Synthesis and reactivity of bis(imido) uranium(VI) cyclopentadienyl complexes†

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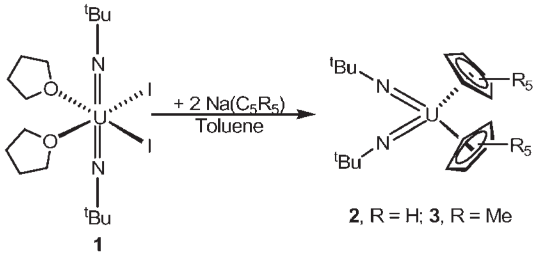
The bis(imido) uranium(VI)–C_5H_5 and –C_5Me_5 complexes $(C_5H_5)_2U(N^tBu)_2$, $(C_5Me_5)_2U(N^tBu)_2$, $(C_5H_5)U(N^tBu)_2(I)$(dmpe), and $(C_5H_5)_2U(N^tBu)_2$(dmpe) can be synthesized from reactions between $U(N^tBu)_2(I)_2(L)_x$ (L = THF, $x = 2$; L = dmpe, $x = 1$) and $Na(C_5R_5)$ (R = H, Me); these complexes represent the first structurally characterized C_5H_5-compounds of uranium(VI) and they further highlight the differences between UO_2^{2+} and the bis(imido) fragment.

Organoactinide complexes have long received attention as potential catalysts for organic transformations.[1–3] Interest in these compounds stems from the ability of the actinide metal centers to attain large formal coordination numbers and unusual coordination geometries; these properties present the potential to promote demanding chemical bond conversions distinctive from their transition metal counterparts. Most of the interest in this area has centered on organometallic complexes of uranium(III) and uranium(IV), in particular complexes which contain C_5H_5 (Cp) and C_5Me_5 (Cp*) ancillary ligands.[4,5] High valent uranium(VI) complexes have attracted attention as a result of their essential role in U(IV)–U(VI)-mediated catalytic transformations. Despite this interest, there are only a few examples of organouranium(VI) complexes. To date, the majority of reported organouranium(VI) complexes have featured C_5Me_5 ancillary ligands, whereas analogous C_5H_5 complexes have yet to be reported. In contrast, uranium(IV)–C_5H_5 complexes have been known for some time but are unstable because they undergo C_5H_5-redistribution reactions which has complicated their use in U(IV)–U(VI) redox chemistry.[6–8] In this communication, we report the synthesis of several bis(imido) uranium(VI)–C_5H_5 and –C_5Me_5 complexes. We have also examined the reactivity of these compounds towards a variety of Lewis bases and investigated the potential of the uranium(VI)–C_5H_5 complexes to undergo redistribution reactions.

We have recently reported the syntheses of a family of uranium(VI) bis(imido) diiodide complexes and found that the addition of alkali metal salts to these complexes exchanges the iodide ligands for other anionic groups.[9,10] Given this reactivity, we investigated the reactions of $U(N^tBu)_2(I)_2(THF)_2$ (**1**) with substituted cyclopentadienides. The addition of two equivalents of $Na(C_5R_5)$ (R = H, Me) to **1** provides $(C_5H_5)_2U(N^tBu)_2$ (**2**) and $(C_5Me_5)_2U(N^tBu)_2$ (**3**), respectively in moderate yields (Scheme 1). The ^1H NMR spectrum of **2** is representative and features singlets for both C_5H_5 (6.13 ppm) and *tert*-butyl imido (1.09 ppm) ligands. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum shows a singlet at 127.2 ppm attributable to the equivalent carbon atoms of the C_5H_5 group. Surprisingly, complex **2** represents the first reported uranium(VI) complex with unsubstituted cyclopentadienyl ligands, and the simple, two step synthetic procedure to generate **2** and **3** from uranium metal is more convenient than the original preparation of **3**.[11,12]

