

# **Reactivity of Tuck-in and Tuck-over Uranium Metallocene Complexes**

Elizabeth Montalvo, Kevin A. Miller, Joseph W. Ziller, and William J. Evans\*

Department of Chemistry, University of California, Irvine, California 92697-2025

Received August 2, 2010

The reactivity of the uranium tuck-in and tuck-over cyclopentadienyl moieties {[ $\eta^5$ : $\eta^1$ -C<sub>5</sub>Me<sub>4</sub>- $CH_2[U]^{2+}$  and  $\{U[\mu-\eta^5:\eta^1-C_5Me_4CH_2]U\}^{6+}$ , respectively, has been investigated by examining the reactivity of  $(C_5Me_5)U[\mu-\eta^5:\eta^1:\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2U(C_5Me_5)_2$ , 1, and  $(C_5Me_5)(\eta^5:\eta^1-C_5Me_4-\eta^5)$  $CH_2$ )(hpp)U [(hpp)<sup>-</sup> = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinato], **2**, with hydrogen, silyl halide, sulfide, amine, and hydrocarbon reagents. The reactivity of 2, which has a single tuck-in reactive site, provides valuable comparisons with that of 1, where the presence of two hydride ligands as well as both tuck-in and tuck-over moieties leads to products in which multiple transformations have occurred. Both 1 and 2 react with H<sub>2</sub> to form hydrides, namely, the  $[(C_5Me_5)_2UH_2]_2/$  $[(C_5Me_5)_2UH]_2$  equilibrium mixture and  $(C_5Me_5)_2(hpp)UH$ , 3, respectively. Attempts to make a simple chloride derivative of 1 with Me<sub>3</sub>SiCl yielded a new tethered metallocene,  $(C_5Me_5)ClU$ - $(\eta^5$ -C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>- $\kappa$ C), **4**, which formally results from a silylmethyl C–H bond activation as well as insertion of the silyl group into the  $U-CH_2$  tuck-in linkage. The trivalent chloride  $[(C_5Me_5)_2UCl]_3$ , 5, is the byproduct of this reaction. This sequence of reactions is probably not initiated by the tuck-in functionality, since 2 does not react with Me<sub>3</sub>SiCl under comparable conditions. Hydride complex 3 reacts readily with Me<sub>3</sub>SiCl to form  $(C_5Me_5)_2(hpp)UCl$ , but  $(C_5Me_5)_2(hpp)UMe$ , 6, requires 100 °C to form the chloride. Complex 1 also displays complicated reactivity with HC=CPh, whereas 2 and 3 react with this substrate to form  $(C_5Me_5)_2(hpp)$ -U(C=CPh), 7, in high yield. Complex 1 converts PhSSPh cleanly to  $(C_5Me_5)_2U(SPh)_2$ , 8, in a reaction that involves S-S cleavage and C-H bond formation. Complex 1 reacts with a 1:1 mixture of PhSSPh and p-tolylSS-p-tolyl to form a 1:2:1 mixture of  $(C_5Me_5)_2U(SPh)_2$ , 8,  $(C_5Me_5)_2U(SPh)_2$ (S-p-tolyl), 9, and  $(C_5Me_5)_2U(S-p-tolyl)_2$ , 10, but the mechanistic implications are compromised by exchange of 8 with 10 to make 9. PhSH, a possible intermediate in a  $\sigma$ -bond metathesis reaction pathway for the 1/PhSSPh reaction, reacts with 1 to form 8. Complex 2 forms a  $\sigma$ -bond metathesis product,  $(C_5Me_4CH_2SPh)(C_5Me_5)(hpp)U(SPh)$ , 11, from PhSSPh that contains a new peralkylated cyclopentadienyl ligand. The reaction of 2 and PhSH forms  $(C_5Me_5)_2(hpp)U(SPh)$ , 12. Complexes 1 and 2 react similarly with PhNH<sub>2</sub> to generate amide products  $(C_5Me_5)_2U(NHPh)_2$ , 13, and  $(C_5Me_5)_2(hpp)_2$ U(NHPh), 14, respectively. No reactions were observed between complex 1 or 2 and methane, benzene, or toluene, but 1 and 2 react with CuI to form (C5Me5)2UI2, 15, and (C5Me5)2(hpp)UI, 16, respectively, in which the CH<sub>2</sub> tuck components have been converted to methyl groups.

#### Introduction

Recent studies of uranium metallocene hydride chemistry<sup>1</sup> generated the bimetallic uranium dihydride complex, **1**, shown in eq 1, which contains pentamethylcyclopentadienyl



ring that has undergone two C–H bond activation reactions to form the first example of a trianionic "tuck-in"<sup>2</sup> "tuck-over"<sup>3–6</sup>

ligand,  $[\mu - \eta^5: \eta^1: \eta^1 - C_5 Me_3(CH_2)_2]^{3-}$ . This complex also provided the first crystallographic evidence on f element tuck-in complexes 25 years after they were first invoked as intermediates in

- (6) Evans, W. J.; Champagne, T. M.; Ziller, J. W. J. Am. Chem. Soc. 2006, 128, 14270.
  - (7) Watson, P. L. J. Am. Chem. Soc. 1983, 105, 6491.
  - (8) Watson, P. L.; Parshall, G. W. Acc. Chem. Res. 1985, 18, 51.
  - (9) Bercaw, J. E. J. Am. Chem. Soc. 1974, 96, 5087.

<sup>\*</sup>Fax: 949-824-2210 Email: wevans@uci.edu.

<sup>(1)</sup> Evans, W. J.; Miller, K. A.; DiPasquale, A. G.; Rheingold, A. L.; Stewart, T. J.; Bau, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5075.

<sup>(2)</sup> Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. J. Am. Chem. Soc. **1987**, 109, 203.

<sup>(3)</sup> Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. Organometallics 1991, 10, 134.

<sup>(4)</sup> Booij, M.; Deelman, B. J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. Organometallics **1993**, *12*, 3531.

<sup>(5)</sup> Evans, W. J.; Perotti, J. M.; Ziller, J. W. Inorg. Chem. 2005, 44, 5820.

<sup>(10)</sup> Schock, L. E.; Brock, C. P.; Marks, T. J. Organometallics 1987, 6, 232.



C-H bond activation of alkanes, eq 2.<sup>7,8</sup> Although tuck-in structures were previously identified by X-ray crystallography



with transition metals<sup>9-16</sup> and several lanthanide tuck-over structures were found,<sup>3-6</sup> f element tuck-in complexes were elusive until **1** was identified.

Not only was the structure of complex **1** unique, it also had unusual reactivity. As shown in Scheme 1, it can function as a multielectron reductant in which the bimetallic compound provides four, six, or eight electrons depending on the substrate. The formal half-reaction for the tuck-in, tuckover, and hydride-based components of these reductions is shown in eq 3. This is an unusual reaction since it requires the hydride ligands to come together with the alkyl anions of the

$$[C_5Me_3(CH_2)_2]^{3-} + 2H^- \rightarrow (C_5Me_5)^- + 4e^-$$
 (3)

tuck-in tuck-over species and then give up electrons and form C-H bonds. This is unusual reactivity for f element

(16) Rybinskaya, M. I.; Kreindlin, A. Z.; Struchkov, Y. T.; Yanovskii, A. I. J. Organomet. Chem. 1989, 359, 233. complexes in which the hydride and alkyl ligands are highly polarized anions:  $R^-$  and  $H^- \rightarrow 2e^- + RH$  would not be expected to be favorable on electrostatic grounds. In fact, Scheme 1 and eq 3 provide the first examples of this type of reactivity with the f elements.

The type of reaction shown in eq 3 would not be considered out of the ordinary for transition metals where less polar bonds and two-electron metal-based redox couples are available. This would be a double reductive elimination reaction in which two C-H bonds are formed and four electrons are transferred to the two metals, Scheme 2a.

However, in the uranium case, this would generate an organometallic  $U^{2+}$  complex, a species that has not yet been isolated and definitively characterized.<sup>17–24</sup> As an alternative, this type of reductive elimination could occur stepwise, Scheme 2b, but this would still involve the unusual coupling of two anions. Obtaining detailed mechanistic data on these aspects of the reactivity of **1** has been challenging due to the presence of four reactive functionalities: the two uranium hydride bonds and the tuck-in and tuck-over alkyl uranium moieties.

<sup>(11)</sup> Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. Organometallics 1987, 6, 1219.

<sup>(12)</sup> Luinstra, G. A.; Teuben, J. H. J. Am. Chem. Soc. 1992, 114, 3361.
(13) Fischer, J. M.; Piers, W. E.; Young, V. G., Jr. Organometallics 1996, 15, 2410.

<sup>(14)</sup> Kreindlin, A. Z.; Dolgushin, F. M.; Yanovsky, A. I.; Kerzina, Z. A.; Petrovskii, P. V.; Rybinskaya, M. I. J. Organomet. Chem. 2000, 616, 106.

<sup>(15)</sup> Beweries, T.; Burlakov, V. V.; Bach, M. A.; Peitz, S.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Pathak, B.; Jemmis, E. D. Angew. Chem., Int. Ed. **2007**, *46*, 6907.

<sup>(17)</sup> Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. J. Am. Chem. Soc. **2000**, *122*, 6108.

<sup>(18)</sup> Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. J. Am. Chem. Soc. **1981**, 103, 6650.

<sup>(19)</sup> Warner, B. P.; Scott, B. L.; Burns, C. J. Angew. Chem., Int. Ed. **1998**, 37, 959.

