Electronic Supplementary Information for:

Uranium-Mediated Reductive Conversion of CO_2 to CO and Carbonate in a Single-Vessel, Closed Synthetic Cycle

Anna-Corina Schmidt[†], *Alexey V. Nizovtsev*[†], *Andreas Scheurer*[†], *Frank W. Heinemann*[†] *and Karsten Meyer**[†]

Friedrich-Alexander-University of Erlangen-Nuremberg, Department of Chemistry and Pharmacy, Inorganic Chemistry, Egerlandstr. 1, 91058 Erlangen, Germany.

* karsten.meyer@chemie.uni-erlangen.de

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General Considerations

All air- and moisture-sensitive experiments were performed under dry dinitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox containing an atmosphere of purified dinitrogen. The glovebox is equipped with a –35 °C freezer. Solvents were purified using a two-column solid-state purification system (Glass Contour System, Irvine, CA), transferred to the glovebox without exposure to air, and stored over molecular sieves and sodium (where appropriate). NMR solvents were obtained packaged under argon and stored over activated molecular sieves and sodium (where appropriate) prior to use. Carbon dioxide (99.8%, used as received) and Nitrogen dioxide (99%, used as received) were purchased from Aldrich. ^{1}H NMR spectra were recorded on a JEOL ECX 400 MHz instrument at a probe temperature of 23 °C. Chemical shifts δ, are reported relative to residual ^{1}H resonances of the solvent in ppm.[1] Due to the complexity of the spectra these are shown as images. Electronic absorption spectra were recorded from 250 to 2200 nm (Shimadzu, UV-3600) in the indicated solvent at room temperature. Magnetization data of crystalline powdered samples (20–30 mg) were recorded with a SQUID magnetometer (Quantum Design) at 10 kOe (2–300 K) and values of the magnetic susceptibility were corrected for the underlying diamagnetic increment by using tabulated Pascal constants, and the effect of the blank sample holders (gelatin capsule/straw). Samples used for magnetization measurement were recrystallized multiple times and checked for chemical composition and purity by elemental analysis (C, H, and N) and ^{1}H NMR spectroscopy. Data reproducibility was carefully checked on three independently synthesized and measured samples. Elemental analyses were obtained using Euro EA 3000 (Euro Vector) and EA 1108 (Carlo-Erba) elemental analyzers in the Chair of Inorganic and General Chemistry at the University Erlangen-Nuremberg (Erlangen, Germany).

Complex Nomenclature Scheme

For clarity, some neopentyl groups are omitted, but are abbreviated with Neop.

[((${}^{\mathrm{Neop,Me}}$ArO)$_3$tacn)U$^{\mathrm{III}}$] (3).

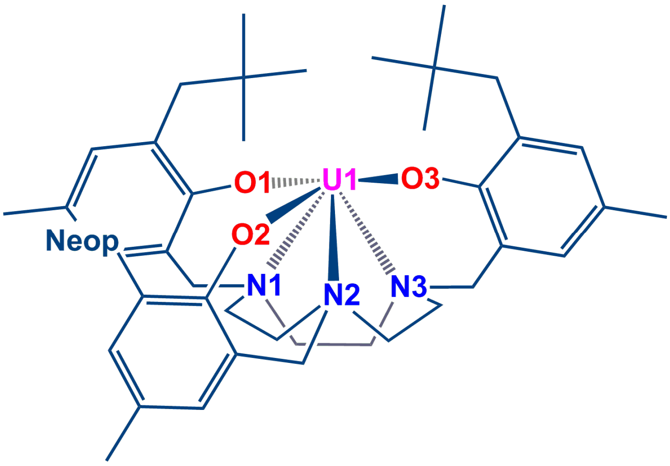


Fig. 1 Labeling of heteroatoms in **3.**

[{((${}^{\mathrm{Neop,Me}}$ArO)$_3$tacn)U$^{\mathrm{IV}}$}$_2$(μ-O)] (4).

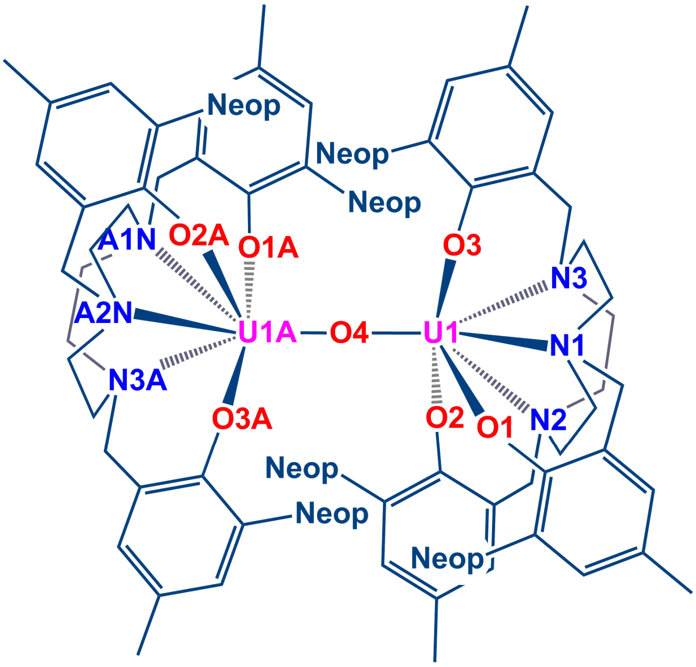


Fig. 2 Labeling of heteroatoms in **4.**

$[\{((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}^{\mathrm{IV}}\}_2\text{-}(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}\mathrm{CO}_3)]$ (5).

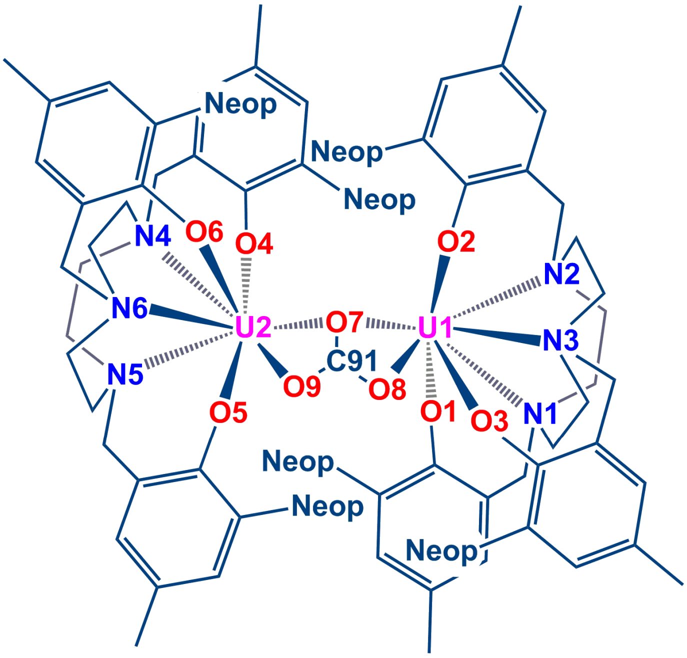


Fig. 3 Labeling of heteroatoms in **5.**

$\{[((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}(\kappa^2\text{-}\mathrm{CO}_3)]\mathrm{K}\}_4$ (6)

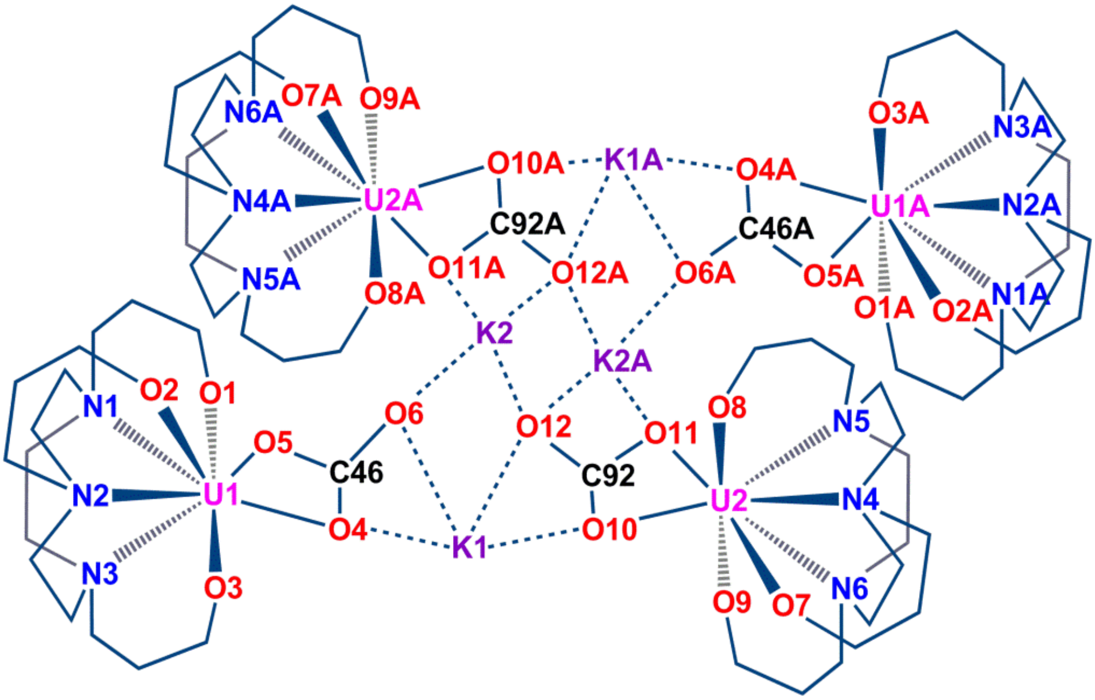
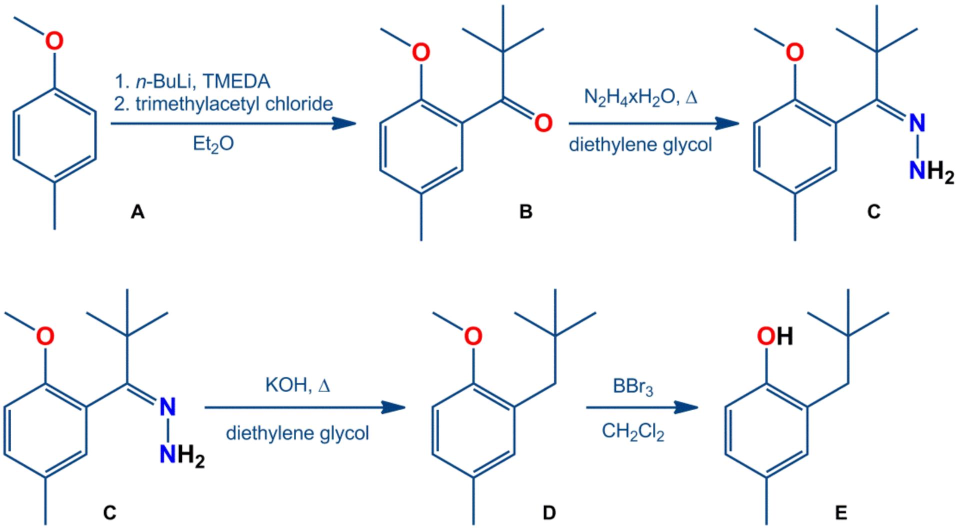


Fig. 4 Labeling of special atoms in **6**. For clarity, parts of the phenolate groups with substituents are omitted.

