In situ generation of uranium alkyl complexes[†]

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A new method for generating uranium alkyl complexes is described. Although homoleptic uranium alkyl complexes are notoriously unstable and difficult to work with, by generating such species in situ, a wide range of alkyl complexes can be accessed from UI₃(THF)₄.

The reactivity of uranium complexes can be substantially modulated by tuning the electronic and steric properties of their ancillary-ligand framework.¹⁻⁹ We have been interested in the reactivity of $d^0 f^n$ metal centers supported by ferrocene ligands¹⁰⁻¹⁷ and proposed that a weak interaction, of donor-acceptor type, takes place between iron and the metal when ferrocene diamides $(NN^{fc} = fc(NSi^{t}BuMe_{2})_{2}, fc = 1,1'$ ferrocenylene, Chart 1) are used.^{18,19} For uranium complexes, we recently reported novel C-H activation reactions by (NN^{fc})U(CH₂Ph)₂, 1^{fc}-U(CH₂Ph)₂, with both benzyl ligands 1^{fc}-U(CH₂Ph)₂ engaging an sp²-C-H bond of of 1-methylimidazole.^{10,20} We have also shown that, after the C-H activation events, a unique cascade of functionalization reactions can be thermally induced.¹⁰

In order to probe whether the reactivity of 1^{fc} -U(CH₂Ph)₂ is unique,²¹ we decided to synthesize analogous dibenzyl complexes of a tridentate, dianionic supporting ligand, 2,6bis(2,6-diisopropylanilidomethyl)pyridine (NN^{py}, Chart 1), because its geometry mimics that of NN^{fc}. Complexes of Ti(IV),²²⁻²⁴ Zr(IV),²⁵⁻²⁸ Ta(V),^{29,30} and lanthanides³¹⁻³³ supported by pyridine-diamide ligands are known.

Dialkyl complexes of Th(IV) supported by NN^{py} have also been reported.34,35 Those complexes were synthesized from KCH₂Ph or LiCH₂SiMe₃ and the respective thorium dichloride, (NN^{py})ThCl₂(DME), which, in turn, was produced in the salt-metathesis reaction between ThCl₄(DME)₂ and Li₂(NN^{py}).^{34,35} The complex 1^{fc}-U(CH₂Ph)₂ was also synthesized by the salt-metathesis reaction of KCH₂Ph and 1^{fc}-I₂(THF),



Chart 1 Pro-ligands used in the present study.

obtained directly from UI₃(THF)₄³⁶⁻³⁸ and [K(OEt₂)₂]₂[NN^{fc}].¹⁸ Since $UI_3(THF)_4^{36-38}$ is a readily available starting material and U-I bonds are weaker and, therefore, easier to involve in salt-metathesis reactions than U-Cl bonds, we decided to follow the same reaction protocol for the synthesis of a (NN^{py})UI₂ starting material, even though the formation of the uranium(IV) complex would require the disproportionation of the uranium(III) complex UI₃(THF)₄.^{1,2,18,39}

The reaction between $[K(OEt_2)_2]_2[NN^{py}]$ and $UI_3(THF)_4$ gave a mixture of products that proved intractable. However, the reaction between [Li(OEt₂)₂]₂[NN^{py}] and UI₃(THF)₄ (eqn (1)) led to the isolation of 1^{py}₂-U.‡ Although 1^{py}₂-U was too insoluble in hydrocarbons or diethyl ether to allow its purification, a single-crystal X-ray diffraction study (see the ESI[†] for details) confirmed the solid-state structure of 1^{py}₂-U.

1.5
$$[Li(OEt_2)]_2[NN^{py}] \xrightarrow[-"U", -Kl]{-"U", -Kl} 1^{py}_2-U$$
 (1)
THF, 16 h, 35%

The analogous 1^{fc} ₂-U is a by-product of the reaction between $UI_3(THF)_4^{36}$ and $[K(OEt_2)_2]_2[NN^{fc}]$ that also gives 1^{fc}-I₂(THF).¹⁸ However, our attempts to modify the conditions for the reaction shown in eqn (1) have not yielded a $(NN^{py})UI_2$ complex. Inspired by a report from the Hayton group on the synthesis of homoleptic uranium alkyl complexes⁴⁰ and encouraged by the fact that (NN^{py})Th(CH₂SiMe₃)₂ was accessible from an *in situ* reaction between "Cl₂Th(CH₂SiMe₃)₂" and H₂(NN^{py}), we decided to pursue the synthesis of uranium alkyl complexes supported by NNpy by generating and not isolating their alkyl precursors.