 <sup>(20)</sup> Arunachalampillai, A.; Crewdson, P.; Korobkov, I.; Gambarotta,
 S. Organometallics 2006, 25, 3856.
 C. S. Franz, P. M. Marka, T. L. Dan, C. S. Wellman,

<sup>(21)</sup> Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. Organometallics **1982**, *1*, 170.

<sup>(22)</sup> Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. J. Am. Chem. Soc. 1979, 101, 5075.

<sup>(23)</sup> Korobkov, I.; Gambarotta, S.; Yap, G. P. A. Angew. Chem., Int. Ed. 2002, 41, 3433.

<sup>(24)</sup> Gambarotta, S.; Scott, J. Angew. Chem., Int. Ed. 2004, 43, 5298.



Recently, a second uranium tuck-in complex,  $(C_5Me_5)$ - $(\eta^5:\eta^1-C_5Me_4CH_2)(hpp)U^{25}$  [(hpp)<sup>-</sup> = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinato], **2**, was isolated, eq 4, that



provides an opportunity to investigate the reactivity of a single U<sup>4+</sup> tuck-in moiety in the absence of additional tuckover and hydride reactive sites as in 1. This report describes the reactivity of the single tuck-in moiety in 2 as well as a comparison of the reactivity of 1 and 2. A rare example of a monometallic uranium hydride,  $(C_5Me_5)_2(hpp)UH$ , 3, was synthesized in the course of these studies, and its reactivity is also described in comparison to that of 1 and 2. The overall study gives the first data on the reactivity of isolated, fully characterized, f element tuck-in complexes and has led to a new tethered uranium metallocene system.

### **Experimental Section**

The manipulations described below were conducted under argon with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium–potassium alloy, degassed by three freeze–pump–thaw cycles, and vacuum-transferred before use.  $(C_5Me_5)U[\mu-\eta^5:\eta^1:\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2U-(C_5Me_5)_2, 1, (C_5Me_5)(\eta^5:\eta^1-C_5Me_4CH_2)(hpp)U, 2, ^{25} (C_5Me_5)_2 (hpp)UR^{25} (R = Me, 6; Et), (C_5Me_5)_2U(SPh)_2, 8, ^{26} [(C_5Me_5)_2 UMe(OTf)]_2, ^{27} and (C_5Me_5)_2UCl_2^{18} were prepared according to$ literature methods. PhSSPh and*p*-tolylSS-*p*-tolyl (Sigma-Aldrich) were sublimed before use. PhSH,*p*-tolylSH, PhNH<sub>2</sub>, $aniline-<math>d_7$ , and HC=CPh (Sigma-Aldrich) were dried over activated 4 A molecular sieves and degassed by three freeze–pump– thaw cycles before use. KS-*p*-tolyl was prepared by deprotonation of *p*-tolylSH with 1 equiv of potassium bis(trimethylsilyl)amide in hexane. Potassium bis(trimethylsilyl)amide (Sigma-Aldrich) was extracted with toluene before use. Hydrogen gas (Praxair), Me<sub>3</sub>SiCl (Sigma-Aldrich), and CuI (Sigma-Aldrich) were used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX500 spectrometer at 25 °C. Due to the paramagnetism of uranium, only resonances that could be unambiguously identified are reported. Infrared spectra were recorded as KBr pellets on a Varian 1000 FTIR spectrophotometer at 25 °C. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS analyzer. GC-MS analyses were performed on a Thermo Trace MS+.

 $[(C_5Me_5)_2UH_x]_2$  from 1. On a high-vacuum line  $(10^{-5} \text{ Torr})$ , H<sub>2</sub> (1 atm) was introduced to a J-Young NMR tube containing a degassed, dark green solution of 1 (14 mg, 0.014 mmol) in C<sub>6</sub>D<sub>6</sub>. After 2 h, H<sub>2</sub> (1 atm) was reintroduced to the J-Young NMR tube to ensure all of the uranium reagent reacted. <sup>1</sup>H NMR spectroscopy showed quantitative conversion of 1 to the previously characterized  $[(C_5Me_5)_2UH_x]_2$  (x = 1, 2; 4.7:1 ratio observed).<sup>18</sup>

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(hpp)UH, 3, from (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(hpp)UEt. On a highvacuum line ( $10^{-5}$  Torr), H<sub>2</sub> (1 atm) was introduced to a Schlenk flask containing a degassed, dark red solution of (C5Me5)2-(hpp)UEt (220 mg, 0.325 mmol) in toluene (20 mL). After 2 h and again after 4 h, H<sub>2</sub> (1 atm) was subsequently reintroduced to the Schlenk flask to ensure all of the uranium reagent reacted. After the Schlenk flask was brought into a glovebox, solvent was removed under vacuum to yield 3 as a dark yellow solid (190 mg, 90%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  18.34 (s,  $\Delta \nu_{1/2}$  = 21 Hz, 2H,  $C_7H_{12}N_3$ ), 5.60 (s,  $\Delta v_{1/2} = 21$  Hz, 2H,  $C_7H_{12}N_3$ ), -0.67 (s,  $\Delta v_{1/2} = 14$  Hz, 30H, C<sub>5</sub>Me<sub>5</sub>), -8.00 (s,  $\Delta v_{1/2}$ 21 Hz, 2H,  $C_7H_{12}N_3$ ), -13.08 (s,  $\Delta v_{1/2} = 35$  Hz, 2H,  $C_7H_{12}N_3$ ), -18.00 (s,  $\Delta \nu_{1/2}$  = 30 Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), -34.91 (s,  $\Delta \nu_{1/2}$  = 31 Hz, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 59.2 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 53.3  $(C_7H_{12}N_3)$ , 50.2  $(C_5Me_5)$ , 28.9  $(C_7H_{12}N_3)$ , 9.7  $(C_7H_{12}N_3)$ , -99.9 (C7H12N3). IR: 2923s, 2899s, 2851s, 2720w, 1548s, 1502s, 1472w, 1452s, 1439m, 1379m, 1358w, 1319m, 1292m, 1260w, 1200s, 1146m, 1111w, 1064m, 1024m, 979w, 898w, 878w, 803w, 727m, 693w, 606w cm<sup>-1</sup>. Anal. Calcd for C<sub>27</sub>H<sub>43</sub>N<sub>3</sub>U: C, 50.07; N, 6.49; H, 6.69. Found: C, 50.15; N, 6.70; H, 6.43.

 $(C_5Me_5)_2(hpp)UD$ , **3D**, from  $(C_5Me_5)_2(hpp)UEt$ . On a highvacuum line  $(10^{-5} \text{ Torr})$ ,  $D_2$  (1 atm) was introduced to a J-Young NMR tube containing a degassed, dark red solution of  $(C_5Me_5)_2(hpp)UEt$  (18 mg, 0.027 mmol) in  $C_6D_6$ . <sup>1</sup>H NMR spectroscopy showed quantitative conversion of starting material to **3D** and deuterium incorporation into the  $(C_5Me_5)^-$  and  $(hpp)^-$  ligands. Only a broad resonance at -0.64 ppm was observed in the <sup>2</sup>H NMR spectrum, consistent with deuterium in the  $(C_5Me_5)^-$ . IR: 2925s, 2897s, 2850s, 2725w, 1546s, 1501s, 1471w, 1452s, 1439m, 1380m, 1359w, 1319m, 1291m, 1260w,

<sup>(25)</sup> Evans, W. J.; Montalvo, E.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *Organometallics* **2010**, *29*, 2104.

<sup>(26)</sup> Lescop, C.; Arliguie, T.; Lance, M.; Nierlich, M.; Ephritikhine, M. J. Organomet. Chem. 1999, 580, 137.

<sup>(27)</sup> Evans, W. J.; Walensky, J. R.; Furche, F.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *Inorg. Chem.* **2008**, *47*, 10169.

1201s, 1146m, 1111w, 1064m, 1025m, 979w, 879w, 808w, 727m, 693w, 605w cm<sup>-1</sup>.

 $(C_5Me_5)_2(hpp)UH$ , 3, from 2. On a high-vacuum line  $(10^{-5}$  Torr), H<sub>2</sub> (1 atm) was introduced to a J-Young NMR tube containing a degassed, brown solution of 2 (16 mg, 0.025 mmol) in C<sub>6</sub>D<sub>6</sub>. After 2 h and again after 4 h, H<sub>2</sub> (1 atm) was subsequently reintroduced to the Schlenk flask to ensure all of the uranium reagent reacted. <sup>1</sup>H NMR spectroscopy showed quantitative conversion of starting material to 3.

 $(C_5Me_5)_2(hpp)UCl$  from 3. Me<sub>3</sub>SiCl (3  $\mu$ L, 0.02 mmol) was added to a J-Young NMR tube containing 3 (15 mg, 0.023 mmol) in C<sub>6</sub>D<sub>6</sub>. The J-Young NMR tube was immediately capped. <sup>1</sup>H NMR spectroscopy showed quantitative conversion of starting material to the previously characterized (C<sub>5</sub>-Me<sub>5</sub>)<sub>2</sub>(hpp)UCl.<sup>28</sup> Me<sub>3</sub>SiH was identified by GC-MS.

