A Mild Protocol To Generate Uranium(IV) Mixed-Ligand Metallocene Complexes using Copper(I) Iodide

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Reaction of the trivalent uranium complexes $(C_5Me_5)_2UI(THF)$ (**1**), $(C_5Me_5)_2U[N(SiMe_3)_2]$ (**3**), $(C_5Me_5)_2U(NPh_2)(THF)$ (**4**), and $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)(THF)$ (**5**) with copper(I) iodide affords the corresponding tetravalent uranium diiodide, amide iodide, and aryloxide iodide complexes $(C_5Me_5)_2UI_2$ (**2**), $(C_5Me_5)_2U[N(SiMe_3)_2](I)$ (**6**), $(C_5Me_5)_2U(NPh_2)(I)$ (**7**) and $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)(I)$ (**8**), respectively. This protocol was also extended to the synthesis of the alkyl iodide complex $(C_5Me_5)_2U(CHPh_2)(I)$ (**10**). The isolation of complex **10** from the in situ generated trivalent uranium alkyl complex $(C_5Me_5)_2U(CHPh_2)(THF)$ (**9**) illustrates the synthetic value of this oxidation procedure in those situations where the uranium(III) metallocene complex cannot be isolated or is unstable. Overoxidation and ligand redistribution are not observed with this Cu-based $U^{III} \rightarrow U^{IV}$ oxidation procedure. Attempted functionalization of the U^{IV} amide iodide complex $(C_5Me_5)_2U[N(SiMe_3)_2](I)$ (**6**) with Me_2Mg afforded the novel azametallacycle $(C_5Me_5)_2U[\eta^2(N,C)\text{-}CH_2SiMe_2N(SiMe_3)]$ (**12**) by intramolecular C−H activation and liberation of methane. Reaction between $(C_5Me_5)_2U(NPh_2)(I)$ (**7**) and Me_2Mg afforded a mixture of the products $(C_5Me_5)_2U(NPh_2)(Me)$ (**13**), $(C_5Me_5)_2UMe_2$ (**14**), and $(C_5Me_5)_2U(NPh_2)_2$ (**15**) at room temperature; heating the mixture smoothly furnished the azametallacycle $(C_5Me_5)_2U[\eta^2(N,C)\text{-}(o\text{-}C_6H_4)NPh]$ (**16**). Similarly, reaction between **14** and $HNPh_2$ at 100 °C produced the azametallacycle **16** by aminolysis and subsequent intramolecular C−H activation.

Introduction

Mixed-ligand metallocene complexes of the type $(C_5Me_5)_2U(X)(Y)$ (where X = halogen, triflate; Y = alkyl, amide, alkoxide/aryloxide, phosphide) have played an important role in the development of organometallic actinide chemistry, serving as convenient starting materials for the preparation of uranium complexes with various functional groups such as hydrides,[1] pyrazolates,[2] imides,[3,4] phosphinidenes,[5] hydrazonates,[6] and ketimides.[7] However, access to this class of molecules is currently limited to very specific reaction chemistries such as (1) redistribution reactions between the dihalide ($(C_5Me_5)_2UCl_2$) and dimethyl ($(C_5Me_5)_2UMe_2$) or diphosphide complexes ($(C_5Me_5)_2U(PR_2)_2$),[1,8] (2) protonolysis of $(C_5Me_5)_2UMe_2$ or $(C_5Me_5)_2U(Me)Cl$ with amines/alcohols/phosphines,[1,8,9] (3) addition of Me_3SiX (X = Cl, Br, I, CN, OTf, N_3) across the U−O bond in $(1,2,4\text{-}{}^tBu_3\text{-}C_5H_2)_2U{=}O$ to give $(1,2,4\text{-}{}^tBu_3\text{-}C_5H_2)_2U(OSiMe_3)(X)$ (X = Cl, Br, I, CN, OTf, N_3),[10] (4) reaction of 1 equiv of $Ph_3C{-}X$ (X = Cl, OTf) with $(C_5Me_5)_2UMe_2$,[6,7] and (5) salt metathesis between 1 equiv of an alkali-metal salt and the dichloride complex $(C_5Me_5)_2UCl_2$.[1,11] While the third route is synthetically limited to oxo compounds, the first, fourth, and fifth procedures are often difficult to control and lead to mixtures of products. Recently, we discovered that U^{IV}−imido complexes could be oxidized and functionalized with copper(I) halides to give the corresponding pentavalent systems (eq 1).[12,13] Based on our interest in the synthesis, reactivity, and electronic structure of actinide complexes,[13−21] we were prompted to explore the use of this Cu-based oxidative functionalization

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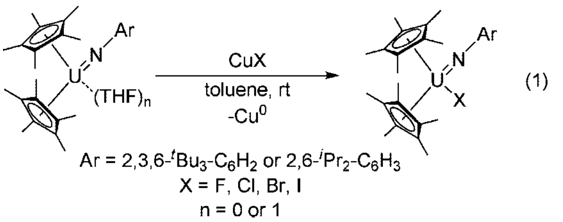
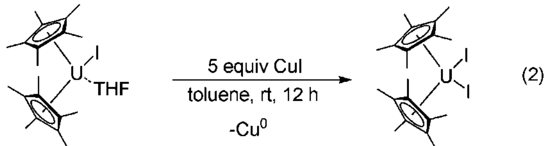
chemistry as a new and versatile method for accessing mixed-ligand U^{IV} metallocene systems.



Herein, we describe our investigations and report the synthesis and characterization of $(C_5Me_5)_2U(I)(X)$ (X = I, $N(SiMe_3)_2$, NPh_2, O-2,6-$^iPr_2$-C_6H_3, $CHPh_2$) from the reaction of copper(I) iodide with the corresponding U^{III} precursor complexes. Importantly, we demonstrate that overoxidation and ligand redistribution are not observed with this Cu-based $U^{III} \rightarrow U^{IV}$ oxidation procedure. While the mixed amide iodide complexes $(C_5Me_5)_2U(I)(X)$ (X = $N(SiMe_3)_2$, NPh_2) are quite stable, the corresponding amide methyl derivatives $(C_5Me_5)_2U(Me)(X)$ (X = $N(SiMe_3)_2$, NPh_2) undergo intramolecular C−H activation chemistry to afford methane and the novel azametallacycles $(C_5Me_5)_2U[\eta^2(N,C)$-$CH_2SiMe_2N(SiMe_3)]$ and $(C_5Me_5)_2U[\eta^2(N,C)$-$(o$-$C_6H_4)NPh]$, respectively. The preparation and characterization of these azametallacycle complexes are also reported in this paper.

