Journal of Organometallic Chemistry 857 (2018) 152–158

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Generation of $Tp^*_2U(N_3)$ from a family of new uranium(III) alkyl complexes

Caleb J. Tatebe, Sara A. Johnson, Matthias Zeller, Suzanne C. Bart*

H. C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States

ARTICLE INFO

Article history:
Received 17 August 2017
Received in revised form
4 September 2017
Accepted 5 September 2017
Available online 7 September 2017

Keywords:
Actinide complexes
Tripodal ligands
Uranium
Alkyl complexes

ABSTRACT

A new family of uranium(III) benzyl species supported by bulky hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) ligands has been synthesized and characterized. These derivatives were synthesized by treating Tp^*_2UI (**1-I**) with various benzylpotassium salts to afford $Tp^*_2U(CH_2$-*para*-*iso*propylphenyl) (**1-*p*-^{i}Pr**), $Tp^*_2U(CH_2$-*para*-*tert*-butylphenyl) (**1-*p*-^{t}Bu**), $Tp^*_2U(CH_2$-*meta*-methoxyphenyl) (**1-*m*-OMe**), and $Tp^*_2U(CH_2$-*ortho*-picolyl) (**1-*o*-Picolyl**). Along with previously reported $Tp^*_2U(CH_2Ph)$ (**1-CH$_2$Ph**), these uranium alkyl complexes can be treated with an equivalent of Me_3SiN_3 to yield $Tp^*_2UN_3$ (**2-N$_3$**), releasing an equivalent of the corresponding benzyltrimethylsilane. All compounds were characterized by multinuclear NMR, IR, and electronic absorption spectroscopies as well as X-ray crystallography.

1. Introduction

The field of organouranium chemistry has been of interest since the mid-twentieth century, when such compounds were predicted to be useful for isotope separation due to their presumed increased volatility [1,2]. While uranium alkyls did not prove their versatility in this realm, these species have been of fundamental interest for comparison to their transition metal counterparts, with most of the strides being made for uranium(IV) derivatives [3–7]. More recently, new synthetic methodologies have allowed access to tri-, penta-, and hexavalent analogues [8].

Efforts in our group have focused on the synthesis, characterization and reactivity of organouranium species in the +3 [9–11] and +4 [12,13] oxidation states. In regard to the former, we have demonstrated that utilizing sterically demanding hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) ligands allows divergence from the bulky $-CH(SiMe_3)_2$ group [3,14–16], which is typically used for U(III), effectively supporting benzyl [9,10], neosilyl [10], and methyl [10] substituents. In the latter case, we have shown that when uranium(IV) centers are benzylated, such species are stable in their homoleptic form, with no bulky ancillary ligands required due to the increased hapticity (η^4) of the benzyl group, which saturates the coordination sphere [13,17,18]. These homoleptic compounds are even tolerant to ring substitution, facilitating isolation of the *p*-^{i}Pr, *p*-^{t}Bu, *m*-OMe, *o*-OMe, and *o*-picoline derivatives [13]. In this study, we sought to combine these systems to determine if the bis(Tp*) uranium(III) derivatives were also tolerant to the same ring substitution, given that uranium(III) is more electron rich and alkyl ligands are generally more reactive towards decomposition pathways. To this end, we employed substituted benzylpotassium salts, KCH_2Ph' (Ph' = *p*-^{i}PrPh, *p*-^{t}BuPh, *m*-OMePh, *o*-picolyl) [13], to generate this new family. These trivalent derivatives were stable and resulted in useful synthons, as treating these members with Me_3SiN_3 afforded $Tp^*_2UN_3$, which is the first monomeric, neutral, trivalent azide derivative for the actinides. Full spectroscopic and structural characterization is discussed for each compound.

2. Results and discussion

Our first experiments were geared towards the synthesis of the new members of the uranium(III) benzyl family. Treating a stirring solution of Tp^*_2UI (**1-I**) with a slight excess (1.20 equiv) of substituted benzylpotassium salt resulted in an immediate color change from dark purple to dark green in each case. After two hours of stirring and subsequent workup, green powders were isolated, assigned as $Tp^*_2UCH_2$Ph' (**1-CH$_2$Ph'**) and characterized using ^{1}H NMR spectroscopy (Scheme 1). The spectra for the first three entries, **1-*p*-^{i}Pr, 1-*p*-^{t}Bu, 1-*m*-OMe,** had similar paramagnetically broadened and shifted features, with the number of resonances and corresponding integration values appropriate for C_{2v} symmetry.

* Corresponding author.
E-mail address: sbart@purdue.edu (S.C. Bart).

http://dx.doi.org/10.1016/j.jorganchem.2017.09.013
0022-328X/

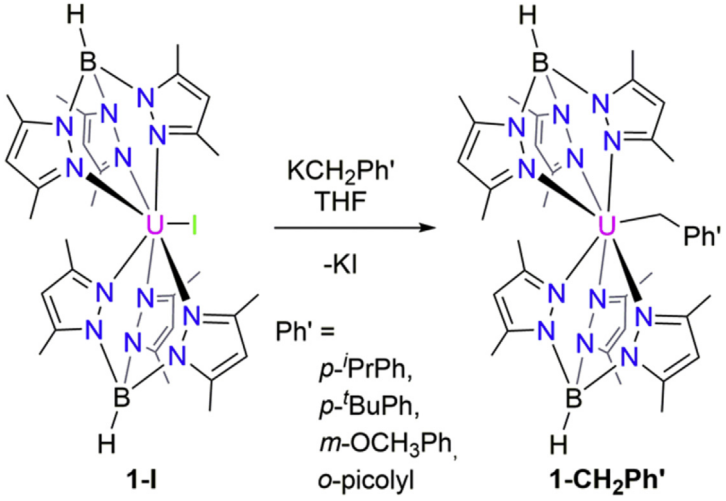
Most notably, the methylene resonances had diagnostic shifts, as these are closest to the paramagnetic uranium center (**1-*p*-^{i}Pr** = 24.42 ppm; **1-*p*-^{t}Bu** = 24.72 ppm; **1-*m*-OMe** = 20.98 ppm). ^{11}B NMR spectroscopy was used to assess the boron environment as well. The products containing the bulky alkyl groups (**1-*p*-^{i}Pr** = −15.6 ppm; **1-*p*-^{t}Bu** = −15.4 ppm) and electron-withdrawing group (**1-*m*-OMe** = −14.0 ppm) have a singlet with chemical shifts that are consistent with Tp*$_2$UCH$_2$Ph (**1-CH$_2$Ph**) (−15.4 ppm) [19].

