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Carbon–Carbon Reductive Elimination from Homoleptic Uranium(IV) Alkyls Induced by Redox-Active Ligands

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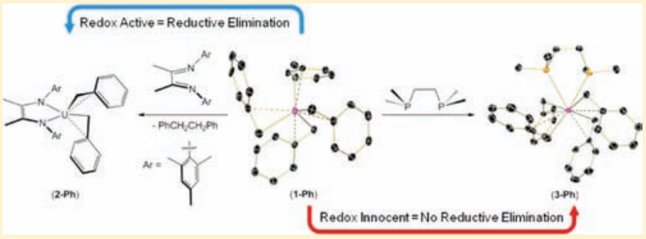
S Supporting Information



ABSTRACT: The synthesis, characterization, and reactivity of the homoleptic uranium(IV) alkyls $U(CH_2C_6H_5)_4$ (**1-Ph**), $U(CH_2\text{-}p\text{-}CH_3C_6H_4)_4$ (**1-*p*-Me**), and $U(CH_2\text{-}m\text{-}(CH_3)_2C_6H_3)_4$ (**1-*m*-Me$_2$**) are reported. The addition of 4 equiv of $K(CH_2Ar)$ (Ar = Ph, $p\text{-}CH_3C_6H_4$, $m\text{-}(CH_3)_2C_6H_3$) to UCl_4 at −108 °C produces **1-Ph** in good yields and **1-*p*-Me** and **1-*m*-Me$_2$** in moderate yields. Further characterization of **1-Ph** by X-ray crystallography confirmed η^4-coordination of each benzyl ligand to the uranium center. Magnetic studies produced an effective magnetic moment of 2.60 μ_B at 23 °C, which is consistent with a tetravalent uranium $5f^2$ electronic configuration. Addition of 1 equiv of the redox-active α-diimine $^{Mes}DAB^{Me}$ ($^{Mes}DAB^{Me}$ = [ArN═C(Me)C(Me)═NAr]; Ar = 2,4,6-trimethylphenyl (Mes)) to **1-Ph** results in reductive elimination of 1 equiv of bibenzyl ($PhCH_2CH_2Ph$), affording $(^{Mes}DAB^{Me})U(CH_2C_6H_5)_2$ (**2-Ph**). Treating an equimolar mixture of **1-Ph** and **1-Ph-*d*$_{28}$** with $^{Mes}DAB^{Me}$ forms the products from monomolecular reductive elimination, **2-Ph**, **2-Ph-*d*$_{14}$**, bibenzyl, and bibenzyl-d_{14}. This is confirmed by ^1H NMR spectroscopy and GC/MS analysis of both organometallic and organic products. Addition of 1 equiv of 1,2-bis(dimethylphosphino)ethane (dmpe) to **1-Ph** results in formation of the previously synthesized $(dmpe)U(CH_2C_6H_5)_4$ (**3-Ph**), indicating the redox-innocent chelating phosphine stabilizes the uranium center in **3-Ph** and prevents reductive elimination of bibenzyl. Full characterization for **3-Ph**, including X-ray crystallography, is reported.

■ INTRODUCTION

In comparison to transition metal alkyls, which have been extensively explored, the synthesis and reactivity of uranium alkyls has not enjoyed such thorough studies. The first series of stable, well-defined σ-bonded organometallics of actinides, Cp_3UR (R = alkyl, aryl, vinyl), was reported by Marks in 1972.[1] Although these compounds decompose via radical pathways, they demonstrate that alkyls can be installed on uranium with common alkylating agents and are stable.[1] Building on this work was the isolation of $Cp^*_2U(CH_3)_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienide), which has been thoroughly studied to test the reactivity of small molecules with uranium–carbon σ-bonds.[2−7] These significant developments in organouranium chemistry have been bolstered by the use of other ligand frameworks, which has facilitated isolation of numerous uranium(IV) alkyl species.[8−18]

Stabilization of homoleptic alkyl species is much more difficult as there is no ancillary ligand present to provide a coordinatively saturated uranium center. Multiple experiments in pursuit of neutral homoleptic uranium(IV) alkyl species have been attempted by treating UCl_4 with 4 equiv of LiR (R = Me, $CH_2{}^tBu$, ^nBu, ^tBu, ^iPr) at low temperatures.[19,20] The desired salt metathesis occurs; however, upon warming, the UR_4 species decompose, resulting in organics formed from β-hydride and C−H reductive elimination pathways, along with uranium metal.[19,20] In subsequent studies, UCl_4 was treated with 4 equiv of LiR (R = ^nBu, ^tBu) followed by stirring for 5−6 days; this did not form the desired tetravalent uranium alkyls but instead served to reduce the uranium center, producing a trivalent uranium hydride.[21] Recently, the homoleptic hexavalent uranium alkyl $U(CH_2SiMe_3)_6$ was synthesized, but is only stable below −25 °C.[22] Although no neutral homoleptic uranium(IV) or -(VI) alkyl species have been crystallographically characterized, in 1989 the first uranium(III) example, $U[CH(SiMe_3)_2]_3$, was reported by Sattelberger and co-workers.[23] Successful synthesis was achieved by the reaction of trivalent $U(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3$ with 3 equiv of $LiCH(SiMe_3)_2$.[23] The stability of $U[CH(SiMe_3)_2]_3$ at ambient temperature is attributed to the steric bulk of the bis(trimethylsilyl)methyl ligands and lack of β hydrogens.

Generation of isolable homoleptic uranium(IV) alkyls has been achieved by the formation of "ate" complexes. Wilkinson first reported that treating UCl_4 with excess LiR produces the tetravalent uranate compounds $[Li(solvent)_4]_2[UR_6]$ (solvent = THF, Et_2O; R = Me, C_6H_5, CH_2SiMe_3) and in the presence of TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), $Li_2UR_6\cdot 7TMEDA$.[24] More recently, Hayton and co-workers have reported a similar series of complexes, including $[Li(DME)_3][U(CH_2SiMe_3)_5]$, $[Li(THF)_4][U(CH_2{}^tBu)_5]$, $[Li(TMEDA)]_2[UMe_6]$, and $\{[K(THF)]_3[K(THF)_2][U(CH_2C_6H_5)_6]_2\}_x$.[25] With the exception of [Li-

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(TMEDA)]$_2$[UMe$_6$], the resulting complexes are thermally stable, presumably due to ionic pair stabilization and steric saturation of the uranium center, making crystallographic characterization of these species possible. Higher valent analogues made by alkylation of $U_2(OEt)_{10}$ with LiR (R = Me, CH_2CMe_3, CH_2SiMe_3) include thermally unstable uranium(V) octa(alkyl) complexes of the type [Li(dioxane)]$_3$[UR$_8$].[24] Successful synthesis of stable pentavalent [Li(THF)$_4$][U(CH$_2$SiMe$_3$)$_6$] was achieved by oxidation of [Li(DME)$_3$][U(CH$_2$SiMe$_3$)$_5$] with 0.5 equiv of I_2, followed by addition of $LiCH_2SiMe_3$.[22]

