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Formation of $(C_5Me_5)_2U(EPh)Me$, $(C_5Me_5)_2U(EPh)_2$, and $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$ from $(C_5Me_5)_2UMe_2$ and PhEEPh (E = S, Se, Te)

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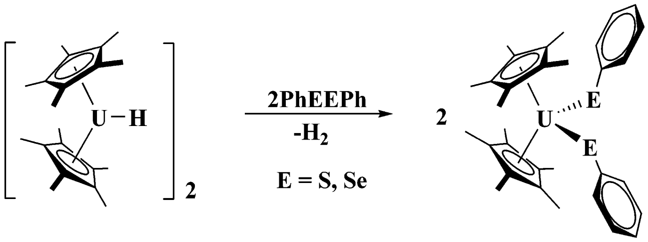
$(C_5Me_5)_2UMe_2$, **1**, reacts with 1 and 2 equiv of PhEEPh (E = S, Se) to form $(C_5Me_5)_2UMe(EPh)$ (E = S, **2**; Se, **3**) and $(C_5Me_5)_2U(EPh)_2$ (E = S, **4**; Se, **5**), respectively, with concomitant formation of MeEPh. Complexes **2**, **3**, and **5** form at ambient temperature, but the synthesis of **4** required heating to 65 °C. Addition of 2 equiv of PhTeTePh to 1 equiv of $(C_5Me_5)_2UMe_2$ generated the tellurium analogue of **4** and **5**, namely, $(C_5Me_5)_2U(TePh)_2$, **6**, but when **1** was reacted with 1 equiv of PhTeTePh, C−H activation of the aryl ring occurred to form $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, **7**, along with MeTePh and CH_4.

Introduction

Recent developments in actinide reduction chemistry have shown that ligand-based reduction involving $(C_5Me_5)^-$, $(BPh_4)^-$, and H^- anions can be combined with metal-based reduction to accomplish multielectron reductions.[1−3] Reductions involving two,[2] three,[1] four,[2,3] six,[2,3] and eight[3] electrons have been observed depending on the substrate and the starting material. Hence, in the formation of $(C_5Me_5)_2U(EPh)_2$ (E = S,[4] Se[3]) from $[(C_5Me_5)_2UH]_2$ in Scheme 1, the two U^{3+} metal ions deliver two electrons and the two H^- ligands deliver two electrons and form H_2 in an overall four-electron process.[3] The reduction in Scheme 1 can also be accomplished with the tetravalent hydrides $[(C_5Me_5)_2UH_2]_2$ and $[(C_5Me_5)_2ThH_2]_2$ in reactions that formally involve only the hydride ions as the reductant,[3] Scheme 2.

These results raised questions about what other ligands in organometallic actinide complexes could accomplish reductions of this type. $(C_5Me_5)_2UMe_2$, **1**, was of interest because it is the precursor to the hydrides above.[5] If the same reduction done by the hydride ligands could be done by the methyl ligands, this would provide access to the reduction products with one less step. Alkyllithium reagents are known to act as reductants in certain cases,[6] so it is not unreasonable to investigate alkyl complexes of other electropositive metals in this regard. Since the PhEEPh substrates constitute easily reducible test cases, their reaction chemistry with $(C_5Me_5)_2UMe_2$, **1**, was investigated. The chalcogen substrates are also good because some of the anticipated reduction products can be easily identified since they are already in the literature.[3,4]

Scheme 1



$$2PhEEPh + 4e^{1-} \longrightarrow 4(PhE)^{1-}$$
$$2[(C_5Me_5)_2U]^{1+} \longrightarrow 2[(C_5Me_5)_2U]^{2+} + 2e^{1-}$$
$$2H^{1-} \longrightarrow H_2 + 2e^{1-}$$

Experimental Section

The manipulations described below were performed under argon with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were dried over Q-5 and molecular sieves and saturated with argon using GlassContour[7] columns. Benzene-d_6 was dried over NaK alloy and vacuum transferred before use. $(C_5Me_5)_2UMe_2$ was prepared as previously described.[5] PhSSPh, PhSeSePh, and PhTeTePh were purchased from Aldrich and sublimed before use. NMR spectra were recorded with a Bruker DRX 500 MHz system. Infrared spectra were recorded as KBr pellets on a Varian 1000 FT-IR instrument. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany. X-ray data collection parameters are given in Table 1, and full crystallographic information is in the Supporting Information.

$(C_5Me_5)_2UMe(SPh)$, 2. PhSSPh (75 mg, 0.34 mmol) in toluene (5 mL) was added to a red solution of **1** (184 mg, 0.344 mmol) in toluene (10 mL). After the mixture was stirred for 12 h, the dark red solution was evaporated to dryness, yielding a red oil. The red oil was dissolved in hexane and cooled to −35 °C. After 4 days, **2** was obtained as dark red crystals. The crystals were washed with cold hexane (−35 °C) and dried under reduced pressure (148 mg, 68%). The hexane wash was dried under reduced pressure, yielding a red oil that displayed additional resonances in the ^1H NMR

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† University of California, Irvine.

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[1] Evans, W. J.; Nyce, G. W.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 240.

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[3] Evans, W. J.; Miller, K. A.; Kozimor, S. A.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, R. L. *Organometallics* **2007**, *26*, 3568.

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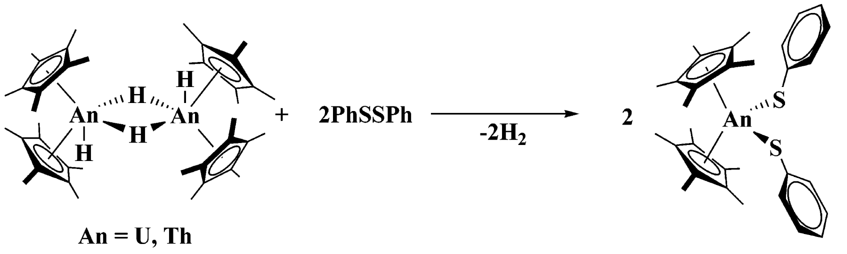
[7] For more information on drying systems, see www.glasscontour.com.