1-*o*-Picolyl displayed a more complicated, C_1 symmetric spectrum, likely due to coordination through the nitrogen atom of the *ortho*-picoline, similar to the uranium(IV) homoleptic species (Fig. S10) [13]. The chemically inequivalent methyl groups of the Tp* appear as 12 singlets (3H each), whereas the C-H pyrazole protons are represented by six resonances (1H each). Aryl protons observed as four singlets between 3.58 and 17.43 ppm are also visible. A broad singlet (2H) observed at −5.56 ppm represents the methylene protons. Two resonances are observed by ^{11}B NMR spectroscopy for **1-*o*-Picolyl** (−13.1, 2.9 ppm) due to the asymmetry imparted by the nitrogen coordination to uranium. Evaluation of the family of **1- CH$_2$Ph'** by IR spectroscopy (KBr pellet) revealed two $\nu_{B\text{-}H}$ stretches (**1-*p*-^{i}Pr** = 2544, 2521 cm^{-1}; **1-*p*-^{t}Bu** = 2545, 2523 cm^{-1}; **1-*m*-OMe** = 2556, 2522 cm^{-1}; **1-*o*-Picolyl** = 2555, 2519 cm^{-1}), which is consistent with other bis(Tp*) U complexes [19–21].

To evaluate the structural properties of these compounds, single crystals of all compounds were grown for analysis by X-ray diffraction (Fig. 1). Unfortunately, suitable crystals of pure **1-*p*-^{t}Bu** were not obtainable; analysis revealed that it was in fact a 0.95:0.05 co-crystal of **1-*p*-^{t}Bu** and **1-I.** In each case, refinement of the data showed the expected Tp*$_2$U(III) benzyl complex with two κ^3-Tp* ligands per uranium center (**1-*p*-^{i}Pr** – U-N$_{pyrazolyl}$: 2.528(3)-2.690(3) Å; **1-*p*-^{t}Bu** – U-N$_{pyrazole}$: 2.517(2)-2.703(2) Å; **1-*m*-OMe** – U-N$_{pyrazolyl}$: 2.524(5)-2.706(5) Å; **1-*o*-Picolyl** – U-N$_{pyrazolyl}$: 2.580(3)-2.736(3) Å) (Table 1). The U-C bonds for the series (**1-*p*-^{i}Pr** = 2.629(4) Å; **1-*p*-^{t}Bu** = 2.632(4) Å; **1-*m*-OMe** = 2.675(15) Å; **1-*o*-Picolyl** = 2.747(4) Å) are within the range of other reported uranium(III) alkyl bond distances, including **1-CH$_2$Ph** (2.57(2) Å) [9], Tp*$_2$U(CH$_2$SiMe$_3$) (2.601(9) Å) [22], Tp*U(CH$_2$Ph)$_2$ (2.615(7), 2.604 (9) Å) [10], U(CH(SiMe$_3$)$_2$)$_3$ (2.48(2) Å) [14], and TpTp*U(CH$_2$Ph) (Tp = hydrotris(pyrazolyl)borate) (2.56(2) Å) [11]. Consistent with the solution ^{1}H NMR spectrum, the solid state molecular structure of **1-*o*-Picolyl** shows pyridine coordination taking on the aza-allyl coordination mode observed for U(CH$_2$*o*-Picolyl)$_4$ [13].

Further characterization by electronic absorption spectroscopy was performed on the family of uranium benzyl derivatives to confirm the +3 oxidation state of its members. All compounds have similar features in the near-infrared (NIR) region, characterized by a relatively intense absorption near 1250 nm (ca. 150 M^{-1}cm^{-1}) with additional broad features up through 1650 nm, consistent for U(III) ions (Fig. 2) [23,24]. Across repeated measurements, **1-*m*-OMe** gave absorbances with lower molar absorptivities than the other benzyl complexes, possibly due to the electronic effects from the methoxy substituent. The UV–visible region displays characteristic spectra similar to **1-CH$_2$Ph**'s previously reported spectra [9].

As expected based on our previous work, this new family of benzyl derivatives, **1-CH$_2$Ph'**, are useful synthons to develop new uranium(III) derivatives. One target was a monomeric, neutral trivalent uranium azide, as previous examples have oxidation states ranging from +4 to +6 or are trivalent anions stabilized by a countercation ([Na(18-crown-6)][Cp'$_3$UN$_3$] (Cp' = C$_5$H$_4$SiMe$_3$)) [25]. Treating dark green THF solutions of **1-CH$_2$Ph'** with one equivalent of azidotrimethylsilane (Me$_3$SiN$_3$) caused an immediate change to blue-green. After 30 min, volatiles were removed, and the resulting oil was washed with *n*-pentane to remove Me$_3$SiCH$_2$Ph' [26–28], affording a blue-green powder assigned as Tp*$_2$UN$_3$ (**2-N$_3$**) (Scheme 2). Analysis by ^{1}H NMR spectroscopy revealed four resonances, consistent with C_{2v} symmetry. Two signals (18H) corresponding to the *endo*-(-15.00 ppm) and *exo*-methyl (1.28 ppm) groups were observed for Tp*, with a singlet (6H) at 7.67 ppm for the Tp*-C*H*. In this case, a very broad singlet (10.12 ppm) was also found for the Tp*-B-*H*. A single boron resonance is observable in the ^{11}B NMR spectrum (10.6 ppm), which is expected for the proposed symmetry. This is shifted from the uranium alkyl starting materials [19] and is consistent with other trivalent uranium complexes [11,23,29]. Two B-H stretches are visible by IR spectroscopy (KBr pellet) (2558, 2523 cm^{-1}), as noted for the **1-CH$_2$Ph'** family. An asymmetric stretch for the terminal azide (2073 cm^{-1}) is consistent with other uranium η^1-azide complexes (2055–2086 cm^{-1}) [30–32]. As for the bis(Tp*)U alkyl



Scheme 1. The preparation of U(III) benzyl compounds from **1-I**.

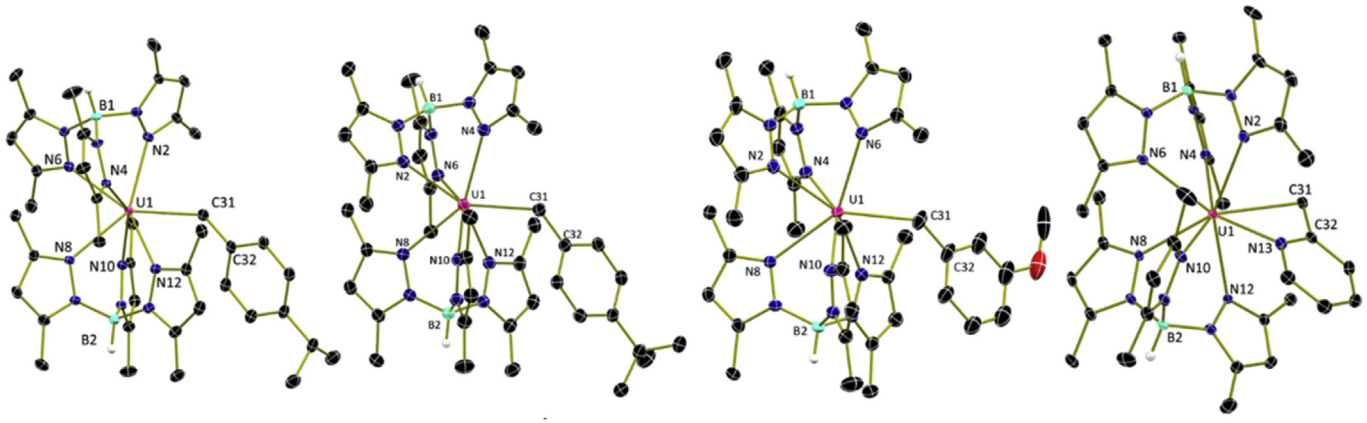


Fig. 1. Molecular structures of **1-*p*-^{i}Pr, 1-*p*-^{t}Bu** × **Tp*$_2$UI**, **1-*m*-OMe**, and **1-*o*-Picolyl** (left to right), displayed with 30% probability ellipsoids. Selected hydrogen atoms, iodine atoms, and co-crystallized solvent molecules have been omitted for clarity.