Synthetic and Spectroscopic Details

4-Methyl-2-neopentylphenol (E)

The phenol $^{\mathrm{Neop,Me}}$ArOH was synthesized in a four-step sequence, starting from 4-methylanisole (**A**) (in comparison to previously reported ligands of our group, 4-methylanisole (**A**) was chosen instead of 4-*tert*-butylanisole in order to decrease solubility of the uranium complexes). The *ortho* lithiation of **A** and subsequent reaction with pivaloyl chloride afforded the corresponding ketone **B**, which was converted *via* hydrazone **C** by Wolff-Kishner reduction (**D**) and removal of the ether protecting group to the desired $^{\mathrm{Neop,MeAr}}$OH (**E**; Scheme 1). Similarly to previously reported ligands, the hexadendate ligand ($^{\mathrm{Neop,Me}}$ArOH)$_3$tacn was obtained *via* Mannich condensation of triazacyclononane, paraform-aldehyde, and $^{\mathrm{Neop,Me}}$ArOH under slightly acidic conditions (Scheme 2).[2]



Scheme 1 Four-step reaction sequence for the synthesis of $^{\mathrm{Neop,Me}}$ArOH (**E**) starting from *p*-methylanisole (**A**).

1-(2-Methoxy-5-methylphenyl)-2,2-dimethylpropan-1-one (B)

Under N_2 atmosphere, 4-methylanisole (**A**) (25.00 mL, 24.2 g, 198.0 mmol) and TMEDA (49.00 mL, 48.02 g, 398.2 mmol) were dissolved in 400 mL abs. ether. The solution was cooled down to –35 °C and *n*-BuLi (100.0 mL, 2.5 M in *n*-hexane, 250.0 mmol) was added rapidly within 6 minutes. The solution was allowed to warm to room temperature and stirred for 5 hours. The pale-yellow solution was cooled down again to –65 °C and trimethylacetyl chloride (46 mL, 35.65 g, 306.8 mmol), dissolved in 150 mL ether, was added within 15 minutes; during addition, the temperature of the reaction mixture should not rise above –60 °C. After complete addition, the solution was warmed to room temperature and stirred for a further 7 hours. Finally, the yellow reaction mixture was quenched by addition of 100 mL of brine and 100 mL of saturated NH_4Cl solution. The collected aqueous phases were washed 3 times with 200 mL ether. The combined organic phases were washed with brine (100 mL) and saturated NH_4Cl solution (100 mL), dried over Na_2SO_4, and the volatiles were evaporated to afford a yellow-brown oil. The oil was chromatographed through a short-plug column of silica (*n*-hexane:ethyl acetate 30:1) to yield a colorless crystalline solid **B** (37.9 g, 183.5 mmol, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.12$ (dd, $^3J = 8.3$ Hz, $^4J = 2.2$ Hz, 1H), 6.82 (d, $^4J = 2.2$ Hz, 1H), 6.79 (d, $^3J = 8.3$ Hz, 1H), 3.78 (s, 3H), 2.29 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 214.2$, 153.1, 131.0, 130.1, 129.5, 126.7, 110.8, 55.4, 44.8, 26.8, 20.4.

EA [$C_{13}H_{18}O_2$, M = 206.28 g/mol]: (calculated) C 75.69%, H 8.80%; (found) C 75.75%, H 9.10%.

(1-(2-Methoxy-5-methylphenyl)-2,2-dimethylpropylidene)hydrazine (C)

B (75.66 g, 0.367 mol) and hydrazine monohydrate (172.4 g, 5.38 mol) were dissolved in 500 mL diethylene glycol and stirred under reflux for 20 hours. After cooling to room temperature the solution was diluted with 400 mL water. KOH (152.2 g, 2.71 mol), dissolved in 1 L of water, was added to the yellowish solution followed by additions of ether (150 mL) and *n*-pentane (150 mL). The aqueous phase was washed 3 times with a mixture of ether and *n*-pentane (1 : 1). The combined organic phases were washed with water and brine, dried over Na_2SO_4, and the volatiles were removed. The obtained yellow-brown oil was dissolved in 50 mL of *n*-hexane and cooled to –40 °C to yield colorless crystals of **C**. After filtration and washing of the first crop of **C**, the filtrate was partially concentrated under vacuum and cooled to –40 °C to yield another batch of **C**. Yield: 42.04 g 190.8 mmol, 52%.

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.14$ (dd, $^3J = 8.5$ Hz, $^4J = 1.9$ Hz, 1H), 6.87 (d, $^3J = 8.5$ Hz, 1H), 6.77 (d, $^4J = 1.9$ Hz, 1H), 4.82 (s, 2H), 3.76 (s, 3H), 2.30 (s, 3H), 1.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.9$, 153.9, 130.2, 130.0, 129.9, 122.4, 111.0, 55.4, 37.9, 28.3, 20.5.

EA [$C_{13}H_{20}N_2O$, M = 220.31 g/mol]: (calculated) C 70.87%, H 9.15%, N 12.72%; (found) C 71.04%, H 9.26%, N 12.68%.

1-Methoxy-4-methyl-2-neopentylbenzene (D)

C (42.05 g, 0.190 mol), KOH (71.82 g, 1.280 mol), and 600 mL diethylene glycol were placed in a three-neck flask equipped with an effective magnetic stirrer, a reflux condenser, a thermometer, and a Dean-Stark trap with an additional reflux condenser. The reaction vessel was heated to 190-205 °C for 3 hours. The yellowish reaction mixture was refluxing during that period, but the internal temperature slowly decreased due to water formation. When the temperature fell below 200 °C, the outlet of the condenser, connected to the three-neck flask, was closed by a stopper. This resulted in a water collection in the Dean-Stark trap and an increase of the temperature of the reaction mixture. When the temperature again reached 205 °C, the outlet of the condenser could be opened. After 4 hours of further reflux, the black reaction mixture was cooled to room temperature, transferred into a separatory funnel together with the Dean-Stark trap content, water (400 mL) and *n*-pentane (200 mL). The separated aqueous phase was washed 4 times with *n*-pentane. The combined organic phases were washed 3 times with water and brine, dried over Na_2SO_4, and evaporated to yield a dark-brown oil **D** which was used for the next step without further purification. Yield: 15.31 g, 79.6 mmol, 42%.

^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.04$ (dd, $^3J = 8.3$ Hz, $^4J = 1.8$ Hz, 1H), 6.96 (d, $^4J = 1.8$ Hz, 1H), 6.82 (d, $^3J = 8.3$ Hz, 1H), 3.81 (s, 3H), 2.59 (s, 2H), 2.34 (s, 3H), 0.98 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 133.1, 128.7, 128.1, 127.2, 110.2, 55.2, 42.6, 32.4, 29.5, 20.5.

4-Methyl-2-neopentylphenol (E)

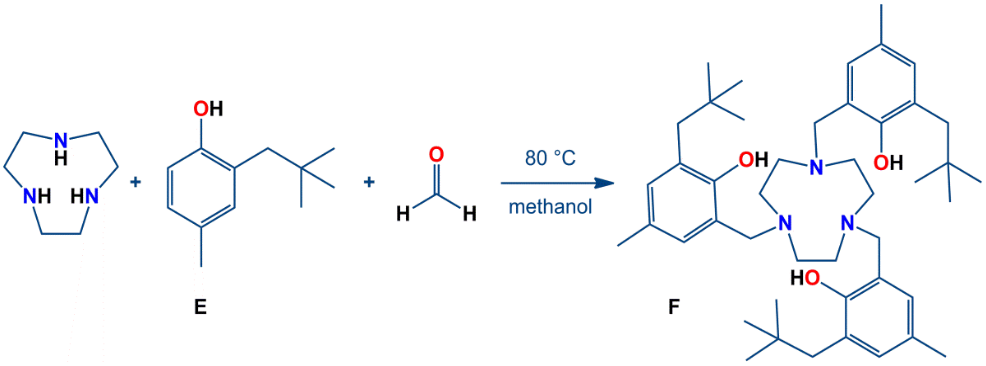
D (16.94 g, 88.1 mmol) was dissolved in 200 mL absolute dichloromethane and cooled to 10 °C. To that brown solution boron tribromide (100 mL, 1.00 mol, 1 M in dichloromethane) was added in one portion. The reaction mixture was stirred at room temperature for 18 hours and poured onto ice (400 g). The aqueous phase was washed 3 times with dichloromethane. The combined organic phases were dried with Na_2SO_4, and concentrated *in vacuo* to give a dark-brown oil. For further purification the oil was distilled *in vacuo* (T = 120 °C/0.05 mbar) to yield **E** as a colorless solid. Yield: 15.39 g, 0.086 mol, 98%.

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.90$ (dd, $^3J = 7.9$ Hz, $^4J = 2.0$ Hz, 1H), 6.88 (d, $^4J = 2.0$ Hz, 1H), 6.70 (d, $^3J = 7.9$ Hz, 1H), 4.54 (s, 1H), 2.50 (s, 2H), 2.28 (s, 3H), 0.97 (s, 9H).

^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 151.8$, 133.3, 129.2, 127.7, 125.3, 115.2, 43.1, 32.6, 29.5, 20.6.

EA [$C_{12}H_{18}O$, M = 178.27 g/mol]: (calculated) C 80.85%, H 10.18%; (found) C 81.07%, H 10.47%.

6,6´,6´´-(1,4,7-Triazonane-1,4,7-triyl)tris(methylene)tris(4-methyl-2-neopentylphenol) (F)



Scheme 2 Synthesis of the neopentyl-substituted chelator ($^{\text{Neop,Me}}$ArOH)$_3$tacn (**F**).

