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Synthesis and Characterization of a Uranium(III) Complex Containing a Redox-Active 2,2′-Bipyridine Ligand

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Hydrotris(3,5-dimethylpyrazolyl)borate uranium(III) diiodide derivatives have been prepared as an entry into low-valent uranium chemistry with these ligands. The bis(tetrahydrofuran) adduct, Tp*$UI_2(THF)_2$ (**1**) (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate), was synthesized by addition of sodium hydrotris(3,5-dimethylpyrazolyl)borate (NaTp*) to an equivalent of $UI_3(THF)_4$. Addition of 2,2′-bipyridine (2,2′-bpy) to **1** displaced the THF molecules producing Tp*UI_2(2,2′-bpy) (**2**). Both derivatives were characterized by ^{1}H NMR and IR spectroscopies, magnetic measurements, and X-ray crystallography. Reduction of both species was attempted with two equivalents of potassium graphite. The reduction of **1** did not result in a clean product, but rather decomposition and ligand redistribution. However, compound **2** was reduced to form Tp^*_2U(2,2′-bpy), **3**, which is composed of a uranium(III) ion with a radical monoanionic bipyridine ligand. This was confirmed by X-ray crystallography, which revealed distortions in the bond lengths of the bipyridine consistent with reduction. Further support was obtained by ^{1}H NMR spectroscopy, which showed resonances shifted far upfield, consistent with radical character on the 2,2′-bipyridine ligand. Future studies will explore the reactivity of this compound as well as the consequences for redox-activity in the bipyridine ligand.

Introduction

The highly reducing nature of uranium makes it a good candidate for the activation of small molecules.[1] The low cost and high availability[2] of depleted uranium warrant the study of this metal for bond activation reactions, as it could potentially be an alternative to precious metals in important chemical transformations. Uranium(III) is especially desirable as it is electron rich and has been demonstrated to activate small molecules including dinitrogen,[3−6] diazoalkanes,[7] azides,[8−16] azobenzene,[17−20] water,[6] and hydrocarbons.[6] Furthermore, the products of activation of carbon dioxide,[21] carbon monoxide,[22−25] and cyclic hydrocarbons[26] by uranium(III) have not been paralleled by transition metals. For example, Meyer[7,27] and Ephritikhine[28] have separately reported uranium(III) species which reduce

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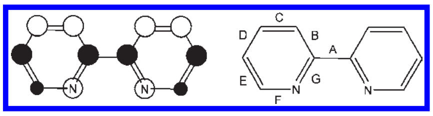
Table 1. Comparison of Bond Distances of 2,2′-Bipyridine in Rare Earth Complexes with Reduced 2,2′-Bipyridine Ligands



Bond	2,2′-bpy[40]	Cp^*_2Sm-(2,2′-bpy)	Cp^*_2Yb-(2,2′-bpy)	Tp^*_2La-(2,2′-bpy)	$[U(NCS)_5$-$(bpy)_2]^-$
A	1.490(3)	1.429(4)	1.44(1)‡ 1.43(1)	1.45(2)	1.391(1) 1.469(1)

‡Two distinct molecules in the unit cell were observed.

organic molecules to form tetravalent uranium(IV) compounds with radical anionic ligands. Other radical compounds have been made by Girolami and Suslick who have reported uranium(IV) bis-porphryn sandwich compounds which are composed of π-radical ligands.[29] The unmatched reactivity of uranium demonstrates this element's unique ability to reduce organics and stabilize some types of ligand radicals.

Controlling the reactivity of the electron-rich uranium(III) center, mediating its ability to perform radical chemistry, and eliminating decomposition reactions are key to harnessing its reducing power for desired bond activations and chemical transformations. Thus redox-active ligands, those that participate in redox chemistry with the metal center, are an attractive choice to control potential radical chemistry. These ligands offer a place for electron-rich metal centers to transfer and store electron density rather than channel this energy for unwanted side reactions. The advantage of using this family of ligands is that the metal center can access the reducing equivalents when necessary, allowing them to be directed toward incoming molecules. Redox-active ligands (also called redox non-innocent or redox-flexible) have been effectively utilized on first row transition metals to prevent unwanted radical chemistry typically observed with these metals,[30] and extensive studies have been performed with multiple analytical techniques to establish ligand involvement on these metal centers.[31−34] Recently, Gambarotta has demonstrated the utility of redox-active ligands to effectively stabilize low-valent uranium centers and has used DFT calculations to establish ligand participation.[35]

One of the most well-known redox-flexible ligands, 2,2′-bipyridine (2,2′-bpy), can accept either one or two electrons into its π^* orbitals. Occupation of the lowest energy LUMO depicted in Table 1 (black and white circles represent orbitals of opposite phases) results in bond distortions in the bipyridine molecule which can be observed by X-ray crystallography. The bonds composed of antibonding interactions (B,D,F,G) in the LUMO lengthen whereas those with the bonding interactions (C,E,A) shorten, with the most striking change occurs for the C−C single bond connecting the two pyridines (A).

A search of the Cambridge Crystallographic Database reveals that as a ligand for *f*-block elements, 2,2′-bipyridine remains predominantly redox innocent, not participating in redox chemistry with the metal center. However, a small number of examples exist where the bipyridine has been reduced. The lanthanide compounds $Cp^*_2Sm(2,2'\text{-}bpy)$,[36] $Cp^*_2Yb(2,2'\text{-}bpy)$,[37] and $Tp^*_2La(2,2'\text{-}bpy)$[38] (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) and the uranium(IV) anion $[U(NCS)_5(2,2'\text{-}bpy)_2]^-$[39] have been established to contain reduced bipyridine radical monoanions based on their structural parameters.