10.1021/om700382a CCC: $37.00

Scheme 2



$$2\text{PhSSPh} + 4\text{e}^{1-} \longrightarrow 4(\text{PhS})^{1-}$$

$$4\text{H}^{1-} \longrightarrow 2\text{H}_2 + 4\text{e}^{1-}$$

Table 1. X-ray Data Collection Parameters for $(C_5Me_5)_2UMe(SPh)$, 2, $(C_5Me_5)_2UMe(SePh)$, 3, $(C_5Me_5)_2U(TePh)_2$, 6, and $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, 7

empirical formula	$C_{27}H_{38}SU$	$C_{27}H_{38}SeU$	$C_{32}H_{40}Te_2U$	$C_{26}H_{34}TeU$
no.	**2**	**3**	**6**	**7**
fw	632.66	679.56	917.87	712.16
temp (K)	155(2)	100(2)	100(2)	100(2)
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a (Å)	11.5327(19)	8.9090(15)	10.1421(16)	8.4434(13)
b (Å)	13.747(2)	17.166(3)	15.659(2)	16.064(3)
c (Å)	31.942(5)	16.484(3)	19.378(3)	17.729(3)
β (deg)	90	100.332(2)	90	93.046(2)
volume (Å^3)	5064.3(14)	2480.1(8)	3077.4(8)	2401.2(6)
Z	8	4	4	4
ρ_{calcd} (Mg/m^3)	1.660	1.820	1.981	1.970
μ (mm^{-1})	6.503	8.023	7.150	7.959
R1 [$I > 2.0\sigma(I)$]^a	0.0277	0.0331	0.0385	0.0238
wR2 (all data)^a	0.0559	0.0794	0.0899	0.0621
absolute struct param	0.005(5)		0.000(5)	

[a] Definitions: $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

spectrum in C_6D_6 that match those of MeSPh (Aldrich). ^{1}H NMR: δ 1.9 (s, 3H, Me), 6.9 (t, 1H, *p*-H), 7.0 (t, 2H, *m*-H), 7.1 (d, 2H, *o*-H). Crystals of **2** suitable for X-ray diffraction were grown at −35 °C from a concentrated hexane solution. ^{1}H NMR (C_6D_6): δ 9.4 (s, 30H, C_5Me_5, $\Delta\nu_{1/2} = 11$ Hz), −3.3 (t, 1H, $^3J_{HH} = 8$ Hz, *p*-H), −4.6 (t, 2H, $^3J_{HH} = 8$ Hz, *m*-H), −41.0 (br s, 2H, *o*-H), −120.9 (s, 3H, U−C*H*$_3$). ^{13}C NMR (C_6D_6): δ −25.8 (C_5*Me*$_5$), 102.0 (*C*$_5$Me$_5$), 120.1 (*o*-phenyl), 91.7 (*m*-phenyl), 124.6 (*p*-phenyl), 129.7 (*ipso*-phenyl), −59.6 (U-*C*H$_3$). IR: 2968m, 2905vs, 2856s, 2726w, 2361w, 1578w, 1474m, 1435s, 1378s, 1102m, 1024m, 802w, 739m, 696m cm^{-1}. Anal. Calcd for $C_{33}H_{43}SU$: C, 51.26; H, 6.05; S, 5.07; U, 37.62. Found: C, 51.26 ; H, 6.11; S, 4.91; U, 37.75.

$(C_5Me_5)_2UMe(SePh)$, 3. As described for **2**, **3** was obtained as red crystals (169 mg, 62%) from PhSeSePh (126 mg, 0.404 mmol) in toluene (8 mL) and **1** (217 mg, 0.405 mmol) in toluene (10 mL). The hexane wash displayed additional resonances in the ^{1}H NMR spectrum in C_6D_6 consistent with MeSePh.[8] ^{1}H NMR: δ 1.9 (s, 3H, Me), 6.9 (t, 2H, *m*-H), 7.0 (t, 1H, *p*-H), 7.3 (d, 2H, *o*-H). Crystals of **3** suitable for X-ray diffraction were grown at −35 °C from a concentrated hexane solution. ^{1}H NMR (C_6D_6): δ 9.7 (s, 30H, C_5Me_5, $\Delta\nu_{1/2} = 11$ Hz), −2.2 (t, 1H, $^3J_{HH} = 8$ Hz, *p*-H), −4.6 (t, 2H, $^3J_{HH} = 8$ Hz, *m*-H), −37.2 (br s, 2H, *o*-H), −117.2 (s, 3H, U-C*H*$_3$). ^{13}C NMR (C_6D_6): δ −26.9 (C_5*Me*$_5$), 104.4 (*C*$_5$Me$_5$), 128.3 (*o*-phenyl), 94.9 (*m*-phenyl), 124.1 (*p*-phenyl), 126.5 (*ipso*-phenyl), −59.3 (U-*C*H$_3$). IR: 3068w, 2979m, 2904s, 2854s, 1575m, 1471s, 1431s, 1379s, 1020s, 1101m, 1066m, 1020s, 905w, 803w, 740s, 696m, 666m cm^{-1}. Anal. Calcd for $C_{33}H_{43}SeU$: C, 47.72; H, 5.64; Se, 11.62; U, 35.03. Found: C, 47.69; H, 5.66; Se, 12.02; U, 34.80.

