Convenient Synthesis, Structure, and Reactivity of $(C_5Me_5)U(CH_2C_6H_5)_3$: A Simple Strategy for the Preparation of Monopentamethylcyclopentadienyl Uranium(IV) Complexes

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A high-yield one-pot synthesis of $(C_5Me_5)U(CH_2C_6H_5)_3$ has been developed and applied to the synthesis of a new organouranium complex possessing a (pentamethylcyclopentadienyl)-bis(cyclopentadienyl) ligand framework, $(C_5Me_5)(C_5H_5)_2U(CH_2C_6H_5)$. Both complexes have been structurally characterized. We also report herein an improved and safer synthesis for the popular uranium starting material UCl_4.

Introduction

Organometallic uranium chemistry has been the subject of an increasing number of investigations over the past two decades, with pentamethylcyclopentadienyl[1] and sterically bulky nitrogen donor[2] ligands frequently being employed as ancillary ligands to both enhance solubility and define or limit the reactive sites in these complexes. Whereas systems such as $(C_5Me_5)_2U$[1] and $(R_2N)_3U$[2] have played a prominent role in these efforts, reports of uranium compounds containing a single pentamethylcyclopentadienyl ancillary ligand are considerably less common.[3] This is unfortunate since monopentamethylcyclopentadienyl uranium complexes offer opportunities for the development of new uranium-mediated chemistry due to the inherent steric and electronic unsaturation of the $(C_5Me_5)U$ framework relative to the bulkier systems. Evidence for this has been provided by Marks and co-workers, who demonstrated that monopentamethylcyclopentadienyl thorium complexes supported on dehydroxylated alumina show enhanced catalytic activity compared with supported bis(pentamethylcyclopentadienyl) thorium and tris(cyclopentadienyl) thorium complexes.[4]

A convenient entry into the monopentamethylcyclopentadienyl uranium framework might be envisioned to be $(C_5Me_5)U(CH_2C_6H_5)_3$, which has been the subject of only a single investigation described by Marks and co-workers in 1982.[5] The previously reported route to this compound involves a multistep and variable (24−60%) yield synthesis which may present a barrier to the development of new chemistry of $(C_5Me_5)U(CH_2C_6H_5)_3$. In our ongoing pursuit to develop synthetic entries toward uranium complexes containing multiply bonded functional groups,[6] we have devised a high-yield, straightforward synthesis of $(C_5Me_5)U(CH_2C_6H_5)_3$. Since $(C_5Me_5)U(CH_2C_6H_5)_3$ provides an attractive entry into both homogeneous and heterogeneous organouranium chemistry, we report the details of our synthesis herein. Furthermore, we demonstrate that $(C_5Me_5)U(CH_2C_6H_5)_3$ can be easily tailored and applied to the synthesis of new uranium(IV) monopentamethylcyclopentadienyl mixed-ring compounds such as the mixed-ring uranium(IV) metallocene complex $(C_5Me_5)(C_5H_5)_2U(CH_2C_6H_5)$. In the course of these studies, we found it desirable to

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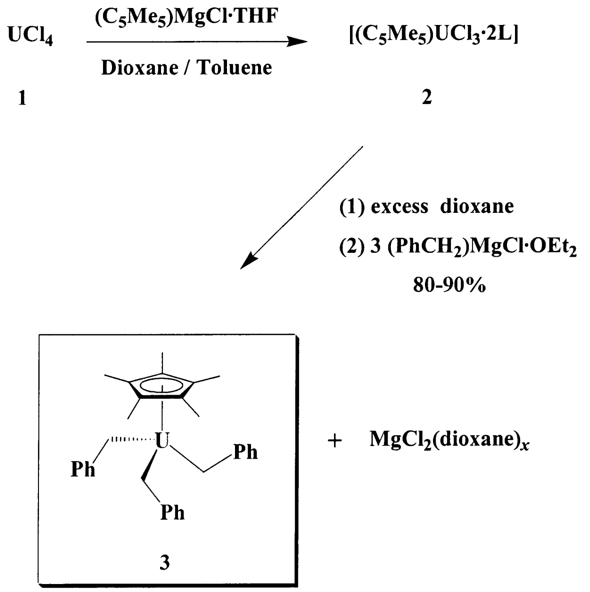
Scheme 1



develop an improved and safer route to the common uranium starting material, UCl_4, which we also report herein.