A comparison of the bond distances for A in these molecules with free 2,2′-bipyridine[40] is presented in Table 1. This distance is indicative of reduction and these values differ significantly by the three σ rule. Although bonds B−G can be compared as well, the error associated with these values causes these distances to be less reliable (distances A−G reported in the Supporting Information, Table S1). As is evident from the tabulated data, the changes in bond distances are quite striking for these compounds as compared to the free ligand, supporting these ligands as monoanionic species. Similar uranium complexes, $Cp^*_2U(2,2'\text{-}bpy)$ and $Cp^{tBu3}_2U(2,2\text{-}bpy)$ (Cp^{tBu3} = η^5-1,2,4-tri-*tert*-butylcyclopentadienide), have been synthesized by Ephritikhine and Andersen, respectively, but no structural evidence to support reduction was provided.[41,42] In the former example, large shifts displayed in the ^{1}H NMR spectrum support formation of a radical monoanionic bipyridine ligand. Based on these interesting compounds, we set out to determine if similar derivatives with the hydrotris(pyrazolyl)borate framework could be identified for uranium. Herein, we report the synthesis and characterization of hydrotris(pyrazolyl)borate uranium diiodide complexes, their ability to undergo ligand substitution chemistry, and the reduction chemistry of these complexes. Characterization of these complexes was accomplished using ^{1}H NMR and IR spectroscopies, magnetometry, and X-ray crystallography, and the results of these studies are reported here.

Experimental Section

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 was equipped with a coldwell designed for freezing samples in liquid nitrogen as well as two −35 °C freezers for cooling samples and crystal-

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lizations. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.[43] Benzene-d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze−pump−thaw cycles. Elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, IN. 2,2′-Bipyridine was purchased from Sigma Aldrich and was dried overnight on the Schlenk line, followed by recrystallization from dry ether. Depleted uranium was purchased from Manufacturing Sciences in Oak Ridge, TN. $UI_3(THF)_4$[44,45] and Tp^*_2UI[46] were prepared according to literature procedures.

^1H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. All chemical shifts are reported relative to the peak for $SiMe_4$ using ^1H (residual) chemical shifts of the solvent as a secondary standard. The spectra for paramagnetic molecules were obtained using an acquisition time of 0.5, 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 magnetic moments were recorded on a Johnson Matthey magnetic susceptibility balance at 20 °C. Solid state infrared spectra were recorded using a Perkin-Elmer FT-IR Spectrum RX I spectrometer. Samples were made by crushing the solids, mixing with dry KBr, and pressing into a pellet.

Single crystals for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of a Rigaku Rapid II image plate diffractometer equipped with a MicroMax002+ high intensity copper X-ray source with confocal optics. Preliminary examination and data collection were performed with Cu Kα radiation (l = 1.54184 Å). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.[47] The structures were solved using the structure solution program PATTY in DIRDIFF99.[48] Refinement was performed on a LINUX PC using SHELX-97.[47] The data were collected at a temperature of 150(1) K.

Synthesis of NaTp*. The procedure for sodium hydrotris(3,5-diphenylpyrazolyl)borate was modified.[49] A 100-mL round-bottomed flask was charged with 0.500 g (0.0132 mol) of $NaBH_4$ and 5.09 g (0.0528 mol) of 3,5-dimethylpyrazole. The flask was fitted with a condenser and was stirred and heated slowly to 250 °C for 12 h until 3 equiv of $H_{2\,(g)}$ evolved. The condenser was used to avoid sublimation of the pyrazole. A white solid formed, and the reaction was removed from heat after the evolution of $H_{2\,(g)}$ ceased. Warm toluene was added to the solid and filtered. The solid was washed with hexane (3 × 20 mL), and was dried under vacuum to afford sodium hydrotris(pyrazolyl)borate as a white solid. Yield: 3.65 g (0.0114 mol, 86%). IR (KBr pellet): B−H, 2452 cm^{-1}. ^1H NMR ($(CD_3)_2{=}O$, 25 °C): $\delta = 2.39$ (s, 18H, CH_3), 5.60 (s, 3H, pyrazole-CH).

Synthesis of $Tp^*UI_2(THF)_2$ (1). A 250-mL round-bottom flask was charged with 1.058 g (1.17 mmol) $UI_3(THF)_4$ and approximately 80 mL of THF. A 20-mL scintillation vial was charged with 0.372 g (1.17 mmol) of NaTp* and 10 mL of THF to dissolve. While stirring, the solution of the ligand was dripped into the solution in the flask, causing it to turn from dark blue to purple. After stirring for 3 h, the solvent was reduced in vacuo, and equal amounts of ether and toluene were added to precipitate the sodium iodide. The solution was filtered over Celite, and the filter cake was washed with ether and toluene until the solvents were pale blue. Removal of the volatiles in vacuo produced a blue−purple solid assigned as $Tp^*UI_2(THF)_2$ (**1**). This crude material was used without further purification. Yield: 1.049 g (96%). Analytically pure material can be obtained by recrystallization from THF. Analysis for $C_{23}H_{38}N_6BI_2O_2U$: Calcd. C, 29.60; H, 4.10; N, 9.00. Found C, 29.49; H, 3.91; N, 8.89. ^1H NMR (C_6D_6, 25 °C): $\delta = -13.9$ (49, 9H, CH_3), 1.3 (15, 8H, CH_2), 2.3 (13, 9H, CH_3), 3.2 (25, 8H, CH_2), 7.9 (10, 1H, CH), 15.9 (126, 1H, BH). IR (KBr pellet): B−H, 2559 cm^{-1}. $\mu_{eff} = 2.9\ \mu_B$.

