Synthesis and Characterization of Hydrotris(3-phenylpyrazolyl)borate Ligands on Low-Valent Uranium

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Abstract

Treating both $\text{UI}_3(\text{THF})_4$ and $\text{UI}_4(\text{dioxane})_2$ with one equivalent of potassium hydrotris(3-phenylpyrazolyl)borate, KTp^{Ph} , resulted in the formation of new low-valent uranium derivatives, $\text{Tp}^{\text{Ph}}\text{UI}_2(\text{THF})_2$ (**1**) and $\text{Tp}^{\text{Ph}}\text{UI}_3$ (**2**), respectively. Spectroscopic characterization of these species shows that the Tp^{Ph} ligand is 1,2-borotropically shifted, causing one phenyl group to point towards the B-H rather than the uranium center. Derivatization of these materials was possible via salt metathesis reactions, and in each case, the borotropically shifted phenyl group is maintained. Treating trivalent **1** with one equivalent of potassium phenoxide, KOPh , afforded trivalent $\text{Tp}^{\text{Ph}}\text{U}(\text{OPh})\text{I}(\text{THF})_2$ (**1-OPh**), whereas, a uranium(IV) derivative, $\text{Tp}^{\text{Ph}}\text{UI}_2(\text{Phpz})(\text{THF})$ (**2-Phpz**), was synthesized by treating **2** with potassium 3-phenylpyrazolide, KPhpz . All compounds were characterized by ^1H and ^{11}B NMR, infrared, and electronic absorption spectroscopies, and where possible, X-ray crystallography.

Keywords: uranium; scorpionate ligands; trivalent; tridentate; tetravalent

Introduction:

Since their discovery, scorpionate ligands have enjoyed widespread use in supporting metals of the *s*-[1–4], *p*-, [5–8] *d*-[9–13] and *f*-blocks [14–17] of the Periodic Table. Their ubiquity is due in part to their steric and electronic tunability, which is easily accomplished by changing the substituted pyrazole ring. Because hydrotris(pyrazolyl)borate (Tp) ligands take up

three metal coordination sites and are anionically charged, they are often considered to be analogous to cyclopentadienyl rings. However, unlike cyclopentadienyl rings, the steric bulk imparted by 3-pyrazole substitutions of Tp ligands generally points along the axis towards the metal rather than to the side, creating a more sterically protected environment.

When steric congestion occurs, Tp ligands have been observed to undergo a variety of rearrangements. For instance, hydrotris(3,5-dimethylpyrazolyl)borate (Tp*), a pyrazole ring can dissociate from the metal center and spin around on the B-N bond, causing association of the B-H to the new sterically accessible metal. This has been noted for the uranium(IV) imido, $\text{Tp}^*_2\text{U}=\text{NAd}$, where the large adamantyl imido substituent causes this rearrangement.[18] Steric pressure can also be relieved through a complete B-N bond scission, followed by bond formation to the other pyrazole nitrogen, known as a 1,2-borotropic shift. This is typically observed for asymmetric pyrazole rings, where one side has a bulky substituent, and the other does not, thus, there is an energetic gain to the rearrangement. This has been noted for the synthesis of hydrotris(3-mesitylpyrazolyl) borate (Tp^{Ms}), where Jordan and co-workers found their synthesis of hafnium and zirconium complexes to experience a 1,2-borotropic shift.[19]

In previous work from our group, we have demonstrated the utility of the Tp* ligand to support low-valent uranium.[18,20–31] However, the steric protection of this ligand is limited due to the small size of the methyl groups. Thus, we sought to explore hydrotris(pyrazolyl)borate with 3-phenylpyrazole rings (Tp^{Ph}), as the large size of the phenyl groups could offer additional protection for the synthesis of small terminally bonded ligands. Herein, we describe our efforts aimed at ligand metallation and characterization of low-valent Tp^{Ph} -uranium species. Spectroscopic and structural studies support a borotropically shifted pyrazole ring for both uranium(III) and uranium(IV).

Materials and Methods:

General Considerations. All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox is 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 using literature procedures with a Seca solvent purification system.[32] Benzene-*d*₆ was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze-pump-thaw cycles. THF-*d*₈ was used as received from Cambridge Isotope Laboratories. 3-Phenyl-1*H*-pyrazole, trimethylamine, and phenol were purchased from Oakwood Chemical and used without further purification. Potassium phenolate (KOPh) was made by the deprotonation of phenol with benzyl potassium. UI₃(THF)₄[33], UI₄(1,4-dioxane)₂[33], and KTp^{Ph}[9] were made according to literature procedures.