Table 1
Selected bond lengths of **1-*p*-^{i}Pr, 1-*p*-^{t}Bu** × **Tp*$_2$UI**, **1-*m*-OMe**, **1-*o*-Picolyl**, and **2-N$_3$**.

	1-*p*-^{i}Pr	1-*p*-^{t}Bu	1-*m*-OMe	1-*o*-Picolyl	2-N$_3$
U1-N2	2.540(3) Å	2.675(2) Å	2.673(4) Å	2.736(3) Å	2.673(3) Å
U1-N4	2.528(3) Å	2.589(2) Å	2.524(5) Å	2.580(3) Å	2.530(3) Å
U1-N6	2.690(3) Å	2.585(2) Å	2.560(5) Å	2.709(3) Å	2.632(3) Å
U1-N8	2.652(3) Å	2.703(2) Å	2.612(5) Å	2.593(3) Å	2.655(3) Å
U1-N10	2.590(3) Å	2.517(2) Å	2.592(5) Å	2.621(3) Å	2.648(3) Å
U1-N12	2.589(3) Å	2.544(2) Å	2.706(5) Å	2.703(3) Å	2.558(3) Å
U1-N13	–	–	–	2.491(3) Å	2.321(4) Å
U1-C31	2.629(4) Å	2.632(4) Å	2.675(15) Å	2.747(4) Å	–

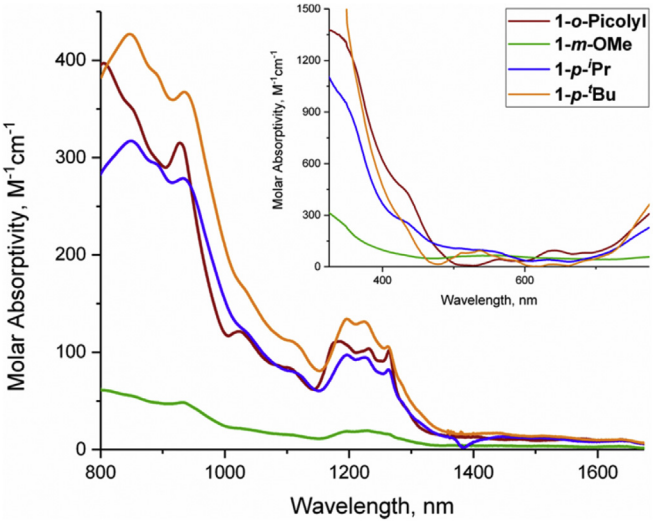


Fig. 2. Electronic absorption spectra of **1-*o*-Picolyl** (red), **1-*m*-OMe** (green), **1-*p*-^{t}Bu** (orange), and **1-*p*-^{i}Pr** (blue) recorded from 300 to 1650 nm in THF at ambient temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

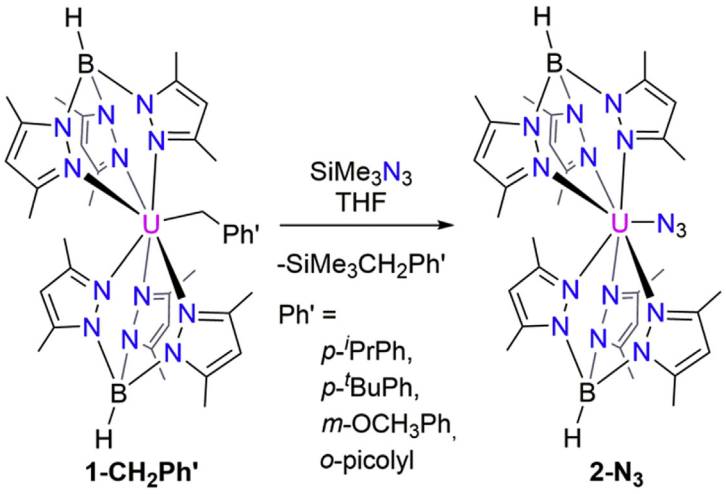
compounds, the electronic absorption spectrum of **2-N$_3$** has an absorption at 1250 nm (ca. 200 $M^{-1}cm^{-1}$) and broad U(III)-like features in the NIR region. In the UV–visible region, there is a strong color-producing band at λ_{max} = 641 nm (1000 $M^{-1}cm^{-1}$) (Fig. 3).

Single, X-ray quality crystals of **2-N$_3$** were obtainable by cooling a concentrated toluene solution to −35 °C. Analysis revealed two κ^3-Tp* ligands on the seven-coordinate uranium center (Fig. 4), with U-$N_{pyrazole}$ bond distances (2.530(6)-2.673(3) Å) (Table 1) consistent with other bis(Tp*) uranium compounds [33,34]. The U-N_{azide} bond length of 2.321(4) Å is significantly shorter than the U-$N_{pyrazole}$ distances, which is expected for a monodentate, monoanionic ligand. There have been U(IV) [31,32,35–46], U(V) [47], and U(VI) [30,48–50] terminal azide complexes reported and bridging U(III) azide complexes [25,51], but to our knowledge, **2-N$_3$** is the first report of a monomeric, terminal U(III) azide complex.

The U1-N13-N14 bond angle (166.0(3)°) is slightly bent, likely due to the crowded bis(Tp*) ligand framework. This U-N_{azide} angle is similar to those observed in other U-N_3 complexes ($Cp^*_2U(N(SiMe_3)_2)(N_3)$ = 163.5(17)° [40]; $((^{Ad}ArO)_3tacn)UN_3$ = 177.2(5)°, $((^{Ad}ArOH)_3tacn$ = 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzyl)1,4,7-triazacyclonone) [35]; $U(N_3)(Tren^{TIPS})$ = 176.0(3)°, ($Tren^{TIPS}$ = tris(triisopropylsilylamidomethyl)amine)) [42]. The linearity of the azide fragment (N13-N14-N15, 178.1(5)°) is expected and consistent with previously reported uranium azide complexes ($Cp^*_2U[N(Ph)(SiMe_3)](N_3)$ = 177.9(10)° [39]; $U(N(SiMe_3)_2)_3(N_3)_2$ = 179.5(4)°) [47]. The intraligand bond distances (N13-N14 = 1.201(6) Å; N14-N15 = 1.154(6) Å) are similar to other reported bond lengths ($Cp^*_2U(O\text{-}2,6\text{-}iPr_2C_6H_3)(N_3)$ − N-N = 1.197(10), 1.172(11) Å) [41] and suggest that any charge is delocalized across all the nitrogen atoms within the azide fragment.