Synthesis of Tp^*UI_2(2,2′-bpy) (2). A 20-mL scintillation vial was charged with 0.133 g (0.143 mmol) of $Tp^*UI_2(THF)_2$. While stirring, a solution of toluene and 0.022 g (0.143 mol) of 2,2′-bipyridine was added, which immediately resulted in the precipitation of a dark solid. The mixture was stirred for an additional hour. The precipitate was collected by vacuum filtration and washed thoroughly with pentane. The solid was transferred to a vial and THF was added to dissolve it. The solution was again filtered by vacuum filtration to remove any insoluble impurities and the filtrate was dried under vacuum to yield Tp^*UI_2(2,2′-bpy) (**2**) as a dark blue solid. Yield: 0.100 g (74%). **2** is temperature sensitive, and must be stored at −35 °C; the blue solid turns brown readily. Elemental analyses were not passing due to the extreme sensitivity of this compound. ^1H NMR (C_6D_6, 25 °C): $\delta = -25.4$ (20, 6H, Tp*-CH_3), −12.9 (20, 3H, Tp*-CH_3), −1.5 (12, 1H, bipy-CH), 2.9 (5, 9H, Tp*-CH_3), 9.0 (6, 3H, pyrazole-CH), 12.8 (14, 1H, bipy-CH), 16.4 (7, 1H, bipy-CH), 16.6 (7, 1H, bipy-CH), 17.9 (14, 1H, bipy-CH), 18.6 (16, 1H, bipy-CH), 23.0 (228, 1H, BH), 24.4 (5, 1H, bipy-CH), 26.5 (17, 1H, bipy-CH). IR (KBr pellet): B−H, 2561 cm^{-1}. $\mu_{eff} = 2.7\ \mu_B$.

Synthesis of Tp^*_2U(2,2′-bpy). A 20-mL scintillation vial was charged with 0.200 g (0.212 mmol) of Tp^*UI_2(2,2′-bpy) and toluene. While stirring, 0.057 g (0.424 mmol) of KC_8 was added. This was stirred for 3 h, after which the dark brown reaction was filtered over Celite to remove graphite from the reaction. Removal of the toluene in vacuo produced 0.080 g (0.081 mmol, 38% based on uranium) of Tp^*_2U(2,2′-bpy).

Independent Synthesis of Tp^*_2U(2,2′-bpy). A 20-mL scintillation vial was charged with 0.150 g (0.156 mmol) of Tp^*_2UI and approximately 5 mL of toluene. Next, 0.024 g (0.156 mmol) of 2,2′-bipyridine was dissolved in 5 mL of toluene and added to the mixture; no color change was observed. Immediately 0.021 g (0.156 mmol) of KC_8 was weighed by difference and added to the vial while stirring. The red−brown mixture was stirred overnight. The graphite was removed by filtration over Celite and a dark brown−red solid was obtained after removal of the toluene in vacuo. Yield = 0.134 g (0.135 mmol, 87%). The reaction proceeds in 3 h using 2 equiv of KC_8. Elemental analyses were not passing due to the extreme sensitivity of this compound. The brown−red solid turns green at room temperature. ^1H NMR (C_6D_6, 25 °C): $\delta = -254.8$ (364, 2H, bipyridine CH), −134.3 (631, 2H, bipyridine CH), −26.0 (16, 6H, Tp*-CH_3), −13.5 (63, 2H), −6.2 (14, 6H, Tp*-CH_3), −5.9 (12, 6H, Tp*-CH_3), −4.7 (250, 2H, BH), −1.6 (9, 6H, Tp*-CH_3), −1.5 (9, 6H, Tp*-CH_3), −1.2 (15, 2H), 6.1 (9, 2H), 12.6 (9, 2H), 16.0 (17, 6H, Tp*-CH_3), 42.6 (64, 2H). IR = 2515, 2545 cm^{-1} (B−H).

Results and Discussion

Synthesis of Uranium(III) Diiodide Complexes. As an entry to uranium(III) ions supported by hydrotris(pyrazolyl)borate ligands, we initially sought to prepare $Tp^*UI_2(THF)_2$. As originally reported by Takats, the synthesis was performed by stirring an equivalent of sodium hydrotris(3,5-dimethylpyrazolyl)borate, NaTp*,

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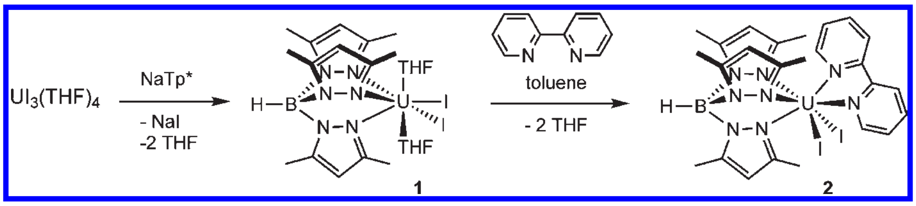
Scheme 1



with $UI_3(THF)_4$ in THF (Scheme 1) and provided the desired product as a blue solid in 97% yield.[50] Takats characterized this product by X-ray crystallography and described an unpublished molecular structure with a seven coordinate uranium center in a distorted capped octahedral geometry.[51]