Results and Discussion

As depicted in Scheme 1, treatment of a toluene slurry of UCl_4 (**1**) with $(C_5Me_5)MgCl{\cdot}THF$ (1 equiv) and dioxane at room temperature generates complex **2** in situ. Subsequent addition of dioxane (excess) and benzylmagnesium chloride (3 equiv) to the solution of **2** affords $(C_5Me_5)U(CH_2C_6H_5)_3$ (**3**). Following workup, the isolated yield for complex **3** is typically 80−90%. Although Marks' preparation of **3** is effective, our protocol circumvents the isolation of $(C_5Me_5)UCl_3$. In addition, the present synthetic scheme also avoids the use of CH_2Cl_2 and $LiCH_2C_6H_5$ and takes advantage of the commercially available reagent benzylmagnesium chloride. The addition of dioxane permits the facile removal of precipitated $MgCl_2(dioxane)_x$ adducts from solution and allows for the straightforward workup and high-yield synthesis of **3**.[7]

Single crystals of **3** suitable for X-ray diffraction were obtained by slow evaporation of a solution of **3** in toluene. As shown in Figure 1, the molecular structure of **3** reveals that the uranium complex is essentially identical to the previously reported thorium(IV) analogue, $(C_5Me_5)Th(CH_2C_6H_5)_3$,[5] with the U(IV) metal center bound to the pentamethylcyclopentadienyl ligand in an η^5-manner and interacting with the three benzyl ligands in a decidedly multihapto fashion. The interaction between the uranium metal center and the pentamethylcyclopentadienyl ligand is unexceptional, and the $U-(C_5Me_5)$ distances ($U-C_{av}$ = 2.83 Å; $C-C_{av}$ = 1.42 Å) compare well with those found in other uranium(IV) complexes.[3a,b] That the three benzyl ligands are bound to the uranium metal center in a multihapto fashion is clearly demonstrated by the metrical parameters associated with the uranium-benzyl linkages (Benzyl ligand #1: U(1)−C(1) = 2.477(18) Å, U(1)−C(2) = 2.814(19) Å, U(1)−C(1)−C(2) = 87.3(11)°, U(1)−C(3) = 3.37(2) Å, U(1)−C(7) = 3.42(2) Å. Benzyl ligand #2: U(1)−C(8) = 2.51(2) Å, U(1)−C(9) = 2.809(19) Å, U(1)−C(8)−C(9) = 85.5(12)°, U(1)−C(10) = 3.47(2) Å, U(1)−C(14) = 3.40(2) Å. Benzyl ligand #3: U(1)−C(15) = 2.53(2) Å, U(1)−C(16) = 2.85(2) Å, U(1)−C(15)−C(16) = 87.0(13)°, U(1)−C(17) = 3.42(2) Å, U(1)−C(21) = 3.50(2) Å). The benzyl groups are best described as η^4, with the strongest secondary interaction occurring between the uranium metal center and the ipso carbon of the coordinated benzyl ligands in addition to weaker unsymmetrical secondary interactions taking place between the uranium and the ortho carbons of the benzyl ligands.

