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Multi-electron reduction facilitated by a trianionic pyridine(diimine) ligand†‡

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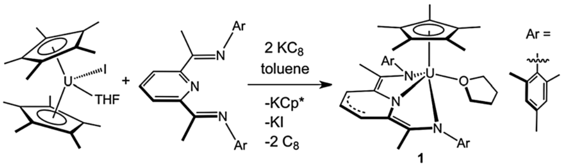
Reduction of $Cp^*_2UI(THF)$ with KC_8 in the presence of a pyridine-(diimine) ligand (PDI) results in the formation of Cp*U(PDI)(THF), which features a triply reduced PDI ligand. This species performs four electron cleavage of azobenzene to generate the uranium bis(imido), $Cp^*(PDI)U(NPh)_2$.

The highly reducing nature of tri- and tetravalent uranium makes it an attractive metal for use in bond activation reactions, but its characteristic radical chemistry must be overcome to make this element catalytically relevant. Redox active ligands[1–4] are known to successfully mediate such processes on main group,[5,6] first row,[7–10] and early transition metals,[11–13] and these ligands have been effectively used on uranium for this purpose. Andersen,[14,15] in addition to our group,[16] has shown that one-electron reduced bipyridine ligands effectively support uranium(III) centres and mediate two electron chemistry. Cummins has demonstrated that bridging aromatic ligands in dimeric uranium species facilitate two electron reduction of diphenyldisulfide.[17] Similar four-electron chemistry has been observed by Evans in the cleavage of azobenzene.[18] In these reactions, dissociation of the redox active ligands occurs.

Recent work from our laboratory has demonstrated the use of the redox-active α-diimine ligand, $^{Mes}DAB^{Me}$ ($^{Mes}DAB^{Me}$ = [ArN═C(Me)-C(Me)═NAr]; Ar = 2,4,6-trimethylphenyl (Mes)), in facilitating two electron reduction of iodomethane[19] and reductive elimination[20] at tetravalent uranium centres. In both cases, the $^{Mes}DAB^{Me}$ ligands store two electrons from the uranium centre, allowing these multi-electron processes to occur. Encouraged by these results, pyridine(diimine) (PDI) ligands were explored for their ability to hold up to three electrons in their conjugated π* orbitals, although this is rarely observed.[21] It was hypothesized that storing more than two electrons in the ligand framework would enhance the reactivity of the uranium centre by generating a highly reduced species that could transfer multiple electrons at a time. Herein we present the synthesis of a reduced pyridine(diimine) uranium species, $Cp^*U(^{Mes}PDI^{Me})(THF)$ ($^{Mes}PDI^{Me}$ = 2,6-((Mes)N═CMe)$_2$-C_5H_3N) and its ability to cleave azobenzene using electrons stored in the ligand framework.[22]

Synthesis of the reduced uranium species was accomplished by treating $Cp^*_2UI(THF)$[23] with one equivalent of $^{Mes}PDI^{Me}$ and stirring for five minutes, with subsequent addition of two equivalents of KC_8. After additional stirring (24 hours) and workup, a brown solid, (**1**), was isolated in 60% yield (eqn (1)). Using a third equivalent of KC_8 resulted in full conversion after 3 hours with higher yields. Lower yields were noted with immediate addition of KC_8 after $^{Mes}PDI^{Me}$. Analysis of **1** by ^1H NMR spectroscopy shows 20 sharp, paramagnetically shifted resonances ranging from −34 to 28 ppm with a prominent Cp* resonance at −2.4 ppm (15H). The remaining peaks integrate to 1H, 2H, and 3H, corresponding to the C*H* and CH_3 groups of PDI and the CH_2 groups of coordinated THF, consistent with an asymmetric $^{Mes}PDI^{Me}$ ligand.