Results and Discussion

As a starting point, the oxidation of $(C_5Me_5)_2UI(THF)$ (**1**) with copper(I) iodide to give $(C_5Me_5)_2UI_2$ (**2**) was performed (eq 2). Complex **2** was obtained in 75% isolated yield as a dark red solid, signifying that the U^{IV}/U^{III} redox couple is accessible to oxidative functionalization chemistry with copper halides. Importantly, **2** was the only observed organometallic product and other compounds resulting from overoxidation or ligand redistribution were not observed. This synthetic protocol is an attractive alternative to current literature procedures for the synthesis of **2**, which is most readily prepared by the halogen exchange reaction between $(C_5Me_5)_2UCl_2$ and either Me_3SiI[22,23] or BI_3;[24] oxidation of $(C_5Me_5)_2UCl(THF)$ with I_2 or alkyl iodides also gives $(C_5Me_5)_2UI_2$,[24] and the benzonitrile adduct $(C_5Me_5)_2UI_2(N{\equiv}CPh)$ has also been prepared from the reaction of $UI_4(N{\equiv}CPh)_4$ with $(C_5Me_5)MgCl(THF)$.[25]



Yield = 75%

Single crystals of **2** suitable for X-ray diffraction were grown from a concentrated tetrahydrofuran solution at −30 °C. The thermal ellipsoid representation of the base-free complex $(C_5Me_5)_2UI_2$ (**2**) is shown in Figure 1, and the crystallographic parameters are presented in Table 1. At 2.9807(9) and 2.9868(9) Å and 95.96(2)°, the respective U−I bond distances and I−U−I angle observed in **2** are comparable to those reported for the structurally similar base-free complex $[1,3$-$(SiMe_3)_2$-$C_5H_3]_2UI_2$: U−I = 2.953(2), 2.954(2) Å, I−U−I = 105.40(8)°.[26] As would be expected, the U−I bond distances in the base-free systems are on average slightly shorter when contrasted with structurally related adduct and anion complexes (e.g. $(C_5Me_5)_2UI_2(N{\equiv}CMe)$, U−I = 3.0536(13), 3.0920(12) Å and I−U−I = 80.13(3)°;[22] $(C_5Me_5)_2UI_2(N{\equiv}C^tBu)$, U−I = 3.0707(8), 3.0732(8) Å and I−U−I = 83.29(2)°;[22] $(C_5Me_5)_2UI_2(N{\equiv}CPh)$, U−I = 2.942(3), 3.092(2) Å and I−U−I = 83.16(7)°;[25] $[(C_5Me_5)_2UI_2]^-$, $U-I_{ave}$ = 3.1038(14) Å[27]) which possess a more electron-rich uranium metal center.

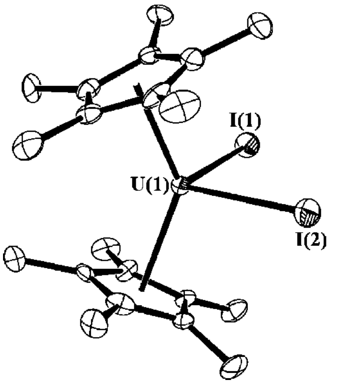


Figure 1. Molecular structure of complex **2** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)−I(1) = 2.9807(9), U(1)−I(2) = 2.9868(9); I(1)−U(1)−I(2) = 95.96(2).

Under conditions identical with those employed for the synthesis of **2**, the U^{III} complexes $(C_5Me_5)_2U[N(SiMe_3)_2]$ (**3**), $(C_5Me_5)_2U(NPh_2)(THF)$ (**4**), and $(C_5Me_5)_2U(O$-2,6-$^iPr_2$-$C_6H_3)(THF)$ (**5**) were all smoothly oxidized with copper(I) iodide to afford the corresponding U^{IV} amide iodide ($(C_5Me_5)_2U[N(SiMe_3)_2](I)$ (**6**) and $(C_5Me_5)_2U(NPh_2)(I)$ (**7**)) and U^{IV} aryloxide iodide ($(C_5Me_5)_2U(O$-2,6-$^iPr_2$-$C_6H_3)(I)$ (**8**)) complexes (Scheme 1).[28]Again, overoxidation and ligand redistribution were not evident in these systems. Following workup by filtration through Celite and crystallization, **6**−**8** were reproducibly isolated as analytically pure solids and characterized by a combination of ^1H NMR, elemental, and mass spectrometric analyses and X-ray crystallography.

This Cu-based oxidative platform also provided a useful entry to an uranium alkyl iodide complex. As shown in Scheme 2, the complex $(C_5Me_5)_2U(CHPh_2)(THF)$ (**9**), prepared in situ from **1** and $KCHPh_2$, was treated with excess CuI to give

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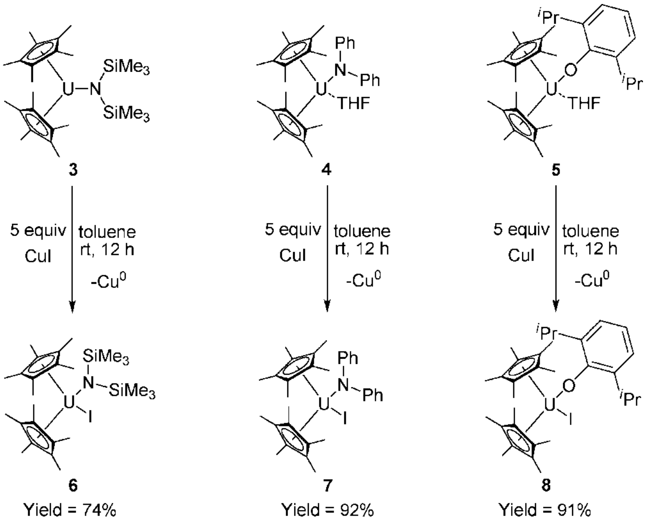
(28) Copper(I) chloride was also effective as an oxidant for the synthesis of $(C_5Me_5)_2U[N(SiMe_3)_2](Cl)$ and $(C_5Me_5)_2U(NPh_2)(Cl)$ from $(C_5Me_5)_2U[N(SiMe_3)_2]$ (**3**) and $(C_5Me_5)_2U(NPh_2)(THF)$ (**4**), respectively, showing the generality of this Cu-based oxidative functionalization platform.