After isolation and characterization of **2-N$_3$**, attempts were made to induce dinitrogen loss to form the corresponding uranium(V) nitrido species. Photolysis using both UV or compact fluorescent lamps produced intractable mixtures of products, with the same result observed after prolonged heating as well. Addition of BPh_3 to **2-N$_3$** also appeared to result in immediate decomposition, giving a complicated NMR spectrum. In each case, there was not an obvious sign of effervescence which would indicate N_2 loss.

Compound **2-N$_3$** is the latest entry into an established family of bis(Tp*) uranium(III) compounds bearing monoanionic ligands, including Tp^*_2UX, where X = CH_3, F, Cl, I. Examining crystallographic data for these species affords an opportunity for a direct comparison of sterics, which can be modeled in a quantitative way using the Solid-G [52,53] program. This analysis uses "numerically calculated ligand steric parameters" from experimentally determined molecular structures to calculate the extent of the uranium coordination sphere that is blocked by its ligands (Table 2). The reported G(complex) value represents the sum of all ligands minus any overlap to give an absolute value for shielding. The percentage of the coordination sphere blocked by the Tp* and X ligands is also given. Based on the G(complex) for this system, we can see an



Scheme 2. Reaction of **1-CH$_2$Ph**′ to afford **2-N$_3$**.

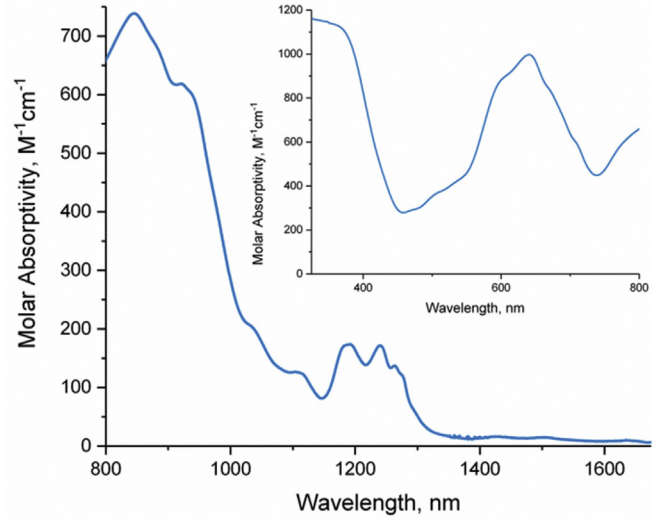


Fig. 3. Electronic absorption spectra of **2-N$_3$** recorded from 300 to 1650 nm in THF at ambient temperature.

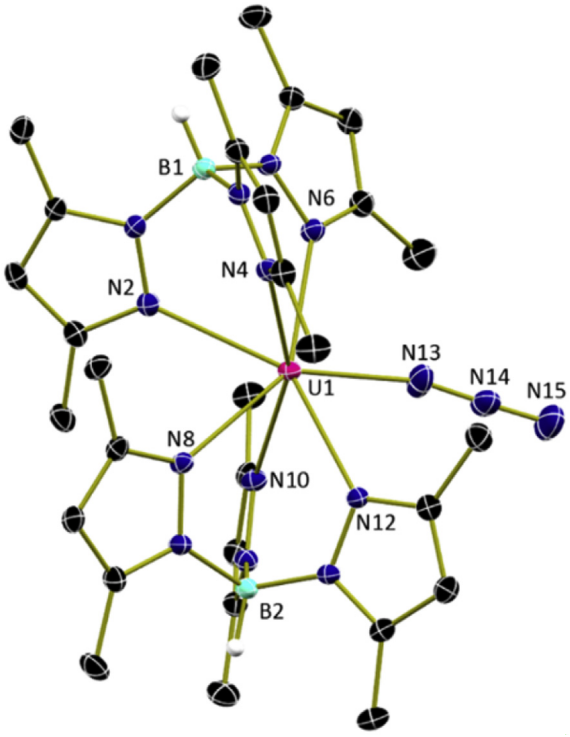


Fig. 4. Molecular structure of **2-N$_3$** displayed with 30% probability ellipsoids. Selected hydrogen atoms and co-crystallized toluene molecules have been omitted for clarity.

expected trend for the halide series (F, Cl, I), in that the larger the halide substituent, the more of the coordination sphere that is blocked. Furthermore, the respective G(complex) values of 85.64% and 85.57% for **2-N$_3$** and Tp*$_2$UCH$_3$ show these derivatives are very similar in their degrees of coordinative saturation, and that this is on par with what is observed for **1-I**. Individually, however, the steric influence of the azide substituent on the uranium(III) ion is the same as for a fluoride substituent due to the affinity of the electropositive uranium for this electron withdrawing ligand.

3. Summary

Overall, we have demonstrated that uranium(III) alkyls, which are typically highly reactive and difficult to make, can be synthesized using the bulky bis(hydrotris(3,5-dimethylpyrazolyl))borate framework. Installation of benzyl groups was possible using substituted benzylpotassium salts, demonstrating that uranium(III) is tolerant to methoxy and pyridyl functional groups. This family was useful for the synthesis of the first monomeric, neutral U(III) azide when treated with Me_3SiN_3, as clean silane elimination occurs. Full spectroscopic and structural analyses reveal the unique features of this interesting trivalent species, which is remarkably stable given its electron-rich uranium center.

4. Experimental section

4.1. General considerations

All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun inert

Table 2
Solid angle parameters obtained from crystallographic data using Solid-G [52,53].

	$Tp^*_2UN_3$	$Tp^*_2UCH_3$ [22]	Tp^*_2UF [29]	Tp^*_2UCl [54]	Tp^*_2UI [55]
G(Tp*), %	38.61	37.60	37.73	37.51	38.42
	38.06	39.40	38.37	37.99	38.64
G(X), %	12.24	10.24	12.25	9.74	10.30
G(complex), %	85.64	85.57	84.72	85.20	85.78

atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as two −35 °C freezers for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated based on literature procedures using a Seca solvent purification system [56]. Benzene-d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze-pump-thaw cycles. Azidotrimethylsilane was purchased from Acros Organics and degassed by three freeze-pump-thaw cycles before use. Benzylpotassium salts [13], Tp^*_2UI (**1-I**) [57],and $Tp^*_2UCH_2Ph$ (**1-CH_2Ph**) [9] were prepared per literature procedures.

^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz ^{11}B NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 96.24 MHz. All chemical shifts are reported relative to the peak for $SiMe_4$, using ^{1}H (residual) chemical shifts of the solvent (C_6D_6: 7.16 ppm) as a secondary standard. ^{11}B chemical shifts are reported relative to the peak for $BF_3 \cdot Et_2O$ (0.0 ppm). The spectra for paramagnetic molecules were obtained by using an acquisition time of 0.5 s, thus the peak widths reported have an error of ±2 Hz. For paramagnetic molecules, the ^{1}H NMR data are reported with the chemical shift, followed by the peak width at half height in Hertz, the integration value, and, where possible, the peak assignment. Elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, Indiana). Solid state infrared spectra were recorded using a Thermo Nicolet 6700 spectrophotometer; samples were made by crushing the solids, mixing with dry KBr, and pressing into a pellet. Electronic absorption spectroscopic measurements were recorded at ambient temperature in sealed 1 cm quartz cuvettes with a Cary 6000i UV-Vis-NIR spectrophotometer.

