Actinide Chemistry

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Challenging the Metallocene Dominance in Actinide Chemistry with a Soft PNP Pincer Ligand: New Uranium Structures and Reactivity Patterns**

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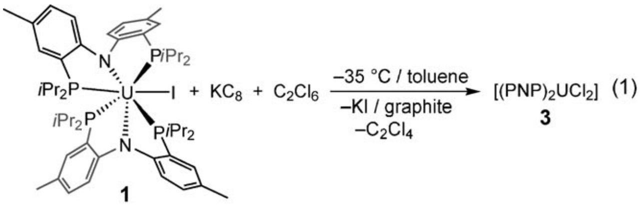
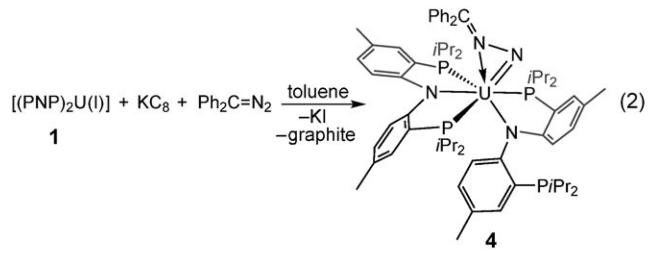
Cyclopentadienyl-based ligand sets, in particular the bis(pentamethylcyclopentadienyl) ligand, are enormously successful frameworks in actinide chemistry and no alternative has proved as fruitful to date.[1] However, the bis(C_5Me_5) framework suffers from inconvenient drawbacks such as the chronic release of the $(C_5Me_5)_2$ dimer upon oxidation of "[$(C_5Me_5)_2U$]" complexes.[2] Inspired by the ability of ligands that combine both hard and soft coordination environments to stabilize highly reactive functional groups (such as alkylidenes, imides, and phosphinidenes) on transition metals and lanthanides,[3] we have extended this strategy to the actinides by using the monoanionic bis[2-(diisopropylphosphino)-4-methylphenyl]amido (PNP) ligand. Compared to the C_5Me_5 ligand, which only displays η^5-coordination to uranium,[4] this soft PNP pincer ligand adopts a variety of coordination modes that range from κ^2-(*P*,*N*) to κ^3-(*P*,*N*,*P'*) and provides more steric crowding and greater electronic density at the metal center.[5] By capitalizing on this versatility, we now demonstrate by using [$(PNP)_2U(I)$] (**1**) and [$(C_5Me_5)_2U(I)(thf)$] (**2**) that the PNP ligand not only promotes unprecedented reactivity patterns for low-valent uranium but also supports new structures for the actinide series that are not available with the C_5Me_5 ligand framework.

Trivalent [$(C_5Me_5)_2U(I)(thf)$] (**2**) in the presence of Na/Hg amalgam or KC_8, a classic uranium(II) synthetic equivalent, is known to provide up to four reducing equivalents.[6] As such, initial studies with **1** were targeted toward establishing the capacity of the bis(PNP) platform to support low-valent uranium chemistry [Eq. (1)]. Treatment of a cold (−35 °C) solution of **1** and KC_8 in toluene with hexachloroethane resulted in an immediate color change from deep green to bright red and formation of the known uranium(IV) [$(PNP)_2UCl_2$] complex[5]; following workup the yield of the isolated product was 96 %. These observations clearly demonstrate that the PNP ligand can indeed support low-valent uranium with the **1**/KC_8 system able to function as a new uranium(II) synthon.



(1)

The ability of the bis(PNP) platform to promote new uranium chemistry was validated by comparing the reactions of **1**/KC_8 and **2**/KC_8 with diphenyldiazomethane. Reaction of **1**/KC_8 with $Ph_2C{=}N_2$ afforded the hydrazonido complex **4,** which was isolated in 98 % yield [Eq. (2)]. To the best of our knowledge, complex **4** represents the first example of an actinide hydrazonido [η^2-(*N*,*N'*)=N−N=CR_2]$^{2-}$ complex and the first example of such a ligand stabilized by a single metal ion.[7] Figure 1 shows the molecular structure of complex **4**, which reveals that the [η^2-(*N*,*N'*)=N−N=CPh_2]$^{2-}$ ligand is stabilized by both a short U=N double bond (U(1)–N(4) = 2.097(5) Å) and an additional U–N dative interaction (U(1)–N(3) = 2.370(5) Å). The U=N linkage is substantially shorter than a uranium(IV)–amide bond (ca. 2.3 Å) and compares well with the few structurally characterized U^{IV} complexes that contain an imido functional group (1.95 Å).[8]



(2)

