LA-UR- 08-7804

Approved for public release; distribution is unlimited.

Title:	Noble Reactions for the Actinides: Safe Gold-Based Access to Organouranium and Azide Complexes
Author(s):	Robert K. Thomson, Christopher R. Graves, Brian L. Scott, and Jaqueline L. Kiplinger*
Intended for:	Angewandte Chemie International Edition

Los Alamos
NATIONAL LABORATORY
EST. 1943

Form 836 (7/06)

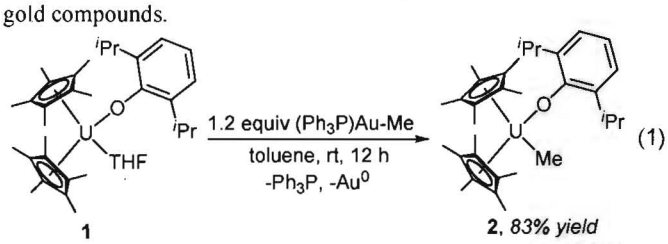
DOI: 10.1002/anie.200((will be filled in by th

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

*Robert K. Thomson, Christopher R. Graves, Brian L. Scott, and Jaqueline L. Kiplinger**

Gold has had a profound impact on organic chemistry; its compounds are spectacular catalysts for many organic transformations involving the formation of C-C, C-O, C-N and C-S bonds,[1,2] and have enabled unprecedented pathways for the functionalization of C-H and C-C bonds.[3,4] In general, 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.[5] We have been developing methods for functionalizing 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 $U^{III} \rightarrow U^{VI}$.[6] Although a logical approach for the direct generation of U-carbon and U-azide bonds, this Cu-based platform is limited in scope as it only works for pure and isolable copper compounds.[7] This is problematic given the instability of organocuprates[8] and copper azides,[9] which can detonate violently as isolated solids.[10] As such, this route has been confined to the synthesis of select uranium phenylacetylide complexes.[6c] Over the past few years, a variety of stable gold(I) alkyl, alkenyl, aryl, alkynyl, and azide complexes have been reported,[11] propelling us to investigate their potential as reagents within the oxidative functionalization platform. Unlike the related Cu^{I} systems, Au^{I} reagents are easily derivatized, and are safe to handle and isolate. Herein, we report that gold(I)-phosphine compounds can undergo a new class of reaction, and are excellent reagents for the oxidative functionalization of uranium with azide and carbon anions.

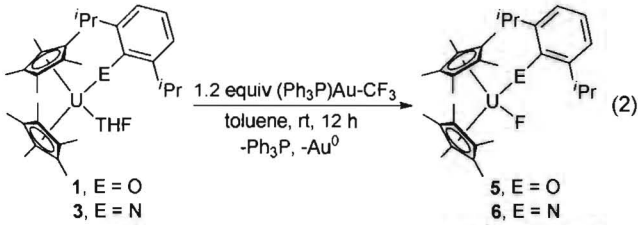
As depicted in Eq. (1), reaction of (Ph_3P)Au-Me with $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(THF)$ (**1**) for 12 h at room temperature results in full conversion of the U^{III} starting material to the U^{IV} methyl derivative $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(Me)$ (**2**) in 83% yield after work-up. Note that in the reaction, the gold plates out of solution allowing for easy separation from the reaction mixture. Although requiring higher temperatures, (Ph_3P)Au-Me also reacts with the uranium(IV) imido complex $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(THF)$ (**3**), and after 12 h at 50 °C affords the known pentavalent uranium methyl complex $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(Me)$ (**4**), as determined by ^{1}H NMR spectroscopy.[6e] To the best of our knowledge these are the first examples demonstrating the oxidation and functionalization of organometallic species using gold compounds.