(1)

Brown crystals of **1** suitable for X-ray crystallography were grown from a concentrated diethyl ether solution at −35 °C (Fig. 1 and 2, Table 1). Refinement of the data showed **1** is $Cp^*U(^{Mes}PDI^{Me})(THF)$ (**1**), which features a uranium centre with

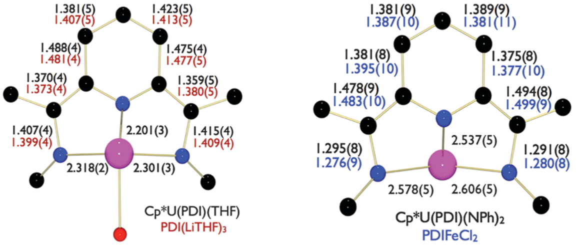


Fig. 1 $^{Mes}PDI^{Me}$ bond distance comparisons in Å for **1** with $PDI(LiTHF)_3$ (left) and **2** with $PDIFeCl_2$ (right).

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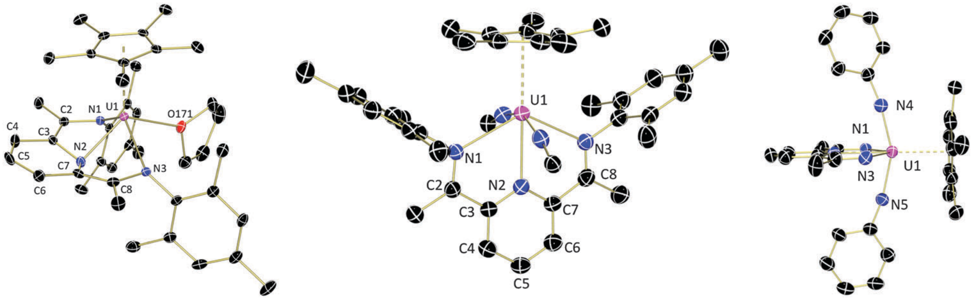


Fig. 2 Molecular structures of **1** (left) and **2** (centre, right) shown with 30% probability ellipsoids. Hydrogen atoms, solvent molecules, and 2nd molecules in asymmetric units have been omitted for clarity. Phenyls (centre) and aryls (right) have also been omitted.

Table 1 Metrical parameters for **1 and 2**

	1 (Å)	**2** (Å)		**1** (Å)	**2** (Å)
U1–N3	2.318(2)	2.578(5)	N3–C8	1.407(4)	1.295(8)
U1–N2	2.201(3)	2.537(5)	N1–C2	1.415(4)	1.291(8)
U1–N1	2.301(3)	2.606(5)	C8–C7	1.370(4)	1.478(9)
U1–O171	2.474(2)	—	C2–C3	1.359(5)	1.494(8)
U1–Ct	2.548	2.577	N2–C7	1.392(4)	1.350(8)
U–N4	—	2.036(5)	N2–C3	1.412(4)	1.348(8)
U–N5	—	1.994(6)	C7–C6	1.488(4)	1.381(8)
			C4–C3	1.475(4)	1.375(8)
			C6–C5	1.381(5)	1.381(9)
			C5–C4	1.423(5)	1.389(9)

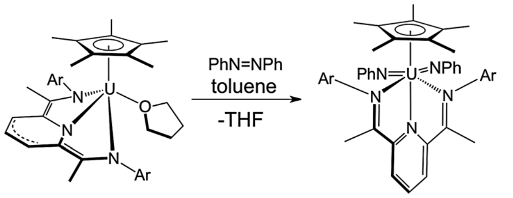
an η^5-Cp* ligand, a tridentate $^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$ ligand, and a coordinated THF molecule. The U–C_{centroid} distance of the Cp* ring is calculated to be 2.548 Å. The datively coordinated THF molecule exhibits a U–O bond distance of 2.474(2) Å, consistent with other low-valent U–O dative bonds.[4]

