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Metal Phosphinidenes

Triamidoamine–Uranium(IV)-Stabilized Terminal Parent Phosphide and Phosphinidene Complexes**

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Abstract: Reaction of $[U(\text{Tren}^{\text{TIPS}})(\text{THF})][\text{BPh}_4]$ (**1**; $\text{Tren}^{\text{TIPS}} = \text{N}\{\text{CH}_2\text{CH}_2\text{NSi}(\text{iPr})_3\}_3$) with NaPH_2 afforded the novel f-block terminal parent phosphide complex $[U(\text{Tren}^{\text{TIPS}})(\text{PH}_2)]$ (**2**; $U\text{--}P = 2.883(2) \text{ \AA}$). Treatment of **2** with one equivalent of $\text{KCH}_2\text{C}_6\text{H}_5$ and two equivalents of benzo-15-crown-5 ether (B15C5) afforded the unprecedented metal-stabilized terminal parent phosphinidene complex $[U(\text{Tren}^{\text{TIPS}})(\text{PH})][\text{K}(\text{B15C5})_2]$ (**4**; $U\text{--}P = 2.613(2) \text{ \AA}$). DFT calculations reveal a polarized-covalent $U\text{--}P$ bond with a Mayer bond order of 1.92.

Terminal metal phosphinidene complexes ($L_nM=PR$) are, despite continued interest, far less developed than their isolobal metal imide and alkylidene counterparts.^[1] Although the first $L_nM=PR$ complex was reported over a quarter of a century ago,^[2] sterically demanding R-groups are required, as $M=PR$ linkages are reactive and require kinetic stabilization.^[3] Certainly, free phosphinidenes (PR) are usually very reactive owing to their triplet ground states and unsaturated valence shells.^[4] Although stabilization of a triplet PR group by a triplet metal fragment to generate a formal $M=P$ bond is an attractive strategy, unlike the well-known $L_nM=NH$ and $L_nM=CH_2$ linkages,^[5] there has never been a structurally authenticated report of a d/f-block metal-stabilized terminal parent phosphinidene $L_nM=PH$,^[6,7] and studies of such

species are limited to computational investigations.^[8] This paucity is underscored by a triplet-singlet energy gap of 22 kcal mol^{-1} for free PH ,^[4b] which has only been observed transiently in the gas phase or low temperature matrices.^[4a,9] Indeed, there is a paucity of well-defined compounds containing a terminal PH group and structurally elucidated examples are confined to the p-block, where the bonding descriptions are open to interpretation, for example, NHC-phosphinidene vs. phosphalkene.^[10]

Herein, we describe the straightforward synthesis and characterization of the first example of a metal-stabilized terminal parent phosphinidene complex. This is only the second actinide terminal phosphinidene complex,^[11,12] and was prepared from the first example of an f-block parent terminal phosphide complex; terminal phosphide complexes are rare, as the sterically unencumbered PH_2 group often bridges metal centers.^[13]

In order to prepare a triplet-PH-derived metal-stabilized terminal parent phosphinidene, we reasoned that a high-oxidation-state metal would be required to engage in a formal $M=PH$ bonding interaction.^[14] We also noted that, as PH is sterically unencumbered, a sterically demanding metal–ligand fragment would be required to compensate for the lack of kinetic protection at phosphorus. Given our success in stabilizing terminal uranium–nitrides,^[15] we identified the $[U(\text{Tren}^{\text{TIPS}})]^{n+}$ ($\text{Tren}^{\text{TIPS}} = \text{N}\{\text{CH}_2\text{CH}_2\text{NSi}(\text{iPr})_3\}_3$) unit as an ideal metal fragment, and NaPH_2 as the ideal PH precursor transfer group. Initial attempts to install PH_2 at uranium using NaPH_2 and $[U(\text{Tren}^{\text{TIPS}})(\text{Cl})]$ failed, presumably because the phosphide cannot displace a strongly bound chloride from uranium. Thus, we utilized $[U(\text{Tren}^{\text{TIPS}})(\text{THF})][\text{BPh}_4]$ (**1**),^[16] as the THF and BPh_4^- groups are labile.^[17] Treatment of **1** with NaPH_2 afforded, after work-up and recrystallization from *iso*-hexane, yellow crystals of the uranium(IV) parent terminal phosphide complex $[U(\text{Tren}^{\text{TIPS}})(\text{PH}_2)]$ (**2**) in 89% yield (Scheme 1). The characterization data for **2** support the proposed formulation.^[16] Notably, the ^{31}P NMR spectrum of **2** exhibits a triplet centered at 595 ppm ($J_{\text{PH}} = 160 \text{ Hz}$), which confirms the presence of PH_2 . The solid-state structure of **2** was determined by X-ray diffraction (Figure 1), which revealed a monomeric structure with a terminal PH_2 unit. The $U\text{--}P$ bond length of $2.883(2) \text{ \AA}$ is slightly longer than the sum of the single bond covalent radii of uranium and phosphorus (2.81 \AA),^[18] and compares to a $U\text{--}P$ bond length of $2.789(4) \text{ \AA}$ in the less encumbered uranium(IV) complex $[U(\text{C}_5\text{Me}_5)_2\{\text{P}(\text{SiMe}_3)_2(\text{Cl})\}]$.^[19]