1 **2**, *83% yield* (1)

The molecular structure of compound **2** is presented in Figure 1 and features a bent-metallocene framework with the aryloxide and methyl ligands contained within the metallocene wedge. At 2.470(6) Å, the U-C_{methyl} distance observed in **2** compares favorably with those found in other structurally characterized uranium(IV) methyl complexes[12] and the metrical parameters for the U-O-C_{aryl} fragment (U-O, 2.126(4) Å; U-O-C, 163.2(4)°) are in good agreement with those found in the related iodide complex, $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(I)$ (U-O, 2.114(6) Å; U-O-C, 166.6(6)).[6d]

We envisioned that use of the analogous $(Ph_3P)Au\text{-}CF_3$ reagent would lead to the corresponding uranium trifluoromethyl complexes.[11a] However, reaction of either $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(THF)$ (**1**) or $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(THF)$ (**3**) with 1.2 equiv $(Ph_3P)Au\text{-}CF_3$ at room temperature resulted in quantitative formation of the fluoride complexes $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(F)$ (**5**)[13] and $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(F)$ (**6**),[6b,14] respectively [Eq. (2)]. We propose that initial oxidation of **1** and **3** occurs as evidenced by the plating of Au^0, resulting in an unstable U-CF_3 moiety which undergoes α-F elimination to give the fluoride 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 the fluoride complexes.



1, E = O
3, E = N

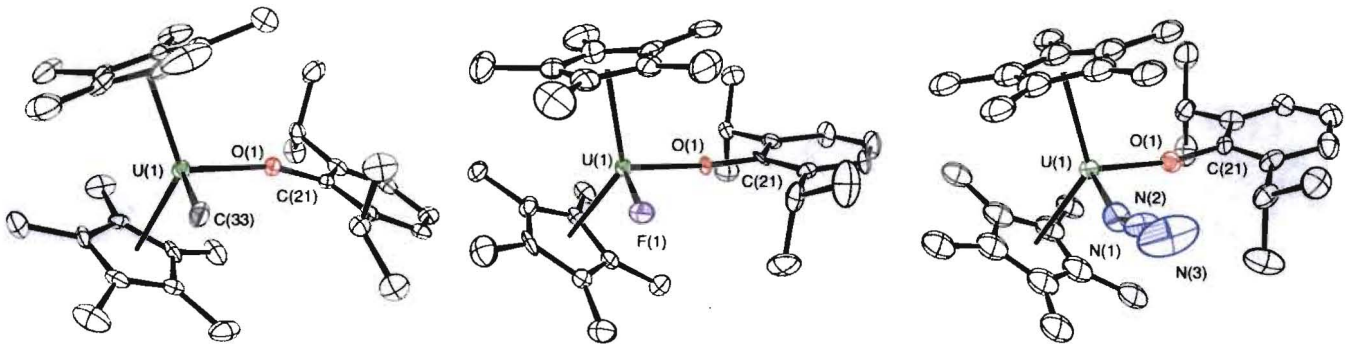
5, E = O
6, E = N (2)

Successful formation of $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(F)$ (**5**) was confirmed by a single crystal X-ray diffraction study. The molecular structure of **5** is given in Figure 1, and is very similar to that for **2**, with the fluoride ligand replacing the methyl ligand. The metrical parameters of the aryloxide ligand (U-O, 2.124(6) Å; U-O-C, 165.4(6)°) are very similar to those obtained for **2**.

[*] Dr. R. K. Thomson, Dr. C. R. Graves, Dr. B. L. Scott, Dr. J. L. Kiplinger
Los Alamos National Laboratory
MS J514, Los Alamos, NM 87545 (USA)
Fax: (+1) 505-667-9905
E-mail: kiplinger@lanl.gov

[**] For financial support of this work, we acknowledge the LANL LDRD Program and G. T. Seaborg Institute (Postdoctoral Fellowships to R.K.T. and C.R.G.), LANL (Director's Postdoctoral Fellowship to C.R.G.), and the Division of Chemical Sciences, Office of Basic Energy Sciences, Heavy Element Chemistry program. The authors thank Dr. Anthony E. Vaughn for executing preliminary reactions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

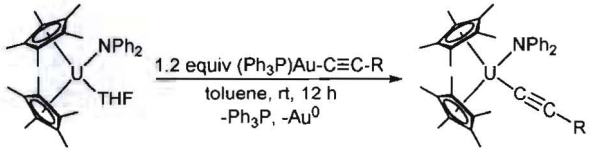


2 5 10

Figure 1. Molecular structures of $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(CH_3)$ (**2**), $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(F)$ (**5**), and $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(N_3)$ (**10**) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (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 (**10**): 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).

