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## COMMUNICATION

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## Isolation of Uranium(III) Primary Phosphido Complexes

Diana Perales<sup>a</sup>, Rina Bhowmick<sup>b</sup>, Matthias Zeller<sup>a</sup>, Pere Miro<sup>b</sup>, Bess Vlaisavljevich<sup>\*b</sup>, and Suzanne C. Bart<sup>\*a</sup>

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**Low-valent uranium(III) primary phosphido complexes supported by hydrotris(3,5-dimethylpyrazolyl)borate (Tp\*) were synthesized with phosphines of varying steric and electronic profiles. Compounds were characterized by multinuclear NMR spectroscopy (<sup>1</sup>H, <sup>11</sup>B, <sup>31</sup>P NMR), infrared spectroscopy, electronic absorption spectroscopy, X-ray crystallography, and quantum chemical calculations.**

The field of uranium-phosphorus bonds has focused on understanding the electronic structure of these species for applications in small molecule activation, separations, and coordination chemistry.<sup>1</sup> Species featuring these bonds are typically more difficult to make compared to their nitrogen counterparts, preventing wide-spread study.<sup>2</sup> Preliminary work indicates that the stability of these compounds is an issue due to the “hard-soft” mismatch of phosphorus with uranium as compared to nitrogen.

Several groups have made strides with the isolation compounds featuring U-P single bonds.<sup>3–6</sup> Bonds derived from primary phosphines are scarce, likely due to the lack of steric protection. Examples of uranium(IV) primary phosphido compounds include Cp\*<sub>2</sub>U[PH-Mes]<sub>2</sub>, recently reported by Walensky<sup>3</sup> and [η<sup>5</sup>-1,3-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>]<sub>2</sub>U(PH-2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)-(OPMe<sub>3</sub>) from Zi and Walter.<sup>7</sup> Liddle has reported a uranium(IV) bridging phosphido complex, [{U(Tren<sup>TIPS</sup>)<sub>2</sub>(μ-PH)] (Tren<sup>TIPS</sup> = N(CH<sub>2</sub>CH<sub>2</sub>-NSi<sup>i</sup>Pr<sub>3</sub>)<sub>3</sub> and the terminal complex, [{U(Tren<sup>TIPS</sup>)(PH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>,<sup>4,8</sup> where-as Marks has generated a dimeric uranium(IV) phosphido, [Cp\*<sub>2</sub>U(OCH<sub>3</sub>)<sub>2</sub>PH]<sub>2</sub>.<sup>5</sup> Uranium(III) primary phosphido examples, Cp\*<sub>2</sub>U(III)(PH-2,4,6-R<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)-(OPMe<sub>3</sub>) (R = <sup>i</sup>Pr, <sup>t</sup>Bu), have also been reported by Zi and Walter.<sup>6</sup>

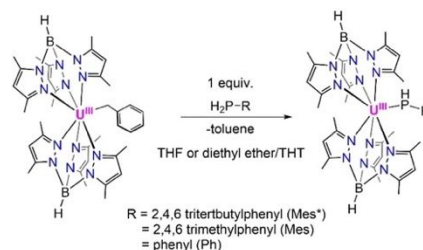
We recently reported a family of bisTp\* uranium(III) anilido species,<sup>9,10</sup> which were converted to uranium(IV) imido complexes using either hydrogen atom transfer (HAT) reagents<sup>10</sup> or a combination of base and oxidant.<sup>9</sup> We sought to understand if other pnictogens, specifically phosphorus, could

react analogously. Herein, we present uranium(III) primary-phosphido complexes from phosphines that vary in sterics and electronics. Reactivity of these compounds towards hydrogen atom transfer is explored. Full characterization, including multinuclear NMR (<sup>1</sup>H, <sup>11</sup>B, <sup>31</sup>P NMR), infrared, and electronic absorption spectroscopies, and X-ray crystallography is reported. Density functional theory computations (M06-L)<sup>11</sup> support a quartet *f*<sup>3</sup> ground state with stronger uranium-pnictogen bonds in the anilido complexes compared to the phosphido complexes. Bond orders,<sup>12–16</sup> energy decomposition analysis (EDA<sup>17</sup>-NOCV<sup>18</sup>), and the quantum theory of atoms in molecules (QTAIM)<sup>19</sup> were employed.