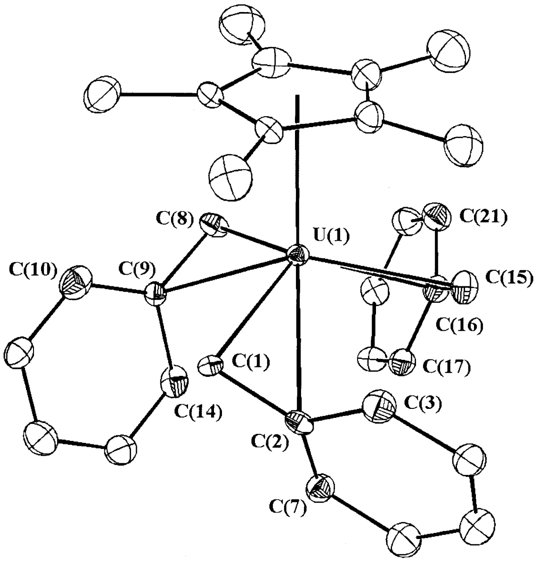


Figure 1. Molecular structure of **3** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): U(1)−C(1) 2.477(18); U(1)−C(8) 2.51(2); U(1)−C(15) 2.53(2); U(1)−C(2) 2.814(19); U(1)−C(9) 2.809(19); U(1)−C(16) 2.85(2); U(1)−C(3) 3.37(2); U(1)−C(7) 3.42(2); U(1)−C(10) 3.47(2); U(1)−C(14) 3.40(2); U(1)−C(17) 3.42(2); U(1)−C(21) 3.50(2); C(1)−C(2) 1.46(3); C(8)−C(9) 1.47(3); C(15)−C(16) 1.44(3); U(1)−C(1)−C(2) 87.3(11); U(1)−C(8)−C(9) 85.5(12); U(1)−C(15)−C(16) 87.0(13); C(1)−U(1)−C(8) 112.4(6); C(1)−U(1)−C(15) 116.6(6); C(8)−U(1)−C(15) 114.0(7).

The proclivity for benzyl ligands to bond in an η^4-mode with actinide metals has been noted by both Marks[5] and Andersen.[8] Two parameters have been defined to quantify the benzyl ligand-to-metal interaction, Δ and Δ′, where $\Delta = [MC_o - MCH_2] - [MC_{ipso} - MCH_2]$ and $\Delta' = [MC_{o'} - MCH_2] - [MC_{ipso} - MCH_2]$ and where MC_o is the shorter metal-to-ortho carbon contact, $MC_{o'}$ is the longer metal-to-ortho contact, MCH_2 is the metal-to-methylene carbon bond length, and MC_{ipso} is the metal-to-ipso carbon bond length.[8] For the f-block metals, Δ and Δ′ have been shown to have comparable values, as would be expected for an η^4-benzyl-to-metal bonding interaction. Table 1 compares and contrasts the Δ and Δ′ values determined for complex **3** with the other

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[7] (a) *Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Marcel Dekker: New York, 1996. (b) This metholodogy has been utilized to prepare a variety of organoactinide complexes, see: England, A. F.; Burns, C. J.; Buchwald, S. L. *Organometallics* **1994**, *13*, 3491−3495.

[8] Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293−298. In this work, Δ and Δ′ values for transition metal benzyl complexes is provided and compared to the actinide benzyl complexes.

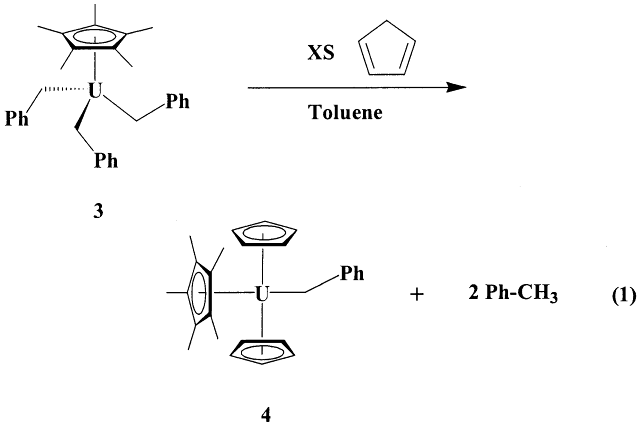
Table 1. Bond Lengths in Actinide Benzyl Complexes