Single crystals of **1-*m*-OMe** and **2-N_3**, suitable for X-ray diffraction, were coated with poly(isobutylene) oil in a drybox and quickly transferred to the goniometer head of a Bruker AXS D8 Quest diffractometer with kappa geometry, an I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon2 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu Kα radiation (λ = 1.54184 Å). Single crystals of **1-*p*-^{i}Pr**, **1-*p*-^{t}Bu** × **1-I**, and **1-*o*-Picolyl**, suitable for X-ray diffraction, were coated with poly(isobutylene) oil in a drybox and quickly transferred to the goniometer head of a Bruker AXS D8 Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator and a Photon200 CMOS area detector. Examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å). Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3 [58]. Complete crystallographic data, in CIF format (CCDC 1567337–1567341), have been deposited with the Cambridge Crystallographic Data Center (CCDC). Additional details for all compounds are given in the SI.

4.2. General synthesis for Tp^*_2U(III) alkyl compounds

A 20 mL scintillation vial was charged with Tp^*_2UI (0.500 g, 0.521 mmol) in 10 mL THF. To this stirring purple solution, an excess of substituted benzyl potassium salt (KCH_2-*p*-^{i}PrPh: 0.112 g, 0.652 mmol; KCH_2-*p*-^{t}BuPh: 0.121 g, 0.652 mmol; KCH_2-*m*-OMePh: 0.104 g, 0.652 mmol; KCH_2pyr: 0.085 g, 0.652 mmol) was added. The color of the solution became dark green after 2 h, after which the green solution was filtered over Celite, and volatiles were subsequently removed *in vacuo*. The resulting green powders were then washed with *n*-pentane (2 × 5 mL) and dried to afford dark green solids identified as **1-*p*-^{i}Pr** (0.458 g, 0.474 mmol, 91% yield), **1-*p*-^{t}Bu** (0.434 g, 0.443 mmol 85% yield), **1-*m*-OMe** (0.417 g, 0.438 mmol, 84% yield), or **1-*o*-Picolyl** (0.424 g, 0.459 mmol, 88% yield). Single crystals suitable for X-ray analysis were grown from a concentrated THF solution (**1-*p*-^{i}Pr**) or diffusion of a concentrated diethyl ether solution into toluene (**1-*p*-^{t}Bu**,**1-*m*-OMe**, **1-*o*-Picolyl**) stored at −35 °C. **1-*p*-^{i}Pr**: Elemental analysis of $C_{40}H_{57}B_2N_{12}U$, Calculated: C, 49.75; H, 5.95; N, 17.41. Found: C, 49.86; H, 5.93; N, 17.02. ^{1}H NMR (C_6D_6, 25 °C): δ (ppm) = −11.19 (24, 18H, Tp*-CH_3), −2.77 (5, 18H, Tp*-CH_3), 0.30 (23, 2H, B-*H*), 5.70 (4, 6H, ^{i}Pr-CH_3), 7.25 (5, 6H, Tp*-C*H*), 9.93 (6, 1H, ^{i}Pr-C*H*), 17.82 (17, 2H, *meta*-C*H*), 24.42 (4, 2H, -CH_2), 26.59 (24, 2H, *ortho*-C*H*). ^{11}B NMR (C_6D_6, 25 °C): δ (ppm) = −15.6. IR (KBr): ν_{B-H} = 2544, 2521 cm^{-1}. **1-*p*-^{t}Bu:** Elemental analysis of $C_{41}H_{59}B_2N_{12}U$ was not performed due to co-crystallization of **1-I**. ^{1}H NMR (C_6D_6, 25 °C): δ (ppm) = −11.29 (23, 18H, Tp*-CH_3), −2.88 (4, 18H, Tp*-CH_3), −0.03 (3, 2H, B-*H*), 5.69 (2, 9H, C(CH_3)$_3$), 7.13 (4, 6H, Tp*-C*H*), 17.89 (71, 2H, *o*-/*m*-C*H*), 24.72 (3, 2H, -CH_2), 26.48 (26, 1H, *m*-/*o*-C*H*). ^{11}B NMR (C_6D_6, 25 °C): δ (ppm) = −15.4. IR (KBr): 2545, 2523 ν_{B-H} = cm^{-1}. **1-*m*-OMe:** Elemental analysis of $C_{38}H_{53}B_2N_{12}OU$, Calculated: C, 47.86; H, 5.60; N, 17.63. Found: C, 47.37; H, 5.58; N, 17.42. ^{1}H NMR (C_6D_6, 25 °C): δ (ppm) = −11.31 (23, 18H, Tp*-CH_3), −2.79 (14, 18H, Tp*-CH_3), −0.07 (3, 2H, B-*H*), 7.15 (6, 6H, Tp*-C*H*), 7.86 (4, 3H, -OCH_3), 10.49 (5, 1H, *o*-/*p*-C*H*), 17.37 (8, 1H, *o*-/*p*-C*H*), 20.98 (1, 2H, -CH_2), 24.90 (24, 1H, *m*-/*o*-C*H*), 27.29 (26, 1H, *m*-/*o*-C*H*). ^{11}B NMR (C_6D_6, 25 °C): δ (ppm) = −14.0. IR (KBr): ν_{B-H} = 2556, 2522 cm^{-1}. **1-*o*-Picolyl:** Elemental analysis of $C_{36}H_{50}B_2N_{13}U$, Calculated: C, 46.77; H, 5.45; N, 19.70. Found: C, 46.71; H, 5.42; N, 19.06. ^{1}H NMR (C_6D_6, 25 °C): δ (ppm) = −27.65 (19, 3H, Tp*-CH_3), −23.68 (21, 3H, Tp*-CH_3), −11.78 (14, 3H, Tp*-CH_3), −11.33 (13, 3H, Tp*-CH_3), −5.56 (3, 2H, -CH_2pyr), −3.84 (7, 3H, Tp*-CH_3), −2.22 (22, 3H, Tp*-CH_3), −0.10 (7, 3H, Tp*-CH_3), 0.02 (7, 1H, Tp*-C*H*), 0.33 (7, 3H, Tp*-CH_3), 1.31 (7, 3H, Tp*-CH_3), 1.40 (16, 1H, Tp*-C*H*), 2.71 (7, 3H, Tp*-CH_3), 3.58 (15, 1H, *p*-C*H*), 3.87 (16, 3H, Tp*-CH_3), 4.37 (8, 1H, Tp*-C*H*), 7.45 (8, 1H, Tp*-C*H*), 8.58 (16, 1H, Tp*-C*H*), 10.86 (8, 1H, Tp*-C*H*), 10.98 (18, 3H, Tp*-CH_3), 11.47 (8, 1H, Tp*-C*H*), 15.53 (8, 1H, *m*-C*H*), 16.35 (8, 1H, *m*-C*H*), 17.43 (35, 1H, *o*-C*H*), 39.71 (26, 1H, Tp*-C*H*). ^{11}B NMR (C_6D_6, 25 °C): δ (ppm) = −13.1, 2.9. IR (KBr): ν_{B-H} = 2555, 2519 cm^{-1}.