 $(C_5Me_5)_2(hpp)UCl$  from  $(C_5Me_5)_2(hpp)UMe$ , 6. Me<sub>3</sub>SiCl  $(2 \mu L, 0.02 \text{ mmol})$  was added to a J-Young NMR tube containing 6 (7 mg, 0.01 mmol) in C<sub>6</sub>D<sub>6</sub>. The J-Young NMR tube was immediately capped. <sup>1</sup>H NMR spectroscopy showed the presence of starting material and resonances consistent with the formation of  $(C_5Me_5)_2(hpp)UCl^{28}$  and Me<sub>4</sub>Si. Upon heating the reaction mixture to 100 °C for 12 h, complete conversion of 6 to  $(C_5Me_5)_2(hpp)UCl^{28}$  was observed.

 $(C_5Me_5)CIU(\eta^5-C_5Me_4CH_2SiMe_2CH_2-\kappa C), 4. Me_3SiCl(76 \mu L),$ 0.60 mmol) was added via syringe to a stirred, dark green solution of 1 (307 mg, 0.302 mmol) in toluene (15 mL). After stirring for 24 h, the dark red solution was centrifuged, separated from a green insoluble powder, and evaporated to dryness, yielding a dark red oil, which was subsequently extracted with pentane to yield 4 as a dark red solid (120 mg, 49%). Dark red crystals of 4 suitable for X-ray diffraction were grown from a concentrated hexane solution at  $-35 \,^{\circ}$ C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.99 (s,  $\Delta \nu_{1/2} = 47$  Hz, 15H, C<sub>5</sub>Me<sub>5</sub>), -4.38 (s,  $\Delta v_{1/2} = 23$  Hz, 2H), -8.91 (s,  $\Delta v_{1/2} =$ 21 Hz, 3H), -16.92 (s,  $\Delta v_{1/2} = 160$  Hz, 3H), -17.68 (s,  $\Delta v_{1/2} = 96$  Hz, 3H), -19.57 (s,  $\Delta v_{1/2} = 106$  Hz, 3H).  $^{13}$ C NMR (C<sub>6</sub>D<sub>6</sub>): δ -21.4 (C<sub>5</sub>Me<sub>5</sub>). IR: 2947s, 2902s, 2859s, 2726w, 1487m, 1438m, 1380m, 1246m, 1164m, 1062w, 1021m, 980w, 856s, 803m, 765w, 722w, 693w cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>37</sub>ClSiU: C, 44.98; H, 6.07. Found: C, 45.08; H, 6.26. The green insoluble byproduct was transferred to a vial using small portions of toluene. The solvent was evaporated to dryness to yield a green powder (90 mg, 14%). The green powder was identified as  $[(C_5Me_5)_2UCl]_3^{22}$  5, on the basis of its <sup>1</sup>H NMR spectrum in THF- $d_8$ , which matched that of  $(C_5Me_5)_2UCl(THF)$ . In a separate experiment in a NMR tube capped with a rubber septum, the volatiles were removed with a syringe, analyzed by GC-MS, and found to contain Me<sub>3</sub>SiH. A J & W Scientific DB-5 column (30 m  $\times$  0.32 mm i.d.  $\times$  0.25  $\mu$ m film thickness) was used with a temperature ramp of 35 °C for 1 min and then 10 °C per min to 290 °C.

 $(C_5Me_5)_2(hpp)U(C \equiv CPh)$ , 7, from 2.  $HC \equiv CPh$  (2  $\mu L$ , 0.02 mmol) was added to a J-Young NMR tube containing 2 (14 mg, 0.022 mmol) in C<sub>6</sub>D<sub>6</sub>. The J-Young tube was capped, and a color change from brown to dark yellow was observed immediately. <sup>1</sup>H NMR spectroscopy showed quantitative conversion of starting material to the previously characterized  $(C_5Me_5)_2(hpp)$ - $U(C \equiv CPh)$ , 7.<sup>25</sup>

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(hpp)U(C=CPh), 7, from 3. HC=CPh (1  $\mu$ L, 0.01 mmol) was added to a J-Young NMR tube containing 3 (7 mg, 0.01 mmol) in C<sub>6</sub>D<sub>6</sub>. The J-Young NMR tube was immediately capped. <sup>1</sup>H NMR spectroscopy showed quantitative conversion of starting material to (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(hpp)U(C=CPh),<sup>25</sup> 7, and a resonance consistent with the formation of H<sub>2</sub> at 4.46 ppm was also observed.

 $(C_5Me_5)_2U(SPh)_2$ , 8, from 1. PhSH (3  $\mu$ L, 0.03 mmol) was added to a J-Young NMR tube containing 1 (7 mg, 0.007 mmol) in  $C_6D_6$ . The J-Young NMR tube was capped, and a color

change from dark green to dark red was observed immediately. <sup>1</sup>H NMR spectroscopy showed the quantitative conversion of starting material to previously characterized (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>-U(SPh)<sub>2</sub>.<sup>26</sup>

(C5Me5)2U(SPh)(S-p-tolyl), 9. PhSH (67 µL, 0.65 mmol) was added to a stirred, dark red solution of  $[(C_5Me_5)_2UMe(OTf)]_2^{27}$ (399 mg, 0.594 mmol) in toluene (15 mL). After the reaction mixture was stirred for 12 h, solvent was removed under vacuum, leaving (C5Me5)2U(SPh)(OTf) as a dark red solid (420 mg, 92%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  12.96 (s,  $\Delta \nu_{1/2} = 22$  Hz, 30H, C<sub>5</sub>*Me*<sub>5</sub>), 0.88 (s,  $\Delta \nu_{1/2} = 15$  Hz, 2H, *Ph*), 0.44 (s,  $\Delta \nu_{1/2} = 19$  Hz, 2H, *Ph*), -6.83 (s,  $\Delta \nu_{1/2} = 18$  Hz, 1H, *Ph*). <sup>13</sup>C NMR  $(C_6D_6)$ :  $\delta$  134.2 (*Ph*), 100.7 (*Ph*), 84.7 (*Ph*), -23.9 ( $C_5Me_5$ ). IR: 3050w, 2986m, 2952m, 2906m, 2860m, 2728w, 1579w, 1471w, 1448w, 1437w, 1355s, 1238s, 1192s, 1162m, 1085w, 1067w, 1024w, 1011m, 983s, 959m, 804w, 766w, 742m, 698m, 632s, 587w, 521w, 504w, 479w, 430w cm<sup>-1</sup>. Subsequently, KS-*p*-tolyl (38 mg, 0.23 mmol) was added to a stirred solution of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>-U(SPh)(OTf) (150 mg, 0.19 mmol) in toluene (15 mL). After the reaction mixture was stirred for 12 h, an insoluble material was removed from the mixture via centrifugation and filtration. Solvent was removed under vacuum, leaving a dark red solid that had a  $^{1}H$  NMR spectrum consistent with the formation of 8, **9** [<sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$  12.82 (s,  $C_5Me_5$ ); other resonances could not be definitively differentiated from those of 8 and 10], and  $(C_5Me_5)_2U(S-p-tolyl)_2$ , 10, in a 1:2.4:1.7 ratio.

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(S-*p*-tolyl)<sub>2</sub>, 10. KS-*p*-tolyl (154 mg, 0.949 mmol) was added to a stirred, dark red solution of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>UCl<sub>2</sub> (262 mg, 0.452 mmol) in toluene (15 mL). After the reaction mixture was stirred for 12 h, an insoluble material was removed from the mixture via centrifugation and filtration. Solvent was removed under vacuum to yield 10 as a dark red solid (288 mg, 84%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 12.70 (s,  $\Delta \nu_{1/2} = 22$  Hz, 30H, C<sub>5</sub>Me<sub>5</sub>), 2.42 (s,  $\Delta \nu_{1/2} = 5$  Hz, 6H, Me), 0.27 (s,  $\Delta \nu_{1/2} = 10$  Hz, 4H, Ph), -32.32 (s,  $\Delta \nu_{1/2} = 27$  Hz, 4H, Ph). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 146.0 (Ph), 102.0 (Ph), 12.9 (Me), -23.9 (C<sub>5</sub>Me<sub>5</sub>). IR: 2972s, 2904s, 2861s, 2728w, 1596w, 1559w, 1488s, 1448m, 1378m, 1243w, 1210w, 1181w, 1120w, 1086s, 1016m, 980w, 842w, 807s, 732s, 696m, 628m, 491w cm<sup>-1</sup>. Anal. Calcd for C<sub>34</sub>H<sub>44</sub>S<sub>2</sub>U: C, 54.10; H, 5.88. Found: C, 53.51; H, 5.86.