$$\begin{array}{c} \text{UI}_{3}(\text{THF})_{4} \\ + 3 \text{ KCH}_{2}\text{Ph} \\ 0.75 \text{ H}_{2}(\text{NN}^{\text{py}}) \end{array} \xrightarrow{\text{THF / Et}_{2}\text{O}} \begin{array}{c} \text{THF / Et}_{2}\text{O} \\ \hline -78 \text{ °C to } 25 \text{ °C} \\ 62\% \end{array} \xrightarrow{\text{(NN}^{\text{py}}) U \xrightarrow{\text{off}^{\text{M}}} \text{Ph} \\ \hline 1^{\text{py}} \text{-U(CH}_{2}\text{Ph})_{2} \end{array} (2)$$

The reaction of $UI_3(THF)_4^{36}$ and three equivalents of KCH₂Ph, followed by the addition of 0.75 equivalents of $H_2(NN^{py})$ at low temperatures, led to the formation of the uranium(IV) dibenzyl complex (NN^{py})U(CH₂Ph)₂, 1^{py}-U(CH₂Ph)₂ (eqn (2)). The reaction was reproducible and allowed the isolation of 1^{py} -U(CH₂Ph)₂ in 54–62% yield consistently. The complex 1^{py}-U(CH₂Ph)₂ was characterized by elemental analysis, ¹H NMR spectroscopy, and X-ray crystallography (Fig. 1).

Interestingly, by changing the stoichiometry and employing two equivalents of KCH₂Ph in a reaction with $UI_3(THF)_4^{36}$ and 0.75 equivalents of $H_2(NN^{py})$, a new product, 1^{py} -UI(CH₂Ph) (Fig. 1), was obtained (eqn (3)). The reaction was also reproducible and occurred consistently in 68-76% yield.

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[†] EElectronic supplementary information (ESI) available: Detailed syntheses, NMR spectra, and crystallographic information. CCDC for 1^{py}₂-U, 1^{py}-U(CH₂Ph)₂, and 1^{py}-UI(CH₂Ph) are 756840, 756841, and 756842, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b927264j



Fig. 1 Thermal-ellipsoid (50% probability) representation of 1^{py} -U(CH₂Ph)₂ (left) and 1^{py} -UI(CH₂Ph) (right). Hydrogen atoms were removed for clarity.

We propose that $U(CH_2Ph)_3(THF)_x$ or $UI(CH_2Ph)_2(THF)_y$, generated *in situ* in the reactions shown in eqn (2) and (3), respectively, reacts with $H_2(NN^{py})$ when the disproportionation to the uranium(IV) product occurs; the disproportionation of either species to uranium(IV) complexes and uranium(0) before the reaction with $H_2(NN^{py})$ is also possible. The formation of 1^{py} -UI(CH₂Ph) is especially noteworthy since our attempts to generate the analogous 1^{fc} -UI(CH₂Ph) from 1^{fc} -I₂(THF) and one equivalent of KCH₂Ph or by comproportionation from 1^{fc} -I₂(THF) and 1^{fc} -U(CH₂Ph)₂ led to equilibrium mixtures containing all three uranium complexes.



Encouraged by the formation of 1^{py} -U(CH₂Ph)₂ and 1^{py} -UI(CH₂Ph), we decided to explore the reaction scope of the *in situ* generation of uranium alkyl complexes. To that end, similar reaction conditions as those presented in eqn (2) were used in order to generate (NN^{fc/})U(CH₂Ph)₂, $1^{fc'}$ -U(CH₂Ph)₂, where NN^{fc/} = fc(NSiMe₃)₂ (Chart 1). Although we had observed the formation of $1^{fc'}$ -I₂(THF) from UI₃(THF)₄³⁶ and [K(OEt₂)₂]₂[NN^{fc'}] previously, the reaction was not reproducible thus prompting us to employ the *tert*-butyldimethyl variant, NN^{fc} = fc(NSi^fBuMe₂)₂.

The reaction between UI₃(THF)₄³⁶ and three equivalents of KCH₂Ph, followed by the addition of 0.75 equivalents of H₂(NN^{fc'}) at low temperatures, led to the formation of (NN^{fc'})U(CH₂Ph)₂, 1^{fc'}-U(CH₂Ph)₂ (Scheme 1), in 51–77% yield, obtained again consistently and reproducibly. Furthermore, the same reaction conditions could be applied to the synthesis of (NN^{fc'})U(CH₂SiMe₃)₂, 1^{fc'}-U(CH₂SiMe₃)₂, in 60–80% yield (Scheme 1), circumventing the need to isolate a halide starting material. The complexes 1^{fc}-U(CH₂SiMe₃)₂ were also synthesized by the present method (Scheme 1) in better yields than those recorded for their syntheses from 1^{fc}-I₂(THF) (84% vs. 52% for 1^{fc}-U(CH₂Ph)₂, 54% vs. 27% for 1^{fc}-U(CH₂SiMe₃)₂).