4.3. Synthesis of $Tp^*_2UN_3$ (2-N_3)

A 20 mL scintillation vial was charged with **1-CH_2Ph'** (**1-CH_2Ph**: 0.300 g, 0.325 mmol; **1-*p*-^{i}Pr**: 0.345 g, 0.357 mmol; **1-*p*-^{t}Bu**: 0.200 g, 0.204 mmol; **1-*m*-OMe**: 0.200 g, 0.210 mmol; **1-*o*-Picolyl**: 0.200 g, 0.216 mmol) in 8 mL THF. To this dark green solution, azidotrimethylsilane (**1-CH_2Ph**: 32.5 μL; **1-*p*-^{i}Pr**: 35.7 μL; **1-*p*-^{t}Bu**: 20.4 μL; **1-*m*-OMe**: 21.0 μL; **1-*o*-Picolyl**: 21.6 μL) was added *via* μsyringe and the solution immediately became blue-green. After 30 min, volatiles were removed *in vacuo*, affording a blue powder. This crude product was washed with *n*-pentane (4 × 5 mL) and

dried again. This resulted in a blue powder (**1-CH_2Ph**: 0.236 g, 0.270 mmol, 83% yield; **1-*p*-^{i}Pr**: 0.242 g, 0.275 mmol, 77%; **1-*p*-^{t}Bu**: 0.112 g, 0.128 mmol, 63%; **1-*m*-OMe**: 0.166 g, 0.190 mmol, 91%; **1-*o*-Picolyl**: 0.152 g, 0.174 mmol, 80%) assigned as $Tp^*_2UN_3$ (**2-N_3**). Elemental analysis of $C_{59}H_{74}B_2N_{15}U$, Calculated: C, 57.25; H, 6.03; N, 13.58. Found C, 56.82; H, 5.93; N, 13.58. ^{1}H NMR (C_6D_6, 25 °C): δ (ppm) = −15.00 (43, 18H, Tp*-CH_3), 1.28 (17, 18H, Tp*-CH_3), 7.67 (20, 6H, Tp*-C*H*), 10.12 (5, 2H, B-*H*). ^{11}B NMR (C_6D_6, 25 °C): δ (ppm) = 10.6. IR (KBr): $\nu_{B\text{-}H}$ = 2558, 2523 cm^{-1}; ν_{N3} = 2073 cm^{-1}.

Acknowledgments

The authors gratefully acknowledge a grant from the National Science Foundation (CHE-1149875, CAREER grant to SCB). This material is based in part upon work supported by the National Science Foundation through the Major Research Instrumentation Program (CHE 1625543) (Funding for the single crystal X-ray diffractometers).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.09.013.