$(C_5Me_5)_2U(SPh)_2$, 4, from $(C_5Me_5)_2UMe_2$, 1. PhSSPh (12 mg, 0.055 mmol) in C_6D_6 was added to an NMR tube containing **1** (15 mg, 0.028 mmol) in C_6D_6. ^{1}H NMR spectroscopy showed conversion of starting material to MeSPh and a 2:3 ratio (by C_5Me_5 resonances) of the previously characterized **4**[4] and **2**, respectively, after 3 days. The NMR tube was flame-sealed under vacuum and heated at 65 °C. After 8 h, ^{1}H NMR spectroscopy showed complete conversion to **4**.[4]

$(C_5Me_5)_2U(SPh)_2$,[4] 4, from $(C_5Me_5)_2UMe(SPh)$, 2. PhSSPh (9 mg, 0.04 mmol) in C_6D_6 was added to an NMR tube containing **2** (25 mg, 0.040 mmol) in C_6D_6. ^{1}H NMR spectroscopy showed MeSPh and partial conversion of **2** to **4**[4] in a 1:1 ratio by C_5Me_5 resonances after 2 days. The NMR tube was flame-sealed and heated at 65 °C. After 8 h, ^{1}H NMR spectroscopy showed complete conversion to **4**.[4]

$(C_5Me_5)_2U(SePh)_2$, 5, from $(C_5Me_5)_2UMe_2$, 1. PhSeSePh (14 mg, 0.044 mmol) in C_6D_6 was added to an NMR tube containing **1** (12 mg, 0.022 mmol) in C_6D_6. ^{1}H NMR spectroscopy showed quantitative conversion of starting material to the previously characterized **5**[3] and MeSePh[8] after 8 h.

$(C_5Me_5)_2U(SePh)_2$, 5, from $(C_5Me_5)_2UMe(SePh)$, 3. PhSeSePh (8 mg, 0.025 mmol) in C_6D_6 was added to an NMR tube containing **3** (17 mg, 0.025 mmol) in C_6D_6. ^{1}H NMR spectroscopy showed quantitative conversion of starting material to the previously characterized **5**[3] and MeSePh[8] after 4 h.

$(C_5Me_5)_2U(TePh)_2$, 6. PhTeTePh (222 mg, 0.542 mmol) in toluene (3 mL) was added to a red solution of **1** (145 mg, 0.271 mmol) in toluene (10 mL). After the mixture was stirred for 12 h, the dark orange solution was evaporated to dryness, yielding a red oil. The red oil was dissolved in hexane (2 mL) and cooled to −35 °C. After 1 day, **6** was obtained as red crystals. The crystals were washed with cold hexane (−35 °C) and dried under reduced pressure (115 mg, 46%). The hexane wash was dried under reduced pressure, yielding a red oil that displayed additional resonances in

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(8) Detty, M. R.; Wood, G. P. *J. Org. Chem.* **1980**, *45*, 80.

the ^{1}H NMR spectrum in C_6D_6 consistent with MeTePh.[9] ^{1}H NMR (C_6D_6): δ 1.8 (s, 3H, Me), 6.9 (t, 2H, *m*-H), 7.0 (t, 1H, *p*-H), 7.5 (d, 2H, *o*-H). Crystals of **6** suitable for X-ray diffraction were grown at −35 °C from a concentrated hexane solution. ^{1}H NMR (C_6D_6): δ 15.1 (s, 30H, C_5Me_5, $\Delta\nu_{1/2} = 18$ Hz), 3.9 (t, 2H, $^3J_{HH} = 8$ Hz, *p*-H), 1.8 (d, 4H, $^3J_{HH} = 8$ Hz, *m*-H), −26.1 (br s, 4H, *o*-H). ^{13}C NMR (C_6D_6): δ −27.7 (C_5Me_5), 127.6 (C_5Me_5), 108.6 (*o*-phenyl), 178.6 (*m*-phenyl), 133.9 (*p*-phenyl), 137.3 (*ipso*-phenyl). IR: 3048w, 2966s, 2900vs, 2727w, 1570vs, 1470vs, 1447m, 1431s, 1379m, 1060s, 1016w, 727s, 691s, 651m cm^{-1}. Anal. Calcd for $C_{32}H_{40}Te_2U$: C, 41.87; H, 4.39; Te, 27.80; U, 25.93. Found: C, 42.07; H, 4.52; Te, 27.5; U, 26.3.

$(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, 7. PhTeTePh (82 mg, 0.200 mmol) in toluene (5 mL) was added to a red solution of **1** (107 mg, 0.200 mmol) in toluene (10 mL). After the mixture was stirred for 12 h, the dark brown solution was evaporated to dryness, yielding a brown oil. The brown oil was dissolved in hexane (2 mL) and cooled to −35 °C. After 1 day, **7** was obtained as brown crystals. The crystals were washed with cold hexane (−35 °C) and dried under reduced pressure (83 mg, 58%). As described above, the hexane wash was dried under reduced pressure, yielding a red oil that displayed additional resonances in the ^{1}H NMR spectrum in C_6D_6 consistent with MeTePh.[9] Crystals of **7** suitable for X-ray diffraction were grown at −35 °C from a concentrated hexane solution. ^{1}H NMR (C_6D_6): δ 5.9 (s, 30H, C_5Me_5, $\Delta\nu_{1/2} = 15$ Hz), 4.1 (t, 1H, $^3J_{HH} =$ 10 Hz, TeC_6H_4), −5.5 (t, 1H, $^3J_{HH} = 8$ Hz, TeC_6H_4), −5.9 (d, 1H, $^3J_{HH} = 10$ Hz, TeC_6H_4), −35.9 (d, 1H, $^3J_{HH} = 10$ Hz, TeC_6H_4). ^{13}C NMR (C_6D_6): δ −35.5 (C_5Me_5), 113.3 (C_5Me_5), −17.0, 57.9, 138.7 152.2, 179.0, 185.3 (TeC_6H_4). IR: 3067w, 3035w, 3017w, 2973s, 2897vs, 2854s, 2724w, 1572w, 1548m, 1484w, 1445s, 1432s, 1390s, 1377vs, 1237s, 1095w, 1018m, 998m, 978m, 801w, 737vs, 692w, 651w, 626w cm^{-1}. Anal. Calcd for $C_{26}H_{34}TeU$: C, 43.85; H, 4.81; Te, 17.92; U, 33.42. Found: C, 43.91; H, 4.96; Te, 17.7; U, 33.6.