Paraformaldehyde (0.44 g, 14.7 mmol) and tacn (0.58 g, 4.5 mmol) were dissolved in 10 mL methanol and stirred under reflux for 2 hours. The yellow solution was cooled to room temperature and $^{\text{Neop,Me}}$ArOH (**E**) (4.14 g, 23.2 mmol), dissolved in 7 mL methanol, was added. The orange solution was refluxed for 60 hours. The obtained emulsion was cooled to 0 °C to form a pale-brown precipitate. The solid was filtered off, taken up in methanol (100 mL), and treated in an ultrasonic bath. This procedure was repeated two times. Finally, the precipitate was filtered off, washed with small amounts of cold acetonitrile, and dried *in vacuo* to yield **F** as a white powder. Yield: 1.30 g (1.86 mmol, 41%).

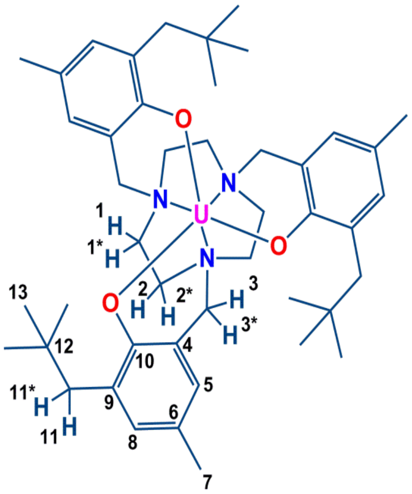
^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.81 (s, 3H), 6.84, 6.62 (s, 6H), 3.66 (s, 6H), 2.81 (s, 12H), 2.55 (s, 6H), 2.22 (s, 9H), 0.97 (s, 27H).

^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 153.6, 132.6, 127.6, 127.0, 126.6, 121.5, 62.8, 55.3, 42.2, 32.7, 29.6, 20.5.

EA [$C_{45}H_{69}N_3O_3$, M = 700.05 g/mol]: (calculated) C 77.13%, H 9.86%, N 5.99%; (found) C 77.25%, H 9.78%, N 6.02%.

Synthesis of [(($^{\text{Neop,Me}}$ArO)$_3$tacn)U$^{\text{III}}$] (3).

A 500 mL round-bottom flask was charged with ($^{\text{Neop,Me}}$ArOH)$_3$tacn (1.00 g, 1.43 mmol) in *n*-hexane (200 mL). While stirring, 1.03 g (1.43 mmol, 1.0 eq.) [((Me$_3$Si)$_2$N)$_3$U], dissolved in 200 mL *n*-hexane, was added dropwise to the colorless solution, resulting in a color change to red-brown. The reaction was stirred for ten minutes, and then filtered over celite. The volatiles were removed *in vacuo*, dissolved in benzene (100 mL) and lyophilized to give 1.21 g (1.30 mmol, 91%) of **3** as a red-brown solid.



^{1}H NMR (400 MHz, C_6D_6): δ = 21.39, –1.93, –3.99, –12.23, –18.48, –22.40 (s, 18H, **1**, **1***, **2**, **2***, **3**, **3***), 11.82, 8.83 (s, 6H, **5**, **8**), 7.06, 5.70 (s, 6H, **11**, **11***), 2.97 (s, 9H, **7**), 2.39 (s, 27H, **13**).

^{13}C NMR (100 MHz, toluene-d_8): δ = 174.9 (3C, **10**), 144.5, 136.3, 134.7, 128.9, 119.8, 117.4, 48.7, 30.4, 26.4, 16.4, 2.19 (42C, **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **11**, **12**, **13**).

EA [$C_{45}H_{66}N_3O_3U$, M = 935.05 g/mol]: (calculated) C 57.80%, H 7.11%, N 4.49%; (found) C 57.94%, H 7.26%, N 4.46%.

Synthesis of [{(($^{\text{Neop,Me}}$ArO)$_3$tacn)U$^{\text{IV}}$}$_2$(μ-O)] (4).

A 20 mL scintillation vial was charged with [(($^{\text{Neop,Me}}$ArO)$_3$tacn)U$^{\text{III}}$] (**3**) (0.100 g, 0.107 mmol) in 15 mL *n*-hexane. While stirring, N_2O was initiated into the red-brown solution, resulting in an extreme color change yielding a green suspension with a light-green precipitate. The reaction was stirred for 10 minutes. The precipitate was filtered off and dried *in vacuo* to give 0.0538 g (0.029 mmol, 52%) of **4** as a light-green solid.

^{1}H NMR (400 MHz, C_6D_6): δ = 122.31, 66.94, 64.64, 20.88, 3.86, 0.30, −2.40, −6.59, −10.14, −20.54, −32.62, −37.55, −102.53.

EA [$C_{90}H_{132}N_6O_7U_2$, M = 1886.10 g/mol]: (calculated) C 57.31%, H 7.05%, N 4.46%; (found) C 56.97%, H 6.94%, N 4.28%.

Synthesis of $[\{((^{Neop,Me}ArO)_3tacn)U^{IV}\}_2(\mu\text{-}CO_3)]$ (5).

A 20 mL scintillation vial was charged with $[((^{Neop,Me}ArO)_3tacn)U^{III}]$ (**3**) (0.304 g, 0.325 mmol) in 15 mL *n*-hexane. While stirring, CO_2 was initiated into the red-brown solution, resulting in an extreme color change yielding a light-green suspension and a colorless precipitate. The reaction was stirred 10 minutes. The precipitate was filtered and dried *in vacuo* to give 0.184 g (0.095 mmol, 59%) of **5** as a colorless solid.

^1H NMR (400 MHz, C_6D_6): $\delta = 42.76, 37.46, 30.45, 27.27, 21.80, 11.05, 6.42, 0.01, -2.35, -4.71, -7.85, -12.90, -16.92, -41.32, -49.12, -59.59, -79.98$.

EA [$C_{91}H_{132}N_6O_9U_2$, M = 1930.11 g/mol]: (calculated) C 56.63%, H 6.89%, N 4.35%; (found) C 56.78%, H 6.91%, N 4.29%.

Reaction conditions for the sequential, synthetic cycle.

In a 20 mL scintillation vial $[((^{Neop,Me}ArO)_3tacn)U^{III}]$ (**3**) (0.100 g, 0.107 mmol) was dissolved in 20 mL benzene. While stirring, CO_2 was initiated into the red-brown suspension, resulting in an extreme color change yielding a light-green solution after a short period of time. After one hour, 0.050 g (0.37 mmol) KC_8 was added and the reaction was stirred for 12 hours, which led to a red-brown suspension. The suspension was filtered through celite to filter off the graphite, excess of KC_8, and free K_2CO_3. This cycle can be repeated under the present, non-optimized conditions five times with decreasing content of complex **3** (because of non-quantitative yields of **5**).

Reaction conditions for a one-pot synthetic cycle and synthesis of $\{[((^{Neop,Me}ArO)_3tacn)U\text{-}(\kappa^2\text{-}CO_3)]K\}_4$ (6).

A 20 mL scintillation vial was charged with $[((^{Neop,Me}ArO)_3tacn)U^{III}]$ (**3**) (0.100 g, 0.107 mmol) and 0.200 g (1.48 mmol) KC_8 in 20 mL benzene. While stirring, CO_2 was initiated into the red-brown suspension over two hours, resulting in a color change yielding a green suspension after stirring over night. The suspension was filtered through celite and dried *in vacuo.* The solid was washed with 5 ml benzene to give to give 0.037 g (0.0085 mmol, 32) of **6** as a green solid. Crystals were obtained by slow evaporation of a solution of **6** in benzene.

^1H NMR (400 MHz, C_6D_6): $\delta = 33.40, 29.68, 25.46, 18.08, 14.20, 3.91, -2.40, -14.58, -30.27, -40.95$.

EA [$C_{184}H_{264}K_4N_{12}O_{24}U_4 \cdot 2.5\ C_6H_6$, M = 4331.92 g/mol]: (calculated) C 55.17%, H 6.49%, N 3.88%; (found) C 55.24%, H 6.60%, N 3.74%.

^{1}H NMR spectra

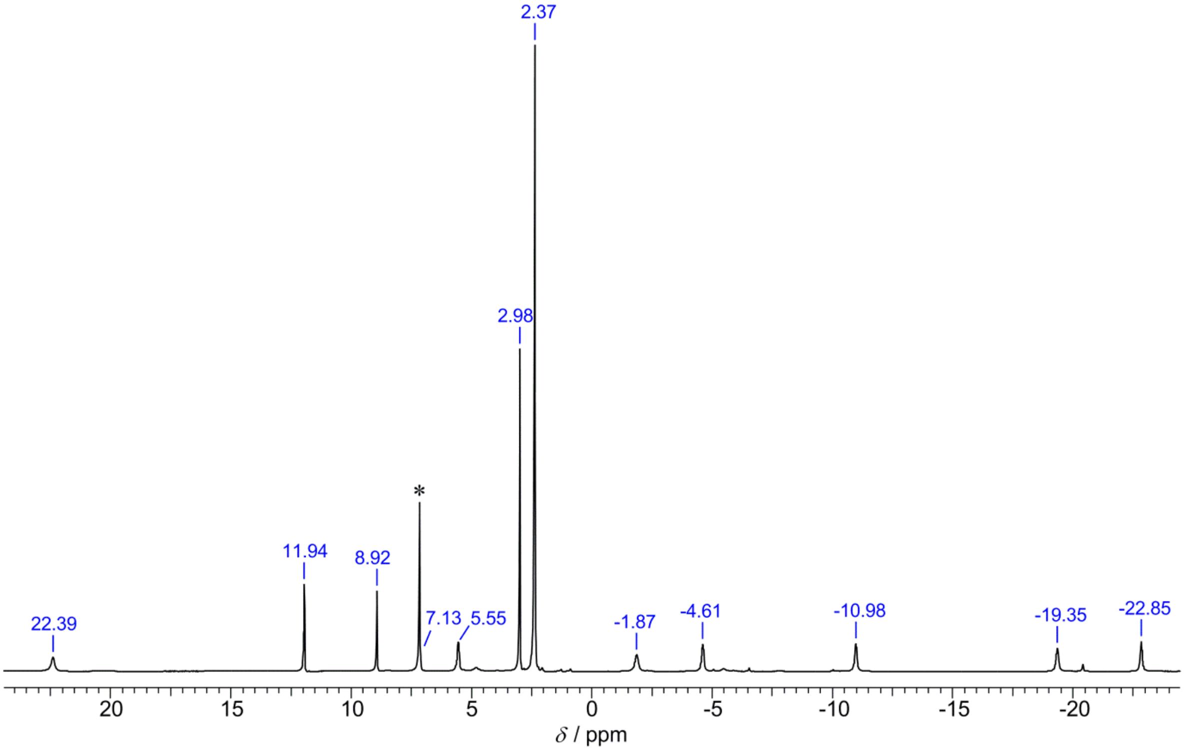


Figure 1 ^{1}H NMR of **3** (400 MHz, C_6D_6).