Takats' synthesis was accomplished in a similar manner in our laboratory using a modified workup procedure (see Experimental Section), and a blue–purple solid assigned as $Tp^*UI_2(THF)_2$ (**1**) (Scheme 1) was isolated in 96% crude yield. Prepared in this way, the compound was pure enough to explore further reactivity. Full characterization of **1** was performed in our laboratory. Infrared spectroscopy confirmed the presence of the ligand in **1**, which displayed a B–H peak at 2559 cm^{-1}, shifted from 2452 cm^{-1} in the free ligand. In addition, solid state magnetic studies on two independently synthesized samples established a magnetic moment of 2.9 μ_B for **1**. Although no magnetic studies have been performed on hydrotris(pyrazolyl)borate uranium(III) complexes, the magnetic moment observed is consistent with previously characterized uranium(III) compounds with other ligand sets.[13,14,52–54]

Because the details of the solid state structure of complex **1** were not originally published by Takats, our laboratory obtained crystallographic data for this compound to confirm the structure. Analysis of crystals of **1** grown from THF, ether, and toluene (~1:1:1) established a seven coordinate uranium center with two THF ligands coordinated (Figure 1, metrical parameters in Table 2). The uranium center has a distorted capped octahedral geometry as originally reported by Takats.[50] The individual U–N ligand distances are within the range expected for uranium(III) hydrotris(pyrazolyl)borate complexes.[55] The average distance of 2.54 Å, however, is the shortest average for uranium(III) hydrotris(pyrazolyl)borate compounds to date.[56] The U–O distances in **1** of 2.582(5) and 2.615(6) Å are similar to those in UI_3THF_4, which range from 2.48(1) to 2.56(1) Å.[44] The uranium–iodide distances in UI_3THF_4 are 3.103(2), 3.119(2), and 3.167(2) Å and are similar to those found in **1**, which are 3.1320(7) and 3.1944(6) Å. The latter distances are slightly longer, most likely due to the increased sterics and rigidity imparted by the hydrotris(pyrazolyl)borate ligand.

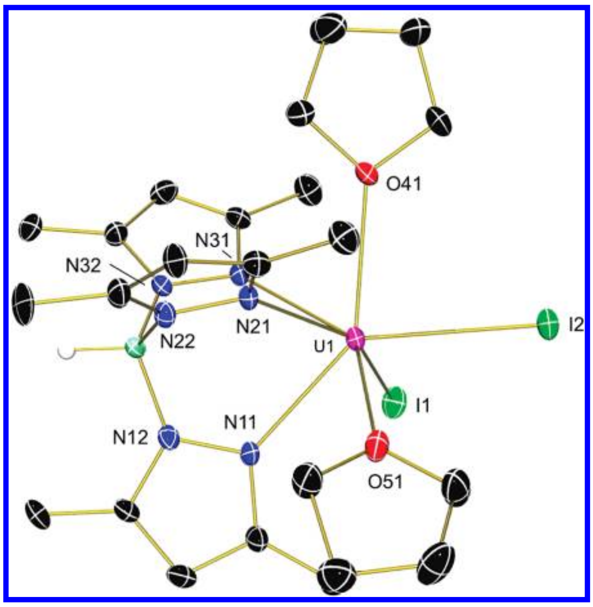


Figure 1. Molecular structure of **1** shown with 30% probability ellipsoids. Selected hydrogen atoms and solvent molecules have been omitted for clarity.

Table 2. Structural Parameters for **1**

	1, length (Å)		**1**, angles (°)
U1–N11	2.521(6)	N11–U1–N21	75.1(2)
U1–N21	2.542(7)	N21–U1–N31	73.9(2)
U1–N31	2.563(7)	N11–U1–N31	73.8(2)
U1–O41	2.582(5)	O41–U1–I1	113.85(16)
U1–O51	2.615(6)	O51–U1–I1	118.76(14)
U1–I1	3.1320(7)	O41–U1–O51	121.5(2)
U1–I2	3.1944(6)	I1–U–I2	85.470(17)

Analysis of a benzene-d_6 solution of **1** by ^1H NMR spectroscopy at 23 °C shows a paramagnetically broadened and shifted, but still assignable, spectrum (Figure 2) demonstrating that in some instances, NMR spectroscopy is a useful tool for the characterization of these complexes. The highly symmetric nature of the proton NMR spectrum indicates the fluxional behavior of **1**, as the capped octahedral geometry does not persist in solution. The resonances for the two methyl groups on the pyrazole rings appear at −13.9 and 2.3 ppm. The pyrazole ring proton (CH) is visible at 7.9, while the B–H proton is shifted to 15.9 ppm. The peaks for the coordinated THF molecules appear at 3.3 to 3.2 ppm, and are broad due to interaction with the uranium center. This spectrum is very similar to that previously reported for Tp^*UCl_2,[57] which lacks coordinated THF ligands.

