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## Phenylsilane as a safe, versatile alternative to hydrogen for the synthesis of actinide hydrides†

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**The thorium and uranium dihydride dimer complexes [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>-An(H)(μ-H)]<sub>2</sub> (An = Th, U) have been easily prepared using phenylsilane, which is an efficient and safer alternative to hydrogen gas. The synthetic utility of this new hydriding method has been demonstrated by the preparation of a variety of organometallic complexes, including, for the first time, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(SMe)<sub>2</sub>, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(C<sub>4</sub>Ph<sub>4</sub>), (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(C<sub>4</sub>Ph<sub>4</sub>), (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThS<sub>5</sub>, and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(bipy) using [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th, U) as multi-electron reductants.**

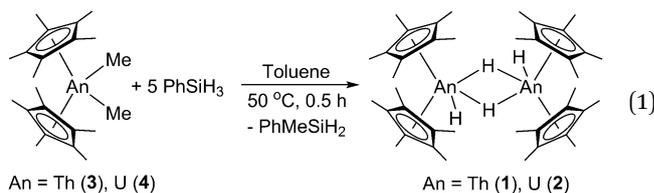
Compared to the hundreds of reported transition metal and lanthanide hydrides, there are only a limited number of thorium and uranium hydride complexes.<sup>1–14</sup> The bis(pentamethylcyclopentadienyl) complexes [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th (1), U (2)) were the first isolable organoactinide hydride complexes;<sup>12</sup> and since their introduction in 1982, they have displayed a palette of chemical reactivity such as the stoichiometric and catalytic hydrogenation of unsaturated substrates,<sup>9,12,15–17</sup> the catalytic dimerization of propylene,<sup>18,19</sup> coupling reactions,<sup>20–22</sup> and multi-electron reductions (following liberation of H<sub>2</sub>).<sup>13,14,23–25</sup>

The chemistry of actinide hydrides is still not well understood. One reason may be that the primary synthetic route for accessing actinide hydride complexes is the hydrogenolysis of alkyl precursors.<sup>26</sup> For example, the classic route to the dihydride dimer complexes 1 and 2 involves treating the known alkyl complexes (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnMe<sub>2</sub> (An = Th (3), U (4)) with H<sub>2</sub>; the uranium derivative (2) must be stored under H<sub>2</sub> as it is prone to loss of H<sub>2</sub> and formation of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(μ-H)]<sub>2</sub> (5).<sup>12,27</sup> Having stable and easy-to-handle liquid surrogates for H<sub>2</sub> as hydriding reagents would be synthetically more

convenient, thereby enabling future progress in the field of actinide hydride chemistry.<sup>28</sup>

Using the [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th (1), U (2)) systems as a platform, we now demonstrate that phenylsilane (PhSiH<sub>3</sub>) is a safe, versatile alternative to H<sub>2</sub> for the synthesis of actinide hydride complexes from the corresponding alkyl precursors. This operationally simple method gives rise to synthetically useful hydrides and importantly only produces volatile, easily separable byproducts. To further add to the scope of the reaction, the method was applied to the synthesis of a variety of thorium and uranium complexes – some for the first time – using 1 or 2 as multi-electron reductants.

As illustrated in eqn (1), quantitative conversion of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnMe<sub>2</sub> (An = Th (3), U (4)) into the corresponding dihydride dimer complexes [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th (1), U (2)) was conveniently achieved in 30 minutes by heating 3 and 4, respectively, with 5 equiv. of PhSiH<sub>3</sub> at 50 °C in toluene solution. When the reactions were monitored by <sup>1</sup>H NMR spectroscopy in C<sub>6</sub>D<sub>6</sub> using an internal standard (Cp<sub>2</sub>Fe for Th; C<sub>6</sub>Me<sub>6</sub> for U), the complete loss of complexes 3 (δ<sub>Th-Me</sub> = -0.19)<sup>12</sup> and 4 (δ<sub>U-Me</sub> = -124),<sup>12</sup> and the quantitative formation of PhMeSiH<sub>2</sub> (δ<sub>Si-H</sub> = q, 4.46)<sup>29</sup> and complexes 1 (δ<sub>Th-H</sub> = 19.43)<sup>12</sup> and 2 (δ<sub>U-H</sub> = -343),<sup>12</sup> were easily confirmed by their respective diagnostic <sup>1</sup>H NMR An-Me, Si-H and An-H chemical shifts.<sup>12</sup> Interestingly, under these reaction conditions, the tetravalent hydrides [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th (1), U (2)) are the only species observed in solution with no evidence for the formation of the trivalent [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(μ-H)]<sub>2</sub> (5) (δ<sub>C<sub>5</sub>Me<sub>5</sub></sub> = -9.37)<sup>12</sup> from 2. Presumably, this is due to the presence of the excess phenylsilane in the reaction mixture. If preferred, the dihydride complexes 1 and 2 can be isolated in 96% and 97% yields, respectively, by simply removing the volatiles from the reaction mixture.