compound	$MC_{ipso}-MCH_2$[a]	MC_o-MCH_2[b]	$MC_{o'}-MCH_2$[c]	Δ[d]	Δ′[e]	reference
$(C_5Me_5)Th(CH_2Ph)_3$ (shortest contacts)	0.29	0.77	1.00	0.48	0.71	5
$(dmpe)Th(CH_2Ph)_4$[f] (shortest contacts)	0.35	0.78	0.39	0.43	0.58	8
$(dmpe)U(CH_2Ph)_3(Me)$[f] (shortest contacts)	0.22	0.55	0.91	0.33	0.69	8
$(C_5Me_5)U(CH_2Ph)_3$ (**3**) (benzyl ligand #1, $U-CH_2 = U(1)-C(1)$)	0.34	0.89	0.94	0.56	0.61	this work
$(C_5Me_5)U(CH_2Ph)_3$ (**3**) (benzyl ligand #2, $U-CH_2 = U(1)-C(8)$)	0.30	0.89	0.96	0.59	0.66	this work
$(C_5Me_5)U(CH_2Ph)_3$ (**3**) (benzyl ligand #3, $U-CH_2 = U(1)-C(15)$)	0.32	0.89	0.97	0.57	0.65	this work

[a] Metal-to-ipso carbon bond length minus metal-to-methylene carbon bond length. [b] Metal-to-shorter ortho carbon bond length minus metal-to-methylene carbon bond length. [c] Metal-to-longer ortho carbon bond length minus metal-to-methylene carbon bond length. [d] $[MC_o - MCH_2] - [MC_{ipso} - MCH_2]$. [e] $[MC_{o'} - MCH_2] - [MC_{ipso} - MCH_2]$. [f] dmpe = 1,2-bis(dimethyldiphosphino)ethane.

known structurally characterized actinide benzyl complexes. The metrical parameters exhibited by complex **3** are comparable with those reported for the other actinide η^4-benzyl systems, which supports the formulation of the ligands in complex **3** as η^4-benzyl ligands.

The reactivity of complex **3** was probed using cyclopentadiene. As shown in eq 1, reaction of a toluene solution **3** with excess cyclopentadiene affords the new mixed-ring metallocene complex **4** as a brown crystalline solid in 86% isolated yield. Although the reaction is rather slow and requires days for completion, ^1H NMR spectroscopy shows that the protonolysis is exceptionally clean with quantitative formation of complex **4**. The ^1H NMR spectrum of **4** is sharp and paramagnetically shifted, which suggests that the complex is a U(IV) species. A noteworthy feature of the ^1H NMR spectrum of **4** is the exceptionally large chemical shift observed for the $U-CH_2$ resonance, which appears as a broad singlet at δ −229.58 ppm. Significant isotropic chemical shifts have been reported for tris(cyclopentadienyl)-uranium(IV) alkyl complexes (e.g., Cp_3UCH_2Ph, δ −213 ppm;[9] Cp_3UCH_2-*p*-Tol, δ −214 ppm;[9] Cp_3UBu, δ −200 ppm).[10] Additionally, the room-temperature electronic absorption spectra for **4**, recorded in toluene solution from 1600 to 300 nm, exhibits several narrow line-width, low molar absorptivity ($<100\ M^{-1}\ cm^{-1}$) transitions and is consistent with the assignment of an f^2 U(IV) metal center.[6d−f]



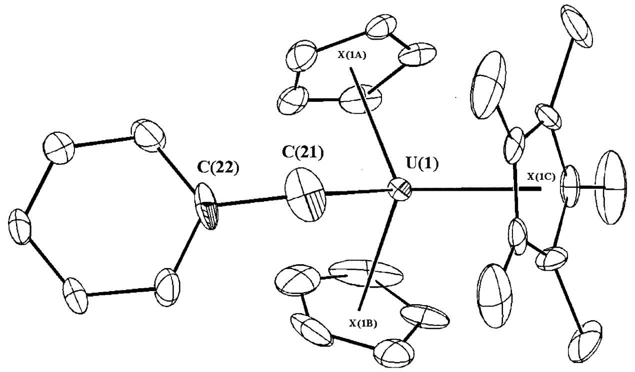


Figure 2. Molecular structure of **4** with thermal ellipsoids at the 25% probability level. Selected bond distances (Å) and angles (deg): U(1)−C(21) 2.485(16); U(1)−C(22) 3.70-(2); C(21)−C(22) 1.51(2); U(1)−X(1A) 2.473; U(1)−X(1B) 2.489; U(1)−X(1C) 2.500; U(1)−C(21)−C(22) 134.0(11); X(1A)−U(1)−X(1B) 113.8; X(1A)−U(1)−X(1C) 119.8; X(1A)−U(1)−C(21) 100.2; C(21)−U(1)−X(1C) 94.9; C(21)−U(1)−X(1B) 106.4; X(1C)−U(1)−X(1B) 116.8.