The molecular structure of **2** was confirmed by X-ray crystallography and found to possess two independent molecules in the asymmetric unit cell. The solid state molecular structure of one of these molecules is shown in Fig. 1 and the geometrical parameters given are the average of the two independent molecules. Both the independent molecules feature a distorted tetrahedral geometry at the uranium center with *cis*-oriented bis(imido) ligands. The average U–N(imido) bond length (1.929(7) Å) is significantly longer than U–N imido bond lengths observed in *trans*-bis(imido) complexes like $U(N^tBu)_2(I)_2(THF)_2$ (1.844(4) Å) and similar to those in other *cis*-bis(imido) uranium(VI) complexes.[11,12] The N1–U1–N2 bond angle for **2** (103.4(3)°) is slightly larger than values observed for other bis(imido) $(C_5Me_5)_2U(NR)_2$ complexes,[11,12] which is most likely a result of steric interactions between the two *tert*-butyl imido ligands. The C_5H_5 ligands assume η^5-bonding modes with U–C_{Cp} bond distances ranging from 2.708(9) to 2.814(14) Å which are similar to those in previously described bis(imido) uranium(VI)–C_5Me_5 complexes.[11] The Cp(centroid)–U–Cp(centroid) angle is 123.7(1)°



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2, R = H; **3**, R = Me

Scheme 1

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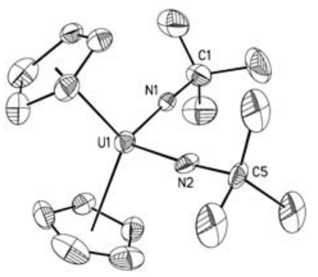


Fig. 1 Molecular structure of one of the independent molecules in the unit cell of $(C_5H_5)_2U(N^tBu)_2$ (**2**). Average bond lengths (Å) and angles (°) for the two independent molecules of **2**: U1–N1 = 1.929(7), N1–U1–N2 = 103.4(3), U–Cp_{cent} = 2.748(10), Cp_{cent}–U–Cp_{cent} = 123.7(1).

which is somewhat smaller than values found in $(C_5Me_5)_2U(NPh)_2$ (141.9°).[11,12]

To gain a better understanding of the coordination chemistry of **2**, the reactions with several Lewis bases were examined. In most cases, the addition of bases such as $OPPh_3$ and pyridine gave no reaction as indicated by ^1H NMR spectroscopy. Interestingly, complex **2** reacts with 1 equiv. of dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) to generate $(C_5H_5)_2U(N^tBu)_2$(dmpe) (**4**, Scheme 2), whereas the addition of dmpe to **3** gives no reaction. The ^1H NMR spectrum of **4** features broad singlets at 1.28 ppm and 1.83 ppm for the dmpe ligand which suggests rapid motion of the uranium–dmpe metallacycle on the NMR timescale. Singlets are also observed at 5.95 ppm and 1.11 ppm and are assigned to the protons of the C_5H_5 and *tert*-butyl imido ligands, respectively. The ^{31}P NMR spectrum of **4** shows a singlet at 84.3 ppm which is shifted significantly downfield from free dmpe (δ = −49 ppm).[13] To our knowledge, **4** represents the first example of a uranium(VI) center stabilized by a dmpe ligand and only the second example of a uranium(VI)–phosphine complex.[10]

The solid state molecular structure of **4** was determined by X-ray crystallography and is shown in Fig. 2. Complex **4** possesses a pseudo-octahedral geometry at the uranium center and a N1–U1–N2 bond angle (154.35(16)°) which lies between those of **2** and the *trans*-bis(imido) complex $U(N^tBu)_2(I)_2(THF)_2$ (**1**).[10] The U–N(imido) bond length in **4** (1.937(4) Å) is comparable to the U–N(imido) bond lengths found in **2** and significantly longer than the average U–N(imido) bond length found in **1** (1.844(4) Å). The C_5H_5 ligands in **4** display η^5-bonding to the U atom with U–C_{Cp} bond distances ranging from 2.824–2.896(5) Å which are significantly longer than bond distances observed for **2** and likely a result of increased steric interactions at the uranium center. The average U–P bond length is 2.999(10) Å, which is shorter than the bond distances in $U(N^tBu)_2(I)_2(PMe_3)_2(THF)$ (U–P(avg.) = 3.059(3) Å) and in the uranium(IV)–dmpe complexes $U(OPh)_4$(dmpe) (U–P avg = 3.104 Å) and $U(CH_2Ph)(Me)_3$(dmpe) (U–P avg = 3.15 Å).[14,15] Complex **5** also features a Cp(centroid)–U–Cp(centroid) angle of 111.0(1)°, which is smaller than the corresponding angle in **2**, the average angles in uranium(IV) complex $(C_5H_5)_3UCl$ (116.7°),[16] and the angles found in $(C_5Me_5)_2U(NPh)_2$.[12]

