Structure of Uranium(V) Methyl and Uranium(VI) Ylide Complexes

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ABSTRACT: Synthesis of rare examples of U(V) methyl and U(IV) ylide complexes are reported. Reaction of the previously reported U(IV) imido complex, $[(C_5Me_5)_2U(py)(=NMes)]$, py = pyridine, Mes = 2,4,6-$Me_3C_6H_2$, with CuI forms the U(V), $[(C_5Me_5)_2U(I)(=NMes)]$. Reaction of the iodo complex with $MgMe_2$ produces the methyl complex, $[(C_5Me_5)_2U(CH_3)(=NMes)]$. The methyl complex was reacted with CH_2PPh_3, surprisingly forming $[(C_5Me_5)_2U(CH_2PPh_3)(=NMes)]$, a U(IV) ylide. These complexes were characterized using spectroscopic methods (NMR, IR, UV-vis-nIR), SQUID magnetometry, X-ray crystallography, and DFT calculations are used to compare the U(V) methyl with the hopeful U(V) carbene ligands.

INTRODUCTION

Actinide-ligand multiple bonds can elucidate the role of the valence orbitals in the structure, bonding, and reactivity of the actinides.[1] While first synthesized over 40 years ago,[2] few actinide-carbon multiple bonds have been reported,[3-12] and most involve the tetravalent oxidation state. All actinide-carbenoid complexes have a U-C bond which is stabilized by a heteroatom,[13-15] typically phosphorus, yielding phosphorano-stabilized carbenes or methandiides.[16-17] Only recently has the Hayton group used an allenylidene ligand to produce short An-C multiple bonds, but the major resonance form was primarily An-C single bond character.[18] Our interest is examining the structure and bonding of actinide complexes with phosphorano-stabilized carbene ligands in higher oxidation states. However, there exists a dearth of starting materials to form high-valent uranium phosphorano-stabilized carbenes.

The Kiplinger group has used uranium(IV) metallocene imido ligand frameworks to make major advances in U(V) chemistry.[19-23] In their pioneering work, they used the previously reported 2,6-$^tBu_2C_6H_3$ and 2,6-$^iPr_2C_6H_3$ substituted imido complexes[24-25] to form U(V) complexes through oxidation of the U(IV) precursor with copper(I) salts. The corresponding halides can be converted from the U(V) iodide, $[(C_5Me_5)_2U(I)\{=N(2,6-^iPr_2C_6H_3)\}]$, to a rare U(V) alkyl, $[(C_5Me_5)_2U(CH_3)\{=N(2,6-^iPr_2C_6H_3)\}]$,[21] using an organomagnesium reagent. We viewed this U(V) alkyl as an excellent starting material to making a phosphorano-stabilized carbene through reaction with an ylide, $CH_2=PPh_3$. To ensure enough space in the equatorial plane for the carbene, we used the known 2,4,6-$Me_3C_6H_2$ (Mes) imido derivative, $[(C_5Me_5)_2U(py)(=NMes)]$[25] and, herein, report the characterization of new U(V) complexes,

$[(C_5Me_5)_2U(X)(=NMes)]$, X = I, Me. However, when the methyl compound is treated with $H_2C=PPh_3$, the surprising result is a U(IV) ylide complex, $[(C_5Me_5)_2U(CH_2PPh_3)(=NMes)]$, and not the U(V) phosphorano stabilized carbene.

RESULTS AND DISCUSSION

Synthesis. In the dark, to a stirring green solution of $[(C_5Me_5)_2U(py)(=NMes)]$ dissolved in toluene at room temperature, five equivalents of CuI were added to produce a black solution. The resulting complex, $[(C_5Me_5)_2U(I)(=NMes)]$, **1**, was obtained as a black microcrystalline solid in 96% yield, eq 1. Complex **1** was
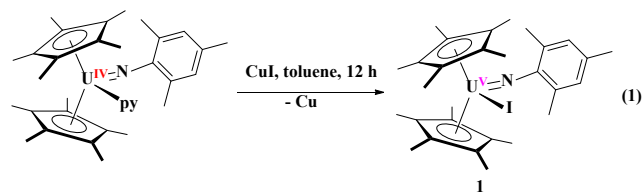