## Results and discussion

The uranium(III) phosphido complexes were made by the elimination of toluene from trivalent Tp\*<sub>2</sub>UBn<sup>20</sup> (**1-Bn**; Bn = benzyl), using primary phosphines, H<sub>2</sub>PR (R = Ph (phenyl), Mes (2,4,6-trimethylphenyl), and Mes\* (2,4,6-tri-<sup>t</sup>Bu-phenyl)), to form Tp\*<sub>2</sub>UPHPh (**2-PPh**), Tp\*<sub>2</sub>UPHMe (**2-PMes**), and Tp\*<sub>2</sub>UPHMe\* (**2-PMes\***) as blue/green or green solids with yields ranging from 51% – 93%. (Scheme 1).

Analysis of **2-PPh**, **2-PMes**, and **2-PMes\*** by <sup>1</sup>H NMR spectroscopy shows paramagnetically broadened and shifted resonances due to the uranium(III) ion. NMR spectra of **2-PPh** and **2-PMes** are similar, with resonances for Ph and Mes groups appearing in the range of +7.48 ppm to +19.45 ppm, whereas signals for the Mes\* group in **2-PMes\*** appear out of the aforementioned range. Resonances for the Tp\* ligands for **2-PPh** and **2-PMes** are similar with peaks appearing in the range



Scheme 1. Synthesis of **2-PPh**, **2-PMes**, and **2-PMes\*** by addition of **1-Bn** to its respective phosphine.

<sup>a</sup>H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907, USA. E-mail: sbart@purdue.edu.

<sup>b</sup>Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069, United States. E-mail: bess.vlaisavljevich@usd.edu.

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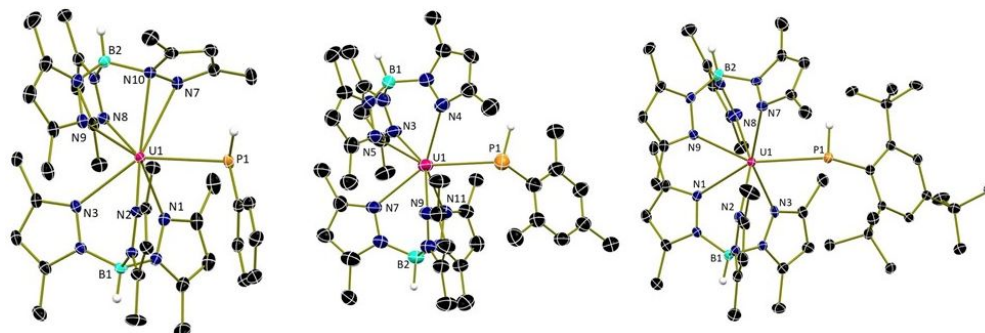


Fig 1. Molecular structures from left to right **2-PPh**, **2-PMes**, and **2-PMes\*** displayed with 30% probability ellipsoids. Selected hydrogen atoms, co-crystallized solvent molecules, and disordered moieties have been omitted for clarity.

of  $-12.87$  ppm to  $+7.48$  ppm, consistent with previously reported  $\text{Tp}^*$  uranium complexes.<sup>10,21</sup> Resonances from the  $\text{Tp}^*$  ligands for **2-PMes\*** are not found, likely due to the paramagnetic uranium(III) and the electron donating effect of the 'Bu's. Broad resonances for the P-H peaks of **2-PPh** ( $-29.3$  ppm), **2-PMes** ( $-31.3$  ppm), and **2-PMes\*** ( $-23.9$  ppm) are shifted upfield relative to the rest of the resonances from the Ph, Mes, or Mes\* units.  $\text{Cp}^*_2\text{U(III)(PH-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2\text{)(OPMe}_3\text{)}$  by Zi and Walter displays a PH resonance at  $4.51$  ppm<sup>6</sup> shifted downfield relative to **2-PPh**, **2-PMes**, and **2-PMes\***, likely due to the deshielding of the base  $\text{OPMe}_3$ . Additionally,  $\text{Cp}^*_2\text{U(IV)[P(H)Mes]}_2$  has a PH resonance at  $-122.9$  ppm,<sup>3</sup> significantly shifted upfield relative to **2-PPh**, **2-PMes**, and **2-PMes\***, likely due to the uranium(IV).