¹H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. ¹¹B NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 96.24 MHz. ¹³C NMR spectra were recorded on a Bruker AV500HD spectrometer equipped with a 5 mm BBFOZ-gradient Cryoprobe Prodigy and operating at 126 MHz. ¹H and ¹³C chemical shifts are reported relative to the peak for SiMe₄, using ¹H residual chemical shifts of the solvent as a secondary standard. ¹¹B chemical shifts are reported relative to BF₃·Et₂O. The spectra for paramagnetic molecules were obtained using an acquisition time of 0.5 s, thus the peak widths reported have an error of ±2 Hz. For paramagnetic molecules, the ¹H 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. 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 measurements were recorded at 294 K in sealed 1 cm quartz cuvettes with a Cary 6000i UV-vis-NIR spectrophotometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc., in Parsippany, NJ or Midwest Microlab LLC in Indianapolis, IN.

Single crystals suitable for X-ray diffraction (**1**×**2-Phpz**, **1-OPh** and **2-Phpz**) were coated with poly(isobutylene) oil in a glovebox. Crystals of **2-Phpz** were transferred to the goniometer head of a Rigaku R-axis curved image plate diffractometer equipped with a MicroMax002+ high-intensity copper X-ray source with confocal optics and examined with Cu K α radiation ($\lambda = 1.54184$ Å). Crystals of **1**×**2-Phpz** and **1-OPh** were transferred to the goniometer head of a Nonius KappaCCD diffractometer equipped with a graphite crystal incident beam monochromator and examined with Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected at low temperature. Data on the KappaCCD instrument were collected using the Nonius Collect software.[34] Data from the R-axis diffractometer were collected using the dtrek option of CrystalClear.[35] All data sets were processed using HKL3000[36] and data were corrected for absorption and scaled using Scalepack.[36] The space groups were assigned using XPREP from the Shelx1 suite of programs[37] and the structures were solved by direct methods with SHELXS[38] and refined by full matrix least squares against F^2 with all reflections using the graphical user interface ShelXle[39] for refinement program SHELXL.[40] H atoms attached to carbon and boron atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for and aromatic C-H, 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH₂ and CH₃ moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}(H)$ values were set to a multiple of

$U_{eq}(C/B)$ with 1.5 for CH_3 , and 1.2 for C-H, CH_2 and B-H units, respectively. Experimental details for each crystal are included in Table 2.

In the co-crystal of **1** and **2-Phpz** a phenylpyrazole and a THF molecule are disordered with each other at a metal coordination site. The disorder is associated with 1:1 disorder of an ether molecule around an inversion center, and the THF/pyrazole disorder was refined as 1:1. The THF molecule was restrained to have a similar geometry as the other not disordered THF molecule in the structure. The 3-phenylpyrazole's geometry was restrained to be similar to that of one of the fragments in the tris pyrazole borate anion. Equivalent bonds in the ether molecule were restrained to be similar. U_{ij} components of ADPs for all disordered atoms were restrained to be similar if closer than 1.7 Å.

In the crystal of pure **2-Phpz** a THF molecule is disordered around an inversion center and induces disorder of two adjacent metal coordinated ligand moieties. The THF molecule was refined to be similar in geometry as the other not disordered THF molecule in the structure, and U_{ij} components of ADPs were restrained to be similar if closer than 1.7 Å. The ligand moieties adjacent to the THF molecule were split in each two 1:1 disordered units. Both moieties of each disordered ligand were each restrained to be similar in geometry, and U_{ij} components of ADPs were restrained to be similar if closer than 1.7 Å.

Preparation of KPhpz: A 20 mL scintillation vial was charged with 0.050 g (0.38 mmol) of benzylpotassium and 5 mL of THF. A second vial was charged with one equivalent 3-phenyl-1*H*-pyrazole (0.38 mmol) and 5 mL of THF. The solution of 3-phenylpyrazole was added dropwise to the stirring solution of benzylpotassium. An instant color change from orange to pale yellow was observed. Solvent was removed by vacuum and the pale yellow solid was washed with pentane. A quantitative yield of **KPhpz** was obtained. Elemental analysis of **KPhpz**: calcd:

C 59.31, H 3.87, N 15.37; found: C 58.88, H 3.93, N 15.20. ^1H NMR ($\text{THF}-d_8$, 25 °C): δ (ppm) = 6.40 (d, 1H, pyrazole-CH), 6.96 (t, 1H, *para*-CH), 7.16 (t, 2H, *ortho*-CH), 7.61 (d, 2H, pyrazole-CH), 7.82 (d, 2H, *meta*-CH). ^{13}C ($\text{THF}-d_8$, 25 °C): δ (ppm) = 151.5, 140.0, 139.2, 128.9, 125.7, 125.1, 100.3.

