

Investigation of the Electronic Structure of Aryl-Bridged Dinuclear U(III) and U(IV) Compounds

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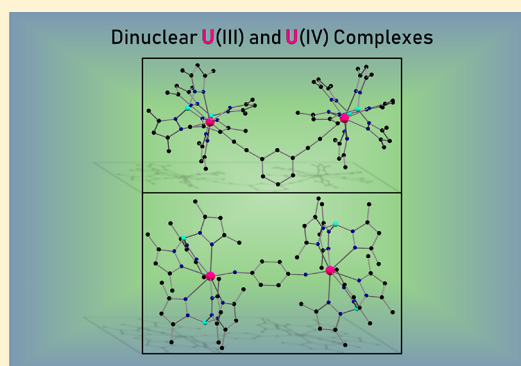
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S Supporting Information

ABSTRACT: A family of dinuclear bis(Tp*) (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) uranium compounds with conjugated organic linkers was synthesized to explore possible electronic communication between uranium ions. Trivalent diuranium phenyl alkynyl compounds, Tp*₂UCC(1,3-C₆H₄)CCUTp*₂ (**2-meta**) or Tp*₂UCC(1,4-C₆H₄)CCUTp*₂ (**2-para**), and tetravalent diuranium phenylimido compounds, Tp*₂U(N-1,3-C₆H₄-N)UTp*₂ (**3-meta**) and Tp*₂U(N-1,4-C₆H₄-N)UTp*₂ (**3-para**), were generated from trivalent Tp*₂UCH₂Ph. All compounds were fully characterized both spectroscopically and structurally. The electronic structures of all derivatives were interrogated using magnetic measurements, electrochemistry, and were the subject of computational analyses. All of these data combined established that little electronic communication exists between the uranium centers in these trivalent and tetravalent diuranium molecules.



INTRODUCTION

Transition metal (TM) species of the type [TM]-(Linker)-[TM] have been extensively studied^{1,2} for their fascinating electron transfer properties.³ Such molecules have potential applicability to serve as molecular wires⁴ and photovoltaic materials.⁵ Diuranium complexes have not undergone such thorough study, but they are gaining in popularity because of their interesting magnetic properties,^{6,7} ability to support surprising bonding motifs,^{8–13} and unprecedented reactivity.^{14–18}

Few examples of uranium complexes linked by conjugated carbon-based or multiply bonded bridging organic frameworks currently exist.^{7,19–23} Andersen and co-workers reported diuranium(V) compounds, Cp'₃U = NC₆H₄N = UCp'₃ (Cp' = η⁵-C₅H₄Me), as both the *meta* and *para* isomers. However, only the *para*-isomer displayed significant antiferromagnetic coupling of the 5f¹ centers, as measured by SQUID magnetometry.¹⁹ Another reported dinuclear U(V) complex from Walensky and co-workers exhibits some coupling between the two uranium centers.²⁴ Di- and trinuclear U(IV) alkynyl compounds have been reported by Shores and co-workers to show weak magnetic communication between the uranium centers,²² while benzoquinoid-bridged U(IV) centers did not exhibit any appreciable communication.²³ Electronic communication between 1,4-phenylenediketimide linked U(IV) centers was observed electrochemically by

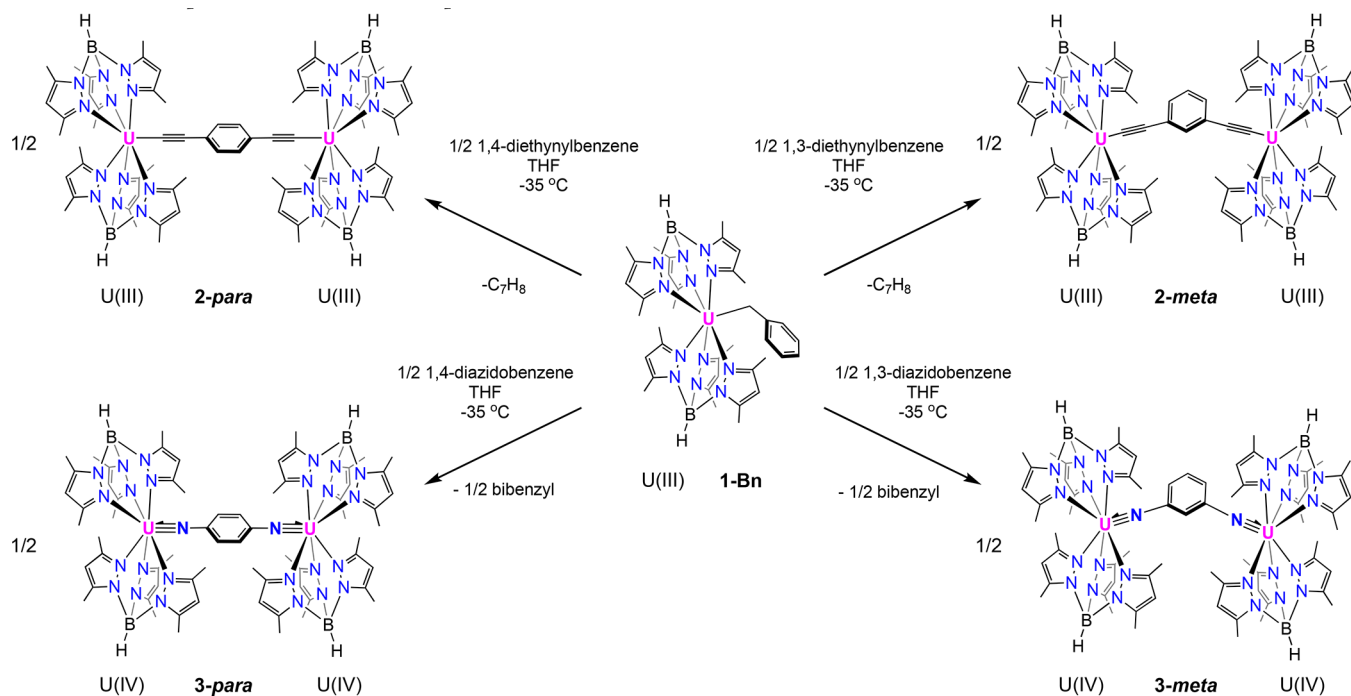
Kiplinger and co-workers.²⁰ Notably rare in this research area is the study of U(III) ions for electronic delocalization and magnetic coupling, presumably because of limitations in the synthesis of U(III)-(linker)-U(III) platforms. Some exceptions to this include inverse sandwich complexes reported by Cummins and Diaconescu¹¹ as well as Liddle,²⁵ which all feature two uranium(III) centers with bridging dianionic arenes. Mazzanti has just recently described a unique nitrido bridged uranium(III) variant that is stabilized by the bulky siloxide ligand, -OSiOtBu.²⁶

Given that the hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) ligand enables access to low-valent uranium alkyl complexes^{27,28} and their reactivity,^{29–34} this ligand framework is an ideal system to study electronic communication in dinuclear molecules of the form [Tp*₂U]-(Linker)-[UTp*₂]. Herein, we report the synthesis of a family of diuranium complexes bridged by either alkynyl (U(III) derivatives) or imido (U(IV) derivatives) linkers. Full structural and spectroscopic characterization of these species is reported. Analysis of electrochemical and magnetic properties as well as computational modeling are used to assess the electronic structures of these unique species.

