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A Crystallizable Dinuclear Tuck-In-Tuck-Over Tuck-Over Dialkyl Tren Uranium Complex and Double Dearylation of BPh_4^- To Give the BPh_2-Functionalized Metallocycle $[U\{N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NSiMe_2CHBPh_2)\}(THF)]$

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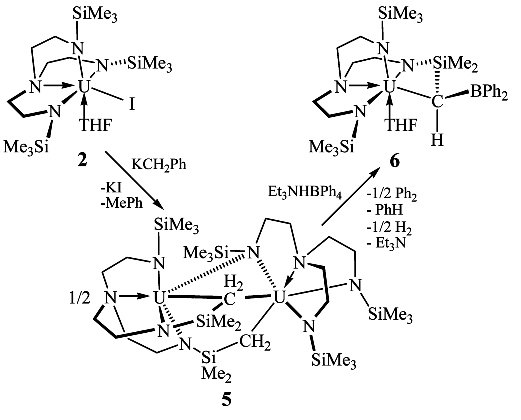
Cyclopentadienyl-based ligands, and the pentamethylcyclopentadienyl ligand in particular, have been enormously successful at supporting novel reactivity patterns in actinide chemistry.[1] In recent years a number of groups have investigated the use of nonmetallocene ligands with uranium(III/IV) chemistry and novel and diverse reactivity profiles have emerged.[2]

Recently, we have investigated the capacity of the $Tren^{TMS}$ ligand $\{N(CH_2CH_2NSiMe_3)_3\}$ to support novel uranium(IV)−metal bonds. We have reported the syntheses of $[(Tren^{TMS})U(X)(THF)]$ (X = Cl, **1**;[3] X = I, **2**[4]) and demonstrated their utility in the preparation of the first structurally authenticated uranium−gallium[3] and −rhenium bonds.[4] However, in preliminary reactions with some transition metal anions, we have noted that KX elimination is not straightforward, and thermolysis is required.

We targeted $[(Tren^{TMS})U(THF)_2][BPh_4]$ (**3**) as a precursor since we reasoned the BPh_4^- anion would be more labile than coordinated halides, and $KBPh_4$ elimination is a proven synthetic method in f-element chemistry.[5] Since $KBPh_4$ does not react with **1** or **2** in THF, we anticipated that treatment of **2** with $KCH_2C_6H_5$ would give the metallocycle $[U\{N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NSiMe_2CH_2)\}(THF)]$ (**4**)[6] which would undergo protonolysis with Et_3NHBPh_4 to afford **3**. Herein, we show that this superficially straightforward chemistry is far more complex, as evidenced by the unprecedented formation of a dinuclear tuck-in-tuck-over tuck-over dialkyl Tren-uranium(IV) complex, and the first example of *double* dearylation of BPh_4^- in a molecular context to give a BPh_2-functionalized metallocycle.

Scheme 1. Synthesis of **5** and **6**



Reaction of **2** with $KCH_2C_6H_5$ proceeds cleanly in toluene to reproducibly give complex **5**, Scheme 1, isolated as yellow crystals from hexane in 54% crystalline yield. A variable-temperature ^1H NMR study and X-ray crystallography enabled us to conclusively identify **5** as a dinuclear tuck-in-tuck-over tuck-over dialkyl,[7] which is further supported by FTIR and CHN data.[8] Monitoring the reaction by ^1H NMR spectroscopy showed the smooth conversion of **2** to **5** with concomitant formation of toluene within minutes. Intermediates were not observed, suggesting the decomposition of the putative benzyl derivative of **2** to **4** and the H^+ transfer/dimerization to form **5** are rapid.[9]

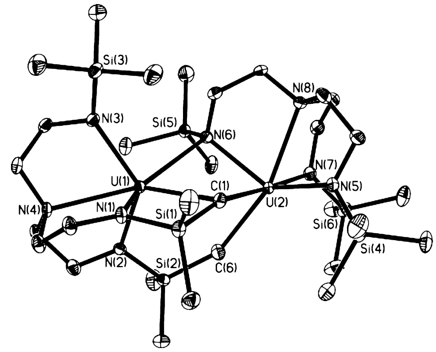


Figure 1. Molecular structure of **5**. Thermal ellipsoids set at 30% probability; hydrogen atoms omitted for clarity. Selected bond lengths (Å): U(1)−N(1) 2.239(3), U(1)−N(2) 2.257(3), U(1)−N(3) 2.292(3), U(1)−N(4) 2.677(3), U(1)−N(6) 2.738(3), U(1)−C(1) 2.667(5), U(2)−N(5) 2.296(4), U(2)−N(6) 2.381(3), U(2)−N(7) 2.267(3), U(2)−N(8) 2.616(3), U(2)−C(1) 2.669(4), U(2)−C(6) 2.493(5).

The molecular structure of **5** is illustrated in Figure 1 with selected bond lengths. The U(2)-Tren ligand is coordinated normally, except for the bridging N(6) center. Bridging Tren amides are known but usually result from alkali metal occlusion.[10] However, the coordination of the U(1)-Tren ligand is unprecedented. In addition to the three anionic amides, two trimethylsilyl groups are metalated. The C(1) center bridges U(1) and U(2) in a tuck-in-tuck-over coordination mode, with essentially identical U−C bond distances of 2.667(5) and 2.669(5) Å. In contrast, terminal C(6) binds in a tuck-over manner with a significantly shorter C(6)−U(2) bond length of 2.493(5) Å. The U−C bond distances compare well to the small number of related metallocyclic uranium(IV)-alkyls.[6b,c] The $U-N_{amide}$ and $-N_{amine}$ bond distances are typical of U(IV)−N bond lengths[11] and are commensurate with their binding modes.

