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Noble Reactions for the Actinides: Safe Gold-Based Access to Organouranium and Azido Complexes

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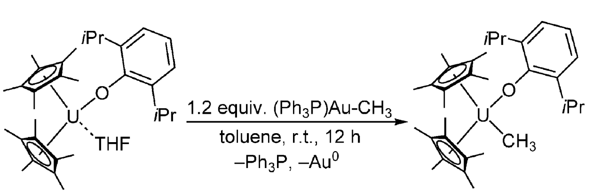
A safe gold-based oxidative functionalization protocol has been developed, which allows access to an assortment of uranium complexes bearing azido- and carbon-functional groups. Alkyl, alkynyl, and azido complexes are accessed in a single step from commercially available or easily prepared gold complexes. This methodology works for $U^{III} \rightarrow U^{IV}$ and $U^{IV} \rightarrow U^{V}$ oxidation. A new high yielding synthetic preparation of $(Ph_3P)Au\text{-}N_3$ is also presented. These reactions proceed rapidly in high yields, and represent a new class of reaction for gold. This work shows that gold chemistry is not just unique for organic transformations and holds great promise for similarly advancing organometallic chemistry.

Introduction

Gold has had a profound impact on organic chemistry with its compounds serving as catalysts for many important transformations.[1,2] In contrast, gold complexes have not been exploited as reagents in organometallic or inorganic chemistry, although a few gold(I) aryl and alkynyl compounds have been reported to undergo transmetalation with transition-metal complexes.[3] We have been developing methods for the functionalization of uranium complexes and have shown that Cu^{I}–X reagents effect the oxidation of uranium with formation of U–X bonds, providing easy chemical control over uranium in oxidation states ranging from $U^{III} \rightarrow U^{V}$.[4] However, this platform is limited in scope as it only works for pure and isolable copper compounds.[5] This is problematic because of the instability of various copper compounds, specifically organocuprates[6] and copper azides,[7] which can detonate violently as isolated solids.[8] Over the past few years, a variety of stable alkyl-, alkenyl-, aryl-, alkynyl-, and azido-gold(I) complexes have been reported,[9] propelling us to investigate their potential as reagents within the oxidative functionalization platform. Unlike the related Cu^{I} systems, these Au^{I} reagents are easily derivatized, and are safe to handle and isolate.[9c,9e] Herein, we report that phosphane-gold(I) complexes are excellent reagents for the oxidative functionalization of uranium with azide and carbon anions, demonstrating a new class of reaction for gold.

Results and Discussion

As depicted in Equation (1), reaction of $(Ph_3P)Au\text{-}CH_3$ with $(C_5Me_5)_2U(O\text{-}2,6\text{-}iPr_2\text{-}C_6H_3)(THF)$ (**1**) for 12 h at room temperature results in full conversion of the U^{III} starting material to the U^{IV} methyl derivative $(C_5Me_5)_2U(O\text{-}2,6\text{-}iPr_2\text{-}C_6H_3)(CH_3)$ (**2**) in 83% yield after workup. Note that, during the reaction, metallic gold plates out of solution, allowing for easy separation from the reaction mixture. Although requiring higher temperatures, $(Ph_3P)Au\text{-}CH_3$ also reacts with the imido-uranium(IV) complex $(C_5Me_5)_2U(=N\text{-}2,6\text{-}iPr_2\text{-}C_6H_3)(THF)$ (**3**), and after 12 h at 50 °C affords the known pentavalent methyluranium complex $(C_5Me_5)_2U(=N\text{-}2,6\text{-}iPr_2\text{-}C_6H_3)(CH_3)$ (**4**), as determined by ^1H NMR spectroscopy.[4e] To the best of our knowledge, these are the first examples demonstrating the oxidation and functionalization of organometallic species by using gold compounds.



