

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 $\text{UI}_3(\text{THF})_4$.

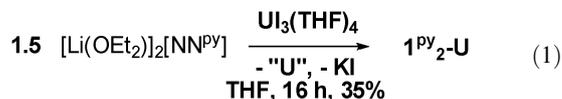
The reactivity of uranium complexes can be substantially modulated by tuning the electronic and steric properties of their ancillary-ligand framework.^{1–9} We have been interested in the reactivity of d^0f^0 metal centers supported by ferrocene ligands^{10–17} and proposed that a weak interaction, of donor–acceptor type, takes place between iron and the metal when ferrocene diamides ($\text{NN}^{\text{fc}} = \text{fc}(\text{NSi}^t\text{BuMe}_2)_2$, $\text{fc} = 1,1'$ -ferrocenylene, Chart 1) are used.^{18,19} For uranium complexes, we recently reported novel C–H activation reactions by ($\text{NN}^{\text{fc}}\text{U}(\text{CH}_2\text{Ph})_2$, $\mathbf{1}^{\text{fc}}\text{-U}(\text{CH}_2\text{Ph})_2$, with both benzyl ligands of $\mathbf{1}^{\text{fc}}\text{-U}(\text{CH}_2\text{Ph})_2$ engaging an $\text{sp}^2\text{-C-H}$ bond 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 $\mathbf{1}^{\text{fc}}\text{-U}(\text{CH}_2\text{Ph})_2$ is unique,²¹ we decided to synthesize analogous dibenzyl complexes of a tridentate, dianionic supporting ligand, 2,6-bis(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 lanthanides^{31–33} supported by pyridine–diamide ligands are known.

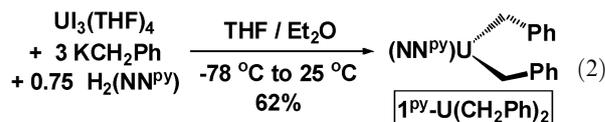
Dialkyl complexes of Th(IV) supported by NN^{py} have also been reported.^{34,35} Those complexes were synthesized from KCH_2Ph or $\text{LiCH}_2\text{SiMe}_3$ and the respective thorium dichloride, ($\text{NN}^{\text{py}}\text{ThCl}_2(\text{DME})$), which, in turn, was produced in the salt-metathesis reaction between $\text{ThCl}_4(\text{DME})_2$ and $\text{Li}_2(\text{NN}^{\text{py}})$.^{34,35} The complex $\mathbf{1}^{\text{fc}}\text{-U}(\text{CH}_2\text{Ph})_2$ was also synthesized by the salt-metathesis reaction of KCH_2Ph and $\mathbf{1}^{\text{fc}}\text{-I}_2(\text{THF})$,

obtained directly from $\text{UI}_3(\text{THF})_4$ ^{36–38} and $[\text{K}(\text{OEt}_2)_2][\text{NN}^{\text{fc}}]$.¹⁸ Since $\text{UI}_3(\text{THF})_4$ ^{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 ($\text{NN}^{\text{py}}\text{UI}_2$) starting material, even though the formation of the uranium(IV) complex would require the disproportionation of the uranium(III) complex $\text{UI}_3(\text{THF})_4$.^{1,2,18,39}

The reaction between $[\text{K}(\text{OEt}_2)_2][\text{NN}^{\text{py}}]$ and $\text{UI}_3(\text{THF})_4$ gave a mixture of products that proved intractable. However, the reaction between $[\text{Li}(\text{OEt}_2)_2][\text{NN}^{\text{py}}]$ and $\text{UI}_3(\text{THF})_4$ (eqn (1)) led to the isolation of $\mathbf{1}^{\text{py}}\text{-U}$.[‡] Although $\mathbf{1}^{\text{py}}\text{-U}$ 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 $\mathbf{1}^{\text{py}}\text{-U}$.



