

# Two-electron reductive reactivity of trivalent uranium tetraphenylborate complexes of $(C_5Me_5)^{1-}$ and $(C_5Me_4H)^{1-}$

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## Abstract

The reductive reactivity of the  $(BPh_4)^{1-}$  ligand in pentamethylcyclopentadienyl  $[(C_5Me_5)_2U][(\mu-\eta^2:\eta^1-Ph)_2BPh_2]$  (**1**) was compared with that of the tetramethyl analog,  $[(C_5Me_4H)_2U][(\mu-\eta^6:\eta^1-Ph)(\mu-\eta^1:\eta^1-Ph)BPh_2]$  (**2**) using PhSSPh as a probe to determine if the mode of  $(BPh_4)^{1-}$  bonding affected the reduction. Both complexes act as two-electron reductants to form  $(C_5Me_4R)_2U(SPh)_2$  [R = Me, **3**; H, **4**], but only in the R = H case could the product be crystallographically characterized. An improved synthesis of **1** from  $[(C_5Me_5)_2UH]$  (**5**) and  $[Et_3NH][BPh_4]$  is also reported as well as its reaction with MeCN that provides another route to the unusual, parallel-ring, uranium metallocene  $[(C_5Me_5)_2U(NCMe)_5][BPh_4]_2$  (**6**).

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**Keywords:** Organouranium; Chalcogens; Organouranium tetraphenylborate

## 1. Introduction

Recent studies of f element reduction chemistry have shown that steric crowding can induce reductive reactivity in normally inert ligands [1–4]. Specifically,  $(C_5Me_5)^{1-}$  can become a one-electron reductant in sterically crowded complexes such as  $(C_5Me_5)_3U$  [5] and  $[(C_5Me_5)_2U]_2(C_6H_6)$  [2] in which the U–C( $C_5Me_5$ ) distances are unusually long [6]. By combining this ligand-based reduction with the reducing  $U^{3+}$  ion, these complexes become capable of multi-electron reduction as shown in the four-electron reduction in Scheme 1 [3].

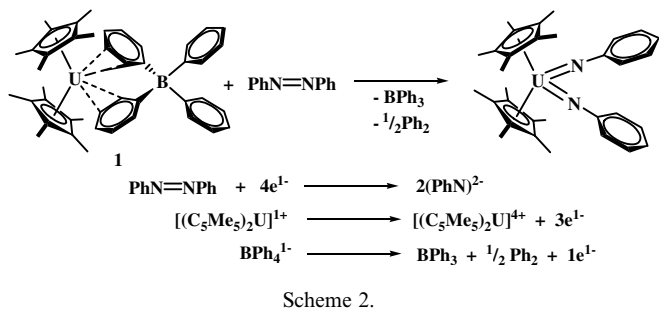
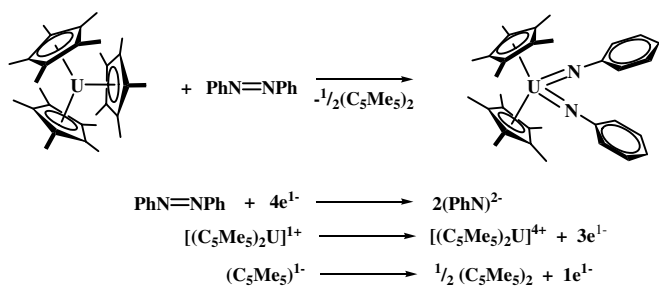
To compare the reactivity of these sterically crowded complexes with a sterically “normal” complex, the reactivity of  $[(C_5Me_5)_2U][(\mu-\eta^2:\eta^1-Ph)_2BPh_2]$  (**1**) [7] was investigated [3]. Surprisingly, **1** can accomplish the same four-electron reduction shown in Scheme 1 by combining a  $U^{3+}$  to  $U^{6+}$  conversion with a  $(BPh_4)^{1-}$  reduction. Although it has been known for decades that  $(BPh_4)^{1-}$

participates in the half reaction shown at the bottom of Scheme 2 [3,8], the reactivity has not been combined with conventional metal based reducing agent to effect multi-electron reduction of this type.