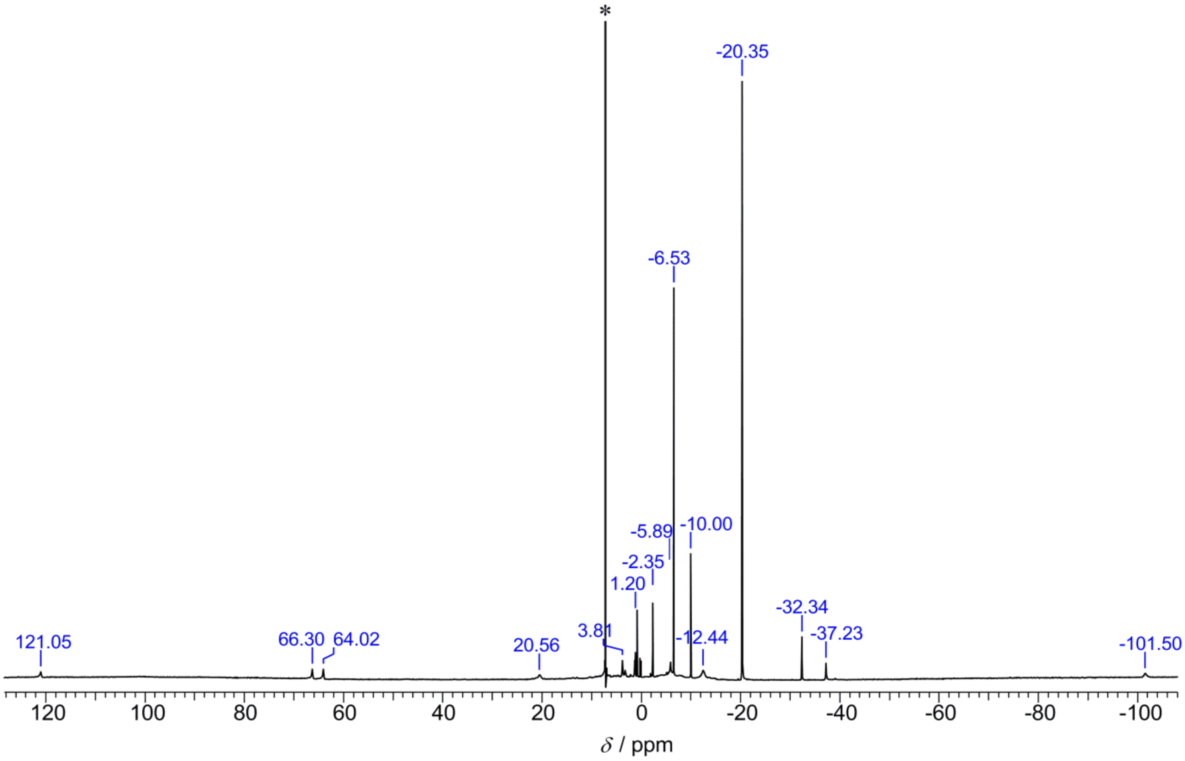


Figure 2 ^{1}H NMR of **4** (400 MHz, C_6D_6).

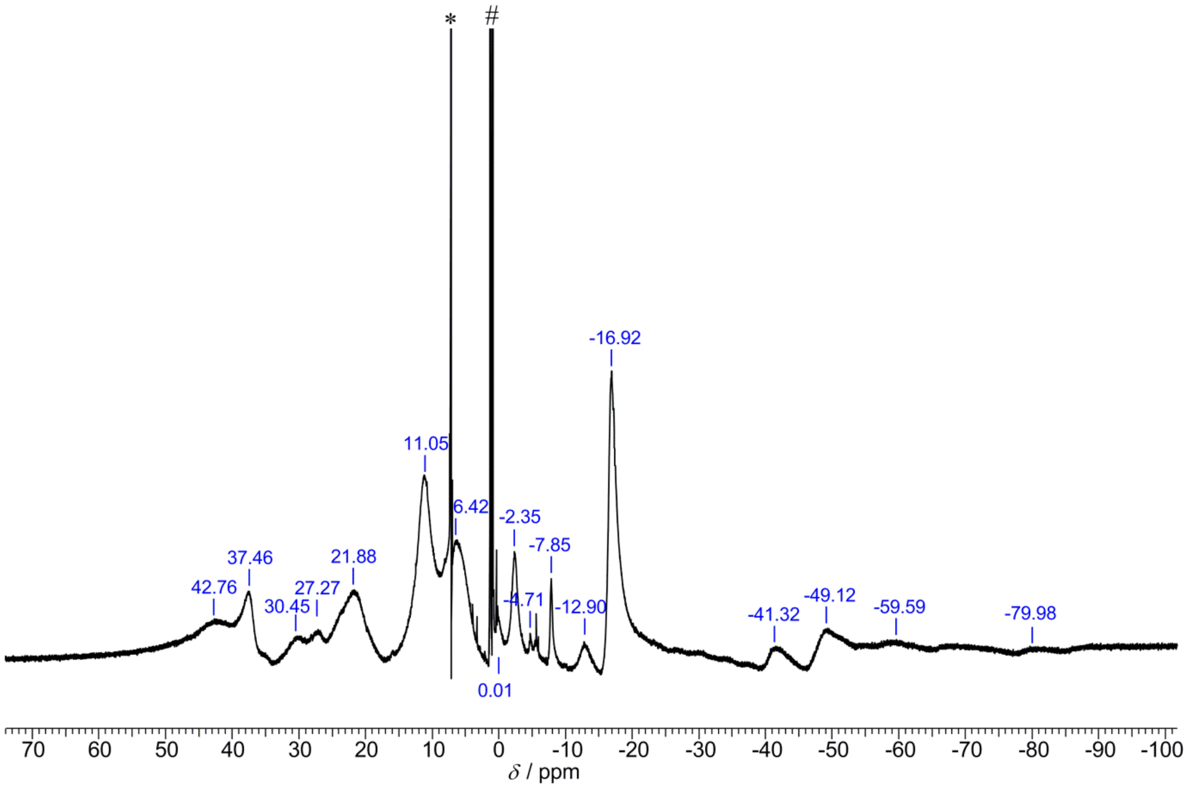


Figure 3 ^{1}H NMR of **5** (400 MHz, C_6D_6, # *n*-hexane).

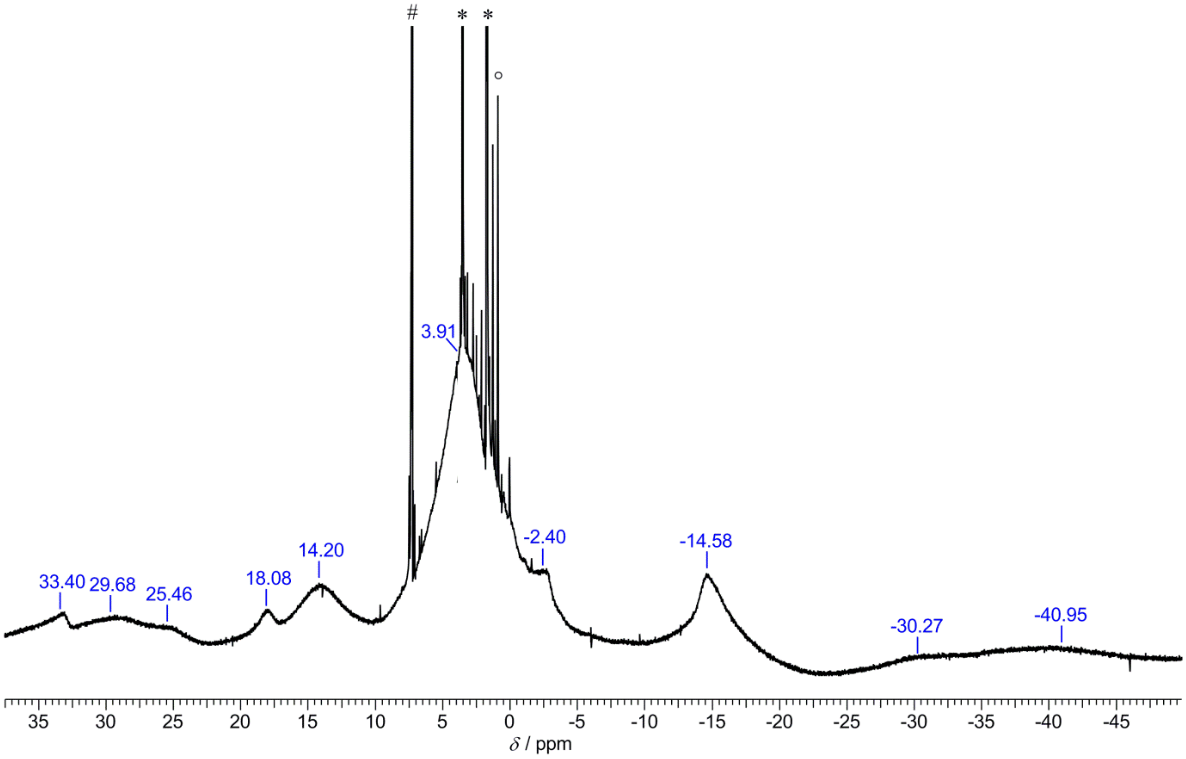


Figure 4 ^{1}H NMR of **6** (400 MHz, THF-d_8, # benzene, ° *n*-hexane).

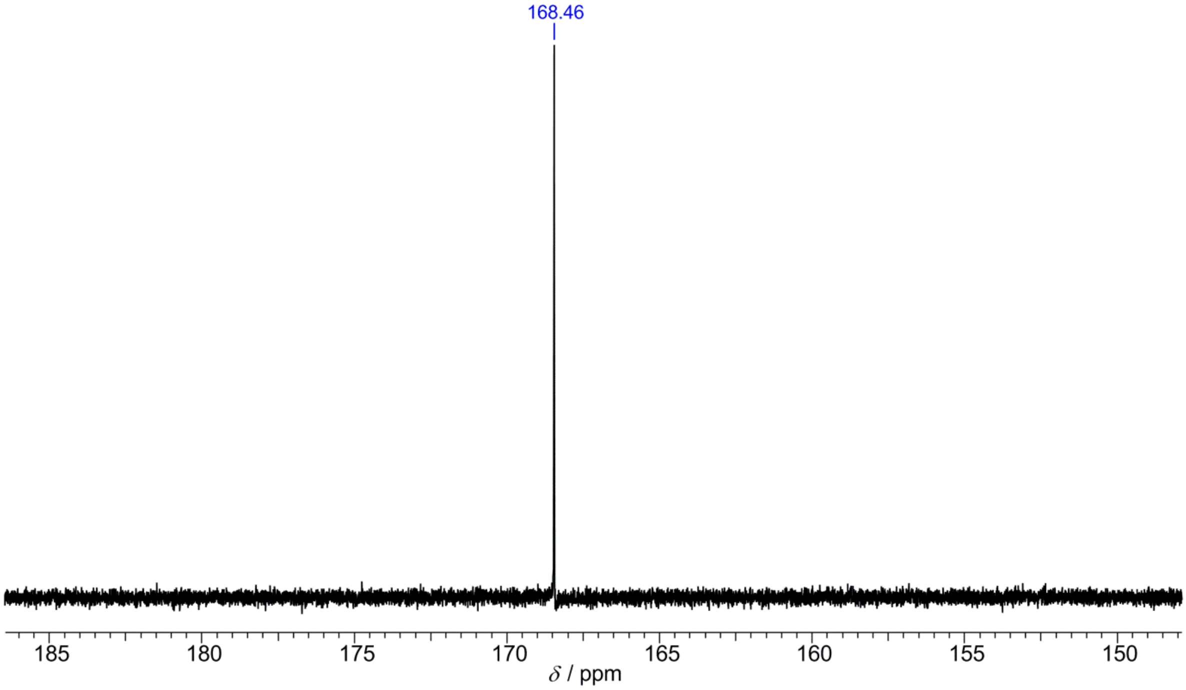


Figure 5 ^{13}C NMR of K_2CO_3 (400 MHz, D_2O).