treated with $[MgMe_2(THF)_2]$ at room temperature to make the U(V) methyl complex, $[(C_5Me_5)_2U(Me)(=NMes)]$, **2**. Complex **2** is obtained in 89% yield as a black microcrystalline solid but decomposes over time, especially in solution. Complex **2** was then treated with an ylide, $H_2C=PPh_3$, and a brown powder was obtained, which we believed was the phosphorano-stabilized carbene complex, $(C_5Me_5)_2U(CHPPh_3)(=NMes)$, **3a**.
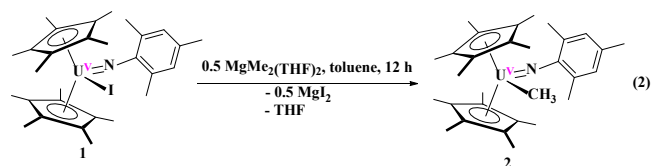
Spectroscopy. The ^{1}H NMR spectrum of **1** and **2** have $(C_5Me_5)^{1-}$ resonances at 5.29 ppm and 2.81 ppm, respectively, similar to the 5.78 ppm and 3.30 ppm observed for $[(C_5Me_5)_2U(I)\{=N(2,6\text{-}^iPr_2C_6H_3)\}]$ and $[(C_5Me_5)_2U(Me)\{=N(2,6\text{-}^iPr_2C_6H_3)\}]$, respectively. The remaining resonances, except for one at -22.1 ppm in complex **2**, which we assign to the methyl group bound to uranium, are similar in **1** and **2**. As noted by Kiplinger, the $(C_5Me_5)^{1-}$ resonance shifts upfield with a more electron-rich uranium center, which we presumed was observed here with the ^{1}H NMR spectrum of the presumed carbene having a $(C_5Me_5)^{1-}$ resonance at -1.02 ppm. We assumed that this was due to significant donation from the carbene, particularly compared to the methyl group.

The UV-Vis-nIR spectra for **1** and **2** are also nearly identical to Kiplinger's analogous compounds.

Structural Analysis. Complexes **1**, **2**, and the presumed carbene were structurally characterized using X-ray diffraction analysis with selected bond distances shown in Table 1. The structure of **1** is as expected with a short U-N bond distance of 1.989(9) Å and U-I bond distance of 3.0443(7) Å, which are nearly identical to those found in Kiplinger's analogous iodide structures, $[(C_5Me_5)_2U(I)(=NAr)]$, Ar = 2,6-$^iPr_2C_6H_3$, U-N: 1.974(7) Å, U-I: 3.0385(7) Å and Ar = 2,6-$^tBu_2C_6H_3$, U-N: 1.975(6) Å, U-I: 3.0116(6) Å. All of Kiplinger and co-workers' U(V) imido halide complexes have U=N-C(ipso) bond angles of 169.6(4)-172.2(9)°, while a near linear 178.4(7)° was found in **1**.
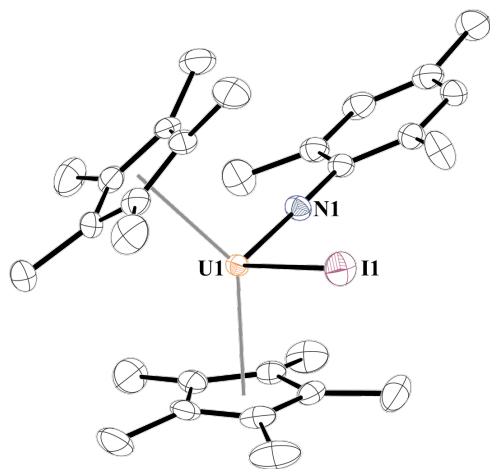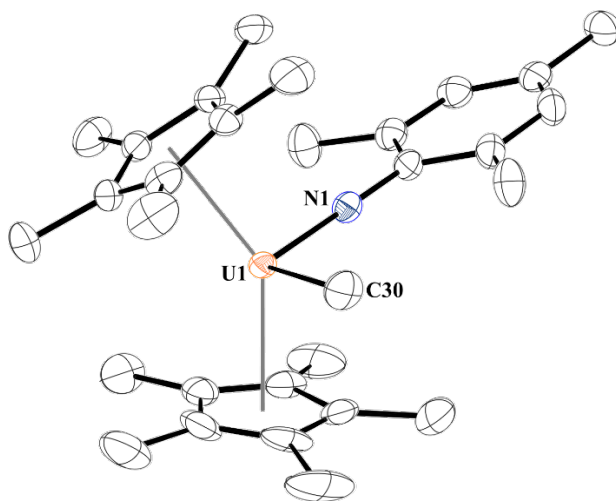