The bond distance for the fluoride ligand in **5** is 2.108(6) Å, which is very similar to those reported for the few other known U(IV) fluoride complexes (~2.08-2.11 Å).[13]

Unlike copper, gold acetylides are easily prepared and stable to isolation as solids.[11d] 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 $(Ph_3P)Au(C{\equiv}C\text{-}R)$ (R = 4-C_6H_4-Me or 4-C_6H_4-CF_3) which affords the corresponding U^{IV}-amide acetylide complexes $(C_5Me_5)_2U(NPh_2)(C{\equiv}C\text{-}4\text{-}C_6H_4\text{-}Me)$ (**8**) and $(C_5Me_5)_2U(NPh_2)(C{\equiv}C\text{-}4\text{-}C_6H_4\text{-}CF_3)$ (**9**), respectively, in good isolated yields [Eq. (3)]. Not only is this a facile 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)-aryloxide system and can tolerate different ancillary ligands.[15]



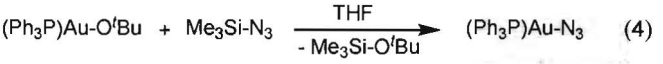
(3)

7

8 R = 4-C_6H_4-Me, ##% *yield*
9 R = 4-C_6H_4-CF_3, ##% *yield*

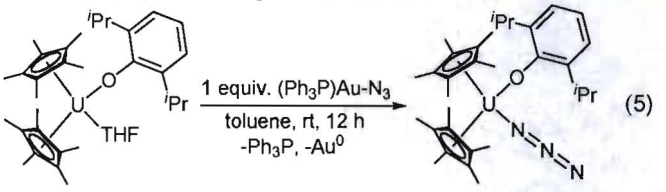
The structure of **8** is consistent with other previously characterized acetylide complexes,[6c,16] featuring a U-C bond distance of 2.418(5) Å and a C≡C bond distance of 1.150(5) Å. The diagnostic C≡C stretch for the acetylide complexes observed in the IR spectra of **8** and **9** (xxxx.x and xxxx.x cm^{-1}, respectively) is likewise similar to that seen for other metal acetylide complexes.

Copper azides are extremely dangerous and explosive,[9] yet gold(I) azide 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 using azide salts (LiN_3, NaN_3) or hydrazoic acid (HN_3), which are hazardous and toxic reagents.[17] However, we found that $(Ph_3P)Au\text{-}N_3$ can be reproducibly prepared in high yield (>80%) by reaction of the known alkoxide $(Ph_3P)Au\text{-}O^tBu$ with $Me_3Si\text{-}N_3$ [Eq. (4)].[18]



(4)

As shown in Eq. (5), $(Ph_3P)Au\text{-}N_3$ is a potent azide transfer reagent which rapidly oxidizes $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(THF)$ (**1**) to the uranium(IV)-azide complex $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(N_3)$ (**10**) in minutes 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 uranium azide complex **10** being isolated in 78% yield after work-up. The transfer of the azide group was monitored by IR spectroscopy, which shows a strong stretch at 2086.2 cm^{-1}, which falls within the typical range for uranium(IV)-azide complexes (2080-2100 cm^{-1}).[19]



(5)

1

10, *78% yield*

Azides are known precursors to uranium nitride complexes,[19,20] which will be critical for understanding the fundamental behavior and properties of the U≡N unit in the potential alternative nuclear fuel uranium nitride. As such, this Au-based protocol creates new opportunities for preparing molecular uranium nitrides by enabling access to novel mixed-ligand azide systems in which the electronic density at the uranium metal center can be easily tuned by changing the ancillary ligand.