(C5Me4CH2SPh)(C5Me5)(hpp)U(SPh), 11. PhSSPh (71 mg, 0.32 mmol) was added to a stirred, brown solution of 2 (209 mg, 0.324 mmol) in toluene (10 mL). After the reaction mixture was stirred for 12 h, solvent was removed under vacuum and a tacky orange solid was obtained, which was triturated with hexane to yield 11 as an orange solid (210 mg, 76%). Orange crystals of 11 suitable for X-ray diffraction were grown from a concentrated ether solution at  $-35 \,^{\circ}$ C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  10.42 (s,  $\Delta v_{1/2}$  = 36 Hz, 1H, Ph), 9.27 (s,  $\Delta v_{1/2} = 27$  Hz, 1H, Ph), 8.57 (s,  $\Delta v_{1/2} =$ 30 Hz, 1H, *Ph*), 8.27 (s,  $\Delta v_{1/2} = 15$  Hz, 2H, C<sub>7</sub>*H*<sub>12</sub>N<sub>3</sub>), 7.41 (s,  $\Delta v_{1/2} = 14$  Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 6.32 (s,  $\Delta v_{1/2} = 10$  Hz, 3H,  $C_5Me_4CH_2SPh$ ), 6.04 (s,  $\Delta v_{1/2} = 9$  Hz, 3H,  $C_5Me_4CH_2SPh$ ), 4.89 (s,  $\Delta v_{1/2} = 8$  Hz, 15H, C<sub>5</sub>Me<sub>5</sub>), 3.98 (s,  $\Delta v_{1/2} = 11$  Hz, 3H, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>SPh), 3.54 (s,  $\Delta v_{1/2} = 28$  Hz, 1H, Ph), 2.59 (s,  $\Delta v_{1/2} = 14$  Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 0.86 (s,  $\Delta v_{1/2} = 11$  Hz, 3H,  $C_5 M e_4 CH_2 SPh$ ), 0.26 (s,  $\Delta v_{1/2} = 30$  Hz, 1H, Ph), -0.21 (s,  $\Delta v_{1/2} = 18$  Hz, 1H, Ph), -1.12 (s,  $\Delta v_{1/2} = 30$  Hz, 1H, Ph), -1.36(s,  $\Delta v_{1/2} = 38$  Hz, 1H, Ph), -1.62 (s,  $\Delta v_{1/2} = 18$  Hz, 2H,  $C_7 H_{12} N_3$ , -2.12 (s,  $\Delta v_{1/2}$  = 36 Hz, 1H, Ph), -3.85 (s,  $\Delta v_{1/2}$  = 21 Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), -4.17 (s,  $\Delta \nu_{1/2} = 16$  Hz, 1H, Ph), -26.24 (s,  $\Delta \nu_{1/2} = 23$  Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  149.8  $(C_7H_{12}N_3)$ , 130.8  $(C_7H_{12}N_3)$ , 129.7  $(C_7H_{12}N_3)$ , 125.8 (Ph), 107.2 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 55.9 (Ph), 54.9 (Ph), 47.2 (Ph), 39.1 (Ph), 4.7 (Ph), -15.2 (Ph), -18.6  $(C_7H_{12}N_3)$ , -31.8  $(C_5Me_4SPh)$ , -34.8 (C<sub>5</sub>Me<sub>4</sub>SPh), -38.4 (C<sub>5</sub>Me<sub>4</sub>SPh), -36.6 (Ph), -41.3 (C<sub>5</sub>Me<sub>5</sub>), -46.4 (C<sub>5</sub>Me<sub>4</sub>SPh), -59.2 (Ph), -62.6 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>). IR: 3048w, 2928s, 2900s, 2851s, 2721w, 1623m, 1574m, 1550s, 1491m, 1472m, 1438s, 1377m, 1317s, 1298m, 1257m, 1208s, 1143m, 1110w, 1081m, 1053w, 1024s, 997w, 997w, 979w, 900w, 880w, 842w, 816w, 738s, 650s, 614w, 534w, 475m, 425w cm<sup>-1</sup>. Anal.

<sup>(28)</sup> Evans, W. J.; Montalvo, E.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *Inorg. Chem.* **2010**, *49*, 222.

Calcd for C<sub>38</sub>H<sub>49</sub>N<sub>3</sub>S<sub>2</sub>U: C, 53.70; N, 4.94; H, 5.81. Found: C, 53.26; N, 5.43; H, 5.95.

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(hpp)U(SPh), 12, from (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(hpp)UMe, 6. PhSH  $(46\,\mu\text{L}, 0.45\,\text{mmol})$  was added to a stirred, dark yellow solution of  $\mathbf{6}^{28}$  (296 mg, 0.447 mmol) in toluene (15 mL). After the reaction mixture was stirred for 12 h, solvent was removed under vacuum, leaving 12 as an orange solid (303 mg, 90%). Yellow crystals of 12 suitable for X-ray diffraction were grown from a concentrated toluene solution at  $-35 \,^{\circ}$ C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 31.50 (s,  $\Delta v_{1/2} = 22$  Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 9.31 (s,  $\Delta v_{1/2} = 18$  Hz, 2H,  $C_7H_{12}N_3$ ), 7.58 (s,  $\Delta v_{1/2} = 12$  Hz, 2H,  $C_7H_{12}N_3$ ), 5.64 (s,  $\Delta v_{1/2} = 9$  Hz, 30H, C<sub>5</sub>Me<sub>5</sub>), 3.83 (s,  $\Delta v_{1/2} = 8$  Hz, 2H, Ph), -0.47 (s,  $\Delta v_{1/2} = 15$  Hz, 1H, *Ph*), -1.29 (s,  $\Delta v_{1/2} = 18$  Hz, 2H, C<sub>7</sub>-H<sub>12</sub>N<sub>3</sub>), -1.98 (s,  $\Delta v_{1/2} = 17$  Hz, 2H, *Ph*), -4.25 (s,  $\Delta v_{1/2} = 16$ Hz, 2H,  $C_7H_{12}N_3$ ), -27.80 (s,  $\Delta\nu_{1/2} = 26$  Hz,  $C_7H_{12}N_3$ ). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 147.3 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 123.5 (Ph), 105.9 (Ph), 55.2  $(C_7H_{12}N_3)$ , 54.3  $(C_7H_{12}N_3)$ , 46.1 (*Ph*), 37.1  $(C_7H_{12}N_3)$ , 32.3 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 0.90 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), -39.1 (C<sub>5</sub>Me<sub>5</sub>). IR: 3058w, 2949s, 2898s, 2850s, 2719w, 1637m, 1574m, 1549s, 1494s, 1472s, 1451s, 1379s, 1319s, 1291m, 1269m, 1201s, 1144m, 1111w, 1082m, 1056m, 1025m, 901w, 898w, 876w, 806w, 739s, 696s, 549w cm<sup>-1</sup> Anal. Calcd for C<sub>33</sub>H<sub>47</sub>N<sub>3</sub>SU: C, 52.44; N, 5.56; H, 6.27. Found: C, 52.50; N, 5.86; H, 5.91. Crystal system: tetragonal; space group:  $P4_3$ ; unit cell dimensions a = 11.2897(12) Å, b = 11.2897(12) Å,

c = 47.192(5) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 90^{\circ}$ ,  $\gamma = 90^{\circ}$ ; V = 6015.0(11) Å<sup>3</sup>. (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(hpp)U(SPh), 12, from 2. PhSH (3  $\mu$ L, 0.03 mmol) was added to a J-Young NMR tube containing 2 (18 mg, 0.028 mmol) in C<sub>6</sub>D<sub>6</sub>. The J-Young tube was capped, and a color change from brown to orange was observed. <sup>1</sup>H NMR spectros-copy showed quantitative conversion of starting material to 12.

 $(C_5Me_5)_2(hpp)U(SPh)$ , 12, from 3 and PhSH. PhSH (2  $\mu$ L, 0.02 mmol) was added to a J-Young NMR tube containing 3 (10 mg, 0.02 mmol) in C<sub>6</sub>D<sub>6</sub>. The J-Young NMR tube was capped, and a color change from dark yellow to orange was observed immediately. <sup>1</sup>H NMR spectroscopy showed quantitative conversion of starting material to 12, and a resonance consistent with the formation of H<sub>2</sub> was also observed.

 $(C_5Me_5)_2(hpp)U(SPh)$ , 12, from 3 and PhSSPh. PhSSPh (3 mg, 0.02 mmol) was added to a J-Young NMR tube containing 3 (9 mg, 0.01 mmol) in  $C_6D_6$ . The J-Young NMR tube was capped, and a color change from dark yellow to orange was observed immediately. <sup>1</sup>H NMR spectroscopy showed quantitative conversion of starting material to 12, and resonances consistent with the formation of PhSH were also observed.

 $(C_5Me_5)_2U(NHPh)_2$ , 13. PhNH<sub>2</sub> (20  $\mu$ L, 0.2 mmol) was added to a stirred, dark green solution of 1 (57 mg, 0.056 mmol) in toluene (10 mL). After the reaction mixture was stirred for 12 h, solvent was removed under vacuum, affording a dark orange oil, which was extracted with hexane to yield 13 as a dark orange solid (28 mg, 36%). The identity of 13 was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that of the previously characterized (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(NHPh)<sub>2</sub>.<sup>29</sup> A resonance consistent with the formation of H<sub>2</sub> was observed in the <sup>1</sup>H NMR spectrum when a similar reaction was carried out in a sealed J-Young NMR tube.