Attempts to isolate the mixed alkyl-iodide uranium complexes supported by ferrocene-diamide ligands have met with little success by using the present method. Although these species formed, as assessed by inspecting ¹H NMR spectra of



Scheme 1 Formation of uranium dialkyl complexes supported by ferrocene-diamide ligands.

aliquots from crude reaction mixtures, they were not the sole products and could not be separated from the dialkyl and diiodide complexes also present.

In conclusion, a general method for the synthesis of uranium(iv) alkyl complexes has been presented. This one-pot procedure starts from a readily available uranium precursor, UI₃(THF)₄, and bypasses the need to isolate halide or homoleptic-alkyl uranium starting materials. The products of all reactions were uranium(iv) complexes, presumably formed by the disproportionation of uranium(iii) intermediates. Both potassium benzyl and lithium alkyl reagents were employed and the ancillary ligands targeted included pyridine and ferrocene-based diamides. We are currently in the process of extending the present procedure to the formation of other uranium alkyl complexes.

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Notes and references

‡ Characterization data for 1^{**Py**}₂-**U**. ¹H NMR (C₆D₆, 500 MHz, 25 °C), δ (ppm): 97.97 (s, 2H, aromatic-CH), 35.22 (s, 4H, aromatic-CH, NCH₂, or CH(CH₃)₂), 25.57 (s, 4H, aromatic-CH, NCH₂, or CH(CH₃)₂), 21.53 (s, 24H, CH(CH₃)₂), 3.47 (s, 2H, aromatic-CH), -5.27 (s, 1H, C₅H₃N), -11.30 (s, 4H, aromatic-CH, NCH₂, or CH(CH₃)₂). Because of its limited solubility, 1^{**Py**}₂-U could not be obtained analytically pure.

Characterization data for 1^{py} -U(CH₂Ph)₂. Yield: 54–62%. ¹H NMR (500 MHz, C₆D₆), δ (ppm): 70.91 (s, 2H, aromatic-CH or CH₂), 63.29 (s, 2H, aromatic-CH or CH₂), 43.18 (s, 2H, aromatic-CH or CH₂), 25.82 (s, 2H, aromatic-CH or CH₂), 19.26 (s, 6H, CH(CH₃)₂), 16.72 (s, 2H, aromatic-CH or CH₂), 13.12 (s, 6H, CH(CH₃)₂), 3.38 (s, 6H, CH(CH₃)₂), 1.34 (s, 2H, aromatic-CH or CH₂), -3.67 (s, 6H, CH(CH₃)₂), -6.91 (s, 2H, aromatic-CH or CH₂), -9.97 (s, 2H, aromatic-CH or CH₂), -11.38 (s, 1H, p-NC₅H₃ or p-C₆H₅), -21.00 (s, 2H, aromatic-CH or CH₂), -66.24 (s, 2H, aromatic-CH or CH₂), -111.21 (s, 2H, aromatic-CH or CH₂). Anal. (%): calcd for C4₅H₅₅N₃U: C, 61.70; H, 6.33; N, 4.80. Found: C, 61.89; H, 6.15; N, 4.79. Characterization data for 1^{py}-UI(CH₂Ph). Yield: 68–76%. ¹H NMR (500 MHz, C₆D₆), δ (ppm): 100.68 (s, 2H, aromatic-CH or CH₂), 96.38 (s, 2H, aromatic-CH or CH₂), 71.58 (s, 2H, aromatic-CH or CH₂), 37.91 (s, 2H, aromatic-CH or CH₂), 28.61 (s, 6H, CH(CH₃)₂), 21.92 (s, 1H, *p*-NC₅H₃, *p*-C₆H₃, or *p*-C₆H₅), 21.68 (s, 1H, *p*-NC₅H₃, *p*-C₆H₃, or *p*-C₆H₅), 16.17 (s, 6H, CH(CH₃)₂), 1.38 (s, 2H, aromatic-CH or CH₂), 0.79 (s, 6H, CH(CH₃)₂), -1.54 (s, 1H, *p*-NC₅H₃, *p*-C₆H₃, or *p*-C₆H₅), -5.98 (s, 2H, aromatic-CH or CH₂), -6.54 (s, 2H, aromatic-CH or CH₂), -8.58 (s, 2H, aromatic-CH or CH₂), -16.13 (s, 1H, *p*-NC₅H₃, *p*-C₆H₃, or *p*-C₆H₅), -16.76 (s, 6H, CH(CH₃)₂), -41.88 (s, 2H, aromatic-CH or CH₂). Anal. (%): calcd for C₃₈H₄₈IN₃U: C, 50.06; H, 5.31; N, 4.61. Found: C, 50.96; H, 5.42; N, 4.27.