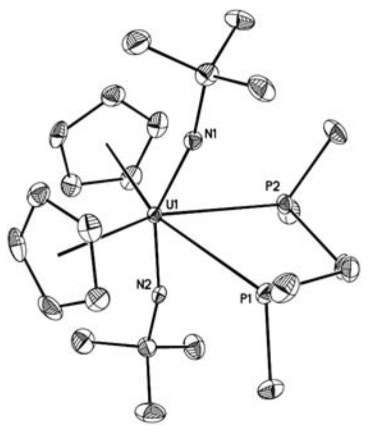
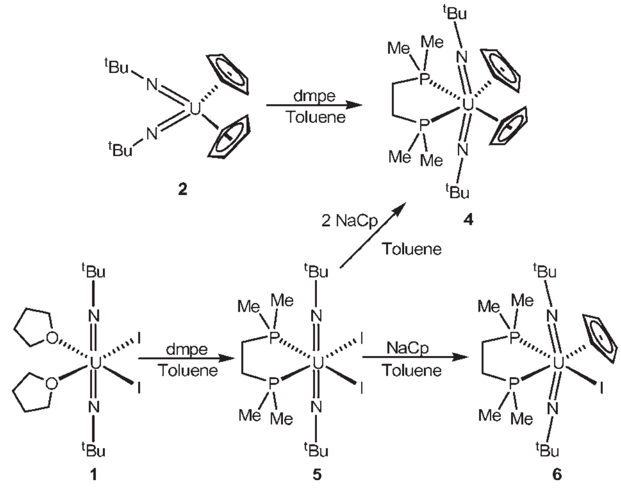


Fig. 2 Molecular structure of $Cp_2U(N^tBu)_2$(dmpe) (**4**). Selected bond lengths (Å) and angles (°): U1–N1 = 1.935(4), U1–N2 = 1.938(4), avg. U–Cp_{cent} = 2.586(5), N1–U1–N2 = 154.35(16), Cp_{cent}–U–Cp_{cent} = 111.0(1).



Scheme 2

Encouraged by the successful isolation of complex **4**, we examined the synthesis of $U(N^tBu)_2(I)_2$(dmpe) (**5**) with a goal to perform metathesis reactions of the iodide ligands with $Na(C_5H_5)$. Complex **5** can be synthesized by the addition of 1 equiv. of dmpe to a CH_2Cl_2 solution of **1**. The ^1H NMR spectrum of **5** shows broad dmpe resonances for both $-CH_3$ and $-CH_2$ substituents and a singlet at 0.58 ppm attributable to the *tert*-imido ligands. The $^{31}P\{^1H\}$ NMR spectrum features a singlet at 64.6 ppm which is upfield from the ^{31}P NMR chemical shift of **4**. Attempts to grow X-ray quality crystals of **5** have so far been unsuccessful; however, NMR spectral data and elemental analysis results agree with the formulation of **5** as depicted in Scheme 2.