Figure 1. Thermal ellipsoid plot of **1** shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Table 1. Selected bond distances (Å) and angles (deg) in complexes **1-3**.

Compound	U-N (Å)	U-X (Å)	U=N-C(ipso) (deg)
1, X = I	1.9597(19)	3.0442(2)	178.38(17)
2, X = CH$_3$	1.972(3)	2.427(4)	177.0(2)
3, X = CH$_2$PPh$_3$	1.997(5)	2.617(5)	177.5(4)
4, X = NMes	1.986(3)	1.986(3)	172.7(2)

Uranium(V) alkyl[26] complexes are exceedingly rare[21] with the only other structurally characterized complexes being $[U(CH_2SiMe_3)_6]^{1-}$,[27] $[U(CH_2SiMe_3)_4(O^tBu)_2]^{1-}$,[27] and $[U(Me)_6]^{1-}$[28] reported by the Hayton and Neidig groups. Therefore, complex **2** is only the fourth structurally characterized U(V) alkyl complex. The U-C(methyl) distance of 2.427(4) Å in **2** is identical to the 2.429(8) Å in $[U(CH_2SiMe_3)_6]^{1-}$ and 2.42(2) Å in $[U(CH_2SiMe_3)_4(O^tBu)_2]^{1-}$ as well as the 2.415(5)-2.452(5) Å in $[U(Me)_6]^{1-}$.


Figure 2. Thermal ellipsoid plot of **2** shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.

The solid-state structure of presumed carbene complex was obtained first chronologically in our study so the long U-C bond of 2.617(5) Å was surprising. For example, the U-C bond distance in a U(VI) methandiide complex, $[U(BIPM^{Dipp})(O^tBu)_3(I)]$, $BIPM^{Dipp} = [C\{PPh_2N(2,4,6\text{-}^iPr_2C_6H_3)\}_2]^{2-}$, has a U-C bond distance of 2.449(7) Å, so we thought that a U(V) complex would have a slightly longer bond distance given that the ionic radius of U(V) is larger than U(VI). The other metric from the crystal structure was the U-C-P bond angle of 160.6(3)° which is larger than the 151.7(4)° in $[U\{N(SiMe_3)_2\}_3(CHPPh_3)]$, but less than the ~166° in $[(C_5Me_5)_2U(X)(CHPPh_3)]$, X = Cl, Br, I, complexes. Larger bond angles typically indicate more covalent bonding which we would expect in a U(V) metal center. In addition, since the hydrogen atoms could not be located by X-ray crystallography, and the ^{1}H NMR spectrum for the proton(s) bound to carbon located at -172 ppm integrated to less than 2 protons (~1.5), which for a paramagnetic metal, could be assigned to one or two

protons, we hoped that this was indeed a U(V) carbene complex. We also rationalized the long U-C bond on the basis the imido ligand would form a stronger covalent bond to the uranium center, thus affording a longer U-C bond distance. To be clear, this logic was at best dangerous and, at its core, scientifically unsound. We include this commentary as a cautionary description of how rationalization for desired results are falsified if one takes a more detailed look.