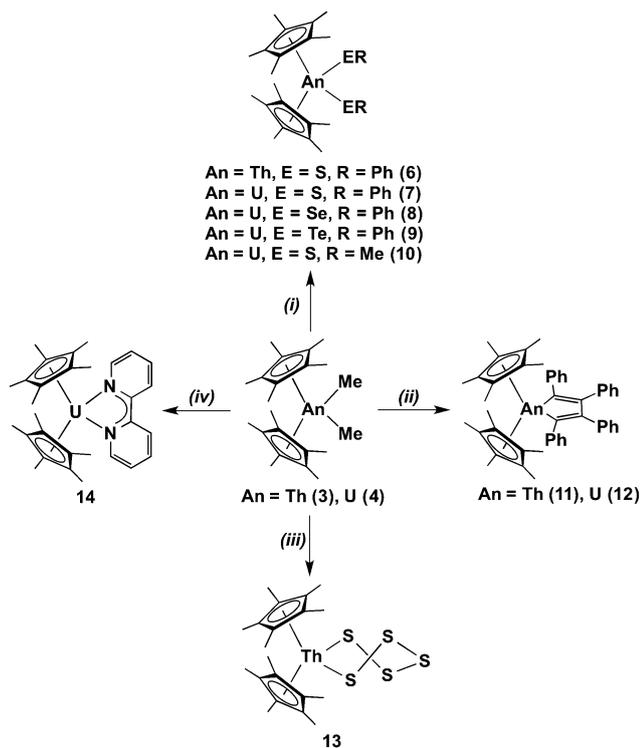


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**Scheme 1** Reagents and conditions: (i) 1 equiv. REER, 5 equiv. PhSiH<sub>3</sub>, toluene, 50 °C, 0.25–5 h, **6** (100% yield), **7** (69% yield), **8** (81% yield), **9** (95% yield), **10** (77% yield); (ii) 2 equiv. PhC≡CPh, 5 equiv. PhSiH<sub>3</sub>, toluene, 50 °C, 3 h, **11** (68% yield), **12** (61% yield); (iii) 0.625 equiv. S<sub>8</sub>, 5 equiv. PhSiH<sub>3</sub>, toluene 50 °C, 0.25 h, 80% yield; (iv) 1 equiv. 2,2'-bipyridine, 5 equiv. PhSiH<sub>3</sub>, toluene, 50 °C, 15 h, 69% yield.

Previously, Evans and co-workers reported that [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th (**1**), U (**2**)), prepared using the traditional H<sub>2</sub> hydriding route, function as multi-electron reductants. To confirm that the chemical integrity of **1** and **2** produced from phenylsilane is maintained, we surveyed their capacity to serve as multi-electron reductants with a wide range of substrates as outlined in Scheme 1. Importantly, control experiments showed that phenylsilane does not reduce any of the substrates used as reagents in Scheme 1. As a starting point, the reductive chemistry of complexes **1** and **2**, generated *in situ* from phenylsilane, was examined with several diaryl and dialkyl dichalcogenides. The reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnMe<sub>2</sub> (An = Th (**3**), U (**4**)) with 5 equiv. of PhSiH<sub>3</sub> and 1 equiv. of PhEPh (E = S, Se, Te) or MeSSMe at 50 °C in toluene afforded PhMeSiH<sub>2</sub>, H<sub>2</sub>, and the known compounds (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(EPh)<sub>2</sub> (An = Th, E = S (**6**); An = U, E = S (**7**); An = U, E = Se (**8**); An = U, E = Te (**9**)) and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(SMe)<sub>2</sub> (**10**). Reaction times and temperatures varied between compounds **6–10**, as did yields. However, this chemistry using the (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnMe<sub>2</sub>/phenylsilane reduction combination provided comparable, and in some cases superior, yields to those previously reported for the syntheses of **6–10**.<sup>13,23,24,30</sup> Although complex **10** has not previously been prepared by hydride-based four-electron reduction chemistry, collectively, these results parallel the chemistry reported by Evans and co-workers for the hydride complexes **1**, **2** and **5** prepared and isolated from the hydrogenolysis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnMe<sub>2</sub> (An = Th (**3**), U (**4**)).<sup>13,23,24,30</sup>

Using this new hydriding method, we were interested in the ability of complexes **1** and **2** to serve as low-valent thorium and

uranium equivalents. We targeted four thorium and uranium molecules that have not been previously prepared from complexes **1** and **2**: (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(C<sub>4</sub>Ph<sub>4</sub>) (An = Th (**11**), U (**12**)), (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThS<sub>5</sub> (**13**) and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(bipy) (**14**).