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Scheme 1. Preparation of *2-para*, *2-meta*, *3-para*, and *3-meta* from *1-Bn*

RESULTS AND DISCUSSION

Preparation of Diuranium Bridging Complexes. In order to synthesize low-valent diuranium complexes with an organic linker, we expanded on our modified preparation of Takats' $\text{Tp}^*_2\text{UCCPh}$.^{31,35} A cold solution (-35°C) of $\text{Tp}^*_2\text{U}(\text{CH}_2\text{Ph})$ (**1-Bn**)²⁷ was treated with one-half an equivalent of cold 1,3-diethynylbenzene (*meta*-DEB) or 1,4-diethynylbenzene (*para*-DEB). Although no color change is noted, a difference in solubility is apparent upon workup. The starting material is readily soluble in diethyl ether, aromatic solvents, and *n*-pentane, but the green powder isolated in this reaction is insoluble in diethyl ether and *n*-pentane (Scheme 1, top). Analyses of C_6D_6 solutions of $\text{Tp}^*_2\text{UCC}(1,3\text{-C}_6\text{H}_4)\text{-CCUTp}^*_2$ (**2-meta**) and $\text{Tp}^*_2\text{UCC}(1,4\text{-C}_6\text{H}_4)\text{-CCUTp}^*_2$ (**2-para**) by ^1H NMR spectroscopy (25°C) revealed eight or five paramagnetically shifted resonances, respectively. Two singlets (36H each) are assigned to the *endo*-(**2-meta**: -13.64 ppm; **2-para**: -12.49 ppm) and *exo*- Tp^* methyl groups (**2-meta**: 0.83 ppm; **2-para**: 1.00 ppm). The pyrazolyl CH is assigned as a singlet (12H: **2-meta**: 7.97 ppm; **2-para**: 8.15 ppm) while a broad singlet appears for the B–H proton of the Tp^* ligands at -14.84 or -14.88 ppm for **2-meta** and **2-para**, respectively. In the ^1H NMR spectrum for **2-meta**, three resonances are observed for the aryl bridge, including a triplet corresponding to one proton (13.40 ppm), a doublet (27.29 ppm) assigned to protons in positions 4 and 6, and a singlet (1H, 34.62 ppm) for the proton in the α position from the two alkynyl carbons (position 2). In the ^1H NMR spectrum for **2-para**, a singlet at 23.99 ppm corresponds to the four protons on the aryl linker. Infrared spectroscopy (KBr pellet) revealed characteristic B–H stretches (**2-meta**: $2554, 2523\text{ cm}^{-1}$; **2-para**: $2559, 2524\text{ cm}^{-1}$) and a single $\text{C}\equiv\text{C}$ absorption (**2-para**: 2046 cm^{-1}), which are consistent with those reported for $\text{Tp}^*_2\text{UCCPh}$.³⁵ Across repeated attempts, the analogous absorption was not observed for **2-meta**.

Single crystals of **2-meta** and **2-para** were grown from concentrated DME (**2-para**) or diethyl ether (**2-meta**) solutions and analyzed using X-ray diffraction to probe the coordination mode. Data refinement revealed that both compounds consisted of two Tp^*_2U units tethered by a DEB unit (Figure 1, Table 1). The range of U–N_{pyrazolyl} bond distances (**2-meta**: $2.546(8)$ – $2.708(9)$ Å; **2-para**: $2.422(18)$ –

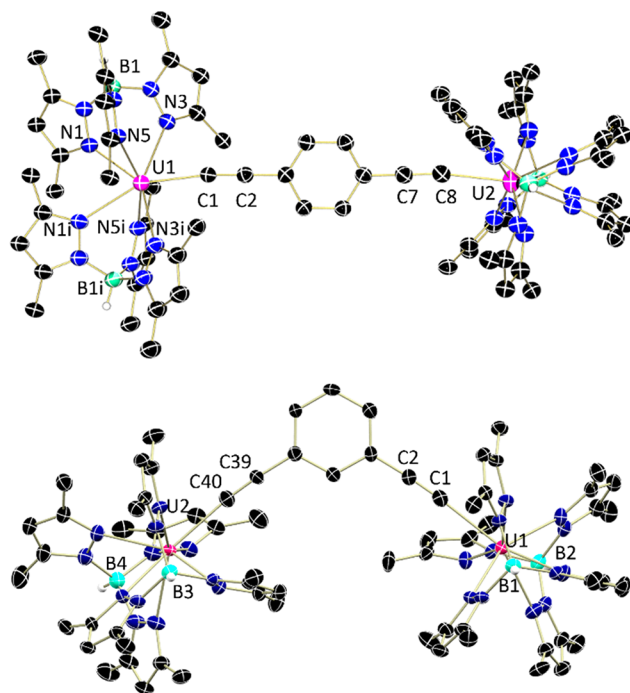


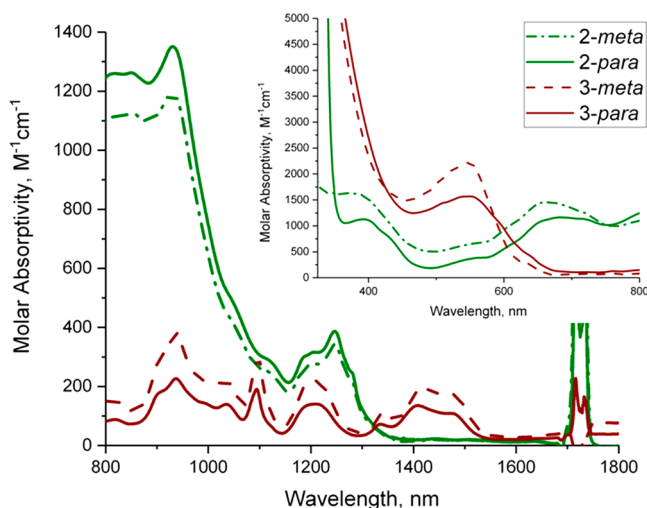
Figure 1. Molecular structures of **2-para** (top) and **2-meta** (bottom) displayed with 30% probability ellipsoids. Selected hydrogen atoms, disorder, and cocrystallized solvent molecules have been omitted for clarity. Symmetry operator (i): $-x, 1/2 - y, z$.