Preparation of $\text{Tp}^{\text{Ph}}\text{UI}_2(\text{THF})_2$ (1): A 20 mL scintillation vial was charged with $\text{UI}_3(\text{THF})_4$ (0.100 g, 0.110 mmol), KTp^{Ph} (0.054 g, 0.110 mmol) and 10 mL THF. The slurry was stirred at room temperature for 2 hours and a color change from blue to bright purple occurred with formation of KI as a white solid. The solution was filtered over Celite and rinsed with THF. The filtrate was dried *in vacuo* and washed with pentane to afford a purple solid (0.083 g, 0.077 mmol, 71% yield). Dark purple crystals suitable for X-ray crystallography were grown from concentrated THF layered with pentane at -35 °C. Elemental analysis of **1**: calcd: C 40.86 H 3.78 N 7.33; found: C 40.08, H 4.11, N 6.68. ^1H NMR (C_6D_6 , 25 °C): δ (ppm) = -12.51 (3, 4H, Tp^{Ph} -CH), 3.73 (105, 4H, endo Tp^{Ph} -*ortho/meta*-CH), 4.44 (110, 8H, THF), 5.79 (8, 4H, endo Tp^{Ph} -*ortho/meta*-CH), 8.01 (5, 2H, exo Tp^{Ph} -CH), 8.22 (23, 2H, endo Tp^{Ph} -*para*-CH), 8.42 (33, 1H, exo Tp^{Ph} -*para*-CH), 8.88 (8H, THF), 10.11 (28, 2H, exo Tp^{Ph} -*ortho/meta*-CH), 14.88 (52, 2H, Tp^{Ph} -*ortho/meta*-CH). ^{11}B NMR (C_6D_6 , 25 °C): δ (ppm) = 20.63. IR (KBr) $\nu_{\text{B-H}}$ = 2511 cm^{-1} .

Preparation of $\text{Tp}^{\text{Ph}}\text{UI}_3$ (2): A 20 mL scintillation vial was charged with $\text{UI}_4(1,4\text{-dioxane})_2$ (0.100 g, 0.108 mmol), KTp^{Ph} (0.052 g, 0.108 mmol), and 10 mL of THF. The orange slurry was stirred at room temperature for 1 hour, upon which time the color changed to bright yellow. The reaction mixture was filtered over Celite to remove KI, and dried under reduced pressure. The residue was washed with pentane (2×10 mL) and dried under vacuum, affording a yellow powder (0.091 g, 0.086 mmol, 79% yield). Compound was not stable enough for elemental analysis. Attempts at obtaining single crystals suitable for X-ray analysis were unsuccessful. ^1H

NMR (C₆D₆, 25 °C): δ (ppm) = -8.17 (3), 5.76 (2), 6.42 (33), 6.96 (23), 7.97 (45), 13.92 (5), 23.25 (29), 49.09 (4), 55.77 (3), 67.01 (4), 81.72 (3). ¹¹B NMR (C₆D₆, 25 °C): δ (ppm) = -2.65. IR (KBr) $\nu_{\text{B-H}}$ = 2490 cm⁻¹.

Preparation of Tp^{Ph}UI(OPh)(THF)₂ (1-OPh): A 20 mL scintillation vial was charged with 0.050 g (0.047 mmol) of **1** and 5 mL of THF and cooled to -108 °C. A second vial was charged with one equivalent of KOPh (0.006 g, 0.047 mmol) and 5 mL of THF and cooled to -108 °C. While thawing, the two solutions were mixed and stirred for 5 minutes at room temperature before being placed in a freezer at -35 °C. The reaction mixture was cooled for 30 minutes and occasionally agitated, over which time the bright purple solution darkened to deep blue. The solution was filtered over Celite to remove KI and dried *in vacuo*, affording a dark blue powder (0.046 g, 0.044 mmol, 95% yield). Black block crystals suitable for X-ray crystallography, were grown from a concentrated THF solution layered with hexane (1:2). Compound was not stable enough for elemental analysis. ¹H NMR (C₆D₆, 25 °C): δ (ppm) = -12.26 (36), -4.96 (132), 5.07 (5), 5.53 (4), 5.84 (6), 6.14 (4), 6.89 (6), 7.29 (6), 8.40 (18), 9.87 (3), 10.41 (10), 13.80 (5), 15.06 (46), 25.38 (3), 31.50 (28). ¹¹B NMR (C₆D₆, 25 °C): δ (ppm) = -15.98. IR (KBr) $\nu_{\text{B-H}}$ = 2496 cm⁻¹.

Alternate preparation of 1-OPh: A 20 mL scintillation vial was charged with 0.050 g (0.047 mmol) of **1**, 6 equivalents of triethylamine (0.279 mmol), and 5 mL of THF. A second vial was charged with one equivalent of phenol (0.005 g, 0.047mmol) and 5 mL of THF. Both solutions were frozen in a coldwell to -108 °C. While thawing, the solution of phenol was added dropwise to the thawing solution of **1**. The reaction was stirred at room temperature for 10 minutes until completely thawed and mixed. Following addition, the reaction mixture was placed in the freezer at -35 °C for two hours and agitated occasionally, causing the bright purple solution to change to

dark blue. The reaction was filtered over Celite to remove triethylammonium iodide and the filtrate was dried under vacuum and washed with pentane to afford **1-OPh** (0.038 g, 0.037 mmol, 80% yield).