It was of interest to determine if this  $(BPh_4)^{1-}$  redox activity was specific to  $(C_5Me_5)^{1-}$  complexes and if it had any dependence on its mode of attachment to  $U^{3+}$ . Accordingly, the reductive reactivity of the tetramethylcyclopentadienyl complex  $[(C_5Me_4H)_2U][(\mu-\eta^6:\eta^1-Ph)(\mu-\eta^1:\eta^1-Ph)BPh_2]$  (**2**) [9] was examined. Complex **2** differs from **1** in that one phenyl group is oriented  $\eta^6$  to  $U^{3+}$  and the other is  $\eta^1$ , whereas **1** has two  $\eta^2$ -phenyl groups. We report here a comparison of  $(BPh_4)^{1-}$  reduction chemistry with **1** and **2**. PhSSPh was used as the substrate since it allows a direct comparison, it expands the range of substrates involved in  $(BPh_4)^{1-}$  reduction chemistry [3], and one of the possible products,  $(C_5Me_5)U(SPh)_2$  had previously been identified by Ephritikhine et al. [10].

Since **1** has proven to be a crucial starting material for recent developments in reduction chemistry [2,3,7], new methods to synthesize this complex were sought. Previously, the synthesis of **1** required multiple steps and alkali metal reduction of  $U^{4+}$  to  $U^{3+}$  [7]. We also report here an improved

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synthesis of **1** from  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  and  $[(\text{C}_5\text{Me}_5)_2\text{UH}]_2$  [11,12] that is more efficient in both time and reagents. Due to the recent synthesis of an unprecedented type of linear metallocene,  $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{NCMe})_5][\text{BPh}_4]_2$  (**6**) [13], complex **1** was reacted with MeCN in an attempt to synthesize a  $\text{U}^{3+}$  analog. This resulted in a new synthetic route to the  $\text{U}^{4+}$  complex.

## 2. Experimental

### 2.1. General procedures

The manipulations described below were performed under argon (unless otherwise noted) with the 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 Glass-Contour [14] columns. Benzene- $d_6$  was dried over NaK alloy and vacuum transferred before use.  $(\text{C}_5\text{Me}_4\text{H})_2\text{UCl}_2$  [11],  $[(\text{C}_5\text{Me}_5)_2\text{UH}]_2$  [11,12]  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  [15] and KSPH [16] were prepared as previously described. PhSSPh was purchased from Aldrich and sublimed before use. MeCN was purchased from Aldrich and distilled over  $\text{CaH}_2$  onto molecular sieves and degassed by three freeze–pump–thaw cycles. NMR spectra were recorded with a Bruker DRX 500 MHz system. Infrared spectra were recorded as thin films on an ASI ReactIR 1000 instrument [17]. Elemental analysis was performed by Analytische Laboratorien, Lindlar, Germany.

### 2.2. Synthesis of $[(\text{C}_5\text{Me}_5)_2\text{U}][(\mu\text{-}\eta^2\text{:}\eta^1\text{-Ph})_2\text{BPh}_2]$ (**1**)

A brown-green solution of  $[(\text{C}_5\text{Me}_5)_2\text{UH}]_2$  (1.35 g, 1.32 mmol) in  $\text{C}_6\text{H}_6$  (30 mL) was added to a stirred white

slurry of  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  (1.12 g, 2.66 mmol) in  $\text{C}_6\text{H}_6$  (15 mL) in a 100 mL round bottom flask. A translucent brown solution immediately formed. The round bottom flask was vented periodically over a period of 8 h. After the mixture was stirred for 12 h, the brown solution was evaporated to dryness yielding **1** as a brown powder (1.89 g, 86%) that was identified by  $^1\text{H}$  NMR spectroscopy [7].

