Expanding the Chemistry of Actinide Metallocene Bromides. Synthesis, Properties and Molecular Structures of the Tetravalent and Trivalent Uranium Bromide Complexes: $(C_5Me_4R)_2UBr_2$, $(C_5Me_4R)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Br)$, and $[K(THF)][(C_5Me_4R)_2UBr_2]$ (R = Me, Et)

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Abstract: The organometallic uranium species $(C_5Me_4R)_2UBr_2$ (R = Me, Et) were obtained by treating their chloride analogues $(C_5Me_4R)_2UCl_2$ (R = Me, Et) with Me_3SiBr. Treatment of $(C_5Me_4R)_2UCl_2$ and $(C_5Me_4R)_2UBr_2$ (R = Me, Et) with $K(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ afforded the halide aryloxide mixed-ligand complexes $(C_5Me_4R)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(X)$ (R = Me, Et; X = Cl, Br). Complexes $(C_5Me_4R)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Br)$ (R = Me, Et) can also be synthesized by treating $(C_5Me_4R)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Cl)$ (R = Me, Et) with Me_3SiBr, respectively. Reduction of $(C_5Me_4R)_2UCl_2$ and $(C_5Me_4R)_2UBr_2$ (R = Me, Et) with KC_8 led to isolation of uranium(III) "ate" species $[K(THF)][(C_5Me_5)_2UX_2]$ (X = Cl, Br) and $[K(THF)_{0.5}][(C_5Me_4Et)_2UX_2]$ (X = Cl, Br), which can be converted to the neutral complexes $(C_5Me_4R)_2U[N(SiMe_3)_2]$ (R = Me, Et). Analyses by nuclear magnetic resonance spectroscopy, X-ray crystallography, and elemental analysis are also presented.

1. Introduction

The bis(cyclopentadienyl) complexes of uranium $(C_5Me_4R)_2UX_2$ (R = Me or Et; X = Cl or I) [1–3], $(1,3\text{-}R'_2C_5H_3)_2UX_2$ and $(1,2,4\text{-}R'_3C_5H_3)_2UX_2$ (R' = ^tBu, $SiMe_3$; X = Cl, I) [4–7] have been known for years, owing to the ease of preparation of reliable chloride and iodide starting materials. With the vast amount of literature attention devoted to $(C_5Me_4R)UX_2$ compounds, it is curious that the corresponding bis(cyclopentadienyl) uranium bromide systems have not been investigated to a similar extent. Considering that the structure and reactivity of these uranium compounds are strongly influenced by the nature of the halide [8], it would be useful to have the $(C_5Me_4R)UBr_2$ congeners available for synthetic actinide chemistry.

Uranium bromide complexes are rare compared to their chloride and iodide counterparts. This is succinctly illustrated in Figure 1, which presents the organometallic tetravalent and trivalent uranium

complexes that have been reported to date. The vast majority of uranium(IV) bromide complexes have been prepared by salt metathesis with either UBr_4 or $UBr_4(NCCH_3)_4$. These compounds include the dicarbollide complex $[Li(THF)_4]_2[(C_2H_{11}B_9)_2UBr_2]$ (**1**) [9]; the cyclopentadienyl complexes $(C_5H_5)_3UBr$ (**2**), $(C_5H_5)UBr_3(L)_2$ (L = $Me_2NC(O)^tBu$ (**3**), $OPPh_3$ (**4**), THF (**5**)), $(C_5H_5)_2UBr_2(L)$ (L = $Me_2NC(O)^tBu$ (**6**), $OPPh_3$ (**7**)), $\{(C_5H_5)UBr_2X[OP(Ph)_2C_2H_4P(O)(Ph_2)]\}_2$ (X = C_5H_5 (**8**), Br (**9**)); and the indenyl complexes $(C_9H_7)_3UBr$ (**10**), $(C_9H_7)UBr_3(OPPh_3)(THF)$ (**11**), $(C_9H_7)UBr_3(THF)_2$ (**12**), $(C_9H_7)UBr_3(OPPh_3)$ (**13**), $[(C_9H_7)UBr_2(NCCH_3)_4][UBr_6]$ (**14**) and $\{[(C_9H_7)UBr(NCCH_3)_4]_2O\}[UBr_6]_2$ (**15**) [10–16]. An alternative method that has been employed to prepare uranium(IV) bromide complexes is halide exchange. For example, $(1,2,4-{}^tBu_3C_5H_2)_2UBr_2$ (**16**) [5] and $(1,3-R_2C_5H_3)_2UBr_2$ (R = $SiMe_3$ (**17**), ${}^tBu$ (**18**)) [4] were prepared by reacting the chloride analogues with excess Me_3SiBr, and (**17**) from its chloride analogue and BBr_3 [7].

In recent years, oxidation chemistry has been developed to access a variety of uranium(IV) bromide complexes such as $(C_5Me_5)_2U(X)(Br)$ (X = $N(SiMe_3)_2$ (**19**) [17], $({}^iPrN)_2C(Me)$ (**20**) [18], $MeNC(Me)NAd$ (**21**) [19]), which were synthesized by treating $(C_5Me_5)_2U(X)$ with CuBr or AgBr. In a similar fashion, $(C_5Me_5)_3U$ was shown to react with benzyl bromide to afford $(C_5Me_5)_3UBr$ (**22**) [20]. The η^2-suldenamido derivative $(C_5Me_5)_2U(\eta^2-{}^tBuNSPh)(Br)$ (**23**) was obtained after long reaction times of chloride complex with MeMgBr [21]. Finally, protonolysis of $(\eta^3-C_3H_5)_4U$ with HBr provided $(\eta^3-C_3H_5)_3UBr$ (**24**) [22].

Reduction chemistry has been the primary method for accessing the handful of known bromide complexes. For example, treatment of $[Li(THF)_4]_2[(C_2H_{11}B_9)_2UBr_2]$ (**1**) [9] and $(1,3-R_2C_5H_3)_2UBr_2$ (R = $SiMe_3$ (**17**), ${}^tBu$ (**18**)) [4] with *tert*-butyl lithium or sodium amalgam gave $[Li(THF)_4]_2[(C_2H_{11}B_9)_2UBr(THF)]$ (**25**) and $[(1,3-R_2C_5H_3)_2UBr]_2$ (R = $SiMe_3$ (**26**), ${}^tBu$ (**27**)), respectively [7,23–25]. Complex $(C_5Me_5)_3UBr$ (**22**) is thermally unstable and leads to isolation of $(C_5Me_5)_2UBr$ (**28**), from which $(C_5Me_5)_2UBr(THF)$ (**29**) can be formed [20]. Finally, $[1,3-(SiMe3)2C5H3]_2UBr(CN^tBu)_2$ (**30**) was obtained by treating complex **26** with excess CN^tBu [26].

Tetravalent Uranium Complexes:
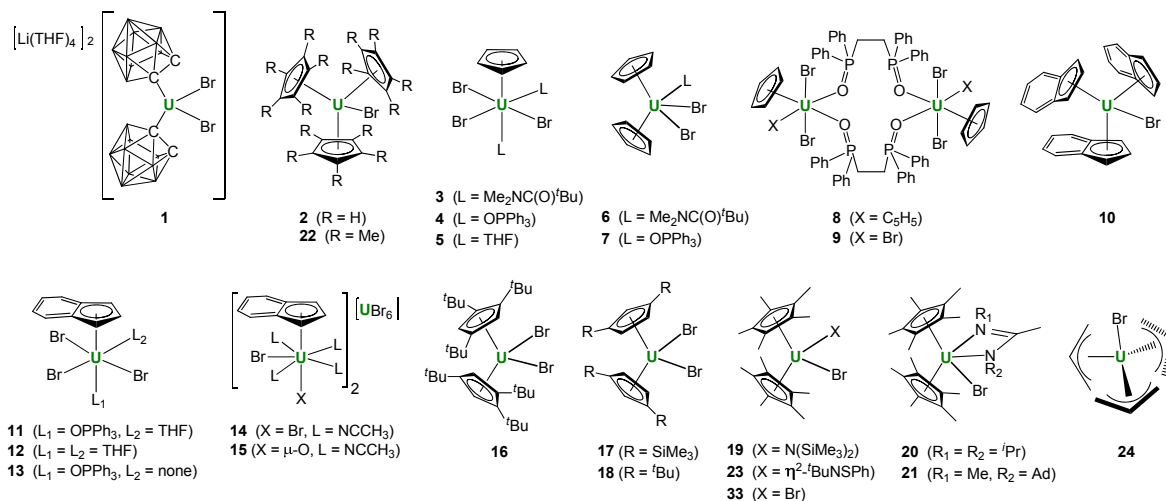
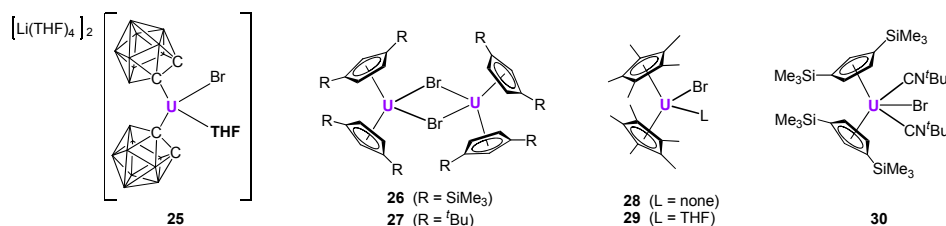*Trivalent Uranium Complexes:*

Figure 1. Structures of known organometallic uranium(IV) and uranium(III) bromide compounds.

Herein, we report the preparation of the bromide complexes $(C_5Me_4R)_2UBr_2$ (R = Me (**33**), Et (**34**)) and show that they and $(C_5Me_4R)_2UCl_2$ (R = Me (**31**), Et (**32**)) can be used as precursors to mixed-ligand species $(C_5Me_4R)_2U(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(X)$ (R = Me, Et; X = Cl and Br) and uranium(III) bromide and chloride "ate" species $[K(THF)_n][(C_5Me_4R)_2UX_2]$ (R = Me, Et; X = Cl, Br; n = 0.5 or 1). In addition, we show that $(C_5Me_4R)_2U[N(SiMe_3)_2]$ can be synthesized from such "ate" species, demonstrating that the $[K(THF)_n][(C_5Me_4R)_2UX_2]$ complexes are useful precursors for the synthesis of neutral uranium(III) compounds. The syntheses of all complexes are discussed and the characterization by ${}^1H$ NMR spectroscopy, melting point, elemental analysis and single crystal X-ray diffraction is provided.