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(hpp)U(NHPh), 14. PhNH<sub>2</sub> (26  $\mu$ L, 0.28 mmol) was added to a stirred, brown solution of 2 (183 mg, 0.0283 mmol) in toluene (10 mL). After the reaction mixture was stirred for 12 h, solvent was removed under vacuum, and a tacky light orange solid was obtained, which was triturated with hexane to yield 14 as a light orange solid (159 mg, 75%). Gold crystals of 14 suitable for X-ray diffraction were grown from a concentrated toluene solution at  $-35 \,^{\circ}$ C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  30.15 (s,  $\Delta \nu_{1/2} =$ 37 Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 28.92 (s,  $\Delta \nu_{1/2} =$  24 Hz, 1H, *Ph*), 22.38 (s,  $\Delta \nu_{1/2} =$  25 Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 5.13 (s,  $\Delta \nu_{1/2} =$  15 Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 0.22 (s,  $\Delta \nu_{1/2} =$  7 Hz, 30H, C<sub>5</sub>Me<sub>5</sub>), -2.37 (s,  $\Delta \nu_{1/2} =$  9 Hz, 2H, *Ph*), -3.24 (s,  $\Delta \nu_{1/2} =$  11 Hz, 2H, *Ph*), -3.54 (s,  $\Delta \nu_{1/2} =$  13 Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), -7.27 (s,  $\Delta \nu_{1/2} =$  20 Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), -9.06 (s,  $\Delta \nu_{1/2} =$  18 Hz, 2H, C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  135.2 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 84.9 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 52.2 (*Ph*), 47.9 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 40.4 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), 27.6 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), -24.7 (C<sub>7</sub>H<sub>12</sub>N<sub>3</sub>), -49.8 (C<sub>5</sub>*Me*<sub>5</sub>), -62.6 (*Ph*), -70.8 (*Ph*). IR: 3331w, 2942s, 2924s, 2897s, 2850s, 2722w, 1618m, 1591s, 1570w, 1544s, 1498m, 1486m, 1540m, 1438m, 1379m, 1357w, 1319m, 1290m, 1274s, 1207m, 1172w, 1144m, 1112w, 1059m, 1026m, 992w, 902w, 837m, 804w, 754m, 725m, 697m, 622w, 580m, 495w, 460w cm<sup>-1</sup>. Anal. Calcd for C<sub>33</sub>H<sub>48</sub>N<sub>4</sub>U: C, 53.65; N, 7.58; H, 6.55. Found: C, 53.59; N, 7.47; H, 6.26.

 $(C_5Me_5)_2(hpp)U(NHPh)$ , 14, from 3. PhNH<sub>2</sub> (2µL, 0.02 mmol) was added to a J-Young NMR tube containing 3 (10 mg, 0.02 mmol) in C<sub>6</sub>D<sub>6</sub>. The J-Young NMR tube was capped, and a color change from dark yellow to orange was observed immediately. <sup>1</sup>H NMR spectroscopy showed quantitative conversion of starting material to 14 and a resonance consistent with the formation of H<sub>2</sub> was also observed.

 $(C_5Me_5)_2UI_2$ , 15. CuI (43 mg, 0.22 mmol) was added to a stirred, dark green solution of 1 (58 mg, 0.057 mmol) in toluene (10 mL). After the reaction mixture was stirred for 12 h, an insoluble material was removed from the mixture via centrifugation and filtration. Solvent was removed under vacuum, leaving 15 as a dark red solid (64 mg, 74%). The identity of 15 was confirmed by comparison of its <sup>1</sup>H NMR spectrum with that of the previously characterized ( $C_5Me_5)_2UI_2$ .<sup>30</sup> Anal. Calcd for  $C_{20}H_{30}I_2U$ : C, 31.51; H, 3.97. Found: C, 31.80; H, 3.52.

 $(C_5Me_5)_2(hpp)UI$ , 16, from 2. CuI (7 mg, 0.04 mmol) was added to a J-Young NMR tube containing 2 (12 mg, 0.018 mmol) in  $C_6D_6$ . The J-Young NMR tube was immediately capped. <sup>1</sup>H NMR spectroscopy showed the formation of the previously characterized ( $C_5Me_5$ )<sub>2</sub>(hpp)UI<sup>25</sup> (23% when Me<sub>4</sub>Si was used as an internal standard) along with other products.

 $(C_5Me_5)_2(hpp)UI$ , 16, from 3. CuI (8 mg, 0.01 mmol) was added to a J-Young NMR tube containing 3 (2 mg, 0.01 mmol) in  $C_6D_6$ . The J-Young NMR tube was immediately capped. <sup>1</sup>H NMR spectroscopy showed the quantitative conversion of starting material to previously characterized ( $C_5Me_5)_2(hpp)UI$ .<sup>25</sup>

X-ray Data Collection, Structure Determination, and Refinement. Crystallographic information on complexes 4, 11, 12, and 14 is summarized in the Supporting Information and Table 1.

#### Results

**Reactions with H<sub>2</sub>.** Since hydrogenolysis of M–C bonds is a characteristic reaction of alkyl complexes of lanthanides and actinides, <sup>18,31–33</sup> the reactivity of **1** and **2** with H<sub>2</sub> was examined. Hydrogen (1 atm) reacts with **1** within 10 min to generate a solution with a complicated <sup>1</sup>H NMR spectrum. However, over the course of 72 h, the spectrum simplifies and only the equilibrium mixture of  $[(C_5Me_5)_2UH_2]_2$  and  $[(C_5Me_5)_2UH]_2$  is observed, <sup>18</sup> eq 5. This is the reverse of the reaction that forms **1**.



Reaction of 1 with  $D_2$  gives products with a <sup>1</sup>H NMR spectrum that is consistent with deuterium incorporation

<sup>(30)</sup> Maynadie, J.; Berthet, J.-C.; Thuery, P.; Ephritikhine, M. Organometallics 2006, 25, 5603.

<sup>(31)</sup> Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. J. Am. Chem. Soc. 1983, 105, 1401.

<sup>(32)</sup> Evans, W. J.; Seibel, C. A.; Ziller, J. W. J. Am. Chem. Soc. 1998, 120, 6745.

<sup>(33)</sup> Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. J. Am. Chem. Soc. **1982**, 104, 2008.

Table 1. X-ray Data Collection Parameters for (0)	$C_5Me_5$ )ClU( $\eta^{\circ}$ - $C_5Me_4CH_2SiN$	$Ae_2CH_2$ - $\kappa C$ ), 4, (C <sub>5</sub> Me <sub>4</sub> CH)	<sub>2</sub> SPh)(C <sub>5</sub> Me <sub>5</sub> )(hpp)U(SPh),
$11, (C_5Me_5)_2$	$_{2}(hpp)U(SPh), 12, and (C_{5}Me_{5})$	) <sub>2</sub> (hpp)U(NHPh), 14	

empirical formula	C23H37ClSiU, 4	$C_{39}H_{51}N_3S_2U$ , 11	$C_{33}H_{47}N_3SU$ , 12	$C_{33}H_{48}N_4U$ , 14
fw	615.10	863.98	755.83	738.78
temperature (K)	153(2)	93(2)	93(2)	93(2)
cryst syst	monoclinic	monoclinic	tetragonal	monoclinic
space group	$P2_1/c$	$P2_1/c$	P43	$P2_1/c$
a (Å)	9.7385(10)	10.0722(4)	11.2897(12)	17.855(2)
$b(\mathbf{A})$	15.5793(16)	17.4433(7)	11.2897(12)	10.7301(14)
$c(\dot{A})$	16.2137(16)	20.8522(9)	47.192(5)	17.385(2)
a (deg)	90	90	90	90
$\beta$ (deg)	104.249(2)	102.2811(5)	90	112.6683(16)
$\gamma$ (deg)	90	90	90	90
volume ( $Å^3$ )	2384.2(4)	3579.7(3)	6015.0(11)	3073.4(7)
Z	4	4	8	4
$\rho_{\text{calcd}}$ (Mg/m <sup>3</sup> )	1.714	1.603	1.669	1.597
$\mu (\text{mm}^{-1})$	6.975	4.682	5.493	5.309
$R1^a (I > 2.0\sigma(I))$	0.0203	0.0248	0.0722	0.0297
wR2 <sup><math>b</math></sup> (all data)	0.0486	0.0516	0.1776	0.0818

 ${}^{a}\mathbf{R}\mathbf{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}\mathbf{w}\mathbf{R}\mathbf{2} = [\sum [w(F_{o}{}^{2} - F_{c}{}^{2})^{2} / \sum [w(F_{o}{}^{2})^{2}]]^{1/2}.$ 

into the  $(C_5Me_5)^-$  ligands, as was previously observed with mixtures of  $[(C_5Me_5)_2UH_2]_2$  and  $[(C_5Me_5)_2UH]_2$ .<sup>18</sup>

Tuck-in complex 2 also reacts with  $H_2$  and generates the terminal hydride  $(C_5Me_5)_2(hpp)UH$ , 3, eq 6. Complex 3 reverts back to 2 upon heating to 110 °C.



Complex 3 can also be generated by hydrogenolysis of the ethyl complex  $(C_5Me_5)_2(hpp)UEt$ , eq 7. Since the ethyl complex is the precursor to 2, complex 3 is more directly made from  $(C_5Me_5)_2(hpp)UEt$ .



Complex **3** had an elemental analysis and spectroscopic characteristics consistent with its formulation as  $(C_5Me_5)_2$ -(hpp)UH, but single crystals suitable for X-ray crystallography were not obtained. Terminal U<sup>4+</sup> hydrides are rare, <sup>34–38</sup> and the only crystallographically characterized examples are  $(C_5H_4^{T}Bu)_3UH^{34}$  and  $[(Me_3Si)_2N]_3UH^{.35}$  Complex **3**, as well as the other new (hpp)<sup>-</sup> complexes described below, **11**, **12**, and **14**, have six (hpp)<sup>-1</sup>H NMR resonances with widespread chemical shifts as well as one  $(C_5Me_5)^-$  resonance. The hydride resonance of **3** could not be located in this paramagnetic system. When the reaction of  $(C_5Me_5)_2$ (hpp)UEt with D<sub>2</sub> was carried out to make **3D**, deuterium incorporation

into the  $(C_5Me_5)^-$  and  $(hpp)^-$  ligands was observed by <sup>1</sup>H NMR spectroscopy. The infrared spectrum of **3D** was similar to that of **3**.<sup>1</sup>

**Reactions with Me<sub>3</sub>SiCl.** The presence of the hydride ligand in **3** was supported by the reaction of **3** with Me<sub>3</sub>SiCl. As shown in eq 8,  $(C_5Me_5)_2(hpp)UCl^{28}$  was formed and the byproduct Me<sub>3</sub>SiH was detected by GC-MS.