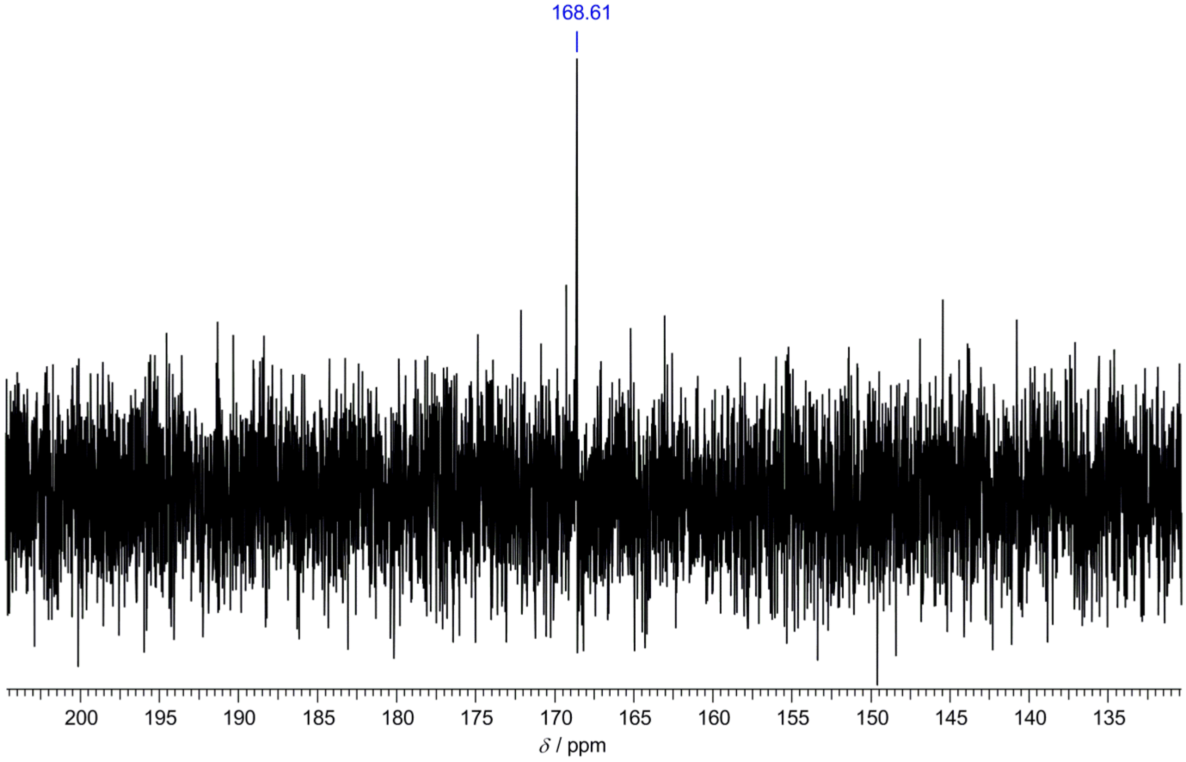


Figure 6 ^{13}C NMR of K_2CO_3 obtained from the cycle (400 MHz, D_2O).

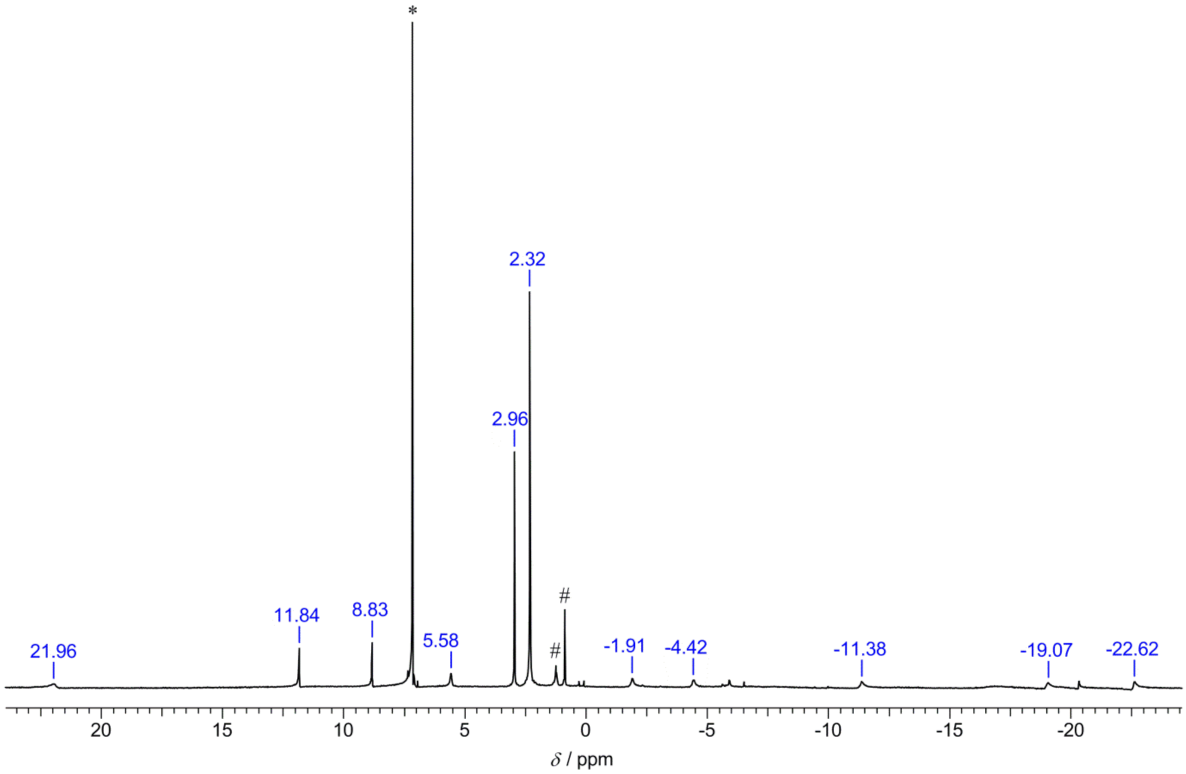


Figure 7 ^{1}H NMR of the reaction mixture (completed cycle of **5** with KC_8 yielding **3**; 400 MHz, C_6D_6, # *n*-hexane).

UV/Vis/NIR

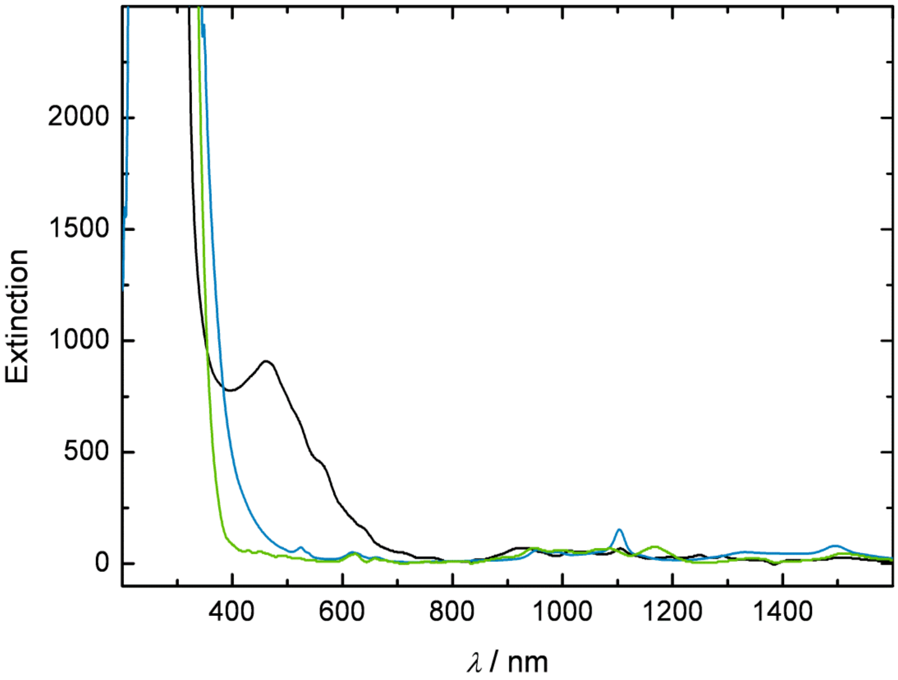


Figure 8 UV/Vis/NIR spectra of **3** in THF with $c = 2.00{\cdot}10^{-4}$ M (black), **4** in THF with $c = 2.00{\cdot}10^{-4}$ M (blue), and **5** in THF with $c = 2.00{\cdot}10^{-4}$ M (green).