Confirmation that the azide group 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 $(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)(N_3)$ (**10**) is similar in constitution to complexes **2** and **5**, but with a linear azide group (N(1)-N(2)-N(3) = 177.4(10)°). Interestingly, the azide 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 other structurally characterized uranium(IV)-azide complexes.[19,20] Also, as for most metal azide complexes, the N(1)-N(2) (1.197(10) Å) and N(2)-N(3)

(1.172(11) Å) bond lengths are similar in **10**, suggesting a degree of delocalization of the π-electron density throughout the azide group.

In conclusion, we have presented a general and versatile Au(I)-based oxidation procedure that enables direct access to U-C and U-N_{azide} bonds. 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 and 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

For full synthetic details of all new complexes prepared, see the Supporting Information.

General Oxidative Functionalization Procedure: *The oxidation of U^{III} complexes with Ph_3PAuX is performed in the same manner regardless of the identity of X. The preparation of $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(N_3)$ (**10**) is given as a generic example.* In a 125 mL Erlenmeyer flask equipped with a vacuum side arm and magnetic stir bar, $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(THF)$ (253 mg, 0.33 mmol, 1 equiv.) was dissolved in 40 mL toluene. To the stirring deep green solution was added solid Ph_3PAuN_3 (167 mg, 0.33 mmol, 1 equiv.), resulting in an immediate color change to dark red. The solution was left to stir for 6 h at room temperature. The deep red solution was filtered through a Celite-padded coarse-porosity fritted disk, and the Celite pad was washed with toluene until the washings were colorless. Excess solvent was removed from the filtrate *in vacuo* to give a dark red solid residue. This was dissolved in hexanes and filtered through a Celite-padded coarse-porosity fritted disk, which was washed with hexanes until the washings were colorless. Excess solvent was removed from the filtrate *in vacuo* to give red-orange crystals. Yield: 190 mg (78%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.69 (1H, d, $^3J_{HH}$ = 7.8 Hz, *m*-Ar-*H*), 7.00 (1H, d, $^3J_{HH}$ = 8.1 Hz, *m*-Ar-*H*), 6.59 (1H, t, $^3J_{HH}$ = 8.0 Hz, *p*-Ar-*H*), 6.05 (30H, s, C_5Me_5), -5.56 (6H, d, $^3J_{HH}$ = 3.9 Hz, ^{i}Pr-C*H*$_3$), -13.18 (6H, s, ^{i}Pr-C*H*$_3$), -32.60 (1H, m, ^{i}Pr-C*H*), -49.03 (1H, m, ^{i}Pr-C*H*). IR (Nujol, cm^{-1}): 2086.2. EIMS (*m/z*): xxx.x. Anal. Calcd. C, 52.81; H, 6.51; N, 5.77. Found: C, xx.xx; H, x.xx; N, x.xx.

Synthesis of Ph_3PAuN_3: In a 125 mL Erlenmeyer flask wrapped with Al foil to exclude light, Ph_3PAuO^tBu (2.12 g, 3.99 mmol, 1 equiv.) was dissolved in 50 mL of THF and stirred at room temperature. To this solution was added a solution of $Me_3Si\text{-}N_3$ (2.30 g, 19.9 mmol, ~5 equiv.) dissolved in THF. After 5 hours the reaction mixture was filtered through Celite, and the filtrate was concentrated to dryness *in vacuo*. 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 and isolated by filtration and dried *in vacuo*. Yield: 1.85 g (93%). This complex is indefinitely stable to decomposition if stored in a dark freezer. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 6.98 (9H, m, *m/p*-Ar-*H*), 6.84 (6H, m, *o*-Ar-*H*). ^{31}P NMR (C_6D_6, 121 MHz, 298 K): δ 30.4. IR (Nujol, cm^{-1}): xxxx.x.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