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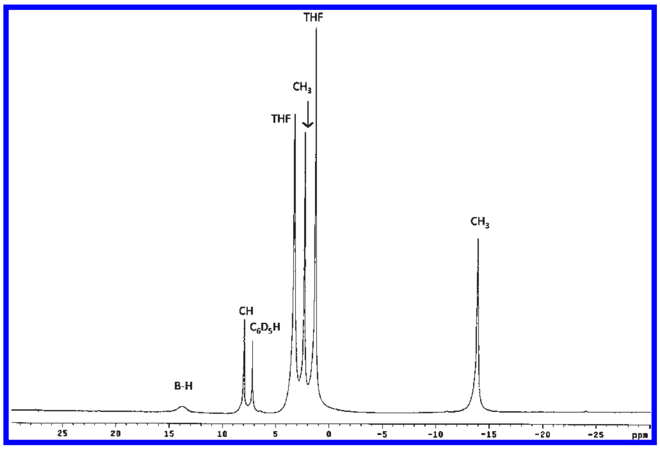

Figure 2. ^{1}H NMR spectrum of **1** in benzene-d_6 at 23 °C.

A tris(tetrahydrofuran) complex, Tp^{iPr2}UI$_2$(THF)$_3$ (Tp^{ipr2} = hydrotris(3,5-diisopropylpyrazolyl)borate, previously synthesized by Santos features two isopropyl substituents on the pyrazole rings. This compound was characterized by ^{1}H NMR (toluene-d_8), and infrared spectroscopies (Nujol) at 23 °C and shows spectroscopic features similar to those of **1**.[58] The pyrazole ring protons in Tp^{iPr2}UI$_2$(THF)$_3$ were equivalent and appeared at 8.52 ppm, while the B−H was observed at 16.0 ppm, and the B−H absorption band appeared at 2550 cm^{-1} in the infrared spectrum (KBr).

Once the hydrotris(pyrazolyl)borate uranium diiodide complex was formed, the next experiments were aimed at ligand substitution reactions with **1** by replacing the THF ligands with a potentially redox-active ligand. Addition of a solution of 2,2′-bipyridine to **1** caused the precipitation of a dark solid assigned as Tp*UI$_2$(2,2′-bpy) (**2**) (Scheme 1). IR spectroscopy revealed an absorption band at 2557 cm^{-1} assignable to the B−H in the complex. Magnetic studies performed on solid samples of **2** established a magnetic moment of 2.7 μ_B at ambient temperature, slightly low compared to compound **1**, but still supporting the formulation of **2** as a uranium(III) compound with a redox-innocent bipyridine ligand.[13,52,53]

Cooling a concentrated THF solution of Tp*UI$_2$(2,2′-bpy) (**2**) produced crystals suitable for X-ray diffraction. Analysis confirmed a seven coordinate uranium center (Figure 3, metrical parameters in Table 3), where the bipyridine ligand bisects the angle of the two iodine ligands for an overall C_s symmetric molecule. The U−N distances for the hydrotris(pyrazolyl)borate ligand are 2.589(6), 2.581(6), 2.578(6) Å, in agreement with the previously synthesized Tp^{iPr2}UI$_2$(2,2′-bpy) which had distances of 2.600(15), 2.564(17), 2.613(15) Å.[58] In addition, the U−N distances for the 2,2′-bipyridine are 2.626(7) and 2.628(7) Å, shorter than those in Tp^{iPr2}UI$_2$-(2,2′-bpy) at 2.663(16) and 2.645(18) Å. The U−I distances are as expected in comparison to the starting material, **1**. The I−U−I angle of 106.241(16)° is much larger compared to that in **1** with two THF ligands where it is 85.470(17)°. The large difference in this angle is due to the change in arrangement of the ligands around the uranium center caused by the chelating nature of the bipyridine ligand.

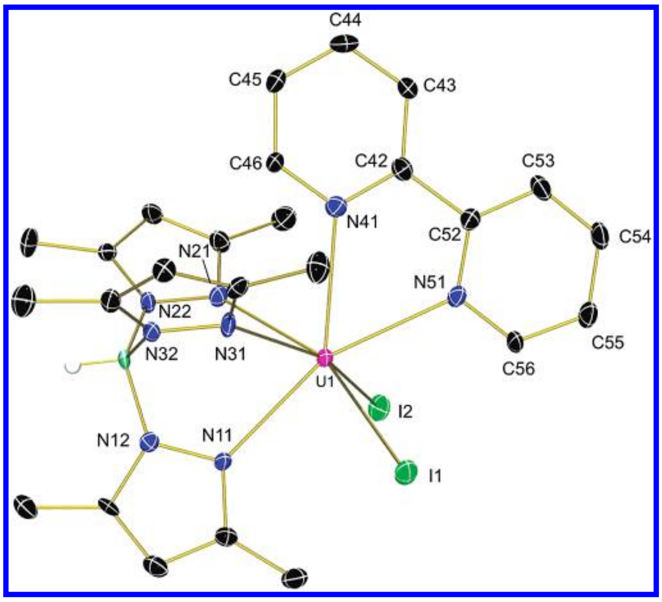

Figure 3. Molecular structure of **2** shown with 30% probability ellipsoids. Solvent and selected hydrogen atoms have been omitted for clarity.