The reaction of 1 with Me<sub>3</sub>SiCl was attempted to obtain a simple derivative with chloride in place of hydride,<sup>39</sup> as was done in eq 8. Alternatively, if 1 reacted as shown in Scheme 2a, products such as  $(C_5Me_5)_2UCl_x(SiMe_3)_y$  (x + y = 2) could result. Uranium chloride bonds do form in this reaction, but the reaction was much more complicated than the two possibilities just presented. The complexity of the reaction demonstrated the potential of the multiple reactive sites in 1 to work in concert to generate unusual results. Specifically, this reaction generates a new type of tethered metallocene,  $(C_5Me_5)CIU(\eta^5-C_5Me_4-CH_2SiMe_2CH_2-\kappa C)$ , **4**, as a major product in which a "Me<sub>2</sub>-SiCH<sub>2</sub>" unit has been inserted into a uranium–methylene bond of the original tuck-in structure, eq 9.



Complex 4 was characterized by spectroscopic and analytical means, and the structure of the tethered cyclopentadienyl

<sup>(34)</sup> Berthet, J. C.; Le Marechal, J. F.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. J. Chem. Soc., Dalton Trans. 1992, 1573.

<sup>(35)</sup> Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1981**, 20, 622.

<sup>(36)</sup> Berthet, J. C.; Le Marechal, J. F.; Ephritikhine, M. J. Chem. Soc., Chem. Commun. 1991, 360.

<sup>(37)</sup> Turner, H. W.; Simpson, S. J.; Andersen, R. A. J. Am. Chem. Soc. 1979, 101, 2782.

<sup>(38)</sup> Baudry, D.; Ephritikhine, M. J. Organomet. Chem. 1988, 349, 123.

<sup>(39)</sup> Reddy, N. D.; Kumar, S. S.; Roesky, H. W.; Vidovic, D.; Magull, J.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem.* **2003**, 442.



**Figure 1.** Thermal ellipsoid plot of  $(C_5Me_5)ClU(\eta^5-C_5Me_4-CH_2SiMe_2CH_2-\kappa C)$ , **4**, drawn at the 50% probability level with hydrogen atoms omitted for clarity.

alkyl ligand ( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>- $\kappa$ C)<sup>2-</sup> was established by X-ray crystallography, Figure 1. The closest related cyclopentadienyl uranium complex, ( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>CH<sub>2</sub>- $\kappa$ C)<sub>2</sub>U,<sup>40</sup> contains ( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>CH<sub>2</sub>- $\kappa$ C)<sup>2-</sup> ligands that differ by a CH<sub>2</sub> unit and were formed by metalation of the silyl group in a (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)<sup>-</sup> precursor. An additional product isolated from the reaction of **1** with Me<sub>3</sub>SiCl is the previously reported trivalent uranium chloride complex [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>UCl]<sub>3</sub>, **5**.<sup>22</sup> Crystallographic data on **4** and the other new complexes reported in this paper fall in the normal ranges and are described in detail only in the Supporting Information.

The reaction observed between 1 and Me<sub>3</sub>SiCl was not simply a " $(C_5Me_5)_2U$ " to  $(C_5Me_5)_2UCl_x(SiMe_3)_v$  conversion, and it appeared that multiple reaction pathways are accessible with this polyfunctional compound. The product composition indicates that C-H bond activation reactivity involving the Me<sub>3</sub>Si group as well as insertion chemistry with the silyl group occurred. C-H bond formation is also indicated since only one of the CH<sub>2</sub> groups in 1 remains in the products. This indicates that one of the tuck-in or tuckover methylene moieties was converted back to a methyl group in the reaction. This methylene to methyl conversion is observed in all of the reactions in Scheme 1. If this C-H bond formation occurred with reduction as shown in Scheme 2b, this could provide a route to the trivalent byproduct  $[(C_5Me_5)_2 UCl_{3}^{22}$  5. To date, we have not been able to separate out these reactions to determine their exact sequence. Several scenarios are reasonable.

The reaction of **1** with Me<sub>3</sub>SiCl was compared with the reactivity of the tuck-in moiety in **2**. Lanthanide and yttrium alkyl complexes are known to react with Me<sub>3</sub>SiCl to form the corresponding chloride complexes,<sup>41</sup> and a similar reaction could occur with **2**. However, no reaction was observed between **2** and Me<sub>3</sub>SiCl at 25 °C. Reactivity is observed after 12 h at 55 °C, but a mixture of products forms and the individual components have not yet been definitively identifiable by X-ray crystallography.

The reactivity of the  $U^{4+}$  methyl complex  $(C_5Me_5)_2(hpp)$ -UMe, **6**,<sup>28</sup> was also examined for comparison with the reactions of **1** and **2**. Complex **6** reacts with Me<sub>3</sub>SiCl at 25 °C to form  $(C_5Me_5)_2(hpp)UCl^{28}$  and  $Me_4Si$ , but the reaction needs to be heated to 100 °C for 12 h to go to completion, eq 10.



**Reactions with HC=CPh.** Complex 1 reacts with phenylacetylene to form multiple products, whereas 2 reacts with this substrate to form  $(C_5Me_5)_2(hpp)U(C=CPh)$ , 7, in quantitative yield, eq 11. The phenylalkynide 7 has previously been made from  $(C_5Me_5)_2(hpp)UCl$  and LiC=CPh<sup>25</sup> and its



preparation via eq 11 was confirmed by <sup>1</sup>H NMR spectroscopy.

Complex 7 can also be synthesized from hydride 3 and  $HC \equiv CPh$ , eq 11, whereas the methyl complex 6 does not react with  $HC \equiv CPh$  under the same reaction conditions. No reactions were observed between complex 1 or 2 and other hydrocarbon reagents such as methane, benzene, or toluene.

**Reactions with PhSSPh.** The reaction of **1** with PhSSPh that forms  $(C_5Me_5)_2U(SPh)_2$ , **8**,<sup>42</sup> Scheme 1, was examined in more detail since it could occur not only by the reductive pathways shown in Scheme 2 but also by a series of  $\sigma$ -bond metathesis reactions as shown in Scheme 3. To form the observed products, the initial reaction of PhSSPh with **1** would have to involve the U–H bonds and have sulfur in the position diagonal to the metal. This would generate PhSH as a byproduct that could subsequently react with the U–C(CH<sub>2</sub> tuck) bonds to form methyl groups and the U–SPh linkages in the product.

Initially, the reaction of **1** with a 1:1 mixture of PhSSPh and *p*-tolylSS-*p*-tolyl was pursued to evaluate the possible presence of an intermediate of formal composition " $(C_5Me_5)_2U$ ". If this reaction proceeded through a " $(C_5Me_5)_2U$ " intermediate, a 1:1 mixture of  $(C_5Me_5)_2U(SPh)_2$ , **8**, and  $(C_5Me_5)_2U(S-p-tolyl)_2$ , **10**, would be expected with no mixed ligand byproduct,  $(C_5Me_5)_2U(SPh)(S-p-tolyl)$ , **9**. However, as described below, exchange reactions interfered with the analysis.

For this study,  $(C_5Me_5)_2U(S-p-tolyl)_2$ , **10**, was synthesized, eq 12, in a reaction analogous to that of  $(C_5Me_5)_2$ -U(SPh)<sub>2</sub>, **8**.<sup>26</sup> The synthesis of **9** was attempted by



(42) Evans, W. J.; Montalvo, E.; Kozimor, S. A.; Miller, K. A. J. Am. Chem. Soc. 2008, 130, 12258.

<sup>(40)</sup> Evans, W. J.; Siladke, N. A.; Ziller, J. W. Chem. Eur. J. 2010, 16, 796.

<sup>(41)</sup> Voskoboynikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. Organometallics **1997**, *16*, 4041.

Scheme 3



generating  $(C_5Me_5)_2U(SPh)(OTf)$  from  $[(C_5Me_5)_2UMe(OTf)]_2$ and PhSH and then reacting the triflate thiolate with KS-*p*tolyl. Unfortunately, this gives a 1:2.4:1.7 mixture of **8**, **9**, and **10** due to ligand exchange, eq 13. Consistent with this result, the

$$\begin{split} \left[(C_5Me_5)_2UMe(OTf)\right]_2 \xrightarrow[-2CH_4]{+2PhSH} & 2(C_5Me_5)_2U(SPh)(OTf) \xrightarrow[-2KOTf]{+2KS-p-tolyl} \\ & 8+9+10 \end{split} \tag{13}$$

combination of **8** with **10** affords **9**, by exchange, eq 14. Hence, although **1** reacts with a 1:1 mixture of PhSSPh and



*p*-tolylSS-*p*-tolyl to form a 1:2:1 mixture of  $(C_5Me_5)_2U(SPh)_2$ , **8**,  $(C_5Me_5)_2U(SPh)(S-$ *p*-tolyl), **9**, and  $(C_5Me_5)_2U(S-$ *p* $-tolyl)_2$ , **10**, eq 15, this result cannot be used to exclude U<sup>2+</sup> intermediates.



The reaction of **2** with PhSSPh was examined to determine how an isolated tuck-in moiety would react with this substrate. Complex **2** reacts with PhSSPh to form the  $\sigma$ -bond metathesis product (C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>SPh)(C<sub>5</sub>Me<sub>5</sub>)(hpp)U(SPh), **11**, eq 16.