In compound **1**, the $^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$ ligand is distorted from planarity, and the uranium centre lies 1.059 Å above the N1–N2–N3 plane. Signs of reduction are noted in the respective N3–C8 and N1–C2 bond distances of 1.407(4) and 1.415(4) Å and the neighboring C8–C7 and C2–C3 bond distances of 1.370(4) and 1.359(5) Å, respectively. These distances are quite different from free PDI ligands, which typically display C_{imine}–N_{imine} distances of 1.28 and C_{imine}–C_{pyridine} distances of 1.50 Å.[24] Instead, the bond distances in **1** are similar to those in ($^{\mathrm{iPr2}}\mathrm{PDI}^{\mathrm{Me}}$)(Li(THF))$_3$ ($^{\mathrm{iPr2}}\mathrm{PDI}^{\mathrm{Me}}$ = 2,6-((2,6-diisopropylphenyl)N=CMe)$_2$C$_5$H$_3$N which is a trianionic $^{\mathrm{iPr2}}\mathrm{PDI}^{\mathrm{Me}}$ ligand (Fig. 1, left).[21a] In this species, the C_{imine}–N_{imine} bonds are 1.399(4) and 1.409(4) Å and the C_{imine}–C_{pyridine} bonds are 1.373(4) and 1.380(5) Å, all very similar to those in compound **1**. These structural distortions indicate population of the PDI π* orbitals, which have an antibonding interaction for the C_{imine}–N_{imine} and a bonding interaction for the adjacent C–C bond. The distances within the pyridine ring in **1** also show deviations from aromaticity. The N2–C7 and N2–C3 bonds have been lengthened to 1.392(4) Å and 1.412(4). Drastic bond distortions can be seen in the C–C distances of the pyridine ring (Table 1). Much like those observed in ($^{\mathrm{iPr2}}\mathrm{PDI}^{\mathrm{Me}}$)(Li(THF))$_3$,[21a] the C_{ortho}–C_{meta} bonds are significantly elongated from free pyridine to 1.488(4) and 1.475(4) Å. Those bonds flanking the *para*-carbon, C4–C5 and C5–C6, are 1.381(5) and 1.423(5) Å, as compared to 1.407(5) and 1.413(5) in ($^{\mathrm{iPr2}}\mathrm{PDI}^{\mathrm{Me}}$)(Li(THF))$_3$. These distances are in agreement with Density Functional Theory calculations performed on ($^{\mathrm{iPr2}}\mathrm{PDI}^{\mathrm{Me}}$)(Li(THF))$_3$, which show an antibonding interaction between C_{ortho}–C_{meta}, explaining the observed elongation, as well as significant electron density on the N and C_{para} of the pyridine, supporting shorter bonds here. The bond distortions observed here are more extreme than those reported by Chirik and coworkers for [Na(15-crown−5)(THF)$_2$]-[($^{\mathrm{iPr}}$PDI)Fe(N$_2$)], which is established to contain a trianionic PDI chelate.[21b] Thus, the distances observed within the ligand framework of **1** support that $^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$ has been reduced to the [PDI]$^{3-}$ oxidation state.

Ligand reduction is further indicated by the U–N bonds, which are shorter than for dative bonds that would accompany coordination of a neutral $^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$ ligand. All three U–N distances in **1** (2.201(3) Å, 2.301(3) Å, and 2.318(2) Å) are in the range of U–N amide bonds,[25,26] indicating anionic coordination to uranium. These data are consistent with neutral **1** as having a tetravalent uranium centre ligated by a monoanionic Cp* and a trianionic $^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$. This is further supported by near-IR data of **1** (pentane) that show sharp, weakly intense absorption bands spanning 1000–2100 nm, characteristic for uranium(IV) species (Fig. S1, ESI‡).[27] Solution magnetic measurements of **1** show a $\mu_{\mathrm{eff}} = 2.3(2)\ \mu_{\mathrm{B}}$ (23 °C), which is somewhat low for U(IV), but this is a noted trend for f-block elements bearing ligands of this type.[28]

The reactivity of **1** was explored to determine if the stored PDI electrons could be used for productive multi-electron chemistry. Treating a toluene solution of **1** with one equiv. of azobenzene followed by stirring for 30 minutes and workup produced a brown solid (**2**) after recrystallization (58%). The ^{1}H NMR spectrum shows several broad, paramagnetically shifted peaks ranging from −11 to 29 ppm signifying a reaction, but this was not useful for structural assignment.