Preparation of $\text{Tp}^{\text{Ph}}\text{UI}_2(\text{3-phenylpyrazole})$ (2-Phpz**):** A 20 mL scintillation vial was charged with **2** (0.050 g, 0.047 mmol) and 5 mL of THF. A second vial was charged with KPhpz (0.010 g, 0.047 mmol) and 5 mL THF. Both vials were cooled to $-35\text{ }^{\circ}\text{C}$; after which the KPhpz solution was added dropwise to **2** while stirring. The reaction mixture was placed in the freezer for 2 hours with frequent agitation. The bright orange-yellow solution slowly lightened to pale yellow. KI was filtered over Celite; crude **2-Phpz** was washed with pentane ($2 \times 5\text{ mL}$) and volatiles were removed *in vacuo* to afford a yellow solid (0.045 g, 0.0392 mmol, 71% yield). Colorless crystals suitable for X-ray crystallography were grown from a THF solution layered with pentane at $-35\text{ }^{\circ}\text{C}$. $\text{C}_{40}\text{H}_{36}\text{BI}_2\text{N}_8\text{OU}$: calcd. C 41.83, N 9.76, H 3.25; found C 41.75, N 9.59, H 3.43. ^1H NMR (C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ (ppm) = -28.87 (20), -3.77 (2), 5.18 (50), 5.79 (5), 6.44 (3), 6.95 (4), 7.23 (8), 8.00 (6), 8.02 (5), 10.70 (8), 15.49 (42), 15.60 (9), 18.73 (712), 22.76 (10), 25.74 (5). ^{11}B NMR (C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ (ppm) = -2.10. IR (KBr) $\nu_{\text{B-H}} = 2482\text{ cm}^{-1}$.

Results and Discussion:

Given our previous synthetic experiences with Tp^* uranium derivatives, we focused our efforts on a more sterically demanding derivative. First, a trivalent derivative was attempted by treating $\text{UI}_3(\text{THF})_4$ with one equivalent of KTp^{Ph} in THF. Following workup, a purple solid was isolated, and analyzed by ^1H NMR spectroscopy. A paramagnetically shifted spectrum was noted, with the number of resonances suggesting asymmetry in the product. Despite this, broad resonances assignable for coordinated THF were visible at 4.44 and 8.88 ppm. One resonance was detected by ^{11}B NMR spectroscopy at -20.63 ppm, which is similar to that observed for

trivalent $\text{Tp}^*\text{U}^{\text{F}}$ at -7.8 ppm. The IR spectrum displays a $\nu_{\text{B-H}}$ absorption at 2511 cm^{-1} , which is shifted from the free ligand (2408 cm^{-1}) and similar to that in $\text{Tp}^*\text{UI}_2(\text{THF})_2$, [28] indicating successful metalation.

The complicated ^1H NMR spectrum of **1** prompted further investigation of the identity of the purple solid by means of X-ray crystallography. Diffraction quality crystals of pure **1** could not be obtained, but 1:1 co-crystals of **1** and **2-Phpz**, where a phenylpyrazole displaces one of the THF molecules at uranium, allowed for the determination of the molecular structure of **1**. Structural characterization revealed that a 1,2-borotropic shift had occurred, in which the boron bond migrated to the other nitrogen. The result is that one phenyl group that typically points toward the uranium center is now oriented in the opposite direction, towards the B-H bond of the scorpionate ligand. Thus, the complicated solution NMR data is rationalized by the asymmetry imparted by the borotropic shift of the pyrazolyl group, which is well preceded for sterically bulky scorpionates.[19,41–53] The geometry of the uranium is distorted trigonal prismatic. The U-N bond distances for Tp^{Ph} in **1** are statistically identical (2.592(6), 2.603(6), 2.567(6) Å) and within the range of what is expected based on Tp^* -uranium derivatives.[20,21,24,31,54–56] The molecular structure also features a I1-U1-I2 angle of $80.96(3)^\circ$, which is slightly smaller than for $\text{Tp}^*\text{UI}_2(\text{THF})_2$, pointing towards a more sterically hindered uranium center in **1**.

Scheme 1. Synthetic scheme for **1**, **2**, **1-OPh**, **2-PhPz**.

Formation of a uranium(IV) derivative of the Tp^{Ph} ligand was also explored. Adding one equivalent of KTp^{Ph} to an orange THF solution of $\text{UI}_4(\text{dioxane})_2$ afforded a pale yellow solid after workup, assigned as $\text{Tp}^{\text{Ph}}\text{UI}_3$ (**2**) (Scheme 1). Although a complicated ^1H NMR spectrum was noted for **2** as in the case of **1**, the single resonance at -44.22 ppm in the ^{11}B NMR spectrum suggested successful metalation. The upfield shift of this resonance as compared to **1** is as expected for a uranium(IV) center, and is in the range of that noted for $\text{Tp}^{\text{Ms}*}\text{UF}_2$ (-63.7 ppm).[20] The infrared spectroscopic data for **2** show a $\nu_{\text{B-H}}$ stretch at 2490 cm^{-1} , which is consistent for a B-H of a scorpionate coordinated to uranium(IV), as in the case of hydrobis(3-mesitylpyrazolyl)(5-mesitylpyrazolyl)borate ($\text{Tp}^{\text{Ms}*}$) $\text{Tp}^{\text{Ms}*}\text{UCl}_3$ (2510 cm^{-1}). Based on the similar spectroscopic features to **1** and $\text{Tp}^{\text{Ms}*}\text{UCl}_3$,[53] we propose the structure of **2** to contain one borotropically shifted pyrazole ring and three iodides completing the coordination sphere. There is no spectroscopic evidence for the presence of coordinated THF molecules. While **1** and