A similar reaction was carried out with PhTeTePh (20 mg, 0.049 mmol) and **1** (26 mg, 0.049 mmol) in C_6D_6 in a sealed J-Young tube. The reaction was followed by ^{1}H NMR spectroscopy. After 20 min, the ^{1}H NMR spectra showed complete conversion of starting materials to new products displaying resonances consistent with MeTePh[9] and $(C_5Me_5)_2$UMe(TePh). ^{1}H NMR (C_6D_6): δ 9.8 (s, 30H, C_5Me_5), −0.2 (t, 1H, *p*-H), −2.5 (t, 2H, *m*-H), −29.9 (br s, 2H, *o*-H), −118.2 (s, 3H, Me). After 16 h the spectrum contained **7** and a resonance at 0.13 ppm consistent with CH_4.

X-ray Data Collection, Structure Solution, and Refinement of 2. A red crystal of approximate dimensions 0.06 × 0.26 × 0.28 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[10] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[11] and SADABS[12] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[13] program. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$, which was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[14] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula unit present ($Z = 8$). Some of the methyl carbon atoms associated with the pentamethylcyclopentadienyl ligand defined by C(28)−C(37) exhibited higher than expected thermal motion. Refinement of a disordered model with these atoms included using multiple components, and partial site-occupancy factors yielded no appreciable improvement. The absolute structure was assigned by refinement of the Flack parameter,[15] 0.005(5).

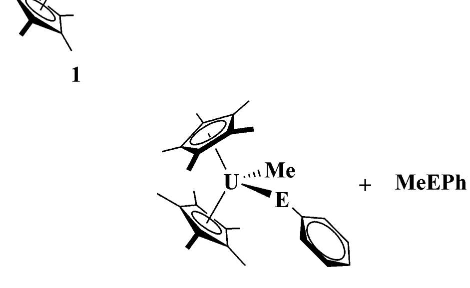
X-ray Data Collection, Structure Solution, and Refinement of 3. A red block 0.10 × 0.07 × 0.02 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. The crystal-to-detector distance was 60 mm and exposure time was 10 s per frame using a scan width of 0.3°. Data collection was 100.0% complete to 25.00° in θ. A total of 20 628 reflections were collected covering the indices $-11 \le h \le 11$, $-22 \le k \le 22$, $-21 \le l \le 21$; 5718 reflections were found to be symmetry-independent, with an R_{int} of 0.0342. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$ (No. 14). The data were integrated using the Bruker SAINT[11] software program and scaled using the SADABS[12] software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

X-ray Data Collection, Structure Solution, and Refinement of 6. A red block 0.22 × 0.22 × 0.08 mm in size was handled as described for **3**. A total of 25,298 reflections were collected covering the indices $-12 \le h \le 13$, $-20 \le k \le 20$, $-25 \le l \le 25$; 7135 reflections were found to be symmetry-independent, with an R_{int} of 0.0581. Indexing and unit cell refinement indicated an orthorhombic lattice. The space group was found to be $P2_12_12_1$. The absolute structure was assigned by refinement of the Flack parameter,[15] 0.000(5). The data were handled as described for **3**.

X-ray Data Collection, Structure Solution, and Refinement of 7. A red crystal 0.30 × 0.30 × 0.24 mm in size was handled as described for **3**. A total of 18 903 reflections were collected covering the indices $-10 \le h \le 10$, $-20 \le k \le 20$, $-22 \le l \le 22$; 5491 reflections were found to be symmetry-independent, with an R_{int} of 0.0265. Indexing and unit cell refinement indicated a monoclinic lattice. The space group was found to be $P2_1/n$. The data were handled as described for **3**.

Results

Reaction Chemistry. $(C_5Me_5)_2$UMe(EPh) (E = S, 2; Se, 3). One equivalent of $(C_5Me_5)_2UMe_2$ reacts with 1 equiv of PhEEPh (E = S, Se) over 12 h to form $(C_5Me_5)_2$UMe(EPh) (E = S, **2**; Se, **3**) and MeEPh, eq 1. Separation of the byproduct,



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E = S, 2; Se, 3

(1)

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[9] Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* **1988**, *7*, 78.

[10] *SMART Software Users Guide*, Version 5.1; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.

[11] *SAINT Software Users Guide*, Version 6.0; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.

[12] Sheldrick, G. M. *SADABS*, Version 2.10; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2002.

[13] Sheldrick, G. M. *SHELXTL*, Version 6.12; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.

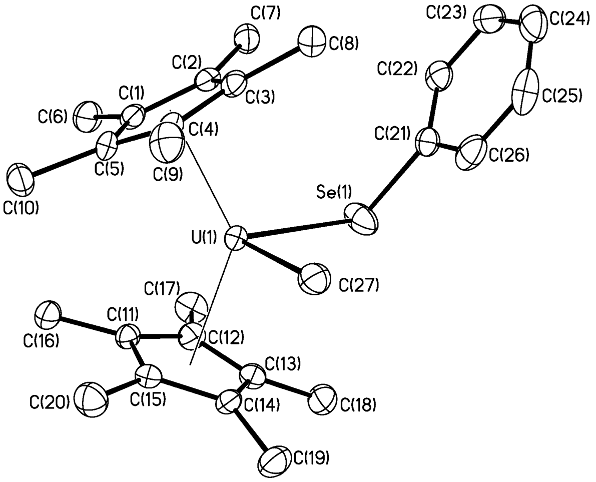


Figure 1. Molecular structure of $(C_5Me_5)_2UMe(SePh)$, **3**, with thermal ellipsoids drawn at the 50% probability level. $(C_5Me_5)_2UMe(SPh)$, **2**, has the same structure.