1

2, *83 % yield*

(1)

The molecular structure of compound **2** features a bent-metallocene framework in which the aryl oxide and methyl ligands are contained within the metallocene wedge (Figure 1). At 2.470(6) Å, the $U–C_{methyl}$ distance observed in **2** compares favorably with those found in other structurally characterized methyluranium(IV) complexes,[10] and the metrical parameters for the $U–O–C_{aryl}$ fragment [U–O,

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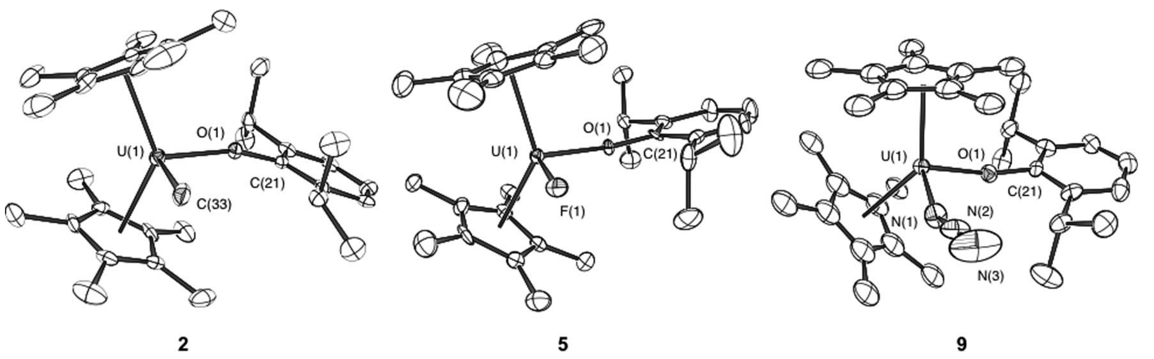
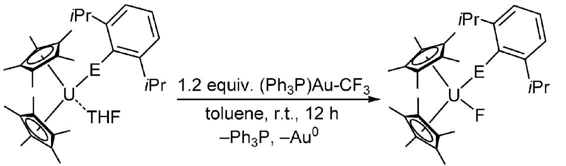


Figure 1. Molecular structures of $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(CH_3)$ (**2**), $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(F)$ (**5**), and $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(N_3)$ (**9**) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **2**: U(1)–O(1) 2.126(4), U(1)–C(33) 2.470(6), U(1)–O(1)–C(21) 163.2(4), O(1)–U(1)–C(33) 98.80(19). For **5**: U(1)–O(1) 2.124(6), U (1)-F(1) 2.108(6), U(1)–O(1)–C(21) 165.4(6), O(1)–U(1)–F(1) 104.1(2). For **9**: U(1)–O(1) 2.117(5), U(1)–N(1) 2.266(7), N(1)–N(2) 1.197(10), N(2)–N(3) 1.172(11), O(1)–U(1)–N(1) 100.7(2), U(1)–O(1)–C(21) 165.2(4), U(1)–N(1)–N(2) 157.9(6), N(1)–N(2)–N(3) 177.4(10).

2.126(4) Å; U–O–C, 163.2(4)°] are in good agreement with those found in the related iodido complex, $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(I)$ [U–O, 2.114(6) Å; U–O–C, 166.6(6)].[4d]

We envisioned that use of the analogous $(Ph_3P)Au\text{-}CF_3$ reagent would lead to the corresponding (trifluoromethyl)uranium complexes.[9a] However, reaction of either $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(THF)$ (**1**) or $(C_5Me_5)_2U(=N\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(THF)$ (**3**) with 1.2 equiv. of $(Ph_3P)Au\text{-}CF_3$ at room temperature resulted in quantitative formation of the fluorido complexes $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(F)$ (**5**)[11] and $(C_5Me_5)_2U(=N\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(F)$ (**6**),[4b,12] respectively [Equation (2)]. We propose that initial oxidation of **1** and **3** occurs as evidenced by the plating out of Au^0, resulting in an unstable $U\text{–}CF_3$ moiety, which undergoes α-F elimination to give the fluorido complexes and presumably difluorocarbene. Independent confirmation that the CF_3 group was successfully transferred to the uranium center by $(Ph_3P)Au\text{-}CF_3$ was obtained from the reaction between **5** and **6** with Me_3SiCF_3, which produced Me_3SiF and regenerated the fluorido complexes.