Table 1. Selected Bond Lengths of *2-meta*, *2-para*, *3-meta*, and *3-para*

bond metric	<i>2-meta</i>	<i>2-para</i>	<i>3-meta</i>	<i>3-para</i>
U=N _{linker}	--	--	1.971(7), 1.980(7) Å	1.973(9) Å
U–C _{linker}	2.486(10), 2.551(8) Å	2.48(2), 2.47(3) Å	--	--
CC _{alkynyl}	1.208(10), 1.206(10) Å	1.29(3), 1.34(4) Å	--	--

2.73(3) Å) falls within the range of previously reported trivalent bis(Tp*)U complexes (2.496–2.764 Å).^{27,36,37} The U–C bonds (*2-meta*: 2.486(10), 2.551(8) Å; *2-para*: 2.48(2), 2.47(3) Å) for both compounds are similar to other trivalent uranium alkyls, including U[CH(SiMe₃)₂]₃ (2.48(2) Å)³⁸ and TpTp*UCH₂Ph (Tp = hydrotris(pyrazolyl)borate; 2.56(2) Å³⁷). The CC_{alkynyl} bonds for *2-meta* (1.208(10), 1.206(10) Å) and *2-para* (1.29(3), 1.34(4) Å) do not differ from each other. The bis(Tp*)U units in *2-para* are aligned in a perpendicular fashion (angle between planes defined by B1–U1–B1ⁱ and B2–U2–B2ⁱ = 89.23°) with the uranium centers separated by 9.064(4) Å. The molecular structure of *2-para* is highly disordered, making further discussion of the organic linker not feasible.

Both alkynyl compounds were studied by electronic absorption spectroscopy. Analysis of THF solutions of *2-para* and *2-meta* at ambient temperature revealed features that are consistent with trivalent U(III) complexes^{28,34} around 1250 nm (400 M^{−1}cm^{−1}), including broad features up to 1650 nm (Figure 2, green). The UV–visible regions (Figure 2,

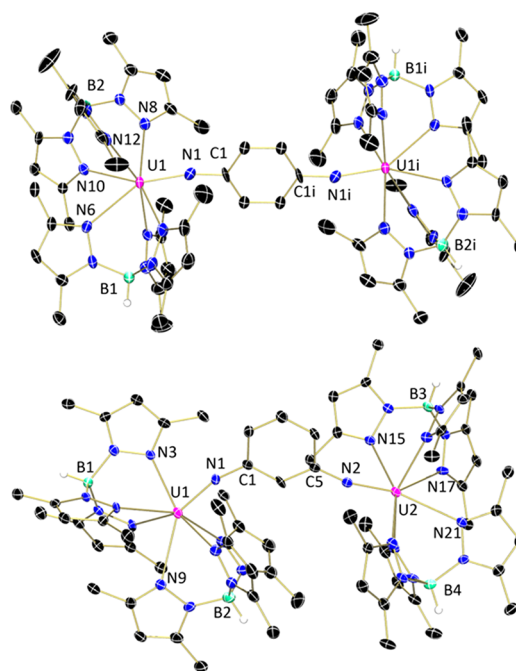
**Figure 2.** Electronic absorption spectra of *2-meta* (green, dashed), *2-para* (green, solid), *3-meta* (maroon, dashed), and *3-para* (maroon, solid) recorded from 300 to 1800 nm in THF at ambient temperature.

inset) for both alkynyl dimers display characteristic absorbances similar to Tp*₂UBn and its derivatives, which are all dark green, U(III) alkyl compounds.^{27,28} This is highlighted by a broad absorption around ~680 nm, which is responsible for the observed green color. Absorbances around ~500–800 nm are established to be color-giving d–f transitions in U(III) systems.³⁹

Generation of dinuclear imido U(IV) derivatives was accomplished using oxidizing azides. One-half of an equivalent of 1,4- or 1,3-diazidobenzene was added to a solution of **1-Bn**,

causing a rapid color change from dark green to red-purple. Effervescence of N₂ was also noted, as is typically observed for azide activation, concurrent with formation of uranium imido complexes (Scheme 1, bottom). The isolated bright red-pink powders were assigned as Tp*₂U(N-1,3-C₆H₄–N)UTp*₂ (*3-meta*) and Tp*₂U(N-1,4-C₆H₄–N)UTp*₂ (*3-para*), respectively. Product characterization by ¹H NMR spectroscopy (C₆D₆, 25 °C) revealed seven and five paramagnetically shifted resonances, for *3-meta* and *3-para*, respectively. The resonances assigned to the aryl bridge are significantly shifted downfield (*3-para*: 121.63 ppm; *3-meta*: 97.07, 97.54, 151.57 ppm). Both compounds have diagnostic B–H absorptions in their corresponding IR spectra (*3-meta*: 2554, 2528 cm^{−1}; *3-para*: 2554, 2527 cm^{−1}).

Structural confirmation of the dinuclear nature of *3-meta* and *3-para* was possible using X-ray crystallography (Figure 3). The U–N_{pyrazolyl} ranges (*3-meta*: 2.531(7)–2.759(7) Å; *3-*

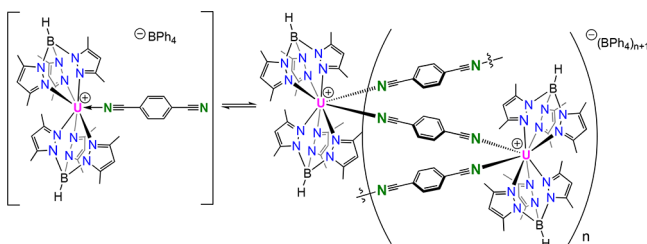
**Figure 3.** Molecular structures of *3-para* (top) and *3-meta* (bottom) shown with 30% probability ellipsoids. Selected hydrogen atoms and cocrystallized solvent molecules have been omitted for clarity.

para: 2.508(7)–2.753(8) Å) are similar to reported tetravalent U compounds with the bis(Tp*) framework (Table 1).^{33,40} The U–N_{imido} bond lengths (*3-meta*: 1.971(7), 1.980(7) Å; *3-para*: 1.973(9) Å) are within the range of previously reported U(IV) imido complexes, including Tp*₂U(Ndetp) (detp = 2,6-diethylphenyl) = 2.004(12) Å,⁴¹ Cp*₂U(NMes*) (Mes* = 2,4,6-tri-*tert*-butylphenyl) = 1.952(12) Å,⁴² and (OPPh₃)₂U(NMes*)Cl₂ = 2.009(3) Å.⁴³ The U–N–C angle of *3-para* is closer to linearity at 168.5(8)°, as compared to *3-meta*. This is notable since the ligand environment of *3-meta* is more crowded, and the imido fragments are only slightly more bent (166.1(6), 163.9(7)°). The change in substitution can be quantified by the distance between the two uranium atoms; *3-meta* (8.165 Å) has a closer U–U distance than *3-para* (9.525 Å). Another quantifiable metric for the two imido compounds is that *3-para* features parallel bis(Tp*)U fragments, but those of *3-meta* have a twist angle of 38.47°.