The reaction between 1 equiv. of $Na(C_5H_5)$ and **5** yields $(C_5H_5)U(N^tBu)_2(I)$(dmpe) (**6**). Complex **4** can also be synthesized by reaction of **5** with 2 equiv. of NaCp. The ^1H NMR spectrum of **6** suggests the molecule possesses C_2-symmetry in solution and features singlets for the C_5H_5 and *tert*-butyl imido resonances at 6.68 ppm and 0.72 ppm, respectively. An asymmetric dmpe ligand is observed with two doublets at 1.64 ppm and 2.26 ppm ($^3J_{P-H}$ = 5 Hz) and a complicated multiplet at 2.62 ppm as is consistent with the protons of the dmpe-methylene backbone. The $^{31}P\{^1H\}$ NMR spectrum of

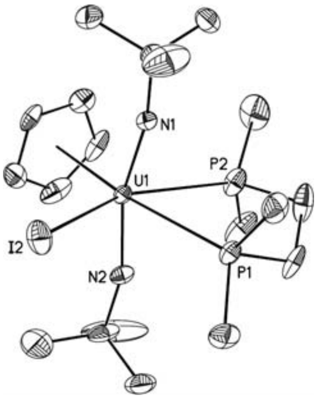


Fig. 3 Molecular structure of CpU(N^{t}Bu)$_2$(I)(dmpe) (**6**). Bond lengths (Å) and angles (°): U1–N1 = 1.883(4), U1–N2 = 1.889(5), U–Cp$_{cent}$ = 2.535(6), U1–P1 = 2.9621(16), U1–P2 = 2.9212(16), N1–U1–N2 = 161.10(19).

6 consists of an AB pattern that would be expected for two inequivalent ^{31}P centers with doublets at 71.3 ppm and 88.3 ppm ($^2J_{P-P}$ = 24 Hz).

The solid state molecular structure of **6** is shown in Fig. 3. Complex **6** possesses a pseudo-octahedral geometry at the uranium center which is similar to **4**. The N1–U1–N2 bond angle of 161.10(19)° is slightly larger than the angle observed in **4**, presumably a result of the decrease in steric interactions at the uranium center. The U–N(imido) bond length in **6** (1.886(5) Å) is comparable to those in the previously described uranium *trans*-bis(imido) complexes.[10] As was observed in **4**, the C_5H_5 ligands in **6** display η^5-bonding to the U atom with U–C_{Cp} bond distances ranging from 2.777(6) to 2.828(6) Å.

$(C_5H_5)_2UX_2$ (X = halide) complexes have demonstrated a strong propensity to undergo disproportionation reactions to form mixtures of $(C_5H_5)_3UX$ and $(C_5H_5)UX_3$.[6–8] The potential for complexes **4** and **6** to undergo C_5H_5-redistribution reactions was addressed in two ways: (1) complex **6** was heated in THF at 60 °C for several hours to determine if disproportionation to **4** and **5** occurs; and (2) complexes **4** and **5** were heated together under similar conditions to determine if conproportionation occurs to yield complex **6**. In both cases, no reactions were observed by ^{1}H NMR spectroscopy.

The reactivity exhibited by **1** is strikingly different from that observed with the uranyl ion. For instance, the reaction of uranyl chloride with K(C_5R_5) (R = H, Me) results in a selective one electron reduction to generate uranyl(v), and not halide metathesis.[17] Interestingly, a pentamethylcyclopentadienyl complex of uranyl has recently been isolated, not *via* metathesis however, but by oxidation of $[(C_5Me_5)_2U(CN)_5]^{3-}$ with pyridine-*N*-oxide.[18] The facile coordination of the soft dmpe ligand to the bis(imido) fragment also illustrates the differences between the two fragments, as phosphine ligands are not known to bind to the hard uranyl ion.[19]

In summary, the first structurally characterized uranium(vi)–C_5H_5 complexes have been synthesized and their reactivity towards several Lewis bases has been investigated. Given the difference in reactivity with dmpe, the differing steric environments established at the uranium(vi) center by C_5H_5 and C_5Me_5 ligands in **2** and **3** have a profound effect on the coordination chemistry of these compounds. These findings show that bis(imido) uranium(vi)–C_5H_5 complexes, like **2**, possess the potential to form higher coordination numbers, which could have a significant impact on the design and use of organouranium(vi) complexes in catalysis. We are currently investigating the potential of these cyclopentadienyl complexes in catalytic processes such as hydroamination and olefin polymerization.

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