark, D. L.; Hayton, T. W.; Kozimor, S. A.; Martin, R. L.; MacInnes, M. M.; Olson, A. C.; Scott, B. L.; Shuh, D. K.; Wilkerson, M. P. Tetrahalide Complexes of the [U(NR)$_2$]$^{2+}$ Ion: Synthesis, Theory, and Chlorine K-Edge X-ray Absorption Spectroscopy. *J. Am. Chem. Soc.* **2013**, *135*, 2279−2290.

(209) Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Clark, D. L.; Kozimor, S. A.; Martin, R. L.; Shuh, D. K.; Tyliszczak, T. New evidence for 5f covalency in actinocenes determined from carbon K-edge XAS and electronic structure theory. *Chem. Sci.* **2014**, *5*, 351−359.

(210) Su, J.; Batista, E. R.; Boland, K. S.; Bone, S. E.; Bradley, J. A.; Cary, S. K.; Clark, D. L.; Conradson, S. D.; Ditter, A. S.; Kaltsoyannis, N.; Keith, J. M.; Kerridge, A.; Kozimor, S. A.; Löble, M. W.; Martin, R. L.; Minasian, S. G.; Mocko, V.; La Pierre, H. S.; Seidler, G. T.; Shuh, D. K.; Wilkerson, M. P.; Wolfsberg, L. E.; Yang, P. Energy-Degeneracy-Driven Covalency in Actinide Bonding. *J. Am. Chem. Soc.* **2018**, *140*, 17977−17984.

(211) Smiles, D. E.; Batista, E. R.; Booth, C. H.; Clark, D. L.; Keith, J. M.; Kozimor, S. A.; Martin, R. L.; Minasian, S. G.; Shuh, D. K.; Stieber, S. C.E.; Tyliszczak, T. The duality of electron localization and covalency

in lanthanide and actinide metallocenes. *Chem. Sci.* **2020**, *11*, 2796−2809.

(212) Qiao, Y.; Ganguly, G.; Booth, C. H.; Branson, J. A.; Ditter, A. S.; Lussier, D. J.; Moreau, L. M.; Russo, D. R.; Sergentu, D.-C.; Shuh, D. K.; Sun, T.; Autschbach, J.; Minasian, S. G. Enhanced 5f-δ bonding in [U(C$_7$H$_7$)$_2$]$^-$: C K-edge XAS, magnetism, and ab initio calculations. *Chem. Commun.* **2021**, *57*, 9562−9565.

(213) Vitova, T.; Pidchenko, I.; Fellhauer, D.; Bagus, P. S.; Joly, Y.; Pruessmann, T.; Bahl, S.; Gonzalez-Robles, E.; Rothe, J.; Altmaier, M.; Denecke, M. A.; Geckeis, H. The role of the 5f valence orbitals of early actinides in chemical bonding. *Nat. Commun.* **2017**, *8*, 16053.

(214) Zegke, M.; Zhang, X.; Pidchenko, I.; Hlina, J. A.; Lord, R. M.; Purkis, J.; Nichol, G. S.; Magnani, N.; Schreckenbach, G.; Vitova, T.; Love, J. B.; Arnold, P. L. Differential uranyl(v) oxo-group bonding between the uranium and metal cations from groups 1, 2, 4, and 12; a high energy resolution X-ray absorption, computational, and synthetic study. *Chem. Sci.* **2019**, *10*, 9740−9751.

(215) Kvashnina, K. O.; Butorin, S. M. High-energy resolution X-ray spectroscopy at actinide M$_{4,5}$ and ligand K edges: what we know, what we want to know, and what we can know. *Chem. Commun.* **2022**, *58*, 327−342.

(216) Kaltsoyannis, N. Does Covalency Increase or Decrease across the Actinide Series? Implications for Minor Actinide Partitioning. *Inorg. Chem.* **2013**, *52*, 3407−3413.

(217) Neidig, M. L.; Clark, D. L.; Martin, R. L. Covalency in f-Element Complexes. *Coord. Chem. Rev.* **2013**, *257*, 394−406.

(218) Sergentu, D.-C.; Autschbach, J. Covalency in actinide(IV) hexachlorides in relation to the chlorine K-edge X-ray absorption structure. *Chem. Sci.* **2022**, *13*, 3194−3207.

(219) Formanuik, A.; Ariciu, A.-M.; Ortu, F.; Beekmeyer, R.; Kerridge, A.; Tuna, A.; McInnes, E. J. L.; Mills, D. P. Actinide covalency measured by pulsed electron paramagnetic resonance spectroscopy. *Nat. Chem.* **2017**, *9*, 578−583.

(220) Lukens, W. W.; Edelstein, N. M.; Magnani, N.; Hayton, T. W.; Fortier, S.; Seaman, L. A. Quantifying the σ and π Interactions between U(V) f Orbitals and Halide, Alkyl, Alkoxide, Amide and Ketimide Ligands. *J. Am. Chem. Soc.* **2013**, *135*, 10742−10754.

(221) Staun, S. L.; Wu, G.; Lukens, W. W.; Hayton, T. W. Synthesis of a heterobimetallic actinide nitride and an analysis of its bonding. *Chem. Sci.* **2021**, *12*, 15519−15527.