MeEPh, from **2** and **3** was accomplished by washing crystals of **2** and **3**, obtained at −35 °C in hexane, with cold hexane (−35 °C). The hexane wash displayed ^1H NMR resonances consistent with MeEPh (E = S, Se[8]). Complexes **2** and **3** were characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis and were completely identified by X-ray crystallography, Figure 1.

$(C_5Me_5)_2U(EPh)_2$ (E = S, 4; Se, 5). When 1 equiv of $(C_5Me_5)_2UMe_2$ was reacted with 2 equiv of PhSeSePh, the previously characterized complex $(C_5Me_5)_2U(SePh)_2$,[3] **5**, was formed along with MeSePh after 8 h. However, when $(C_5Me_5)_2UMe_2$ was reacted with 2 equiv of PhSSPh at room temperature over a period of 3 days, complete conversion of starting material to $(C_5Me_5)_2U(SPh)_2$, **4**, a complex previously reported by Ephritikhine et al.,[4] did not occur. Instead, ^1H NMR spectroscopy revealed that both $(C_5Me_5)_2UMe(SPh)$, **2**, and $(C_5Me_5)_2U(SPh)_2$,[4] **4**, were present in a 3:2 ratio, respectively. After heating the mixture at 65 °C for 8 h, complete conversion to **4**[4] was observed by ^1H NMR spectroscopy.

$(C_5Me_5)_2U(EPh)_2$ (E = S,[4] Se[3]) can also be formed in a stepwise manner from $(C_5Me_5)_2UMe(EPh)$ (E = S, Se) with 1 equiv of PhEEPh (E = S, Se), respectively. However, heating the reaction of $(C_5Me_5)_2UMe(SPh)$ and PhSSPh was required in order to achieve complete conversion to $(C_5Me_5)_2U(SPh)_2$,[4] Scheme 3.

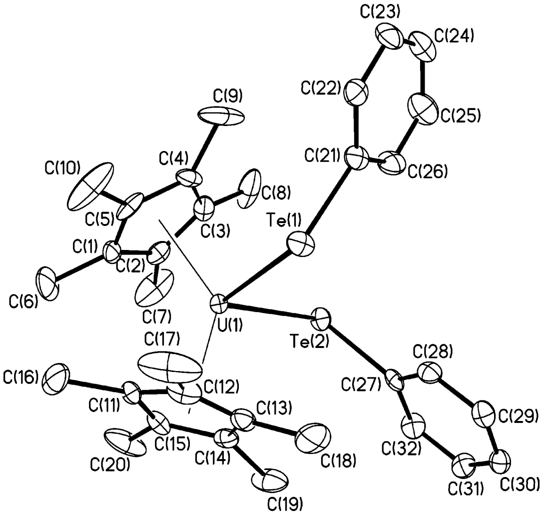


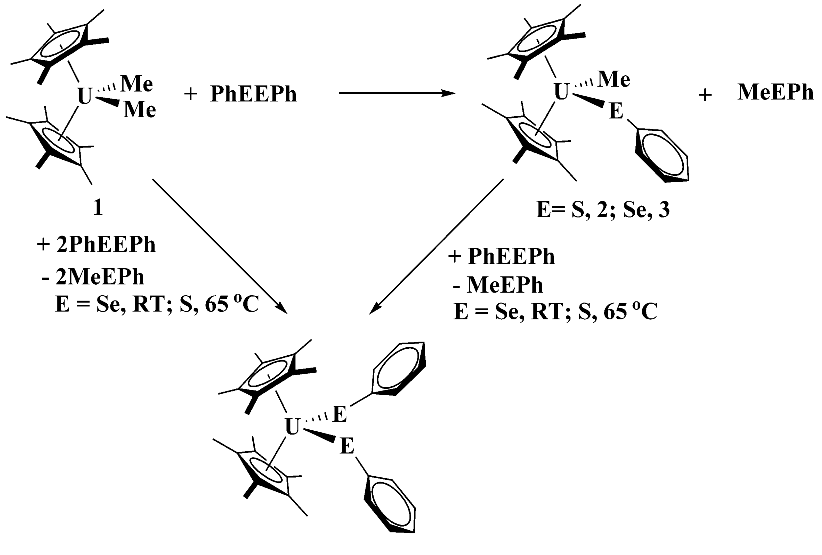
Figure 2. Molecular structure of $(C_5Me_5)_2U(TePh)_2$, **6**, with thermal ellipsoids drawn at the 50% probability level.

$(C_5Me_5)_2U(TePh)_2$, 6, and $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, 7. $(C_5Me_5)_2UMe_2$ reacts with 2 equiv PhTeTePh to form $(C_5Me_5)_2U(TePh)_2$, **6**, in a reaction analogous to the formation of **5** from **1**, Scheme 3. A byproduct was separated as described for the sulfur and selenium analogues that displayed resonances in its ^1H NMR spectrum consistent with MeTePh.[9] The identity of $(C_5Me_5)_2U(TePh)_2$, **6**, was confirmed by X-ray crystallography, Figure 2.