2. Results and Discussion

Synthesis: Our study takes advantage of the halide exchange reagent, trimethylsilyl bromide, Me_3SiBr. The compounds $(C_5Me_4R)_2UBr_2$ (R = Me (**33**), Et (**34**)) were obtained by treating $(C_5Me_4R)_2UCl_2$ (R = Me (**31**), Et (**32**)) with excess Me_3SiBr (Scheme 1) similar to the method reported by Andersen for the preparation of the bent cyclopentadienyl species $(1,3\text{-}R'_2C_5H_3)_2UBr_2$ [4] and $(1,2,4\text{-}R'_3C_5H_2)_2UBr_2$ [5] (R' = ${}^tBu$, $SiMe_3$). Complexes **33** and **34** can be obtained in 96% and 90% yield, respectively, using this procedure, but it is important to add fresh Me_3SiBr three times to the reaction mixture and to let the mixture react for at least 12 h each time. Lower time intervals and/or lesser number of treatments lead to incomplete reactions. The uranium(IV) bromide complex $(C_5Me_5)_2UBr_2$ (**33**) has been mentioned before, but no experimental data for this compound were provided [20,27]. To the best of our knowledge, this is the first time that compounds **33** and **34** have been fully characterized. The ${}^1H$ Nuclear Magnetic Resonance (NMR) spectrum of **33** in benzene-d_6 shows a singlet at 15.70 ppm, which is intermediate in value compared to $(C_5Me_5)_2UCl_2$ (13.5 ppm) [3] and $(C_5Me_5)_2UI_2$ (17.9 ppm) [28–30]; while that of complex **34** shows four singlets corresponding to the three inequivalent methyl groups (25.1, 15.6 and 13.1 ppm) and the methylene group (0.31 ppm) of the C_5Me_4Et ligand. The ${}^1H$ NMR shifts of **34** are also downfield compared to the analogous $(C_5Me_4Et)_2UCl_2$ (22.9, 13.8 and −2.8 ppm, respectively) and $(C_5Me_4Et)_2U(CH_3)_2$ (14.1, 5.6, 5.1 and −4.3 ppm, respectively) [31].
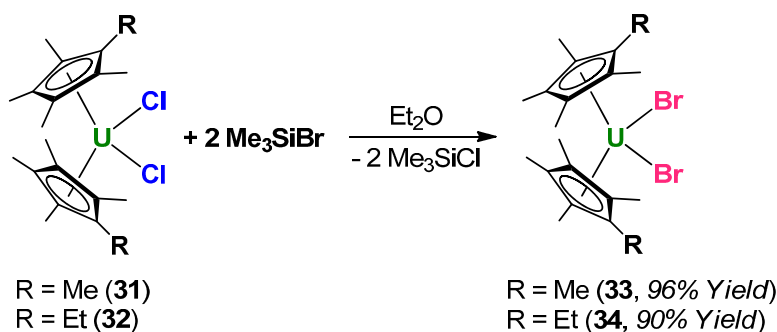
Scheme 1. Synthesis of the uranium(IV) bromide complexes $(C_5Me_4R)_2UBr_2$ (R = Me (**33**), Et (**34**)) by halide exchange with trimethylsilyl bromide.

The X-ray structure of complexes **33** and **34** are shown in Figure 2. The U(1)–Br(1) bond lengths of **33** (2.7578(5) Å) and **34** (2.7607(4) and 2.7609(4) Å) fall within the range of known neutral U(IV) terminal bromides (2.734(1)–2.831(7) Å) [6,7,9,16,32–45] and the Br(1)–U(1)–Br(2) bond angles of **33** (97.64(3)°) and **34** (96.224(14)°) are similar to those of $(C_5Me_5)_2UX_2$ (X = Cl (97.9(4)°), I (95.96(2)°)) [1,2] and [1,3-(SiMe3)2C5H3]2UBr2 (94.60(4)°) [4], but larger than most non-cyclopentadienyl-based complexes containing *cis*-bromide ligands (75.48(8)–103.83(12)°) [6,7,9,16,32–45]. The U(1)–C_{Cent} distances for **33** (2.438(4) Å) and **34** (2.444(2) Å) fall within the typical distances for C_5Me_5-based complexes (2.393–2.562 Å) [1,2,31,46–50]. Similarly, the $C_{Cent(1)}$–U(1)–$C_{Cent(2)}$ bond angles of **33** (137.57(15)°) and **34** (138.50(8)°) fall within the known range for bis(pentamethylcyclopentadienyl)-based complexes (126.2–142.6°) [1,2,31,46–50].

As outlined in Scheme 2, the halide complexes **31–34** react with bulky aryloxides such as K[O-2,6-^{i}Pr$_2$C$_6$H$_3$] to yield the corresponding halide aryloxide mixed-ligand complexes in excellent yields, (C$_5$Me$_4$R)$_2$U(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(Cl) (**35**, R = Me, 92%; **36**, R = Et, 90%) and (C$_5$Me$_4$R)$_2$U(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(Br) (**37**, R = Me, 99%; **38**, R = Et, 96%). Complex **35** has been previously synthesized by oxidation of (C$_5$Me$_4$R)$_2$U(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(THF) with CuCl [8]. Synthesis of the halide aryloxide mixed-ligand complexes **35–38** by salt metathesis not only complements the known oxidative synthetic route to **35**, but also helps to introduce complexes **36–38** here for the first time. Finally, similar to the synthesis of complexes **33** and **34**, treatment of **35** and **36** with excess Me$_3$SiBr in THF also yields **37** and **38** in 93% and 91% yields, respectively (Scheme 3).
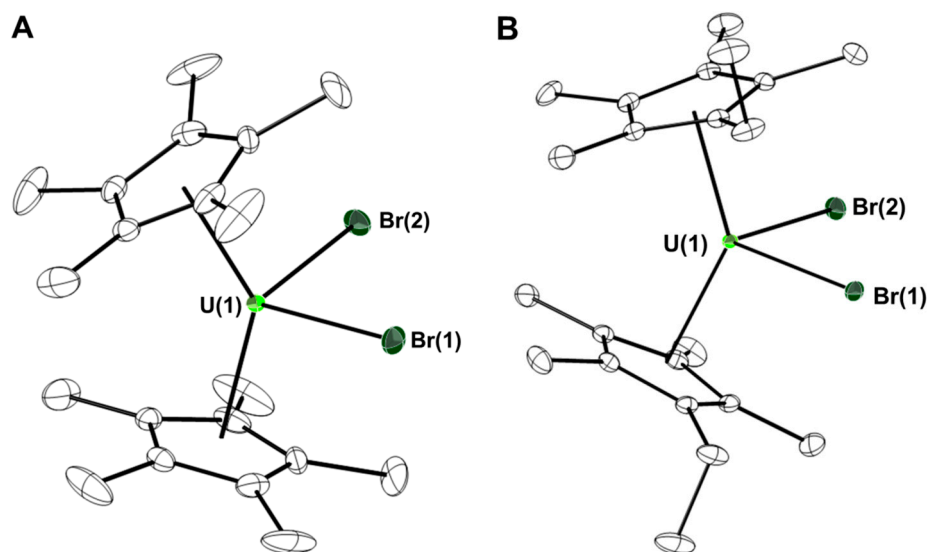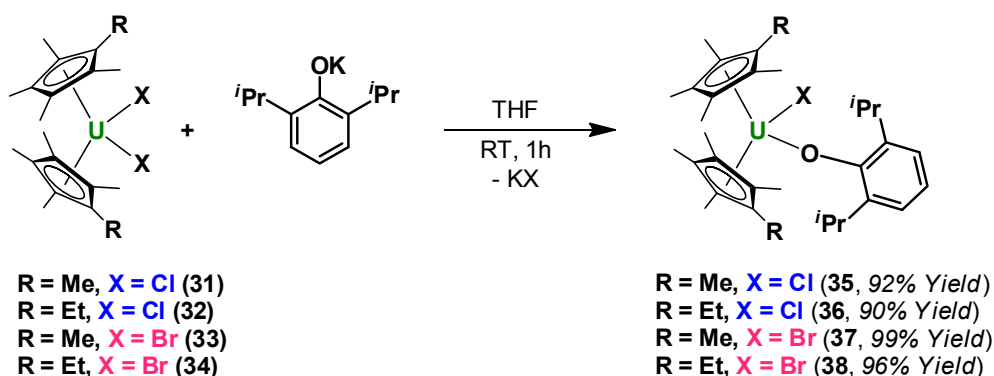

Figure 2. Molecular structure of (C$_5$Me$_5$)$_2$UBr$_2$ (**33**) (**A**) and (C$_5$Me$_4$Et)$_2$UBr$_2$ (**34**) (**B**) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for **33**: U(1)–Br(1), 2.7578(5); U(1)–C$_{Cent}$, 2.438(4); Br(1)–U(1)–Br(2), 97.64(3); C$_{Cent(1)}$–U(1)–C$_{Cent(2)}$, 137.57(15). For **34**: U(1)–Br(1), 2.7609(4); U(1)–Br(2), 2.7607(4); U(1)–C$_{Cent}$, 2.444(2); Br(1)–U(1)–Br(2), 96.224(14); C$_{Cent(1)}$–U(1)–C$_{Cent(2)}$, 138.50(8).

R = Me, **X = Cl** (**31**)
R = Et, **X = Cl** (**32**)
R = Me, **X = Br** (**33**)
R = Et, **X = Br** (**34**)

R = Me, **X = Cl** (**35**, *92% Yield*)
R = Et, **X = Cl** (**36**, *90% Yield*)
R = Me, **X = Br** (**37**, *99% Yield*)
R = Et, **X = Br** (**38**, *96% Yield*)

Scheme 2. Synthesis of the halide aryloxide mixed-ligand uranium(IV) complexes (C$_5$Me$_4$R)$_2$U(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(Cl) (R = Me (**35**), Et (**36**)) and (C$_5$Me$_4$R)$_2$U(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(Br) (R = Me (**37**), Et (**38**)) by salt metathesis.
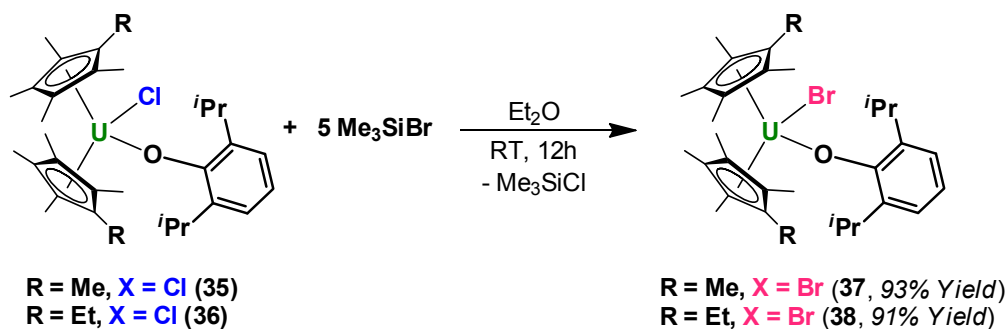
Scheme 3. Synthesis of the bromide aryloxide mixed-ligand uranium(IV) complexes $(C_5Me_4R)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Br)$ (R = Me (**37**), Et (**38**)) by halide exchange with trimethylsilyl bromide.

It is worth mentioning that in the family of the halide aryloxide series of compounds $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(X)$ (X = F, Cl, Br, I), the bromide complex is the only member that has not been previously reported [2,8,48]. Comparison of the methyl proton resonance of C_5Me_5 by ^1H NMR spectroscopy reveals an upfield shift in the order I (9.85 ppm) < Br (8.76 ppm) < Cl (7.85 ppm) << F (3.19 ppm). This trend has been observed before in other cyclopentadienyl complexes and it is directly correlated with the π-donating ability of the halide ligand [51]. Similarly, comparison of the methyl peaks of the C_5Me_4Et ligand of **36** (11.9, 8.5, 7.8, 7.8 and 6.6 ppm) and **38** (11.9, 9.11, 9.07, 8.3 and 7.8 ppm) shows the same pattern, where the peak positions of $(C_5Me_4Et)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Br)$ appear downfield from those of $(C_5Me_4Et)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Cl)$.