2 are air and moisture sensitive, these compounds show excellent resilience under inert atmosphere, as both are stable at room temperature for hours and are stable for weeks when stored at -35 °C.

In order to assess the reactivity of the Tp^{Ph} uranium iodide compounds which feature the unusual borotropic shift, alkoxide and pyrazole derivatives were made. For trivalent **1**, the phenoxide derivative was targeted to take advantage of the high oxophilicity of uranium. Treating **1** with one equivalent of potassium phenoxide caused a color change from bright purple to deep blue over thirty minutes (Scheme 1, top). After workup, to remove the KI, a blue/black solid was isolated and assigned as $\text{Tp}^{\text{Ph}}\text{U}(\text{OPh})\text{I}(\text{THF})_2$ (**1-OPh**). This species can also be synthesized by the addition of phenol to **1** in the presence of triethylamine, however the removal of KI is easier than $[\text{HNEt}_3][\text{I}]$ and leads to a larger yield and cleaner product. The ^1H NMR spectrum shows similar asymmetry as seen with **1**, **2**, and **2-Phpz**. The protons of the phenoxide appear (*para*-CH:15.06, *ortho/meta*-CH: 25.38, *ortho/meta*-CH: 31.50 ppm) similarly shifted as those found for Tp^*UOPh (*para*-CH:18.35, *meta*-CH: 21.26, *ortho*-CH: 42.57 ppm). [23] The ^{11}B NMR spectrum displays one resonance (-0.85 ppm), which is consistent with trivalent Tp^*UF [20] and other Tp^* -uranium (III) complexes.[31] The IR spectrum reveals an absorption at 2496 cm^{-1} , assignable to the B-H for the coordinated ligand. Overall, **1-OPh** is thermally sensitive, decomposing at room temperature over the course of a day.

In order to explore the coordination mode of Tp^{Ph} in **1-OPh**, black block crystals suitable for X-ray crystallography were grown from a concentrated THF solution layered with hexane (1:2). Analysis showed the expected seven-coordinate uranium(III) phenoxide compound, with two additional THF molecules completing the coordination sphere. The structural geometry is observed to be distorted pentagonal bipyramidal. The borotropically shifted pyrazole ring is

maintained and is in a *trans* position to the aryloxy. The U-O_{aryloxy} distance, 2.184(2) Å, and angle, 162.6(2)°, is on the order of other scorpionate uranium(III) aryloxy species, including Tp*₂UOMes, (2.159(10) Å, 168.2(10)°).[53] The U-N distances are within error of those for **1**, as well as trivalent Tp*-U derivatives,[20,21,24,31,54–56].

Derivatization of **2** was also explored. In this case, formation of the phenylpyrazole derivative, Tp^{Ph}UI₂(3-phenylpyrazole) (**2-Phpz**), was targeted, since a similar adduct is known for the more common Tp*-uranium system, Tp*₂U(3,5-dimethylpyrazole).[55] Synthesis of the desired species was accomplished by treating **2** with a single equivalent of KPhpz in THF at -35 °C (Scheme 1). Compound **2-Phpz** is stable at room temperature over several hours. Analysis by ¹H NMR spectroscopy shows a highly asymmetrical spectrum featuring broad, paramagnetically shifted resonances. Once again, confirmation of the Tp^{Ph} ligand coordinated to uranium was obtained by ¹¹B NMR spectroscopy (-2.10 ppm) and IR spectroscopy (ν_{B-H} = 2482 cm⁻¹).

The solid state structure of **2-Phpz** was elucidated using X-ray crystallography, following work up, colorless crystals were grown from THF layered with pentane at -35 °C (Figure 1, Table 1). Refinement of the data showed the targeted Tp^{Ph}-uranium compound, with two iodide and one 3-phenylpyrazole ligands. One molecule of THF completes the coordination sphere giving the molecule a slightly distorted trigonal prismatic geometry. A disordered interstitial THF molecule imparts disorder onto the coordinated phenylpyrazole in **2-Phpz** (*vide supra*). As for **1** and **1-OPh**, the borotropically shifted phenylpyrazole ring is maintained, as in the case of the synthesis of Tp^{Ms*}U[N(SiMe₃)₂]Cl₂. [53]

Figure 1: Molecular structures of **1** (left), **1-OPh** (middle) and **2-Phpz** (right), displayed with 30% probability. All disorder, selected hydrogen atoms, co-crystallized moieties and solvent molecules are omitted for clarity.