### 2.3. Synthesis of $(\text{C}_5\text{Me}_5)_2\text{U}(\text{SPh})_2$ (**3**) from $[(\text{C}_5\text{Me}_5)_2\text{U}][(\mu\text{-}\eta^2\text{:}\eta^1\text{-Ph})_2\text{BPh}_2]$ (**1**)

PhSSPh (13 mg, 0.060 mmol) in  $\text{C}_6\text{H}_6$  (2 mL) was added to **1** (50 mg, 0.060 mmol) in  $\text{C}_6\text{H}_6$  (5 mL) and stirred for 12 h. The resulting red solution was evaporated to dryness to yield a dark red oil that contained **3** [10] by  $^1\text{H}$  NMR spectroscopy and another product that displayed a single  $\text{C}_5\text{Me}_5$  resonance at 9.4 ppm of intensity equal to that of the  $\text{C}_5\text{Me}_5$  resonance of **3**.

The 9.4 ppm resonance was consistent with the  $^1\text{H}$  NMR resonance of the product obtained by reacting **1** with 1 equiv. of KSPH as follows. Compound **1** (95 mg, 0.13 mmol) in toluene (5 mL) was added to a white slurry of KSPH (19 mg, 0.13 mmol) in toluene (5 mL) and stirred for 24 h. Brown insoluble materials were removed by centrifugation and the solvent was removed under vacuum to yield a dark red oil that displayed a single resonance at 9.4 ppm in the  $^1\text{H}$  NMR spectrum. Repeated attempts to crystallize this product for X-ray analysis and to make solid derivatives suitable for elemental analysis were not successful.

### 2.4. Synthesis of $(\text{C}_5\text{Me}_4\text{H})_2\text{U}(\text{SPh})_2$ (**4**) from $(\text{C}_5\text{Me}_4\text{H})_2\text{UCl}_2$

A dark red solution of  $(\text{C}_5\text{Me}_4\text{H})_2\text{UCl}_2$  (150 mg, 0.27 mmol) in toluene (10 mL) was added to a white slurry of KSPH (81 mg, 0.54 mmol) in toluene (10 mL) and stirred for 12 h. Brown insoluble materials were removed by centrifugation, and the solvent was removed under vacuum to form a dark orange oil. This was dissolved in hexane and cooled to  $-35^\circ\text{C}$ . After 2 days, **4** was obtained as red crystals (124 mg, 65%). Crystals of **4** suitable for X-ray diffraction were grown at  $-35^\circ\text{C}$  from a concentrated solution in hexane.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  26.5 (s, 12H,  $\text{C}_5\text{Me}_4\text{H}$ ,  $\Delta\nu_{1/2} = 17$  Hz),  $-4.8$  (s, 12H,  $\text{C}_5\text{Me}_4\text{H}$ ,  $\Delta\nu_{1/2} = 13$  Hz), 2.9 (t, 2H,  $^3J_{\text{HH}} = 8$  Hz, *p*-H), 2.5 (br t, 4H, *m*-H),  $-24.6$  (s with broad shoulder, 6H, *o*-H,  $\text{C}_5\text{Me}_4\text{H}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.6 ( $\text{C}_5\text{Me}_4\text{H}$ ), 183.3 ( $\text{C}_5\text{Me}_4\text{H}$ ), 106.0 (*m*-phenyl), 132.9 (*p*-phenyl), 142.3 (*o*-phenyl), 129.7 ( $\text{C}_5\text{Me}_4\text{H}$ ), 128.9 ( $\text{C}_5\text{Me}_4\text{H}$ ), 126.0 ( $\text{C}_5\text{Me}_4\text{H}$ ). IR: 2961m, 2910s, 2856s, 1720w, 1579m, 1476s, 1444s, 1382m, 1320m, 1258vs, 1085vs, 1011vs, 957m, 865m, 784vs, 741s, 695vs, 676vs  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{30}\text{H}_{36}\text{S}_2\text{U}$ : C, 51.57; H, 5.19; S, 9.18; U, 34.06. Found: C, 51.32; H, 5.02; S, 9.00; U, 33.80%.