Magnetic Measurements. The magnetic susceptibility of the product of the reaction of [(C5Me5)2U(Me)(=NMes)], **2**, with H2C=PPh3 is shown in Figure 3a, and that of the reaction of [(C5Me5)2U(THF)(=NMes)] with H2C=PPh3 is shown in Figure 3b. Both reaction products display the same magnetic susceptibility and are assumed to be the same product. From 2 K to 12 K, χT is linear in T at all fields and the y intercept is 0 emu K. This behavior is consistent with a singlet ground state ($\mu_{eff} = 0$ μ_B) with an excited state ~30 cm^{-1} above the ground state. The singlet ground state with a magnetic excited state indicates that the product has a 5f^2 or 5f^4 electronic configuration of which the most likely is 5f^2. The susceptibility is not consistent with U(III), U(V), or U(VI). Above 70 K, χT is linear in T, which implies that no further excited states become thermally populated below 300 K. Therefore, the magnetic susceptibility measurement establishes that both products are the same compound and both are 5f^2 systems. Variable temperature magnetic susceptibility measurements were also done on 1 (see Supporting Information) and showed it was consistent with a 5f^1 electron configuration.
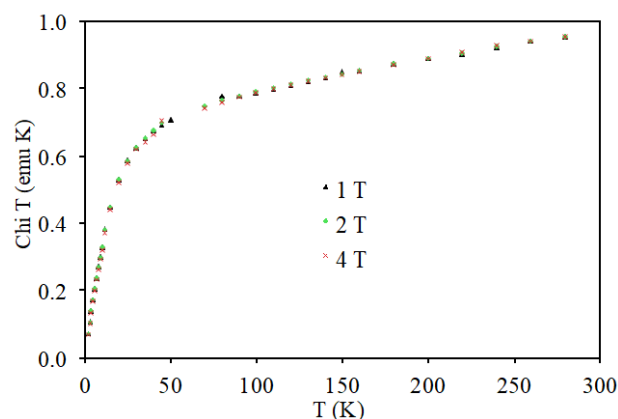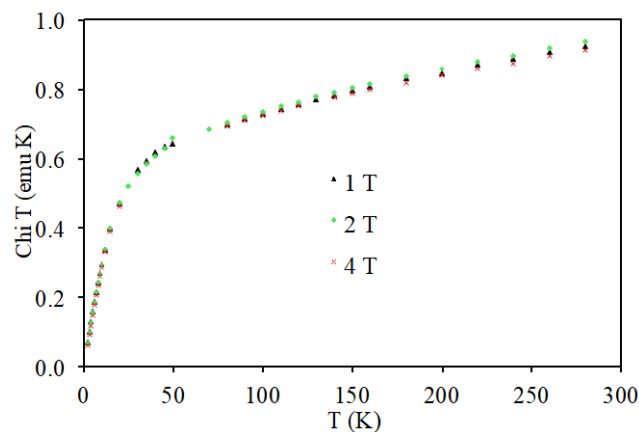
Figure 3. (a, top) Magnetic susceptibility of the product of the reaction of [(C5Me5)2U(Me)(=NMes)] with H2C=PPh3. (b, bottom) Magnetic susceptibility of the product of the reaction of [(C5Me5)2U(THF)(=NMes)] with H2C=PPh3.