We treated **2** with benzyl potassium and 2,2,2-cryptand to afford $[U(\text{Tren}^{\text{TIPS}})(\text{PH})(\text{K-2,2,2-cryptand})]$ (**3**) in 80% yield as black crystals after work-up and recrystallization from *iso*-

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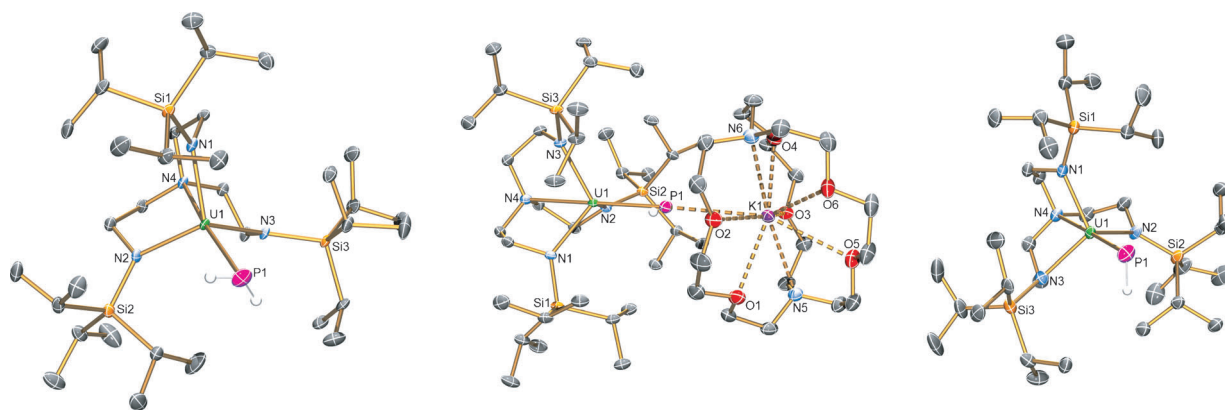
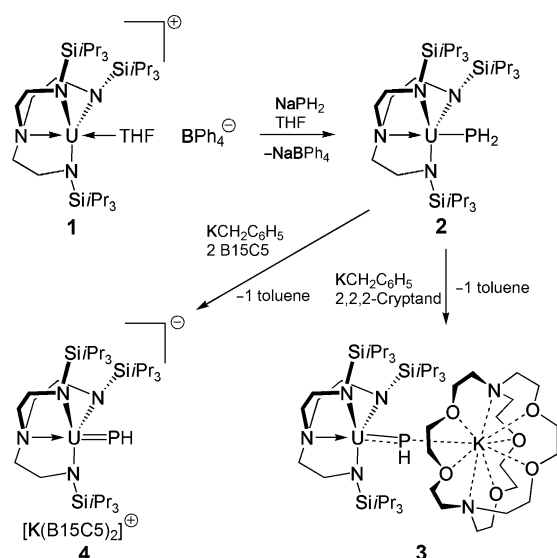