### 2.5. Synthesis of $(C_5Me_4H)_2U(SPh)_2$ (**4**) from $[(C_5Me_4H)_2U][(\mu-\eta^6:\eta^1-Ph)(\mu-\eta^1:\eta^1-Ph)BPh_2]$ (**2**)

PhSSPh (10 mg, 0.046 mmol) in  $C_6D_6$  was added to an NMR tube containing **2** (37 mg, 0.046 mmol) in  $C_6D_6$ . The color immediately changed from brown to red. After 12 h, the  $^1H$ ,  $^{13}C$ ,  $^{11}B$  NMR spectra showed complete conversion of starting materials to **4** and  $BPh_3$ .

### 2.6. Synthesis $[(C_5Me_5)_2U(NCMe)_5][BPh_4]_2$ (**6**)

In a nitrogen filled glovebox, **1** (100 mg, 0.12 mmol) was dissolved in 10 mL of MeCN and allowed to stir for 12 h. The resulting brown-green solution was reduced to 5 mL under vacuum and cooled to  $-35^\circ C$ . After 5 days, **6** was obtained as black crystals (21 mg, 26%) that were identified by X-ray crystallography and  $^1H$  NMR spectroscopy [13].

### 2.7. X-ray data collection and refinement for $(C_5Me_4H)_2U(SPh)_2$ (**4**)

A red crystal of approximate dimensions  $0.13 \times 0.17 \times 0.25$  mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART [18] program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT [19] and SADABS [20] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL [21] program. The diffraction symmetry was  $2/m$  and the systematic absences were consistent with the monoclinic space groups  $Cc$  and  $C2/c$ . It was later determined that the centrosymmetric space group  $C2/c$  was correct. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-

squares techniques. The analytical scattering factors [22] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined ( $x$ ,  $y$ ,  $z$  and  $U_{iso}$ ). At convergence,  $wR_2 = 0.0456$  and  $GOF = 1.075$  for 442 variables refined against 6674 data. As a comparison for refinement on  $F$ ,  $R_1 = 0.0192$  for those 5874 data with  $I > 2.0\sigma(I)$ . Details are given in Table 1.

## 3. Results

### 3.1. Reduction of PhSSPh

$[(C_5Me_5)_2U][(\mu-\eta^2:\eta^1-Ph)_2BPh_2]$  (**1**) reacts within 12 h with PhSSPh to form  $(C_5Me_5)_2U(SPh)_2$  (**3**) a complex previously reported by Ephritikhine et al. from the reaction of  $(C_5Me_5)_2UCl_2$  and NaSPh [10]. No crystallographic data were obtained in that study although numerous sulfur donor atom complexes of uranium have been crystallographically characterized [10,23,24] and, in our hands, crystals of **3** were also elusive. The  $^1H$  NMR spectrum of the product of the reaction of **1** and PhSSPh also revealed another product with a  $(C_5Me_5)^{1-}$  resonance at 9.4 ppm. This complex also did not crystallize, but could be obtained as a single product from the reaction of **1** and KSPH. On the basis of this reaction chemistry, the 9.4 ppm complex was expected to be the trivalent phenylsulfide,  $[(C_5Me_5)_2U(SPh)]_n$ , but it could only be isolated as a tacky oil. Attempts to make crystalline base adducts or derivatives by  $CO_2$  insertion, a reaction useful with the lanthanide analogs,  $[(C_5Me_5)_2Ln(SPh)]_2$  [25], were not successful. The  $^1H$  and  $^{13}C$  NMR spectrums of the reaction of **1** and PhSSPh also displayed resonances consistent with  $BPh_3$ , however, resonances of the other expected byproduct  $Ph_2$ , were not observed. Although biphenyl has been observed in other reductions involving uranium complexes of  $(BPh_4)^{1-}$  [3], it was not observed in this case. The fate of the phenyl radicals required by the stoichiometry is unknown.