Table 1. Crystallographic Experimental Parameters for 2, 6, 8, 12, and 16

	2	6	8	12	16
formula	$C_{20}H_{30}I_2U$	$C_{27.5}H_{51.5}INSiU$	$C_{32}H_{47}IOU$	$C_{26}H_{48}NSi_2U$	$C_{32}H_{44}NU$
a (Å)	8.5406(16)	9.760(2)	16.5602(17)	8.753(3)	9.2465(9)
b (Å)	16.293(3)	17.856(4)	18.6484(19)	15.573(5)	10.8850(11)
c (Å)	15.827(3)	18.371(4)	19.595(2)	11.017(3)	13.7791(14)
α (deg)	90.00	95.73(3)	90	90	86.5926(14)
β (deg)	98.717(2)	100.47(3)	90	110.857(5)	80.0815(14)
γ (deg)	90.00	93.31(3)	90	90	80.0828(15)
V (Å^3)	2176.9(7)	3122.9(11)	6051.3(11)	1403.2(7)	1345.1(2)
Z	4	4	8	2	2
formula wt (g/mol)	762.27	817.30	812.63	668.86	680.71
space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$P2_1/m$	$P\bar{1}$
T (K)	120(1)	141(2)	120(1)	120(1)	120(1)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
D_{calcd} (g cm^{-3})	2.326	1.738	1.784	1.583	1.681
μ (mm^{-1})	10.291	6.279	6.407	5.882	6.054
R1 ($I > 2\sigma(I)$)	0.0476	0.0264	0.0359	0.0787	0.0374
wR2 (all data)	0.1401	0.0496	0.0739	0.2123	0.0875
GOF (F^2)	1.194	0.983	1.029	1.539	0.826

Scheme 1. Synthetic Routes for Tetravalent Uranium Mixed-Ligand Metallocene Amide Iodide and Aryloxide Iodide Complexes



$(C_5Me_5)_2U(CHPh_2)(I)$ (**10**) in 89% isolated yield over two steps. Although the intermediate U^{III}−alkyl complex **9** was not isolated, analysis of the reaction mixture by ^{1}H NMR revealed a sharp signal at δ −3.30 ppm, corresponding to the C_5Me_5 ligand protons. The trivalent amide and aryloxide starting materials **3**−**5** display similar C_5Me_5 ligand proton resonances.[29−32] The Ar−H resonances in **9** were not observed at room temperature. Since overoxidation and ligand redistribution are not detected in the high-yield formation of complex **10** from **9**, this reaction sequence is noteworthy, as it nicely demonstrates how the Cu-based oxidation chemistry can be valuable in those situations where the uranium(III) metallocene complex cannot be isolated or is unstable, thereby dramatically expanding its utility.

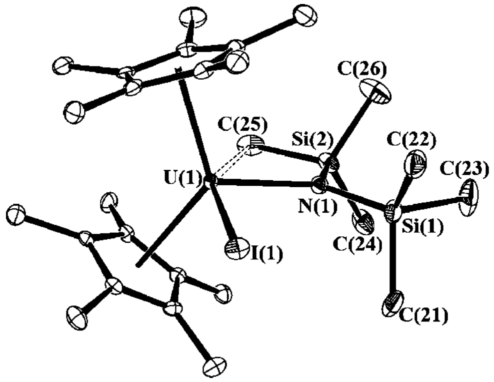


Figure 2. Molecular structure of one of the molecules found in the unit cell for complex **6** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)−N(1) = 2.288(3), U(1)−I(1) = 3.0253(9), Si(1)−C(21) = 1.866(4), Si(1)−C(22) = 1.874(4), Si(1)−C(23) = 1.881(4), Si(2)−C(24) = 1.890(4), Si(2)−C(25) = 1.886(4), Si(2)−C(26) = 1.886(4), U(1)−C(25) = 3.280(4); N(1)−U(1)−I(1) = 93.41(8), U(1)−N(1)−Si(1) = 130.26(15), U(1)−N(1)−Si(2) = 113.80(14), N(1)−Si(2)−N(1) = 108.35(15), N(1)−U(1)−C(25) = 61.2(1), U(1)−C(25)−Si(2) = 76.8(1). Bond distances for the other molecule present in the unit cell can be found in the Supporting Information.

The ^{1}H NMR spectra for complexes **6**−**8** and **10** are consistent with those reported for other U^{IV} metallocene systems[1,3,6,20]—all four complexes have sharp signals corresponding to the C_5Me_5 ligand protons and paramagnetically shifted resonances for the other protons in the compounds. Interestingly, the ^{1}H NMR spectrum of **6** shows three different $SiMe_3$ environments at δ 9.22, 4.83, and −109.70 ppm in a 3:2:1 ratio. The highly upfield resonance at δ −109.70 ppm, which has an integration of three protons, is consistent with restricted rotation of the $SiMe_3$ group about one of the two N−Si axes due to the presence of an agostic[33] U···H−C interaction between one of the Si−Me groups and the uranium center. This interaction is also observed in the solid-state structural data for complex **6** (vide infra). Agostic U···H−C interactions have been previously reported for both $[N(SiMe_3)_2]_3U(S\text{-}2,6\text{-}Me_2\text{-}C_6H_3)$[34] and $(C_5Me_5)U[N(SiMe_3)_2]_2$[35] (vide infra). Complex **7** also has a highly upfield shifted Ar-H proton (δ −146.83)

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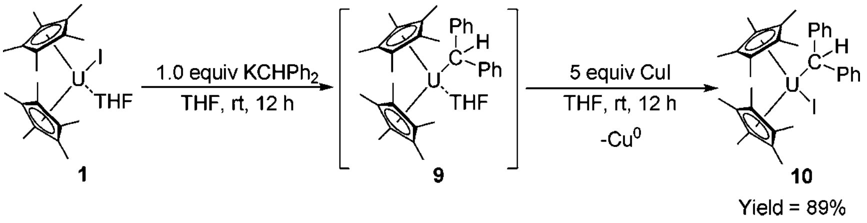
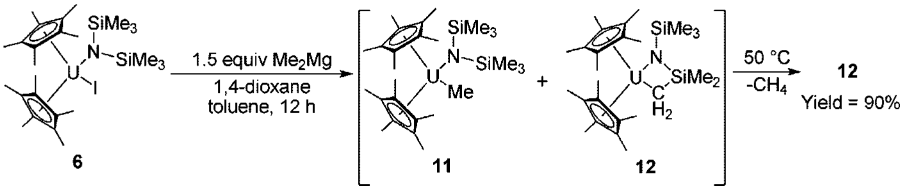
Scheme 2. Synthetic Route for the Tetravalent Uranium Alkyl Iodide Complex $(C_5Me_5)_2U(CHPh_2)(I)$ (10)