Characterization data for $1^{fc'}$ -U(CH₂Ph)₂. Yield: 51–77%. ¹H NMR (300 MHz, C₆D₆), δ (ppm): 47.86 (s, 18H, Si(CH₃)₃), -8.21 (s, 4H, C₅H₄ or C₆H₅), -11.92 (s, 2H, p-C₆H₅), -17.19 (s, 4H, C₅H₄ or C₆H₅), -17.75 (s, 4H, C₅H₄ or C₆H₅), -34.49 (s, 4H, C₅H₄ or C₆H₅). Anal. (%): calcd for C₃₀H4₀FeN₂Si₂U: C, 46.27; H, 5.18; N, 3.60. Found: C, 45.92; H, 5.19; N, 3.50.

Characterization data for $1^{\text{fe'}}$ -U(CH₂SiMe₃)₂. Yield: 60–80%. ¹H NMR (300 MHz, C₆D₆), δ (ppm): 64.04 (s, 18H, SiC(CH₃)₃), -21.84 (s, 4H, C₅H₄), -30.40 (s, 18H, Si(CH₃)₃), -43.38 (s, 4H, C₅H₄). Anal. (%): calcd for C₂₄H₄₈FeN₂Si₄U: C, 37.39; H, 6.28; N, 3.63. Found: C, 37.28; H, 6.10; N, 3.16.

Characterization data for 1^{fc} -U(CH₂SiMe₃)₂. Yield: 87%. ¹H NMR (300 MHz, C₆D₆), δ (ppm): 64.53 (s, 12H, Si(CH₃)₂), 40.27 (s, 18H, Si(CH₃)₃), -22.22 (s, 4H, C₅H₄), -32.83 (s, 18H, Si(CH₃)₃), -44.34 (s, 4H, C₅H₄). Anal. (%): calcd for C₃₀H₆₀FeN₂Si₄U: C, 42.14; H, 7.07; N, 3.28. Found: C, 42.22; H, 6.92; N, 3.16.

Crystal data for 1^{py}_2 -U: C₆₂H₈₂N₆U·0.8(C₆H₁₄), monoclinic, space group C2/c, a = 19.828(2) Å, b = 22.158(2) Å, c = 14.7466(16) Å, $\beta = 108.964(1)^\circ$, V = 6127.3(11) Å³, Z = 4, $\mu = 2.693$ mm⁻¹, F(000) = 2496, T = 100(2) K, 30847 measured reflections, 9054 unique ($R_{\text{int}} = 0.0281$), $R_1 = 0.0255$, w $R_2 = 0.0651$ for $I > 2\sigma(I)$.

Crystal data for 1^{py} -U(CH₂Ph)₂: C₄₅H₅₅N₃U·OC₄H₁₀, triclinic, space group $P\bar{1}$, a = 10.5281(10) Å, b = 12.7043(12) Å, c = 17.9213(16) Å, $\beta = 105.205(1)^{\circ}$, V = 2213.0(4) Å³, Z = 2, $\mu = 3.705$ mm⁻¹, F(000) = 960, T = 100(2) K, 22255 measured reflections, 12383 unique ($R_{\text{int}} = 0.0196$), $R_1 = 0.0313$, $wR_2 = 0.0806$ for $I > 2\sigma(I)$.

Crystal data for 1^{py}-UI(CH₂Ph): C₃₈H₄₈N₃IU·0.5(C₁₄H₁₂), monoclinic, space group $P2_1/c$, a = 11.3927(15) Å, b = 13.9847(19) Å, c = 25.077(3) Å, $\beta = 95.235(2)^\circ$, V = 3978.7(9) Å³, Z = 4, $\mu = 4.890$ mm⁻¹, F(000) = 1956, T = 100(2) K, 26600 measured reflections, 6513 unique ($R_{int} = 0.0829$), $R_1 = 0.0397$, w $R_2 = 0.0769$ for $I > 2\sigma(I)$.

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