In contrast to the pentamethylcyclopentadienyl chemistry, the tetramethylcyclopentadienyl analog,  $[(C_5Me_4H)_2U][(\mu-\eta^6:\eta^1-Ph)(\mu-\eta^1:\eta^1-Ph)BPh_2]$  (**2**) reacts with PhSSPh to form only one uranium metallocene complex  $(C_5Me_4H)_2U(SPh)_2$  (**4**), Eq. (1) and  $BPh_3$ . Again, biphenyl was not observed in the  $^1H$  and  $^{13}C$  NMR spectra. To aid in the identification of **4**, this complex was made independently from  $(C_5Me_4H)_2UCl_2$  and KSPH, Eq. (2). In contrast to **3**, complex **4** readily crystallizes to give the structure shown in Fig. 1.

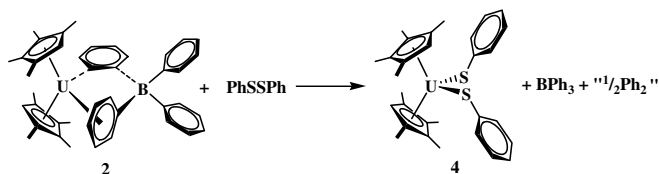


Table 1  
X-ray data collection parameters for  $(C_5Me_4H)_2U(SPh)_2$  (**4**)

Compound	<b>4</b>
Empirical formula	$C_{30}H_{36}S_2U$
Formula weight	698.74
Temperature (K)	163(2)
Crystal system	Monoclinic
Space group	$C2/c$
$a$ (Å)	16.2886(12)
$b$ (Å)	14.0086(10)
$c$ (Å)	24.7932(18)
$\alpha$ (°)	90
$\beta$ (°)	106.0030(10)
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	5438.1(7)
$Z$	8
$\rho_{calc}$ (Mg/m <sup>3</sup> )	1.707
$\mu$ (mm <sup>-1</sup> )	6.139
$R_1^a$ [ $I > 2.0\sigma(I)$ ]	0.0192
$wR_2^b$ (all data)	0.0456

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

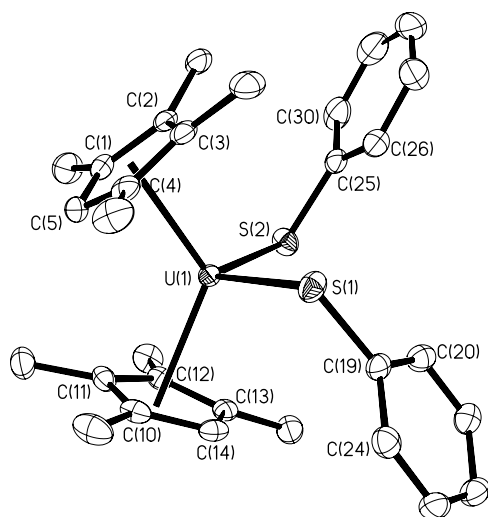
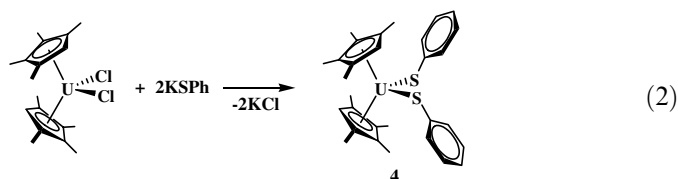


Fig. 1. Molecular structure of  $(C_5Me_4H)_2U(SPh)_2$  (**4**) with thermal ellipsoids drawn at the 50% probability level.

Table 2  
Selected bond distances (Å) and angles (°) for  $(C_5Me_4H)_2U(SPh)_2$  (**4**)

Bond distance (Å)	
U(1)–S(1)	2.6845(7)
U(1)–S(2)	2.6967(7)
U(1)–Cnt1	2.448
U(1)–Cnt2	2.437
S(1)–C(19)	1.776(3)
S(2)–C(25)	1.775(3)
Bond angle (°)	
Cnt1–U(1)–S(1)	97.7
Cnt1–U(1)–S(2)	112.4
Cnt2–U(1)–S(1)	110.3
Cnt2–U(1)–S(2)	98.0
Cnt1–U(1)–Cnt2	128.9
C(19)–S(1)–U(1)	104.44(9)
C(25)–S(2)–U(1)	108.57(9)
S(1)–U(1)–S(2)	109.12(2)