The hydrazonido [η^2-(*N*,*N'*)=N−N=CPh_2]$^{2-}$ ligand is formed by the two-electron reduction of diphenyldiazomethane. The N−N bond of the reduced $Ph_2C{=}N_2$ unit (N(3)–N(4) 1.359(7) Å) is substantially elongated compared to that in uncomplexed diazoalkanes (1.12–1.13 Å)[9] and is slightly longer than that reported for the [η^2-(*N*,*N'*)-N-N=CPh_2]$^{\bullet-}$ ligand in [$(t\mathrm{BuArO})_3(\mathrm{tacn})U\{\eta^2\text{-}(N,N')\text{-N-N-CPh}_2\}$] (1.338(5) Å; tacn = 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane).[10] In fact, the N(3)–N(4) bond distance in **4** is longer than those observed for the imido ligands in [$(C_5Me_5)_2U(=N-N=CPh_2)(=N\text{-}2,4,6\text{-}t\mathrm{Bu}_3\text{-}C_6H_2)$]

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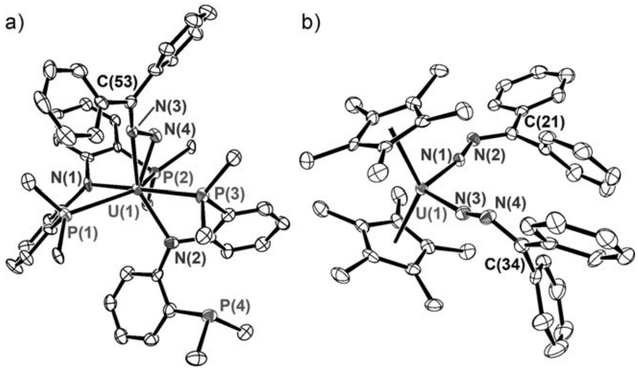
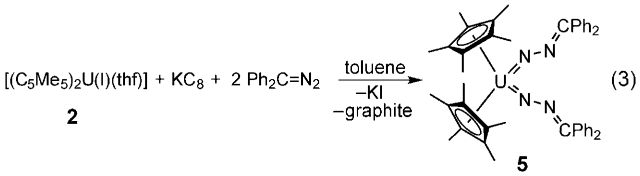


Figure 1. Molecular structure of complexes **4** (a) and **5** (b) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms and methyl groups on the PNP ligands are omitted for clarity. Selected bond distances [Å] and angles [°] for **4**: U(1)–N(3) 2.375(5), U(1)–N(4) 2.097(5), N(3)–N(4) 1.359(7), N(3)–C(53) 1.302(8). For **5**: U(1)–N(1) 1.999(4), U(1)–N(3) 2.018(4), N(1)–N(2) 1.315(6), N(3)–N(4) 1.324(5), N(2)–C(21) 1.314(6), N(4)–C(34) 1.305(6); N(3)-U(1)-N(1) 103.26(16).

(1.308(8) Å)[11] and in **5** (1.315(6), 1.324(5) Å, see below). This bond lengthening is accompanied by a shortening of the C=N bond from 1.32–1.33 Å in uncomplexed diazoalkanes[9] to 1.302(8) Å for C(53)–N(3) in **4**. The same shortening is observed in $[(C_5Me_5)_2U(=N-N=CPh_2)(=N\text{-}2,4,6\text{-}t\text{Bu}_3\text{-}C_6H_2)]$ (1.310(10) Å)[11] and in **5** (1.314(6), 1.305(6) Å), but not for the radical anion ligand in $[(t\text{BuArO})_3(\text{tacn})U\{\eta^2\text{-}(N,N')\text{-N-N-CPh}_2\}]$ (1.333(6) Å), as expected for a $[\eta^2\text{-}(N,N')\text{-N-N=CPh}_2]^{\cdot-}$ radical anion compared to a $[\eta^2\text{-}(N,N')\text{=N}-\text{N=CPh}_2]^{2-}$ dianion.[10] Finally, the coordination sphere of the uranium(IV) center[12] in **4** is completed by two PNP ligands in κ^3-(*P,N,P′*) and κ^2-(*P,N*) coordination modes.[13] This is the first example of such a coordination environment for the bis(PNP) framework and illustrates the flexibility of this ligand set to accommodate various electronic and steric environments which are needed to enable new reactivity patterns for uranium.