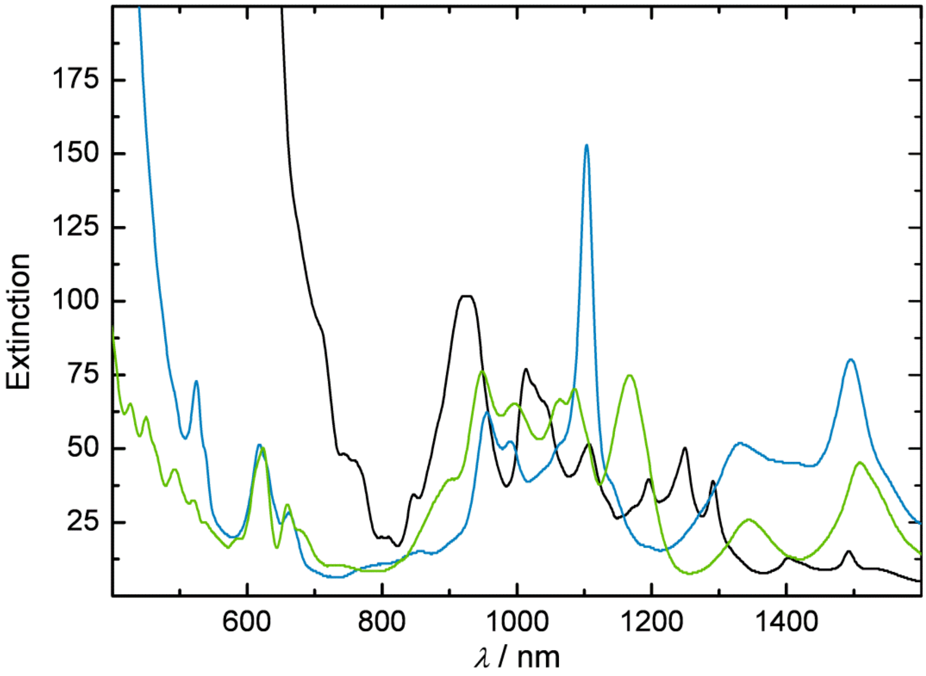


Figure 9 UV/Vis/NIR spectra of **3** in THF with $c = 2.00{\cdot}10^{-3}$ M (black), **4** in THF with $c = 2.00{\cdot}10^{-4}$ M (blue), and **5** in THF with $c = 2.00{\cdot}10^{-3}$ M (green).

SQUID Magnetization

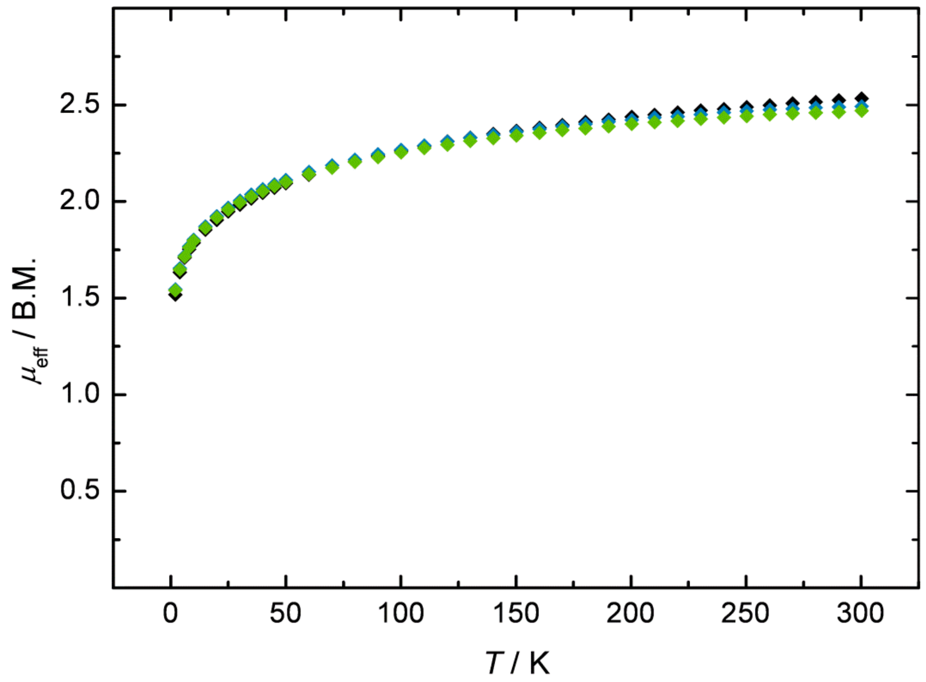


Figure 10 SQUID magnetization measurements of **3**. For reproducibility, three measurements of independently synthesized samples (black, green, blue) are shown.

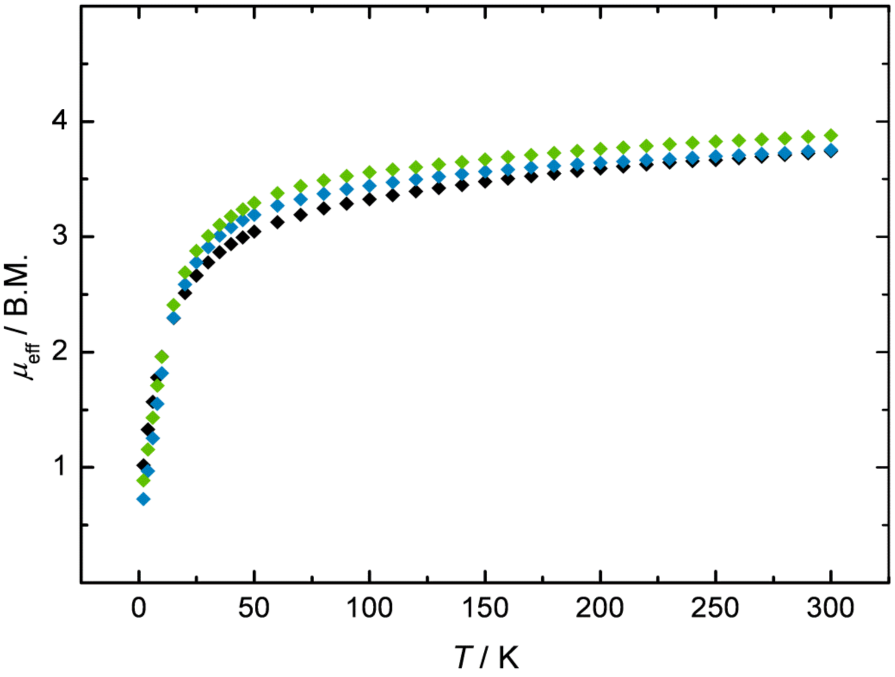


Figure 11 SQUID magnetization measurements of **4**. For reproducibility, three measurements of independently synthesized samples (black, green, blue) are shown.

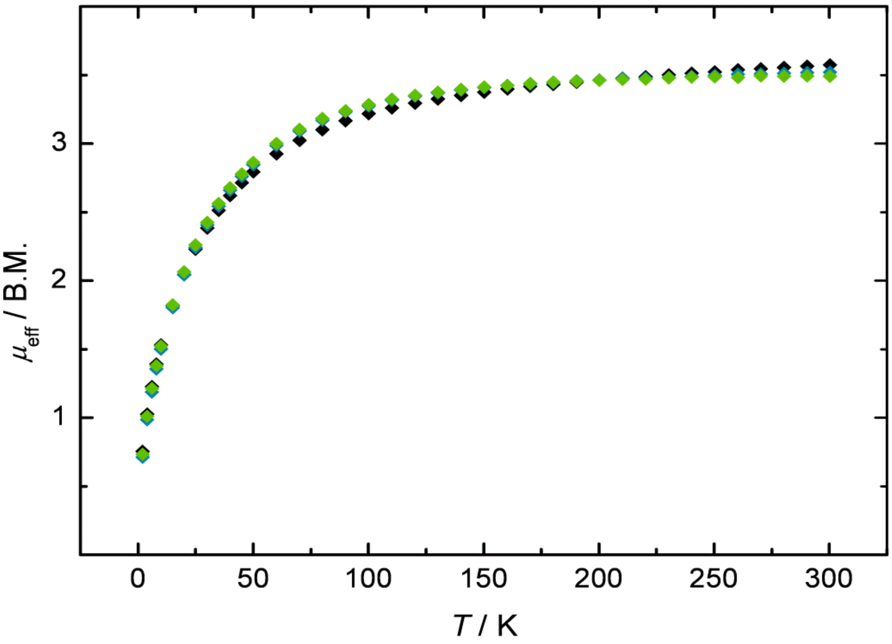


Figure 12 SQUID magnetization measurements of **5**. For reproducibility, three measurements of independently synthesized samples (black, green, blue) are shown.

X-Ray Crystal Structure Determinations

Crystallographic Details for $[\{((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}\}_2\text{-}(\mu\text{-O})]$ · benzene (4 · benzene)

CCDC-886105:

Block-shaped single crystals of the light-green, dinuclear uranium(IV/IV) complex $[\{((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}\}_2\text{-}(\mu\text{-O})]$ (**4**) suitable for X-ray diffraction were obtained from slow diffusion of *n*-hexane into a benzene solution as benzene solvate. A suitable single crystal of approximately 0.16 × 0.14 × 0.08 mm size was coated with protective perfluoropolyether oil and mounted on a MiTeGen micromount. Intensity data were collected at 100 K on a Bruker Kappa APEX 2 *iμS* duo diffractometer using Mo*K*α radiation ($\lambda = 0.71073$ Å) and QUAZAR focussing Montel optics. Data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied on the basis of multiple scans (SADABS 2008/1).[3] The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12).[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to the equivalent isotropic displacement parameter of the corresponding carrier atom by a factor of either 1.2 or 1.5. The dinuclear complex is situated on a twofold axis (Wyckoff position 4*d*) and exhibits crystallographically imposed C_2 molecular symmetry. The compound crystallized with one molecule of benzene that is situated on a crystallographic inversion center (Wyckoff position 4*a*). Selected geometric parameters of **4** · benzene are summarized in Table 1. Crystallographic data, data collection, and refinement details are summarized in Table 5.

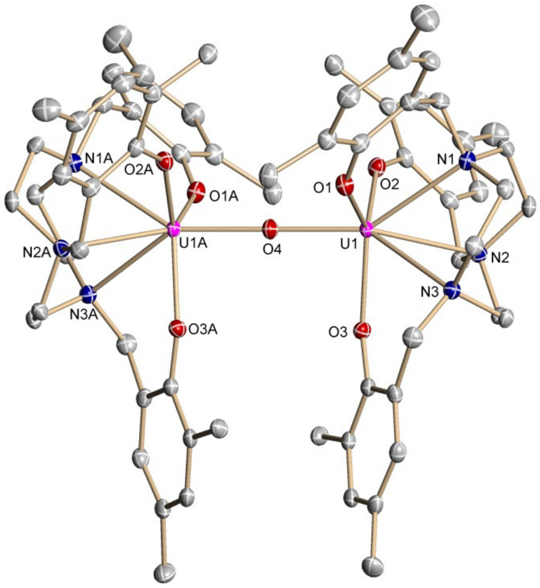


Figure 13 Solid-state molecular structure of **4** in crystals of $[\{((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}\}_2(\mu\text{-O})]$ · benzene. *t*-Bu fragment of neopentyl groups, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

Table 1 Selected bond distances [Å] and angles [°] for [{($^{\text{Neop,Me}}$ArO)$_3$tacn)U}$_2$(μ-O)] · benzene (**4** · benzene).