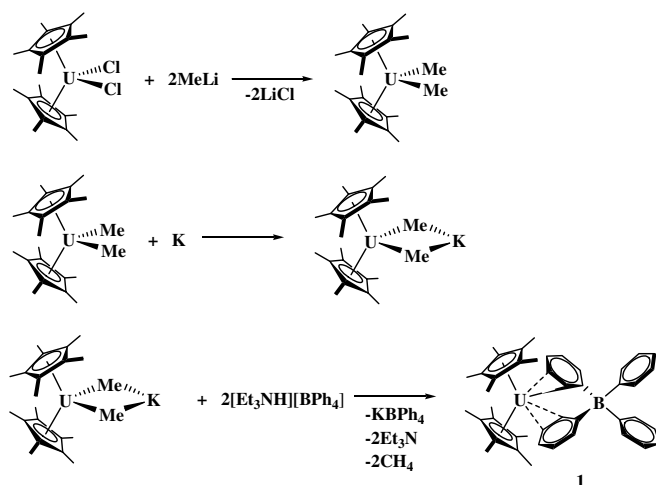


Complex **4** has a typical uranium bent metallocene structure in which the two  $(C_5Me_4H)^{1-}$  rings and the two  $(PhS)^{1-}$  ligands define a distorted tetrahedron around the  $U^{4+}$  center. The bonding parameters are normal for eight-coordinate tetravalent uranium complexes. For example, the 2.443 Å average U– $(C_5Me_4H)$  ring centroid distance is similar to the 2.444, 2.429, and 2.42 Å distances in  $(C_5Me_4H)_2UMe_2$  [9],  $(C_5Me_4H)_2UMeCl$  [9], and  $(C_5Me_4H)_2UCl_2$  [9], respectively.

The 2.691(6) Å average U–S distance in **4** is equivalent to the 2.687(2)–2.700(2) Å U–S distances in the bis(dithiolen) complex  $[Na(18-crown-6)][U(C_8H_8)(C_4H_4S_4)_2]$  [23] crystallographically characterized by Ephritikhine et al. The U–S average in **4** is also 0.056 Å shorter than the analogue in  $(C_5Me_5)_2Th(SPh)_2$  [12] consistent with the 0.05 Å difference in the Shannon ionic radii of eight-coordinate  $U^{4+}$  and  $Th^{4+}$  [26]. It is also shorter than the 2.7997(7) and 2.8011(7) Å U–Se distances in  $(C_5Me_5)_2U(SePh)_2$  [12] consistent with the 0.14 Å difference in Shannon ionic radii of  $S^{2-}$  and  $Se^{2-}$  [26]. The U–S–C(Ph) angles are close to tetrahedral: 104.4(1)° and 108.6(1)° (see Table 2).

### 3.2. Improved synthesis of $[(C_5Me_5)_2U][(\mu-\eta^2:\eta^1-Ph)_2BPh_2]$ (**1**)

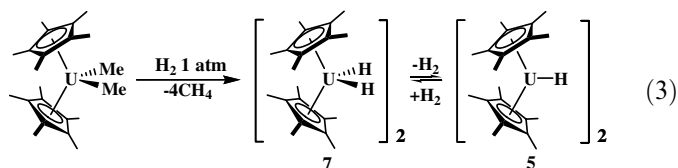
Complex **1** was previously made by the sequence of reactions shown in Scheme 3.  $(C_5Me_5)_2UMe_2$ , formed from  $(C_5Me_5)_2UCl_2$  and MeLi, reacts with potassium sand over



Scheme 3.