Table 3. Bond Distances (Å) for **2** and **3**

	2	**3**		**2**	**3**
U1−N11	2.589(6)	2.646(8)	**A** C42−C52	1.511(11)	1.409(13)
U1−N21	2.581(6)	2.596(7)	**B** C42−C43	1.380(11)	1.437(13)
U1−N31	2.578(6)	2.691(8)	**C** C43−C44	1.373(12)	1.352(15)
U1−N41	2.626(7)	2.592(8)	**D** C44−C45	1.380(12)	1.406(15)
U1−N51	2.628(7)	2.565(8)	**E** C45−C46	1.378(12)	1.379(14)
U1−N61	--	2.567(8)	**F** N41−C46	1.337(10)	1.360(12)
U1−N71	--	2.633(7)	**G** N41−C42	1.351(10)	1.375(12)
U1−N81	--	2.703(7)	**B** C52−C53	1.380(11)	1.429(13)
			C C53−C54	1.365(12)	1.344(14)
			D C54−C55	1.387(13)	1.407(14)
			E C55−C56	1.404(11)	1.383(13)
			F N51−C56	1.341(10)	1.373(11)
			G N51−C52	1.353(10)	1.401(11)

Comparison of the bond distances within the 2,2′-bipyridine ligand in **2** with the values in Table 1 establish it as a uranium(III) species with a neutral bipyridine chelator. The C−C single bond distance in **2**, denoted as **A** in Table 1, is 1.511(11) in **2** and is consistent with the value for free bipyridine. The same distances for the reduced ligands in Table 1 are much shorter, confirming that no reduction has taken place in the bipyridine ligand in **2**. In addition, the C−N and C−C bond distances in **2** are as predicted by comparison to the bond distances in free bipyridine, bonds B−G listed in Table S1. Thus, because the distances are equivalent to the free molecule, the bipyridine ligand is a neutral chelator on the uranium center in **2**, establishing it is a trivalent uranium ion.

Once the molecular structure of **2** was established (Figure 3), the ^{1}H NMR spectrum was more easily interpreted. Based on the solid state structure presented in Figure 3, compound **2** has a mirror plane containing the bipyridine rings and the bottom pyrazole ring which bisects the angles of both the remaining pyrazole rings and the two iodide ligands. Thus, in the ^{1}H NMR spectrum, there is a resonance for the two equivalent methyl groups pointing toward the bipyridine ligand visible

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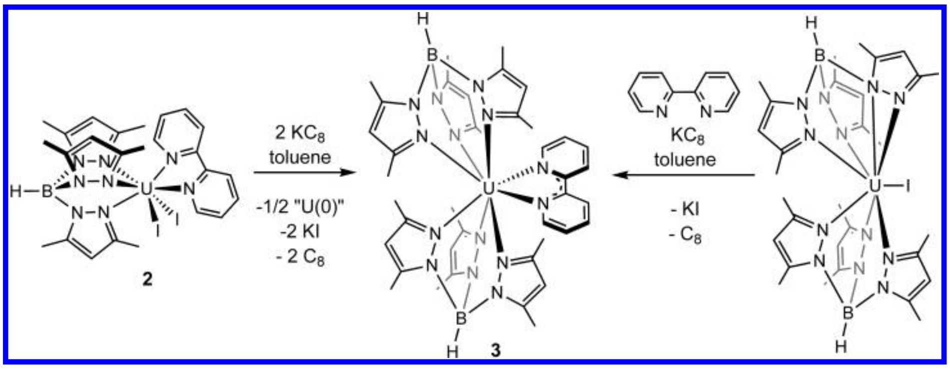
[58] Maria, L.; Domingos, A.; Galvao, A.; Ascenso, J.; Santos, I. *Inorg. Chem.* **2004**, *43*, 6426–6434.

Scheme 2



at −25.42 ppm, while the remaining methyl group on the inequivalent ring appears at −12.91 ppm. The methyl groups on the pyrazole ring paralleling the B−H bond (5 position) appear equivalent despite the fact that one of them is in a different chemical environment. This peak, representing the accidental equivalence of these protons, appears at 2.93 ppm in the spectrum and has the correct integration for 9 protons. The pyrazole ring protons on the hydrotris(pyrazolyl)borate ligand are also accidentally equivalent and appear at 9.0 ppm. The 8 inequivalent protons for the bipyridine ligand have resonances integrating to one proton each appearing in the range of 12.8 to 26.5 ppm. The relatively narrow distribution of the resonances supports the formulation of this compound as a uranium(III) complex with a neutral 2,2′-bipyridine ligand, since reduced 2,2′-bipyridine ligands on rare earth elements have been demonstrated to have resonances shifted far upfield.[59]

Reduction Chemistry. Establishing the neutral 2,2′-bipyridine ligand in **2** prompted us to explore if 2,2′-bipyridine is capable of acting as a redox active ligand in complexes with this framework, and if using the redox-innocent THF ligand influences the reduction chemistry in any way. To study these possibilities, chemical reduction was attempted by addition of potassium graphite to both diiodide complexes, **1** and **2**. Two equivalents of KC$_8$ were added to a stirring purple toluene solution of **1**. After stirring for 3 h and workup, analysis by ^{1}H NMR spectroscopy revealed that mostly decomposition had occurred, along with a small amount ($<$10%) of ligand redistribution to form Tp*$_2$UI, a compound previously synthesized by Takats.[46]

Using the same reaction conditions, the reduction chemistry of compound **2** was explored. After 3 h of stirring in toluene and workup, a brown−red solid was obtained, albeit in low yields (Scheme 2). Analysis by ^{1}H NMR spectroscopy revealed formation of a clean product, **3**. Using pentane for reduction chemistry required stirring overnight for conversion to the same product given the low solubility of **2**. Analysis of the product by IR spectroscopy revealed two absorption bands assignable to B−H peaks, at 2515 and 2545 cm^{-1}, indicating that a uranium center with two hydrotris(pyrazolyl)borate ligands had been formed (Scheme 2).