Previous studies from our group have shown that the  $^{11}\text{B}$  NMR signal for  $\text{Tp}^*$  can indicate the oxidation state on the Uranium where a shift from 0 to  $-10$  ppm is indicative of uranium(III) and shifts of  $-50$  to  $-70$  ppm are indicative of uranium(IV).<sup>10,21</sup> The  $^{11}\text{B}$  NMR spectroscopic data shows broad resonances for **2-PPh** ( $-2.9$  ppm), **2-PMes** ( $-0.6$  ppm), and **2-PMes\*** ( $-1.2$  ppm), which are shifted from the starting material (**1-Bn** =  $-15.4$  ppm) and consistent with previously reported bis $\text{Tp}^*$  uranium(III) compounds. The  $^{31}\text{P}$  NMR spectroscopic data shows broad resonances for **2-PPh** ( $2345$  ppm), **2-PMes** ( $2802$  ppm), and **2-PMes\*** ( $2910$  ppm).  $\text{Cp}^*_2\text{U(III)(PH-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2\text{)(OPMe}_3\text{)}$  by Zi and Walter displays a PH signal ( $71.1$  ppm) significantly shifted upfield relative to the complexes reported here, likely a result of the bound  $\text{OPMe}_3$ .<sup>6</sup>

Infrared spectroscopic data for **2-PPh**, **2-PMes**, and **2-PMes\*** show two  $\nu_{\text{B-H}}$  absorptions ( $2486$  to  $2561$   $\text{cm}^{-1}$ ), similar to previously reported bis $\text{Tp}^*$  uranium species.<sup>10,21</sup> The P-H absorption is visible for **2-PPh** ( $2267$   $\text{cm}^{-1}$ ), **2-PMes** ( $2322$   $\text{cm}^{-1}$ ), and **2-PMes\*** ( $2364$   $\text{cm}^{-1}$ ), confirming the phosphido species. The PH stretch increases in energy as substituents become more electron donating.<sup>22,23</sup>

Single crystals were grown from concentrated THF at  $-35$  °C (**2-PPh**),  $\text{Et}_2\text{O}$  at  $-35$  °C (**2-PMes**), or diffusion of pentane into toluene at  $-35$  °C (**2-PMes\***) and analyzed by X-ray crystallography (Fig. 1). Solving and refining the data shows that **2-PMes** and **2-PMes\*** have distorted monocapped trigonal prismatic uranium ions with two  $\kappa^3\text{-Tp}^*$  ligands, with  $\text{U-N}_{\text{pyrazole}}$  distances ranging from  $2.487(10)$  to  $2.788(4)$  Å. **2-PPh** displays a side-on interaction with one pyrazole that is a capped octahedron with  $\text{U-N}$  distances ranging from  $2.518(3)$  to  $2.841(3)$  Å. Regardless of geometry, all the  $\text{U-N}$  distances are consistent with other bis $\text{Tp}^*$  uranium(III) complexes.<sup>10,20</sup>

The  $\text{U-P}$  distances range from  $3.0456(8)$  Å to  $2.9815(16)$  Å, and lengthens as the phosphido substituent becomes smaller, where **2-PPh** ( $3.0456(8)$  Å) has the longest bond, **2-PMes** ( $3.016(4)$  Å) is shorter, and **2-PMes\*** ( $2.9815(16)$  Å) is the shortest. In comparison,  $\text{Cp}^*_2\text{U(III)(PH-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2\text{)(OPMe}_3\text{)}$  ( $\text{U-P}$ :  $3.031(1)$ )<sup>6</sup> by Zi and Walter, is slightly longer than **2-PPh**, **2-PMes**, and **2-PMes\***, likely due to the effect of the bound  $\text{OPMe}_3$ . Tetravalent species  $\text{Cp}^*_2\text{U[P(H)Mes]}_2$  ( $\text{U-P}$ :  $2.7768(12)$  Å),<sup>3</sup> and  $\{[\text{U}(\text{Tren}^{\text{TIPS}})]_2(\mu\text{-PH})\}$  ( $\text{U-P}$ :  $2.8187(12)$  and  $2.8110(12)$  Å),<sup>4</sup> are  $\sim 0.25$  Å shorter, consistent with the smaller uranium(IV) ion relative to uranium(III).