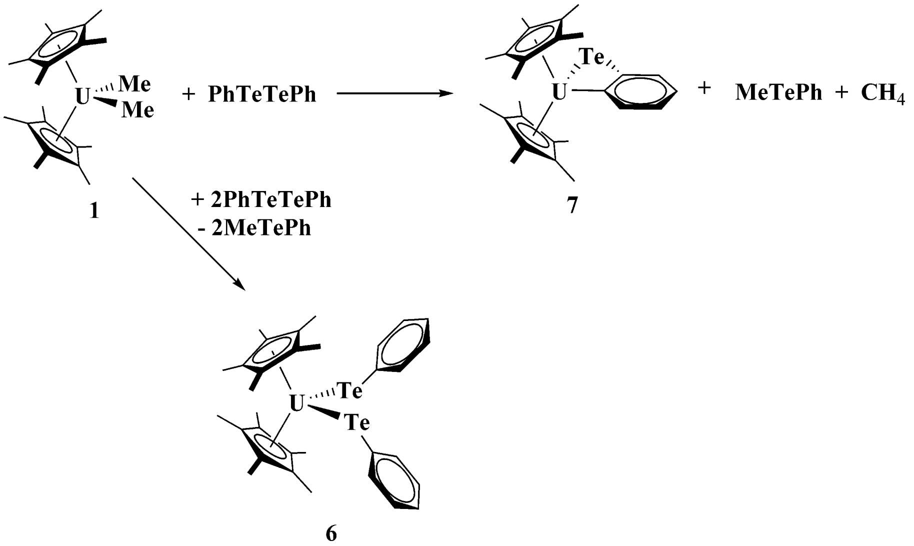
However, when $(C_5Me_5)_2UMe_2$, **1**, was treated with 1 equiv of PhTeTePh, the expected product, $(C_5Me_5)_2UMe(TePh)$, analogous to **2** and **3**, was not isolated. Instead, C−H activation of the aryl ring occurred to form $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, **7**, CH_4, and MeTePh, Scheme 4. Complex **7** was characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis and was completely identified by X-ray crystallography, Figure 3.

When the reaction of **1** with 1 equiv of PhTeTePh was monitored by ^1H NMR spectroscopy, an intermediate that displayed ^1H NMR resonances consistent with $(C_5Me_5)_2UMe$-

Scheme 3



Scheme 4



(TePh) was observed, but $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, **7**, CH_4, and MeTePh were the only products after 16 h. Hence, in this tellurium system, the $(C_5Me_5)_2UMe(TePh)$ intermediate can react in two ways. In the presence of PhTeTePh, complex **6** is formed in competition with the metalation reaction to form **7**. Since **6** is formed in high yield, the aryl metalation reaction to form **7** appears to be slow compared to the reaction with PhTeTePh to make **6**.

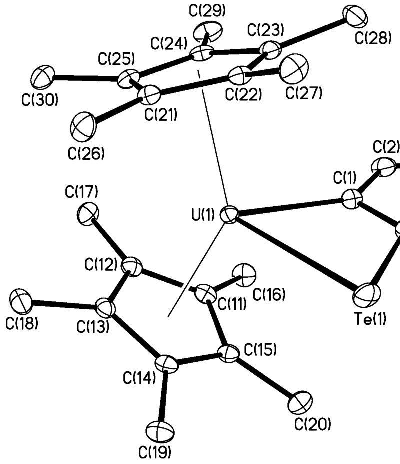


Figure 3. Molecular structure of $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, **7**, with thermal ellipsoids drawn at the 50% probability level.

Structure. The X-ray crystal structures of **2**, **3**, **6**, and **7** display conventional metallocene metrical parameters for eight-coordinate tetravalent uranium complexes of this type, Tables 1−3. The U−C(C_5Me_5) average distances of 2.74(2), 2.73(1), 2.72(3), and 2.73(3) Å for **2**, **3**, **6**, and **7**, respectively, are within the broad range of 2.71(2) to 2.80(5) Å observed for eight-coordinate tetravalent uranium metallocenes.[16]

The 2.708(2) Å U−S distance in **2** is equivalent to the 2.695(4) Å U−S(terminal ligand) distance in $(C_5Me_5)_3U(SMe)$[17] and the 2.687(2)−2.700(2) Å U−S distances in the bis(dithiolene) complex $[Na(18\text{-crown-}6)][(C_8H_8)U(C_4H_4S_4)_2]$.[18] These are shorter than the U−S(bridging ligand) distances of 2.806(3)−2.894(3) Å in $[(C_8H_8)U(\mu\text{-}SCHMe_2)]_2$[19] as expected. The U−S distance in **2** is also 0.04 Å shorter than the analogue in $(C_5Me_5)_2Th(SPh)_2$.[3] This is consistent with the 0.05 Å difference in the Shannon ionic radii of eight-coordinate U^{4+} and Th^{4+}.[20] The U−S distance in **2** is shorter than the 2.777(1)−2.791(1) Å U−S distances in trivalent $[(C_5Me_5)_2U(S^iPr)_2]^-$.[21]

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2UMe(SPh)$, 2,[a] and $(C_5Me_5)_2UMe(SePh)$, 3

	2 E = S	3 E = Se
U(1)−E(1)	2.7060(14)	2.8432(7)
U(2)−E(2)	2.7101(14)	
U1−C(21): U(1)−C(27)	2.427(5)	2.438(5)
U(2)−C(48)	2.400(5)	
E(1)−C(22): E(1)−C(21)	1.772(5)	1.920(5)
E(2)−C(49)	1.763(6)	
U(1)−Cnt1	2.463	2.452
U(1)−Cnt2	2.459	2.459
U(2)−Cnt3	2.463	
U(2)−Cnt4	2.455	
U(1)−C(C_5Me_5) range	2.713(4)−2.757(5)	2.716(5)−2.762(5)
U(1)−C(C_5Me_5) average	2.74(1)	2.73(1)
U(2)−C(C_5Me_5) range	2.685(6)−2.769(5)	
U(2)−C(C_5Me_5) average	2.73(2)	
C(21)−U(1)−E(1): C(27)−U(1)−E(1)	102.87(14)	98.11(13)
C(48)−U(2)−E(2)	98.21(14)	
U(1)−E(1)−C(22): U(1)−E(1)−C(21)	105.77(16)	104.79(15)
U(2)−E(2)−C(49)	110.45(19)	

[a] Complex **2** has two crystallographically independent molecules in the unit cell.