Organometallics with more than one alkyl group are attractive for chemical transformations that involve reductive elimination, and these species are commonly made from second and third row transition metals. These metals have suitable redox potentials to effectively perform this two-electron process while generating stable, reduced products.[26] In contrast, lanthanides and actinides typically undergo one-electron chemistry, such as M−C homolytic cleavage, preventing their use for reductive elimination processes that require multielectron transfer. Several examples of reductive elimination in uranium systems have been reported; however, this type of two-electron process has not been extensively studied for this element. Seyam observes C−C reductive elimination from hexavalent $UO_2(C_6H_5)_2$, resulting in formation of biphenyl.[27] However, alkyl analogues of the type UO_2R_2 (R = CH_3, vinyl, ^{n}Bu, ^{t}Bu, ^{i}Pr) decompose by β-hydrogen/C−H reductive eliminations or through H abstraction by alkyl radicals. More recently, the uranium(IV) dihydride dimer [Cp*$_2$UH$_2$]$_2$ and the uranium(IV) "tuck-in, tuck-over" complex Cp*U[μ-η^5:η^1:η^1-C$_5$Me$_3$(CH$_2$)$_2$](μ-H)$_2$UCp*$_2$ have been demonstrated to undergo H−H and C−H reductive eliminations, respectively, making them masked forms of the low-valent [Cp*$_2$U] fragment.[28] This reactive intermediate performs multielectron reductions of organic substrates.[28]

Because reductive eliminations involve a two-electron redox change, the electron-rich products can be unstable. Redox-active ligands are attractive for stabilizing such reactive fragments through the use of energetically low-lying π^* orbitals for electron storage, thereby increasing the metal oxidation state and preventing unwanted side reactions.[29] These ligands are distinguished from π acids such as carbon monoxide, as they can accept discrete numbers of electrons from a metal center, and these reducing equivalents can be accessed later for further chemistry. α-Diimines are effective as they can house up to two electrons per metal center, generating the dianionic ene-diamide framework.[30] These ligands have been extensively studied on main group,[31−33] transition,[34−38] and lanthanide[39,40] metals. Only recently have they been explored for actinides. Kiplinger and co-workers reported the use of the related dpp-BIAN (dpp-BIAN = 1,2-bis(2,6-diisopropylphenylimino)-acenaphthylene) systems on uranium, and have established that these ligands can be reduced by either one or two electrons by the uranium center.[41]

Recently, we reported reduced uranium species supported by the α-diimine, ^{Mes}DAB^{Me} {^{Mes}DAB^{Me} = [ArN=C(Me)C(Me)=NAr]}, where Ar = 2,4,6-trimethylphenyl (Mes). In the complexes (^{Mes}DAB^{Me})$_2$U(THF) and Cp$_2$U(^{Mes}DAB^{Me}), the α-diimine ligands are reduced by two electrons, making the ene-diamide resonance form the major contributor.[42] This was confirmed by X-ray crystallography, and studies using electronic absorption and X-ray absorption spectroscopies support tetravalent uranium centers in both compounds.[42]

Encouraged by the ability of reduced α-diimine ligands to support uranium(IV) centers, these ligands were examined for their ability to induce carbon−carbon reductive elimination at uranium and effectively support organouranium products. Herein, we report the synthesis and structural characterization of the thermally stable homoleptic uranium(IV) alkyl, U(CH$_2$Ph)$_4$, along with several of its derivatives. Studies which explore the ability of these species to undergo carbon−carbon reductive elimination in the presence of the redox-active ^{Mes}DAB^{Me} and the redox-innocent 1,2-bis(diphenylphosphino)-ethane were also performed.

■ EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive manipulations were performed by using standard Schlenk techniques or in an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a coldwell designed for freezing samples in liquid nitrogen as well as two −35 °C freezers for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated by using literature procedures.[43] Benzene-d_6 and toluene-d_8 were purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by 3 freeze−pump−thaw cycles. Potassium *tert*-butoxide, *n*-butyllithium, and 1,2-bis(dimethylphosphinoethane) were purchased from Sigma Aldrich and used with no further purification. *p*-Xylene and mesitylene were purchased from Sigma Aldrich, dried over CaH_2, and distilled. U_3O_8 was purchased from IBI Chemicals in Boca Raton, FL and used as received. UCl_4,[15] K(CH$_2$C$_6$H$_5$),[44] KCH$_2$-*p*-CH$_3$C$_6$H$_4$,[45] K(CD$_2$C$_6$D$_5$),[46] and ^{Mes}DAB^{Me} [47] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. All chemical shifts are reported relative to the peak for SiMe$_4$, using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. The spectra for paramagnetic molecules were obtained by using an acquisition time of 0.5, thus the peak widths reported have an error of ±2 Hz. For paramagnetic molecules, the ^{1}H NMR data are reported with the chemical shift, followed by the peak width at half height in hertz, the integration value, and where possible, the peak assignment. Solid state magnetic moments were recorded on a Johnson Matthey magnetic susceptibility balance at 23 °C. Publishable elemental analyses could not be obtained on **1-Ph**, **2-Ph**, **3-Ph**, **1-*p*-Me**, and **1-*m*-Me$_2$** due to the highly reactive nature of these species which did not survive shipping or delivery.

Single crystals for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of either a Rigaku Rapid II image plate diffractometer equipped with a MicroMax002+ high intensity copper X-ray source with confocal optics (compound **1-Ph**), or a Nonius KappaCCD diffractometer with a molybdenum source equipped with a graphite crystal, incident beam monochromator (compound **3-Ph**). Preliminary examination and data collection were performed with either Cu Kα radiation (λ = 1.54184 Å) (**1-Ph**) or Mo Kα radiation (λ = 0.71073 Å) (**3-Ph**). Cell constants for data collection were obtained from least-squares refinement. The space group was identified with use of the program XPREP.[48] The structures were solved by using the structure solution program PATTY in DIRDIFF99.[49] Refinement was performed on a LINUX PC, using SHELX-97.[48] The data were collected at a temperature of 150(1) K.

The capillary gas chromatography/mass spectrometry analyses were carried out with an Agilent 5975C (Agilent Laboratories, Santa Clara, CA) mass spectrometer system. Typical electron energy was 70 eV with the ion source temperature maintained at 250 °C. The individual components were separated by using a 30 m HP-5 capillary column (250 μm i.d. × 0.25 μm film thickness). The initial column temperature was set at 35 °C (for 3 min) and programmed to reach 280 °C with a ramp of 10.0 deg/min. The flow rate was set at 1 mL/min and the injector was set at 250 °C.