Scheme 3. Synthesis of the U^{IV} Metallacycle $(C_5Me_5)_2U[\eta^2(N,C)\text{-}CH_2SiMe_2N(SiMe_3)]$ (12)



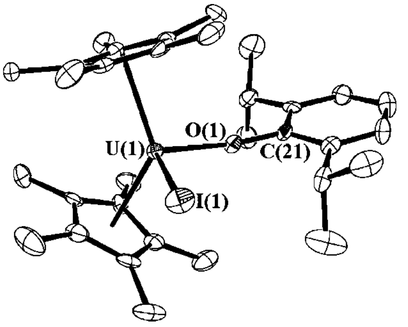


Figure 3. Molecular structure of one of the molecules found in the unit cell for complex **8** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)−O(1) = 2.114(6), U(1)−I(1) = 3.0366(7), O(1)−C(21) = 1.372(10); O(1)−U(1)−I(1) = 104.87(15), U(1)−O(1)−C(21) = 166.6(6). Bond distances for the other molecule present in the unit cell can be found in the Supporting Information.

relative to the other proton signals, suggesting that an agostic interaction may also be present in this system.

The identities of compounds **6** and **8** were confirmed by single-crystal X-ray crystallography studies. Single crystals were not obtained for **7** or **10**, but their formulation is consistent with ^{1}H NMR, mass spectrometric, and elemental analyses. Compound **6** crystallized with two independent, but structurally similar, molecules in the unit cell. As shown in Figure 2, the molecule features a bent-metallocene framework with the $N(SiMe_3)_2$ and iodide ligands contained within the metallocene wedge. The $U-N_{amide}$ (2.288(3) Å) and U−I (3.0253(9) Å) bond distances observed in **6** fall in the ranges observed for other organometallic uranium complexes having $U-N_{amide}$[31,35−37] and U−I linkages.[38] The most notable feature of the $N(SiMe_3)_2$ ligand structure is the presence of a short U−C contact observed between the uranium center and one of the methyl groups. Corroborating the solution ^{1}H NMR data, the U(1)−C(25) distance of 3.280(4) Å indicates that an agostic U···H−C interaction is present in the solid state. This is further supported by the different U−N−Si geometric parameters—at 113.80(14)° the U(1)−N(1)−Si(2) angle is significantly smaller than the U(1)−N(1)−Si(1) angle of 130.26(15)°. Such U···H−C interactions have been reported for other uranium systems that possess a $N(SiMe_3)_2$ ligand.[34,35,39] The $(C_5Me_5)U[N(SiMe_3)_2]_2$ complex features two U···H−C interactions in the solid state, as evidenced by close U···C contacts (2.86(2), 2.80(2) Å) and decreased U−N−Si angles for the interacting (106.3(11), 101.5(9)°) versus noninteracting (134.2(12), 132.4(12)°) groups.[35] Although the U−C distances observed for $(C_5Me_5)U[N(SiMe_3)_2]_2$ are much shorter than those seen for **6**, the distances reported for the three agostic U···H−C interactions in the $[N(SiMe_3)_2]_3U(S\text{-}2,6\text{-}Me_2\text{-}C_6H_3)$ complex (3.158−3.539 Å) are much more in accord with our findings. Decreased U−N−Si angles (109.5−117.2° versus 127.8−134.4°) were also hallmarks for these U···H−C interactions in the $[N(SiMe_3)_2]_3U(S\text{-}2,6\text{-}Me_2\text{-}C_6H_3)$ complex.[34] An agostic interaction has also been reported for the homoleptic alkyl complex $U[CH(SiMe_3)_2]_3$, which contained a short U−C (3.09(2) Å) bond distance.[39] Although neutron diffraction and theoretical studies suggest that such agostic interactions in similar lanthanide complexes result from β-Si−C rather than γ-C−H interactions, these conclusions were based on significant differences in the Si−C bond distances[40] and such an interpretation cannot be made in the present case, where the Si−C distances are all statistically comparable.

Complex **8** also crystallized with two independent but structurally similar complexes in the unit cell (Figure 3). Interestingly, the geometric parameters observed for **8** are statistically indistinguishable from those obtained for the structurally related U^V complex $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)({=}O)$,[30] with both complexes having close to linear $U-O-C_{aryl}$ bond angles (166.6(6) and 169.7(5)°, respectively). The U−O bond distance of 2.114(6) Å seen for **8** is also comparable to that seen for $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)({=}O)$ (2.135(5) Å) and is positioned well in the range of those observed for other U^{IV} aryloxide complexes (e.g. $IU(O\text{-}2,6\text{-}{}^tBu_2\text{-}C_6H_3)_3$,[41] U−O = 2.092(8), 2.102(8), 2.114(11) Å; [N(Si-

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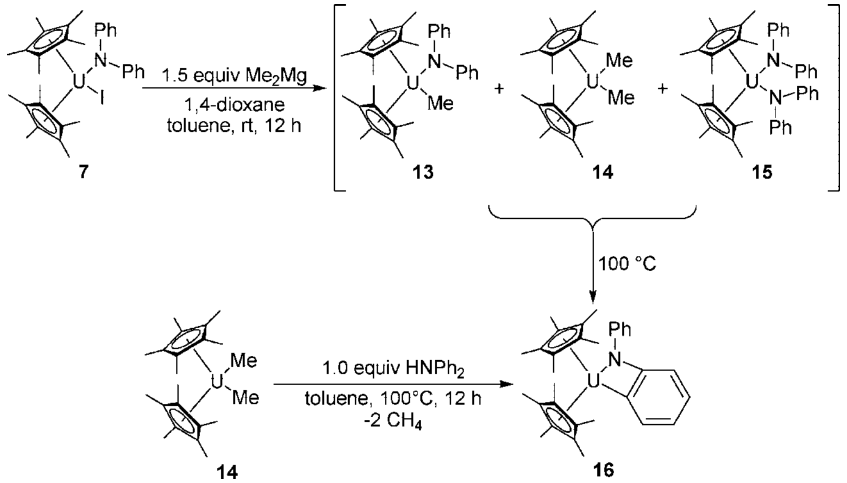
(41) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; McKee, S. D.; Smith, W. H. *Inorg. Chem.* **1994**, *33*, 4245–4254.