Examination of the electronic absorption spectra for complexes **3** show distinct features as compared to what was observed for **2**. Both **3-meta** and **3-para** display sharp, weak f–f transitions in the near-IR region from ca. 880–1550 nm, which are characteristic of uranium(IV) ions (Figure 2, maroon). This is in contrast to U(III) ions, where these absorptions are much more broad. Complexes **3** display absorbances at ~549 nm that are of slightly lower energy than the monomeric species Tp^*_2UNR (R = benzyl, *p*-tolyl, 2,6-diethylphenyl),⁴¹ but are responsible for the red-violet color of these powders.

With the structural characterization of dinuclear U(III) and U(IV) compounds completed, we sought to expand the library to include a bridged U(III) species with a datively bound linker for structural comparisons. Stirring 1,4-dicyanobenzene with a solution of $[\text{Tp}^*_2\text{U}(\text{THF})][\text{BPh}_4]$ (**1-THF**) (full details of the preparation of **1-THF** are in the SI) produced a color change from purple to blue. Upon workup, a blue solid was isolated (Scheme 2), but it was largely insoluble in aromatic solvents.

Scheme 2. Equilibrium of **4-n**



Characterization of this blue compound by IR spectroscopy (KBr pellet) revealed B–H (2554, 2528 cm^{-1}) and nitrile (2239 cm^{-1}) absorptions. Interestingly, analysis by X-ray crystallography did not show a dinuclear uranium complex bridged through a single dicyanobenzene unit as expected, but instead, an extended structure where each uranium atom is bound to two dicyanobenzene ligands (Figure S21), assigned as $[\text{Tp}^*_2\text{U}(\text{NCPhCN})]_n[\text{BPh}_4]_n$ (**4-n**).

Upon dissolution of **4-n** in acetonitrile- d_3 , a color change to green is noted, and ^1H NMR spectroscopy shows dissociated 1,4-dicyanobenzene and paramagnetically shifted resonances assigned as $[\text{Tp}^*_2\text{U}(\text{MeCN})_2][\text{BPh}_4]$ (**1-MeCN**). Independent preparation of **1-MeCN** was accomplished by treating an acetonitrile solution of Tp^*_2UI with an equivalent of KBPh_4 .

To compare the binding modes of **4-n** and **1-MeCN**, single crystals were obtained from a concentrated acetonitrile solution (**1-MeCN**) or by layering THF and *n*-pentane (5:1) (**4-n**) (–35 °C for both) (Figure S21, Figure S26). Both molecular structures feature eight-coordinate uranium ions with two Tp^* ligands with U–N_{pyrazolyl} distances (**1-MeCN**: 2.533(5)–2.675(6) Å; **4-n**: 2.529(4)–2.635(4) Å) that fall into the range of the bond lengths for **2** and **3** (Table S1). Both compounds feature one tetraphenylborate anion per uranium ion and two neutrally bound acetonitrile molecules to uranium forming a square antiprismatic geometry. The U–N_{nitrile} bond lengths (**1-MeCN**: 2.693(7), 2.705(7) Å; **4-n**: 2.677(4), 2.696(4) Å) are indicative of neutral interactions and consistent with reported distances for nitrile coordination ($\text{Tp}^*_2\text{UI}_3(\text{NCMe}) = 2.557(6)$ Å).⁴⁴ The molecular structure of **1-MeCN** proves to be unique as an extended structure is observed for **4-n**.

Computation. Elucidation of the electronic structures of **2-para**, **2-meta**, **3-meta**, and **3-para** was aided using density functional theory (DFT) at the B3LYP level, which has been used effectively for examining orbital interactions in actinide complexes.^{45–47} For ease in computing, the crystal structures were truncated by replacing the methyl groups on Tp^* to hydrogen atoms. The agreement between experimental and computational bond distances is good with all distances within 0.05 Å. The calculated bond distances are slightly shorter due to the truncation which diminishes steric factors in these complexes. For uranium(III) alkynyl complexes, **2-para** and **2-meta**, the septet state was found to be the lowest in energy. Little covalent character is observed as evidenced by the spin density of 2.99 for both compounds. Uranium(III), f^3 complexes should display a spin density of 3.00 (having three unpaired electrons), but since no deviation was found, this supports negligible metal–ligand covalent interaction. We can also compare this spin density to that of **1-Bn**, for which no metal–ligand multiple bonding should be present. Indeed, the spin density for **1-Bn** is 3.00. Uranium(IV), f^2 imido complexes **3-para** and **3-meta**, should exhibit spin densities of 2.00 (having two unpaired electrons); however, spin densities of 2.18 are observed for both compounds, indicating a higher degree, albeit very slight, of metal–ligand covalent interaction due to the uranium–nitrogen multiple bond. This result is expected, given that the corresponding U(IV) terminal oxo, $\text{Tp}^*_2\text{U}(\text{O})$, has a calculated spin density of 2.13.⁴⁰

The lowest energy conformation for **3-para** was found to be a quintet ground state with C_2 -symmetry, therefore the molecular orbitals are degenerate. The HOMO-5, HOMO-6, and HOMO-34 are shown in Figure 4 which represent the two π bonds and σ bond, respectively, that comprise the uranium–imido bond.

Magnetometry. In order to gain insight into the possibility of electronic communication between uranium ions in **2-meta/para** and **3-meta/para**, the magnetic properties of these

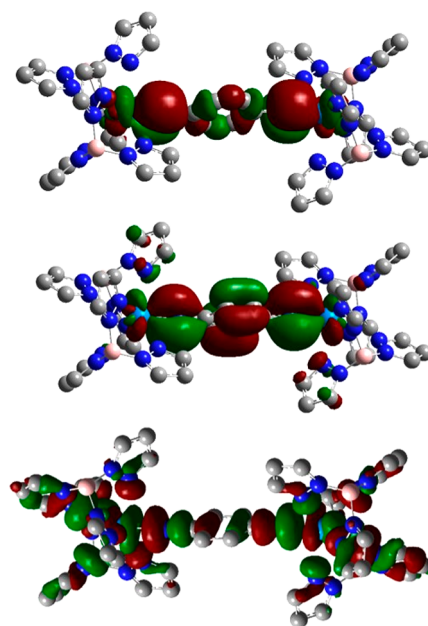


Figure 4. One σ (bottom, HOMO-34) and two π (top, HOMO-5, and middle, HOMO-6) orbitals that comprise the uranium–nitrogen triple bond in **3-para** are shown (isolevel = 0.02).

species were probed by collecting variable temperature magnetic susceptibility data in the solid state (Figure 5).