The structure of **11** was determined by X-ray crystallography and is shown in Figure 2. The <sup>1</sup>H NMR spectrum of **11** contained one  $(C_5Me_5)^-$  resonance along with four resonances, each of which integrated to three protons corresponding to the methyl groups in the  $(C_5Me_4CH_2SPh)^$ ligand. In addition, ten  $(C_6H_5)^-$  resonances were observed as well as six (hpp)<sup>-</sup> resonances typical for  $(C_5Me_5)_2$ (hpp)-UX (X = Cl, Me, N<sub>3</sub>, C=CPh, Et, Ph, I).<sup>25,28</sup> The IR spectrum of **11** contains a C–N stretch arising from the (hpp)<sup>-</sup> ligand at 1550 cm<sup>-1</sup>. The other new (hpp)<sup>-</sup> complexes presented



Figure 2. Thermal ellipsoid plot of  $(C_5Me_4CH_2SPh)(C_5Me_5)$ -(hpp)U(SPh), 11, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

in this paper, **3**, **12**, and **14**, have analogous C–N stretches at 1549, 1544, and 1548 cm<sup>-1</sup>, respectively.<sup>43</sup>

In contrast to the reaction of **2** in eq 16,  $(C_5Me_5)_{2^-}$ (hpp)UMe, **6**, does not react with PhSSPh at 25 °C.<sup>28</sup> However, the hydride complex **3** reacts with PhSSPh to form  $(C_5Me_5)_2$ (hpp)U(SPh), **12**, and PhSH, eq 17.



**Reactions with PhSH.** The observation of  $\sigma$ -bond metathesis reactivity with the single tuck-in moiety in **2** and the hydride in **3** suggested that the reactions in Scheme 3 should be examined further. The necessary intermediate in that scheme, PhSH, was the next substrate studied. With a p $K_a$  of 10.3 (DMSO),<sup>44</sup> PhSH is on the protonolysis end of the continuum of reactions that can be formally viewed as  $\sigma$ -bond metatheses. It has previously been shown that **1** reacts with PhOH (p $K_a = 18$ , DMSO)<sup>44</sup> to form (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(OPh)<sub>2</sub>.<sup>1</sup> As shown in eq 18, **1** reacts cleanly with PhSH to generate an analogous product, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(SPh)<sub>2</sub>, **8**. Complex **8** was also obtained from **1** and PhSSPh, Scheme 1.



(43) Wilkins, J. D. J. Organomet. Chem. 1974, 80, 349.
(44) Bordwell, F. G.; McCallum, R. J.; Olmstead, W. N. J. Org. Chem. 1984, 49, 1424.



Figure 3. Thermal ellipsoid plot of  $(C_5Me_5)_2(hpp)U(SPh)$ , 12, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Complex 2 also reacts cleanly with PhSH to form the protonolysis product  $(C_5Me_5)_2(hpp)U(SPh)$ , 12, eq 19. Complex 12 can be more conveniently synthesized from the reaction of PhSH with  $(C_5Me_5)_2(hpp)UH$ , 3, or  $(C_5Me_5)_2(hpp)UMe$ , 6, eq 19. The connectivity of 12 was determined by X-ray crystallography, Figure 3.



**Reactions with PhNH<sub>2</sub>.** Reactions with PhNH<sub>2</sub> ( $pK_a = 30.6$ , DMSO) were examined since polyfunctional **1** had the potential to make (=NPh)<sup>2-</sup> imide products as well as (NHPh)<sup>-</sup> analogues of the PhSH and PhOH reactions. As shown in eq 20, the bis(amide) complex (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(NHPh)<sub>2</sub>,<sup>29</sup> **13**, was isolated rather than the imide. When complex **1** was reacted with aniline- $d_7$ , incorporation of deuterium into the (C<sub>5</sub>Me<sub>5</sub>)<sup>-</sup> ligand was observed by <sup>1</sup>H NMR spectroscopy.



Complex **2** similarly reacts with PhNH<sub>2</sub> to make the amide complex  $(C_5Me_5)_2(hpp)U(NHPh)$ , **14**, eq 21. Complex **14** can also be made from  $(C_5Me_5)_2(hpp)UH$ , **3**, and PhNH<sub>2</sub>, eq 21, but it was not accessible from  $(C_5Me_5)_2(hpp)UMe$ , **6**, and PhNH<sub>2</sub>. The X-ray crystal structure of **14** is shown in Figure 4.



Figure 4. Thermal ellipsoid plot of  $(C_5Me_5)_2(hpp)U(NHPh)$ , 14, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.



**Reactions with CuI.** Reactions of 1 and 2 with CuI were examined since CuI has recently been shown to be an excellent reagent to convert  $U^{4+}$  alkyls to iodides in quantitative yields with elimination of the corresponding alkane, e.g., eq 22.<sup>25,45</sup> Kiplinger and co-workers have also shown that copper salts can oxidize  $U^{4+}$  metallocenes, e.g., eq 23.<sup>46-49</sup>



The main products isolated from reactions of **1** and **2** with CuI are not oxidation products, but are instead the iodide complexes  $(C_5Me_5)_2UI_2$ , **15**, eq 24, and  $(C_5Me_5)_2(hpp)UI_2^{25}$ 

<sup>(45)</sup> Evans, W. J.; Walensky, J. R.; Ziller, J. W. Organometallics 2010, 29, 101.

<sup>(46)</sup> Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. J. Am. Chem. Soc. 2007, 129, 11914.

<sup>(47)</sup> Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. Organometallics 2008, 27, 3335.

<sup>(48)</sup> Graves, C. R.; Vaughn, A. E.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2008**, *47*, 11879.

<sup>(49)</sup> Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. J. Am. Chem. Soc. 2008, 130, 5272.

**16**, eq 25, respectively. The generation of a mixture of products differs from the reactivity observed for the monoalkyl  $(C_5Me_5)_2(hpp)UR$  (R = Me, 6; C=CPh, Ph, Et) complexes with CuI, where the  $(C_5Me_5)_2(hpp)UI$  complex is formed in quantitative yields. However, the hydride complex **3** reacts with CuI to form **16** in quantitative yield, eq 26.



Competition Experiments. In attempts to examine the relative rates of tuck-in versus hydride reactivity, competition experiments between 2 and 3 with PhSH and PhNH<sub>2</sub> were conducted. Since HX substrates can react with the U-H bond in 3 to form U–X and  $H_2$  and the  $H_2$  can in turn convert the U-C tuck-in bond in 2 to U-H by hydrogenolysis as described in the first part of the Results section, this reaction can be complicated. However, if the rate of reaction of the tuck-in moiety is much faster than that of the hydride, this is not a problem. When a 1:1 mixture of 2 and 3 was reacted with 1 equiv of PhSH in an open scintillation vial (to avoid building up a concentration of H<sub>2</sub>), the <sup>1</sup>H NMR spectrum of this reaction showed the presence of 2 and 3 in a 1:3 ratio and resonances consistent with the formation of 12. When a 1:1 mixture of 2 and 3 was reacted with 1 equiv of PhNH<sub>2</sub> under similar conditions, <sup>1</sup>H NMR spectroscopy showed only 3 and resonances consistent with the formation of 14. Hence, in both of these reactions, the tuck-in complex disappears faster than the hydride complex. Since reaction of the hydride complex 3 with PhSH or PhNH<sub>2</sub> can generate hydrogen as a byproduct that can also lead to the disappearance of 2, it cannot unequivocally be stated that the tuck-in reacts faster. However, the data indicate that the tuck-in reacts at least at rates comparable to that of the hydride since all of the hydride would have to react first to generate enough hydrogen to eliminate the tuck-in complex by the competing hydrogenolysis reaction.

## Discussion

Correlations between the reactivities of the tuck-in tuckover dihydride  $(C_5Me_5)U[\mu-\eta^5:\eta^1:\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2 U(C_5Me_5)_2$ , **1**, and the tuck-in complex  $(C_5Me_5)(\eta^5:\eta^1-C_5 Me_4CH_2)(hpp)U$ , **2**, are highly dependent upon the particular substrate examined. This discussion will be structured starting with the most similar observed reactivity going to the least similar.

The reactions with H<sub>2</sub> appear to be directly analogous. Hydrogenolyses of U–C tuck-in and tuck-over bonds in 1, eq 5, and U–C tuck-in bonds in 2, eq 6, are observed and form the expected hydride products. This is typical U–C(alkyl) reactivity and can be explained as a  $\sigma$ -bond meta-thesis, eq 27 (X = H). The reactivity of these U–C



linkages seems to be similar regardless of tuck-in or tuckover structure, and the hydrogenolyses occur in the presence of other reactive ligands. Since this is a hydride-forming reaction and the other reactive ligands are hydrides, it makes sense that this should be the most analogous set of reactions. Although these hydrogenolyses are superficially straightforward, the reactions with deuterium that show exchange into  $(C_5Me_5)^-$  and  $(hpp)^-$  ligands indicate that considerable dynamic behavior is occurring with hydrogen in these systems. Exchange of deuterium into the rings in 1 has precedent in the chemistry of the uranium hydrides,  $[(C_5Me_5)_2UH_x]_2$ ,<sup>18</sup> but the deuterium exchange into  $(hpp)^-$  hydrogen sites has not been previously reported. This facile hydrogen transfer makes it difficult to pinpoint the reactivity of the hydride ligands in 1.