Electronic Structure Calculations. The optimized geometry of the phosphorano-stabilized carbene, **3a**, showed a U-C bond distance of 2.29 Å, over 0.3 Å shorter than the one obtained from the crystal structure at 2.617(5) Å. The calculations also predicted U-C(Me) distance of 2.41 Å in **2**, which is in good agreement to the observed 2.427(4) Å. At this point, we realized that the structure obtained from reaction of **2** with CH2PPh3 was a U(IV) ylide, [(C5Me5)2U(=NMes)(CH2PPh3)], **3**, eq 3, which, while disheartening, is the first reported U(IV) ylide. The calculated U-C distance in **3** is 2.70 Å. The only other uranium ylide complex is from the Hayton group, [U{N(SiMe3)2}3(CH2PPh3)], a uranium(III) complex with a U-C bond distance of 2.686(6) Å,[3] which is expectedly longer than the U-C distance in **3** given the larger ionic radius of U(III) versus U(IV).[29] Structural and bonding properties of
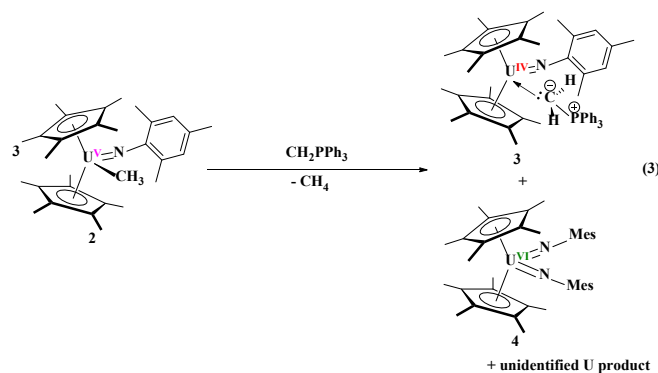
complexes **2**, **3**, and the hypothetical carbene, **3a**, were investigated. To investigate bonding, QTAIM (Quantum Theory of Atoms in Molecules) analysis was performed on the PBE0-derived electron density. Taking the difference between the uranium atomic number (Z=92) and corrected localization index (λ + 60-electrons) gave oxidation numbers of +4.95 and +5.01 for **2** and **3a** respectively, in agreement with the expected +5 formal oxidation state. A calculated oxidation state (Mulliken charge?) of +4.30 is found for **3**, consistent with the +4 formal oxidation state. Overall, simulations reveal a covalency trend. Covalency is greatest between uranium and CHPPh3 in 3a, followed by CH3 in **2** and then CH2PPh3 in **3**. This decreasing covalency trend correlates with increasing bond lengths, 2.29 Å, 2.41 Å, 2.70 Å respectively, and further correlates with decreasing DI (Delocalization Index) values, 0.91 a.u, 0.68 a.u and 0.33 a.u. High U-C covalency in **3a** is explained by a π-interaction confirmed by inspecting NBOs (figure 4), which is not present in **2** or **3**, and explains the non-zero ellipticity of 0.26 a.u typical of double bonds. Complex **2** shows a single σ-bonding NBO as expected for a U-CH3 bond and has a non-zero ρ_{BCP} value indicating an accumulation of electron density at the bond critical point. The U-C π-bonding interaction in **3a** explains the higher degree of electron sharing (DI) as compared to **2**, as well as the shorter bond length.

Complex **3** presents limited U-C covalency, confirmed by the absence of a U-C NBO and having the lowest U-C DI value. The bond also has a near-zero ρ_{BCP} value (0.04 a.u), meaning there is effectively no accumulation of electron density at the bond critical point. These findings are all indicative of limited covalency.

QTAIM metrics for U-N bonding are similar across complexes **1-3**, meaning a change in carbon ligand has little effect on U-N bonding across the complexes. U-N DI values are larger than U-C bonds in all three complexes, indicating stronger covalency in U-N bonds as compared to U-C. Complex **3a** presents a slightly lower U-N DI value which also coincides with an increased localization index on the uranium and nitrogen centers. A change in oxidation state between complex **2** and **3**, has resulted in slightly decreased U-N covalent sharing and a localization of electron density onto uranium and nitrogen as compared with **2** and **3a**. Though this does not drastically affect the bond length which remains comparable to that of **2** and **3a**. NBOs reveal U-N bonding consists of two perpendicular π-bonding interactions which would satisfy the cylindrical electron density expected from the near-zero ellipticity values reported.