First, the coupling of PhC≡CPh to (C<sub>4</sub>Ph<sub>4</sub>)<sup>2-</sup> by complexes **1** and **2** was examined. Reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnMe<sub>2</sub> (An = Th (**3**), U (**4**)) with 5 equiv. PhSiH<sub>3</sub> and 2 equiv. of PhC≡CPh at 50 °C in toluene afforded PhMeSiH<sub>2</sub>, H<sub>2</sub>, and the previously reported metal-lacyclopentadiene complexes (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(C<sub>4</sub>Ph<sub>4</sub>) (An = Th (**11**), U (**12**)) in 68% and 61% isolated yields, respectively (Scheme 1). In these reactions, both complexes **1** and **2** are functioning as four-electron reductants. The formation of complexes **11** and **12** establishes that the (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnMe<sub>2</sub>/phenylsilane reduction combination provides an attractive synthetic strategy for accessing chemistry previously reported for very reactive low-valent uranium and thorium species. For example, the reductive coupling of PhC≡CPh to (C<sub>4</sub>Ph<sub>4</sub>)<sup>2-</sup> to prepare complex **12** has been achieved in the past, but requires either sterically crowded complexes such as (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U,<sup>31</sup> [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U][[(μ-Ph)<sub>2</sub>BPh<sub>2</sub>]]<sub>2</sub>,<sup>31</sup> and [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U]<sub>2</sub>(μ-η<sup>6</sup>:η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>31</sup> (which are capable of transferring multiple electrons to a substrate), or the reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>UCl<sub>2</sub> combined with excess reducing equivalents provided by Na/Hg,<sup>27</sup> and KC<sub>8</sub>,<sup>27</sup> or salt metathesis between (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>UCl<sub>2</sub> and 1,4-dilithiotetraphenylbutadiene.<sup>12</sup> Although complex **12** has been known for nearly 30 years, only very recently has the synthesis of the thorium analogue (**11**) been realized. Walter and co-workers reported that (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(C<sub>4</sub>Ph<sub>4</sub>) (**11**) can be prepared from the reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThCl<sub>2</sub> and 2 equiv. of PhC≡CPh in the presence of 5 equiv. of KC<sub>8</sub>.<sup>32</sup>

The synthesis of complexes (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThS<sub>5</sub> (**13**) and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(bipy) (**14**) were initially reported by Ryan in 1986,<sup>33</sup> and Ephritikhine in 2005,<sup>34</sup> respectively. Complex **14** is unique as it contains a trivalent uranium metal center coordinated to a redox-active bipy ligand (bipy = 2,2'-bipyridine). Previously, it was found that reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThCl<sub>2</sub> with Li<sub>2</sub>S<sub>5</sub> formed the rare thorium pentasulfide complex **13**; whereas, **14** was synthesized from the reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(I)(bipy) with excess Na/Hg or KC<sub>8</sub>.<sup>34,35</sup> We now demonstrate that complexes **13** and **14** can be easily prepared from the corresponding hydrides [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th (**1**), U (**2**)) (Scheme 1). For example, reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThMe<sub>2</sub> (**3**) with 5 equiv. PhSiH<sub>3</sub> and 0.625 equiv. of S<sub>8</sub> at 50 °C in toluene resulted in an immediate color change from red-orange to bright yellow, along with the formation of PhMeSiH<sub>2</sub>, H<sub>2</sub>, and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThS<sub>5</sub> (**13**) (δ<sub>C<sub>5</sub>Me<sub>5</sub></sub> = 2.04)<sup>33</sup> in 80% isolated yield. Similarly, the reaction of **4** with 5 equiv. of PhSiH<sub>3</sub> and 2,2'-bipyridine at 50 °C in toluene for 15 h gave (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(bipy) (**14**) in 69% isolated yield after workup.<sup>34,35</sup>

In conclusion, we have shown that the tetravalent thorium and uranium hydrides [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th (**1**), U (**2**)) can be easily and efficiently prepared from the corresponding alkyl precursors (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnMe<sub>2</sub> and PhSiH<sub>3</sub>. This new organosilane method obviates the need for H<sub>2</sub> gas or pyrophoric reductants (*e.g.*, sodium amalgam, potassium graphite, *etc.*) and provides a potent synthetic tool for preparing actinide hydride complexes. Using this approach, we have expanded the synthetic profile of the hydride complexes [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(H)(μ-H)]<sub>2</sub> (An = Th, U) by using them to prepare, for the first time, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(SMe)<sub>2</sub>, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(C<sub>4</sub>Ph<sub>4</sub>), (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(C<sub>4</sub>Ph<sub>4</sub>), (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThS<sub>5</sub>, and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(bipy). Further studies examining the

generality of this chemistry, with other ligand frameworks and in other areas of the periodic table, are currently underway.

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