The reactions of increasingly polar element—H bonds will be considered next. The reaction of HC=CPh with 2 to form the alkynide  $(C_5Me_5)_2(hpp)U(C=CPh)$ , 7, eq 11, is another example of a straightforward  $\sigma$ -bond metathesis reaction of the type typical for f element—C bonds. As is common in  $\sigma$ -bond metathesis, hydrogen is in the position diagonal to the metal and only U–alkynide and CH<sub>2</sub>—H bonds result in the product. The alternative would form U–H and CH<sub>2</sub>–C=CPh bonds and generate a  $(C_5Me_2CH_2C=CPh)^$ ligand.

The observation that the hydride  $(C_5Me_5)_2(hpp)UH$ , 3, can also react with HC=CPh to make 7, eq 11, is consistent with the result that the analogous reaction with 1 gives multiple products. Both hydride and tuck-in moieties in 1 can react with HC=CPh, and when several of these reactive sites are present, multiple products can form. The fact that the methyl complex  $(C_5Me_5)_2(hpp)UMe$ , 6, does not react with HC=CPh suggests that the U-C(tuck-in) bond is more reactive than a simple U-C alkyl linkage. This would be expected on the basis of ring strain and the steric availability and longer bond distance of the U-C(tuck-in) bond versus the U-C(Me) bond in 6, a complex that has been shown to have low reactivity.<sup>28</sup>

The reaction of **2** with PhNH<sub>2</sub> also appears to be a straightforward  $\sigma$ -bond metathesis, eq 27 (X = NHPh), with hydrogen in the position diagonal to the metal. Since **2** has only one reactive U-element bond for  $\sigma$ -bond metathesis, a (NHPh)<sup>-</sup> product, **14**, is cleanly formed, eq 21. The hydride complex, **3**, also reacts with PhNH<sub>2</sub> to form the amide complex **14**, eq 21. Since **1** has four U-element bonds that can participate in  $\sigma$ -bond metathesis, i.e., tuck-in U-C, tuck-over U-C, and two U-H linkages, it was conceivable



that  $(=NPh)^{2^{-}}$  products could result. However, the net result is analogous to that of **2** with only an  $(NHPh)^{-}$ product being formed, eq 20. This result could arise in several ways that, at present, are indistinguishable.  $\sigma$ -Bond metathesis could occur with all four reactive sites to make the observed four U–NHPh bonds, two C–H bonds, and 2 equiv of H<sub>2</sub>. Alternatively, hydride-alkyl anion elimination could occur according to Scheme 2 to re-form the (C<sub>5</sub>Me<sub>5</sub>)<sup>-</sup> methyl groups and U<sup>2+</sup> or U<sup>3+</sup> intermediates, and these could reduce PhNH<sub>2</sub> to form (PhNH)<sup>-</sup> and H<sub>2</sub>.

The reactivity of PhSH with 1 and 2 is similar to that for PhNH<sub>2</sub>. Both complexes give the products expected from  $\sigma$ -bond metathesis, eqs 18, 19, and 27 (X = SPh). The reaction of 2 and 3 with PhSH shows that tuck-in and hydride functionalities can effect this reaction cleanly. With 1 there again is ambiguity in terms of  $\sigma$ -bond metathesis or reductive elimination pathways involving lower oxidation states.

PhSSPh is not a common  $\sigma$ -bond metathesis substrate since it does not have a hydrogen or silicon to put in the diagonal position of a four-centered intermediate.<sup>50–53</sup> However,  $\sigma$ -bond metathesis-like reactivity of PhEEPh

(E = S, Se, Te) has been reported with  $(C_5Me_5)_2UMe_2$ , e.g., eq 28.<sup>54</sup> The reaction of **2** with PhSSPh, eq 19,



cleanly generates a  $\sigma$ -bond metathesis product, (C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>SPh)(C<sub>5</sub>Me<sub>5</sub>)(hpp)U(SPh), **11**. Again, this indicates that U–C(tuck-in) bonds can participate in  $\sigma$ -bond metathesis reactions like U–Me bonds, eq 28. In contrast to the reactions described so far in this section, complex **1** does not make a product directly analogous to that of **2**, as (C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>SPh)<sup>-</sup> products are not observed. Since **1** reacts with PhSSPh to give (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(SPh)<sub>2</sub>, **8**, with SPh only attached to U and no (C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>SPh)<sup>-</sup> ligands, the hydrides must react faster with PhSSPh than the tuck-in and tuck-over units if  $\sigma$ -bond metathesis is occurring. However, the PhSSPh reaction with **1** could proceed by reductive elimination, Scheme 2, an option not available to **2**.

Evidence supporting higher reactivity for U–H bonds versus tuck-in U–C bonds is also found in the reactions of 2 and 3 with Me<sub>3</sub>SiCl. The tuck-in complex 2 does not react

<sup>(50)</sup> Perrin, L.; Eisenstein, O.; Maron, L. New J. Chem. 2007, 31, 549.

<sup>(51)</sup> Perrin, L.; Maron, L.; Eisenstein, O. Inorg. Chem. 2002, 41, 4355.

<sup>(52)</sup> Perrin, L.; Maron, L.; Eisenstein, O.; Tilley, T. D. Organometallics 2009, 28, 3767.

<sup>(53)</sup> Werkema, E. L.; Andersen, R. A.; Yahia, A.; Maron, L.; Eisenstein, O. *Organometallics* **2009**, *28*, 3173.

<sup>(54)</sup> Evans, W. J.; Miller, K. A.; Ziller, J. W.; DiPasquale, A. G.; Heroux, K. J.; Rheingold, A. L. Organometallics **2007**, *26*, 4287.

with Me<sub>3</sub>SiCl at 25 °C, but the hydride, 3, cleanly converts to  $(C_5Me_5)_2(hpp)UCl$ , eq 8. The analogous reaction of 1 with Me<sub>3</sub>SiCl shows how complicated the reactivity of this multifunctional complex can be. The chloride ligands in the reaction products,  $(C_5Me_5)ClU(\eta^5-C_5Me_4CH_2SiMe_2CH_2 \kappa C$ ), 4, and [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>UCl]<sub>3</sub>, 5, are consistent with the replacement of hydride by chloride in eq 9. However, the formation of a  $U^{3+}$  product clearly shows that reductive reaction pathways are accessible from 1. In addition, the formation of the  $(\eta^5 - C_5 Me_4 CH_2 Si Me_2 CH_2 - \kappa C)^{2-}$  ligand indicates that C-H activation is also accessible in this system.  $\sigma$ -Bond metathesis of Me<sub>3</sub>SiCl with a tuck-in or tuck-over U-C bond could make a  $(\eta^5$ -C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>SiMe<sub>3</sub>)<sup>-</sup> intermediate that is subsequently converted to the observed  $(\eta^5-C_5-Me_4CH_2SiMe_2CH_2-\kappa C)^{2-}$  ligand by  $\sigma$ -bond metathesis with either the remaining U-C tuck-in or tuck-over bond or the hydride ligands. Metalation of silylmethyl groups in ( $\eta^5$ -C<sub>5</sub>-Me<sub>4</sub>SiMe<sub>3</sub>)<sup>-</sup> by U–Me bonds has recently been reported.<sup>40</sup> Scheme 4 shows one route to the products, but many pathways are possible.

In contrast to the reactions discussed above, where the hydride ligands appear to be more reactive than the tuck U-C bond, competition reactions between tuck-in 2 and hydride 3 with PhSH and PhNH<sub>2</sub> suggest that the tuck-in reacts as fast as, if not faster than, the hydride complex. Hence, as stated in the first paragraph of the Discussion section, the reactivity is substrate dependent.

The final reactions to be discussed involve CuI. The reaction of **2** with CuI to make  $(C_5Me_5)_2(hpp)UI$ , **16**, eq 25, is quite unusual in that the hydrogen source is unknown. Reactions of CuI with  $(C_5Me_5)_2[^{i}PrNC(Me)-N'Pr-\kappa^2N,N']UMe^{45}$  and  $(C_5Me_5)_2(hpp)UR^{25}$  ( $R = Me, C \equiv$  CPh, Ph, Et) in deuterated solvents have also been observed to form an RH byproduct without a clear source of hydrogen.

The reaction of 1 with CuI, eq 24, gives analogous U–I bonds in the product, but in this case the hydrogen that combines with the U–CH<sub>2</sub> linkages to form U–Me units could be the hydride ligands in 1. These reactions can involve reductive elimination reactions in which CuI is reduced by lower oxidation state uranium intermediates.

#### Conclusion

Comparison of the reactivity of tuck-in tuck-over dihydride 1, tuck-in 2, hydride 3, and methyl 6 shows that the reactions of these functionalities can be quite substrate dependent. Both  $\sigma$ -bond metathesis/protonolysis and reductive elimination pathways are possible. Hydride ligands appear to be more reactive with Me<sub>3</sub>SiCl and PhSSPh than tuck functionalities, but PhSH and PhNH<sub>2</sub> appear to react at least as fast with tuck moieties as with hydride ligands. Interestingly, none of these isolable tuck functional groups show reactivity with alkanes or arenes, substrates that originally led to the identification of tuck-in moieties.

Acknowledgment. We thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy for support. This research was facilitated in part by a National Physical Science Consortium Fellowship and by stipend support from Los Alamos National Laboratory (to E.M.). We thank Dr. John Greaves for assistance with the GC-MS studies.

**Supporting Information Available:** X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.