Scheme 4. Profile of the Reaction between $(C_5Me_5)_2U(NPh_2)(I)$ (7) and Me_2Mg



$Me_3)_2]_3U(O\text{-}2,6\text{-}{}^tBu_2\text{-}C_6H_3)$,[42] U–O = 2.145(8) Å). The U–I bond distance of 3.0366(7) Å observed for **8** is unexceptional and can be compared with that observed in complex **6** and other tetravalent uranium iodide complexes.

Interestingly, attempts to alkylate $(C_5Me_5)_2U[N(SiMe_3)_2](I)$ (**6**) with Me_2Mg gave a mixture of products at room temperature after 12 h.[43] Although complex **6** was entirely consumed, the major product of the reaction was the novel metallacycle $(C_5Me_5)_2U[\eta^2(N,C)\text{-}CH_2SiMe_2N(SiMe_3)]$ (**12**) (82% by ^1H NMR), not the anticipated product $(C_5Me_5)_2U[N(SiMe_3)_2](Me)$ (**11**). An NMR signal at δ 8.26 ppm (18% by ^1H NMR) in the range expected for the C_5Me_5 ligand protons of **11** was also observed as the minor product of the reaction. We propose that **11** is formed as an intermediate in the salt metathesis reaction and that a subsequent intramolecular C–H activation reaction with elimination of methane[44] affords the metallacycle **12**. Upon heating at 50 °C for 12 h in toluene **12** is formed quantitatively under indentical reaction conditions and can be obtained in 90% isolated yield (Scheme 3).

As illustrated in Scheme 4, the reaction between $(C_5Me_5)_2U(NPh_2)(I)$ (**7**) and Me_2Mg also formed a mixture of products at room temperature.[43] While the desired product $(C_5Me_5)_2U(NPh_2)(Me)$ (**13**, 25% by NMR) could be observed in the reaction mixture by ^1H NMR spectroscopy, the major product was $(C_5Me_5)_2UMe_2$ (**14**, 50% by NMR), in addition to another organometallic, $(C_5Me_5)_2U(NPh_2)_2$ (**15**, 25% by NMR).[45] While $(C_5Me_5)_2UMe_2$ is a known compound,[1] the identity of $(C_5Me_5)_2U(NPh_2)_2$ (**15**) was confirmed by an NMR reaction between $(C_5Me_5)_2U(NPh_2)(I)$ (**7**) and 1.2 equiv of $KNPh_2$, which showed a single resonance corresponding to the C_5Me_5 protons at δ 11.28 ppm. In analogy to the formation of $(C_5Me_5)_2U[\eta^2(N,C)\text{-}CH_2SiMe_2N(SiMe_3)]$ (**12**), when this mixture of **13**, **14**, and **15** was heated to 100 °C, the complex $(C_5Me_5)_2U[\eta^2(N,C)\text{-}(o\text{-}C_6H_4)NPh]$ (**16**) was formed as the sole organometallic product. Presumably, intramolecular C–H activation from both **13** and **15** with elimination of methane and diphenylamine, respectively, gives the metallacycle product **16**. A subsequent protonolysis reaction between **14** and $HNPh_2$ followed by C–H activation accounts for the consumption of the dialkyl complex. To confirm that this is a possibility, $(C_5Me_5)_2UMe_2$ (**14**) was treated with 1 equiv of diphenylamine at 100 °C, which cleanly gave the metallacycle $(C_5Me_5)_2U[\eta^2(N,C)\text{-}(o\text{-}C_6H_4)NPh]$ (**16**) as the sole organometallic product. Additionally, heating $(C_5Me_5)_2U(NPh_2)_2$ (**15**) at 100 °C also affords the azametallacycle $(C_5Me_5)_2U[\eta^2(N,C)\text{-}(o\text{-}C_6H_4)NPh]$ (**16**) and diphenylamine.

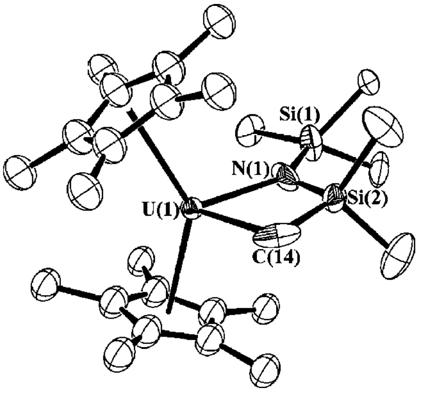


Figure 4. Molecular structure of complex **12** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)–N(1) = 2.221(8), U(1)–C(14) = 2.52(2); U(1)–N(1)–Si(1) = 136.2(5), U(1)–N(1)–Si(2) = 100.7(4), U(1)–C(14)–Si(2) = 86.6(7), N(1)–U(1)–C(14) = 70.5(4), Si(1)–N(1)–Si(2) = 123.1(6), N(1)–Si(2)–C(14) = 102.2(8).

Similar alkanolysis chemistry has been observed for the uranium phosphide complexes $(C_5Me_5)_2U[P(SiMe_3)_2](Me)$ and $(C_5Me_5)_2U(PPh_2)(Me)$, with thermolysis giving the corresponding phosphametallacycles $(C_5Me_5)_2U[\eta^2(P,C)\text{-}CH_2SiMe_2P(SiMe_3)]$ and $(C_5Me_5)_2U[\eta^2(P,C)\text{-}(o\text{-}C_6H_4)PPh]$, respectively, although for these systems much higher temperatures were required.[8,11] Further, this cyclometalation pathway is not unique for these bis(pentamethylcyclopentadienyl) U^{IV} methyl amide and methyl phosphide mixed-ligand systems. The actinide tris(amide) complexes $[N(SiMe_3)_2]_3AnR$ (An = Th, U; R = H, Me) readily expel either H_2 or CH_4 at elevated temperatures to give the azametallacycles $[N(SiMe_3)_2]_2An[\eta^2(N,C)\text{-}CH_2SiMe_2N(SiMe_3)]$ (An = Th, U).[46,47] Analogous chemistry was observed for the homoleptic U^{IV} amide complex $U[N(SiMe_3)_2]_4$ formed in situ between the reaction of UCl_4 with 4 equiv of NaN-

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[42] Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger, A. P.; Streib, W. E.; Van der Sluys, W. G.; Watkin, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 10811–10821.

[43] Excess Me_2Mg was utilized to ensure complete consumption of the uranium starting material.