Mechanistic Details. We began investigating this reaction in more detail as the crude NMR spectrum shows the formation of multiple products. The reaction was done in a J. Young NMR tube in C_6D_6 and monitored by ^{1}H NMR spectroscopy. Methane, CH_4, is observed in the spectrum indicating that the ylide is indeed being deprotonated by the methyl attached to the metal center. No growth of $C(H)(D)=PPh_3$ was observed, indicating the U(V) carbene does not deprotonate the deuterated benzene to form the ylide with concomitant reduction. To assess whether a radical reaction maybe occurring, the reaction of TEMPO with **2** was attempted, but yielded no reaction. Hence, this is complicated reaction. One striking feature of the ^{1}H NMR spectrum was a sharp resonance at 4.51 ppm. Coincidentally, our group has also been examining the electrochemistry of uranium(VI) bis(imido) complexes[30] whose $(C_5Me_5)^{1-}$ resonances are located between 4-5 ppm.[31-32] Indeed, the remaining resonances of $(C_5Me_5)_2U(=NMes)_2$, **4**, were also identified, specifically resonances at 6.86, 7.96, and 8.50 ppm for each methyl group as well as 8.96 and 9.40 ppm for the *meta*-phenyl hydrogens. Complex **4** can also be independently synthesized in good yield from the reaction of $[(C_5Me_5)_2UCl_2]$ with $MesN_3$ in the presence of excess potassium graphite. Therefore, the reaction of $[(C_5Me_5)_2U(=NMes)(CH_3)]$, **2**, with $H_2C=PPh_3$ involves the disproportionation of U(V) to form the U(IV) ylide, **3**, and a U(VI) bis(imido), **4**. Still, another paramagnetic product has not been identified or isolated yet as observed in the ^{1}H NMR spectrum, and the stoichiometry of eq 3 is not accurate.

CONCLUSION

In summary, we have used a U(IV) framework established by Burns, $[(C_5Me_5)_2U(=NMes)(py)]$, to form the U(V) complex, $[(C_5Me_5)_2U(=NMes)(I)]$, in a similar manner to Kiplinger. This complex was used to isolate only the second U(V) methyl complex, $[(C_5Me_5)_2U(=NMes)(CH_3)]$, and only the fourth U(V)-$C(sp^3)$ bond. However, upon reaction of the U(V) methyl complex with $H_2C=PPh_3$, a U(IV) ylide compound was formed instead of the U(V) carbene. While not the desired U(V) carbene, it is the first U(IV) ylide and only the second actinide ylide complex reported.

EXPERIMENTAL

General considerations. All manipulations were performed under an inert atmosphere of N_2 using standard glovebox and Schlenk line techniques. All solvents were dried over activated molecular sieves and alumina column in solvent purification system by MBRAUN, USA. $[(C_5Me_5)_2U(=N-2,4,6-Me_3C_6H_2)(py)]$,[25] $[Mg(CH_3)_2(THF)_2]$,[33] and CH_2PPh_3[3] were prepared according to literature procedures. Copper(I) iodide (Aldrich) was used as received. NMR experiments were performed on either a 300 MHz Bruker AvII, a 500 MHz, or a 600 MHz Bruker Advance spectrometer. [1]H chemical shifts are reported in ppm referenced internally to solvent impurities.[34] [31]P chemical shifts are reported in ppm referenced externally to 85% H_3PO_4 at 0 ppm. Deuterated benzene (Cambridge Isotope) was dried over 4Å molecular sieves and degassed through 3 cycles of freeze-pump-thaw. IR spectra were collected on a Nicolet Summit Pro FT-IR spectrometer prepared as KBr pellets. Elemental analyses were performed on a Carlo Erba 1108 elemental analyzer, outfitted with an A to D converter for analysis using Eager Xperience software.

Caution! Depleted uranium (primarily U-238) is an α emitting radiometal with a half-life of 4.47×10^9 years. All work was performed in a radiological laboratory with appropriate personal protective and counting equipment.

Synthesis of $(C_5Me_5)_2U(=N-2,4,6-Me_3C_6H_2)(I)$, 1. Complex **1** was synthesized from a modified procedure.[19] A 20 mL scintillation vial was charged with $(C_5Me_5)_2U(=N-2,4,6-Me_3C_6H_2)(py)$ (443 mg, 0.61 mmol), toluene (*ca.* 10 mL), and a stir bar. To this stirring solution, a slurry of copper (I) iodide (580 mg, 3.04 mmol) in toluene (*ca.* 5 mL) was added at room temperature and allowed to stir overnight. The resulting solution was filtered through Celite and dried *in vacuo*. The residue was then extracted with pentane (*ca.* 3 x 50 mL) and filtered through Celite padded medium porous frit. Removal of solvent yielded a black microcrystalline solid (455 mg, 96%). ^{1}H NMR (600 MHz, C_6D_6): δ 5.29 (s, 30H, C_5Me_5), 15.1 (s, 3H, $Me_3C_6H_2$), 25.0 (s, 1H, $Me_3C_6H_2$), 30.5 (s, 1H, $Me_3C_6H_2$), 32.9 (s, 3H, $Me_3C_6H_2$), 45.5 (s, 3H, $Me_3C_6H_2$). IR (KBr, cm^{-1}): 2966 (m), 2903 (m), 2855 (m), 1469 (w), 1457 (m), 1433 (m), 1420 (m), 1384 (s), 1247 (w), 1236 (m), 1142 (w), 1095 (vs), 1021 (w), 957 (w), 884 (w), 855 (m), 804 (w). Anal. Calcd for $C_{29}H_{41}UNI$: C, 45.32; H, 5.38; N, 1.82. Found: C, 45.38; H, 5.66; N, 1.98.