Keywords: uranium · oxidation · gold · azide · organometallic

[1] A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180-3211.
[2] A. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239-3265.
[3] For representative examples of applied C-H activation by gold complexes see: (a) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem., Int. Ed.* **2000**, *39*, 2285-8. (b) Z. Li, Z. Shi, C. He, *J. Organomet. Chem.* **2005**, *690*, 5049-54. (c) C. Wei, C.-J. Li, *J. Am. Chem. Soc.* **2003**, *125*, 9584-5.
[4] For representative examples of applied C-C activation by gold complexes see: (a) Y. Liu, F. Song, S. Guo, *J. Am. Chem. Soc.* **2006**, *128*, 11332-3. (b) D. Xing, B. Guan, G. Cai, Z. Fang, L. Yang, Z. Shi, *Org. Lett.* **2006**, *8*, 693-6.
[5] (a) M. Contel, M. Stol, M. A. Casado, G. P. M. van Klink, D. D. Ellis, A. L. Spek, G. van Koten, *Organometallics*, **2002**, *21*, 4556-9. (b) M. Stol, D. J. M. Snelders, H. Kooijman, A. L. Spek, G. P. M. van Klink, G. van Koten, *Dalton Trans.*, **2007**, 2589-93. (c) M. Ferrer, L. Rodriguez, O. Rossell, J. C. Lima, P. Gomez-Sal, A. Martin, *Organometallics*, **2004**, *23*, 5096-9.
[6] (a) C. R. Graves, B. L. Scott, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2007**, *129*, 11914-5. (b) C. R. Graves, P. Yang, S. A. Kozimor, A. E. Vaughn, D. L. Clark, S. D. Conradson, E. J. Schelter, B. L. Scott, J. D. Thompson, P. J. Hay, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2008**, *130*, 5272-85. (c) C. R. Graves, B. L. Scott, D. E. Morris, J. L. Kiplinger, *Organometallics*, **2008**, *27*, 3335-7. (d) C. R. Graves, E. J. Schelter, T. Cantat, B. L. Scott, J. L. Kiplinger, *Organometallics*, **2008**, *27*, 5371-8. (e) C. R. Graves, A. E. Vaughn, E. J. Schelter, B. L. Scott, J. D. Thompson, D. E. Morris, J. L. Kiplinger, *Inorg. Chem.* **2008**, *27*, 5371-8. (f) For an example of U^V-U^{VI} oxidation, see: J. M. Boncella and coworkers, personal communication.
[7] Attempted oxidation of $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(THF)$ (**3**) using *in-situ* formed CuMe from the reaction of CuI and $MgMe_2$ resulted in a mixture of both $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(Me)$ (**4**) and $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(I)$ by ^{1}H NMR spectroscopy.
[8] B. H. Lipshutz, in *Organometallics in Synthesis*, 2nd Edition (Ed: M. Schlosser), WILEY-VCH, Weinheim, **2002**, pp. 717-8.
[9] *Energetic Materials: Physics and chemistry of inorganic azides*, Vol. 1 (Eds. H. D. Fair, R. F. Walker), Plenum Press, New York, **1977**.
[10] Related silver azide complexes are also known to be highly toxic and are unstable/explosive. For representative references, see: Reference 9 and B. P. Aduev, E. D. Aluker, V. G. Kriger, Y. A. Zakharov, *Solid State Ionics*, **1997**, *101-3*, 33-6.
[11] For some examples of these functionalities on gold, see: (a) Y. Usui, J. Noma, M. Hirano, S. Komiya, *Inorg. Chim. Acta.* **2000**, *309*, 151-4. (b) D. V. Partyka, J. B. Updegraff, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics*, **2007**, *26*, 183-6. (c) D. V. Partyka, M. Zeller, A. D. Hunter, T. G. Gray, *Angew. Chem., Int. Ed.* **2006**, *45*, 8188-91. (d) W. Lu, N. Zhu, C.-M. Che, *J. Am. Chem. Soc.* **2003**, *125*, 16081-8. (e) W. Beck, T. M. Klapotke, P. Klufers, G. Kramer, C. M. Rienacker, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1669-74.
[12] (a) W. J. Evans, K. A. Miller, J. W. Ziller, A. G. DiPasquale, K. J. Heroux, A. L. Rheingold, *Organometallics*, **2007**, *26*, 4287-93. (b) E. Barnea, T. Andrea, M. Kapon, J.-C. Berthet, M. Ephritikhine, M. S. Eisen, *J. Am. Chem. Soc.* **2004**, *126*, 10860-1. (c) K. C. Jantunen, C. J. Burns, I. Castro-Rodriguez, R. E. Da Re, J. T. Golden, D. E. Morris, B. L. Scott, F. L. Taw, J. L. Kiplinger, *Organometallics*, **2004**, *23*, 4682-92. (d) W. J. Evans, S. A. Kozimor, W. R. Hillman, J. W. Ziller, *Organometallics*, **2005**, *24*, 4676-83.
[13] $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(F)$ (**5**) was independently synthesized by the oxidative functionalization of $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(THF)$ (**1**) with CuF_2. See the Supporting Information for details. For some other examples of uranium fluorides, see: (a) W. J. Evans, G. W. Nyce, M. A. Johnston, J. W. Ziller, *J. Am. Chem. Soc.* **2000**, *122*, 12019-20. (b) W. W. Lukens, S. M. Beshouri, L. L. Blosch, A. L. Stuart, R. A. Andersen, *Organometallics*, **1999**, *18*, 1235-46. (c) R. R. Ryan, R. A. Penneman, B. Kanellakopulos, *J. Am. Chem. Soc.* **1975**, *97*, 4258-60. (d) G. Zi, L. Jia, E. L. Werkema, M. D. Walter, J. P. Gottfriedsen, R. A. Andersen, *Organometallics*, **2005**, *24*, 4251-64. (e) S. Kannan, M. A. Moody, C. L. Barnes, P. B. Duval, *Inorg. Chem.* **2006**, *45*, 9206-12.
[14] $(C_5Me_5)_2U(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(F)$ (**6**) was identified and characterized using ^{1}H NMR spectroscopy. Full characterization of this complex has been previously reported in reference 6b.
[15] $(Ph_3P)Au(4\text{-}C_6H_4\text{-}Me)$ and $(Ph_3P)Au(C_6H_5)$ complexes with sp^2 Au-C bonds were prepared. Although oxidation of the U^{III} precursors to U^{IV} was successful as evidenced by a color change from green to red, the corresponding U^{IV} complexes are inherently unstable and decomposed.
[16] (a) J. L. Atwood, C. F. Hains Jr., M. Tsutsui, A. E. Gebala, *J. Chem. Soc., Chem. Commun.* **1973**, 452-3. (b) J. L. Atwood, M. Tsutsui, N. Ely, A. E. Gebala, *J. Coord. Chem.* **1976**, *5*, 209-15. (c) R. Boaretto,