Compound **37** crystallizes with two asymmetric units in the crystal lattice and the structures are shown in Figure 3. The U–Br bond distances (2.7951(12) and 2.8023(12) Å) are somewhat longer than those of **33** (2.7578(5) Å) and **34** (U(1)–Br(1) = 2.7609(4) and U(1)–Br(2) = 2.7607(4) Å), but still fall within the range of the known neutral U–Br complexes (2.734(1)–2.831(7) Å) [6,7,9,16,33–45]. The U–O bond distances of **37** (2.110(7) and 2.134(7) Å) are similar to those of the known halide and pseudohalide derivatives $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(X)$ (X = F (2.124(6) Å), Cl (2.110(5) Å), I (2.114(6) Å), N$_3$ (2.117(5) Å) and CH$_3$ (2.126(4) Å)) [2,48,50]. Likewise, the U–O–C$_{ipso}$ and O–U–Br bond angles of **37** (U–O–C$_{ipso}$ = 166.9(6) and 61.7(6)°; O–U–Br = 104.64(18)° and 104.04(17)°) compare favorably with the known complexes $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(X)$ (X = F: U–O–C$_{ipso}$ = 165.4(6)°, O–U–F = 104.1(2)°; X = Cl: U–O–C$_{ipso}$ = 164.0(4)°, O–U–Cl = 102.06(14)°; X = I: U–O–C$_{ipso}$ = 166.6(6)°, O–U–I = 104.87(15)°; X = N$_3$: U–O–C$_{ipso}$ = 165.2(4)°, O–U–N = 100.7(2)° and X = CH$_3$: U–O–C$_{ipso}$ = 163.2(4)°, O–U–CH$_3$ = 98.80(19)°). Finally the U–C$_{Cent}$ bond distances and the C$_{Cent}$–U–C$_{Cent}$ bond angles of **37** (U–C$_{Cent}$ = 2.47(1), 2.46(1) and 2.45(1) Å; C$_{Cent}$–U–C$_{Cent}$ = 134.7(3)° and 133.2(2)°) are comparable with those of other bis(pentamethylcyclopentadienyl) complexes (U–C$_{Cent}$ = 2.420–2.562 Å; C$_{Cent}$–U–C$_{Cent}$ = 126.2–142.6°) [1,2,31,46–50] and to the other $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(X)$ derivatives (X = F: U–C$_{Cent}$ = 2.444(2)–2.451(1) Å, C$_{Cent}$–U–C$_{Cent}$ = 135.8–135.9°; X = Cl: U–C$_{Cent}$ = 2.444(3)–2.457(3) Å; C$_{Cent}$–U–C$_{Cent}$ = 133.1–134.5°; X = I: U–C$_{Cent}$ = 2.447(3)–2.456(4) Å; C$_{Cent}$–U–C$_{Cent}$ = 133.5–133.6°; X = N$_3$: U–C$_{Cent}$ = 2.505(3)–2.532(3) Å; C$_{Cent}$–U–C$_{Cent}$ = 133.2°; X = CH$_3$: U–C$_{Cent}$ = 2.466(2)–2.471(3) Å; C$_{Cent}$–U–C$_{Cent}$ = 134.0°) [2,48,50].
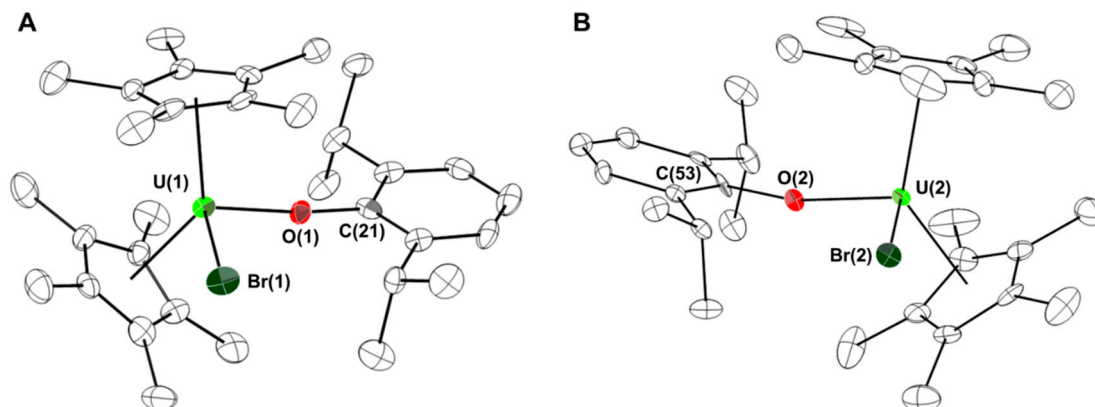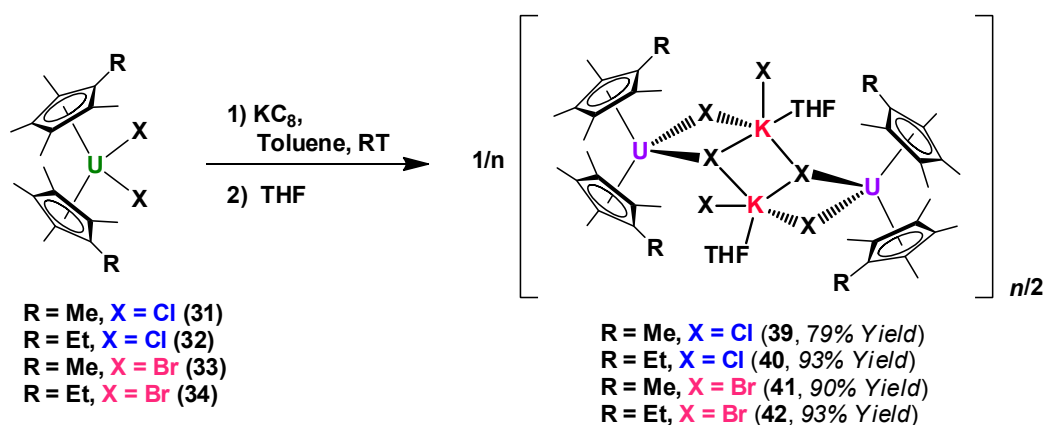
Figure 3. Molecular structures of the two crystallographically-independent $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Br)$ (**37**) complexes (**A** and **B**) with thermal ellipsoids projected at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): U(1)–O(1), 2.110(7); U(2)–O(2), 2.134(7); U(1)–Br(1), 2.7951(12); U(2)–Br(2), 2.8023(12); U(1)–$C_{Cent(1)}$, 2.47(1); U(1)–$C_{Cent(2)}$, 2.46(1); U(2)–$C_{Cent(3)}$, 2.45(1); U(2)–$C_{Cent(4)}$, 2.46(1); Br(1)–U(1)–O(1), 104.64(18); Br(2)–U(2)–O(2), 104.04(17); U(1)–O(1)–C(21), 166.9(6); U(2)–O(2)–C(53), 161.7(6); $C_{Cent(1)}$–U(1)–$C_{Cent(2)}$, 134.7(3); $C_{Cent(3)}$–U(2)–$C_{Cent(4)}$, 133.2(2).

Treatment of the uranium(IV) dihalide complexes **31–34** with one equivalent of KC_8 in toluene at room temperature affords the corresponding uranium(III) chloride and bromide "ate" species $[K(THF)_n][(C_5Me_4R)_2UX_2]$ (**39**, X = Cl, R = Me, *n* = 1; **40**, X = Cl, R = Et, *n* = 0.5; **41**, X = Br, R = Me, *n* = 1; **42**, X = Br, R = Et, *n* = 0.5) as illustrated in Scheme 4. During the course of the reaction, the vivid red-maroon color of complexes **31–34** changes to an insoluble green solid. After workup, all complexes were isolated in good to excellent yields (**39** (79%), **40** (93%), **41** (90%) and **42** (93%)).

R = Me, **X = Cl** (**31**)
R = Et, **X = Cl** (**32**)
R = Me, **X = Br** (**33**)
R = Et, **X = Br** (**34**)

R = Me, **X = Cl** (**39**, *79% Yield*)
R = Et, **X = Cl** (**40**, *93% Yield*)
R = Me, **X = Br** (**41**, *90% Yield*)
R = Et, **X = Br** (**42**, *93% Yield*)

Scheme 4. Synthesis of uranium(III) complexes $[K(THF)][(C_5Me_5)_2UX_2]$ (X = Cl (**39**), Br (**41**)) and $[K(THF)_{0.5}][(C_5Me_4Et)_2UX_2]$ (X = Cl (**40**), Br (**42**)) by KC_8 reduction of the corresponding uranium(IV) dihalides.

Complexes **41** and **42** are rare examples of trivalent uranium bromides. A truncated form of the solid-state structure of compound **41** is shown in Figure 4. The complex is best described as a polymer with potassium ions linking the uranium centers with potassium–bromide bridges. The geometry at each uranium center is pseudo tetrahedral, while that at each potassium is distorted trigonal pyramidal. The K–Br bond lengths of **41** (3.1684(14), 3.1671(14), 3.2577(15) and 3.2477(15) Å) are comparable to those reported for other compounds with K–Br interactions (2.988(11)–3.844(3) Å) [52–66]. The U–Br bond lengths of **41** (U–Br = 2.9126(6) and 2.8953(6) Å)

are comparable to the few known U(III) bromides in the literature: $\{[1,3\text{-}(SiMe3)2C5H3]_2UBr\}_2$
(**26**, U–Br = 2.93(1) and 2.94(1) Å) [24], $[U(Br)_2(H_2O)_5(NCMe)_2][Br]$ (U–Br = 3.074(4) Å) [37],
$[Li(THF)_4]_2[(C_2H_{20}B_9)_2U(Br)(THF)]$ (**25**, U–Br = 2.883(2) Å) [25], $[1,3\text{-}(SiMe3)2C5H3]_2U(Br)(CN^tBu)_2$
(**30**, U–Br = 2.8761(10) Å) [26] and $[UBr_3(DME)_2]_2$ (U–Br = 2.898(2), 2.887(2), 3.016(2) and
3.098(2) Å) [40] and are longer than those of **33** (U–Br = 2.7578(5) Å) and **34** (U–Br = 2.7609(4) and
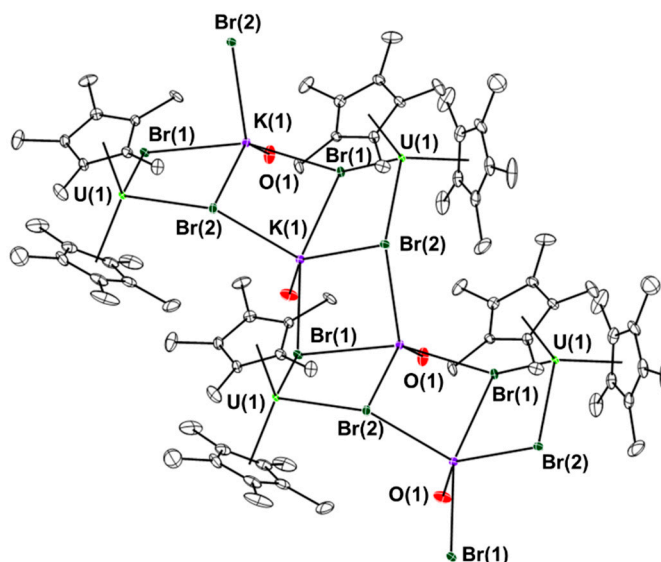2.7607(4) Å).

Figure 4. Solid state structure (30% probability ellipsoids) of a tetrameric unit of
$[K(THF)][(C_5Me_5)_2UBr_2]$ (**41**) Hydrogen atoms and the carbon atoms of THF molecules are omitted
for clarity. Selected bond distances (Å) and bond angles (°): U(1)–Br(1), 2.9126(6); U(1)–Br(2),
2.8953(6); K(1)–Br(1), 3.1681(14), 3.2577(15); K(1)–Br(2), 3.1671(14), 3.2477(15); K(1)–O(1), 2.641(6);
U(1)–$C_{Cent(1)}$, 2.495(7); U(1)–$C_{Cent(2)}$, 2.485(7); Br(1)–U(1)–Br(2), 88.841(19); Br(1)–K(1)–Br(2), 114.32(15),
87.50(4), 87.35(3), 77.35(3); Br(1)–K(1)–O(1), 85.26(14), 93.41(16); Br(2)–K(1)–O(1), 100.91(18), 132.49(19);
$C_{Cent(1)}$–U(1)–$C_{Cent(2)}$, 136.6(3).