In order to elucidate the structure of **2**, X-ray quality crystals grown from a concentrated toluene solution at −35 °C were analyzed. Refinement of the crystallographic data revealed the structure of **2** as the pyridine(diimine) bis(imido) uranium species, Cp*U(PDI)(NPh)$_2$ (**2**) (Fig. 2, Table 1). Compound **2** has two phenyl imido substituents with short U–N bonds (1.993(6) and 2.035(5) Å) consistent with multiple bond character. These bonds are in agreement with other high-valent uranium–imido bonds,[29–31] and are longer than those reported for U(VI) *trans*-bis(imido) species, which have U–N bond lengths of 1.81–1.88 Å.[32–37] The U–N bonds in **2** most closely match with those for the uranium(V) bis(imido), U(NDipp)$_2$Cl(^{t}Bu$_2$bpy)$_2$ (Dipp = 2,6-diisopropylphenyl), reported by Boncella, with U–N distances of 1.977(4) and 1.980(4) Å.[29] The arrangement of the imido substituents in **2** enforces an N–U–N angle of 154.2(2)°, smaller than those noted for all other uranium bis(imido) complexes (161.10(19)–180.0(3)°).[29,32–37] This is most likely due to steric pressure imparted by the Cp* ring. The U–N_{imido}–C bond angles (169.1(5)° and 170.1(5)°) are nearly linear, indicative of nitrogen lone pair bonding to uranium. The Cp* ring in **2** adopts an η^5 coordination mode, with a U–$C_{centroid}$ distance of 2.577 Å.



(2)

A striking difference from **1** is that in **2**, the three nitrogen atoms of the $^{Mes}PDI^{Me}$ ligand are coplanar with the uranium centre. The respective N1–C2 and N3–C8 bond distances of 1.291(8) and 1.295(8) Å are consistent with C–N double bonds and show no signs of reduction. Likewise, the neighboring C2–C3 and C8–C7 bonds of 1.494(8) and 1.478(9) Å are similar to C–C single bonds and as expected for the $[PDI]^0$ oxidation state. Furthermore, aromaticity has been restored to the pyridine ring as indicated by the C–C and C–N bond distances. While no crystallographic data is known for free $^{Mes}PDI^{Me}$, a comparison of bond distances can be made to $^{Mes}PDI^{Me}FeCl_2$,[38] which is established to have a neutral supporting ligand (Fig. 1, right). In this compound, the N–C_{imine} distances are 1.276(9) and 1.280(8) Å, while the C_{imine}–$C_{pyridine}$ distances are 1.483(10) and 1.499(9) Å, all of which agree with compound **2**. The pyridine ring in $^{Mes}PDI^{Me}FeCl_2$ is aromatic as is observed for **2**.

The uranium–nitrogen distances for $^{Mes}PDI^{Me}$ ligand within **2** of 2.606(5), 2.537(5), and 2.578(5) Å are as expected for dative linkages, also supporting the $^{Mes}PDI^{Me}$ chelate is neutral. Ligand reduction through occupation of π*-orbitals would create shorter distances as in **1**. With $^{Mes}PDI^{Me}$ ligand, Cp* and imido substituents, compound **2** can be formulated as pentavalent, as is confirmed by the paramagnetic ^{1}H NMR spectrum. This is further supported by the solution magnetic moment of 1.75(1) μ_B (23 °C), which is consistent with other uranium(V) species.[30,31]

The formation of **2** from **1** shows the utility of the redox-active ligand in the four electron reduction of azobenzene. In **1**, the $^{Mes}PDI^{Me}$ ligand is reduced by three electrons, as indicated by X-ray crystallography. In **2**, the PDI ligand is neutral, supporting the idea that the three reducing equivalents housed in $^{Mes}PDI^{Me}$ are critical for the observed N=N bond cleavage. Further, the uranium oxidation state changes from +4 to +5 in the reaction, showing that the metal centre is the origin of the fourth reducing equivalent. Therefore, the $^{Mes}PDI^{Me}$ ligand facilitates multi-electron chemistry that is rarely observed with uranium. Further, in contrast to previous work in this area, the redox-active ligand is retained throughout the reaction, rather than sacrificed, and may play a role in subsequent reactivity. Future work will focus on the utility of $^{Mes}PDI^{Me}$ in functionalization of the strong U–N_{imido} multiple bond as well as expanding the scope of these multi-electron reactions for organometallic transformations.

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