Table 1. Select bond distances of **1**, **2-Phpz**, and **1-OPh**.

Bond Distances (Å)	Tp ^{Ph} UI ₂ (THF) ₂ (1)	Tp ^{Ph} UI ₂ (Phpz)(THF) (2-Phpz)	Tp ^{Ph} UI(OPh)(THF) ₂ (1-OPh)
U1-N1	2.567(6)	2.599(7)	2.594(3)
U1-N3	2.603(6)	2.537(8)	2.654(3)
U1-N5	2.592(6)	2.610(7)	2.660(3)
U1-N5	U1-I1: 3.2112(13) U1-I2: 3.1798(11)	U1-I1: 3.2100(8) U1-I2: 3.2014(8)	U1-N7: 2.60(3) U1-O1: 2.184(2) U1-I1: 3.2574(6)

Table 2. Experimental details

For all structures: triclinic, $P\bar{1}$. Absorption was corrected for by multi-scan methods, *SCALEPACK*.^[36] H-atom parameters were constrained.

	2-Phpz	1-OPh	1×2-Phpz
CCDC dep. #	1488925	1488926	1488924
Crystal data			
Chemical formula	2(C ₄₀ H ₃₇ BI ₂ N ₈ OU)·C ₄ H ₈ O	C ₄₁ H ₄₃ BI ₂ N ₆ O ₃ U·2(C ₄ H ₈ O)	C ₃₅ H ₃₈ BI ₂ N ₆ O ₂ U·C ₄₀ H ₃₇ BI ₂ N ₈ OU·C ₄ H ₁₀ O
<i>M_r</i>	2368.94	1187.76	2299.89

Temperature (K)	200	100	100
a, b, c (Å)	10.1939 (6), 11.1350 (7), 20.6212 (11)	10.7202 (16), 13.358 (3), 17.347 (2)	9.938 (2), 10.961 (2), 20.389 (4)
α, β, γ (°)	103.257 (4), 92.522 (4), 110.858 (5)	93.094 (6), 91.403 (5), 105.086 (9)	100.04 (3), 94.71 (3), 109.75 (3)
V (Å ³)	2108.6 (2)	2392.9 (8)	2034.3 (8)
Z	1	2	1
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	22.68	4.09	5.55
Crystal shape	Chip	Block	Plate
Colour	Purple	Black	Purple
Crystal size (mm)	$0.20 \times 0.10 \times 0.05$	$0.45 \times 0.31 \times 0.27$	$0.45 \times 0.25 \times 0.07$
Data collection			
Diffractometer	Rigaku Rapid II curved image plate diffractometer	Nonius Kappa CCD diffractometer	Nonius Kappa CCD diffractometer
$T_{\min}, T_{\max}$	0.032, 0.322	0.175, 0.405	0.233, 0.697
No. of measured, independent and observed [$I >$ $2\sigma(I)$] reflections	7349, 7349, 6203	50782, 12119, 10688	23790, 9776, 7655
R_{int}	0.077	0.035	0.054
Refinement			
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.049, 0.130, 1.10	0.028, 0.060, 1.09	0.053, 0.146, 1.04
No. of reflections	7349	12119	9776
No. of parameters	706	569	572
No. of restraints	755	0	303
	$w = 1/[\sigma^2(F_o^2) +$ $(0.0544P)^2 +$ $18.1672P]$ where $P = (F_o^2 +$ $2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) +$ $7.8802P]$ where $P = (F_o^2 +$ $2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) +$ $(0.0777P)^2 +$ $9.8252P]$ where $P = (F_o^2 +$ $2F_c^2)/3$

Computer programs: *CrystalClear*-SM Expert 2.1 b32[35], Nonius Collect[34], *HKL-3000* [36], *SHELXS97*[38], *SHELXL2014/7*,[40] *SHELXL* Rev714[39], *SHELXL* Rev761.[39]

To gain insight into the electronic structures of the new Tp^{Ph} family of compounds, **1**, **1-OPh**, **2**, and **2-Phpz**, electronic absorption spectroscopy was employed. Data for all compounds were recorded from 300 to 1800 nm in THF at ambient temperature (Figure 2). For **1** and **1-OPh**, the visible region shows weak color-producing bands at 526 nm ($119 \text{ M}^{-1}\text{cm}^{-1}$) and 505 nm ($46 \text{ M}^{-1}\text{cm}^{-1}$), respectively. The near-infrared region displays weak and poorly defined f - f transitions for **1** and **1-OPh**, which has been seen with previously reported uranium (III) complexes.[20,23,26–28,30,31] In contrast, the visible region for **2** and **2-Phpz** displays broad, weak absorptions as expected for uranium(IV) species, similar to yellow $\text{Tp}^*_2\text{U}(\eta^2\text{-S}_2)$. [29] The near-infrared region for **2** and **2-Phpz** shows sharp, weak f - f transitions indicative of uranium (IV) ions.[18]

Figure 2: Electronic absorption spectra of **1**, **2**, **1-OPh**, **2-Phpz** recorded from 300 to 1800 nm in THF at ambient temperature.