Synthesis of KCH_2-*m*-$(CH_3)_2C_6H_3$. The procedure for *m*-dimethylbenzyl potassium was previously reported.[50] ^1H NMR (C_4D_8O, 25 °C) δ 1.63 (s, 2H, CH_2), 2.19 (s, 6H, CH_3), 5.23 (s, 1H, *p*-Ph-CH), 6.69 (s, 2H, *o*-Ph-CH).

Synthesis of $U(CH_2C_6H_5)_4$ (1-Ph). A 20 mL scintillation vial was charged with 0.122 g (0.321 mmol) of UCl_4, and 2 mL of THF, then frozen in the coldwell. A second 20 mL scintillation vial was charged with 0.168 g (1.29 mmol) of $KCH_2C_6H_5$ and 10 mL of THF and frozen in the same manner. Both vials were removed from the coldwell and combined upon thawing while stirring. The THF was *immediately* removed in vacuo. Upon addition of the red-orange $KCH_2C_6H_5$ solution, the UCl_4 solution changed from green to dark red. The residue was taken up in diethyl ether and filtered over Celite. The Celite pad was washed with diethyl ether until the washings ran clear (about 30−40 mL). Removal of solvent in vacuo afforded dark red powder (0.149 g, 0.247 mmol, 77%) assigned as $U(CH_2C_6H_5)_4$ (**1-Ph**). Single, X-ray quality crystals were grown in a concentrated solution of ether at −35 °C. ^1H NMR (C_6D_6, 25 °C) δ −30.41 (37, 8H, CH_2), −13.99 (19, 8H, *o*-Ph-CH), 0.39 (t, 6 Hz, 4H, *p*-Ph-CH), 9.48 (17, 8H, *m*-Ph-CH). μ_{eff} = 2.60 μ_B (23 °C).

Synthesis of $U(CH_2$-*p*-$CH_3C_6H_4)_4$ (1-*p*-Me). A 20 mL scintillation vial was charged with 0.172 g (0.452 mmol) of UCl_4 and 2 mL of THF, then frozen in the coldwell. A second 20 mL scintillation vial was charged with 0.263 g (1.81 mmol) of KCH_2-*p*-$CH_3C_6H_4$ and 10 mL of THF and frozen in the same manner. Both vials were removed from the coldwell and combined upon thawing while stirring. Upon addition of the red KCH_2-*p*-$CH_3C_6H_4$ solution, the UCl_4 solution changed from green to dark brown. The THF was immediately removed in vacuo. The residue was taken up in diethyl ether and filtered over Celite. Removal of solvent in vacuo afforded a dark brown oil. Subsequent washings with pentane afford a brown solid (0.118 g, 0.179 mmol, 40%) assigned as $U(CH_2$-*p*-$CH_3C_6H_4)_4$ (**1-p-Me**). ^1H NMR (C_6D_6, 25 °C) δ −30.42 (35, 8H, CH_2), −14.03 (18, 8H, *o*-Ph-CH), 9.26 (11, 8H, *m*-Ph-CH), 9.64 (2, 12H, *p*-CH_3).

Synthesis of $U(CH_2$-*m*-$(CH_3)_2C_6H_3)_4$ (1-*m*-Me₂). A 20 mL scintillation vial was charged with 0.150 g (0.395 mmol) of UCl_4 and 2 mL of THF, then frozen in the coldwell. A second 20 mL scintillation vial was charged with 0.251 g (1.58 mmol) of $K(CH_2$-*m*-$(CH_3)_2C_6H_3)$ and 10 mL of THF and frozen in the same manner. Both vials were removed from the coldwell and combined upon thawing while stirring. Upon addition of the bright yellow $K(CH_2$-*m*-$(CH_3)_2C_6H_3)$ solution, the UCl_4 solution changed from green to dark red. The THF was immediately removed in vacuo. The residue was taken up in diethyl ether and filtered over Celite. Removal of solvent in vacuo afforded a dark red oil. Subsequent washings with pentane afforded a red solid (0.125 g, 0.175 mmol, 44%) assigned as $U(CH_2$-*m*-$(CH_3)_2C_6H_3)_4$ (**1-*m*-Me₂**). ^1H NMR (C_6D_6, 25 °C) δ −23.74 (37, 8H, CH_2), −19.98 (13, 8H, *o*-Ph-CH), −5.23 (3, 24H, *m*-CH_3), −0.78 (4, 4H, *p*-CH_3).

Synthesis of $(^{Mes}DAB^{Me})U(CH_2C_6H_5)_2$ (2-Ph). A 20 mL scintillation vial was charged with 0.103 g (0.171 mmol) of **1-Ph** and 5 mL of diethyl ether, then frozen in the coldwell. Upon thawing 0.055 g (0.171 mmol) of $^{Mes}DAB^{Me}$ solid was added while stirring. The red solution was stirred for approximately 15 min and the color of the reaction became brighter. Removal of the solvent in vacuo, followed by filtering with pentane and drying afforded a dark red powder (0.098 g, 0.132 mmol, 74%) assigned as $(^{Mes}DAB^{Me})U(CH_2C_6H_5)_2$ (**2-Ph**). ^1H NMR (C_6D_6, 25 °C) δ −42.20 (67, 6H), −35.20 (10, 6H), −26.57 (7, 2H), −3.76 (13, 2H), −1.86 (6, 2H), 0.02 (5, 2H), 2.43 (6, 6H), 5.41 (16, 2H), 5.94 (21, 2H), 10.78 (4, 2H), 18.96 (5, 1H), 23.87 (6, 2H), 26.77 (10, 6H), 42.38 (11, 1H).

Synthesis of $Cp_2U(^{Mes}DAB^{Me})$[16] from 2-Ph. A J-Young NMR tube was charged with 0.010 g (0.013 mmol) of $(^{Mes}DAB^{Me})U(CH_2C_6H_5)_2$ and benzene-d_6. To this was added 2.2 μL (0.027 mmol) of cyclopentadiene, then the solution was shaken periodically for 15 min until the solution turned brown from red. ^1H NMR spectroscopy confirmed the formation of $Cp_2U(^{Mes}DAB^{Me})$[16] and toluene in quantitative yields.

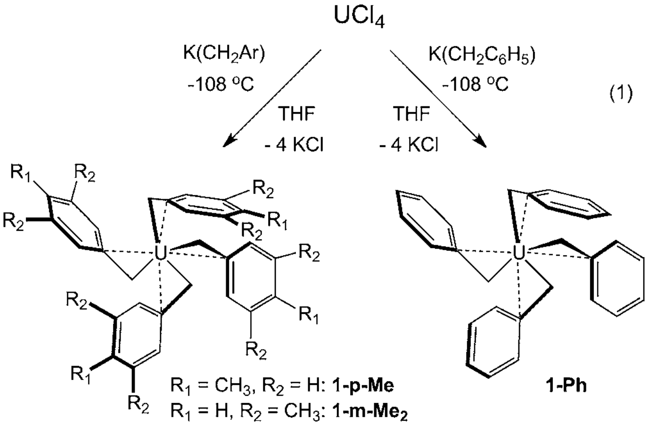
Synthesis of $U(CD_2C_6D_5)_4$ (1-Ph-d_{28}). $U(CD_2C_6D_5)_4$ was prepared in the same manner as for **1-Ph**. ^2H NMR (THF, 25 °C) δ −29.95 (8H, CH_2), −10.89 (8H, *o*-Ph-CH), 1.87 (4H, *p*-Ph-CH), 8.18 (8H, *m*-Ph-CH).