In addition, the U–C_{Cent} bond distances of **41** (2.495(7) and 2.485(7) Å) are comparable to those
of **33** (2.438(4) Å), **34** (2.444(2) Å), and **37** (2.45(1), 2.46(1) and 2.47(1) Å). Finally, the C_{Cent}–U–C_{Cent}
bond angle of **41** (136.6(3)°) is similar to those of compounds **33** (137.57(15)°), **34** (138.50(8)°) and **37**
(137.7(3)°), as well as other $(C_5Me_5)_2U(X)_2$ complexes (121.1–146.1°) [29,67–81].

Few other similar types of complexes have been reported in the past. For instance, Marks and
co-workers reported that Na/Hg reduction of $(C_5Me_5)_2UCl_2$ formed $[Na(THF)_2][(C_5Me_5)_2UCl_2]$ [72],
but no structure was presented and two other examples reported by Lappert and co-workers show
monomeric motifs for $[M(THF)_2][\{1,3\text{-}(Me_3Si)_2C_5H_3\}_2UCl_2]$ (M = Li or Na) [7]. The polymeric structure
of **41** can be explained by the presence of the considerably larger potassium ions, *versus* lithium and
sodium adducts, which yield monomeric complexes.

As shown in Scheme 5, the synthetic utility of the "ate" complexes $[K(THF)][(C_5Me_4R)_2UX_2]$
(**39**–**42**) was demonstrated by their reaction with one equivalent of $Na[N(SiMe_3)_2]$ in toluene to afford
$(C_5Me_4R)_2U[N(SiMe_3)_2]$ (R = Me, (**43**), Et (**44**)) in good yields (76%–86%).
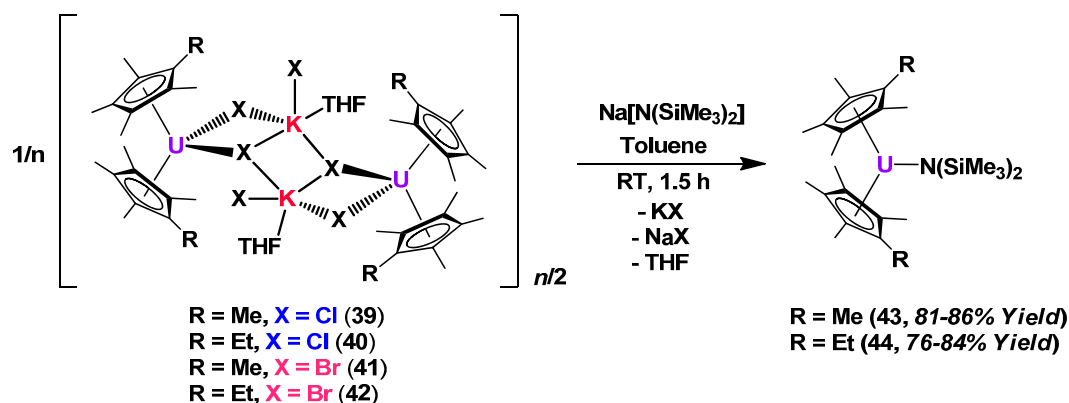
Scheme 5. Preparation of neutral uranium(III) complexes $(C_5Me_4R)_2U[N(SiMe_3)_2]$ (R = Me, (**43**), Et (**44**)).

3. Experimental Section

3.1. General Synthetic Considerations

Unless otherwise noted, all reactions and manipulations were performed at ambient temperatures in a recirculating Vacuum Atmospheres NEXUS model inert atmosphere (N_2) drybox equipped with a 40 CFM Dual Purifier NI–Train. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer at room temperature. Chemical shifts for ^1H NMR spectra were referenced to solvent impurities [82]. Melting points were determined with a Mel-Temp II capillary melting point apparatus equipped with a Fluke 50 S K/J thermocouple using capillary tubes flame-sealed under N_2; values are uncorrected. Elemental Analyses were performed by ALS Environmental (Tucson, AZ, USA) or Atlantic Microlab, Inc. (Norcross, GA, USA).

3.2. Materials

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich, Saint Louis, MO, USA), neutral alumina (Aldrich), and 3 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 220 °C for 48 h prior to use. All solvents (Aldrich), benzene-d_6 and THF-d_8 (Cambridge Isotopes, Tewksbury, MA, USA) were purchased anhydrous and dried over KH for 48 h, passed through a column of activated alumina, and stored over activated 3 Å molecular sieves prior to use. HO-2,6-$^iPr_2C_6H_3$ (Aldrich) was dried with activated 3 Å molecular sieves prior to use. Potassium metal (Aldrich) was rinsed with hexane, dried and used immediately. Me_3SiBr (Aldrich), graphite (Aldrich) and $Na[N(SiMe_3)_2]$ (Aldrich) were used as received. $(C_5Me_5)_2UCl_2$ (**31**) [3], $(C_5Me_4Et)_2UCl_2$ (**32**) [31], and K[O-2,6-$^iPr_2C_6H_3$] [30] were prepared according to literature procedures.

3.3. Caution

Depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47×10^9 years; manipulations and reactions should be carried out in monitored fume-hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

3.4. Synthetic Procedures

$(C_5Me_5)_2UBr_2$ (33): A 20 mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2UCl_2$ (**31**) (0.301 g, 0.518 mmol) and Et_2O (5 mL). To this solution, Me_3SiBr (0.397 g, 2.59 mmol) was added dropwise. The reaction mixture was stirred at ambient temperature for 12 h and the volatiles were removed under reduced pressure. Et_2O (5 mL) and Me_3SiBr (0.397 g, 2.59 mmol) were added again and the solution was left stirring at ambient temperature for another 12 h and the volatiles were

removed under reduced pressure. Et_2O (5 mL) and Me_3SiBr (0.397 g, 2.59 mmol) were added for the third and final time and the reaction mixture was stirred at ambient temperature for 12 h and the volatiles were removed under reduced pressure. The resulting residue was dissolved in toluene (15 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red colored filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_5)_2UBr_2$ (**33**) as a red solid (0.333 g, 0.498 mmol, 96%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution at ambient temperature. ^1H NMR (benzene-d_6, 298 K): δ 15.70 (s, 30H, $v_{1/2}$ = 111.8 Hz, C_5Me_5). m.p. 276–278 °C. Anal. calcd. for $C_{20}H_{30}Br_2U$ (mol. wt. 668.29): C, 35.94; H, 4.52. Found: C, 35.20, H, 4.42.

$(C_5Me_4Et)_2UBr_2$ (34): A 20 mL scintillation vial was charged with a stir bar, $(C_5Me_4Et)_2UCl_2$ (**32**) (0.500 g, 0.823 mmol) and Et_2O (5 mL). To this solution Me_3SiBr (0.630 g, 4.12 mmol) was added dropwise. The reaction mixture was stirred at ambient temperature for 12 h and the volatiles were removed under reduced pressure. Et_2O (5 mL) and Me_3SiBr (0.630 g, 4.12 mmol) were added again and the solution was left stirring at ambient temperature for another 12 h and the volatiles were removed under reduced pressure. Et_2O (5 mL) and Me_3SiBr (0.630 g, 4.12 mmol) were added for the third and final time and the reaction mixture was stirred at ambient temperature for 12 h and the volatiles were removed under reduced pressure. The resulting residue was dissolved in toluene (15 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red colored filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_4Et)_2UBr_2$ (**34**) as a red solid (0.515 g, 0.740 mmol, 90%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution at ambient temperature. ^1H NMR (benzene-d_6, 298 K): δ 25.06 (s, 6H, $v_{1/2}$ = 43.3 Hz, CH_2CH_3), 15.57 (s, 12H, $v_{1/2}$ = 95.7 Hz, CH_3), 13.06 (s, 12H, $v_{1/2}$ = 93.8 Hz, CH_3), 0.31 (s, 4H, $v_{1/2}$ = 112.5 Hz CH_2). m.p. 160–162 °C. Anal. calcd. for $C_{22}H_{34}Br_2U$: C, 37.95; H, 4.92. Found: C, 37.59; H, 5.05.

$(C_5Me_5)_2U(O-2,6-^iPr_2C_6H_3)(Cl)$ (35): A 20 mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2UCl_2$ (**29**) (0.149 g, 0.257 mmol), $K[O-2,6-^iPr_2C_6H_3]$ (0.056 g, 0.257 mmol) and THF (5 mL). The reaction mixture was stirred at ambient temperature for 35 min and the volatiles were removed under reduced pressure. The resulting residue was dissolved in toluene (10 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_5)_2U(O-2,6-^iPr_2C_6H_3)(Cl)$ (**35**) as a red solid (0.170 g, 0.236 mmol, 92%). The ^1H NMR spectrum collected in benzene-d_6 was consistent with data previously reported for complex **35** [8]. ^1H NMR (C_6D_6, 298 K): δ 8.37 (d, 1H, *m*-Ar-*H*), 8.35 (d, 1H, *m*-Ar-*H*), 7.85 (s, 30H, $C_5(CH_3)_5$), 7.06 (t, 1H, *p*-Ar-*H*), −6.01 (s, 6H, CH(C*H*$_3$)$_2$), −12.37 (s, 6H, CH(C*H*$_3$)$_2$), −35.74 (m, 1H, C*H*(CH$_3$)$_2$), −44.65 (m, 1H, C*H*(CH$_3$)$_2$).

$(C_5Me_4Et)_2U(O-2,6-^iPr_2C_6H_3)(Cl)$ (36): A 20 mL scintillation vial was charged with a stir bar, $(C_5Me_4Et)_2UCl_2$ (**32**) (0.300 g, 0.494 mmol), $K[O-2,6-^iPr_2C_6H_3]$ (0.107 g, 0.494 mmol) and THF (5 mL). The reaction mixture was stirred at ambient temperature for 35 min and the volatiles were removed under reduced pressure. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red colored filtrate was collected and the volatiles were removed under reduced pressure. The resulting red oil was dissolved in hexane (5 mL) and passed through a Celite-padded coarse-porosity fritted filter. The red filtrate was collected, the volatiles were removed under reduced pressure and the oily product triturated three times with acetonitrile (5 mL) to give $(C_5Me_4Et)_2U(O-2,6-^iPr_2C_6H_3)(Cl)$ (**36**) as a red solid (0.332 g, 0.443 mmol, 90%). ^1H NMR (benzene-d_6, 298 K): δ 11.87 (s, 6H, $v_{1/2}$ = 13.6 Hz, CH_3), 8.49 (s, 6H, $v_{1/2}$ = 5.9 Hz, CH_3), 8.26 (d, 1H, J_{HH} = 8.5 Hz, *m*-Ar-C*H*), 8.15 (d, 1H, J_{HH} = 8.5 Hz, *m*-Ar-C*H*), 7.82 (s, 6H, $v_{1/2}$ = 13.6 Hz, CH_3), 7.78 (s, 6H, $v_{1/2}$ = 13.6 Hz, CH_3), 6.91 (t, 1H, J_{HH} = 8.5 Hz, *p*-Ar-*H*), 6.58 (s, 6H, $v_{1/2}$ = 4.7 Hz, CH_3), −0.55 (s, 2H, $v_{1/2}$ = 29 Hz, CH_2), −1.37 (s, 2H, $v_{1/2}$ = 29 Hz, CH_2), −5.85 (d, 6H, J_{HH} = 3.6 Hz, CH(C*H*$_3$)$_2$), −12.75 (s, 6H, $v_{1/2}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), −35.67 (m, 1H, C*H*(CH$_3$)$_2$), −46.81 (s, 1H, $v_{1/2}$ = 28.6 Hz, C*H*(CH$_3$)$_2$). m.p. 92–95 °C. Anal. calcd. for $C_{34}H_{51}ClOU$ (mol. wt. 749.25): C, 54.50; H, 6.86. Found: C, 54.08; H, 7.16.