Fewer U−Se distances are available for comparison with **3**. In contrast to the over 100 crystallographically characterized U−S complexes in the Cambridge Crystallographic Data Base, only four[22−24] crystallographically characterized U−Se complexes are reported. None of these are metallocenes that allow for direct comparison. However, the 2.8432(7) Å U−Se distance in **3** is 0.14 Å longer than the 2.708(2) Å U−S distance in **2**,

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2U(TePh)_2$, 6, and $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, 7

6		7	
U(1)−Te(1)	3.0383(6)	U(1)−Te(1)	2.9648(4)
U(1)−Te(2)	3.0504(6)	U(1)−C(1)	2.352(4)
U(1)−Cnt1	2.458	U(1)−Cnt1	2.439
U(1)−Cnt2	2.450	U(1)−Cnt2	2.447
Te(1)−C(21)	2.117(8)	Te(1)−C(6)	2.195(4)
Te(2)−C(27)	2.125(8)	C(6)−C(1)	1.396(5)
Cnt1−U(1)−Te(1)	96.53	Cnt1−U(1)−Te(1)	109.47
Cnt1−U(1)−Te(2)	118.84	Cnt2−U(1)−Te(1)	109.85
Cnt2−U(1)−Te(1)	111.06	Cnt1−U(1)−C1(1)	101.56
Cnt2−U(1)−Te(2)	97.37	Cnt2−U(1)−C(1)	102.64
Cnt1−U(1)−Cnt2	134.58	Cnt1−U(1)−Cnt2	138.34
C(21)−Te(1)−U(1)	109.7(2)	C(6)−Te(1)−U(1)	65.73(10)
C(27)−Te(2)−U(1)	109.69(18)	Te(1)−C(6)−C(1)	124.1(3)
Te(1)−U(1)−Te(2)	101.848(19)	C(6)−C(1)−U(1)	96.8(2)
U(1)−C(C_5Me_5) range	2.682(7)−2.780(8)	Te(1)−U(1)−C(1)	72.80(1)
U(1)−C(C_5Me_5) average	2.72(3)	U(1)−C(C_5Me_5) range	2.781(3)−2.6879(4)
		U(1)−C(C_5Me_5) average	2.73(3)

which is in agreement with the 0.14 Å difference in the Shannon ionic radii of S^{2-} and Se^{2-}.[20] The 2.8432(7) Å U−Se distance in **3** is similar to the 2.8004(7) Å average U−Se distance in $(C_5Me_5)_2U(SePh)_2$.[3]

There are even fewer crystallographically characterized U−Te complexes for comparison with **6** and **7**. The only example of a crystallographically characterized U−Te complex in the literature, $U\{N(TeP^iPr_2)_2\}_3$,[25] reported by Neu and co-workers, has a 3.16(3) Å U−Te distance. The 3.044(6) Å average U−Te distance in **6** is 0.12 Å shorter, but the coordination environment is quite different. The U−Te distance in **6** is also 0.24 Å longer than the average U−Se distance in **5**, which is in agreement with the 0.23 Å difference in Shannon ionic radii of Te^{2-} and Se^{2-}.[20] The 2.747(2) Å average Th−S distance in $(C_5Me_5)_2Th(SPh)_2$[3] is 0.30 Å shorter than the average U−Te distance in **6**. This is in agreement with the expected 0.37 Å difference in Shannon ionic radii of Te^{2-} and S^{2-} [20] and the 0.05 Å difference in the ionic radii of eight-coordinate U^{4+} and Th^{4+}.[20] The 2.9648(4) Å U−Te distance in **7** is 0.11 Å shorter than the U−Te distance in **6**. This may be due to the chelating nature of the $(TeC_6H_4)^{2-}$ ligand.

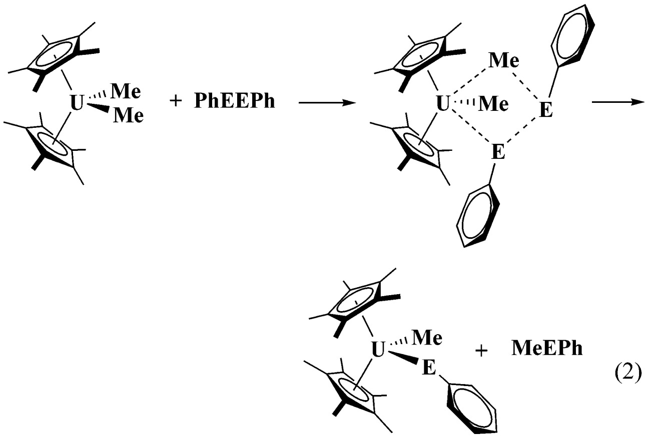
The U−E−C(*ipso*) angles in **2** and **3** decrease from S to Se with values of 105.77(16)° and 110.45(19)° for **2**, which has two crystallographically independent molecules in the unit cell, and 104.79(15)° for **3**. The decrease in angle from **2** to **3** is similar to that in the solvated samarium benzene chalcogenolate series, $(C_5Me_5)_2Sm(EPh)THF$ (E = S, Se, Te).[26] In this series, the U−E−C(*ipso*) angles for S, Se, and Te complexes are 120.82(17)°, 118.51(14)°, and 112.49(6)°, respectively. The 109.70(5)° average U−Te−C(*ipso*) angle in $(C_5Me_5)_2U(TePh)_2$, **6**, is 3° smaller than the 113(1)° U−Se−C(*ipso*) angle in **5**, which follows the trend that was observed for the U−E−C(*ipso*) angles in **2**, **3**, and $(C_5Me_5)_2Sm(EPh)THF$.[26]