Synthesis of $(C_5Me_5)_2U(=N-2,4,6-Me_3C_6H_2)(Me)$, 2. Complex **2** was synthesized from a modified procedure.[21] A 20 mL scintillation vial was charged with **1** (433 mg, 0.56 mmol), toluene (*ca.* 10 mL), and a stir bar. To this stirring solution, $Mg(CH_3)_2(THF)_2$ (112 mg, 0.56 mmol) in toluene (*ca.* 5 mL) was added at room temperature, followed by 1,4-dioxane (*ca.* 0.5 mL), and allowed to stir overnight. The resulting solution was filtered through Celite and dried *in vacuo*. The residue was then extracted with pentane (*ca.* 3 x 50 mL) and filtered through Celite padded medium porous frit. Removal of solvent yielded

a black microcrystalline solid (330 mg, 89%). ^{1}H NMR (600 MHz, C_6D_6): δ -22.1 (s, 3H, U-CH_3), 2.81 (s, 30H, C_5Me_5), 3.97 (s, 3H, $Me_3C_6H_2$), 20.3 (s, 1H, $Me_3C_6H_2$), 28.6 (s, 4H, $Me_3C_6H_2$ and $Me_3C_6H_2$), 50.3 (s, 3H, $Me_3C_6H_2$). IR (KBr, cm^{-1}): 2967 (m), 2906 (m), 2857 (m), 1438 (w), 1384 (m), 1243 (w), 1145 (w), 1021 (vs), 853 (w), 800 (w). Anal. Calcd for $C_{30}H_{44}U_1N_1$: C, 54.87; H, 6.75; N, 2.13. Found: C, 55.07; H, 6.90; N, 1.98.

Synthesis of $(C_5Me_5)_2U(=N-2,4,6-Me_3C_6H_2)(CH_2PPh_3)$, 3. Method A: A 100 mL Schlenk bomb flask was charged with $(C_5Me_5)_2U(=N-2,4,6-Me_3C_6H_2)(Me)$ (286 mg, 0.43 mmol), $CH_2=PPh_3$ (120 mg, 0.43 mmol), toluene (*ca.* 20 mL), and a stir bar. The flask was sealed with Teflon valve and heated to 60 °C in an oil bath for 24 hours. The resulting solution was concentrated, filtered through Celite, and placed in the freezer (-15 °C) for several days. The product crystallized out in batches as black crystals (200 mg, 50%). **Method B:** A 20 mL scintillation vial was charged with $(C_5Me_5)_2U(=N-2,4,6-Me_3C_6H_2)(py)$ (202 mg, 0.28 mmol), toluene (*ca.* 10 mL), and a stir bar. To this stirring solution, $CH_2=PPh_3$ (78 mg, 0.28 mmol) in toluene was added at room temperature and stirred for 2 hours. Removal of solvent yielded the product as a black microcrystalline solid in quantitative yield. X-ray quality crystals were grown from a concentrated toluene solution at -15 °C. ^{1}H NMR (500 MHz, C_6D_6): δ -172.3 (s, 2H, CH_2PPh_3), -7.25 (s, 6H, CHPPh_3), -1.02 (s, 30H, C_5Me_5), 4.02 (s, 3H, CHPPh_3), 4.09 (s, 6H, CHPPh_3), 7.48 (s, 3H, $Me_3C_6H_2$), 30.4 (s, 3H, $Me_3C_6H_2$), 37.8 (s, 1H, $Me_3C_6H_2$), 46.0 (s, 1H, $Me_3C_6H_2$), 56.7 (s, 3H, $Me_3C_6H_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ -100.5. IR (KBr, cm^{-1}): 2962 (m), 2902 (m), 2852 (m), 1491 (w), 1438 (s), 1406 (w), 1384 (m), 1294 (m), 1264 (m), 1163 (w), 1131 (w), 1114 (vs), 997 (w), 885 (m), 822 (w), 745 (m), 701 (w), 693 (m). Anal. Calcd for $C_{48}H_{58}U_1N_1P_2$: C, 62.87; H, 6.27; N, 1.53. Found: C, 63.16; H, 6.40; N, 1.87.