The analogous $\mathbf{1}^{\text{fc}}\text{-U}$ is a by-product of the reaction between $\text{UI}_3(\text{THF})_4$ ³⁶ and $[\text{K}(\text{OEt}_2)_2][\text{NN}^{\text{fc}}]$ that also gives $\mathbf{1}^{\text{fc}}\text{-I}_2(\text{THF})$.¹⁸ However, our attempts to modify the conditions for the reaction shown in eqn (1) have not yielded a ($\text{NN}^{\text{py}}\text{UI}_2$) complex. Inspired by a report from the Hayton group on the synthesis of homoleptic uranium alkyl complexes⁴⁰ and encouraged by the fact that ($\text{NN}^{\text{py}}\text{Th}(\text{CH}_2\text{SiMe}_3)_2$) was accessible from an *in situ* reaction between “ $\text{Cl}_2\text{Th}(\text{CH}_2\text{SiMe}_3)_2$ ” and $\text{H}_2(\text{NN}^{\text{py}})$, we decided to pursue the synthesis of uranium alkyl complexes supported by NN^{py} by generating and not isolating their alkyl precursors.



The reaction of $\text{UI}_3(\text{THF})_4$ ³⁶ and three equivalents of KCH_2Ph , followed by the addition of 0.75 equivalents of $\text{H}_2(\text{NN}^{\text{py}})$ at low temperatures, led to the formation of the uranium(IV) dibenzyl complex ($\text{NN}^{\text{py}}\text{U}(\text{CH}_2\text{Ph})_2$, $\mathbf{1}^{\text{py}}\text{-U}(\text{CH}_2\text{Ph})_2$) (eqn (2)). The reaction was reproducible and allowed the isolation of $\mathbf{1}^{\text{py}}\text{-U}(\text{CH}_2\text{Ph})_2$ in 54–62% yield consistently. The complex $\mathbf{1}^{\text{py}}\text{-U}(\text{CH}_2\text{Ph})_2$ was characterized by elemental analysis, ¹H NMR spectroscopy, and X-ray crystallography (Fig. 1).

Interestingly, by changing the stoichiometry and employing two equivalents of KCH_2Ph in a reaction with $\text{UI}_3(\text{THF})_4$ ³⁶ and 0.75 equivalents of $\text{H}_2(\text{NN}^{\text{py}})$, a new product, $\mathbf{1}^{\text{py}}\text{-UI}(\text{CH}_2\text{Ph})$ (Fig. 1), was obtained (eqn (3)). The reaction was also reproducible and occurred consistently in 68–76% yield.

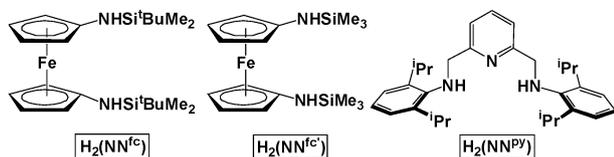


Chart 1 Pro-ligands used in the present study.

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† Electronic supplementary information (ESI) available: Detailed syntheses, NMR spectra, and crystallographic information. CCDC for $\mathbf{1}^{\text{py}}\text{-U}$, $\mathbf{1}^{\text{py}}\text{-U}(\text{CH}_2\text{Ph})_2$, and $\mathbf{1}^{\text{py}}\text{-UI}(\text{CH}_2\text{Ph})$ are 756840, 756841, and 756842, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b927264j

Characterization data for $1^{\text{py}}\text{-UI}(\text{CH}_2\text{Ph})$. Yield: 68–76%. ^1H NMR (500 MHz, C_6D_6), δ (ppm): 100.68 (s, 2H, aromatic-CH or CH_2), 96.38 (s, 2H, aromatic-CH or CH_2), 71.58 (s, 2H, aromatic-CH or CH_2), 37.91 (s, 2H, aromatic-CH or CH_2), 28.61 (s, 6H, $\text{CH}(\text{CH}_3)_2$), 21.92 (s, 1H, $p\text{-NC}_5\text{H}_3$, $p\text{-C}_6\text{H}_3$, or $p\text{-C}_6\text{H}_5$), 21.68 (s, 1H, $p\text{-NC}_5\text{H}_3$, $p\text{-C}_6\text{H}_3$, or $p\text{-C}_6\text{H}_5$), 16.17 (s, 6H, $\text{CH}(\text{CH}_3)_2$), 1.38 (s, 2H, aromatic-CH or CH_2), 0.79 (s, 6H, $\text{CH}(\text{CH}_3)_2$), -1.54 (s, 1H, $p\text{-NC}_5\text{H}_3$, $p\text{-C}_6\text{H}_3$, or $p\text{-C}_6\text{H}_5$), -5.98 (s, 2H, aromatic-CH or CH_2), -6.54 (s, 2H, aromatic-CH or CH_2), -8.58 (s, 2H, aromatic-CH or CH_2), -16.13 (s, 1H, $p\text{-NC}_5\text{H}_3$, $p\text{-C}_6\text{H}_3$, or $p\text{-C}_6\text{H}_5$), -16.76 (s, 6H, $\text{CH}(\text{CH}_3)_2$), -41.88 (s, 2H, aromatic-CH or CH_2). Anal. (%): calcd for $\text{C}_{38}\text{H}_{48}\text{IN}_3\text{U}$: C, 50.06; H, 5.31; N, 4.61. Found: C, 50.96; H, 5.42; N, 4.27.