(C$_5$Me$_5$)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Br) (37): Method A: From (C$_5$Me$_5$)$_2$UBr$_2$. A 20 mL scintillation vial was charged with a stir bar, (C$_5$Me$_5$)$_2$UBr$_2$ (**33**) (0.100 g, 0.150 mmol), K[*O*-2,6-^{i}Pr$_2$C$_6$H$_3$] (0.0324 g, 0.150 mmol) and THF (5 mL). The reaction mixture was stirred at ambient temperature for 1 h and the volatiles were removed under reduced pressure. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red filtrate was collected and the volatiles were removed under reduced pressure to give (C$_5$Me$_5$)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Br) (**37**) as a red solid (0.113 g, 0.148 mmol, 99%).

Method B: From (C$_5$Me$_5$)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Cl). A 20 mL scintillation vial was charged with a stir bar, (C$_5$Me$_5$)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Cl) (**35**) (0.102 g, 0.141 mmol), Et$_2$O (5 mL) and Me$_3$SiBr (0.108 g, 0.707 mmol). The reaction mixture was stirred at ambient temperature for 12 h and the volatiles were removed under reduced pressure. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red filtrate was collected and the volatiles were removed under reduced pressure to give (C$_5$Me$_5$)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Br) (**37**) as a red solid (0.100 g, 0.131 mmol, 93%). Single crystals suitable for X-ray diffraction were obtained from a 50 mM toluene solution at −35 °C. ^{1}H NMR (benzene-d_6, 298 K): δ 9.41 (d, 1H, J_{HH} = 8.6 Hz, *m*-Ar-*H*), 9.07 (d, 1H, J_{HH} = 8.6 Hz, *m*-Ar-*H*), 8.76 (s, 30H, C$_5$(C*H*$_3$)$_5$), 7.40 (t, 1H, J_{HH} = 8.7 Hz, *p*-Ar-*H*), −5.89 (d, 6H, J_{HH} = 3.8 Hz, CH(C*H*$_3$)$_2$), −11.68 (s, 6H, CH(C*H*$_3$)$_2$), −35.67 (m, 1H, C*H*(CH$_3$)$_2$), −42.99 (m, 1H, C*H*(CH$_3$)$_2$). m.p. 214–216 °C. Anal. calcd. for C$_{32}$H$_{47}$BrOU (mol. wt. 765.65): C, 50.20; H, 6.19. Found: C, 49.46, H, 5.98.

(C$_5$Me$_4$Et)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Br) (38): Method A: From (C$_5$Me$_4$Et)$_2$UBr$_2$. A 20 mL scintillation vial was charged with a stir bar, (C$_5$Me$_4$Et)$_2$UBr$_2$ (**34**) (0.100 g, 0.144 mmol), K[*O*-2,6-^{i}Pr$_2$C$_6$H$_3$] (0.0311 g, 0.144 mmol) and THF (5 mL). The reaction mixture was stirred at ambient temperature for 1 h and the volatiles were removed under reduced pressure. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red filtrate was collected and the volatiles were removed under reduced pressure. The resulting red oil was dissolved in hexane (5 mL) and passed through a Celite-padded coarse-porosity fritted filter. The red filtrate was collected, the volatiles removed under reduced pressure and the oily product triturated three times with acetonitrile (5 mL) to give (C$_5$Me$_4$Et)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Br) (**38**) as a red solid (0.110 g, 0.139 mmol, 96%).

Method B: From (C$_5$Me$_4$Et)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Cl). A 20 mL scintillation vial was charged with a stir bar, (C$_5$Me$_4$Et)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Cl) (**36**) (0.100 g, 0.133 mmol), Et$_2$O (5 mL) and Me$_3$SiBr (0.102 g, 0.667 mmol). The reaction mixture was stirred at ambient temperature for 12 h and the volatiles were removed under reduced pressure. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red filtrate was collected and the volatiles were removed under reduced pressure. The resulting red oil was triturated with acetonitrile (3 mL) to give (C$_5$Me$_4$Et)$_2$U(*O*-2,6-^{i}Pr$_2$C$_6$H$_3$)(Br) (**38**) as a red solid (0.096 g, 0.121 mmol, 91%). ^{1}H NMR (benzene-d_6, 298 K): δ 11.92 (s, 6H, $v_{1/2}$ = 14.0 Hz, C*H*$_3$), 9.11 (s, 6H, $v_{1/2}$ = 5.3 Hz, C*H*$_3$), 9.07 (s, 6H, $v_{1/2}$ = 5.3 Hz, C*H*$_3$), 8.96 (d, 1H, J_{HH} = 8.3 Hz, *m*-Ar-C*H*), 8.33 (s, 6H, $v_{1/2}$ = 13.6 Hz, C*H*$_3$), 7.77 (s, 6H, $v_{1/2}$ = 5.4 Hz, C*H*$_3$), 7.23 (t, 1H, J_{HH} = 8.7 Hz, *p*-Ar-*H*), 0.35 (s, 2H, $v_{1/2}$ = 27 Hz, C*H*$_2$), −0.52 (s, 2H, $v_{1/2}$ = 31 Hz, C*H*$_2$), −5.72 (d, 6H, J_{HH} = 3.2 Hz, CH(C*H*$_3$)$_2$), −12.15 (s, 6H, $v_{1/2}$ = 7.0 Hz, CH(C*H*$_3$)$_2$), −35.62 (m, 1H, C*H*(CH$_3$)$_2$), −45.56 (m, 1H, C*H*(CH$_3$)$_2$). m.p. 69–72 °C. Anal. calcd. for C$_{34}$H$_{51}$BrOU (mol. wt. 793.70): C, 51.45; H, 6.48. Found: C, 51.51; H, 6.65.

KC$_8$: This is a modification of literature procedures [83,84]: A 20 mL scintillation vial was charged with potassium metal (0.040 g, 1.03 mmol) and graphite (0.099 g, 8.26 mmol) in an nitrogen atmosphere glove box. The reaction mixture was stirred with a spatula at 100 °C until the solid was completely bronze in color (~5 min), yielding quantitative solid KC$_8$ (0.140 g, 1.03 mmol, 100%).

[K(THF)][(C$_5$Me$_5$)$_2$UCl$_2$] (39): A 20 mL scintillation vial was charged with a stir bar, (C$_5$Me$_5$)$_2$UCl$_2$ (**31**) (0.600 g, 1.03 mmol), KC$_8$ (0.140 g, 1.03 mmol), and toluene (10 mL). The reaction mixture was stirred at ambient temperature for 4 h, yielding a green precipitate. The reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter. The toluene-insoluble green solid, which was collected on the Celite-padded fritted filter was dissolved by adding THF

(15 mL). The green filtrate was collected and the volatiles were removed under reduced pressure to give [K(THF)][(C$_5$Me$_5$)$_2$UCl$_2$] (**39**) as a green solid (0.560 g, 0.405 mmol, 79%). Single crystals suitable for X-ray diffraction were grown from a saturated THF solution at −35 °C. ^{1}H-NMR (THF-d_8, 298 K): δ 3.62 (8H, m, THF-CH_2), 1.78 (8H, m, THF-CH_2), −5.49 (60H, $v_{1/2}$ = 52 Hz, C$_5$(CH_3)$_5$). m.p. 230.0 °C (Decomp). Anal. calcd. for C$_{48}$H$_{76}$Cl$_4$K$_2$O$_2$U$_2$ (mol. wt. 1381.18): C, 41.74; H, 5.55. Found: C, 41.41; H, 5.30.

[K(THF)$_{0.5}$][(C$_5$Me$_4$Et)$_2$UCl$_2$] (40): A 20 mL scintillation vial was charged with a stir bar, (C$_5$Me$_4$Et)$_2$UCl$_2$ (**32**) (0.500 g, 0.823 mmol), KC$_8$ (0.111 g, 0.823 mmol), and toluene (10 mL). The reaction mixture was stirred at ambient temperature for 2 h, yielding a green precipitate. The reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter. The insoluble green solid on the Celite-padded coarse-porosity fritted filter. The toluene-insoluble green solid, which was collected on the Celite-padded frit was dissolved by adding THF (15 mL). The green filtrate was collected and the volatiles were removed under reduced pressure to give [K(THF)$_{0.5}$][(C$_5$Me$_4$Et)$_2$UCl$_2$] (**40**) as a green solid (0.549 g, 0.764 mmol, 93%). ^{1}H NMR (THF-d_8, 298 K): d 11.39 (s, 6H, $v_{1/2}$ = 29.0 Hz, CH$_2$CH_3), 3.62 (m, 4H, THF-CH_2), 1.79 (m, 4H, THF-CH_2), −4.61 (s, 12H, $v_{1/2}$ = 58.6 Hz, CH_3), −5.79 (s, 4H, $v_{1/2}$ = 87.3 Hz, CH_2), −6.43 (s, 12H, $v_{1/2}$ = 60.0 Hz, CH_3). m.p. 189–192 °C (Decomp). Anal. calcd. for C$_{48}$H$_{76}$Cl$_4$K$_2$OU$_2$ (mol. wt. 1365.18): C, 42.43; H, 5.61. Found: C, 42.54; H, 6.04.

[K(THF)][(C$_5$Me$_5$)$_2$UBr$_2$] (41): A 20 mL scintillation vial was charged with a stir bar, (C$_5$Me$_5$)$_2$UBr$_2$ (**33**) (0.263 g, 0.393 mmol), KC$_8$ (0.0530 g, 0.393 mmol), and toluene (10 mL). The reaction mixture was stirred at ambient temperature for 3 h, yielding a green precipitate. The reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter. The toluene-insoluble green solid, which was collected on the Celite-padded fritted filter was dissolved by adding THF (15 mL). The green filtrate was collected and the volatiles were removed under reduced pressure to give [K(THF)][(C$_5$Me$_5$)$_2$UBr$_2$] (**41**) as a green solid (0.275 g, 0.353 mmol, 90%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a THF solution at ambient temperature. ^{1}H NMR (THF-d_8, 298 K): δ 3.62 (m, 4H, THF-CH_2), 1.78 (m, 4H, THF-CH_2), −3.42 (s, 30H, $v_{1/2}$ = 84.5 Hz, C$_5$(CH_3)$_5$). m.p. 190–192 °C (Decomp). Anal. calcd. for C$_{48}$H$_{76}$Br$_4$K$_2$O$_2$U$_2$ (mol. wt. 1558.99): C, 36.98; H, 4.91. Found: C, 37.00; H, 4.98.

[K(THF)$_{0.5}$][(C$_5$Me$_4$Et)$_2$UBr$_2$] (42): A 20 mL scintillation vial was charged with a stir bar, (C$_5$Me$_4$Et)$_2$UBr$_2$ (**34**) (0.300 g, 0.431 mmol), KC$_8$ (0.058 g, 0.431 mmol), and toluene (10 mL). The reaction mixture was stirred at ambient temperature for 2 h, yielding a green precipitate. The reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter. The toluene-insoluble green solid, which was collected on the Celite-padded fritted filter was dissolved by adding in THF (10 mL). The green colored filtrate was collected and the volatiles were removed under reduced pressure. The resulting solid was triturated twice with hexane (3 mL) to give [K(THF)$_{0.5}$][(C$_5$Me$_4$Et)$_2$UBr$_2$] (**42**) as a green solid (0.323 g, 0.400 mmol, 93%). ^{1}H NMR (THF-d_8, 298 K): δ 13.61 (s, 6H, $v_{1/2}$ = 76.5 Hz, CH$_2$CH_3), 3.62 (m, 4H, THF-CH_2), 1.79 (m, 4H, THF-CH_2), −3.10 (s, 12H, $v_{1/2}$ = 131.9 Hz, CH_3), −4.23 (s, 12H, $v_{1/2}$ = 135.8 Hz, CH_3), −4.47 (s, 4H, CH_2). m.p. 189–191 °C (Decomp). Anal. calcd. for C$_{48}$H$_{76}$Br$_4$K$_2$OU$_2$ (mol. wt. 1542.99): C, 37.36; H, 4.96. Found: C, 37.61; H, 5.23.