Synthesis of $[(C_5Me_5)_2U(=NMes)_2]$, 4.

Crystal Structure Refinement: Single crystal XRD data for **1**, **3**, and **4** were collected on a Bruker D8 Venture diffractometer equipped with a Photon II CMOS area detector or Photon 100 CMOS area detector (Bruker AXS, Madison, WI) using Mo-Kα radiation from a microfocus source. Data for **2** was collected on a Bruker X8 Prospector diffractometer equipped with an Apex II CCD area detector (Bruker AXS, Madison, WI, USA) using Cu-Kα radiation from a microfocus source. Crystals were cooled to the collection temperatures under streams of cold N$_2$ using Oxford Cryostream 700 and Cryostream 800 cryostats (Oxford Cryosystems, Oxford, UK). Hemispheres of unique data were collected using strategies of scans about the omega and phi axes with 0.5° frame widths. Unit cell determination, data collection, data reduction, absorption correction and scaling, and space group determination were performed using the Apex3 software suite (Bruker AXS)[35]. Structures were solved using either direct methods as implemented in SHELXS[36] or an iterative dual space approach as implemented in SHELXT[37]. Structures were refined by full-matrix least squares refinement against F^2 using SHELX with anisotropic thermal displacement parameters on all full-occupancy non-hydrogen atoms.[38] In **2** a cyclopentadienyl ligand was found to be disordered over two positions related by rotation about the metal-centroid axis; the occupancies were fixed at 75% and 25% with the minor conformer refined isotropically. Hydrogen atoms for the coordinating P-CH$_2^-$ group in **3** were modeled by refining difference map peaks in chemically realistic positions with distance restraints.

All other hydrogen atoms were placed in calculated positions with their coordinates and thermal parameters constrained to ride on the carrier atoms. Olex2 was used as a graphical interface for model building and refinement programs[39].

Computational Details. Complexes **2**, **3**, and **3a** were optimized from the basis of an XRD-derived complex. TURBOMOLE V6.6[40] was utilized for geometry optimizations at the DFT level, implementing the PBE0 hybrid GGA exchange-correlation functional[41-42] paired with Aldrichs def2-TZVP basis set for light elements (H,C,N,P).[43] For uranium, the basis set of def-TZVP and associated 60-electron effective core potential was utilized.[43-44] This model chemistry has successfully been implemented in previous studies on f-element complexes.[45-47] Convergence of local energetic minima with C1 symmetry was confirmed by vibrational frequency analysis. Optimized uranium(V) structures were confirmed to be doublet multiplicity, with electronic structures having spin-squared expectation values of 0.805 and 0.822 for **1** and **2** respectively. Given an open-shell treatment, a degree of spin-contamination is to be expected, with these values being sufficiently close to the 0.75 value for a pure doublet. Complex **3** was confirmed to have triplet multiplicity with spin-squared expectation value of 2.027. Bonding was investigated using quantum theory of atoms in molecules (QTAIM) analysis[48] using the AIMALL V19.02.13 software suite[49] as well as orbital analysis using version 6.0.13 of the NBO6 program.[50]

ASSOCIATED CONTENT

Supporting Information

Spectra, further computational and magnetic measurement details and results. Crystal structure data is available from the Cambridge Crystallographic Data Center (CCDC nos. 2235221-2235224).

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