Characterization data for $1^{\text{fe}}\text{-U}(\text{CH}_2\text{Ph})_2$. Yield: 51–77%. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 47.86 (s, 18H, $\text{Si}(\text{CH}_3)_3$), -8.21 (s, 4H, C_5H_4 or C_6H_5), -11.92 (s, 2H, $p\text{-C}_6\text{H}_3$), -17.19 (s, 4H, C_5H_4 or C_6H_5), -17.75 (s, 4H, C_5H_4 or C_6H_5), -34.49 (s, 4H, C_5H_4 or C_6H_5). Anal. (%): calcd for $\text{C}_{30}\text{H}_{40}\text{FeN}_2\text{Si}_2\text{U}$: C, 46.27; H, 5.18; N, 3.60. Found: C, 45.92; H, 5.19; N, 3.50.

Characterization data for $1^{\text{fe}}\text{-U}(\text{CH}_2\text{SiMe}_3)_2$. Yield: 60–80%. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 64.04 (s, 18H, $\text{Si}(\text{CH}_3)_3$), -21.84 (s, 4H, C_5H_4), -30.40 (s, 18H, $\text{Si}(\text{CH}_3)_3$), -43.38 (s, 4H, C_5H_4). Anal. (%): calcd for $\text{C}_{24}\text{H}_{48}\text{FeN}_2\text{Si}_4\text{U}$: C, 37.39; H, 6.28; N, 3.63. Found: C, 37.28; H, 6.10; N, 3.16.

Characterization data for $1^{\text{fe}}\text{-U}(\text{CH}_2\text{SiMe}_3)_2$. Yield: 87%. ^1H NMR (300 MHz, C_6D_6), δ (ppm): 64.53 (s, 12H, $\text{Si}(\text{CH}_3)_2$), 40.27 (s, 18H, $\text{Si}(\text{CH}_3)_3$), -22.22 (s, 4H, C_5H_4), -32.83 (s, 18H, $\text{Si}(\text{CH}_3)_3$), -44.34 (s, 4H, C_5H_4). Anal. (%): calcd for $\text{C}_{30}\text{H}_{60}\text{FeN}_2\text{Si}_4\text{U}$: 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 : $\text{C}_6_2\text{H}_{82}\text{N}_6\text{U}\cdot 0.8(\text{C}_6\text{H}_{14})$, monoclinic, space group $\text{C}2/c$, $a = 19.828(2)$ 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, 30 847 measured reflections, 9054 unique ($R_{\text{int}} = 0.0281$), $R_1 = 0.0255$, $wR_2 = 0.0651$ for $I > 2\sigma(I)$.

Crystal data for $1^{\text{py}}\text{-U}(\text{CH}_2\text{Ph})_2$: $\text{C}_{45}\text{H}_{55}\text{N}_3\text{U}\cdot \text{OC}_4\text{H}_{10}$, 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, 22 255 measured reflections, 12 383 unique ($R_{\text{int}} = 0.0196$), $R_1 = 0.0313$, $wR_2 = 0.0806$ for $I > 2\sigma(I)$.

Crystal data for $1^{\text{py}}\text{-UI}(\text{CH}_2\text{Ph})$: $\text{C}_{38}\text{H}_{48}\text{N}_3\text{U}\cdot 0.5(\text{C}_{14}\text{H}_{12})$, monoclinic, space group $\text{P}2_1/c$, $a = 11.3927(15)$ 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, 26 600 measured reflections, 6513 unique ($R_{\text{int}} = 0.0829$), $R_1 = 0.0397$, $wR_2 = 0.0769$ for $I > 2\sigma(I)$.

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