P. Roussel, A. J. Kingsley, I. J. Munslow, C. J. Sanders, N. W. Alcock, P. Scott, *Chem. Commun.* **1999**, 1701-2.

[17] (a) W. Beck, W. P. Fehlhammer, P. Poellmann, H. Schachl, *Chem. Ber.* **1969**, *102*, 1976-87. (b) D. I. Nichols, A. S. Charleston, *J. Chem. Soc. A.* **1969**, *17*, 2581-3.

[18] B. R. Sutherland, K. Folting, W. E. Streib, D. M. Ho, J. C. Huffman, K. G. Caulton, *J. Am. Chem. Soc.* **1987**, *109*, 3489-90.

[19] (a) J.-C. Berthet, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, *J. Organomet. Chem.* **1991**, *420*, C9-11. (b) I. Castro-Rodriguez, K. Olsen, P. Gantzel, K. Meyer, *J. Am. Chem. Soc.* **2003**, *125*, 4565-71. (c) M.-J. Crawford, A. Ellern, P. Mayer, *Angew. Chem. Int. Ed.* **2005**, *44*, 7874-8.

[20] (a) W. J. Evans, S. A. Kozimor, J. W. Ziller, *Science*, **2005**, *309*, 1835-8. (b) G. Nocton, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed.* **2008**, *47*, 3040-2. (c) W. J. Evans, K. A. Miller, J. W. Ziller, J. Greaves, *Inorg. Chem.* **2007**, *46*, 8008-18.