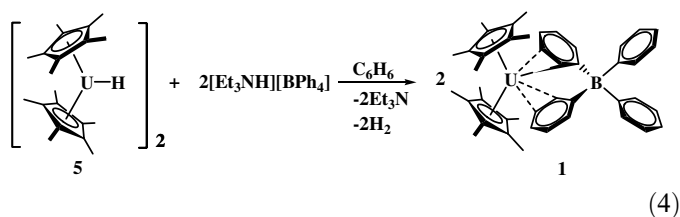
four days to form  $(C_5Me_5)_2UMe_2K$  [7]. This compound was subsequently treated with  $[Et_3NH][BPh_4]$  to form **1** in 82% overall yield. Although this process produces **1** in high yield, it is limited in that, in our hands, only small quantities, ca. 500 mg, can be successfully synthesized at one time. When the synthesis of larger quantities of  $(C_5Me_5)_2UMe_2K$  is attempted, we find that the reaction of  $(C_5Me_5)_2UMe_2$  and K is not complete.

An alternative route to **1** was envisioned using the  $U^{3+}$  hydride  $[(C_5Me_5)_2UH]_2$  [11,12] (**5**) and 2 equiv. of  $[Et_3NH][BPh_4]$ . Complex **5** is made from the same  $(C_5Me_5)_2UMe_2$  precursor as **1**. The hydride route to **1** initially seemed problematic since **5** is made in a mixture containing  $[(C_5Me_5)_2UH_2]_2$  [11] (**7**), Eq. (3). This mixture of hydrides could give both  $U^{3+}$  and  $U^{4+}$  ( $BPh_4$ ) $^{1-}$  products.



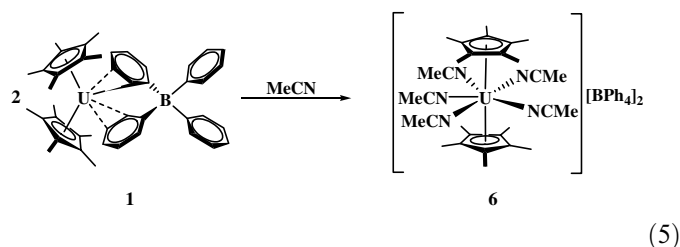
Recently, however, it was found that **5** could be isolated in nearly pure form. Removal of solvent from a toluene solution of **7** followed by dissolution in hexane, removal of solvent, and finally dissolution in toluene and removal of solvent generates a brown-green solid that analyzes by  $^1\text{H}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$  as **5** [12].

To test these ideas, **5** was treated with 2 equiv. of  $[\text{Et}_3\text{NH}][\text{BPh}_4]$ . Complex **1** was formed in high yield (94%) and purity on the basis of  $^1\text{H}$  NMR spectroscopy, Eq. (4). Samples of **1** prepared by this route have also proven to be good precursors to  $(\text{C}_5\text{Me}_5)_3\text{U}$  [5],  $[(\text{C}_5\text{Me}_5)_2\text{U}]_2(\text{C}_6\text{H}_6)$  [2],  $[(\text{C}_5\text{Me}_5)_2\text{U}(\mu\text{-N})\text{U}(\mu\text{-N}_3)(\text{C}_5\text{Me}_5)_2]_4$  [27], and  $(\text{C}_5\text{Me}_5)_2\text{-U}(\text{C}_4\text{Ph}_4)$  [3]. Complex **1** can now be prepared in three days starting from  $(\text{C}_5\text{Me}_5)_2\text{UCl}_2$  instead of six days and it can be done on a 2 g scale.



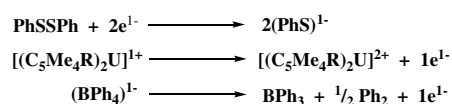
### 3.3. New synthesis of $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{NCMe})_5][\text{BPh}_4]_2$ (**6**)

Complex **1** was treated with MeCN to determine if a trivalent analog of  $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{NCMe})_5][\text{BPh}_4]_2$  [13] (**6**) could be isolated. Complex **6** is unusual because it is the first actinide metallocene to be found to have parallel pentamethylcyclopentadienyl rings, i.e. a  $180^\circ$  ( $\text{C}_5\text{Me}_5$  ring centroid)–An–( $\text{C}_5\text{Me}_5$  ring centroid) angle. Crystalline material was obtained from **1** in neat MeCN, but X-ray crystallographic analysis revealed that it was the tetravalent metallocene **6**, Eq. (5). The byproduct of the oxidation of the trivalent precursor was not readily identified.