That complex **3** participates in protonolysis chemistry with relatively weak carbon acids to give the new metallocene system is rather interesting.[11] It appears that the reaction is dictated by steric factors, since only two C_5H_5 rings are transferred to the uranium metal center even in the presence of excess cyclopentadiene. The driving force for this transformation can be explained by comparing the pK_a's for toluene (p$K_a \approx 41$) and cyclopentadiene (p$K_a \approx 16$).[12] As a weak acid, toluene serves as an excellent leaving group for the stronger carbon acid cyclopentadiene and suggests that this simple methodology may be readily extended to other carbon acids with pK_a's less than that of toluene. Accordingly, complex **3** also reacts with pentamethylcyclopentadiene to give the previously reported $(C_5Me_5)_2U(CH_2C_6H_5)_2$.[1a]

Complex **4** has been structurally characterized (Figure 2). The molecular structure of **4** reveals a distorted tetrahedral coordination environment about the uranium metal center, which is common for all compounds of the type $(C_5R_5)_3MX$ (R = H, alkyl).[13] The uranium metal center is encased by one C_5Me_5 ring ($U-C_{av}$ =

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[9] Brandi, G.; Brunelli, M.; Lugli, G.; Mazzei, A. *Inorg. Chim. Acta* **1973**, *7*, 319−322.

[10] Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529−5539.

[11] Little is known about the chemical reactivity of complex **3**. It has been noted that **3** reacts with alcohols, formaldehyde, and H_2 to give alkoxide and hydride complexes. See ref 5.

[12] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 297−298.

2.77 Å; C−C$_{av}$ = 1.38 Å) and two C_5H_5 rings (U−C$_{av}$ = 2.74, 2.75 Å; C−C$_{av}$ = 1.37, 1.42 Å), which all interact with the metal center in an η^5-manner. These metrical parameters compare well with those found in other tris(ligand) uranium(IV) metallocene complexes (e.g., Cp_3UCl, U−C$_{av}$ = 2.74 Å;[14] $(C_5Me_4H)_3UCl$, U−C$_{av}$ = 2.79 Å;[15] $(C_5Me_5)_3UCl$, U−C$_{av}$ = 2.83 Å).[16] The benzyl ligand is bound to the metal center in an η^1-fashion (U(1)−C(21) = 2.485(16) Å, U(1)−C(22) = 3.70(2) Å, U(1)−C(21)−C(22) = 134.0(11)°) and displays no secondary interactions between the arene ring and the uranium metal center. However, the larger than tetrahedral angle about the α-carbon atom is curious and could suggest the presence of an α-agostic interaction.[17] Similar structural findings have been reported for the related tris(cyclopentadienyl) complexes Cp_3UBu (U−C(1)−C(2) = 127.9(19)°) and $Cp_3U(CH_2\text{-}p\text{-tol})$ (U−C(1)−C(2) = 128.5(13)°).[18]

In summary, the synthetic methodology provided in this contribution offers a convenient one-pot synthesis of $(C_5Me_5)U(CH_2C_6H_5)_3$. This new approach affords $(C_5Me_5)U(CH_2C_6H_5)_3$ in high-yield, making it an attractive starting material readily available in multigram quantities for uranium metallocene chemistry. Preliminary reactivity studies show that $(C_5Me_5)U(CH_2C_6H_5)_3$ can be readily manipulated for the synthesis of novel monopentamethylcyclopentadienyl uranium(IV) systems. We are presently exploring its use in the preparation of a variety of mixed-ring uranium metallocene complexes.