[44] A peak in the ^1H NMR spectrum for the reaction between $(C_5Me_5)_2U[N(SiMe_3)_2](I)$ (**6**) and Me_2Mg in C_6D_6 had a signal at δ 0.14 ppm corresponding to CH_4.

[45] The C_5Me_5 resonances observed in the ^1H NMR corresponding to $(C_5Me_5)_2U(NPh_2)(Me)$ (**13**), $(C_5Me_5)_2UMe_2$ (**14**), and $(C_5Me_5)_2U(NPh_2)_2$ (**15**) are located at δ 8.50, 5.27, and 11.28 ppm, respectively.

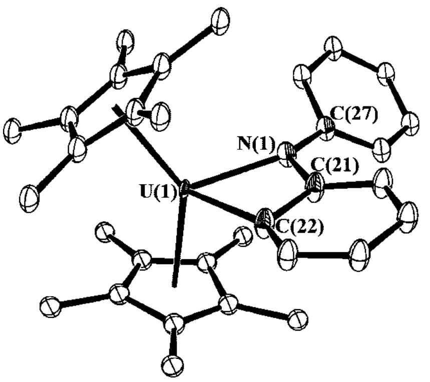

Figure 5. Molecular structure of complex **16** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)−N(1) = 2.239(5), U(1)−C(22) = 2.342(7); U(1)−N(1)−C(21) = 93.9(4), U(1)−N(1)−C(21) = 93.9(4), U(1)−N(1)−C(27) = 142.9(4), N(1)−U(1)−C(22) = 62.7(2), N(1)−C(21)−C(22) = 114.2(6).

$(SiMe_3)_2$.[48] Finally, at elevated temperatures, the thorium dialkyl complexes $(C_5Me_5)_2Th(CH_2EMe_3)_2$ (E = C, Si) eliminate CMe_4 and $SiMe_4$, respectively, to give the corresponding cyclometalated products $(C_5Me_5)_2Th[\eta^2(C,C)\text{-}CH_2EMe_2CH_2]$.[49,50]

The metallacyles **12** and **16** were both characterized by single-crystal X-ray diffraction. Thermal ellipsoid plots are shown in Figures 4 (**12**) and 5 (**16**), and crystallographic experimental parameters are provided in Table 1. Both complexes exhibit a bent-metallocene framework with the newly formed metallacyclic ligands contained within the metallocene wedge. The structure of **12** is similar to that of the previously reported phosphorus analogue $(C_5Me_5)_2U[\eta^2(P,C)\text{-}CH_2SiMe_2P(SiMe_3)]$. The two have similar U−CH_2 bond distances (2.52(2) and 2.415(20) Å, respectively) and X−U−CH_2 angles (86.6(7) and 78.7(5)°, respectively). At 2.221(8) and 2.239(5) Å, the $U-N_{amide}$ bond lengths observed in **12** and **16** agree well with similar parameters obtained for other uranium amides.[51]

Conclusions

Oxidative functionalization of trivalent uranium organometallic complexes with copper(I) iodide provides a simple and mild method for synthesizing the corresponding U^{IV} iodide complexes in good yield. This new approach works on a variety of U^{III} complexes to give not only the basic U^{IV} diiodide but also amide iodide, aryloxide iodide, and alkyl iodide complexes, making it an attractive synthetic alternative to the existing routes for the preparation of mixed-ligand metallocene complexes of the type $(C_5Me_5)_2U(X)(Y)$ (where X = halogen and Y = alkyl, amide, aryloxide, etc.). The isolation of the alkyl iodide complex $(C_5Me_5)_2U(CHPh_2)(I)$ (**10**) from the in situ generated trivalent uranium alkyl complex $(C_5Me_5)_2U(CHPh_2)(THF)$ (**9**) demonstrates the synthetic utility of this oxidation method for those situations where the U^{III} metallocene complex cannot be isolated or is unstable. Importantly, neither overoxidation nor ligand redistribution chemistry is observed with this Cu-based oxidative functionalization protocol. We are presently exploring its efficacy on an assortment of non-metallocene actinide systems.

Experimental Section

General Considerations. Reactions and manipulations were performed in either a recirculating 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 overnight at 150 °C before use. All NMR spectra were obtained in C_6D_6 using a Bruker Avance 300 MHz spectrometer. Chemical shifts for ^1H NMR spectra were referenced to solvent impurities. 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 obtained at the University of California, Berkeley Mass Spectrometry Facility, using a VG ProSpec (EI) mass spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer Series II 2400 CHNS analyzer. X-ray data were collected using either a Bruker APEX2 or Bruker P4/CCD diffractometer. Details regarding data collection are provided in the CIF files given in the Supporting Information. Structural solution and refinement was achieved using the SHELXL97 program suite.[52]

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Benzene-d_6 (Aldrich) was purified by passage through activated alumina and storage over activated 4 Å molecular sieves prior to use. Celite (Aldrich), alumina (Brockman I, Aldrich), and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. All solvents (Aldrich) were purchased anhydrous and were dried over KH for 24 h, passed through a column of activated alumina, and stored over activated 4 Å molecular sieves prior to use. $(C_5Me_5)_2UI(THF)$ (**1**),[35] $(C_5Me_5)_2U(NPh_2)(THF)$ (**4**),[29] $(C_5Me_5)_2U(O\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)(THF)$ (**5**),[30] $(C_5Me_5)_2UMe_2$ (**14**),[1] $KCHPh_2$,[53] and Me_2Mg[54] were prepared according to literature procedures.

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 fume hoods or in an inert-atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

Synthesis of $(C_5Me_5)_2UI_2$ (2). A 125 mL sidearm flask equipped with a stir bar was charged with $(C_5Me_5)_2UI(THF)$ (**1**; 0.50 g, 0.70 mmol) and toluene (50 mL). CuI (0.67 g, 3.5 mmol) was added to the dark green solution, and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered through a Celite-padded coarse-porosity frit

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(46) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728–7729.

(47) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991–2995.

(48) Dormond, A.; El Bouadili, A.; Aaliti, A.; Moise, C. *J. Organomet. Chem.* **1985**, *288*, C1−C5.

(49) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357–7360.

(50) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *250*, 237–246.