Crossover Experiment of 1-Ph and 1-Ph-d_{28}. A 20 mL scintillation vial was charged with 0.020 g (0.033 mmol) of $U(CH_2Ph)_4$, 0.022 g (0.033 mmol) of $U(CD_2C_6D_5)_4$, and 5 mL of diethyl ether. While the reaction mixture was stirred, 0.020 g (0.066 mmol) of $^{Mes}DAB^{Me}$ was weighed by difference and added as a solid. After 15 min of stirring the color of the solution turned bright red. The resulting solution was filtered through an alumina column with diethyl ether to separate the organic products (yellow) from uranium metal (black). Capillary gas chromatography/mass spectrometry analyses indicated the formation of bibenzyl (*m*/*z* 182) and bibenzyl-d_{14} (*m*/*z* 196) with no formation of bibenzyl-d_7, the crossover product.

Synthesis of $(dmpe)U(CH_2C_6H_5)_4$ (3-Ph). A 20 mL scintillation vial was charged with 0.086 g (0.143 mmol) of **1-Ph** and 10 mL of diethyl ether. While stirring, 24.0 μL (0.143 mmol) of 1,2-bis(dimethylphosphinoethane) (dmpe) was added, causing an immediate color change to bright red. Removal of the solvent in vacuo afforded a dark red powder (0.098 g, 0.130 mmol, 91%) assigned as $(dmpe)U(CH_2C_6H_5)_4$ (**3-Ph**). Single, X-ray quality crystals were grown in a concentrated solution of diethyl ether at −35 °C. ^1H NMR (C_7D_8, 25 °C) δ −15.38 (789), −0.68 (333), 1.33 (118), 2.898 (860), 7.20 (561). ^1H NMR (C_7D_8, −40 °C) δ −80.43 (849, 4H), −21.21 (161, 2H), −7.97 (26, 4H), −3.82 (30, 2H), −3.63 (30, 2H), 0.79 (20, 6H, P-CH_3), 1.25 (83, 4H), 4.35 (26, 4H), 4.80 (63, 2H), 7.44 (100, 6H, P-CH_3), 9.46 (46, 4H), 38.22 (359, 4H). μ_{eff} = 2.70 μ_B (23 °C).

■ RESULTS AND DISCUSSION

Initial experiments were aimed at the synthesis of homoleptic uranium(IV) alkyl species. Although previous studies have demonstrated the instability of these species at room temperature,[19,21] the successful formation of the uranium(III) alkyl, $Tp^*_2UCH_2Ph$,[51] indicated that benzyl ligands may serve to effectively stabilize homoleptic uranium(IV) alkyls for isolation at room temperature. Mixing thawing THF solutions of UCl_4 and 4 equiv of benzyl potassium affords a dark red solid assigned as $U(CH_2C_6H_5)_4$ (**1-Ph**) after workup in 77% yield (eq 1). Analysis of **1-Ph** by ^1H NMR spectroscopy in benzene-d_6 shows a paramagnetically shifted and broadened spectrum (Figure 1). The three singlets with integration values for 8 protons are observed at −30.41, −13.99, and 9.48 ppm and are assigned as methylene, *o*-Ph, and *m*-Ph hydrogens, respectively. A triplet assignable to the *p*-Ph hydrogens (J_{HH} = 6.0 Hz) is also observable at 0.39 ppm, integrating to an area equivalent to 4 protons. Splitting in the para resonance is visible due to its distance from the paramagnetic uranium center.



(1)

Single, X-ray quality crystals of **1-Ph** were obtained by cooling a concentrated diethyl ether solution to −35 °C. The

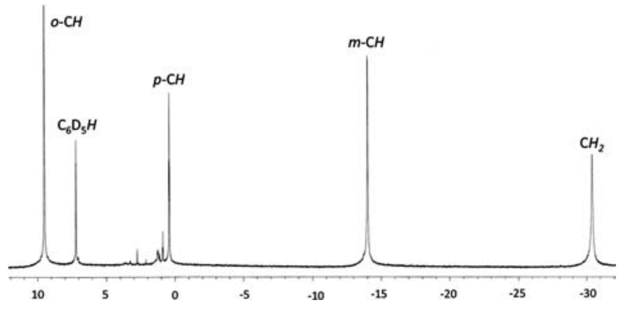


Figure 1. ^1H NMR spectrum of **1-Ph** recorded in benzene-d_6 at 23 °C.

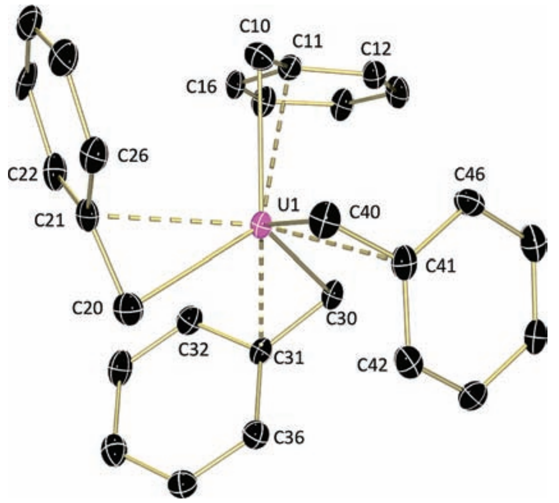


Figure 2. Molecular structure of **1-Ph** shown with 30% probability ellipsoids. Hydrogen atoms and cocrystallized solvent molecules have been omitted for clarity.

molecular structure is presented in Figure 2 (structural parameters in Table 1) and shows a pseudo-four-coordinate uranium center with four benzyl ligands. The U−C distances for the methylene carbons range from 2.446(7) to 2.462(7) Å, and are on the order of those previously reported for other uranium(IV) benzyl methylene carbon distances (2.456−2.538 Å).[5,8,12,15,17,25,52−57] These distances compare well with the U−C methylene distances in $\{[K(THF)]_3[K(THF)_2][U(CH_2C_6H_5)_6]_2\}_x$, which range from 2.50(2) to 2.57(2) Å,[25] as well as those for $U(CH(SiMe_3)_2)_3$.[23] The uranium *ipso* carbon bond lengths in **1-Ph** range from 2.700(8) to 2.839(7) Å, and are comparable to previously reported uranium(IV) benzyl species.[8,15,58] The molecular structure of **1-Ph** is significant, as previous neutral homoleptic uranium(IV) alkyls have eluded structural characterization.[19]