Experimental Section

General Comments. Unless otherwise noted, reactions and manipulations were performed at 20 °C in a recirculating Vacuum Atmospheres Model HE-553-2 inert atmosphere (N_2 or He) drybox with a MO-40-2 Dri-Train or using standard Schlenk and high-vacuum-line techniques. Glassware was dried overnight at 150 °C before use. Reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Celite (Aldrich) and alumina (Brockman I, Aldrich) were dried in vacuo at 250 °C for 48 h prior to use. Toluene (Fisher), hexanes (Fisher), diethyl ether (Fisher), and tetrahydrofuran (Fisher) were passed through a column of activated alumina (A2, 12 × 32, Purify) under nitrogen pressure and sparged with N_2 prior to use.[19] Dioxane (Aldrich) was degassed, passed through a short column (5−6 cm) of activated alumina, and stored over 4 Å molecular sieves prior to use. Uranium tetrachloride was prepared using a modification to the literature procedure published by Suttle and Hermann,[20] which is detailed below. $(C_5Me_5)MgCl\cdot THF$ was prepared according to literature procedures.[1a] $(C_6H_5CH_2)MgCl$ (1.0 M diethyl ether solution, Aldrich) was used as received. Deuterated solvents (Cambridge Isotope Laboratories) were purified by storage over activated 4 Å molecular sieves or sodium metal and then degassed by three freeze−pump−thaw cycles prior to use. All other reagents were ACS reagent grade and used as received and obtained as follows: uranium(VI) oxide dihydrate (Cerac) and hexachloropropene (Aldrich) and anhydrous methylene chloride (Aldrich).

Synthesis of UCl_4 (1). The following synthesis was found to be a *safer*[20] and more convenient alternative to the published procedure.[21] On a Schlenk-line, a 250 mL three-neck round-bottomed flask equipped with a condenser (outfitted with a nitrogen inlet) and a thermometer was charged with hexachloropropene (110 mL, 780 mmol, 1.765 g/mL) and a stir bar. Under a strong nitrogen flow, the flask was heated to 190 °C, and two small portions (spatula tip, ca. 0.3 g) of uranium(VI) oxide dihydrate were added. A cloudy yellow mixture was produced. (*Note*: This is a radical-initiated reaction; efficient stirring is *critical* to smoothly initiate the reaction.) Heating was continued at 190 °C. Gas evolution was observed and the mixture changed color from yellow to dark orange. Small portions (spatula tip, ca. 0.3 g) of $UO_3\cdot 2H_2O$ were *carefully* added to the hot reaction mixture until all of the $UO_3\cdot 2H_2O$ (10.591 g, 32.89 mmol) was exhausted. With each addition of $UO_3\cdot 2H_2O$, a vigorous reaction ensues, as evidenced by a significant amount of foaming and smoke which is produced as the reaction mix changes color from orange to dark red. Once addition of the $UO_3\cdot 2H_2O$ was complete, the reaction mixture was heated at reflux (190 °C) overnight (12 h), during which time the red dissolved UCl_5 was gradually converted to insoluble green UCl_4 (**1**). The reaction mixture was then cooled to room temperature and taken into an inert atmosphere drybox and filtered. The crude UCl_4 was collected and washed with 160 mL of methylene chloride in 20 mL portions (or until the washings go from dark red to colorless); this removes hexachloropropene and other soluble impurities that adhere to the UCl_4. The crude product was collected and the volatiles were removed under reduced pressure overnight to afford **1** as a green solid (12.25 g, 32.23 mmol, 98%).