The U−C(Me) distances, 2.41(1) Å for **2** and 2.438(7) Å for **3**, are similar to U−C(Me) distances in $(C_5Me_5)_2UMe_2$,[27,28] 2.424(7) and 2.414(7) Å, $(C_5Me_4H)_2UMe_2$,[29] 2.426(2) Å, and $(C_5Me_4H)_2UMeCl$,[29] 2.38(2) Å. The 2.352(4) Å U−C(1) distance in **7** is shorter than these U−C(Me) distances, but again this may be due to the chelation of the ligand. However, this is close to the range previously observed for uranium−aryl bonds, 2.386(3) to 2.561(13) Å.[30,31]

The four-membered U−Te−C(6)−C(1) ring in **7** is roughly planar, with U(1) deviating from the Te−C(6)−C(1) plane by 0.3342 Å. This is similar to the situation in the $(C_5Me_5)_2MR(\eta^2\text{-}ONC_5H_4)$ (M = U, Th; R = CH_3, CH_2Ph)[30] complexes involving a metalated pyridine ring, where uranium is 0.0698 Å and thorium is 0.0770 Å out of the O−N−C plane.

Discussion

The purpose of this study was to determine if $(C_5Me_5)_2UMe_2$, **1**, would react with PhEEPh reagents to make the same $(C_5Me_5)_2U(EPh)_2$ products, **5** (E = S) and **6** (E = Se), formed by $[(C_5Me_5)_2UH]_2$ in Scheme 1 and $[(C_5Me_5)_2UH_2]_2$ in Scheme 2. Complexes **5** and **6** are formed from **1**, but the mechanisms of the reactions are apparently very different from the hydride reactions. The methyl groups in **1** do not act like the hydride ligands in Schemes 1 and 2, which formally provide one electron per hydride and eliminate dihydrogen. If the methyl group provided an electron and formed methyl radicals, ethane or methane would be the expected products. Instead, MeEPh is observed as the byproduct. The MeEPh byproduct could be formed by a σ-bond metathesis mechanism involving U−Me and E−E bonds, eq 2. This type of reaction was previously observed in the reaction of $[(^tBuC_5H_4)_2Ln(\mu\text{-}Me)]_2$ (Ln = Y, Lu) with REER (E = S, Se; R = Ph, ^nBu, $^tBuCH_2Ph$) that forms MeER and $[(^tBuC_5H_4)_2Ln(\mu\text{-}ER)]_2$.[32]



(2)

In the case of $(C_5Me_5)_2UMe_2$, the formation of **5** and **6** can be effected stepwise by controlling the stoichiometry. Hence, reactions with 1 equiv of PhEEPh provided the mono-chalcogen

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intermediates, $(C_5Me_5)_2UMe(EPh)$, **2** (E = S) and **3** (E = Se). These react with an additional equivalent of PhEEPh to make **4** and **5**, respectively. The formation of **2**, **3**, and **6** all occur at ambient temperature, but formation of the dithiolate **5** requires heating. This can be rationalized by the fact that a S−S bond is more difficult to activate than a Se−Se bond and $(C_5Me_5)_2UMe(SPh)$ has a less sterically accessible U−Me bond than $(C_5Me_5)_2UMe_2$.

The reaction of 2 equiv of PhTeTePh with $(C_5Me_5)_2UMe_2$ gives the $(C_5Me_5)_2U(TePh)_2$ product, **6**, analogous to **4** and **5**. However, only ^{1}H NMR evidence was obtained for $(C_5Me_5)_2UMe(TePh)$, the tellurium analogue of **2** and **3**. In the absence of additional PhTeTePh, this complex eliminates methane to make the C−H activation product $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$, **7**. Metalation of arene rings has been previously observed in organoactinide chemistry with $(C_5Me_5)_2AnR_2$ (An = U, Th; R = Me, CH_2Ph) and pyridine *N*-oxide, a reaction that generates metalated $(C_5Me_5)_2AnR(\eta^2\text{-}ONC_5H_4)$ products.[30] Pyridine has also been metalated by $(C_5Me_5)_2AnMe_2$ (An = U, Th)[31] and $U[N(CH_2CH_2NSiMe_2Bu^t)_2(CH_2CH_2NSiMeBu^tCH_2)]$.[33] Although this ortho-metalation reactivity is well precedented, it is not clear why this is observed only in the PhTeTePh reaction and not with the S and Se analogues. The longer U−Te bond provides a slightly different metrical arrangement between the methyl group and the ortho-hydrogen in a $(C_5Me_5)_2UMe(EPh)$ complex, but the long bond would lead to less steric crowding. Usually, the more crowded systems eliminate alkanes more readily, as in the formation of Schrock carbene and carbyne complexes.[34−38]

Conclusion

$(C_5Me_5)_2UMe_2$ reacts with 2 equiv of PhEEPh to form $(C_5Me_5)_2U(EPh)_2$ (E = S, Se, Te) in one less step than is required from $[(C_5Me_5)_2UH_2]_2$ starting materials, since $(C_5Me_5)_2UMe_2$ is the precursor to the hydrides. The reaction pathway for the methyl precursors is not analogous to that of the hydride complexes since MeEPh byproducts are formed that are consistent with σ-bond metathesis and $(C_5Me_5)_2UMe(EPh)$ intermediates can be isolated for S and Se. The reactions provide facile, halide-free routes to the relatively rare examples of molecular compounds containing U−Se and U−Te bonds. In contrast to the S and Se analogues, $(C_5Me_5)UMe(TePh)$ generates a C−H activation product, $(C_5Me_5)_2U(\eta^2\text{-}TeC_6H_4)$.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: X-ray diffraction details (CIF) and X-ray data collection, structure solution, and refinement of compounds **2**, **3**, **6**, and **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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