## 4. Discussion

Both **1** and **2** function as two-electron reductants with PhSSPh to generate the corresponding phenylsulfide complexes,  $(\text{C}_5\text{Me}_4\text{R})_2\text{U}(\text{SPh})_2$  ( $\text{R} = \text{Me}, \text{H}$ ), by combining  $(\text{BPh}_4)^{1-}$  reduction chemistry with reduction by  $\text{U}^{3+}$ . Scheme 4 shows the half reactions involved. Hence, the  $(\text{BPh}_4)^{1-}$  ligand can function as a reductant along with  $\text{U}^{3+}$  when it arises from a  $[(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph})\text{BPh}_2]^{1-}$  complex as well as a  $[(\mu\text{-}\eta^2\text{:}\eta^1\text{-Ph})_2\text{BPh}_2]^{1-}$  compound. This reactivity also occurs in both  $(\text{C}_5\text{Me}_5)^{1-}$  and



Scheme 4.

$(\text{C}_5\text{Me}_4\text{H})^{1-}$  complexes. Apparently, this two-electron reduction reactivity for the  $(\text{BPh}_4)^{1-}/\text{U}^{3+}$  combination is not connected with some special aspect of the  $(\text{C}_5\text{Me}_5)^{1-}$  complexes. This contrasts with the sterically induced reduction chemistry of  $(\text{C}_5\text{Me}_5)_3\text{M}$  compounds [6] which does not occur with the less sterically crowded  $(\text{C}_5\text{Me}_4\text{H})_3\text{M}$  analogs [9,28,29].

The  $(\text{C}_5\text{Me}_5)^{1-}$  and  $(\text{C}_5\text{Me}_4\text{H})^{1-}$  complexes do differ in the crystallinity of the products: the  $(\text{C}_5\text{Me}_4\text{H})^{1-}$  products crystallize more readily in this system. In addition, the  $(\text{C}_5\text{Me}_4\text{H})^{1-}$  system provides as single product, **4**, rather than the mixture obtained with the  $(\text{C}_5\text{Me}_5)^{1-}$  reaction. The special aspects of  $(\text{C}_5\text{Me}_4\text{H})^{1-}$  in f element chemistry have been noted before [30].

The synthesis of **1** from  $[(\text{C}_5\text{Me}_5)_2\text{UH}]_2$  (**5**) is much improved over the multi-step route previously used to make this useful precursor. The synthesis of the paralleling metallocene  $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{NCMe})_5][\text{BPh}_4]_2$  (**6**) from **1** does not represent an improved synthesis since **6** can also be obtained from  $(\text{C}_5\text{Me}_5)_2\text{UME}_2$  [13], a precursor to **1**. However, the formation of **6** from **1** may indicate that it is a thermodynamically favorable end product of bis(pentamethylcyclopentadienyl) uranium  $\text{U}^{4+}$  chemistry in acetonitrile despite its unusual structure.

## 5. Conclusion

Both  $[(\text{C}_5\text{Me}_5)_2\text{U}][(\mu\text{-}\eta^2\text{:}\eta^1\text{-Ph})_2\text{BPh}_2]$  and  $[(\text{C}_5\text{Me}_5)_2\text{U}][(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph})\text{BPh}_2]$  function as two-electron reductants with PhSSPh to form  $(\text{C}_5\text{Me}_4\text{R})_2\text{U}(\text{SPh})_2$  products. The reductive chemistry of the  $(\text{BPh}_4)^{1-}$  ligand is not affected by either its solid state mode of coordination or the ancillary ligands in this case.

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## Appendix A. Supplementary material

CCDC 633748 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.04.046](https://doi.org/10.1016/j.jorganchem.2007.04.046).

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