Synthesis of $(C_5Me_5)U(CH_2C_6H_5)_3$ (3). A 125 mL Erlenmeyer flask equipped with a stir bar was charged with UCl_4 (1.558 g, 4.10 mmol), dioxane (4.0 mL, 46.9 mmol, 1.034 g/mL), and toluene (40 mL). To the resulting green slurry was added $(C_5Me_5)MgCl\cdot THF$ (1.100 g, 4.12 mmol) with additional toluene (40 mL). The resulting red slurry was stirred at room temperature for 12 h. To the resulting dark brick red mixture was sequentially added dioxane (5.0 mL, 58.7 mmol, 1.034 g/mL) and benzylmagnesium chloride (1.0 M solution in Et_2O, 15 mL, 15 mmol), which afforded a dark brown colored solution that was stirred at room temperature for 3 h. The mixture was then filtered through a Celite-padded coarse frit to remove the insoluble salts. The reddish brown filtrate was collected and the volatiles were removed under reduced pressure to give a brown solid. This solid was taken up in toluene/hexane (20 mL/20 mL) and filtered through a Celite-padded coarse frit to remove the insoluble salts. The filtrate was collected and the volatiles were removed under reduced pressure. This last step

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(20) We have experienced some safety issues with the published UCl_4 synthesis which involves heating a "one-pot" mixture of $UO_3\cdot 2H_2O$ and hexachloropropene to high temperatures. In our hands, different lots of $UO_3\cdot 2H_2O$ have initiated at different temperatures (presumably a consequence of variable surface area and waters of hydration with different $UO_3\cdot 2H_2O$ batches), which has led to unexpected thermal excursions of reagent from the reaction vessel. We have found that this can be avoided using the following procedure, which entails the portionwise addition of $UO_3\cdot 2H_2O$ to a hot hexachloropropene solution and allows for control of the reaction.

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was repeated to afford **3** as a dark brown crystalline solid (2.364 g, 1.023 mmol, 90%). ^{1}H NMR (C_6D_6, 300 MHz, 21 °C): δ 6.56 (t, J = 6.9 Hz, 2H meta), 3.52 (br s, 2H, U-CH_2), 0.13 (t, J = 7.5 Hz, 1H, para), −0.49 (s, 15H, Cp*-CH_3), −21.33 (br s, 2H, ortho). UV−vis/NIR (ϵ, M^{-1} cm^{-1}, toluene): 419 (sh) (3250), 594 (sh) (800), 684 (sh) (350), 1107 (113), 1167 (179), 1430 (26), 1570 (30). Mp = 119−121 °C. MS (EI, 70 eV): m/z 556 (M − $C_7H_7^+$).

Synthesis of (C_5Me_5)(C_5H_5)$_2$U($CH_2C_6H_5$) (4). A 125 mL Erlenmeyer flask equipped with a stir bar was charged with (C_5Me_5)U($CH_2C_6H_5$)$_3$ (**3**) (0.689 g, 1.07 mmol) and toluene (60 mL). To the dark brown solution was added freshly cracked cyclopentadiene via syringe (0.189 mL, 2.25 mmol, 0.80 g/mL). The brown solution was stirred at room temperature for 6 days. The reaction mixture was then filtered through a Celite-padded coarse frit, the filtrate was collected, and the volatiles were removed under reduced pressure to give crude **4** as a dark brown solid. Recrystallization from toluene (3 mL) and hexanes (15 mL) at −30 °C afforded **4** as a black crystalline solid (0.546 g, 0.918 mmol, 86%). ^{1}H NMR (C_6D_6, 300 MHz, 21 °C): δ 8.13 (s, 15H, Cp*-CH_3), 2.81 (t, J = 7.5 Hz, 2H, meta), −1.75 (t, J = 6.9 Hz, 1H, para), −6.36 (s, 10H, Cp-H), −22.51 (d, J = 7.5 Hz, ortho), −229.58 (br s, 2H, U-CH_2). UV−vis/NIR (ϵ, M^{-1} cm^{-1}, toluene): 467 (20), 494 (sh) (20), 511 (100), 546 (20), 575 (sh), 599 (10), 621 (10), 648 (10), 680 (42), 709 (34), 728 (11), 740 (sh) (5), 768 (3), 796 (3), 810 (3), 939 (45), 1005 (62), 1036 (75), 1053 (5), 1078 (107), 1140 (48), 1184 (sh) (30), 1227 (55), 1336 (95), 1375 (sh) (25), 1481 (11), 1499 (sh) (5). Mp = 192−194 °C (dec). MS (EI, 70 eV): m/z 594 (M − H^+), 529 (M − $C_5H_6^+$), 504 (M − $C_7H_7^+$). Anal. Calcd for $C_{27}H_{32}U$ (594.58 g/mol): C, 54.54; H, 5.42. Found: C, 54.70; H, 5.60.