**2-PPh**, **2-PMes**, and **2-PMes\*** have  $\text{U-P-C}$  angles ranging from  $112.11(10)$  to  $134.34(17)^\circ$ , and become more acute as the phosphido substituent becomes less sterically bulky where **2-PPh** ( $112.11(10)^\circ$ ) has the most acute angle, **2-PMes** ( $129.5(5)^\circ$ ) is slightly more obtuse, and **2-PMes\*** ( $134.34(17)^\circ$ ) is the most obtuse. The uranium(III) anilido complexes,  $\text{Tp}^*_2\text{UNHMe}$  (**2-NMes**),<sup>10</sup> and  $\text{Tp}^*_2\text{UNHMe}^*$  (**2-NMes\***)<sup>10</sup>, are more linear than **2-PPh**, **2-PMes**, and **2-PMes\***, likely due to lone pair donation.<sup>10</sup>

During the synthesis **2-PMes\***, THF ring-opening occurs to produce  $\text{Tp}^*_2\text{UO}(\text{CH}_2)_4\text{PHMe}^*$  (**3-PMes\***). Compound **3-PMes\*** can be made either by introducing THF to **2-PMes\*** or by addition of  $\text{H}_2\text{PMes}^*$  to **1-Bn** in THF, both resulting in high yields (Scheme S1). Lewis acidic metals ring-opening THF is well known in actinide,<sup>24,25</sup> lanthanide,<sup>26,27</sup> and transition metal<sup>28,29</sup>

chemistries, but Little's  $\beta$ -diketiminate yttrium complex,  $[\text{HC}(\text{C}(\text{CH}_3)\text{-NAr})_2\text{Y}(\text{THF})]$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ),<sup>26</sup> is of particular interest as it behaves in a similar fashion as **2-PMes\*** when attempting to make a yttrium phosphido complex. Instead, the ring-opened THF product,  $[\text{HC}(\text{C}(\text{CH}_3)\text{NAr})_2\text{Y}\{\text{O}(\text{CH}_2)_4\text{P}(\text{H})\text{Ar}^*\}\text{-}(\text{I})(\text{THF})]$ , forms with a PHAr\* unit terminally bound to the THF carbon chain, analogous to **3-PMes\***.<sup>26</sup>

The <sup>1</sup>H NMR spectrum of **3-PMes\*** is paramagnetically broadened and shifted due to the uranium(III),  $f^3$  ion. The protons of activated THF were found between +9 ppm to +43 ppm. The <sup>11</sup>B NMR spectroscopic data shows broad resonances for **3-PMes\*** (−5.9 ppm), which are shifted from **2-PMes\***. The <sup>31</sup>P NMR spectroscopic data displays a signal at −64.0 ppm, which is shifted from **2-PMes\*** and is similar to  $[\text{HC}(\text{C}(\text{CH}_3)\text{-NAr})_2\text{Y}\{\text{O}(\text{CH}_2)_4\text{P}(\text{H})\text{Ar}^*\}\text{-}(\text{I})(\text{THF})]$ .<sup>26</sup> Infrared spectroscopic data for **3-PMes\*** show two  $\nu_{\text{B-H}}$  stretching vibrations, 2554 and 2527  $\text{cm}^{-1}$ , confirming two Tp\* ligands are present. The  $\nu_{\text{P-H}}$  stretching vibration is visible at 2390  $\text{cm}^{-1}$ , confirming the PHMes\* unit is retained. This is shifted from **2-PMes\*** by 26  $\text{cm}^{-1}$ , and is attributed to the distance of the P-H unit from the uranium(III).

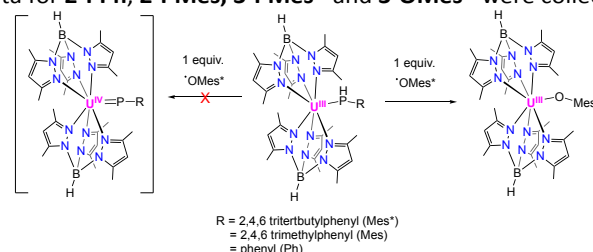
Structural properties of **3-PMes\*** were evaluated single crystals grown from concentrated diethyl ether at −35 °C (Figure S24). Refinement of the data shows a seven-coordinate distorted monocapped trigonal prismatic uranium ion that feature two  $\kappa^3\text{-Tp}^*$  ligands per uranium, with U-N distances ranging from 2.596(3) to 2.737(3) Å which is consistent with U-N distances for other bisTp\* uranium(III) complexes.<sup>9,20</sup> The U-O distance (2.157(2) Å) and U-O-C bond angle (156.5(2)°) in **3-PMes\*** is consistent with other uranium(III) alkoxides.<sup>30</sup>