Two parameters to effectively determine the hapticity of benzyl substituents in actinide complexes have been defined using bond distances, Δ and Δ′, where $\Delta = [MC_o{-}CH_2] - [MC_{ipso}{-}MCH_2]$ and $\Delta' = [MC_o'{-}MCH_2] - [MC_{ipso}{-}CH_2]$.[8] MC_o is the shorter metal-to-ortho carbon contact length, MC_o' is the longer metal-to-ortho contact length, MCH_2 is the metal-to-methylene carbon bond length, and MC_{ipso} is the metal-to-ipso carbon bond length.[8] When Δ and Δ′ are comparable in magnitude, then the benzyl groups are coordinated in an η^4 fashion to the metal. A comparison of the values of Δ and Δ′ for structurally characterized published actinide benzyl complexes and **1-Ph** is presented in Table 2. Previously reported complexes by Marks,[59] Andersen,[8] and Kiplinger and Burns[15] bond in an η^4-mode according to this convention. The metrical parameters Δ and Δ′ for **1-Ph** are consistent with these literature examples, supporting η^4 coordination of all four benzyl ligands.

Table 2. Structural Parameters for Actinide Benzyl Compounds

compd	$MC_{ipso}-MCH_2$	MC_o-MCH_2	$MC_o'-MCH_2$	Δ	Δ′	ref
$Cp^*Th(CH_2Ph)_3$[a]	0.29	0.77	1.00	0.48	0.71	59
(dmpe) $Th(CH_2Ph)_4$[a]	0.35	0.78	0.39	0.43	0.58	8
(dmpe) $U(CH_2Ph)_3(Me)$[a]	0.22	0.55	0.91	0.33	0.69	8
$Cp^*U(CH_2Ph)_3$[a]	0.34	0.89	0.94	0.56	0.61	15
$U(CH_2Ph)_4$ U1−C10	0.39	0.95	0.98	0.56	0.59	this work
$U(CH_2Ph)_4$ U1−C20	0.31	0.84	0.86	0.53	0.55	this work
$U(CH_2Ph)_4$ U1−C30	0.30	0.75	0.91	0.45	0.61	this work
$U(CH_2Ph)_4$ U1−C40	0.24	0.71	0.83	0.47	0.59	this work
(dmpe) $U(CH_2Ph)_4$ U2−C220	0.68	1.30	1.40	0.62	0.72	this work
(dmpe) $U(CH_2Ph)_4$ U2−C230	0.33	0.79	1.00	0.46	0.67	this work
(dmpe) $U(CH_2Ph)_4$ U2−C240	0.77	1.33	1.61	0.56	0.84	this work
(dmpe) $U(CH_2Ph)_4$ U2−C250	0.93	1.63	1.76	0.70	0.83	this work

[a]Shortest contacts.

Table 1. Metrical Parameters for 1-Ph and 3-Ph

1-Ph						3-Ph					
bond	length (Å)	bond (U−*o*-C)	contact	angle	angle (deg)	bond	length (Å)	bond (U−*o*-C)	contact	angle	angle (deg)
U1−C10	2.446(7)	U1−C12	3.420	U1−C10−C11	89.4(4)	U2−C220	2.523(8)	U2−C222	3.921	U2−C220−C221	102.7(5)
U1−C20	2.454(8)	U1−C16	3.392			U2−C230	2.461(8)	U2−C226	3.826		
U1−C30	2.477(7)	U1−C22	3.293	U1−C20−C21	86.0(4)	U2−C240	2.460(9)	U2−C232	3.466	U2−C230−C231	87.0(5)
U1−C40	2.462(7)	U1−C26	3.316			U2−C250	2.495(8)	U2−C236	3.252		
U1−C11	2.839(7)	U1−C32	3.229	U1−C30−C31	85.7(4)	U2−C221	3.197	U2−C242	3.787	U2−C240−C241	108.3(6)
U1−C21	2.762(7)	U1−C36	3.386			U2−C231	2.790	U2−C246	4.070		
U1−C31	2.777(6)	U1−C42	3.171	U1−C40−C41	82.7(4)	U2−C241	3.233	U2−C252	4.253	U2−C250−C251	116.2(5)
U1−C41	2.700(8)	U1−C46	3.289			U2−C251	3.427	U2−C256	4.126		

Magnetic data were collected at room temperature for multiple independently synthesized samples of **1-Ph** in order to establish its behavior and support the tetravalent oxidation state. The effective magnetic moment for **1-Ph** is measured to be 2.60 μ_B, which is similar to the room temperature magnetic moments of other uranium(IV) complexes ranging from 2.5 to 3.1 μ_B.[25,41,60−62]

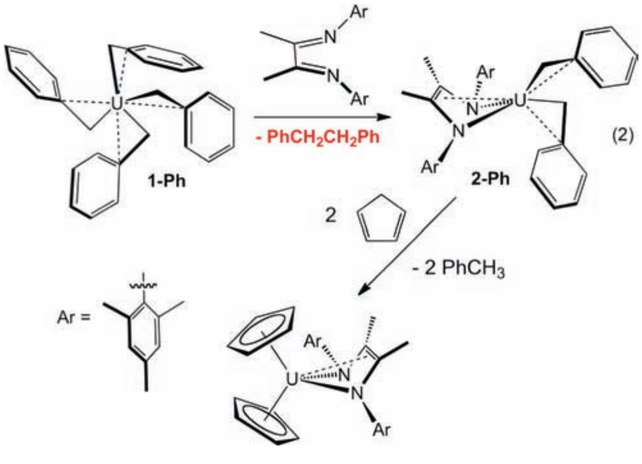
Compound **1-Ph** is stable at room temperature in solution for a short time. After 1 h, decomposition is detectable by ^{1}H NMR spectroscopy and the presence of a small amount of uranium metal on the bottom of the vial. After 5 h in benzene-d_6 solution at 22.5 °C, no $U(CH_2Ph)_4$ could be detected by ^{1}H NMR spectroscopy, only toluene and bibenzyl (85.5:14.5) were present. Performing the decomposition studies in both the light and dark showed no effect on the rate of decomposition or in the organic product distribution, indicating thermal instability. Storage of **1-Ph** is possible at −35 °C either in the solid state (1 month) or in solution (5 days). Although the formation of a small amount of bibenzyl indicates that some C−C reductive elimination occurs, the primary mode of decomposition is by homolytic scission of the U−C bond, producing toluene.