Conclusions:

In summary, we have synthesized uranium complexes bearing the Tp^{Ph} scorpionate ligand. Treating these ligands with $\text{UI}_3(\text{THF})_4$ and $\text{UI}_4(1,4\text{-dioxanes})_2$ salts resulted in metalation and a simultaneous ligand isomerization through a 1,2-borotropic shift. Further derivatization was possible via salt metathesis, and in each case, the borotropically shifted pyrazole group was maintained. All oxidation states were maintained throughout the course of the study, with no unwanted redox chemistry occurring. The new uranium species presented here expand upon the family of scorpionate uranium compounds previously known. These unique species can adjust the steric environment of the uranium center by displacement of the phenyl rings from the coordination sphere.

References:

- [1] O. Michel, H.M. Dietrich, R. Litlabø, K.W. Törnroos, C. Maichle-Mössner, R. Anwander, *Organometallics* 31 (2012) 3119–3127.
- [2] M.H. Chisholm, N.W. Eilerts, J.C. Huffman, S.S. Iyer, M. Pacold, K. Phomphrai, *J. Am. Chem. Soc.* 122 (2000) 11845–11854.

- [3] Y. Sohrin, H. Kokusen, S. Kihara, M. Matsui, Y. Kushi, M. Shiro, *J. Am. Chem. Soc.* 115 (1993) 4128–4136.
- [4] R. Han, G. Parkin, *Inorg. Chem.* 31 (1992) 983–988.
- [5] C.A. Dodds, A.R. Kennedy, J. Reglinski, M.D. Spicer, *Inorg. Chem.* 43 (2004) 394–395.
- [6] Z. Ciunik, T. Ruman, M. Lukasiewicz, S. Wolowiec, *J. Mol. Struct.* 690 (2004) 175–180.
- [7] A. Frazer, B. Piggott, M.B. Hursthouse, M. Mazid, *J. Am. Chem. Soc.* 116 (1994) 4127–4128.
- [8] G. Ferguson, M.C. Jennings, F.J. Lalor, C. Shanahan, *Acta Crystallogr., Sect. C* 47 (1991) 2079–2082.
- [9] D.M. Eichhorn, W.H. Armstrong, *Inorg. Chem.* 29 (1990) 3607–3612.
- [10] A. Dehestani, A. Wu, R. Hayoun, W. Kaminsky, J.M. Mayer, *Inorg. Chim. Acta* 362 (2009) 4534–4538.
- [11] K. Mashima, T. Oshiki, K. Tani, *Organometallics* 16 (1997) 2760–2762.
- [12] K. Michiue, T. Oshiki, K. Takai, M. Mitani, T. Fujita, *Organometallics* 28 (2009) 6450–6457.
- [13] A. Kremer-Aach, W. Kläui, R. Bell, A. Strerath, H. Wunderlich, D. Mootz, *Inorg. Chem.* 36 (1997) 1552–1563.
- [14] J. Cheng, M.J. Ferguson, J. Takats, *J. Am. Chem. Soc.* 132 (2010) 2–3.
- [15] D. Schädle, C. Maichle-Mössmer, C. Schädle, R. Anwander, *Chem.-Eur. J.* 21 (2015) 662–670.
- [16] J.L. Galler, S. Goodchild, J. Gould, R. McDonald, A. Sella, *Polyhedron* 23 (2004) 253–262.
- [17] A.C. Hillier, Zhang, G.H. Maunder, S.Y. Liu, T.A. Eberspacher, M. V. Metz, R.