Figure 1. Molecular structures of $[U(\text{Tren}^{\text{TIPS}})(\text{PH}_2)]$ (**2**, left), one of the four independent molecules in the asymmetric unit of $[U(\text{Tren}^{\text{TIPS}})(\text{PH})][\text{K}(\text{B15C5})_2]$ (**3**, center), and the anionic component of $[U(\text{Tren}^{\text{TIPS}})(\text{PH})][\text{K}(\text{B15C5})_2]$ (**4**, right). Displacement ellipsoids set at 50% probability. Non-phosphorus-bound hydrogen atoms and minor disorder components are omitted for clarity. Selected bond lengths [Å]: **2**, U1–P1 2.883(2), U1–N1 2.241(4), U1–N2 2.259(3), U1–N3 2.233(3), U1–N4 2.633(3); **3**, U1–P1 2.661(2), U1–N1 2.312(3), U1–N2 2.287(3), U1–N3 2.310(3), U1–N4 2.716(3), K1–P1 3.575(2); **4**, U1–P1 2.613(2), U1–N1 2.326(3), U1–N2 2.320(3), U1–N3 2.320(3), U1–N4 2.692(3).



Scheme 1. Synthesis of **2–4**. B15C5 = benzo-15-crown-5 ether.

hexane (Scheme 1). The characterization data for **3** support the proposed formulation,^[16] and the ^{31}P NMR spectrum exhibits a broad resonance at 2460 ppm (fwhm = 440 Hz, J_{PH} not resolved). To determine whether the phosphinidene in **3** was terminal, we analyzed the structure by X-ray diffraction (Figure 1). However, although the potassium ion is coordinated by the cryptand, it is not sequestered from the phosphinidene. The U=P distance was found to be 2.661(2) Å, which is ca. 0.22 Å shorter than the U–P distance in **2**. The long P–K distance of 3.575(2) Å must be regarded as a weak interaction.

The failure of 2,2,2-cryptand to abstract the potassium ion in **3** is surprising, but the long P–K distance suggested that a separated ion pair might be feasible. Noting the prior success of a conjugate acid deprotonation method to afford a terminal molybdenum carbide,^[20] we treated **2** with benzyl potassium and two equivalents of benzo-15-crown-5 ether

(B15C5) and, after work-up and recrystallization from toluene, isolated the uranium(IV) terminal parent phosphinidene complex $[U(\text{Tren}^{\text{TIPS}})(\text{PH})][\text{K}(\text{B15C5})_2]$ (**4**) in 89% yield as black crystals.^[16] An X-ray diffraction study confirmed the identity of **4** (Figure 1). The U=P distance of 2.613(2) Å is ca. 0.05 Å shorter than the U=P distance in **3**, perhaps reflecting the weak P–K interaction in **3**. It is germane to note that the sum of the double bond covalent radii of uranium and phosphorus is 2.36 Å,^[21] thus the U=P distance in **4** lies midway between the sum of the covalent single and double bond radii values. For comparison, uranium–phosphorus distances of 2.743(1) and 2.562(3) Å were observed in $[\text{U}(\text{C}_5\text{Me}_5)_2(\text{OMe})_2(\mu\text{-PH})]$,^[12] and $[\text{U}(\text{C}_5\text{Me}_5)_2(\text{P-2,4,6-}t\text{Bu}_3\text{C}_6\text{H}_2)(\text{OPMe}_3)]$,^[11] respectively. The U–N distances are consistent with the uranium(IV) formulation.^[22] The phosphinidene hydrogen atom in **4** could be located in the difference electron density map revealing a U–P–H angle of 118.8(9)°, which suggests a formal U=P bond, as would be expected.

Unlike **2** and **3**, complex **4** is silent in the ^{31}P NMR spectrum, presumably because of a stronger uranium–phosphorus interaction resulting in paramagnetic line-broadening. The ^1H NMR spectrum of **4** spans the range of +46 to –10 ppm, and exhibits four Tren-ligand resonances, which is consistent with C_{3v} symmetry on the NMR timescale. The FTIR spectrum of **4** exhibits an absorption at 2360 cm^{-1} , which we attribute to a terminal PH stretch. The UV/Vis/NIR electronic absorption spectrum of **4** exhibits broad absorptions in the range 25 000–10 000 cm^{-1} ,^[16] which accounts for its black color and weak ($\epsilon \approx 25 \text{ M}^{-1} \text{ cm}^{-1}$) bands in the 10 000–5000 cm^{-1} region that are characteristic of uranium(IV).^[23] The solution magnetic moment of **4** in C_6D_6 at 298 K is 2.98 μ_{B} . The solid-state magnetic moment of **4** at 298 K measured by SQUID magnetometry is 2.45 μ_{B} ,^[16] which is consistent with the solution-phase magnetic data. The magnetic moment decreases smoothly with decreasing temperature to 1.04 μ_{B} at 1.8 K and tending to zero; this is consistent with uranium(IV), which is a magnetic singlet at low temperature. The data are similar to those of **2** and **3**, which is