With the successful synthesis of **1-Ph**, isolation of other uranium tetrabenzyl derivatives was attempted to determine if more ring substitution influenced stability. The methyl-substituted benzyl potassium reagents KCH_2-*p*-$CH_3C_6H_4$[45] and KCH_2-*m*-$(CH_3)_2C_6H_3$[50] were prepared according to literature procedures, and ^{1}H NMR spectroscopic data for the latter are reported in the Experimental Section. In an analogous manner to **1-Ph**, two new complexes, **1-*p*-Me** and **1-*m*-Me$_2$**, were prepared by stirring 4 equiv of the respective salts and UCl_4 at −108 °C. However, upon workup, isolated yields of 40% and 44%, respectively, were obtained. The lower yield as compared to **1-Ph** is most likely due to longer workup times for isolation required as a result of the increased solubility imparted by the methyl substituents on the benzyl ligands. This thermal decomposition is noted by formation of di-*p*-methylbibenzyl and *p*-xylene for **1-*p*-Me** and 3,3′,5,5′-tetramethylbibenzyl and mesitylene for **1-*m*-Me$_2$**. The products from C−C reductive elimination are minor in the decomposition of these complexes as is the case with **1-Ph**.

Analyses by ^{1}H NMR spectroscopy in benzene-d_6 were performed on **1-*p*-Me** and **1-*m*-Me$_2$** (Figures S1 and S2, Supporting Information) and show paramagnetically shifted and broadened spectra. For **1-*p*-Me**, three singlets with integration values for 8 protons are observed at −30.41, −14.03, and 9.26 ppm and assigned as methylene, *o*-Ph, and *m*-Ph hydrogens, respectively. A singlet (12H) assignable to the *p*-CH_3 is also observable at 9.64 ppm. For **1-*m*-Me$_2$**, two singlets with integration values for 8 protons are observed at −37.49 and −19.98 ppm and are assigned as methylene and *o*-Ph hydrogens, respectively. A singlet assignable to *m*-CH_3 is observable at −5.23 ppm, integrating to an area equivalent to 24 protons. Another singlet with an integration value of 4 is observed at −0.78 and is assigned as *p*-Ph protons. Since **1-*p*-Me** and **1-*m*-Me$_2$** have similar NMR spectroscopic features to **1-Ph**, X-ray crystallographic data were not obtained.

The synthesis of $U(CH_2C_6H_5)_4$ and its methylated derivatives contributes to the family of other homoleptic tetrabenzyl organometallic compounds, including $Th(CH_2C_6H_5)_4$[63] and the group (IV) counterparts, $Zr(CH_2C_6H_5)_4$ and $Hf(CH_2C_6H_5)_4$.[64−66] Characterization of these transition metal derivatives by ^{1}H NMR spectroscopy reveals strong aromatic proton shifts indicative of interactions between the aromatic rings and the corresponding metal centers. X-ray crystallography confirms this interaction as the average metal−methylene−ipso carbon bond angles for Zr and Hf are contracted to 91° and 93°, respectively, deviating from the expected 109.5° angle for a tetrahedral carbon center.[66] Compound **1-Ph** exhibits larger distortions in metal−methylene−ipso carbon bond angles, 82.7(4)° to 89.4(4)° (Table 1), indicating stronger interactions of aromatic rings to the uranium center in comparison to the Zr and Hf analogues. However, this interaction does not impart the same degree of stability as seen for Zr and Hf. The instability in the uranium analogue is most likely a result of the larger radius of uranium and greater ionic character of the metal−methylene carbon bonds in **1-Ph** as compared to the transition metal analogues. Decomposition of $Zr(CH_2C_6H_5)_4$ and $Hf(CH_2C_6H_5)_4$ occurs at high temperatures in hydrocarbon solvents with toluene as the primary organic product.

With a family of neutral homoleptic uranium(IV) alkyls in hand, the ability of these complexes to undergo carbon−carbon reductive elimination was explored. If reductive elimination occurs for $U(CH_2Ph)_4$, bibenzyl would be formed along with either an unstable divalent uranium fragment or uranium metal. It was hypothesized that the unstable low-valent organometallic product of reductive elimination from $U(CH_2Ph)_4$ could be circumvented by using a redox-active ligand, which would provide a place to store electrons. The bulky α-diimine, $^{Mes}DAB^{Me}$, was chosen for this purpose as this ligand and its derivatives have been successfully demonstrated to support tetravalent uranium in its reduced dianionic form.[41,42] Addition of 1 equiv of $^{Mes}DAB^{Me}$ to **1-Ph** resulted in an immediate color change to bright red and extrusion of bibenzyl, which was confirmed by ^{1}H NMR spectroscopy (eq 2). No formation of toluene from U−C homolytic cleavage was noted. Performing the reaction in the presence of the internal standard ferrocene showed that after complete consumption of $U(CH_2Ph)_4$, 92% of the expected bibenzyl was produced by integration. The new organometallic uranium species, assigned as $(^{Mes}DAB^{Me})U(CH_2Ph)_2$ (**2-Ph**), was analyzed by ^{1}H NMR spectroscopy and showed a paramagnetically shifted and broadened spectrum with 14 resonances ranging from −42.20 to 42.38 ppm; these data indicate inequivalency in the molecule. The inequivalent protons are due to a π interaction between the uranium center and the new carbon−carbon double bond in the ligand framework generated by ligand reduction to the ene-diamide resonance structure. This causes the ligand backbone to bend upward toward the uranium center, which in turn creates

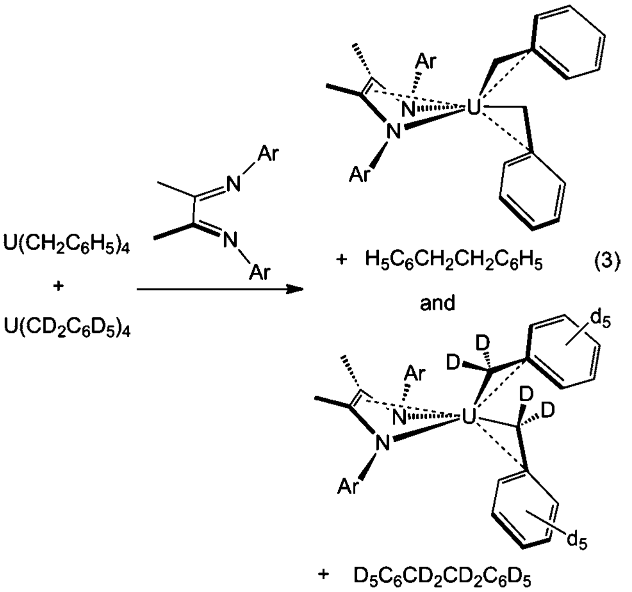


inequivalency in the benzyl groups (eq 2), affording a C_1 symmetric molecule in solution. Two resonances at 42.38 and 18.96 ppm integrate for one proton each, consistent with two different *p*-H's from the inequivalent benzyl ligands. The aryl methyl protons and the methyl backbone are represented as four resonances integrating to six, and the remaining signals for the molecule integrate for two protons, and are indistinguishable. Exclusive formation of bibenzyl over toluene indicates that the redox-active α-diimine ligand plays an important role in inducing multielectron elimination from this U(IV) species. Carbon−carbon reductive elimination was also noted in the presence of 2 equiv of 2,2′-bipyridine; however, no tractable organometallic product was generated.