THF ring-opening is not observed for **2-PPh** or **2-PMes**, even at elevated temperatures. As nucleophilicity increases with increasing basicity and size, it is not a surprise that the most basic phosphido unit, PHMes\*, can facilitate the transformation while the smaller and less basic nitrogen analogue (NHMes\*) and the weaker base phosphorus units, PPh and PMes, cannot. The analogous transformation was attempted with the softer sulfur analogue, tetrahydrothiophene (THT). Treating **1-Bn** with  $\text{H}_2\text{PMes}^*$  in the presence of THT led to formation of **2-PMes\*** in high yield but not a ring-opened product. No THT-opening was observed for **2-PPh** and **2-PMes**, likely due to the oxophilicity of uranium.

Synthesis of uranium(IV) phosphinidenes was explored by addition of HAT reagents to **2-PPh**, **2-PMes**, and **2-PMes\***. These reagents successfully convert uranium(III) anilido species to uranium(IV) imido complexes.<sup>10</sup> Treating **2-PPh**, **2-PMes**, and **2-PMes\*** with 2,4,6-tri-*t*-Bu-phenoxy radical exclusively formed  $\text{Tp}^*_2\text{UOMes}^*$  (**3-OMes\***) in quantitative yield. The phosphorus containing product was not identified, but formation of  $\text{H}_2\text{PMes}^*$  and  $\text{Mes}^*\text{-P=P-Mes}^*$  was ruled out since it was not detected via <sup>1</sup>H or <sup>31</sup>P NMR spectroscopy. Compound **3-OMes\*** was independently synthesized by addition of HOMes\* to **1-Bn** (Scheme 2). Single crystals suitable for high quality crystallographic analysis were not obtainable for **3-OMes\***, but connectivity was confirmed (Figure S25). Analysis of **3-OMes\*** by <sup>1</sup>H NMR spectroscopy shows a paramagnetically broadened and shifted spectrum, whereas the <sup>11</sup>B NMR spectrum shows a broad resonance at −14.9 ppm. Infrared spectroscopic data for

**3-OMes\*** displays two  $\nu_{\text{B-H}}$  stretching vibrations at 2560 and 2531  $\text{cm}^{-1}$ , showing the two Tp\* ligands are present while the absence of the O-H stretching vibration supports formation of the **3-OMes\***. When trityl radical was added to **2-PPh**, **2-PMes**, and **2-PMes\***, unidentifiable products formed. Oxidative deprotonation with a mixture of  $\text{I}_2$  and potassium tert-butyl-(dimethylsilyl)amide (KTSA) was also unsuccessful regardless of order of addition, producing  $\text{Tp}^*_2\text{UI}$  in quantitative yield, observed via <sup>1</sup>H NMR spectroscopy.

The optical properties of **2-PPh**, **2-PMes**, **2-PMes\***, **3-OMes\***, and **3-PMes\*** were examined using electronic absorption spectroscopy. The spectra for **2-PPh**, **2-PMes**, **2-PMes\*** were measured in toluene (Figure S20) but additional data for **2-PPh**, **2-PMes**, **3-PMes\*** and **3-OMes\*** were collected



Scheme 2. Synthesis of **3-OMes\***

in THF (Figure S21-S23). All the uranium(III) complexes exhibit analogous broad and poorly defined  $f\text{-}f$  transitions in the near-infrared range (800–1600 nm), consistent with previously reported bisTp\* uranium(III) compounds, supporting the uranium(III) oxidation state.<sup>9,20</sup> In the visible region, a broad colour producing charge transfer band is present at ~580 nm for the blue/green solutions of **2-PPh** and **2-PMes**, ~650 nm for the green solution of **2-PMes\*** and **3-OMes\***, and ~640 nm for the green solution of **3-PMes\***.