Table 1: Selected computed DFT, NBO, and QTAIM data for **2–4**.

| Entry ^[a] | Bond lengths and indices | | Atomic spin densities and charges | | | NBO σ -component ^[g] | | | NBO π -component ^[g] | | | QTAIM ^[h] | | | |
|----------------------|--------------------------|------------------|-----------------------------------|----------------------|----------------------|--|-------|---------------|-------------------------------------|-------|---------------|----------------------|----------------------------|-----------------|---------------------------|
| | U–P ^[b] | B ^[c] | m_U ^[d] | q_U ^[e] | q_P ^[f] | P [%] | U [%] | U 7s/7p/5f/6d | P [%] | U [%] | U 7s/7p/5f/6d | $\rho(\mathbf{r})$ | $\nabla^2\rho(\mathbf{r})$ | $H(\mathbf{r})$ | $\varepsilon(\mathbf{r})$ |
| 2 | 2.9250 | 0.84 | 2.31 | 2.61 | –0.54 | 87.4 | 12.6 | 2:2:45:51 | – | – | – | 0.05 | 0.04 | –0.01 | 0.01 |
| 3 | 2.6718 | 1.61 | 2.36 | 2.53 | –1.18 | 82.8 | 17.2 | 2:0:48:50 | 79.1 | 20.9 | 0:1:62:37 | 0.07 | 0.07 | –0.02 | 0.22 |
| 4 | 2.6209 | 1.92 | 2.41 | 2.32 | –1.16 | 75.9 | 24.1 | 0:0:80:20 | 72.1 | 27.9 | 0:1:69:30 | 0.08 | 0.07 | –0.03 | 0.20 |

[a] All molecules geometry optimized without symmetry constraints at the spin-unrestricted LDA VWN BP TZP/ZORA level. [b] Calculated U–P distances [Å]. [c] Mayer bond indices. [d] MDC-m α -spin densities on uranium. [e] MDC-q charges on uranium. [f] MDC-q charges on phosphorus. [g] Natural Bond Orbital (NBO) analyses. [h] QTAIM topological electron density [$\rho(\mathbf{r})$], Laplacian [$\nabla^2\rho(\mathbf{r})$], electronic energy density [$H(\mathbf{r})$], and ellipticity [$\varepsilon(\mathbf{r})$] bond critical point data.

commensurate with the formal uranium oxidation state of +4 for all these complexes.

In order to probe the nature of the U=PH linkages in **3** and **4**, we conducted single-point energy calculations on the geometry optimized structures of **3** and the anion component of **4** (Table 1). The calculated bond lengths and angles are within 0.05 Å and 2° of the experimentally determined structures, and therefore we conclude that the calculated structures represent qualitative models of the electronic structures of **3** and **4**. For comparison, we calculated the electronic structure of **2** (Table 1). The calculated MDC_q charges for uranium (2.32–2.61) are typical of Tren–uranium(IV) complexes.^[24] The phosphorus charges reflect the changes from mono-anionic phosphide in **2** to dianionic phosphinidenes in **3** and **4**. The uranium spin densities span 2.31–2.41 and together with the charges support the notion of increased donation of electron density from the ligands in the order **4** > **3** > **2**, as would be expected from the progression of terminal phosphinidene to pseudo-bridging phosphinidene to phosphide. The calculated Mayer bond order for **4** is 1.92, which is consistent with a double bond interaction (cf. bond orders of 1.61 for **3** and 0.84 for **2**). The HOMO and HOMO-1 of **2–4** are each singly occupied and of essentially pure 5f character, as expected for ³H₄ uranium centers. For **3** and **4** the HOMO-2 and HOMO-3 represent the principal π - and σ -components, respectively, of the U=P bond, which for **4** are illustrated in Figure 2. In order to exclusively probe the U=P linkages, we studied them with Natural Bond Orbital (NBO) analysis, which identified σ - and π -bonding interactions. For **4**,

the σ -bond comprises 24% uranium and 76% phosphorus character and the π -bond is composed of 72% phosphorus and 28% uranium character. It is notable that the NBO data suggest a dominance of 5f orbital contributions in the bonding, as observed in uranium–nitrides^[14] and uranium–carbenes.^[25] Although the K–P distance in **3** is long, it is evident from a comparison of the U=P bond data in Table 1 that coordination of potassium to the phosphinidene perturbs the U=P bond through the polarization of electron density towards the potassium center.