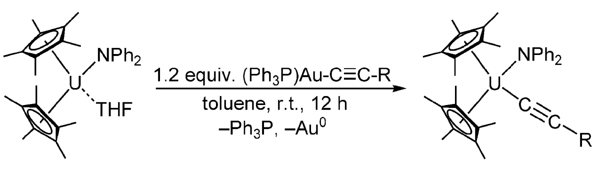
(2)

1, E = O
3, E = N

5, E = O
6, E = N

The molecular structure of **5** is provided in Figure 1 and is analogous to that for **2**. The metrical parameters of the aryl oxide ligand [U–O, 2.124(6) Å; U–O–C, 165.4(6)°] are comparable to those obtained for **2**, and the U–F bond length of 2.108(6) Å is in agreement with the handful of structurally characterized fluorido-U^{IV} complexes.[11]

Unlike copper, gold acetylides can easily be prepared and are stable to isolation as solids.[9d] As such, this Au-based protocol enables access to a spectrum of electronically diverse –C≡C–R functional groups as exemplified by the reaction of $(C_5Me_5)_2U(NPh_2)(THF)$ (**7**) with $(Ph_3P)Au[C{\equiv}C\text{-}(4\text{-}C_6H_4\text{-}CH_3)]$ which affords the corresponding amido-U^{IV} acetylide complex $(C_5Me_5)_2U(NPh_2)[C{\equiv}C\text{-}(4\text{-}C_6H_4\text{-}CH_3)]$ (**8**) in good isolated yield [Equation (3)]. Not only does this provide a direct route to a variety of previously inaccessible uranium acetylide complexes, but it also demonstrates that this Au-based oxidative functionalization chemistry is not unique to the U^{III}-aryl oxide system and can tolerate different ancillary ligands.[13]



(3)

7

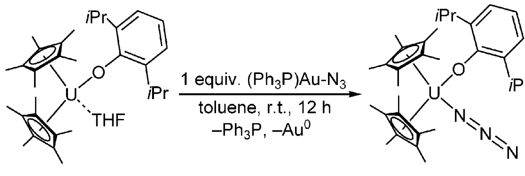
8 R = 4-C_6H_4-CH_3,
74 % yield

The structure of **8** is consistent with other previously characterized acetylide complexes,[4c,14] featuring a U–C bond length of 2.418(5) Å and a C≡C bond length of 1.150(5) Å. The diagnostic C≡C stretch for the acetylide complex observed in the IR spectrum of **8** (2059 cm^{-1}) is likewise similar to that seen for other metal acetylide complexes.[4c,14]

Copper azides are extremely dangerous and shock-sensitive,[7] yet azidogold(I) complexes such as $(Ph_3P)Au\text{-}N_3$ are stable and easily manipulated. The synthesis of $(Ph_3P)Au\text{-}N_3$ has traditionally been accomplished by using azide salts (LiN_3, NaN_3) or hydrazoic acid (HN_3), which are hazardous and toxic reagents.[15] However, we found that $(Ph_3P)Au\text{-}N_3$ can be conveniently prepared in high yield (>80%) by reaction of the known alkoxide $(Ph_3P)Au\text{-}OtBu$ with $Me_3Si\text{-}N_3$ [Equation (4)].[16]

$$(Ph_3P)Au\text{-}OtBu + Me_3Si\text{-}N_3 \xrightarrow[-\,Me_3Si\text{-}OtBu]{THF} (Ph_3P)Au\text{-}N_3 \qquad (4)$$