Although formation of **2-Ph** results in a protected metal center stabilized by the reduced ene-diamide ligand, the benzyl ligands remain highly reactive. At room temperature, compound **2-Ph** is isolable, but decomposes over an hour in solution. No further C−C coupling is observed for **2-Ph**, instead toluene is the main organic product as confirmed by ^{1}H NMR spectroscopy. Further addition of a second equivalent of $^{\text{Mes}}$DAB$^{\text{Me}}$ does not result in formation of another equivalent of bibenzyl; instead, the same decomposition products are noted. Because single crystals of **2-Ph** could not be obtained, further characterization was accomplished by taking advantage of the basic nature of the benzyl ligands using protonation. Addition of 2 equiv of cyclopentadiene to a stirring solution of **2-Ph** caused a color change from red to brown. After workup, characterization by ^{1}H NMR spectroscopy confirmed the formation of $Cp_2U(^{\text{Mes}}\text{DAB}^{\text{Me}})$[42] in quantitative conversion with the expected amount of toluene based on integration against a ferrocene internal standard (eq 2). The formation of $Cp_2U(^{\text{Mes}}\text{DAB}^{\text{Me}})$ occurs via protonation of the benzyl ligands in **2-Ph** by the acidic cyclopentadienyl hydrogens and supports the assignment as $(^{\text{Mes}}\text{DAB}^{\text{Me}})U(CH_2Ph)_2$.

The addition of $^{\text{Mes}}$DAB$^{\text{Me}}$ to both **1-*p*-Me** and **1-*m*-Me$_2$** results in the loss of 1 equiv each of di-*p*-methylbibenzyl and 3,3′,5,5′-tetramethylbibenzyl, respectively, as a result of C−C reductive elimination. This reactivity is analogous to that of **1-Ph**, indicating that the C−C reductive elimination is a general transformation for this family. However, the reactivity of this family diverges upon attempts to isolate organometallic complexes similar to **2-Ph** for both **1-*p*-Me** and **1-*m*-Me$_2$**. Upon formation of **2-*p*-Me** and **2-*m*-Me$_2$**, homolytic cleavage of the remaining U−C bonds occurs rapidly, producing 2 equiv of *p*-xylene or mesitylene, respectively. This increased propensity for bond scission is most likely due to the electron-donating character of the methyl-substituted benzyl groups as compared to the unsubstituted benzyls in **2-Ph**.

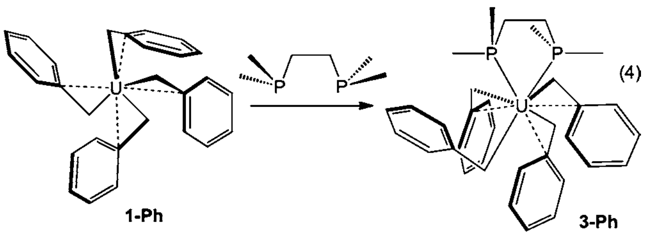
To gain insight into the mechanism for reductive elimination, a crossover experiment was performed with **1-Ph** and its deuterated analogue, $U(CD_2C_6D_5)_4$ (**1-Ph-*d*$_{28}$**) (eq 3). Compound **1-Ph-*d*$_{28}$** was synthesized in an analogous manner to **1-Ph** with benzyl potassium-d_7. Using a similar procedure to that for synthesis of **2-Ph**, equimolar amounts of **1-Ph** and **1-Ph-*d*$_{28}$** were mixed, followed by addition of 2 equiv of $^{\text{Mes}}$DAB$^{\text{Me}}$ in diethyl ether upon thawing. After 15 min of stirring, the solvent was removed in vacuo, and analysis of this mixture by GC/MS confirmed the presence of bibenzyl and bibenzyl-d_{14}. The crossover product, bibenzyl-d_7, was not observed by mass spectrometry. Further, the ^{1}H NMR spectrum of the reaction mixture shows no splitting in the methylene peak at 2.76 ppm, as would be expected if deuterium was incorporated into the adjacent methylene peak. The formation of bibenzyl-d_{14} in the crossover experiment was also confirmed by ^{2}H NMR spectroscopy. These results corroborate that carbon−carbon reductive elimination of bibenzyl occurs from a single uranium center.



Analogous studies have been performed with use of group (IV) derivatives. Klosin et al. reports the addition of α-diimines to $Zr(CH_2C_6H_5)_4$ and $Hf(CH_2C_6H_5)_4$ produces bibenzyl en route to highly active ethylene polymerization catalysts.[67,68] In these systems, migration of a benzyl group to the α-diimine backbone generates the isolable imino-amido tris(benzyl) complexes, $(ArN{=}C(Me)C(Me)(CH_2Ph)NAr)M(CH_2Ph)_3$ (M = Zr, Hf; Ar = 2,6-diisopropylphenyl (DIPP)).[69] Upon thermolysis, elimination of bibenzyl is noted, forming $(^{\text{DIPP}}\text{DAB}^{\text{Me}})M(CH_2Ph)_2$ in analogy to **2-Ph**. The authors observe a weak bonding interaction between the newly formed ligand carbon−carbon double bond by X-ray crystallography. To rule out that this mechanism is operable for the uranium system, decomposition studies following the addition of $^{\text{Mes}}$DAB$^{\text{Me}}$ to **1-Ph** were performed. Analysis by ^{1}H NMR spectroscopy and GC/MS of the free ligand showed the α-diimine starting material with no additional benzyl group, ruling out benzyl radical migration to the ligand backbone in the uranium system.

Studies with TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)-oxyl) were utilized to test for radical reductive elimination from the imino-amido hafnium derivative, $(ArN{=}C(Me)C(Me)(CH_2Ph)NAr)Hf(CH_2Ph)_3$.[69] These studies were conducted by heating to induce reductive elimination in the presence of 6 equiv of TEMPO, which produced nearly quantitative amounts of TEMPO−CH_2Ph and trace bibenzyl in support of a radical mechanism. To ascertain the reactivity of TEMPO with uranium alkyls, a control experiment was performed to determine if the U−C bonds were susceptible to attack by this reagent. Addition of 6 equiv of TEMPO to $U(CH_2Ph)_4$ *immediately* produced 78% TEMPO−CH_2Ph and 22% bibenzyl by integration with an internal standard (ferrocene), indicating that benzyl abstraction from uranium is a major pathway (see Table S1, Supporting Information). This ratio is similar to that observed for the decomposition of $U(CH_2Ph)_4$ over 5 h. The same ratio of TEMPO was used for the reductive elimination experiment in the presence of $^{\text{Mes}}$DAB$^{\text{Me}}$. In this case, 65% TEMPO−CH_2Ph and 35% bibenzyl were quantified, showing that additional bibenzyl, the product from two-electron reductive elimination, is formed in the presence of the *α*-diimine ligand.