(C$_5$Me$_5$)$_2$U[N(SiMe$_3$)$_2$] (43): Method A: From [K(THF)][(C$_5$Me$_5$)$_2$UCl$_2$]. A 20 mL scintillation vial was charged with a stir bar, [K(THF)][(C$_5$Me$_5$)$_2$UCl$_2$] (**39**) (0.100 g, 0.148 mmol), Na[N(SiMe$_3$)$_2$] (0.027 g, 0.148 mmol), and toluene (5 mL). The reaction mixture was stirred at ambient temperature for 1 h, and the volatiles were removed under reduced pressure. The resulting residue was dissolved in hexane (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The gray filtrate was collected and the volatiles were removed under reduced pressure to give (C$_5$Me$_5$)$_2$U[N(SiMe$_3$)$_2$] (**43**) as a gray solid (0.085 g, 0.127 mmoles, 86%).

Method B: From [K(THF)][(C$_5$Me$_5$)$_2$UBr$_2$]. A 20 mL scintillation vial was charged with a stir bar, [K(THF)][(C$_5$Me$_5$)$_2$UBr$_2$] (**41**) (0.100 g, 0.128 mmol), Na[N(SiMe$_3$)$_2$] (0.024 g, 0.128 mmol), and toluene (5 mL). The reaction mixture was stirred at ambient temperature for 1 h and the volatiles were removed under reduced pressure. The resulting residue was dissolved in hexane (5 mL) and filtered

through a Celite-padded coarse-porosity fritted filter. The gray filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_5)_2U[N(SiMe_3)_2]$ (**43**) as a gray solid (0.065 g, 0.097 mmol, 76%). The ^1H NMR spectrum collected in benzene-d_6 was consistent with data previously reported for complex **43** [85]. ^1H NMR (benzene-d_6, 298 K): δ −5.69 (30H, s, $C_5(CH_3)_5$), −25.57 (18H, s, Si(CH_3)$_3$).

$(C_5Me_4Et)_2U[N(SiMe_3)_2]$ (44): Method A: From $[K(THF)_{0.5}][(C_5Me_4Et)_2UCl_2]$. A 20 mL scintillation vial was charged with a stir bar, $[K(THF)_{0.5}][(C_5Me_4Et)_2UCl_2]$ (**40**) (0.100 g, 0.139 mmol), $Na[N(SiMe_3)_2]$ (0.026 g, 0.139 mmol), and toluene (5 mL). The reaction mixture was stirred at ambient temperature for 1 h, and the volatiles were removed under reduced pressure. The resulting residue was dissolved in hexane (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The gray filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_4Et)_2U[N(SiMe_3)_2]$ (**44**) as a gray solid (0.079 g, 0.113 mmol, 81%).

Method B: From $[K(THF)_{0.5}][(C_5Me_4Et)_2UBr_2]$. A 20 mL scintillation vial was charged with a stir bar, $[K(THF)_{0.5}][(C_5Me_4Et)_2UBr_2]$ (**42**) (0.100 g, 0.124 mmol), $Na[N(SiMe_3)_2]$ (0.023 g, 0.124 mmol), and toluene (5 mL). The reaction mixture was stirred at ambient temperature for 1 h, and the volatiles were removed under reduced pressure. The resulting residue was dissolved in hexane (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The gray filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_4Et)_2U[N(SiMe_3)_2]$ (**44**) as a gray solid (0.073 g, 0.104 mmol, 84%). The ^1H NMR spectrum collected in benzene-d_6 was consistent with data previously reported for complex **44** [85]. ^1H NMR (benzene-d_6, 298 K): δ 10.28 (6H, s, CH_2CH_3), 4.03 (4H, s, CH_2CH_3), −5.62 (12H, s, CH_3), −6.52 (12H, s, CH_3), −25.48 (18H, s, Si(CH_3)$_3$).

X-ray Crystallography: Data for **33**, **34**, and **41** were collected on a Bruker D8 Quest diffractometer, with a CMOS detector in shutterless mode. The crystals were cooled to 100 K employing an Oxford Cryostream liquid nitrogen cryostat. Data for **37** were collected on a Bruker D8 diffractometer, with an APEX II CCD detector. The crystal was cooled to 140 K using a Bruker Kryoflex liquid nitrogen cryostat. Both data collections employed graphite monochromatized MoKα (λ = 0.71073 Å) radiation. Cell indexing, data collection, integration, structure solution, and refinement were performed using Bruker and SHELXTL software [86–89]. CIF files representing the X-ray crystal structures of **33**, **34**, **37** and **41** (Supplementary files) have been submitted to the Cambridge Crystallographic Database as submission numbers CCDC 1428938–1428941.

4. Conclusions

In summary, we have expanded the family of organouranium bromides with the preparation of the tetravalent and trivalent uranium bromide complexes $(C_5Me_4R)_2UBr_2$, $(C_5Me_4R)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Br)$, and $[K(THF)][(C_5Me_4R)_2UBr_2]$ (R = Me, Et). The uranium(IV) compounds were easily accessed by treating the corresponding chloride analogues with excess Me_3SiBr. The uranium(IV) chloride complexes were all easily obtained from UCl_4 and their halide substitution chemistry with Me_3SiBr constitutes a practical and efficient route to new bromide derivatives, even in the presence of alkoxide ligands.

The reduction of $(C_5Me_4R)_2UX_2$ complexes with one equivalent of KC_8 allowed for the isolation of the uranium(III) species $[K(THF)][(C_5Me_5)_2UX_2]$ and $[K(THF)_{0.5}][(C_5Me_4Et)_2UX_2]$, which can be converted to the neutral uranium(III) complexes $(C_5Me_4R)_2U[N(SiMe_3)_2]$ upon treatment with $Na[N(SiMe_3)_2]$. Halide and anion compatibility can be very important in the synthesis of organouranium complexes, and this work provides new options for the actinide synthetic chemistry toolbox.

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References

1. Spirlet, M.R.; Rebizant, J.; Apostolidis, C.; Kanellakopulos, B. Bis(cyclopentadienyl) actinide(IV) compounds. I. The structure of dichlorobis(pentamethyl-η^5-cyclopentadienyl)uranium(IV) and dichlorobis(pentamethyl-η^5-cyclopentadienyl)thorium(IV). *Acta Crystallogr. Sect. C Cryst. Commun.* **1992**, *48*, 2135–2137. [CrossRef]

2. Graves, C.R.; Schelter, E.J.; Cantat, T.; Scott, B.L.; Kiplinger, J.L. A mild protocol to generate uranium(IV) mixed-ligand metallocene complexes using copper(I) iodide. *Organometallics* **2008**, *27*, 5371–5378. [CrossRef]

3. Fagan, P.J.; Manriquez, J.M.; Maatta, E.A.; Seyam, A.M.; Marks, T.J. Synthesis and properties of bis(pentamethylcyclopentadienyl) actinide hydrocarbyls and hydrides. A new class of highly reactive f-element organometallic compounds. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667. [CrossRef]

4. Lukens, W.W., Jr.; Beshouri, S.M.; Blosch, L.L.; Stuart, A.L.; Andersen, R.A. Preparation, solution behavior, and solid-state structures of $(1,3\text{-}R_2C_5H_3)_2UX_2$, where R is CMe_3 or $SiMe_3$ and X is a one-electron ligand. *Organometallics* **1999**, *18*, 1235–1246. [CrossRef]

5. Zi, G.; Jia, L.; Werkema, E.L.; Walter, M.D.; Gottfriedsen, J.P.; Andersen, R.A. Preparation and reactions of base-free bis(1,2,4-tri-*tert*-butylcyclopentadienyl)uranium oxide, Cp'_2UO. *Organometallics* **2005**, *24*, 4251–4264. [CrossRef]

6. Blake, P.C.; Lappert, M.F.; Taylor, R.G.; Atwood, J.L.; Hunter, W.E.; Zhang, H. Synthesis, spectroscopic properties and crystal structures of $[ML_2Cl_2]$ [M = Th or U; L = $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$] and $[UL_2X_2]$ (X = Br, I or BH_4). *Dalton Trans.* **1995**, 3335–3341. [CrossRef]

7. Blake, P.C.; Lappert, M.F.; Taylor, R.G.; Atwood, J.L.; Zhang, H. Some aspects of the coordination and organometallic chemistry of thorium and uranium (M^{III}, M^{IV}, U^V) in +3 and +4 oxidation states. *Inorg. Chim. Acta* **1987**, *139*, 13–20. [CrossRef]

8. Thomson, R.K.; Graves, C.R.; Scott, B.L.; Kiplinger, J.L. Organometallic uranium(IV) fluoride complexes: Preparation using protonolysis chemistry and reactivity with trimethylsilyl reagents. *Dalton Trans.* **2010**, *39*, 6826–6831. [CrossRef] [PubMed]

9. Rabinovich, D.; Haswell, C.M.; Scott, B.L.; Miller, R.L.; Nielsen, J.B.; Abney, K.D. New dicarbollide complexes of uranium. *Inorg. Chem.* **1996**, *35*, 1425–1426. [CrossRef] [PubMed]

10. Spirlet, M.R.; Rebizant, J.; Apostolidis, C.; Andreetti, G.D.; Kanellakopulos, B. Structure of tris(cyclopentadienyl)uranium bromide. *Acta Crystallogr. C* **1989**, *45*, 739–741. [CrossRef]

11. Goffart, J.; Fuger, J.; Gilbert, B.; Hocks, L.; Duyckaerts, G. On the indenyl compounds of actinide elements Part I: Triindenylthorium bromide and triindenyluranium bromide. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 569–583. [CrossRef]

12. Goffart, J.; Piret-Meunier, J.; Duyckaerts, G. On the indenyl compounds of actinide elements: Part V: Some oxygen-donor complexes of indenyl actinide halides. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 233–244. [CrossRef]

13. Spirlet, M.R.; Rebizant, J.; Goffart, J. Structure of tris(1-3-η-Indenyl)uranium bromide. *Acta Crystallogr. C* **1987**, *43*, 354–355. [CrossRef]

14. Bagnall, K.W.; Edwards, J. Uranium(IV) substituted poly(pyrazol-1-yl) borate complexes. *J. Less Common Met.* **1976**, *48*, 159–165. [CrossRef]

15. Bagnall, K.W.; Edwards, J.; Tempest, A.C. Some oxygen-donor complexes of cyclopentadienyluranium(IV) halides. *Dalton Trans.* **1978**, 295–298. [CrossRef]

16. Beeckman, W.; Goffart, J.; Rebizant, J.; Spirlet, M.R. The first cationic indenyl-f-metal complexes with pentagonal bipyramidal geometry. Crystal structures of $[C_9H_7UBr_2(CH_3CN)_4]_2^+[UBr_6]^{2-}$ and $[\{C_9H_7UBr(CH_3CN)_4\}_2O]^{2+}[UBr_6]^{2-}$. *J. Organomet. Chem.* **1986**, *307*, 23–37. [CrossRef]

17. Thomson, R.K.; Scott, B.L.; Morris, D.E.; Kiplinger, J.L. Synthesis, structure, spectroscopy and redox energetics of a series of uranium(IV) mixed-ligand metallocene complexes. *C. R. Chim.* **2010**, *13*, 790–802. [CrossRef]

18. Evans, W.J.; Walensky, J.R.; Ziller, J.W. Reaction chemistry of the U^{3+} metallocene amidinate $(C_5Me_5)_2[^iPrNC(Me)N^iPr]U$ including the isolation of a uranium complex of a monodentate acetate. *Inorg. Chem.* **2010**, *49*, 1743–1749. [CrossRef] [PubMed]