Indeed, different chemistry is observed in the reaction of **2**/KC_8 and $Ph_2C{=}N_2$, which gives the bis(imido) uranium(VI) complex **5** in 94% yield of isolated product; two equivalents of the oxidant are needed for the completion of the reaction [Eq. (3)]. The molecular structure of **5** features two imido



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ligands obtained by the formal two electron reduction of each diphenyldiazomethane (Figure 1). As noted for **4**, this reduction results in a significant lengthening of the N–N bonds and a shortening of the C=N bonds of the diazoalkane. The U=N double bonds are characterized by short U–N bond distances (U(1)–N(1) = 1.999(4), U(1)–N(3) = 2.018(4) Å), which are in agreement with those found in the related $[(C_5Me_5)_2U(=N-N=CPh_2)(=N\text{-}2,4,6\text{-}t\text{Bu}_3\text{-}C_6H_2)]$[11] and other $[(C_5Me_5)_2U^{VI}]$ bis(imido) complexes (average U=N = 1.98 Å).[14]

The mechanisms of these two transformations were probed to determine the origin of the difference in reactivity between the [(PNP)$_2$U(I)] (**1**) and $[(C_5Me_5)_2U(I)(thf)]$ (**2**) systems. Compound **2** is known to be a two-electron reductant and the active species in the reductive cleavage of azobenzene (to give $[(C_5Me_5)_2U(=NPh)_2]$) and the reductive coupling of diphenylacetylene (to give $[(C_5Me_5)_2U\{\kappa^2\text{-}(C,C')\text{-CPh=CPh-CPh=CPh}\}]$.[6] In the absence of KC_8 or Na/Hg amalgam, complex **2** reacts with one equivalent of $Ph_2C{=}N_2$ to produce 0.5 equivalents of **5** and 0.5 equivalents of $[(C_5Me_5)_2U(I)_2]$ (**6**) [Eq. (4)].

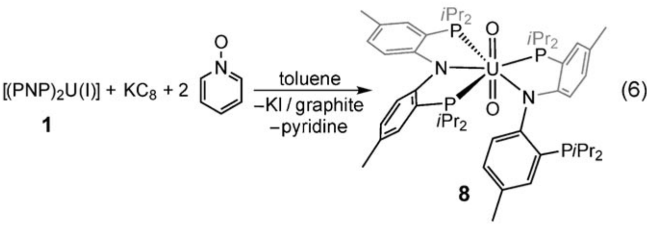
$$\underset{\mathbf{2}}{[(C_5Me_5)_2U(I)(thf)]} + Ph_2C{=}N_2 \xrightarrow{\text{toluene}} 0.5\ \mathbf{5} + 0.5\ \underset{\mathbf{6}}{[(C_5Me_5)_2U(I)]_2} \qquad (4)$$

Similarly, in the absence of KC_8, addition of $Ph_2C{=}N_2$ to one equivalent of **1** yielded a 50:50 mixture of **4**/(PNP)$_2$U(I)$_2$ (**7**) to leave 0.5 equivalents of $Ph_2C{=}N_2$ unreacted [Eq. (5)].[15]

$$\underset{\mathbf{1}}{[(PNP)_2U(I)]} + Ph_2C{=}N_2 \xrightarrow[0.5\ Ph_2C=N_2]{\text{toluene}} 0.5\ \mathbf{4} + 0.5\ \underset{\mathbf{7}}{[(PNP)_2U(I)]_2} \qquad (5)$$

The combination of these observations suggests that the active species are the uranium(III) complexes **1** and **2**, which can accomplish the two-electron reduction of the substrate. As such, the role of the exogenous reductant (KC_8) is merely to regenerate the active uranium(III) species by reducing **6** to **2** and **7** to **1**. The difference in the observed reactivity is likely to arise from the different redox behavior of the uranium(IV) complexes obtained by reaction with the diphenyldiazomethane oxidant (that is, $[(C_5Me_5)_2U{=}N-N{=}CPh_2]$ versus $(PNP)_2U[\eta^2\text{-}(N,N')\text{=N}-\text{N=CPh}_2]$ (**4**)).

To determine whether the reduction chemistry with **1** was limited to the formation of uranium(IV) complexes, its reaction with stronger oxidants was explored. A dramatic distinction between PNP and C_5Me_5 as supporting ligands is seen in the reactivity of **1** and **2** with pyridine-*N*-oxide. Addition of one equivalent of pyridine-*N*-oxide to a solution of **1** in toluene led to the complete consumption of pyridine-*N*-oxide and formation of pyridine, 0.5 equivalents of **7**, and 0.5 equivalents of the new uranium(VI) complex **8**, which showed that two equivalents of the oxidant had reacted. In fact, reaction of **1**/KC_8 with two equivalents of pyridine-*N*-oxide smoothly produced complex **8** as the only uranium complex, which was isolated in 85% yield [Eq. (6)]. This



8

transformation decisively illustrates the ability of **1** to act as a four-electron reductant and to support uranium(VI).