(51) For representative U−N bond lengths for complexes containing a uranium−amide linkage, see: (a) $U[N(SiMe_3)_2]_3$, $U-N_{amide}$ = 2.320(4) Å: Stewart, J. L.; Andersen, R. A. *Polyhedron* **1998**, *17*, 953–958. (b) $(C_5Me_5)_2U[N(SiMe_3)_2]$, $U-N_{amide}$ = 2.352(2) Å: Evans, W. J.; Nyce, G. W; Forrestal, K. J.; Ziller, J. W. *Organometallics* **2002**, *21*, 1050–1055. (c) $(C_5Me_5)_2U[NH(2,6\text{-}Me_2\text{-}C_6H_3)]_2$, $U-N_{amide}$ = 2.276(6) Å: Straub, T.; Frank, W.; Reis, G. J.; Eisen, M. S. *J. Chem. Soc., Dalton Trans.* **1996**, 2541–2546. (d) $[N(SiMe_3)_2]_3U({=}NSiMe_3)(F)$, $U-N_{amide}$ = 2.217(17)−2.252(17) Å; $[N(SiMe_3)_2]_3U({=}NC_6H_5)(F)$, $U-N_{amide}$ = 2.206(7)−2.226(6) Å: Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237–3238.

(52) (a) Bruker AXS SAINT 7.06, Integration Software; Bruker Analytical X-ray Systems, Madison, WI, 2003. (b) Sheldrick, G. M. SADABS 2.03, Program for Adsorption Correction; University of Göttingen, Göttingen, Germany, 2001. (c) Sheldrick, G. M. SHELXTL 5.10, Structure Solution and Refinement Package; University of Göttingen, Göttingen, Germany, 1997.

(53) Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Organometallics* **2006**, *25*, 2696–2699.

(54) Tobia, D.; Baranski, J.; Rickborn, B. *J. Org. Chem.* **1989**, *54*, 4253–4256.

and the volatiles were removed from the filtrate. The residue was extracted into hexane (50 mL) and the extract filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give **2** as a red solid (0.40 g, 0.53 mmol, 75%). Spectroscopic characterization of **2** matched literature data.[23] ^{1}H NMR ($\mathrm{C_6D_6}$, 298 K): δ 20.34 (30H, $\mathrm{C_5}Me_5$). X-ray-quality samples of **2** were obtained by recrystallization from a concentrated tetrahydrofuran solution at −30 °C.

Synthesis of $(\mathrm{C_5Me_5})_2\mathrm{U[N(SiMe_3)_2]}$ (3). A 125 mL sidearm flask equipped with a stir bar was charged with $(\mathrm{C_5Me_5})_2\mathrm{UI(THF)}$ (**1**; 1.0 g, 1.4 mmol) and toluene (50 mL). $\mathrm{KN(SiMe_3)_2}$ (0.28 g, 1.4 mmol) was added to the dark green solution, and the reaction mixture was stirred at room temperature. After 1 h, the reaction mixture was filtered through a Celite-padded coarse-porosity frit and the volatiles were removed from the filtrate. The residue was extracted into hexane (50 mL) and the extract filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give **3** as a dark green solid (0.81 g, 1.2 mmol, 86%). Spectroscopic characterization of **3** matched literature data.[31,32] ^{1}H NMR ($\mathrm{C_6D_6}$, 298 K): δ −5.73 (30H, $\mathrm{C_5}Me_5$), −25.59 (18H, $\mathrm{Si}Me_3$).

Synthesis of $(\mathrm{C_5Me_5})_2\mathrm{U[N(SiMe_3)_2](I)}$ (6). A 125 mL sidearm flask equipped with a stir bar was charged with $(\mathrm{C_5Me_5})_2\mathrm{U[N(SiMe_3)_2]}$ (**3**; 0.5 g, 0.75 mmol) and toluene (50 mL). CuI (0.72 g, 3.8 mmol) was added to the dark green solution, and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered through a Celite-padded coarse-porosity frit and the volatiles were removed from the filtrate. The residue was extracted into hexane (50 mL) and the extract filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give **6** as a red solid (0.44 g, 0.56 mmol, 74%). ^{1}H NMR ($\mathrm{C_6D_6}$, 298 K): δ 12.84 (30H, $\mathrm{C_5}Me_5$), 9.22 (9H, $\mathrm{Si}Me_3$), 4.83 (6H, $\mathrm{Si}Me_2$), −109.70 (3H, $\mathrm{Si}Me$). Anal. Calcd for $\mathrm{C_{26}H_{48}NSi_2IU}$ (mol wt 795.77): C, 39.24; H, 6.08; N, 1.76. Found: C, 39.25; H, 6.06; N, 1.69. Mp: 249−251 °C. MS (EI, 70 eV): *m/z* 794 ($[\mathrm{M}-\mathrm{H}]^+$). X-ray-quality samples of **6** were obtained by recrystallization from a concentrated hexane solution at −30 °C.

Synthesis of $(\mathrm{C_5Me_5})_2\mathrm{U(NPh_2)(I)}$ (7). A 125 mL sidearm flask equipped with a stir bar was charged with $(\mathrm{C_5Me_5})_2\mathrm{U(NPh_2)(THF)}$ (**4**; 0.25 g, 0.33 mmol) and toluene (50 mL). CuI (0.31 g, 1.6 mmol) was added to the dark green solution, and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered through a Celite-padded coarse-porosity frit and the volatiles were removed from the filtrate. The residue was extracted into hexane (50 mL) and the extract filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give **7** as a red solid (0.25 g, 0.31 mmol, 92%). ^{1}H NMR ($\mathrm{C_6D_6}$, 248 K): δ 16.93 (30H, $\mathrm{C_5}Me_5$), 5.94 (1H, Ar-*H*), 5.15 (2H, Ar *H*), −3.54 (1H, Ar *H*), −5.75 (2H, Ar *H*), −8.44 (1H, Ar *H*), −8.70 (1H, Ar *H*), −17.28 (1H, Ar *H*), −146.83 (1H, Ar *H*). Anal. Calcd for $\mathrm{C_{32}H_{40}NIU}$ (mol wt 803.60): C, 47.83; H, 5.02; N, 1.74. Found: C, 47.47; H, 5.20; N, 1.65. Mp: 297−299 °C.