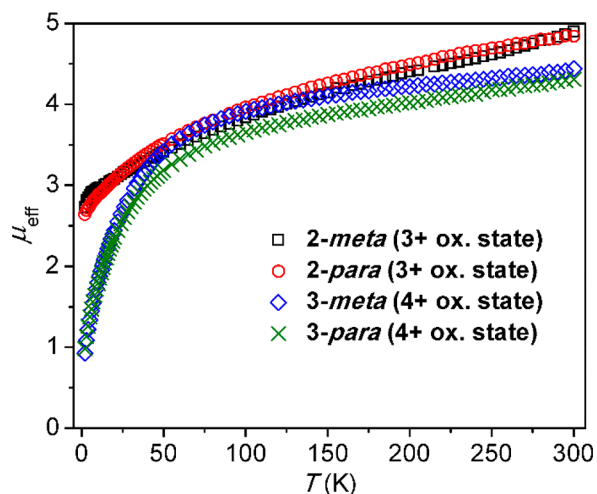


Figure 5. Temperature-dependent magnetic susceptibility data. Compound **2-para** (red circle) and **3-meta** (blue diamond) and **3-para** (green $\times$) collected at 1000 Oe; compound **2-meta** (black square) collected at 5000 Oe.

Previous examples have demonstrated that bridged actinide ions can show magnetic superexchange coupling through conjugated linkers, such as those from Andersen,¹⁹ Long,⁴⁸ and Shores.²² However, this is not always the case,^{23,49} and thus, potential communication was evaluated for this system.

Compound **2-para** shows a room temperature $\chi_M T$ value of $2.93 \text{ cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 4.84$), which decreases monotonically across all temperatures until 2 K, where the $\chi_M T$ value reaches $0.87 \text{ cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 2.64$). These data are consistent with the presence of two U(III) ions, as the expected room temperature $\chi_M T$ value for two noninteracting $4f_{7/2}$ ground states is $3.29 \text{ cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 5.13$).⁵⁰ A magnetic saturation experiment (1.8 K) shows near-saturation at $1.61 \mu_B$ with an applied field of 50 kOe (Table 2 and Figure S41), further suggesting the presence of two U(III) ions in **2-para**.⁷ Meanwhile, **2-meta** shows analogous data over the applied temperature range; magnetization data collected at 1.8 K also support the presence of two U(III) ions.

Given that temperature-dependent magnetic behaviors are similar to free ions, we would expect that the ions in **2-para** and **2-meta** are magnetically noninteracting. However, since the interactions can result in subtle effects on magnetic susceptibility values, a subtraction method reported by Rinehart *et al.* was applied to further investigate the potential for magnetic exchange coupling in the dinuclear species.²² As part of this analysis, magnetic data were collected for the corresponding mononuclear species, $\text{Tp}^*_2\text{UCCPh}$:³¹ as expected, this compound shows magnetic properties typical

for mononuclear U(III) complexes (Figure S40).⁵⁰ After subtraction of the mononuclear data from those obtained for **2-para** or **2-meta**, the resultant susceptibility data do not indicate significant interactions between the U(III) ions for either **2-para** or **2-meta** (Figures S49, S50). In addition, no reasonable fits are obtained when using PHI⁵¹ to fit the subtracted data to extract an intramolecular coupling constant (J) value. The closest intermolecular U...U distances are 9.064(4) and 9.9665(6) Å for **2-para** and **2-meta**, respectively, which are likely far enough separated to preclude through-space magnetic interactions between ions. The molecular structure obtained in the solid state does not display obvious H-bonding or π -stacking interactions, eliminating other communication pathways between U(III) ions in these alkynyl-bridged species.

The magnetic data for **3-para** and **3-meta** show typical trends for dinuclear U(IV) complexes with redox-innocent ligands that have multiple bonding character.^{22,50} At room temperature, the susceptibility products give values of 2.32 and $2.46 \text{ cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 4.31$ and 4.44), respectively (Figure 5, Table 2). Upon cooling, values for **3-para** and **3-meta** decrease gradually until around 100 K, where the downturn becomes pronounced, reaching respective values of 0.12 and 0.11 $\text{cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 0.98$ and 0.94) at 2 K. To further confirm the ground states for **3-para** and **3-meta**, magnetization data were collected (1.8 K) up to an applied field of 50 kOe. Consistent with U(IV) ions, these data are small in magnitude (0.35 and $0.33 \mu_B$ for **3-para** and **3-meta**, respectively) and do not saturate. Typically, magnetization values for a U(IV), $5f^2$ ion approach $0 \mu_B$ at low temperature due to thermal depopulation, but generally, they show some occupation of magnetic excited states at higher temperatures.

To address the question of possible magnetic exchange for **3-para** and **3-meta**, the same subtraction method used for **2-para** and **2-meta** was applied using $\text{Tp}^*_2\text{U}(\text{N-pTolyl})$ ⁴¹ as the mononuclear surrogate (Figure S44).⁴⁸ Attempts to fit these data with PHI⁵¹ were unsuccessful using a J tensor in the applied Hamiltonian. Furthermore, no obvious inflection point is observed in a plot of the χ_M vs T data (Figure S35, S36), indicating no long-range magnetic ordering. Thus, we conclude that the uranium ions in dinuclear **3-meta/para** are likely magnetically noninteracting.

Electrochemistry. The potential for electronic communication in dinuclear **2-meta/para** and **3-meta/para** was also probed using electrochemistry (Figure 6). For trivalent **2-para** and **2-meta**, the cyclic voltammograms display a single, two-electron oxidation process A (U^{III} to U^{IV}) within the potential solvent window (potentials provided in Table 3). The two potentials are similar and are comparable to results reported by Shores and co-workers for *para*- and *meta*-diethynylbenzene bridged U(IV) ($\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^t\text{BuMe}_2)_3$) complexes.²² The oxidation potentials of **2-para** and **2-meta** compared to **1-Bn** are anodically shifted, which is indicative of decreased electron density around the U(III) ion, likely due to the replacement of

Table 2. Selected Magnetic Properties for the Dinuclear Complexes **2-meta/para** and **3-meta/para**

complex	$\chi_M T$ ($\text{cm}^3 \text{ K mol}^{-1}$) 300 K, (μ_{eff})	per ion $\chi_M T$ ($\text{cm}^3 \text{ K mol}^{-1}$) 300 K, (μ_{eff})	$\chi_M T$ ($\text{cm}^3 \text{ K mol}^{-1}$) 2 K, (μ_{eff})	per ion $\chi_M T$ ($\text{cm}^3 \text{ K mol}^{-1}$) 2 K, (μ_{eff})	M (μ_B) 50 kOe, 1.8 K
2-para	2.93 (4.84)	1.47 (3.43)	0.87 (2.64)	0.44 (1.88)	1.61
2-meta	3.00 (4.90)	1.50 (3.46)	0.93 (2.73)	0.47 (1.94)	1.73
3-para	2.32 (4.31)	1.66 (3.64)	0.12 (0.98)	0.06 (0.69)	0.33
3-meta	2.47 (4.44)	1.24 (3.15)	0.11 (0.93)	0.06 (0.69)	0.35