As shown in Equation (5), $(Ph_3P)Au\text{-}N_3$ is an excellent azide transfer reagent that rapidly oxidizes $(C_5Me_5)_2U(O\text{-}2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)(THF)$ (**1**) to the azidouranium(IV) complex $(C_5Me_5)_2U(O\text{-}2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)(N_3)$ (**9**) at room temperature. Again, gold metal plates out of solution and is accompanied by a dramatic color change from dark green to dark red with the new azidouranium complex **9** being isolated in 78% yield after workup. The transfer of the azido ligand was monitored by IR spectroscopy; a strong stretch is observed at 2086 cm^{-1}, which falls within the typical range for azidouranium(IV) complexes (2080–2100 cm^{-1}).[17]



(5)

1

9, *78 % yield*

Confirmation that the azido ligand had been oxidatively transferred from $(Ph_3P)Au\text{-}N_3$ to uranium was obtained by a single-crystal X-ray diffraction study (Figure 1). The molecular structure for $(C_5Me_5)_2U(O\text{-}2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)(N_3)$ (**9**) is similar in constitution to those of complexes **2** and **5**, and has a linear azide group [N(1)–N(2)–N(3) 177.4(10)°]. Interestingly, the azido ligand is bent with respect to the uranium(IV) center, with a U(1)–N(1)–N(2) bond angle of 157.9(6)°. The U(1)–N(1) bond length of 2.266(7) Å is comparable to those in other structurally characterized azidouranium(IV) complexes.[17] Also, as for most azido-metal complexes, the N(1)–N(2) [1.197(10) Å] and N(2)–N(3) [1.172(11) Å] bond lengths are similar in **9**, suggesting a degree of delocalization of the π-electron density throughout the azide group.

Conclusions

In conclusion, we have presented a general and versatile gold(I)-based oxidation procedure that enables direct access to U–C and U–N_{azide} functional groups. The gold reagents are nontoxic, easily derivatized, and safe to handle and isolate. This reaction manifold represents a powerful strategy that complements existing azide transfer, lithium, and magnesium alkylation methods and does not appear to be limited by metal oxidation state or ancillary ligands. Clearly, gold chemistry is not just unique for organic transformations and holds great promise for similarly advancing organometallic chemistry.

Experimental Section

General: Unless otherwise noted, reactions and manipulations were performed either in a Vacuum Atmospheres NEXUS model inert-atmosphere (N_2) drybox equipped with a 40CFM Dual Purifier NI-Train, or using standard Schlenk techniques. Glassware was dried in an oven at 150 °C overnight prior to use. All NMR spectra were collected with a Bruker Avance 300 MHz NMR spectrometer. Chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to solvent impurities and ^{31}P{^{1}H} NMR spectra were referenced to external H_3PO_4 (δ = 0.00 ppm). Melting points were determined with a Mel-Temp II capillary melting point apparatus equipped with a Fluke 50S K/J thermocouple using capillary tubes flame-sealed under nitrogen; values are uncorrected. Mass spectrometric (MS) analyses were performed at the University of California, Berkeley Mass Spectrometry Facility, with a VG ProSpec (EI) mass spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, with a Perkin–Elmer Series II 2400 CHNS analyzer.

Materials: Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. [D$_6$]-Benzene (Aldrich, anhydrous) and [D$_8$]THF (Cambridge Isotope Laboratories) were purified by storage over activated 4-Å molecular sieves under N_2 prior to use. Celite (Aldrich), alumina (Aldrich, Brockman I) and 4-Å molecular sieves (Aldrich) were dried under reduced pressure at 250 °C for 48 h prior to use. All solvents (Aldrich) were purchased in "anhydrous" quality and treated with KH for 24 h, passed through a column of activated alumina, and stored over activated 4-Å molecular sieves prior to use. The following compounds were prepared according to literature procedures: $(C_5Me_5)_2U(O\text{-}2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)(THF)$ (**1**),[18] $(C_5Me_5)_2U(=N\text{-}2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)(THF)$ (**3**),[18] $(C_5Me_5)_2U(NPh_2)(THF)$ (**7**).[4c]