19. Evans, W.J.; Walensky, J.R.; Ziller, J.W. Reactivity of methyl groups in actinide metallocene amidinate and triazenido complexes with silver and copper salts. *Organometallics* **2010**, *29*, 101–107. [CrossRef]

20. Evans, W.J.; Nyce, G.W.; Johnston, M.A.; Ziller, J.W. How much steric crowding is possible in tris(η^5-pentamethylcyclopentadienyl) complexes? Synthesis and structure of $(C_5Me_5)_3UCl$ and $(C_5Me_5)_3UF$. *J. Am. Chem. Soc.* **2000**, *122*, 12019–12020. [CrossRef]

21. Danopoulos, A.A.; Hankin, D.M.; Cafferkey, S.M.; Hursthouse, M.B. η^2-Sulfenamido complexes of uranium. *Dalton Trans.* **2000**, 1613–1615. [CrossRef]

22. Lugli, G.; Mazzei, A.; Poggio, S. High 1,4-*cis*-polybutadiene by uranium catalysts, 1. Tris(π-allyl)uranium halide catalysts. *Makromol. Chem.* **1974**, *175*, 2021–2027. [CrossRef]

23. Lukens, W.W., Jr.; Beshouri, S.M.; Stuart, A.L.; Andersen, R.A. Solution structure and behavior of dimeric uranium(III) metallocene halides. *Organometallics* **1999**, *18*, 1247–1252. [CrossRef]

24. Blake, P.C.; Lappert, M.F.; Taylor, R.G.; Atwood, J.L.; Hunter, W.E.; Zhang, H. A complete series of uranocene(III) halides $[(UCp''_2X)_n]$ [X = F, Cl, Br, or I; Cp'' = η^5-$C_5H_3(SiMe_3)_2$]; Single-crystal X-ray structure determinations of the chloride and bromide (n = 2, X^- = μ-Cl, μ-Br). *Chem. Commun.* **1986**, 1394–1395. [CrossRef]

25. De Rege, F.M.; Smith, W.H.; Scott, B.L.; Nielsen, J.B.; Abney, K.D. Electrochemical properties of bis(dicarbollide)uranium dibromide. *Inorg. Chem.* **1998**, *37*, 3664–3666. [CrossRef] [PubMed]

26. Beshouri, S.M.; Zalkin, A. Bis[η^5-bis(trimethylsilyl)cyclopentadienyl]bromouranium(III) bis(tert-butyl isocyanide). *Acta Crystallogr. C* **1989**, *C45*, 1221–1222. [CrossRef]

27. Finke, R.G.; Hirose, Y.; Gaughan, G. $(C_5Me_5)_2UCl \cdot$ tetrahydrofuran. Oxidative-addition and related reactions. *Chem. Commun.* **1981**, 232–234. [CrossRef]

28. Maynadié, J.; Berthet, J.-C.; Thuéry, P.; Ephritikhine, M. An unprecedented type of linear metallocene with an f-element. *J. Am. Chem. Soc.* **2006**, *128*, 1082–1083. [CrossRef] [PubMed]

29. Maynadie, J.; Berthet, J.-C.; Thuery, P.; Ephritikhine, M. From bent to linear uranium metallocenes: Influence of counterion, solvent, and metal ion oxidation state. *Organometallics* **2006**, *25*, 5603–5611. [CrossRef]

30. Monreal, M.J.; Thomson, R.K.; Cantat, T.; Travia, N.E.; Scott, B.L.; Kiplinger, J.L. $UI_4(1,4$-dioxane$)_2$, $[UCl_4(1,4$-dioxane$)]_2$, and $UI_3(1,4$-dioxane$)_{1.5}$: Stable and versatile starting materials for low- and high-valent uranium chemistry. *Organometallics* **2011**, *30*, 2031–2038. [CrossRef]

31. Schelter, E.J.; Veauthier, J.M.; Graves, C.R.; John, K.D.; Scott, B.L.; Thompson, J.D.; Pool-Davis-Tournear, J.A.; Morris, D.E.; Kiplinger, J.L. 1,4-Dicyanobenzene as a scaffold for the preparation of bimetallic actinide complexes exhibiting metal–metal communication. *Chem. Eur. J.* **2008**, *14*, 7782–7790. [CrossRef] [PubMed]

32. LeMarechal, J.F.; Villiers, C.; Charpin, P.; Nierlich, M.; Lance, M.; Vigner, J.; Ephritikhine, M. Anionic tricyclopentadienyluranium(III) complexes. Crystal structure of $[Cp_3UClUCp_3][Na(18$-Crown-6$)(THF)_2]$ (Cp = η-C_5H_5). *J. Organomet. Chem.* **1989**, *379*, 259–269. [CrossRef]

33. Du Preez, J.G.H.; Gellatly, B.J.; Jackson, G.; Nassimbeni, L.R.; Rodgers, A.L. The chemistry of uranium. Part 23. Isomorphous tetrachlorobis(hexamethylphosphoramide)uranium(IV) and tetrabromobis(hexamethylphosphoramide)uranium(IV). *Inorg. Chim. Acta* **1978**, *27*, 181–184. [CrossRef]

34. Du Preez, J.G.H.; Zeelie, B.; Casellato, U.; Graziani, R. The chemistry of uranium. Part 34. Structural and thermal properties of UX_4L_2 complexes (X = Cl and Br; L = *N,N,N',N'*-tetramethylurea). *Inorg. Chim. Acta* **1986**, *122*, 119–126. [CrossRef]

35. Du Preez, J.G.H.; Rohwer, H.E.; van Brecht, B.J.A.M.; Zeelie, B.; Casellato, U.; Graziani, R. The chemistry of uranium. Part 41. Complexes of uranium tetrahalide, with emphasis on iodide, and triphenylphosphine oxide, tris(dimethylamino)phosphine oxide or tris(pyrrolidinyl)phosphine oxide. Crystal structure of tetrabromobis[tris(pyrrolidinyl)phosphine oxide]uranium(IV). *Inorg. Chim. Acta* **1991**, *189*, 67–75.

36. Du Preez, J.G.H.; Gouws, L.; Rohwer, H.; van Brecht, B.J.A.M.; Zeelie, B.; Casellato, U.; Graziani, R. The chemistry of uranium. Part 42. Cationic uranium(IV) complexes $UX_2L_4Y_2$ (X = Cl, Br or I; Y = ClO_4 or BPh_4; L = bulky strong neutral *O*-donor ligand) and [$U(ClO_4)_4(OAsPh_3)_4$]: Crystal structures of [UX_2L_4][BPh_4]$_2$ (L = tris(pyrrolidine-1-yl)phosphine oxide, X = Br or I). *Dalton Trans.* **1991**, 2585–2593. [CrossRef]

37. Zych, E.; Starynowicz, P.; Lis, T.; Drozdzynski, J. Crystal structure and spectroscopic properties of ammonium bis(acetonitrile)pentaaquadibromouranium dibromide. *Polyhedron* **1993**, *12*, 1661–1667. [CrossRef]

38. Berthet, J.-C.; Siffredi, G.; Thuéry, P.; Ephritikhine, M. Controlled chemical reduction of uranyl salts into $UX_4(MeCN)_4$ (X = Cl, Br, I) with Me_3SiX reagents. *Eur. J. Inorg. Chem.* **2007**, *2007*, 4017–4020. [CrossRef]

39. Caira, M.R.; de Wet, J.F.; Du Preez, J.G.H.; Gellatly, B.J. The crystal structures of hexahalouranates. I. Bis(triphenylethylphosphonium) hexachlorouranate(IV) and bis(triphenylethylphosphonium) hexabromouranate(IV). *Acta Crystallogr. B* **1978**, *34*, 1116–1120. [CrossRef]

40. Schnaars, D.D.; Wu, G.; Hayton, T.W. Reactivity of UH_3 with mild oxidants. *Dalton Trans.* **2008**, 6121–6126. [CrossRef] [PubMed]

41. Bombieri, G.; Benetollo, F.; Bagnall, K.W.; Plews, M.J.; Brown, D. Triphenylphosphine oxide complexes of actinide tetrahalides. Crystal and molecular structure of *trans*-tetrabromobis(triphenylphosphine oxide)uranium(IV). *Dalton Trans.* **1983**, 343–348. [CrossRef]

42. De Wet, J.F.; Caira, M.R. Structure and bonding in octahedral uranium(IV) complexes of the type $UX_4 \cdot 2L$ (X = halogen, L = unidentate, neutral oxygen donor). Part 1. The crystal structures of tetrabromobis(*NN*′-dimethyl-*NN*′-diphenylurea)uranium(IV) and α- and β-tetrachlorobis (*NN*′-dimethyl-*NN*′-diphenylurea)uranium(IV). *Dalton Trans.* **1986**, 2035–2041. [CrossRef]

43. De Wet, J.F.; Caira, M.R. Structure and bonding in octahedral uranium(IV) complexes of the type $UX_4 \cdot 2L$ (X = halogen, L = unidentate, neutral oxygen donor). Part 2. The crystal structures of tetrachlorobis[tris(pyrrolidinyl)phosphine oxide]-, tetrachlorobis (di-isobutyl sulphoxide)-, and tetrabromobis(triphenylarsine oxide)-uranium(IV). *Dalton Trans.* **1986**, 2043–2048. [CrossRef]

44. Kepert, D.; Patrick, J.; White, A. Structure and stereochemistry in "f-block" complexes of high coordination number. VI. Crystallographic characterizations of bis[(1,1-dimethyl-3-oxobutyl)triphenyl-phosphonium] hexabromouranate(IV) and tetrabromobis[ethane-1,2-diylbis(diphenylarsine) oxide]uranium(IV). *Aust. J. Chem.* **1983**, *36*, 469–476.

45. Jantunen, K.C.; Batchelor, R.J.; Leznoff, D.B. Synthesis, characterization, and organometallic derivatives of diamidosilyl ether thorium(IV) and uranium(IV) halide complexes. *Organometallics* **2004**, *23*, 2186–2193. [CrossRef]

46. Evans, W.J.; Miller, K.A.; Ziller, J.W.; Greaves, J. Analysis of uranium azide and nitride complexes by atmospheric pressure chemical ionization mass spectrometry. *Inorg. Chem.* **2007**, *46*, 8008–8018. [CrossRef] [PubMed]

47. Dietrich, H.M.; Ziller, J.W.; Anwander, R.; Evans, W.J. Reactivity of $(C_5Me_5)_2UMe_2$ and $(C_5Me_5)_2UMeCl$ toward group 13 alkyls. *Organometallics* **2009**, *28*, 1173–1179. [CrossRef]

48. Thomson, R.K.; Graves, C.R.; Scott, B.L.; Kiplinger, J.L. Noble reactions for the actinides: Safe gold-based access to organouranium and azido complexes. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1451–1455. [CrossRef]

49. Thomson, R.K.; Graves, C.R.; Scott, B.L.; Kiplinger, J.L. Straightforward and efficient oxidation of tris(aryloxide) and tris(amide) uranium(III) complexes using copper(I) halide reagents. *Inorg. Chem. Commun.* **2011**, *14*, 1742–1744. [CrossRef]

50. Thomson, R.K.; Graves, C.R.; Scott, B.L.; Kiplinger, J.L. Uncovering alternate reaction pathways to access uranium(IV) mixed-ligand aryloxide-chloride and alkoxide-chloride metallocene complexes: Synthesis and molecular structures of $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(Cl)$ and $(C_5Me_5)_2U(O\text{-}^tBu)(Cl)$. *Inorg. Chim. Acta* **2011**, *369*, 270–273. [CrossRef]

51. Graves, C.R.; Yang, P.; Kozimor, S.A.; Vaughn, A.E.; Clark, D.L.; Conradson, S.D.; Schelter, E.J.; Scott, B.L.; Thompson, J.D.; Hay, P.J.; *et al.* Organometallic uranium(V)-imido halide complexes: From synthesis to electronic structure and bonding. *J. Am. Chem. Soc.* **2008**, *130*, 5272–5285. [CrossRef] [PubMed]