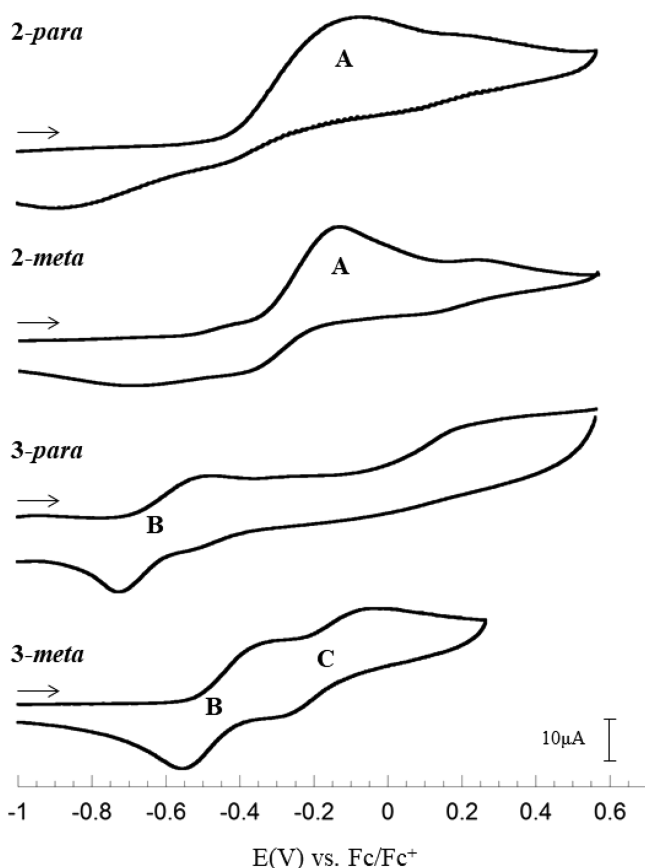


Figure 6. Cyclic voltammograms (CVs) recorded for compounds 2–3 in 0.1 M THF solution of Bu₄NOTf at a scan rate of 0.10 V s^{−1}.

Table 3. Redox Potentials (V, vs Fc/Fc⁺) for 1-Bn, 2-*para*, 2-*meta*, 3-*para*, and 3-*meta*

compound	(A) U(IV/III)	(B) U(V/IV) ($E_{p,a} - E_{p,c}$, i_c/i_a)	(C) U(V/IV) ($E_{p,a} - E_{p,c}$, i_c/i_a)
1-Bn	−0.31	–	–
2- <i>para</i>	−0.07	–	–
2- <i>meta</i>	−0.14	–	–
3- <i>para</i>	–	−0.60 (0.20, 0.60)	–
3- <i>meta</i>	–	−0.46 (0.19, 0.86)	−0.15 (0.19, 0.68)

the strong σ -donor benzyl ligand with the π -accepting alkynyl linker.

The tetravalent imido derivatives, 3-*para* and 3-*meta*, were analyzed analogously. The CV for 3-*para* possesses a single two-electron quasi-reversible oxidation B (U^{IV} to U^V), whereas that for 3-*meta* shows two stepwise one electron events - a reversible couple at B and an irreversible couple at C (U^{IV} to U^V). Thus, the general trend in electron density at the uranium ion is 3-*meta/para* > 1-Bn > 2-*meta/para*. Similar trends in electron density were reported by Kiplinger and co-workers for a series of mononuclear U^V complexes, [(Cp*)₂U(=N–Ar)(X)] (X = Cl, Me, C₂Ph, N=CPh₂; Ar = dipp, Mes*).^{52,53} Variation of electrolytes, solvents, and working electrodes lead only to ill-defined waves or had little effect on the voltammograms of 1-Bn (Figure S51), 1-THF (Figure S53), 2-*meta/para*, and 3-*meta/para*.

The higher valent metal centers of 3-*meta* and 3-*para* are more oxidized than 2-*meta* and 2-*para* and are stabilized by their metal–ligand multiple bonding environments;⁵² therefore, they have access to a greater range of oxidation states

under electrochemical conditions. Measurements using varying scan rates were taken for 3-*meta* and 3-*para* (Figure S52). For 3-*meta*, the peak current (i_p) increases linearly with the square root of the scan rate ν (V s^{−1}), while the peak-to-peak separation increases. This behavior is consistent with a nonsurface bound, quasi-reversible electrochemical process. Furthermore, after rinsing and transferring the working electrode to a fresh electrolyte solution, no detectable electrochemical features appear in the CVs of any U(Tp*) compounds, suggesting that there are no strongly adsorbed surface species,^{54,55} and that the analyte solution remains homogeneous throughout voltammetry experiments. The second oxidation (C) of 3-*meta* is likely the result of a reversible electron transfer followed by a slow chemical reaction involving the loss of a coligand, or a conformational change of the Tp* ligand on uranium. At scan rates approaching 0.5 V s^{−1}, the second reduction of 3-*meta* becomes chemically reversible, indicating moderate stability of higher oxidation states under electrochemical conditions (Figure S52). Varying scan rate measurements for 3-*para* did not lead to improved reversibility, suggesting an accelerated rate of decomposition occurs upon oxidation.

Based on its voltammogram, the first oxidation of 2-*para* is broader than expected for a single-electron process and as compared to that for 2-*meta*. This broadening of the $E_{p,a}$ potential in 2-*para* may be attributed to a weak degree of charge transfer between both uranium centers. The stepwise potential observed for 3-*meta* is a clear indication of a stronger electrostatic contribution than electronic resonance. The distance between uranium ions (3-*para* U1–U2 9.524(3) Å and 3-*meta* U1–U2 8.165(1) Å) overpowers any resonance advantage gained from structural connectivity (i.e., *para* vs *meta*). Similar observations were reported for a series of bimolecular U(IV/IV) tris(amide) complexes, where enhanced coupling was observed across the *meta* diethynylbenzene bridge over the *para* isomer.²³ In a recent report by Arnold and co-workers involving bimolecular U(IV/IV) quinoid complexes, stepwise potentials were noted and proposed to be the result of geometrical changes at the uranium rather than electronic resonance contributions.⁵⁶

CONCLUSIONS

In summary, dinuclear U(III) and U(IV) compounds were successfully prepared using organic linkers and Tp*₂U as a supporting scaffold. Two uranium(III) alkynyl-bridged compounds (2-*meta* and 2-*para*) were synthesized via protonation chemistry, and join other examples of low-valent bridging uranium species.^{9,12,18} The dinuclear U(IV) imido compounds (3-*meta* and 3-*para*) were synthesized using aryldiazides, which furnished the desired bridging species in high yields. Magnetic studies and electronic absorption spectroscopy were integral to this study, as they were able to support the oxidation state assignments in all compounds. Overall, spectroscopic, structural, computational, magnetic, and electrochemical characterization established the noninteracting nature of the uranium ions in these systems and demonstrated that there is little electronic communication between uranium ions in all bridged species reported here.