Density functional theory (DFT) calculations were performed on **2-PPh**, **2-PMes**, and **2-PMes\*** and their nitrogen analogues  $\text{Tp}^*_2\text{UNH}(\text{phenyl})$ <sup>30</sup> (**2-NPh**), **2-NMes**, and **2-NMes\***. Geometries are in excellent agreement with experiment, reproducing the trends noted earlier (Table S6). The ground state is a uranium-centred  $f^3$  quartet that is well-separated from the lowest doublet and sextet states (Table S7). Second-order multireference calculations (CASPT2) confirm the quartet ground state and support subsequent analysis with single-reference DFT methods (Table S17). The unique capped octahedron observed in **2-PPh** was retained in optimizations starting from the crystal structure. The geometry of **2-PPh** was reoptimized starting from the seven-coordinate geometry observed for the other complexes. The experimentally observed capped octahedron lies 2.2 kcal/mol lower in energy. On the other hand, the trend is reversed in **2-NPh** and the capped octahedron is less favorable by 2.6 kcal/mol (Table S8). This suggests that the phosphine is sufficiently weak and there is an electronic effect encouraging an additional nitrogen from Tp\* to coordinate. Moreover, the capped octahedral geometry was lower in energy for all of the phosphido complexes, albeit by only a few kcal/mol, in contrast with the measured structure. This suggests that the formation of the capped octahedron is indeed an electronic effect due to the nature of the pnictogen;

however, not so strong that packing effects are unimportant in determining the final geometry.

In the anilido complexes, a  $\sigma$  and  $\pi$  interaction were observed along the U-N bond. Specifically, in **2-NPh**, the U contribution is 9.9% and the N contribution is 45.8% in the  $\pi$  interaction while the U contribution is higher in  $\sigma$  interaction at 37.5% with a N contribution of 42.3% (Figure S26). On the other hand, no  $\pi$  interaction is observed in **2-PPh**. The  $\sigma$  orbital has a much larger contribution (53.8%) from the P with only 15.2 % from uranium (Figure S26). These differences between the pnictogen centres were also observed in the other complexes (Figures S27 and S28) and consistent with phosphorus being a weaker Lewis base. Subsequent energy decomposition analysis (EDA) using the so-called natural orbitals for chemical valence (NOCV) approach supports this as well. The U-N bonds exhibited a 59.2% orbital contribution, on average, while the U-P bonds showed only 44.3%. An average interaction energy along the uranium-pnictogen bond of -139 kcal/mol and -114 kcal/mol for the U-N and U-P complexes, respectively, was also computed (Table S15). The  $\sigma$  and  $\pi$ -like interactions in the anilido complexes also appeared in the NOCV density deformation plots (Figures S32 - S34) suggesting that higher orbital contributions was, in part, due to the " $\pi$ -like" mixing resulting in stronger U-N bonds compared to U-P bonds. Note that the NOCV results suggest a redistribution of electron density between the metal and ligand and not a straightforward ligand to metal donation. Nevertheless, these results are consistent with the shorter and stronger bonds observed experimentally for the anilido complexes.

Finally, the uranium-pnictogen bonds were also studied by QTAIM and bond order analysis. Bond critical points (BCPs) were identified for all U-P and U-N bonds leading to the assignment of a polar dative bond. At the BCP, both the total density and bond degree, a measure of covalency, were higher at the BCP for the nitrogen species (Table S13). Nalewajski-Mrozek (N-M) bond orders were 1.252 on average for the anilido complexes and 1.018 for the phosphido complexes (Table S14). This is consistent with the presence of a larger covalent contribution to bonding in the anilido complexes, including the presence of interactions with weak but meaningful  $\pi$ -character.

## Conclusions

A series of uranium(III) primary-phosphido complexes with varying steric and electronic profiles have been isolated, which are the first examples of base-free derivatives. Multinuclear NMR ( $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{31}\text{P}$ ) spectroscopy supports the formation of the new complexes while UV-Vis/NIR and crystallography supports the uranium(III) oxidation state. The corresponding uranium-anilido bonds are stronger and have larger covalent contributions than the analogous phosphido bonds. The interesting structure observed in the **2-PPh** complex is reproduced by DFT modeling and is attributed to an electronic effect due to the use of a weaker Lewis base as the ligand.

## Conflicts of interest

There are no conflicts to declare.

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