References

[1] H. Gilman, Some personal notes on more than one-half century of organometallic chemistry, Adv. Organomet. Chem. 7 (1969) 1–52, http://dx.doi.org/10.1016/S0065-3055(08)60291-9.
[2] H. Gilman, R.G. Jones, E. Bindschadler, D. Blume, G. Karmas, G.A. Martin, J.F. Nobis, J.R. Thirtle, H.L. Yale, F.A. Yoeman, Organic compounds of uranium. I. 1,3-Dicarbonyl chelates, J. Am. Chem. Soc. 78 (1956) 2790–2792, http://dx.doi.org/10.1021/ja01593a038.
[3] T.J. Marks, A.M. Seyam, Stable uranium(IV) alkyl and aryl complexes, J. Am. Chem. Soc. 94 (1972) 6545–6546, http://dx.doi.org/10.1021/ja00773a050.
[4] S. Fortier, B.C. Melot, G. Wu, T.W. Hayton, Homoleptic uranium(IV) alkyl complexes: synthesis and characterization, J. Am. Chem. Soc. 131 (2009) 15512–15521, http://dx.doi.org/10.1021/ja906516e.
[5] N.R. Andreychuk, S. Ilango, B. Vidjayacoumar, D.J.H. Emslie, H.A. Jenkins, Uranium(IV) alkyl complexes of a rigid dianionic NON-donor ligand: synthesis and quantitative alkyl exchange reactions with alkyllithium reagents, Organometallics 32 (2013) 1466–1474, http://dx.doi.org/10.1021/om301136f.
[6] J.L. Kiplinger, D.E. Morris, B.L. Scott, C.J. Burns, Convenient synthesis, structure, and reactivity of $(C_5Me_5)U(CH_2C_6H_5)_3$: a simple strategy for the preparation of monopentamethylcyclopentadienyl uranium(IV) complexes, Organometallics 21 (2002) 5978–5982, http://dx.doi.org/10.1021/om0206610.
[7] S. Duhovic, M.J. Monreal, P.L. Diaconescu, Reactions of aromatic heterocycles with uranium alkyl complexes, Inorg. Chem. 49 (2010) 7165–7169, http://dx.doi.org/10.1021/ic1009835.
[8] S.A. Johnson, S.C. Bart, Achievements in uranium alkyl chemistry: celebrating sixty years of synthetic pursuits, Dalton Trans. 44 (2015) 7710–7726, http://dx.doi.org/10.1039/C4DT01621A.
[9] E.M. Matson, W.P. Forrest, P.E. Fanwick, S.C. Bart, Functionalization of carbon dioxide and carbon disulfide using a stable uranium(III) alkyl complex, J. Am. Chem. Soc. 133 (2011) 4948–4954, http://dx.doi.org/10.1021/ja110158s.
[10] E.M. Matson, W.P. Forrest, P.E. Fanwick, S.C. Bart, Synthesis and reactivity of trivalent $Tp^*U(CH_2Ph)_2$ (THF): insertion vs oxidation at low-valent uranium–carbon bonds, Organometallics 32 (2013) 1484–1492, http://dx.doi.org/10.1021/om301139h.
[11] E.M. Matson, J.J. Kiernicki, P.E. Fanwick, S.C. Bart, Expanding the family of uranium(III) alkyls: synthesis and characterization of mixed-ligand derivatives, Eur. J. Inorg. Chem. 2016 (2016) 2527–2533, http://dx.doi.org/10.1002/ejic.201501251.
[12] S.J. Kraft, P.E. Fanwick, S.C. Bart, Carbon–carbon reductive elimination from homoleptic uranium(IV) alkyls induced by redox-active ligands, J. Am. Chem. Soc. 134 (2012) 6160–6168, http://dx.doi.org/10.1021/ja209524u.
[13] S.A. Johnson, J.J. Kiernicki, P.E. Fanwick, S.C. Bart, New benzylpotassium reagents and their utility for the synthesis of homoleptic uranium(IV) benzyl derivatives, Organometallics 34 (2015) 2889–2895, http://dx.doi.org/10.1021/acs.organomet.5b00212.
[14] W.G. Van der Sluys, C.J. Burns, A.P. Sattelberger, First example of a neutral homoleptic uranium alkyl. Synthesis, properties, and structure of U[CH(SiMe3)2]3, Organometallics 8 (1989) 855–857, http://dx.doi.org/10.1021/om00105a051.
[15] P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam, T.J. Marks, Synthesis and properties of bis(pentamethylcyclopentadienyl) actinide hydrocarbyls and hydrides. A new class of highly reactive f-element organometallic compounds, J. Am. Chem. Soc. 103 (1981) 6650–6667, http://dx.doi.org/10.1021/ja00412a021.
[16] T.J. Marks, A.M. Seyam, J.R. Kolb, Synthesis, chemistry, and spectroscopy of some tris(pentahapto-cyclopentadienyl)uranium(IV) alkyl and aryl compounds, J. Am. Chem. Soc. 95 (1973) 5529–5539, http://dx.doi.org/10.1021/ja00798a018.
[17] G. Li Manni, J.R. Walensky, S.J. Kraft, W.P. Forrest, L.M. Pérez, M.B. Hall, L. Gagliardi, S.C. Bart, Computational insights into uranium complexes supported by redox-active α-diimine ligands, Inorg. Chem. 51 (2012) 2058–2064, http://dx.doi.org/10.1021/ic202522w.
[18] S.J. Kraft, P.E. Fanwick, S.C. Bart, Exploring the insertion chemistry of tetrabenzyluranium using carbonyls and organoazides, Organometallics 32 (2013) 3279–3285, http://dx.doi.org/10.1021/om400197j.
[19] C.J. Tatebe, M. Zeller, S.C. Bart, [2π+2π] cycloaddition of isocyanates to uranium(IV) imido complexes for the synthesis of U(IV) κ^2-ureato compounds, Inorg. Chem. 56 (2017) 1956–1965, http://dx.doi.org/10.1021/acs.inorgchem.6b02547.
[20] E.M. Matson, J.J. Kiernicki, N.H. Anderson, P.E. Fanwick, S.C. Bart, Isolation of a uranium(III) benzophenone ketyl radical that displays redox-active ligand behaviour, Dalton Trans. 43 (2014) 17885–17888, http://dx.doi.org/10.1039/C4DT01636J.
[21] J.J. Kiernicki, R.F. Higgins, S.J. Kraft, M. Zeller, M.P. Shores, S.C. Bart, Elucidating the mechanism of uranium mediated diazene N=N bond cleavage, Inorg. Chem. 55 (2016) 11854–11866, http://dx.doi.org/10.1021/acs.inorgchem.6b01922.
[22] E.M. Matson, W.P. Forrest, P.E. Fanwick, S.C. Bart, Use of alkylsodium reagents for the synthesis of trivalent uranium alkyl complexes, Organometallics 31 (2012) 4467–4473, http://dx.doi.org/10.1021/om3002763.
[23] S.A. Johnson, C.J. Tatebe, S. Gonzalez, M. Zeller, S.C. Bart, Synthesis and characterization of hydrotris(3-phenylpyrazolyl)borate ligands on low-valent uranium, Polyhedron 125 (2017) 107–112, http://dx.doi.org/10.1016/j.poly.2016.09.024.
[24] E.M. Matson, M.D. Goshert, J.J. Kiernicki, B.S. Newell, P.E. Fanwick, M.P. Shores, J.R. Walensky, S.C. Bart, Synthesis of terminal uranium(IV) disulfido and diselenido compounds by activation of elemental sulfur and selenium, Chem.-Eur. J. 19 (2013) 16176–16180, http://dx.doi.org/10.1002/chem.201303095.
[25] J.-C. Berthet, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, Tricyclopentadienyluranium azide complexes, J. Organomet. Chem. 420 (1991) C9–C11, http://dx.doi.org/10.1016/0022-328X(91)80271-K.
[26] W. Li, G. Gao, Y. Gao, C. Yang, W. Xia, Direct oxidation of the C(sp^2)–C(sp^3) bond from benzyltrimethylsilanes to phenols, Chem. Commun. 53 (2017) 5291–5293, http://dx.doi.org/10.1039/C7CC01868A.
[27] C. Raviola, D. Ravelli, S. Protti, M. Fagnoni, Methoxy-substituted α, n -didehydrotoluenes. Photochemical generation and polar vs diradical reactivity, J. Am. Chem. Soc. 136 (2014) 13874–13881, http://dx.doi.org/10.1021/ja507735u.
[28] R.L. Scholl, G.E. Maciel, W.K. Musker, Silicon-29 chemical shifts of organosilicon compounds, J. Am. Chem. Soc. 94 (1972) 6376–6385, http://dx.doi.org/10.1021/ja00773a021.
[29] C.L. Clark, J.J. Lockhart, P.E. Fanwick, S.C. Bart, Synthesis of low-valent uranium fluorides by C–F bond activation, Chem. Commun. 51 (2015) 14084–14087, http://dx.doi.org/10.1039/C5CC05049A.
[30] B.C. Stobbe, D.R. Powell, R.K. Thomson, Schiff base thorium(IV) and uranium(IV) chloro complexes: synthesis, substitution and oxidation chemistry, Dalton Trans. 46 (2017) 4888–4892, http://dx.doi.org/10.1039/C7DT00580F.
[31] E.P. Wildman, J.P.A. Ostrowski, D.M. King, W. Lewis, S.T. Liddle, Uranium–halide and –azide derivatives of the sterically demanding triamidoamine ligand $Tren^{TPS}$ [$Tren^{TPS}$={$N(CH_2CH_2NSiPh_3)_3$}$^{3-}$], Polyhedron 125 (2017) 2–8, http://dx.doi.org/10.1016/j.poly.2016.07.001.
[32] W.J. Evans, E. Montalvo, J.W. Ziller, A.G. DiPasquale, A.L. Rheingold, Uranium metallocene complexes of the 1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-*a*] pyrimidinato ligand, $(hpp)^-$, Inorg. Chem. 49 (2010) 222–228, http://dx.doi.org/10.1021/ic901790t.
[33] S.J. Kraft, J.R. Walensky, P.E. Fanwick, M.B. Hall, S.C. Bart, Crystallographic evidence of a base-free uranium(IV) terminal oxo species, Inorg. Chem. 49 (2010) 7620–7622, http://dx.doi.org/10.1021/ic101136j.
[34] S.J. Kraft, P.E. Fanwick, S.C. Bart, Synthesis and characterization of a uranium(III) complex containing a redox-active 2,2′-bipyridine ligand, Inorg. Chem. 49 (2010) 1103–1110, http://dx.doi.org/10.1021/ic902008w.
[35] I. Castro-Rodriguez, H. Nakai, L.N. Zakharov, A.L. Rheingold, K. Meyer, A linear, O-coordinated 1-CO_2 bound to uranium, Science 305 (2004) 1757–1759, http://dx.doi.org/10.1126/science.1102602.
[36] I. Castro-Rodríguez, K. Olsen, P. Gantzel, K. Meyer, Uranium tris-aryloxide derivatives supported by triazacyclononane: engendering a reactive uranium(III) center with a single pocket for reactivity, J. Am. Chem. Soc. 125 (2003) 4565–4571, http://dx.doi.org/10.1021/ja028342n.
[37] O.P. Lam, S.M. Franke, H. Nakai, F.W. Heinemann, W. Hieringer, K. Meyer, Observation of the inverse trans influence (ITI) in a Uranium(V) imide coordination complex: an experimental study and theoretical evaluation, Inorg. Chem. 51 (2012) 6190–6199, http://dx.doi.org/10.1021/ic300273d.
[38] G. Zi, L. Jia, E.L. Werkema, M.D. Walter, J.P. Gottfriedsen, R.A. Andersen, Preparation and reactions of base-free bis(1,2,4-tri-*tert*-butylcyclopentadienyl)uranium oxide, Cp'$_2$UO, Organometallics 24 (2005) 4251–4264, http://dx.doi.org/10.1021/om050406q.
[39] R.K. Thomson, B.L. Scott, D.E. Morris, J.L. Kiplinger, Synthesis, structure,