- McDonald, Â. Domingos, N. Marques, V.W. Day, A. Sella, J. Takats, *Inorg. Chem.* 40 (2001) 5106–5116.
- [18] E.M. Matson, M.G. Crestani, P.E. Fanwick, S.C. Bart, *Dalton Trans.* 41 (2012) 7952.
- [19] K. Michiue, R.F. Jordan, *Organometallics* 23 (2004) 460–470.
- [20] C.L. Clark, J.J. Lockhart, P.E. Fanwick, S.C. Bart, *Chem. Commun.* 51 (2015) 14084–14087.
- [21] S.J. Kraft, P.E. Fanwick, S.C. Bart, *Inorg. Chem.* 49 (2010) 1103–1110.
- [22] S.J. Kraft, J.R. Walensky, P.E. Fanwick, M.B. Hall, S.C. Bart, *Inorg. Chem.* 49 (2010) 7620–7622.
- [23] E.M. Matson, A.T. Breshears, J.J. Kiernicki, B.S. Newell, P.E. Fanwick, M.P. Shores, J.R. Walensky, S.C. Bart, *Inorg. Chem.* 53 (2014) 12977–12985.
- [24] E.M. Matson, P.E. Fanwick, S.C. Bart, *Eur. J. Inorg. Chem.* 2 (2012) 5471–5478.
- [25] E.M. Matson, P.E. Fanwick, S.C. Bart, *Organometallics* 30 (2011) 5753–5762.
- [26] E.M. Matson, W.P. Forrest, P.E. Fanwick, S.C. Bart, *J. Am. Chem. Soc.* 133 (2011) 4948–4954.
- [27] E.M. Matson, W.P. Forrest, P.E. Fanwick, S.C. Bart, *Organometallics* 32 (2013) 1484–1492.
- [28] E.M. Matson, W.P. Forrest, P.E. Fanwick, S.C. Bart, *Organometallics* 31 (2012) 4467–4473.
- [29] E.M. Matson, M.D. Goshert, J.J. Kiernicki, B.S. Newell, P.E. Fanwick, M.P. Shores, J.R. Walensky, S.C. Bart, *Chem.-Eur. J.* 19 (2013) 16176–16180.
- [30] E.M. Matson, J.J. Kiernicki, N.H. Anderson, P.E. Fanwick, S.C. Bart, *Dalton Trans.* 43 (2014) 17885–17888.

- [31] E.M. Matson, J.J. Kiernicki, P.E. Fanwick, S.C. Bart, *Eur. J. Inorg. Chem.* 2016 (2016) 2527–2533.
- [32] A.B. Pangborn, M. a. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics* 15 (1996) 1518–1520.
- [33] M.J. Monreal, R.K. Thomson, T. Cantat, N.E. Travia, B.L. Scott, J.L. Kiplinger, *Organometallics* 30 (2011) 2031–2038.
- [34] Nonius, (1998).
- [35] Rigaku Corp., (2014).
- [36] Z. Otwinowski, W. Minor, in: *Methods Enzymol.*, 1997, pp. 307–326.
- [37] Bruker Advanced X-ray Solutions, (2003).
- [38] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 64 (2008) 112–122.
- [39] C.B. Hübschle, G.M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* 44 (2011) 1281–1284.
- [40] G.M. Sheldrick, *Acta Crystallogr., Sect. C* 71 (2015) 3–8.
- [41] M. Cano, J. V. Heras, C.J. Jones, J.A. McCleverty, S. Trofimenko, *Polyhedron* 9 (1990) 619–621.
- [42] M.H. Chisholm, N.W. Eilerts, J.C. Huffman, *Inorg. Chem.* 35 (1996) 445–450.
- [43] P. Cui, Y. Chen, M. V. Borzov, *Dalton Trans.* 39 (2010) 6886.
- [44] L.R. Kadel, J.R. Bullinger, R.R. Baum, C.E. Moore, D.L. Tierney, D.M. Eichhorn, *Eur. J. Inorg. Chem.* 2016 (2016) 2543–2551.
- [45] M. Kumar, E.T. Papish, M. Zeller, A.D. Hunter, *Dalton Trans.* 40 (2011) 7517.
- [46] F.A. Kunrath, R.F. de Souza, O.L. Casagrande, N.R. Brooks, V.G. Young, *Organometallics* 22 (2003) 4739–4743.
- [47] D.D. LeCloux, M.C. Keyes, M. Osawa, V. Reynolds, W.B. Tolman, *Inorg. Chem.* 33

- (1994) 6361–6368.
- [48] L. Maria, Â. Domingos, I. Santos, *Inorg. Chem.* 42 (2003) 3323–3330.
- [49] N. Romero, L. Vendier, C. Dinoi, M. Etienne, *Dalton Trans.* 43 (2014) 10114.
- [50] T. Ruman, Z. Ciunik, S. Wołowiec, *Eur. J. Inorg. Chem.* 2003 (2003) 2475–2485.
- [51] S. Trofimenko, J.C. Calabrese, P.J. Domaille, J.S. Thompson, *Inorg. Chem.* 28 (1989) 1091–1101.
- [52] J.M. White, V.W.L. Ng, D.C. Clarke, P.D. Smith, M.K. Taylor, C.G. Young, *Inorg. Chim. Acta* 362 (2009) 4570–4577.
- [53] M. Silva, Â. Domingos, A. Pires de Matos, N. Marques, S. Trofimenko, *J. Chem. Soc., Dalton Trans.* (2000) 4628–4634.
- [54] Â. Domingos, N. Marques, A.P. De Matos, I. Santos, M. Silva, *Polyhedron* 11 (1992) 2021–2025.
- [55] M.A. Antunes, Â. Domingos, I.C. Santos, N. Marques, J. Takats, *Polyhedron* 24 (2005) 3038–3045.
- [56] M.A. Antunes, G.M. Ferrence, Â. Domingos, R. McDonald, C.J. Burns, J. Takats, N. Marques, *Inorg. Chem.* 43 (2004) 6640–6643.