Caution! *Depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47×10^9 years. Manipulations and reactions should be carried out in monitored fumehoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.*

Caution! *Me_3SiN_3 should always be handled with caution under anhydrous conditions, as hydrolysis can lead to formation of toxic HN_3. While we have not observed any explosive behavior with $(Ph_3P)Au\text{-}N_3$ or $(C_5Me_5)_2U(O\text{-}2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)(N_3)$ (**9**), all azido complexes are potentially shock sensitive and should be handled with great care using personal protection precautions.*

Synthesis of $(Ph_3P)Au\text{-}N_3$: A 125-mL side-arm flask (wrapped with Al foil to exclude light) equipped with a stir bar was charged with $(Ph_3P)Au\text{-}OtBu$ (2.12 g, 3.99 mmol) and THF (50 mL) at room temperature. To this stirring solution was added a THF (10 mL) solution of $Me_3Si\text{-}N_3$ (2.30 g, 19.9 mmol). After 5 h the reaction mixture was filtered through a Celite-padded coarse-porosity filter, the filtrate collected and the volatiles removed under reduced pressure to give an off-white residue. *Note*: Allowing this reaction to proceed for longer periods of time generally results in low yields through decomposition. The off-white residue was washed with hexanes (35 mL), collected by filtration and dried under reduced pressure to give $(Ph_3P)Au\text{-}N_3$ as a white solid (1.85 g, 3.69 mmol, 93%). This complex is indefinitely stable if stored in a dark freezer at –30 °C. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 6.98 (m, 9 H, *m*/*p*-Ar-*H*), 6.84 (m, 6 H, *o*-Ar-*H*) ppm. ^{31}P NMR (121 MHz, [D$_6$]benzene, 25 °C): δ = 30.4 ppm. IR (Nujol): $\tilde{\nu}$ = 2053 cm^{-1}.

General $(Ph_3P)Au\text{-}X$ Oxidative Functionalization Procedure Demonstrated by the Synthesis of $(C_5Me_5)_2U(O\text{-}2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)(N_3)$ (9): A

125-mL side-arm flask equipped with a stir bar was charged with $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(THF)$ (**1**) (0.253 g, 0.33 mmol) and toluene (40 mL). To the stirring deep green solution was added solid $(Ph_3P)Au\text{-}N_3$ (0.167 g, 0.33 mmol), resulting in an immediate color change to dark red. The solution was stirred at room temperature for 12 h, filtered through a Celite-padded coarse-porosity filter (Celite pad was washed with toluene until the washings were colorless, ca. 10 mL), filtrate collected and volatiles removed under reduced pressure to give a dark red solid residue. This solid was dissolved in hexanes (20 mL), filtered through a Celite-padded coarse-porosity filter (washed with hexanes until the washings were colorless, ca. 10 mL), filtrate collected, and volatiles removed under reduced pressure to give $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(N_3)$ (**9**) as a red-orange crystalline solid (0.190 g, 0.26 mmol, 78 %). ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 7.69 (d, *J* = 8 Hz, 1 H, *m*-Ar-*H*), 7.00 (d, *J* = 8 Hz, 1 H, *m*-Ar-*H*), 6.59 (t, *J* = 8 Hz, 1 H, *p*-Ar-*H*), 6.05 (s, 30 H, C_5Me_5), –5.56 (d, *J* = 4 Hz, 6 H, *i*Pr-C*H*$_3$), –13.18 (s, 6 H, *i*Pr-C*H*$_3$), –32.60 (m, 1 H, *i*Pr-C*H*), –49.03 (m, 1 H, *i*Pr-C*H*) ppm. IR (Nujol): $\tilde{\nu}$ = 2086 cm^{-1}. M.p. 238–242 °C.