Crystallographic Details for (C_5Me_5)U($CH_2C_6H_5$)$_3$ (3). A black crystal (0.25 × 0.12 × 0.12 mm) grown by slow evaporation of a toluene solution of **3** was mounted from Paratone N oil (Exxon) onto a glass fiber under argon gas flow and placed on a Bruker P4/CCD diffractometer, equipped with a Bruker LT-2 temperature device. A hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. A total of 37 913 reflections ($-9 \leq h \leq 9$, $0 \leq k \leq 32$, $0 \leq l \leq 19$) were collected at T = 203(2) K in the θ range of 1.3−22.5°, of which 6380 were unique (R_{int} = 0.071); Mo Kα radiation (λ = 0.71073 Å). Data collection and initial indexing and cell refinement were handled using SMART[22] software. Frame integration and final cell parameter calculations were carried out using SAINT[23] software. The data were corrected for absorption using the DIFABS[24] program. The structure was solved using direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares procedures. All non-hydrogen anisotropic temperature factors were restrained to approximate isotropic behavior using the ISOR option in SHELXTL, and hydrogen atoms were treated as idealized contributions. Difference Fourier maps revealed the presence of residual electron density consistent with minor static rotational disorder of the molecule, but this disorder could not be fit with any realistic model. The absorption coefficient was 6.303 mm^{-1}. The least-squares refinement converged normally with residuals of R1 = 0.1180 ($I > 2\sigma(I)$), wR2 = 0.1767, and GOF = 3.331 (F^2); $C_{31}H_{36}U$ (646.63 g/mol), space group $P2_1/n$, monoclinic a = 9.556(2) Å, b = 30.725(8) Å, c = 17.877(5) Å, β = 100.351(5)°, V = 5163(2) Å^3, Z = 8, F(000) = 2512, ρ_{calcd} = 1.664 g cm^{-3}. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.[25]

Crystallographic Details for (C_5Me_5)(C_5H_5)$_2$U($CH_2C_6H_5$) (4). A brown crystal (0.25 × 0.21 × 0.21 mm) grown by slow evaporation of a hexane solution of **4** was mounted from Paratone N oil (Exxon) onto a glass fiber under argon gas flow and placed on a Bruker P4/CCD diffractometer, equipped with a Bruker LT-2 temperature device. A hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. A total of 7046 reflections ($-9 \leq h \leq 9$, $0 \leq k \leq 32$, $0 \leq l \leq 19$) were collected at T = 203(2) K in the θ range of 1.8−23.3°, of which 3237 were unique (R_{int} = 0.068); Mo Kα radiation (λ = 0.71073 Å). Data collection and initial indexing and cell refinement were handled using SMART[22] software. Frame integration and final cell parameter calculations were carried out using SAINT[23] software. The data were corrected for absorption using the DIFABS[24] program. The structure was solved using direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares procedures. All non-hydrogen anisotropic temperature factors were restrained to approximate isotropic behavior using the ISOR option in SHELXTL, and hydrogen atoms were treated as idealized contributions. The absorption coefficient was 7.192 mm^{-1}. The least-squares refinement converged normally with residuals of R1 = 0.0540 ($I > 2\sigma(I)$), wR2 = 0.1356, and GOF = 1.027 (F^2); $C_{27}H_{32}U$ (594.56 g/mol), space group $P2_1/n$, monoclinic a = 8.099(3) Å, b = 19.261(6) Å, c = 14.495(5) Å, β = 92.016(5)°, V = 2259.7(12) Å^3, Z = 4, F(000) = 1144, ρ_{calcd} = 1.748 g cm^{-3}. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.[25]

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Supporting Information Available: X-ray crystallographic information for **3** and **4** (PDF and CIF). The material is available free of charge via the Internet at http://pubs.acs.org.

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