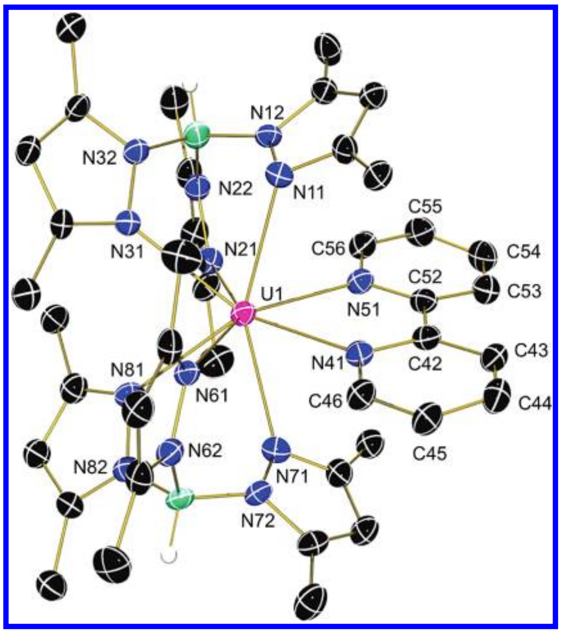


Figure 4. Molecular structure of **3** shown with 30% probability ellipsoids. Solvent and selected hydrogen atoms have been omitted for clarity.

Further characterization of the reduced product, **3**, by X-ray crystallography was performed with dark brown block crystals grown from a saturated THF/ether solution (60:40) cooled to −35 °C (Figure 4 and Table 3). Analysis revealed the product as Tp*$_2$U(2,2′-bpy), **3**, containing an 8 coordinate uranium center, the result of ligand redistribution during the reduction process. Examination of the U−N bond distances shows that in *each* hydrotris(pyrazolyl)borate ligand there is one very long U−N bond. These unusual rings have U−N distances of 2.691(8) and 2.703(7) Å, both much longer than the distances observed for the other rings of the ligands which are 2.646(8), 2.596(7), 2.567(8), and 2.633(7) Å. The uranium−nitrogen distances for the bipyridine ligand in **3** are shorter than those for **2** and Tp^{iPr2}UI$_2$(2,2′-bpy), supporting formation of the 2,2′-bipyridine as a reduced ligand.

Comparison of the bond distances within the bipyridine ligands in **2** and **3** presented in Table 3 indicate that reduction of this ligand has occurred in **3**. Bond **A** has a distance of 1.511(11) Å in **2** with the neutral ligand, but the distance shortens drastically to 1.409(13) in **3** in accord with occupation of the π* LUMO. In addition, there is lengthening of the **B**, **D**, and **F** bonds as predicted

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(59) Mehdoui, T.; Berthet, J.-C.; Thuery, P.; Salmon, L.; Riviere, E.; Ephritikhine, M. *Chem.—Eur. J.* **2005**, *11*, 6994–7006.

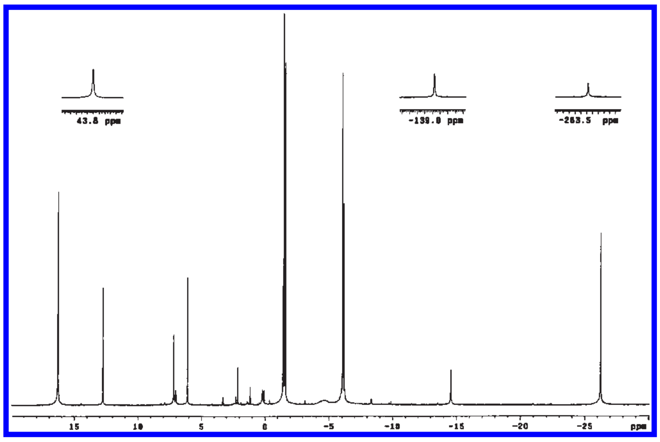

Figure 5. ^{1}H NMR Spectrum of **3** in benzene-d_6 at 23 °C.

from the LUMO diagram (Tables 1 and S1) and as compared to **2**. Contraction of bonds **C** and **E** as compared to free 2,2′-bipyridine and **2** is also observed (see Tables 3 and S1, supporting information). Compound **3** is similar to the previously generated lanthanide compound, Tp*$_2$La(2,2′-bpy),[38] which contains a lanthanide(III) center and monoanionic radical bipyridine ligand.

An independent synthesis of **3** was devised to make the compound more efficiently and in higher yields (Scheme 2). Reduction of Tp*$_2$UI[46] using 1 equiv of potassium graphite and stirring overnight in toluene in the presence of 2,2′-bipyridine easily generated the desired compound, **3**, improving the yield to 87% from the original 38%. This reaction proceeds to completion in 3 h when 2 equiv of potassium graphite are used. Increasing the yield of the reaction allowed isolation of this material and bulk recrystallization for magnetic measurements. The magnetic moment of compound **3** was measured on several independently synthesized solid samples, and determined to be 3.2 μ_B at 20 °C, slightly high for a uranium(III) species but still within range. To our knowledge, there are no magnetic data published for other uranium(III) complexes with radical ligands for comparison.