^1H NMR Experiment for the Reaction of $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(THF)$ (1) with $(Ph_3P)Au\text{-}CF_3$: A [D$_6$]benzene (ca. 0.5 mL) solution of $(Ph_3P)Au\text{-}CF_3$ (0.035 g, 0.066 mmol) was added by pipette with stirring to a 20 mL scintillation vial charged with $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(THF)$ (**1**) (0.050 g, 0.066 mmol) and [D$_6$]benzene (ca. 1 mL) at room temperature, resulting in an immediate color change from dark green to a dark red solution. Analysis by ^1H NMR revealed complete conversion to complex $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(F)$ (**5**). ^1H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = –45.33 (br, 1 H, C*H*Me$_2$), –11.45 (s, 7 H, C*H*Me$_2$, CH*Me*$_2$), –1.71 (s, 6 H, CH*Me*$_2$), 3.19 (s, 30 H, C$_5$*Me*$_5$), 4.13 (d, *J* = 8 Hz, 1 H, *m*-Ar-*H*), 6.30 (t, *J* = 8 Hz, 1 H, *p*-Ar-*H*), 6.75 (d, *J* = 8 Hz, 1 H, *m*-Ar-*H*) ppm.

Synthesis of $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(F)$ (5) by Oxidation of $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(THF)$ (1) with CuF_2: A 125-mL side-arm flask equipped with a magnetic stir bar was charged with $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(THF)$ (**1**) (0.75 g, 0.99 mmol) and toluene (35 mL). To the dark green solution solid CuF_2 (0.20 g, 1.98 mmol) was added resulting in an immediate color change to dark red. After stirring at room temperature for 12 h, the reaction mixture was filtered through a Celite-padded coarse porosity frit, and the Celite pad was washed with toluene (10 mL) until the washings went colorless. The filtrate was collected and the volatiles were removed under reduced pressure to give a red oily residue. This material was dissolved in hexane (35 mL) and the resulting solution was filtered through a Celite-padded coarse porosity frit, and the Celite pad was washed with hexane (10 mL) until the washings went colorless. The filtrate was collected and the volatiles removed under reduced pressure to give a tarry red solid. Trituration with TMS_2O (10 mL) and drying gave $(C_5Me_5)_2U(O\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(F)$ (**5**) as a dark red microcrystalline solid (0.65 g, 0.92 mmol, 93 %). X-ray quality crystals of **5** were obtained from either saturated TMS_2O or hexane solutions at –35 °C. ^1H NMR (300 MHz, [D$_6$]benzene, 25°): δ = –45.47 (br, 1 H, C*H*Me$_2$), –11.50 (s, 6 H, CH*Me*$_2$), –11.36 (br, 1 H, C*H*Me$_2$), –1.73 (s, 6 H, CH*Me*$_2$), 3.18 (s, 30 H, C$_5$*Me*$_5$), 4.14 (d, *J* = 8 Hz, 1 H, *m*-Ar-*H*), 6.31 (t, *J* = 8 Hz, 1 H, *p*-Ar-*H*), 6.77 (d, *J* = 8 Hz, 1 H, *m*-Ar-*H*) ppm. MS (EI, 70 eV): *m/z* 704 [M$^+$]. $C_{32}H_{47}FOU$ (704.74): calcd. C 54.54, H 6.72; found C 54.47, H 6.95.

Supporting Information (see also the footnote on the first page of this article): Full details regarding the synthesis and characterization of complexes **2** and **8**, as well as the results from NMR-tube experiments described herein.

CCDC-714038 (for **2**), -714039 (for **5**), -714040 (for **8**), and -714041 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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[5] Attempted oxidation of $(C_5Me_5)_2U(=N\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(THF)$ (**3**) using in situ-formed CuMe from the reaction of CuI and $MgMe_2$ resulted in a mixture of both $(C_5Me_5)_2U(=N\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(Me)$ (**4**) and $(C_5Me_5)_2U(=N\text{-}2,6\text{-}i Pr_2\text{-}C_6H_3)(I)$ by ^1H NMR spectroscopy.[4a,4e]

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