52. Gowda, B.T.; Foro, S.; Shakuntala, K. Potassium *N*-bromo-4-chlorobenzenesulfonamidate monohydrate. *Acta Crystallogr. E* **2011**, *67*, m962. [CrossRef] [PubMed]

53. Tonshoff, C.; Merz, K.; Bucher, G. Azidocryptands—Synthesis, structure, and complexation properties. *Org. Biomol. Chem.* **2005**, *3*, 303–308. [CrossRef] [PubMed]

54. Mahoney, J.M.; Nawaratna, G.U.; Beatty, A.M.; Duggan, P.J.; Smith, B.D. Transport of alkali halides through a liquid organic membrane containing a ditopic salt-binding receptor. *Inorg. Chem.* **2004**, *43*, 5902–5907. [CrossRef] [PubMed]

55. Jaroschik, F.; Nief, F.; le Goff, X.-F.; Ricard, L. Isolation of stable organodysprosium(II) complexes by chemical reduction of dysprosium(III) precursors. *Organometallics* **2007**, *26*, 1123–1125. [CrossRef]

56. Fender, N.S.; Fronczek, F.R.; John, V.; Kahwa, I.A.; McPherson, G.L. Unusual luminescence spectra and decay dynamics in crystalline supramolecular $[(A18C6)_4MBr_4][TlBr_4]_2$ (A = Rb, K; M = 3d element) complexes. *Inorg. Chem.* **1997**, *36*, 5539–5547. [CrossRef]

57. Danis, J.A.; Lin, M.R.; Scott, B.L.; Eichhorn, B.W.; Runde, W.H. Coordination trends in alkali metal crown ether uranyl halide complexes: The series $[A(Crown)]_2[UO_2X_4]$ where A = Li, Na, K and X = Cl, Br. *Inorg. Chem.* **2001**, *40*, 3389–3394. [CrossRef] [PubMed]

58. Jia, Y.-Y.; Liu, B.; Liu, X.-M.; Yang, J.-H. Syntheses, structures and magnetic properties of two heterometallic carbonates: $K_2Li[Cu(H_2O)_2Ru_2(CO_3)_4X_2]\cdot 5H_2O$ (X = Cl, Br). *CrystEngComm* **2013**, *15*, 7936–7942. [CrossRef]

59. Linti, G.; Li, G.; Pritzkow, H. On The chemistry of gallium: Part 19. Synthesis and crystal structure analysis of novel complexes containing Ga–FeCp(CO)$_2$-fragments. *J. Organomet. Chem.* **2001**, *626*, 82–91. [CrossRef]

60. Wu, F.; Tong, H.; Li, Z.; Lei, W.; Liu, L.; Wong, W.-Y.; Wong, W.-K.; Zhu, X. A white phosphorescent coordination polymer with Cu_2I_2 alternating units linked by benzo-18-crown-6. *Dalton Trans.* **2014**, *43*, 12463–12466. [CrossRef] [PubMed]

61. Gibney, B.R.; Wang, H.; Kampf, J.W.; Pecoraro, V.L. Structural evaluation and solution integrity of alkali metal salt complexes of the manganese 12-metallacrown-4 (12-MC-4) structural type. *Inorg. Chem.* **1996**, *35*, 6184–6193. [CrossRef]

62. Gao, X.; Zhai, Q.-G.; Li, S.-N.; Xia, R.; Xiang, H.-J.; Jiang, Y.-C.; Hu, M.-C. Two anionic $[Cu^I_6X_7]_n^{n-}$ (X = Br and I) chain-based organic–inorganic hybrid solids with *N*-substituted benzotriazole ligands. *J. Solid State Chem.* **2010**, *183*, 1150–1158. [CrossRef]

63. Amo-Ochoa, P.; Jiménez-Aparicio, R.; Perles, J.; Torres, M.R.; Gennari, M.; Zamora, F. Structural diversity in paddlewheel dirhodium(II) compounds through ionic interactions: Electronic and redox properties. *Cryst. Growth Des.* **2013**, *13*, 4977–4985. [CrossRef]

64. Yan, H.; Jang, H.B.; Lee, J.-W.; Kim, H.K.; Lee, S.W.; Yang, J.W.; Song, C.E. A chiral-anion generator: Application to catalytic desilylative kinetic resolution of silyl-protected secondary alcohols. *Angew. Chem. Int.* **2010**, *49*, 8915–8917. [CrossRef] [PubMed]

65. Molcanov, K.; Kojic-Prodic, B.; Babic, D.; Zilic, D.; Rakvin, B. Stabilisation of tetrabromo- and tetrachlorosemiquinone (bromanil and chloranil) anion radicals in crystals. *CrystEngComm* **2011**, *13*, 5170–5178. [CrossRef]

66. Neumüller, B.; Gahlmann, F. Mesityltrifluorogallate. Die kristallstrukturen von Cs[MesGaF$_3$] und K[MesInBr$_3$]. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1897–1904. [CrossRef]

67. Schelter, E.J.; Wu, R.; Scott, B.L.; Thompson, J.D.; Morris, D.E.; Kiplinger, J.L. Mixed valency in a uranium multimetallic complex. *Angew. Chem. Int.* **2008**, *47*, 2993–2996. [CrossRef] [PubMed]

68. Evans, W.J.; Kozimor, S.A.; Hillman, W.R.; Ziller, J.W. Synthesis and structure of the bis(tetramethylcyclopentadienyl)uranium metallocenes $(C_5Me_4H)_2UMe_2$, $(C_5Me_4H)_2UMeCl$, $[(C_5Me_4H)_2U][(\mu-\eta^6:\eta^1-Ph)(\mu-\eta^1:\eta^1-Ph)BPh_2]$, and $[(C_5Me_4)SiMe_2(CH_2CH=CH_2)]_2UI(THF)$. *Organometallics* **2005**, *24*, 4676–4683. [CrossRef]

69. Mehdoui, T.; Berthet, J.-C.; Thuery, P.; Salmon, L.; Riviere, E.; Ephritikhine, M. Lanthanide(III)/actinide(III) differentiation in the cerium and uranium complexes $[M(C_5Me_5)_2(L)]^{0,+}$ (L = 2,2′-bipyridine, 2,2′:6′,2″-terpyridine): Structural, magnetic, and reactivity studies. *Chem. Eur. J.* **2005**, *11*, 6994–7006. [CrossRef] [PubMed]

70. Mehdoui, T.; Berthet, J.-C.; Thuery, P.; Ephritikhine, M. The distinct affinity of cyclopentadienyl ligands towards trivalent uranium over lanthanide ions. evidence for cooperative ligation and back-bonding in the actinide complexes. *Dalton Trans.* **2005**, 1263–1272. [CrossRef] [PubMed]

71. Mehdoui, T.; Berthet, J.-C.; Thuery, P.; Ephritikhine, M. The remarkable efficiency of *N*-heterocyclic carbenes in lanthanide(III)/actinide(III) differentiation. *Chem. Commun.* **2005**, 2860–2862. [CrossRef] [PubMed]

72. Fagan, P.J.; Manriquez, J.M.; Marks, T.J.; Day, C.S.; Vollmer, S.H.; Day, V.W. Synthesis and properties of a new class of highly reactive trivalent actinide organometallic compounds. derivatives of bis(pentamethylcyclopentadienyl)uranium(III). *Organometallics* **1982**, *1*, 170–180. [CrossRef]

73. Cendrowski-Guillaume, S.M.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. New actinide hydrogen transition metal compounds. Synthesis of [K($C_{12}H_{24}O_6$)][(η-C_5Me_5)$_2$(Cl)UH_6Re(PPh_3)$_2$] and the crystal structure of its benzene solvate. *Chem. Commun.* **1994**, 1655–1656. [CrossRef]

74. Evans, W.J.; Kozimor, S.A.; Ziller, J.W. Methyl displacements from cyclopentadienyl ring planes in sterically crowded (C_5Me_5)$_3$M complexes. *Inorg. Chem.* **2005**, *44*, 7960–7969. [CrossRef] [PubMed]

75. Evans, W.J.; Kozimor, S.A.; Ziller, J.W. Bis(pentamethylcyclopentadienyl) U(III) oxide and U(IV) oxide carbene complexes. *Polyhedron* **2004**, *23*, 2689–2694. [CrossRef]

76. Evans, W.J.; Kozimor, S.A.; Ziller, J.W.; Kaltsoyannis, N. Structure, reactivity, and density functional theory analysis of the six-electron reductant, [(C_5Me_5)$_2$U]$_2$(μ-η^6:η^6-C_6H_6), synthesized via a new mode of (C_5Me_5)$_3$M reactivity. *J. Am. Chem. Soc.* **2004**, *126*, 14533–14547. [CrossRef] [PubMed]

77. Evans, W.J.; Nyce, G.W.; Forrestal, K.J.; Ziller, J.W. Multiple syntheses of (C_5Me_5)$_3$U. *Organometallics* **2002**, *21*, 1050–1055. [CrossRef]

78. Roger, M.; Belkhiri, L.; Thuéry, P.; Arliguie, T.; Fourmigué, M.; Boucekkine, A.; Ephritikhine, M. Lanthanide(III)/actinide(III) differentiation in mixed cyclopentadienyl/dithiolene compounds from X-ray diffraction and density functional theory analysis. *Organometallics* **2005**, *24*, 4940–4952. [CrossRef]

79. Arliguie, T.; Lescop, C.; Ventelon, L.; Leverd, P.C.; Thuéry, P.; Nierlich, M.; Ephritikhine, M. C–H and C–S bond cleavage in uranium(III) thiolato complexes. *Organometallics* **2001**, *20*, 3698–3703. [CrossRef]

80. Boisson, C.; Berthet, J.C.; Ephritikhine, M.; Lance, M.; Nierlich, M. Synthesis and crystal structure of [U(η-C_5Me_5)$_2$(OC_4H_8)$_2$][BPh_4], the first cationic cyclopentadienyl compound of uranium(III). *J. Organomet. Chem.* **1997**, *533*, 7–11. [CrossRef]

81. Manriquez, J.M.; Fagan, P.J.; Marks, T.J.; Vollmer, S.H.; Day, C.S.; Day, V.W. Pentamethylcyclopentadienyl organoactinides. trivalent uranium organometallic chemistry and the unusual structure of bis(pentamethylcyclopentadienyl)uranium monochloride. *J. Am. Chem. Soc.* **1979**, *101*, 5075–5078. [CrossRef]

82. Fulmer, G.R.; Miller, A.J.M.; Sherden, N.H.; Gottlieb, H.E.; Nudelman, A.; Stoltz, B.M.; Bercaw, J.E.; Goldberg, K.I. NMR chemical shifts of trace impurities: Common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist. *Organometallics* **2010**, *29*, 2176–2179. [CrossRef]

83. Lalancette, J.M.; Rollin, G.; Dumas, P. Metals intercalated in graphite. I. Reduction and oxidation. *Can. J. Chem.* **1972**, *50*, 3058–3062. [CrossRef]

84. Bergbreiter, D.E.; Killough, J.M. Reactions of potassium-graphite. *J. Am. Chem. Soc.* **1978**, *100*, 2126–2134. [CrossRef]

85. 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. [CrossRef] [PubMed]

86. APEX II 1.08, Bruker AXS, Inc. Madison, WI, USA, 2004. 53719.

87. SAINT+ 7.06, Bruker AXS, Inc. Madison, WI, USA, 2003. 53719.

88. SADABAS 2.03, University of Göttingen, Göttingen, Germany, 2001.

89. SHELXTL 5.10, Bruker AXS, Inc. Madison, WI, USA, 1997. 53719.