Single-crystal X-ray diffraction confirmed that **8** consists of a uranyl moiety supported by two PNP ligands in κ^3-(*P,N,P′*) and κ^2-(*P,N*) coordination modes (Figure 2), which makes it the first uranyl phosphine complex. The U−P bond lengths in **8** (U(1)–P(1) = 3.066(3), U(1)–P(3) = 3.017(3), U(1)–P(4) = 2.984(3) Å) compare well with those reported for $[U(I)_2({=}NtBu)_2(thf)(PMe_3)_2]$ (U–P = 3.075(3), 3.042(2) Å).[16] The uranium–oxo bond lengths are short, with U(1)–O(1) = 1.791(6) Å and U(1)–O(2) = 1.808(6) Å, which is typical for uranyl complexes.[17] It is noteworthy that the formation of **8** represents only the second rational synthesis of a uranyl fragment from a low-valent uranium precursor; the other reported example relies on the oxidation of $[U(I)_3(thf)_3]$ using pyridine-*N*-oxide to form $[UO_2(I)_2(py)_3]$.[18]

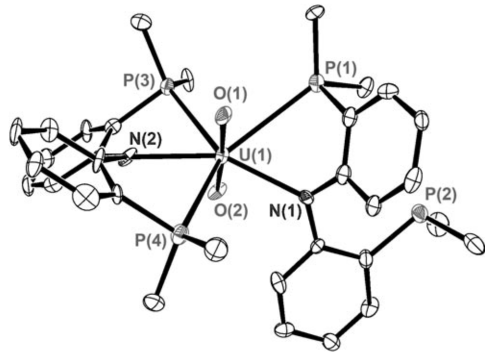
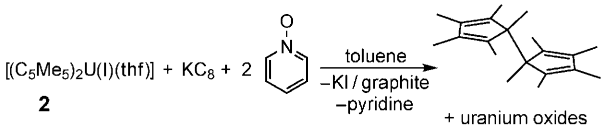


Figure 2. Molecular structure of complex **8** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms and methyl groups are omitted for clarity. Selected bond distances [Å] and angles [°]: U(1)–P(1) 3.066(3), U(1)–P(3) 3.017(3), U(1)–P(4) 2.984(3), U(1)–O(1) 1.791(6), U(1)–O(2) 1.808(6), U(1)–N(1) 2.405(7), U(1)–N(2) 2.402(8); O(1)-U(1)-O(2) 177.0(3).

Finally, for purposes of comparison, the same reaction using **2**/KC_8 instead of **1** was found to produce the dimer $(C_5Me_5)_2$ as the only C_5Me_5-containing compound [Eq. (7)].



(7)

This finding implies the generation of an unstable hexavalent $(C_5Me_5)_2U({=}O)_2$ complex that is reduced by the $C_5Me_5^-$ ligand to produce $(C_5Me_5)_2$ and uranium oxides.[2a,8] In contrast, the stability of **8** reinforces the hypothesis that the PNP ligand, as a better donor and a more flexible ligand than C_5Me_5, can support structures that are simply not accessible with the bis(C_5Me_5) ligand framework.

In conclusion, the work presented here demonstrates that the PNP ligand is capable of supporting not only low-valent uranium but also high-valent species and represents an exciting alternative for promoting reaction chemistry and structural motifs at uranium that are simply not available for the C_5Me_5 ligand set. As evidenced by the formation of the uranyl complex **8**, the PNP ligand is able to support U^{VI} and efforts are now directed towards exploiting systems such as **4** as entries to actinide metallanitrene and nitride chemistry.[19]

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[13] Retention of the κ^3-(*P*,*N*,*P'*) and κ^2-(*P*,*N*) coordination modes for the two PNP ligands in **4** in solution was demonstrated by using ^1H and ^{31}P NMR spectroscopy.

[14] A Cambridge Structural Database search identified four bis-(C_5Me_5)–uranium(VI) imido structures with an average U=N bond length of 1.98 Å (range 0.09 Å). For specific references, see: a) $[(C_5Me_5)_2U(=NPh)_2]$, U–N = 1.952(7) Å: D. S. J. Arney, C. J. Burns, D. C. Smith, *J. Am. Chem. Soc.* **1992**, *114*, 10068–10069; b) $[(C_5Me_5)_2U(=NAd)_2]$ (Ad = 1-adamantyl), U–N = 1.94(2), 1.96(2) Å: reference [6a]; c) $[(C_5Me_5)_2U(=O)(=N\text{-}2,6\text{-}i\text{Pr}_2C_6H_3)]$, U–N = 1.988(4) Å: D. S. J. Arney, C. J. Burns, *J. Am. Chem. Soc.* **1993**, *115*, 9840–9841; d) $[(C_5Me_5)_2U(=N{-}N{=}CPh_2)(=N\text{-}2,4,6\text{-}t\text{Bu}_3\text{-}C_6H_2)]$, U–N = 2.031(6), 1.987(5) Å: reference [11].

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