To gain further insight into the uranium–phosphorus linkages in **2–4** we employed Bader’s Atoms in Molecules (QTAIM) to analyze the topological electron density [$\rho(\mathbf{r})$], the Laplacian of the electron density [$\nabla^2\rho(\mathbf{r})$], and the electronic energy density $H(\mathbf{r})$ of the charge distribution (defined as $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$ where $G(\mathbf{r})$ is the kinetic energy density and $V(\mathbf{r})$ is the potential energy). In each case, a 3,–1 bond critical point (BCP) was identified (Table 1). These BCP data are consistent with predominantly electrostatic bonding with modest covalent contributions, and are consistent with greater bonding interactions for the formal U=P bonds in **3** and **4** compared to the formal single bond in **2**. The calculated ellipticity parameters [$\varepsilon(\mathbf{r})$] for the U=P bonds in **3** and **4** confirm the presence of double-bonding interactions. Specifically, for a cylindrical σ -bond the ellipticity is 0, and for a bond with a π -contribution the ellipticity is > 0. The ellipticity values for the C–C bonds in ethane, benzene, and ethene are calculated to be 0.0, 0.23, and 0.45, respectively.^[26] Although it should be recognized that the dipolar U⁺–P(H)[–] resonance form will contribute to the electronic structure of the U=PH linkages, the ellipticity values for **3** and **4** are similar to that of benzene and the calculated bond order is close to two. This suggests that the uranium–phosphorus bonds in **3** and **4** are composed of σ - and π -components, and that the U=PH bond resonance form may dominate. Lastly, we note a surprising, given the differences in covalency of 4f and early 5f complexes, similarity of the computational data for 5f **3** and **4** compared to our recently reported 4f cerium(IV)–carbene complex [Ce{C(PPh₂NSiMe₃)₂}(ODipp)₂] (Dipp = 2,6-*i*Pr₂C₆H₃), which exhibits a Ce=C bond.^[27]

To conclude, we have reported the straightforward synthesis and characterization of the first structurally authenticated metal-stabilized terminal parent phosphinidene complex, thus extending the range of metal–parent imide L_nM=NH and alkylidene L_nM=CH₂ complexes to include the L_nM=

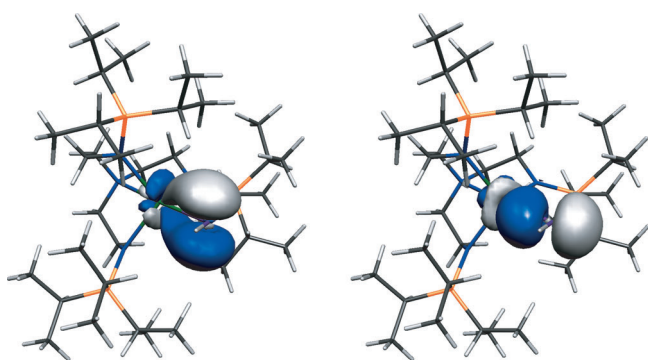


Figure 2. α -spin Kohn Sham orbitals that represent the principal components of the U=P bond in **4**. Left: HOMO-2 (225a, –0.608 eV); Right: HOMO-3 (224a, –0.692 eV).

PH linkage. This complex is only the second example of an actinide terminal phosphinidene complex, and was prepared from the first example of an f-block parent terminal phosphide complex. Complex **4** is potentially a precursor to the uranium terminal phosphido $U=PH$ linkage, which has only been experimentally observed in matrix isolation experiments and probed computationally,^[28] and this work suggests that heavier pnictide $L_nU=EH$ linkages (E = As, Sb) may also be accessible. Studies to these ends are ongoing in our laboratories.

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