To further probe the role of the redox-active ligand in reductive elimination from **1-Ph**, the redox-innocent chelating phosphine, 1,2-bis(dimethylphosphino)ethane (dmpe), was used. Upon addition, immediate brightening of the dark red solution occurred, indicating progression of the reaction. While a minimal amount of bibenzyl was observed by ^{1}H NMR spectroscopy due to decomposition of a small portion of **1-Ph**, there was far less than 1 equiv, supporting that dmpe does not induce reductive elimination, but rather chelates to the uranium center. The product, assigned as (dmpe)U(CH_2Ph)$_4$ (**3-Ph**), was isolated as a red solid in 91% yield (eq 4). Heating **3-Ph** does not induce C−C reductive elimination, but only serves to decompose the compound; toluene is formed exclusively, with no evidence for bibenzyl formation. Thus, in this case, the dmpe ligand does not support a uranium(IV) center that is capable of carbon−carbon reductive elimination.



(4)

Compound **3-Ph** was previously synthesized by salt metathesis of benzyllithium with (dmpe)$_2$UCl$_4$, but no structural characterization was reported.[8] In our hands, single crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution of **3-Ph** to −35 °C (Figure 3, stuctural parameters in Table 1). Analysis showed two molecules in the asymmetric unit, each with a distorted trigonal prismatic geometry, with the dmpe ligand forming one edge of a single triangle. The uranium−methylene carbon bond distances for the benzyl ligand are similar to those for **1-Ph** and range from 2.460(9) to 2.523(8) Å, whereas those for (dmpe)U(CH_2Ph)$_3$(CH_3) have distances of 2.46(1) to 2.56(1) Å.[8] Following the same bonding analysis as for **1-Ph**, each benzyl ligand in **3-Ph** is coordinated in an η^4 fashion as calculated from the metrical parameters in Table 1.[8] Tetravalent uranium complexes containing one or two dmpe ligands have been structurally characterized and have U−P distances ranging from 2.999(10) to 3.174(3) Å;[8,58,70−74] in comparison, the U−P distances in **3-Ph** of 3.060(2) and 3.070(2) Å are consistent with those of both phosphorus atoms coordinated to the uranium center.

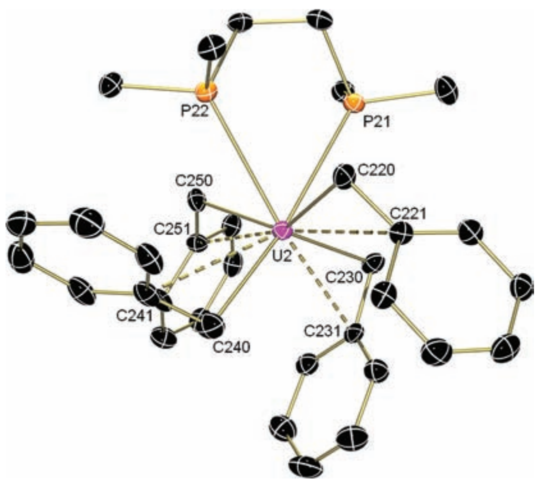


Figure 3. Molecular structure of **3-Ph** shown with 30% probability ellipsoids. Hydrogen atoms, solvent molecules, and a second cocrystallized molecule have been omitted for clarity.

Analysis of **3-Ph** by ^{1}H NMR spectroscopy at 25 °C shows five broad peaks ranging from −15.38 to 7.20 ppm, attributed to dynamics in solution. To gain more structural information, variable-temperature ^{1}H NMR characterization of **3-Ph** was performed. Upon cooling to −40 °C, 12 paramagnetically shifted sharp resonances ranging from −80.43 to 38.22 ppm are baseline resolved. The number and intensity of peaks indicates a C_s symmetric molecule. The methyl protons for the dmpe ligand appear at 0.79 and 7.44 ppm. Resonances for the methylene CH_2's, *o*-phenyl-H's, and *m*-phenyl-H's appear at −80.43, −7.97, 1.25, 4.35, 9.46, and 38.22 ppm based on integration. The remaining four resonances correspond to two *p*-phenyl-H's and two methylene dmpe backbone CH_2's which appear at −21.21, −3.82, 3.63, and 4.80 ppm and are indistinguishable based on shift alone. Cooling the sample slows the dynamic process on the NMR time scale, providing data consistent with the solid state structure.

Magnetic data for **3-Ph** were collected at room temperature for comparison to **1-Ph**. The effective magnetic moment for **3-Ph** is 2.70 μ_B (23 °C), which is consistent with **1-Ph** and previously reported uranium(IV) complexes.[25,41,60−62]

Addition of the redox innocent dmpe to **1-Ph** does not result in reductive elimination, and the analogous amine, TMEDA, shows no reaction or chelation. Reductive elimination of bibenzyl from **1-Ph** is induced exclusively with redox-active ^{Mes}DAB^{Me}. This contrast in reactivity is attributed to the accessibility of the energetically low-lying π^* ligand LUMO, which can store two electrons from the uranium to maintain the +4 oxidation state after elimination of bibenzyl. Thus, a multielectron reduction of the ligand, which changes its character from soft to hard, facilitates the formation of **2-Ph**. Computational studies are currently underway to gain further insight to the pathway by which bibenzyl elimination from **2-Ph** occurs.

■ CONCLUSIONS

The homoleptic tetravalent uranium alkyls **1-Ph**, **1-*p*-Me**, and **1-*m*-Me$_2$** were synthesized and structurally and spectroscopically characterized. These complexes are the first neutral homoleptic tetravalent uranium alkyls that are stable and can be handled at room temperature. The observed extrusion of bibenzyl and its derivatives from **1-Ph**, **1-*p*-Me**, and **1-*m*-Me$_2$** upon addition of the redox-active ^{Mes}DAB^{Me} ligand demonstrates a rare example of carbon−carbon reductive elimination from a monomeric uranium compound. The redox-flexibility of the *α*-diimine ligand serves to generate the stable uranium(IV) organometallic product, **2-Ph**, by storing two electrons in the ligand framework. This forms a hard ene-diamide ligand and maintains the uranium +4 oxidation state throughout the reductive elimination process. A crossover experiment with the deuterated isotopologue, **1-Ph-*d*$_{28}$**, eliminates the possibility of an intermolecular radical process. The advantage of redox-activity is further highlighted with the use of the redox-inflexible dmpe ligand, which stabilizes the tetraalkyl species through chelation and does not promote chemistry at the U−C bond. In addition to supporting C−C bond formation, the redox-flexible $^{Mes}DAB^{Me}$ facilitates multielectron processes at single uranium centers. Thus, redox-active ligands are a promising class for supporting fundamental organometallic reactions at thermodynamically stable uranium(IV) centers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR data for uranium tetrabenzyl derivatives, CIFs, and X-ray crystallography experimental. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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