Synthesis of $(\mathrm{C_5Me_5})_2\mathrm{U(O\text{-}2,6\text{-}{}^{\mathit{i}}Pr_2\text{-}C_6H_3)(I)}$ (8). A 125 mL sidearm flask equipped with a stir bar was charged with $(\mathrm{C_5Me_5})_2\mathrm{U(O\text{-}2,6\text{-}{}^{\mathit{i}}Pr_2\text{-}C_6H_3)(THF)}$ (**5**; 0.50 g, 0.66 mmol) and toluene (50 mL). CuI (0.63 g, 3.3 mmol) was added to the dark green solution, and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered through a Celite-padded coarse-porosity frit and the volatiles were removed from the filtrate. The residue was extracted into hexane (50 mL) and the extract filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give **8** as a red solid (0.49 g, 0.60 mmol, 91%). ^{1}H NMR ($\mathrm{C_6D_6}$, 298 K): δ 10.85 (1H, d, *J* = 8 Hz), 10.20 (1H, d, *J* = 8 Hz), 9.85 (30H, $\mathrm{C_5}Me_5$), 7.97 (1H, t, *J* = 8 Hz), −5.60 (6H, $\mathrm{CH}Me_2$), −10.71 (6H, $\mathrm{CH}Me_2$), −35.02 (1H), −40.69 (1H). Anal. Calcd for $\mathrm{C_{32}H_{47}OIU}$ (mol wt 812.65): C, 47.30; H, 5.83. Found: C, 47.69; H, 6.01. Mp: 280−282 °C. MS (EI, 70 eV): *m/z* 812 (M^+). X-ray-quality samples of **8** were obtained by recrystallization from a concentrated hexane solution at −30 °C.

Synthesis of $(\mathrm{C_5Me_5})_2\mathrm{U(CHPh_2)(I)}$ (10). A 125 mL sidearm flask equipped with a stir bar was charged with $(\mathrm{C_5Me_5})_2\mathrm{UI(THF)}$ (**1**; 0.25 g, 0.35 mmol) and tetrahydrofuran (50 mL). $\mathrm{KCHPh_2}$ (0.073 g, 0.35 mmol) was added to the dark green solution, and the reaction mixture was stirred at room temperature. After 12 h the reaction mixture was filtered through a Celite-padded coarse-porosity frit and CuI (0.33 g, 1.75 mmol) was added to the filtrate. The resulting mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered through a Celite-padded coarse-porosity frit and the volatiles were removed from the filtrate. The residue was extracted into hexane (50 mL) and the extract filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give **10** as a red solid (0.25 g, 0.31 mmol, 89%). ^{1}H NMR ($\mathrm{C_6D_6}$, 248 K): δ 33.03 (2H), 15.41 (2H), 7.80 (2H), 4.41 (30H, $\mathrm{C_5}Me_5$), 3.42 (1H), 0.93 (2H), −1.39 (1H), −50.01 (1H). Anal. Calcd for $\mathrm{C_{33}H_{41}IU}$ (mol wt 802.61): C, 49.38; H, 5.15. Found: C, 49.12; H, 5.35. Mp = 97−99 °C.

Synthesis of $(\mathrm{C_5Me_5})_2\mathrm{U}[\eta^2(N,C)\text{-}\mathrm{CH_2SiMe_2N(SiMe_3)}]$ (12). A 150 mL thick-walled Schlenk tube equipped with Teflon valve and a stir bar was charged with $(\mathrm{C_5Me_5})_2\mathrm{U[N(SiMe_3)_2](I)}$ (**6**; 0.25 g, 0.31 mmol) and toluene (50 mL). $\mathrm{Me_2Mg}$ (0.026 g, 0.47 mmol) was added as a white powder. The reaction vessel was sealed and removed from the drybox to a fume hood, where it was placed in a 50 °C oil bath. After 12 h, the reaction mixture was removed from heat, cooled to room temperature, and brought back into the drybox. The reaction mixture was filtered through a Celite-padded coarse-porosity frit, and the volatiles were removed from the filtrate. The residue was extracted into hexane (50 mL) and the extract filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give **12** as a red solid (0.19 g, 0.28 mmol, 90%). ^{1}H NMR ($\mathrm{C_6D_6}$, 298 K): δ 15.75 (6H, $\mathrm{Si}Me_2$), 5.56 (2H, $\mathrm{U{-}C}H_2\mathrm{Si}$), 1.99 (9H, $\mathrm{Si}Me_3$), 1.29 (30H, $\mathrm{C_5}Me_5$). Anal. Calcd for $\mathrm{C_{26}H_{47}NSi_2U}$ (mol wt 667.86): C, 46.76; H, 7.09; N, 2.10. Found: C, 48.11; H, 7.34; N, 1.91. Mp: 134−136 °C. MS (EI, 70 eV): *m/z* 667 (M^+). X-ray-quality samples of **12** were obtained by recrystallization from either a concentrated hexane or toluene solution at −30 °C.

Synthesis of $(\mathrm{C_5Me_5})_2\mathrm{U}[\eta^2(N,C)\text{-}(o\text{-}\mathrm{C_6H_4})\mathrm{NPh}]$ (16). A 150 mL thick-walled Schlenk tube equipped with a Teflon valve and a stir bar was charged with $(\mathrm{C_5Me_5})_2\mathrm{UMe_2}$ (**14**; 0.50 g, 0.92 mmol) and toluene (100 mL). Diphenylamine (0.16 g, 0.92 mmol) was added, and the reaction vessel was sealed and removed from the drybox to a fume hood, where it was placed in a 100 °C oil bath. After 12 h, the reaction mixture was removed from heat, cooled to room temperature, and brought back into the drybox. The reaction was filtered though a Celite-padded coarse-porosity frit, and the volatiles were removed from the filtrate. The crude product was extracted into hexane (50 mL), the extract was filtered through a Celite-padded coarse-porosity frit, and the volatiles were removed under reduced pressure to give **16** as a brown solid (0.57 g, 0.85 mmol, 92%). ^{1}H NMR ($\mathrm{C_6D_6}$, 298 K): δ 15.72 (1H, d, *J* = 8 Hz), 8.42 (1H, t, *J* = 8 Hz), 5.06 (2, t, *J* = 6 Hz), 2.92 (1H, t, *J* = 6 Hz), 0.89 (30H, $\mathrm{C_5}Me_5$), −7.91 (1H, d, *J* = 7 Hz), −11.27 (2H, d, *J* = 8 Hz), −25.08 (1H, d, *J* = 7 Hz). Anal. Calcd for $\mathrm{C_{32}H_{39}NU}$ (mol wt 675.69): C, 56.88; H, 5.82; N, 2.07. Found: C, 56.74; H, 5.70;

N, 2.27. Mp: 79−81 °C. MS (EI, 70 eV): *m/z* 675 (MH^+). X-ray-quality samples of **16** were obtained by recrystallization from a concentrated hexane solution at −30 °C.

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Supporting Information Available: >CIF files giving crystallographic details for complexes **2**, **6**, **8**, **12**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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