The results of this study are in contrast to those for dinuclear U(V), f^I compounds, such as those reported by Andersen,¹⁹ Boncella,⁵⁷ and Mazzanti,¹⁸ which do show interaction between uranium ions. While no electronic communication was noted in the cases of the trivalent and

tetravalent compounds reported here, these observations are consistent with other U(IV) examples.^{58,59} Future studies will be aimed at exploring the possibility of magnetic resonance in these systems.

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 is equipped with a cold well designed for freezing samples in liquid nitrogen as well as two $-35\text{ }^{\circ}\text{C}$ freezers for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.⁶⁰ Deuterated solvents were purchased from Cambridge Isotope Laboratories. Benzene- d_6 was dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles. Acetonitrile- d_3 was distilled from CaH_2 prior to use. THF- d_8 was filtered over alumina and stored on Na^0 . $\text{Tp}^*_2\text{U}(\text{CH}_2\text{Ph})$ (**1-Bn**),²⁷ $\text{Tp}^*_2\text{UCCPh}$,³¹ 1,4-diethynylbenzene,⁶¹ 1,4-diazidobenzene,^{62,63} and 1,3-diazidobenzene^{63,64} were prepared according to literature procedures. 1,3-Diethynylbenzene (Sigma) and KBPh_4 (Alfa Aesar) were purchased from commercial sources. 1,3-Diethynylbenzene was degassed by three freeze–pump–thaw cycles and filtered over dry alumina before use.

^1H 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 96.24 MHz. All chemical shifts are reported relative to the peak for SiMe_4 , using ^1H (residual) chemical shifts of the solvent ($\text{C}_6\text{D}_6 = 7.16\text{ ppm}$; $\text{CD}_3\text{CN} = 1.94\text{ ppm}$) as a secondary standard. 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 $\pm 2\text{ Hz}$. 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. ^{11}B chemical shifts are reported relative to the peak for $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.0 ppm). All voltammetric data were obtained under inert atmosphere conditions using external electrical ports of the MBraun inert drybox. All data were obtained using a Gamry Instruments Interface 1000 model potentiostat using the Gamry Instruments Laboratory software. All samples were collected in THF with 1.0 mM $[\text{Bu}_4\text{N}][\text{OTf}]$ in 4 mL of dry THF. Solutions were analyzed in 10 mL beakers, consisting of a 3 mm glassy carbon working electrode, a Pt wire counter electrode, and an Ag wire quasi-reference electrode. Potentials were corrected using a ferrocene standard at the end of runs. Elemental analyses were performed by the UIUC Microanalysis Laboratory or Midwest-Microlab, LLC. Electronic absorption spectroscopic measurements were recorded at ambient temperature in sealed 1 cm quartz cuvettes with a Cary 6000i UV–vis–NIR spectrophotometer. Infrared spectra were recorded using a Thermo Nicolet iS5 FT-IR spectrometer. Samples were mixed with dry KBr and recorded.

Magnetic susceptibility data were collected using a Quantum Design MPMS XL SQUID magnetometer. All sample preparations were performed inside a dinitrogen-filled glovebox (MBRAUN Labmaster 130). Powdered microcrystalline samples were loaded into polyethylene bags and sealed in the glovebox. The bags that contained compounds **2-meta**, **2-para**, and $\text{Tp}^*_2\text{UCCPh}$ were subsequently sealed in an additional polyethylene bag to ensure inert conditions as these complexes showed heightened air-sensitivity. After sealing in the bags, the samples were inserted into a straw and transported to the magnetometer under dinitrogen. Ferromagnetic impurities were checked through a variable field analysis (0 to 10 kOe) of the magnetization at 100 K (Figures S24–S29), which showed that for **2-para**, **3-meta**, and **3-para** major ferromagnetic impurities were likely not present. As a precaution, the variable temperature magnetic susceptibility data for **2-meta**, $\text{Tp}^*_2\text{UCCPh}$, and $\text{Tp}^*_2\text{U}(\text{N-}p\text{Tolyl})$ were collected at 5000 Oe due to nonlinearity in the low field magnetization data collected at 100 K. Magnetic susceptibility data were collected at temperatures ranging from 2 to

300 K (Figure 5). Reproducibility of magnetic susceptibility data was assessed through measurements on two different batches for all compounds (with the exception of $\text{Tp}^*_2\text{UCCPh}$). Relative consistency at all temperatures was observed for all samples (Figures S30–S34). Magnetization measurements were collected at 1.8 K while varying the applied field up to 50 kOe (Figures S41–S42). Fits acquired with the program PHI⁵¹ to determine a potential coupling constant for **2-meta**, **2-para**, **3-meta**, and **3-para** used a spin Hamiltonian with the general form: $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. Data were corrected for the diamagnetic contributions of the sample holder and bag by subtracting empty containers; diamagnetic corrections for the sample were calculated using Pascal's constants.⁶⁵

The electronic structures of complexes **1–4** were examined using the Gaussian16 suite of software⁶⁶ at the B3LYP⁶⁷ (Becke-3⁶⁸ exchange and Lee–Yang–Parr⁶⁹ correlation functional) level. All structures were truncated by replacing methyl substituents with hydrogen atoms, and stationary points were determined to be global minima using analytical frequency calculations with the Stuttgart/Dresden triple- ζ quality basis set⁷⁰ and the corresponding effective core potential (ECP) for uranium. The Pople double- ζ quality basis set, 6-31G, was used for all remaining atoms. Bader's Atoms in Molecules (AIM) analysis was performed using Multiwfn.