The ^{1}H NMR spectrum of **3** at ambient temperature in benzene-d_6 is presented in Figure 5. This spectrum shows a total of 15 peaks resulting from two equivalent hydrotris(pyrazolyl)borate ligands in solution. This is not expected based on the molecular structure, as the ligands are not equivalent in the solid state structure. However, fluxional behavior of the pyrazole rings in solution causes the equivalence of these protons. Several peaks for residual solvent appear in the diamagnetic region, between 0 and 10 ppm in Figure 5. Because of the inequivalent methyl groups, resonances for six different methyl groups on the hydrotris(pyrazolyl)borate ligand are observed, each integrating to 6 protons. In addition, three peaks integrating to two protons each are observed for the protons on equivalent pyrazole rings, and one broad peak for the two B−H protons is visible. The bipyridine protons are equivalent from one side of the molecule to the other and the resonances are visible throughout the spectrum. A striking feature of this spectrum is the far shift of two resonances, appearing at −254.8 and −134.3 ppm in the spectrum. Previously mentioned rare earth complexes containing reduced bipyridine ligands with radical character also show shifts in the ^{1}H NMR spectrum of this magnitude. The cerium compound, Cp*$_2$Ce(2,2′-bpy),[59] which has a radical monoanionic 2,2′-bipyridine ligand, displays peaks ranging from −26.91 to −253.11 ppm while the uranium version, Cp*$_2$U(bpy)[59] has peaks ranging from 0.25 to −93.91 ppm in the ^{1}H NMR spectrum, consistent with the large shifts observed for **3**, supporting the formulation of the 2,2′-bipyridine ligand as a radical monoanionic ligand.

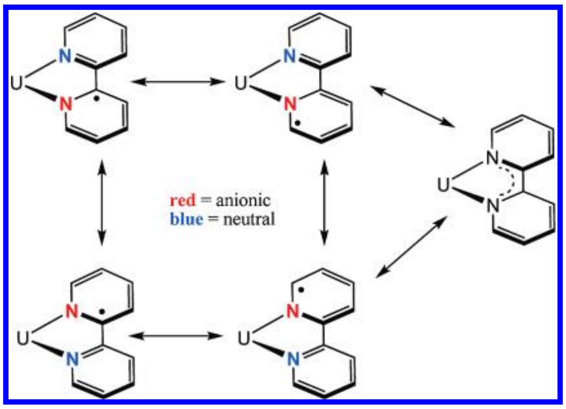

Figure 6. Resonance forms of the uranium center with reduced 2,2′-bipyridine ligand.

In addition to the already reported compounds containing reduced bipyridine ligands, similar radical containing terpyridine ligands have been reported on uranium. Ephritikhine has synthesized the corresponding uranium compound, Cp*$_2$U(terpyridine),[59] while Kiplinger reports a similar reduced terpyridine ligand in a Cp*$_2$U(terpyridine) fragment of a higher order multinuclear species.[60] Both of these complexes display typical crystallographic distances for reduced terpyridine ligands, namely shortening of the C−C bonds connecting the pyridine rings; the magnetic behavior at low temperature for Cp*$_2$U(terpyridine)[59] also supports formation of a ligand radical.

Complexes with the polypyridine radical ligands represent a unique class of compounds in which electron rich metals are stabilized by backbonding into the π* orbitals of the polypyridine. Although radicals are present in these molecules, the delocalization of these species throughout the polypyridine framework (Figure 6) offers a unique stabilization, keeping these radical species from behaving like typical organic radicals that are often prone to atom abstraction and decomposition reactions. It is our hope that the stability imparted by the delocalization into the redox active ligand allows these radicals to exist long enough to perform further desired chemistry.

Conclusions

Uranium(III) hydrotris(pyrazolyl)borate diiodide complexes have been synthesized as an entry into low-valent uranium chemistry with these ligands. New spectroscopic and structural data have been presented for Tp*UI$_2$(THF)$_2$. Ligand substitution was accomplished easily by addition of 2,2′-bipyridine to this species, producing Tp*UI$_2$(2,2′-bpy). Spectroscopic, magnetic, and structural data support the formulation of the bipyridine as a neutral chelating ligand,

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(60) Schelter, E. J.; Wu, R.; Scott, B. L.; Thompson, J. D.; Morris, D. E.; Kiplinger, J. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 2993–2996.

maintaining the trivalent oxidation state. The reduction chemistry of these compounds was explored to determine the role of the supporting ligand in stabilizing low-valent uranium species. Reduction of Tp*$UI_2(THF)_2$ resulted in a small amount of ligand redistribution as well as decomposition of the starting material, indicating that the THF ligands do not stabilize reduced uranium. However, reduction of Tp*UI_2(2,2′-bpy) with two equivalents of potassium graphite resulted clean in ligand redistribution as well as reduction of the 2,2′-bipyridine ligand to produce $Tp*_2U$(2,2′-bpy), where bipyridine is a radical monoanion. This was confirmed by comparison to other structurally characterized *f*-block element compounds with reduced polypyridine ligands. Future studies will concentrate on the spectroscopic analysis of uranium(III) species with radical ligands as well as the consequences of radical ligands for the reactivity of this uranium(III) center.

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Supporting Information Available: Crystallographic details and a full table of reduced bipyridine bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.