[{($^{\text{Neop,Me}}$ArO)$_3$tacn)U}$_2$(μ-O)] · benzene (**4** · benzene)	
U1 – O4	2.0869(2)
U1 – O1, O2, O3	2.231(2), 2.204(2), 2.230(2)
U1 – N1, N2, N3	2.733(2), 2.693(2), 2.734(2)
U1$_{\text{out of plane shift}}$	-0.136
U1 – O4 – U1A	180.0(2)

Crystallographic Details for [{($^{\text{Neop,Me}}$ArO)$_3$tacn)U}$_2$-(μ-O)] · 2 *n*-hexane (4 · 2 *n*-hexane)

CCDC-886104:

In a similar way as for **4** · benzene single crystals of the light-green, dinuclear uranium(IV/IV) complex [{($^{\text{Neop,Me}}$ArO)$_3$tacn)U}$_2$-(μ-O)] (**4**) were also obtained from slow diffusion of *n*-hexane into a benzene solution as *n*-hexane solvate. A suitable single crystal of approximately 0.45 × 0.36 × 0.24 mm size was coated with protective perfluoropolyether oil and mounted on the tip of a glass fiber. Intensity data were collected at 100 K on a Bruker Smart APEX 2 diffractometer using graphite monochromatized Mo*K*α radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied on the basis of multiple scans (SADABS 2008/1).[3] The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12).[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to the equivalent isotropic displacement parameter of the corresponding carrier atom by a factor of either 1.2 or 1.5. The dinuclear complex is situated on a twofold axis and exhibits crystallographically imposed C_2 molecular symmetry. One arm of the ligand was disordered, two alternative orientations were refined resulting in occupancies of 53.6(6) for C34 – C45 and 46.4(6)% for C34A – C45A, respectively. The compound crystallized with a total of two molecules of *n*-hexane that were distributed over three crystallographic sites. All of the solvent molecules were disordered. Two of the hexane molecules were situated on crystallographic inversion centres (independent atoms C101 – C105 and C201 – C203) while the third hexane (independent atoms C301 – C305) was located on a crystallographic twofold axis running through C301. No H atoms were included in the structure model for these disordered *n*-hexanes. Selected geometric parameters of **4** · 2 *n*-hexane are summarized in Table 2. Crystallographic data, data collection, and refinement details are summarized in Table 5.

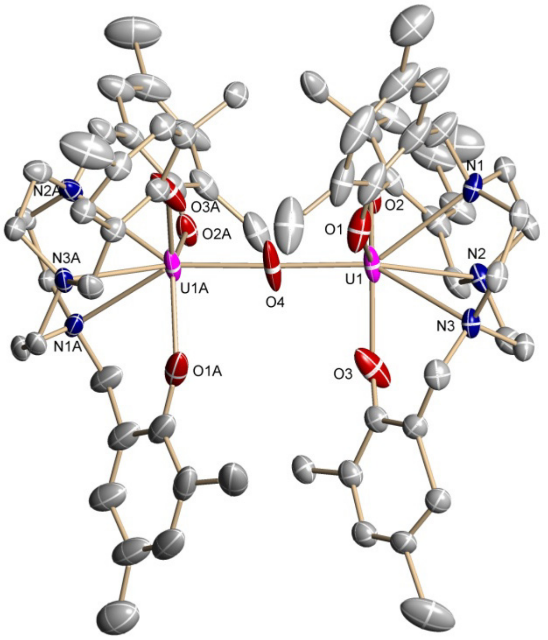


Figure 14 Solid-state molecular structure of **4** in crystals of $[\{((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}\}_2(\mu\text{-O})]$ · 2 *n*-hexane. *t*-Bu fragment of neopentyl groups, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

Table 2 Bond lengths [Å] and angles [°] for $[\{((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}\}_2(\mu\text{-O})]$ · 2 *n*-hexane (**4** · 2 *n*-hexane).

$[\{((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}\}_2(\mu\text{-O})]$ · 2 *n*-hexane (**4** · 2 *n*-hexane)	
U1 – O4	2.0909(5)
U1 – O1, O2, O3	2.227(6), 2.203(5), 2.209(7)
U1 – N1, N2, N3	2.720(6), 2.732(6), 2.705(6)
$\mathrm{U1}_{\text{out of plane shift}}$	-0.103
U1 – O4 – U1A	176.8(4)

Crystallographic Details for [{((${}^{\mathrm{Neop,Me}}$ArO)$_3$tacn)U}$_2$-(μ-CO$_3$)] · 2.5 benzene (5 · 2.5 benzene)

CCDC-886106:

Single crystals of the light-green, dinuclear uranium(IV/IV) complex [{((${}^{\mathrm{Neop,Me}}$ArO)$_3$tacn)U}$_2$-(μ-CO$_3$)] (**5**) suitable for X-ray diffraction were obtained from a slow diffusion of *n*-hexane into a benzene solution in form of prisms. A suitable single crystal of approximately 0.25 × 0.20 × 0.12 mm size was coated with protective perfluoropolyether oil and mounted on the tip of a glass fiber. Intensity data were collected at 100 K on a Bruker Smart APEX 2 diffractometer using graphite monochromatized Mo*K*α radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied on the basis of multiple scans (SADABS 2008/1).[3] The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12).[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to the equivalent isotropic displacement parameter of the corresponding carrier atom by a factor of either 1.2 or 1.5. The compound crystallized with a total of 2.5 molecules of benzene with half a solvent molecule being situated on a crystallographic inversion center. For atom C45 (terminal methyl group) ISOR restraints were applied. Selected geometric parameters of **5** are summarized in Table 3. Crystallographic data, data collection, and refinement details are summarized in Table 5.

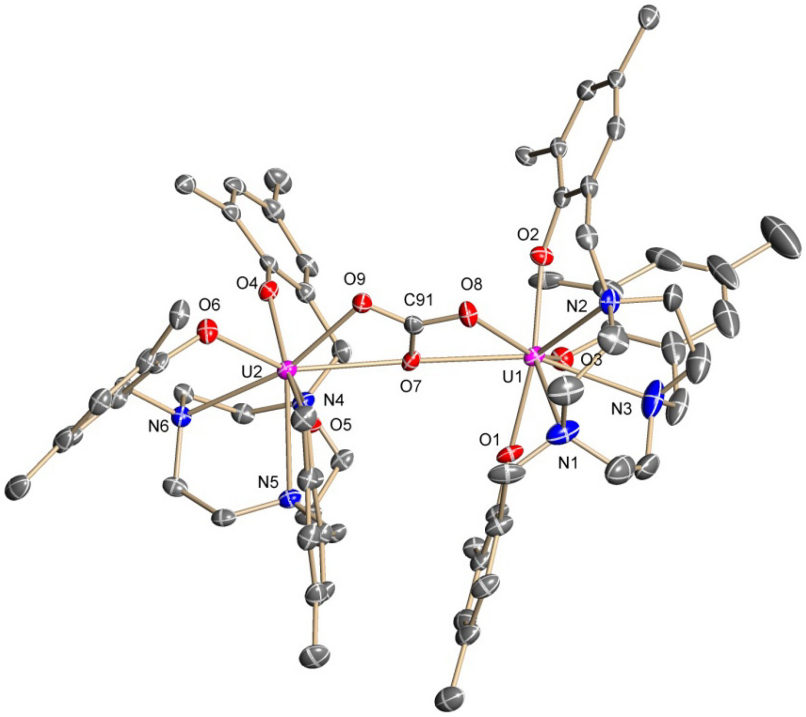


Figure 15 Solid-state molecular structure of **5** in crystals of [{((${}^{\mathrm{Neop,Me}}$ArO)$_3$tacn)U}$_2$(μ-CO$_3$)] · 2.5 benzene. *t*-Bu fragment of neopentyl groups, hydrogen atoms, and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are at the 40% probability level.

Table 3 Selected bond distances [Å] and angles [°] for [{((${}^{\mathrm{Neop,Me}}$ArO)$_3$tacn)U}$_2$(*μ*-CO$_3$)] · 2.5 benzene (**5** · 2.5 benzene).

[{((${}^{\mathrm{Neop,Me}}$ArO)$_3$tacn)U}$_2$(*μ*-CO$_3$)] · 2.5 benzene (**5** · 2.5 benzene)	
U1 – O7, O8	2.616(3), 2.430(3)
U2 – O7, O9	2.663(3), 2.375(3)
U1 – O1, O2, O3	2.190(3), 2.149(3), 2.239(3)
U2 – O4, O5, O6	2.158(3), 2.171(3), 2.213(3)
U1 – N1, N2, N3	2.704(4), 2.748(4), 2.669(4)
U2 – N4, N5, N6	2.722(4), 2.776(4), 2.717(4)
$\mathrm{U1_{out\ of\ plane\ shift}}$	-0.333
$\mathrm{U2_{out\ of\ plane\ shift}}$	-0.314
U1 – O7 – U2	175.8(2)
O7 – U1 – O8	50.9(1)
O7 – U2 – O9	51.3(1)
C91 – O7, O8, O9	1.274(5), 1.274(5), 1.277(5)

Crystallographic Details for $\{[((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}(\kappa^2\text{-}\mathrm{CO}_3)]\mathrm{K}\}_4 \cdot$ 18 benzene (6 · 18 benzene)

CCDC-886107:

Block-shaped single crystals of the light-green, tetranuclear uranium(IV) complex $\{[((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\text{-}\mathrm{tacn})\mathrm{U}(\kappa^2\text{-}\mathrm{CO}_3)]\mathrm{K}\}_4$ (**6**) suitable for X-ray diffraction were obtained by slow evaporation of a benzene solution. A suitable single crystal of approximately 0.60 × 0.40 × 0.30 mm size was coated with protective perfluoropolyether oil and mounted on the tip of a glass fiber. Intensity data were collected at 100 K on a Bruker Smart APEX 2 diffractometer using graphite monochromatized Mo*K*α radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied on the basis of multiple scans (SADABS 2008/1).[3] The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12).[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to the equivalent isotropic displacement parameter of the corresponding carrier atom by a factor of either 1.2 or 1.5. The tetranuclear complex is situated on a crystallographic inversion centre. The compound crystallized with a total of 18 molecules of benzene (9 independent molecules). Selected geometric parameters of **6** · 18 benzene are summarized Table 4. Crystallographic data, data collection, and refinement details are summarized in Table 5.