(222) Nguyen, T. H.; Paul, E. L.; Lukens, W. W.; Hayton, T. W. Evaluating f-Orbital Participation in the U^V=E Multiple Bonds of [U(E)(NR$_2$)$_3$] (E = O, NSiMe$_3$, NAd; R = SiMe$_3$). *Inorg. Chem.* **2023**, *62*, 6447−6457.

(223) Hrobárik, P.; Hrobáriková, V.; Greif, A. H.; Kaupp, M. Giant Spin-Orbit Effects on NMR Shifts in Diamagnetic Actinide Complexes: Guiding the Search of Uranium(VI) Hydride Complexes in the Correct Spectral Range. *Angew. Chem., Int. Ed.* **2012**, *51*, 10884−10888.

(224) Seaman, L. A.; Hrobárik, P.; Schettini, M. F.; Fortier, S.; Kaupp, M.; Hayton, T. W. A Rare Uranyl(VI)-Alkyl Ate Complex [Li-(DME)$_{1.5}$]$_2$[UO$_2$(CH$_2$SiMe$_3$)$_4$] and Its Comparison with a Homoleptic Uranium(VI)-Hexaalkyl. *Angew. Chem., Int. Ed.* **2013**, *52*, 3259−3263.

(225) Smiles, D. E.; Wu, G.; Hrobárik, P.; Hayton, T. W. Use of ^{77}Se and ^{125}Te NMR Spectroscopy to Probe Covalency of the Actinide-Chalcogen Bonding in [Th(E$_n$){N(SiMe$_3$)$_2$}$_3$]$^-$ (E = Se, Te; N = 1, 2) and Their Oxo-Uranium(VI) Congeners. *J. Am. Chem. Soc.* **2016**, *138*, 814−825.

(226) Smiles, D. E.; Wu, G.; Hrobárik, P.; Hayton, T. W. Synthesis, Thermochemistry, Bonding, and ^{13}C NMR Chemical Shift Analysis of a Phosphorano-Stabilized Carbene of Thorium. *Organometallics* **2017**, *36*, 4519−4524.

(227) Rungthanaphatsophon, P.; Huang, P.; Walensky, J. R. Phosphorano-Stabilized Carbene Complexes with Short Thorium(IV)- and Uranium(IV)-Carbon Bonds. *Organometallics* **2018**, *37*, 1884−1891.

(228) Mullane, K. C.; Hrobárik, P.; Cheisson, T.; Manor, B. C.; Carroll, P. J.; Schelter, E. J. ^{13}C NMR Shifts as an Indicator of U-C Bond

Covalency in Uranium(VI) Acetylide Complexes: An Experimental and Computational Study. *Inorg. Chem.* **2019**, *58*, 4152−4163.

(229) Staun, S. L.; Sergentu, D. C.; Wu, G.; Autschbach, J.; Hayton, T. W. Use of ^{15}N NMR Spectroscopy to Probe Covalency in a Thorium Nitride. *Chem. Sci.* **2019**, *10*, 6431−6436.

(230) Sergentu, D. C.; Kent, G. T.; Staun, S. L.; Yu, X.; Cho, H.; Autschbach, J.; Hayton, T. W. Probing the Electronic Structure of a Thorium Nitride Complex by Solid-State ^{15}N NMR Spectroscopy. *Inorg. Chem.* **2020**, *59*, 10138−10145.

(231) Du, J.; Hurd, J.; Seed, J. A.; Balázs, G.; Scheer, M.; Adams, R. W.; Lee, D.; Liddle, S. T. [31]P Nuclear Magnetic Resonance Spectroscopy as a Probe of Thorium-Phosphorus Bond Covalency: Correlating Phosphorus Chemical Shift to Metal-Phosphorus Bond Order. *J. Am. Chem. Soc.* **2023**, *145*, 21766−21784.

(232) Brown, J. L.; Batista, E. R.; Boncella, J. M.; Gaunt, A. J.; Reilly, S. D.; Scott, B. L.; Tomson, N. C. A Linear trans-Bis(imido) Neptunium-(V) Actinyl Analog: $Np^V(NDipp)_2({}^tBu_2bipy)_2Cl$ (Dipp = $2,6\text{-}{}^iPr_2C_6H_3$). *J. Am. Chem. Soc.* **2015**, *137*, 9583−9586.

(233) Dutkiewicz, M. S.; Goodwin, C. A. P.; Perfetti, M.; Gaunt, A. J.; Griveau, J.-C.; Colineau, E.; Kovács, A.; Wooles, A. J.; Caciuffo, R.; Walter, O.; Liddle, S. T. A Terminal Neptunium(V)-Mono(Oxo) Complex. *Nat. Chem.* **2022**, *14*, 342−349.

(234) Goodwin, C. A. P.; Wooles, A. J.; Murillo, J.; Lu, E.; Boronski, J. T.; Scott, B. L.; Gaunt, A. J.; Liddle, S. T. Carbene complexes of neptunium. *J. Am. Chem. Soc.* **2022**, *144*, 9764−9774.

(235) Murillo, J.; Seed, J. A.; Wooles, A. J.; Oakley, M. S.; Goodwin, C. A. P.; Gregson, M.; Dan, D.; Chilton, N. F.; Gaunt, A. J.; Kozimor, S. A.; Liddle, S. T.; Scott, B. L. Carbene complexes of plutonium: structure, bonding, and divergent reactivity to lanthanide analogs. *J. Am. Chem. Soc.* **2024**, *146*, 4098−4111.