Single crystals of **2-para** and **3-para** suitable 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 $K\alpha$ radiation ($\lambda = 1.54184\text{ \AA}$). Crystals of **3-meta** were transferred to the goniometer head of a Bruker APEX II CCD diffractometer and analyzed at 100 K using monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) with the omega scan technique. Single crystals of **1-MeCN** and **2-meta** were transferred to the goniometer head of a Bruker Quest diffractometer equipped with a single crystal curved graphite incident beam monochromator and a Photon100 CMOS area detector. Examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Data were collected, unit cells determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 or Apex3 suites of programs. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs and refined by full matrix least-squares against F^2 with all reflections using Shelxl 2014 or Shelxl 2017⁷¹ and the graphical interface Shelxle. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1852443–1852445, 1852447–1852450 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $\text{Tp}^*_2\text{UCCPhCCUTp}^*_2$ (2-meta**, **2-para**).** A 20 mL scintillation vial was charged with $\text{Tp}^*_2\text{UCH}_2\text{Ph}$ (**1-Bn**) (0.250 g, 0.271 mmol) and 5 mL of THF and cooled to $-35\text{ }^{\circ}\text{C}$. A separate vial was charged with half an equivalent of 1,3-diethynylbenzene (0.017 g, 0.135 mmol) or 1,4-diethynylbenzene (0.017 g, 0.135 mmol) in 5 mL of THF and cooled to $-35\text{ }^{\circ}\text{C}$. The solution of diethynylbenzene was added to the thawing solution of **1-Bn** and allowed to warm to room temperature. After 30 min, volatiles were removed in vacuo. The resulting solid was washed with cold n -pentane ($2 \times 10\text{ mL}$), and dried to afford green powder assigned as $\text{Tp}^*_2\text{UCC}(1,3\text{-C}_6\text{H}_4)\text{-CCUTp}^*_2$ (**2-meta**) (0.206 g, 0.115 mmol, 85%) or $\text{Tp}^*_2\text{UCC}(1,4\text{-C}_6\text{H}_4)\text{-CCUTp}^*_2$ (**2-para**) (0.218 g, 0.122 mmol, 90%). Single, X-ray quality crystals were obtained from a concentrated THF solution stored at $-35\text{ }^{\circ}\text{C}$ (**2-meta**) or from a concentrated 1,2-dimethoxyethane solution stored at $-35\text{ }^{\circ}\text{C}$ (**2-para**).

2-meta. ^1H NMR (benzene- d_6 , $25\text{ }^{\circ}\text{C}$): $\delta = -14.84$ (4, 2H, B-H), -13.64 (6, 2H, B-H), -12.58 (19, 36H, Tp^*-CH_3), 0.83 (4, 36H, Tp^*-CH_3), 7.97 (11, 12H, Tp^*-CH), 13.40 (t, 1H, aryl-CH, $J = 6\text{ Hz}$), 27.29 (d, 2H, aryl-CH, $J = 7\text{ Hz}$), 34.62 (9, 1H, aryl-CH). ^{11}B NMR (benzene- d_6 , ambient temperature): $\delta = 5.47$. IR (KBr pellet) ν (B–H) = $2547, 2523\text{ cm}^{-1}$. Elemental analysis of $\text{C}_{70}\text{H}_{92}\text{N}_{24}\text{B}_4\text{U}_2$:

Calculated, C, 47.00; H, 5.18; N, 18.79. Found, C, 46.62; H, 5.34; N, 18.01.

2-para. ^1H NMR (benzene- d_6 , 25 °C): δ = −14.88 (3, 4H, B-H), −12.49 (25, 36H, Tp^*-CH_3), 1.00 (11, 36H, Tp^*-CH_3), 8.15 (11, 12H, Tp^*-CH), 23.99 (11, 4H, aryl-CH). ^{11}B NMR (benzene- d_6 , ambient temperature): δ = −3.67, −2.56. IR (KBr pellet) ν (B-H) = 2559, 2524, 2046 ($\text{C}\equiv\text{C}$) cm^{-1} . Elemental analysis of $\text{C}_{70}\text{H}_{92}\text{N}_{24}\text{B}_4\text{U}_2$: Calculated, C, 47.00; H, 5.18; N, 18.79. Found, C, 47.08; H, 5.36; N, 18.55.

Synthesis of $\text{Tp}_2^*\text{UNPhNUTp}_2^*$ (3-*meta*, 3-*para*). A 20 mL scintillation vial was charged with **1-Bn** (0.325 g, 0.352 mmol) and 5 mL of THF and then frozen. A separate vial was charged with half an equivalent of 1,3-diazidobenzene (0.028 g, 0.175 mmol) or 1,4-diazidobenzene (0.028 g, 0.175 mmol) in 5 mL of THF and frozen. On thawing, the solution of azide was added to the thawing solution of **1-Bn** resulting in an immediate color change from green to deep red-purple. After 15 min, volatiles were removed in vacuo. The resulting solid was washed with *n*-pentane and dried to afford red-purple powder assigned as $\text{Tp}_2^*\text{UN}(1,3\text{-C}_6\text{H}_4)\text{NUTp}_2^*$ (3-*meta*) (0.298 g, 0.168 mmol, 95%) or $\text{Tp}_2^*\text{UN}(1,4\text{-C}_6\text{H}_4)\text{NUTp}_2^*$ (3-*para*) (0.289 g, 0.163 mmol, 93%). Single, X-ray quality crystals of either 3-*meta* or 3-*para* were obtained by slow diffusion of diethyl ether into a concentrated THF solution at −35 °C.

3-*meta*. ^1H NMR (benzene- d_6 , ambient temperature): δ = −18.59 (120, 4H, B-H), −6.60 (19, 36H, Tp^*-CH_3), 7.00 (57, 12H, Tp^*-CH), 11.75 (163, 36H, Tp^*-CH_3), 98.36 (22, 2H, 4,6-Ph-CH), 98.82 (11, 1H, 5-Ph-CH), 153.63 (51, 1H, 2-Ph-CH). ^{11}B NMR (benzene- d_6 , ambient temperature): δ = −61.02. IR (KBr pellet) ν = 2554, 2528 cm^{-1} (B-H). Elemental analysis of $\text{C}_{66}\text{H}_{92}\text{N}_{26}\text{B}_4\text{U}_2$: Calculated, C, 44.81; H, 5.24; N, 20.59. Found, C, 45.33; H, 5.31; N, 19.78.

3-*para*. ^1H NMR (benzene- d_6 , ambient temperature): δ = −15.64 (140, 4H, B-H), −3.48 (7, 36H, Tp^*-CH_3), 10.04 (17, 12H, Tp^*-CH), 12.31 (62, 36H, Tp^*-CH_3), 121.23 (27, 4H, Ph-CH). ^{11}B NMR (benzene- d_6 , ambient temperature): δ = −58.84. IR (KBr pellet) ν = 2554, 2527 cm^{-1} (B-H). Elemental analysis of $\text{C}_{66}\text{H}_{92}\text{N}_{26}\text{B}_4\text{U}_2$: Calculated, C, 44.81; H, 5.24; N, 20.59. Found, C, 44.88; H, 4.99; N, 19.61.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-
met.8b00794.

Additional experimental procedures, NMR, IR, and electronic absorption spectra, tabulated X-ray parameters, magnetic data, CV plots, and geometry optimization tables (PDF)

Cartesian coordinates for complex **1-Bn** (XYZ)

Cartesian coordinates for complex **2-*meta*** (XYZ)

Cartesian coordinates for complex **2-*para*** (XYZ)

Cartesian coordinates for complex **3-*meta*** (XYZ)

Cartesian coordinates for complex **3-*para*** (XYZ)

Accession Codes

CCDC 1852443–1852445 and 1852447–1852450 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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