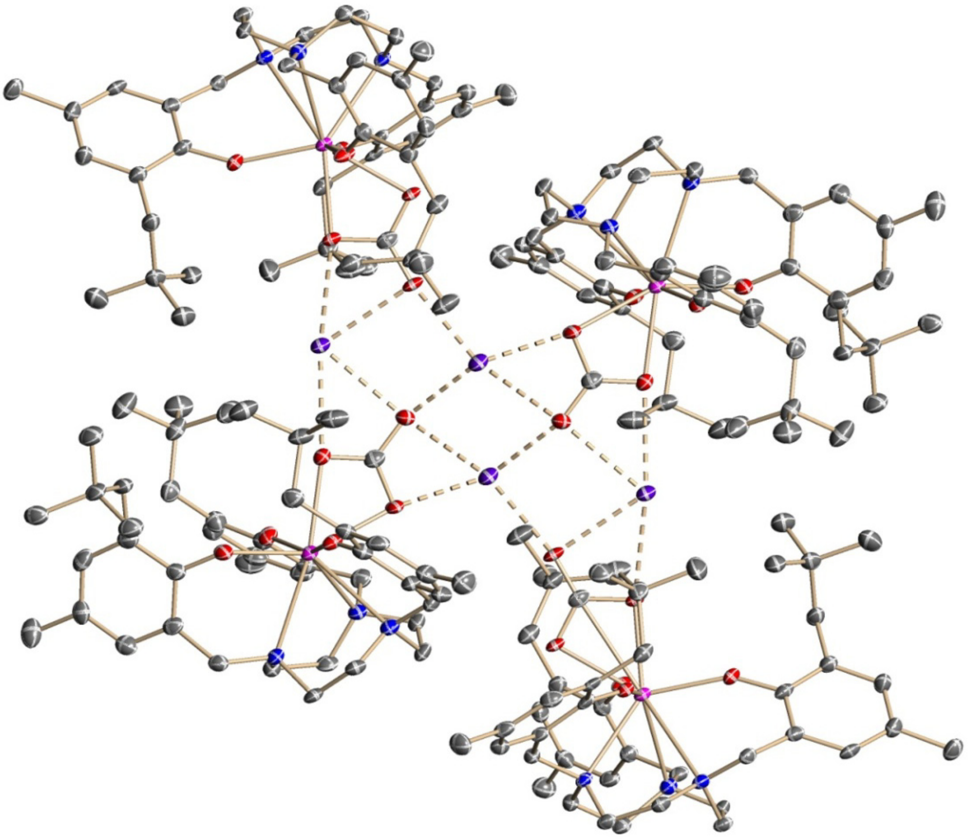


Figure 16 Solid-state molecular structure of **6** in crystals of $\{[((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}(\kappa^2\text{-}\mathrm{CO}_3)]\mathrm{K}\}_4 \cdot 18$ benzene. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are at the 50% probability level.

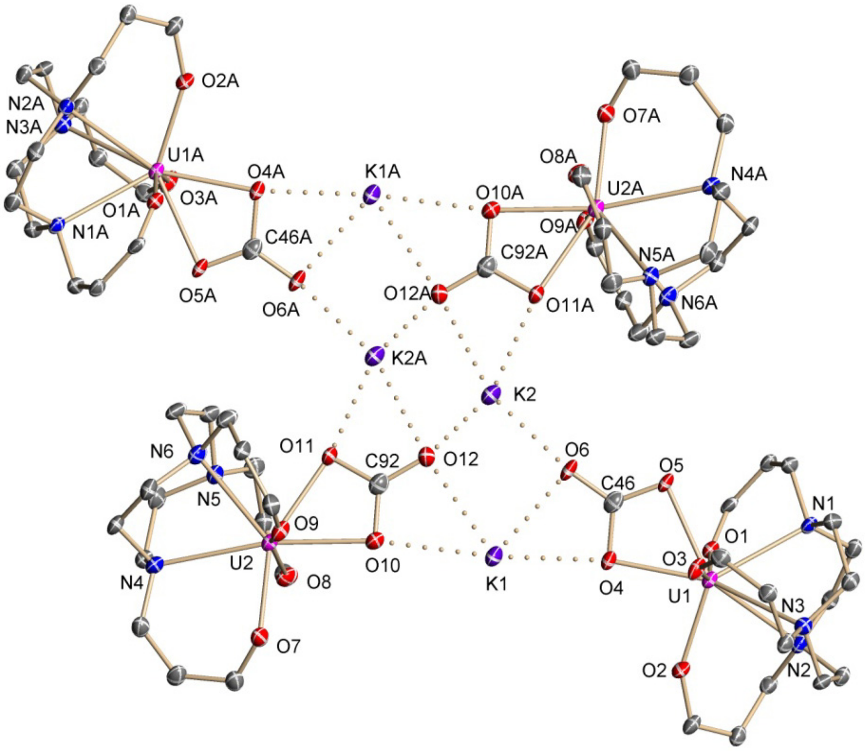


Figure 17 Core structure of $\{[((^{\mathrm{Neop,Me}}\mathrm{ArO})_3\mathrm{tacn})\mathrm{U}(\kappa^2\text{-}\mathrm{CO}_3)]\mathrm{K}\}_4 \cdot 18$ benzene (**6** · 18 benzene).

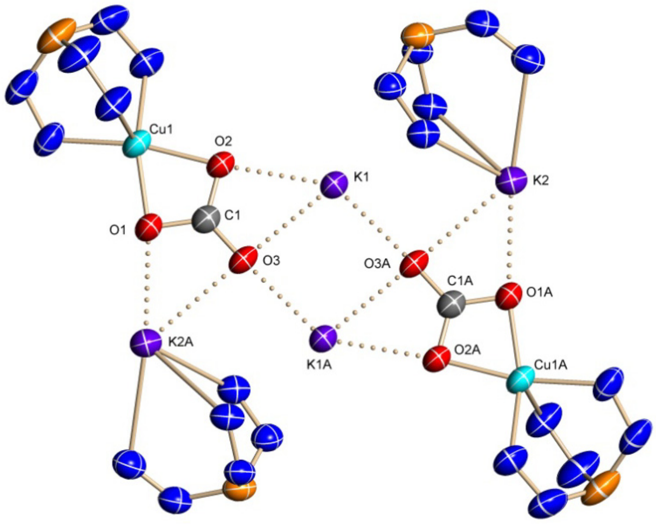


Figure 18 For comparison, core structure of [Tp^{CF_3,CH_3}CuK(μ_4-CO$_3$)KTp^{CF_3,CH_3}]$_2$.[5]

Table 4 Selected bond distances [Å] and angles [°] for {[((^{Neop,Me}ArO)$_3$tacn)U(κ^2-CO$_3$)]K}$_4$ · 18 benzene (**6** · 18 benzene).

{[((^{Neop,Me}ArO)$_3$tacn)U(κ^2-CO$_3$)]K}$_4$ · 18 benzene (**6** · 18 benzene)	
U1 – O4, O5	2.360(3), 2.421(3)
U2 – O10, O11	2.410(3), 2.398(3)
U1 – O1, O2, O3	2.187(3), 2.173(3), 2.176(3)
U2 – O7, O8, O9	2.248(3), 2.179(3), 2.141(3)
U1 – N1, N2, N3	2.630(4), 2.896(4), 2.810(4)
U2 – N4, N5, N6	2.703(4), 2.745(4), 2.767(4)
U1$_{\text{out of plane shift}}$	-0.229
U2$_{\text{out of plane shift}}$	-0.381
O4 – U1 – O5	54.9(2)
O10 – U2 – O11	54.5(2)
C46 – O4, O5, O6	1.328(6), 1.283(6), 1.255(6)
C92 – O10, O11, O12	1.294(6), 1.311(6), 1.258(6)
K1 – O4, O6, O10, O12	2.715(3), 2.716(4), 2.766(3), 2.751(3)
K2 – O6, O12, O11A$^{\#}$, O12A$^{\#}$	2.516(3), 2.579(4), 2.639(4), 2.813(3)

$^{\#}$ symmetry: $-x, -y+1, -z+1$

Table 5 Crystallographic data, data collection, and refinement details for **4** · benzene, **4** · 2 *n*-hexane, **5** · 2.5 benzene, and **6** · 18 benzene

	4 · benzene **CCDC-886105**	**4** · 2 *n*-hexane **CCDC-886104**	**5** · 2.5 benzene **CCDC-886106**	**6** · 18 benzene **CCDC-886107**
Empirical formula	$C_{96}H_{138}N_6O_7U_2$	$C_{102}H_{160}N_6O_7U_2$	$C_{106}H_{147}N_6O_9U_2$	$C_{292}H_{372}K_4N_{12}O_{24}U_4$
Mol. weight	1964.18	2058.42	2125.36	5542.55
Crystal size [mm^3]	0.16×0.14×0.08	0.45×0.36×0.24	0.25×0.20×0.12	0.60×0.40×0.30
Temperature [K]	100	100	100	100
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic
Space group	*Pnna* (no. 52)	*C*2/*c* (no. 15)	$P2_1/n$ (no. 14)	*P*-1 (no. 2)
a [Å]	16.300(2)	23.955(2)	17.0385(2)	18.9925(4)
b [Å]	21.497(3)	20.947(2)	23.9304(3)	20.0409(4)
c [Å]	25.420(3)	23.302(3)	24.1626(3)	21.8950(4)
α [°]	90	90	90	71.285(1)
β [°]	90	117.653(2)	95.986(1)	65.118(1)
γ [°]	90	90	90	63.811(1)
V [Å^3]	8907 (2)	10357(2)	9798.3(2)	6690.0(2)
Z	4	4	4	1
ρ_{calc} [g/cm^3]	1.465	1.320	1.441	1.376
μ [mm^{-1}]	3.689	3.175	3.361	2.541
F (000)	3984	4216	4324	2844
T_{min}; T_{max}	0.627; 0.746	0.597; 0.746	0.631; 0.746	0.614; 0.746
2θ interval [°]	$2.9 \leq 2\theta \leq 56.9$	$5.1 \leq 2\theta \leq 52.8$	$4.6 \leq 2\theta \leq 51.8$	$4.1 \leq 2\theta \leq 55.8$
Collected reflections	148203	43578	150266	122215
Independent reflections; R_{int}	11173; 0.0791	10559; 0.0775	21565; 0.0811	31153; 0.0732
Observed reflections [$I \geq 2\sigma(I)$]	8160	6169	16522	20804
No. refined parameters	513	710	1132	1501
wR_2 (all data)	0.0568	0.1568	0.0868	0.1145
R_1 [$I \geq 2\sigma(I)$]	0.0254	0.0505	0.0390	0.0453
GooF on F^2	1.028	1.344	1.015	1.095
$\Delta\rho_{\mathrm{max/min}}$	1.103 / – 0.781	2.394 / – 2.467	7.031 / – 2.910	3.072 / – 1.445

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