Treatment of **5** with 2 equiv of Et_3NHBPh_4 does not give **3**. Instead, the tuck-in metallocycle **6** was isolated as pale green crystals in 52% crystalline yield, Scheme 1, and the characterization data support its formulation.[8]

The molecular structure of **6** is depicted in Figure 2 with selected bond lengths. The U(1)−C(1) bond distance of 2.644(9) Å compares well to **5** and related metallocyclic uranium(IV)-alkyls.[6] The $U-N_{amido}$ and $U-N_{amine}$ bond lengths of 2.244(6) (av.) and 2.573(6) Å are typical of U(IV)−N bond distances.[11] The U(1)−N(1) bond is short at 2.193(6) Å, and the bite angle of the tuck-in arm is acute at 68.7(2)° [*cf.* 86.41(17)° in **5**]. The boron center is trigonal planar [$\Sigma\angle = 360°$] and the B(1)−C(1) distance of 1.493(11) Å is short, suggesting B−C multiple bond character. For comparison, average $B-CH_2$ and $B-C_{Ph}$ bond lengths of 1.444 and 1.576 Å were reported for $[Mes_2BCH_2][Li(12\text{-crown-}4)_2]$[12] and BPh_3.[13] To further

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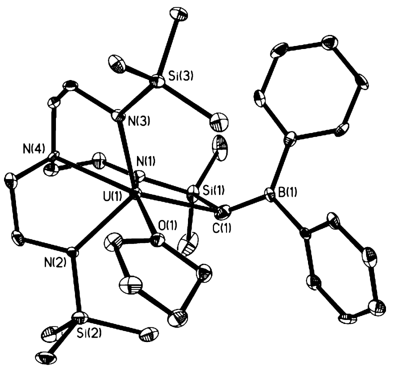

Figure 2. Molecular structure of **6**. Thermal ellipsoids set at 30% probability; hydrogen atoms omitted for clarity. Selected bond lengths (Å): U(1)−N(1) 2.193(6), U(1)−N(2) 2.262(6), U(1)−N(3) 2.277(6), U(1)−N(4) 2.573(6), U(1)−C(1) 2.644(9), U(1)−O(1) 2.565(5), B(1)−C(1) 1.493(11), B(1)−C(16) 1.596(11), B(1)−C(22) 1.591(12).

validate **6** and probe the B(1)−C(1) bond we carried out DFT calculations on a full model of **6**.[8] The calculation reproduced the metrical parameters and inspection of the Kohn−Sham orbitals, and Mayer bond orders (B−C = 1.33) confirm the manifestation of a B(1)−C(1) π-bond perturbed by the polarizing uranium center.

$$\begin{aligned}&2RCH_2^- + 2Et_3NH^+ + 2BPh_4^- \rightarrow \\ &2RC(H)BPh_2^- + 2Et_3N + Ph_2 + 2PhH + H_2\end{aligned} \tag{1}$$

$$BPh_4^- \rightarrow BPh_2^+ + Ph_2 + 2e^- \tag{2}$$

$$BPh_4^- \rightarrow BPh_3 + 1/2Ph_2 + e^- \tag{3}$$

$$BPh_4^- + H^+ \rightarrow BPh_3 + PhH \tag{4}$$

$$2S\text{-}BPh_3 \rightarrow S\text{-}BPh_2^+ + BPh_4^- + S \tag{5}$$

To shed light on the formation of **6**, we analyzed the reaction mother liquor using GC-MS, which revealed the presence of benzene and biphenyl.[8] Thus, the overall reaction can be represented by eq 1. Monitoring the reaction by variable temperature ^{1}H NMR spectroscopy showed conversion of **5** to **6**, and no intermediates were observed.[8,14] The stoichiometry of eq 1 suggests that eqs 2−5[15] should be considered (S = solvent): (i) formation of BPh_2^+, eq 2, appears unlikely but could be facilitated by a redox active uranium center, and this would account for the generation of Ph_2 and BPh_2; (ii) eq 3 is known for BPh_4^- and accounts for the formation of Ph_2;[16] (iii) attack of BPh_3 by a carbanion center with extrusion of Ph^- (or PhH) seems unlikely on steric grounds, but this cannot be ruled out;[17] (iv) formation of C_6H_6 may be accounted for with eq 4, point (iii), or direct extrusion of Ph^- from BPh_4^- which then abstracts H^+ from Et_3NH^+ or the cyclometalated arm in an acid−base reaction;[18] (v) previous electrochemical studies have demonstrated that eq 5 is viable,[15] which would sustain eqs 3 and 4, generate a BPh_2^+ of sufficient reactivity to allow nucleophilic attack by a carbanion center, and regenerate BPh_4^- which is a potential source of Ph^-.

The formation of **6** is remarkable and is, as far as we are aware, the first example of double dearylation of BPh_4^- in a molecular context.[15] The reason why the use of BPh_4^- as a counteranion is avoided in homogeneous catalysis is open to debate. It is usually assumed that BPh_4^- can block incoming substrates by weak coordination.[19] The BPh_4^- anion can also become metalated.[20] Monodearylation of BPh_4^- (eq 3) has been recognized as another potentially detrimental role for BPh_4^-.[16] The *double* dearylation reactivity of BPh_4^- described here adds to the growing list of possible reactions that should be contemplated when using BPh_4^-.

To conclude, the unprecedented dinuclear tuck-in-tuck-over tuck-over dialkyl Tren-uranium(IV) complex **5** extends the palate of novel chemistry which may be achieved with uranium and nonmetallocene ligands, and the BPh_2-functionalized complex **6** reveals a new double dearylation reaction for the BPh_4^- anion.

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Supporting Information Available: Experimental, X-ray and computational data for **5** and **6**. This material is free of charge via the Internet at http://pubs.acs.org.

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