spectroscopy and redox energetics of a series of uranium(IV) mixed-ligand metallocene complexes, C. R. Chim. 13 (2010) 790–802, http://dx.doi.org/10.1016/j.crci.2010.04.008.
[40] R.K. Thomson, T. Cantat, B.L. Scott, D.E. Morris, E.R. Batista, J.L. Kiplinger, Uranium azide photolysis results in C–H bond activation and provides evidence for a terminal uranium nitride, Nat. Chem. 2 (2010) 723–729, http://dx.doi.org/10.1038/nchem.705.
[41] R.K. Thomson, C.R. Graves, B.L. Scott, J.L. Kiplinger, Noble reactions for the actinides: safe Gold-based access to organouranium and azido complexes, Eur. J. Inorg. Chem. 2009 (2009) 1451–1455, http://dx.doi.org/10.1002/ejic.200900034.
[42] D.M. King, F. Tuna, E.J.L. McInnes, J. McMaster, W. Lewis, A.J. Blake, S.T. Liddle, Isolation and characterization of a uranium(VI)–nitride triple bond, Nat. Chem. 5 (2013) 482–488, http://dx.doi.org/10.1038/nchem.1642.
[43] A.N. Dame, M.S. Bharara, C.L. Barnes, J.R. Walensky, Synthesis of thorium(IV) and uranium(IV) salicylaldiminate pseudo-halide complexes, Eur. J. Inorg. Chem. 2015 (2015) 2996–3005, http://dx.doi.org/10.1002/ejic.201500378.
[44] L. Maria, I.C. Santos, V.R. Sousa, J. Marçalo, Uranium(III) redox chemistry assisted by a hemilabile bis(phenolate) cyclam ligand: uranium–nitrogen multiple bond formation comprising a trans-$\{RN{=}U(VI){=}NR\}^{2+}$ complex, Inorg. Chem. 54 (2015) 9115–9126, http://dx.doi.org/10.1021/acs.inorgchem.5b01547.
[45] M.-J. Crawford, A. Ellern, P. Mayer, UN_{21}^{3-}: a structurally characterized binary actinide heptaazide anion, Angew. Chem. Int. Ed. 44 (2005) 7874–7878, http://dx.doi.org/10.1002/anie.200502484.
[46] G. Nocton, J. Pécaut, M. Mazzanti, A nitrido-centered uranium azido cluster obtained from a uranium azide, Angew. Chem. Int. Ed. 47 (2008) 3040–3042, http://dx.doi.org/10.1002/anie.200705742.
[47] S. Fortier, G. Wu, T.W. Hayton, U(IV) and U(V) azide complexes supported by amide or aryloxide ligands, Dalton Trans. 39 (2010) 352–354, http://dx.doi.org/10.1039/B909879H.
[48] R. Haiges, M. Vasiliu, D.A. Dixon, K.O. Christe, The Uranium(VI) Oxoazides $[UO_2(N_3)_2 \cdot CH_3CN]$, $[(bipy)_2(UO_2)_2(N_3)_4]$, $[(bipy)UO_2(N_3)_3]^{2-}$, $[UO_2(N_3)_4]$, Chem.-Eur. J. 23 (2017) 652–664, http://dx.doi.org/10.1002/chem.201604154.
[49] F.G. Sherif, A.M. Awad, The structure of uranyl azide—its instability constant in aqueous solutions, J. Inorg. Nucl. Chem. 19 (1961) 94–100, http://dx.doi.org/10.1016/0022-1902(61)80051-1.
[50] A.L. Tamasi, P. Rungthanapathsophon, A.N. Dame, M.A. Moody, C.L. Barnes, M.P. Wilkerson, J.R. Walensky, Pseudo-halide uranyl salicylaldiminate complexes including the isolation of a rare uranyl azide, J. Coord. Chem. 69 (2016) 1904–1913, http://dx.doi.org/10.1080/00958972.2016.1189544.
[51] I. Castro-Rodriguez, K. Meyer, Carbon dioxide reduction and carbon monoxide activation employing a reactive uranium(III) complex, J. Am. Chem. Soc. 127 (2005) 11242–11243, http://dx.doi.org/10.1021/ja053497r.
[52] I.A. Guzei, M. Wendt, An improved method for the computation of ligand steric effects based on solid angles, Dalton Trans. (2006) 3991–3999, http://dx.doi.org/10.1039/b605102b.
[53] I.A. Guzei, M. Wendt, Program Solid-G, 2004.
[54] M.A. Antunes, Â. Domingos, I.C. Santos, N. Marques, J. Takats, Synthesis and characterization of uranium(III) compounds supported by the hydrotris(3,5-dimethyl-pyrazolyl)borate ligand: crystal structures of $[U(TpMe_2)_2(X)]$ complexes (X = OC_6H_2-2,4,6-Me_3, dmpz, Cl), Polyhedron 24 (2005) 3038–3045, http://dx.doi.org/10.1016/j.poly.2005.06.025.
[55] M.A. Antunes, I.C. Santos, H. Bolvin, L.C.J. Pereira, M. Mazzanti, J. Marçalo, M. Almeida, Crystal structure diversity in the bis[hydrotris(3,5-dimethylpyrazolyl)borate]iodouranium(III) complex: from neutral to cationic forms, Dalton Trans. 42 (2013) 8861, http://dx.doi.org/10.1039/c3dt50753j.
[56] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, Safe and convenient procedure for solvent purification, Organometallics 15 (1996) 1518–1520, http://dx.doi.org/10.1021/om9503712.
[57] Y. Sun, R. McDonald, J. Takats, V.W. Day, T.A. Eberspacher, Synthesis and structure of bis[hydrotris(3,5-dimethylpyrazolyl)borato]iodouranium(III), $U[HB(3,5\text{-}Me_2pz)_3]_2I$: unprecedented side-on interaction involving a hydrotris(pyrazolyl)borate ligand, Inorg. Chem. 33 (1994) 4433–4434, http://dx.doi.org/10.1021/ic00098a005.
[58] Apex3 v2016.9-0, Bruker Advanced X-ray Solutions, 2016.