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Isocyanide Adducts of Tri- and Tetravalent Uranium Metallocenes Supported by Tetra(isopropyl)cyclopentadienyl Ligands[†]

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Abstract

Reaction of the uranium(III) metallocenium salt $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$ with *tert*-butyl isocyanide (*t*BuNC) yielded the dicationic uranium(IV) complex $[(Cp^{iPr4})_2U(CN^tBu)_4][B(C_6F_5)_4]_2$ (**1**), which displays a linear metallocene geometry. Use of crude mixtures of $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$, which contain a soluble source of iodide, led instead to isolation of the monocationic uranium(IV) iodide complex $[(Cp^{iPr4})_2U(I)(CN^tBu)_2][B(C_6F_5)_4]$ (**2**). Adduct formation with no change in oxidation state was observed upon addition of *t*BuNC to the neutral uranium(III) species $(Cp^{iPr4})_2UI$, resulting in isolation of $(Cp^{iPr4})_2U(I)(CN^tBu)$ (**3**). X-ray crystallographic and IR spectroscopic studies both showed effects ascribed to the presence of multiple strongly donating isocyanide ligands in **1**.

Introduction

The chemistry of trivalent uranium has developed rapidly in the past few decades as new synthetic routes have provided facile access to uranium(III) starting materials.¹⁻⁷ Much of the interest in this oxidation state of uranium stems from its ability to act as a potent reductant for a variety of transformations with small molecules.^{1,8-11} Given the fundamental importance of

metallocene chemistry to the development of actinide chemistry,¹²⁻¹⁴ the uranium(III) metallocenium salts $[(C_5Me_4R)_2U][(\mu-Ph)_2BPh_2]$ ($R = H, Me, SiMe_3$) represent an important class of low-valent uranium synthons.¹⁵⁻¹⁷ The redox and ligand substitution reactivity of these species continues to be the focus of many studies.^{15,17-27}

Recently, the first base-free uranium(III) metallocenium cations $[(Cp^{iPr5})_2U][B(C_6F_5)_4]$ and $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$ ($Cp^{iPr5} = C_5(iPr)_5$, $Cp^{iPr4} = C_5(iPr)_4H$) were reported.^{28,29} To-date, the reactivity of these species is minimal, amounting to coordination of 1,2-dimethoxyethane (DME) to $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$ to form the Lewis adduct $[(Cp^{iPr4})_2U(DME)][B(C_6F_5)_4]$.²⁹ As a part of our continuing studies using the $(Cp^{iPr4})_2U$ fragment with both uranium(III) and uranium(IV),²⁹⁻³¹ we sought to expand the reactivity of the $[(Cp^{iPr4})_2U]^+$ cation.

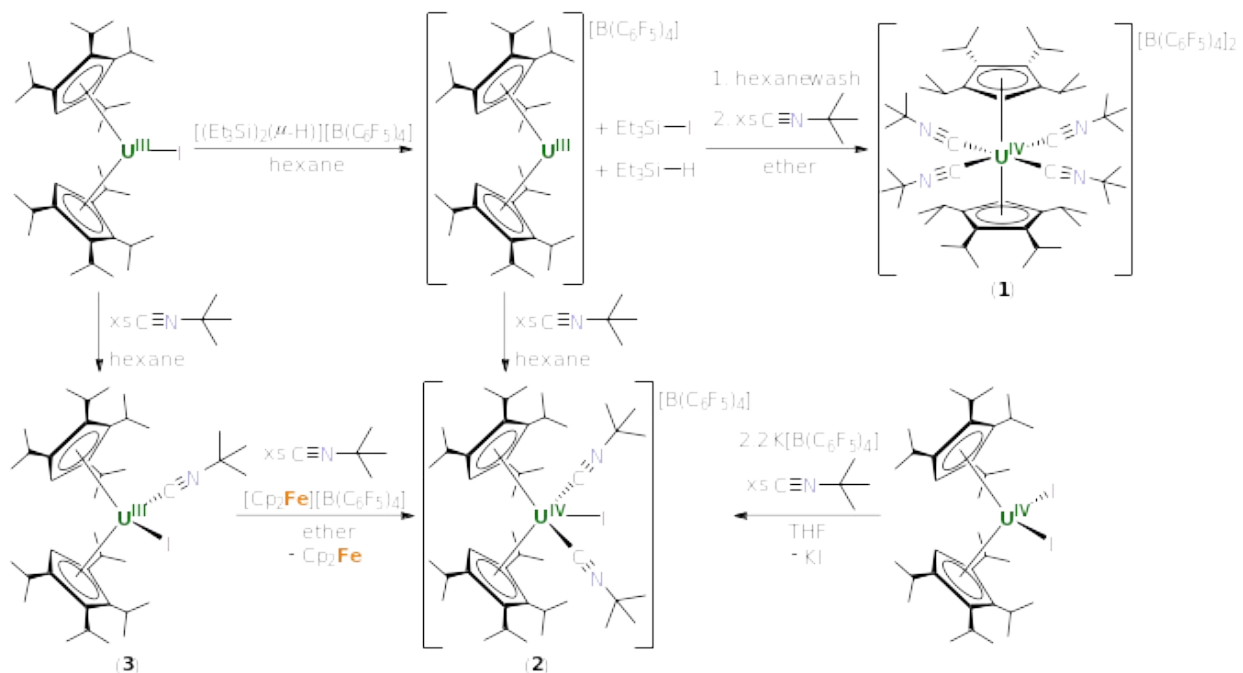
Here, we describe the behavior of $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$ toward *tert*-butyl isocyanide (*t*-BuNC), which, in contrast to reactions with DME, produced uranium(IV) complexes as the only isolable species. Intriguingly, we observed different products from the reaction between the metallocenium complex and *t*-BuNC depending on whether or not an iodide source was present.

Results and Discussion

Addition of excess *t*-BuNC to an ether solution of $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$ led to rapid precipitation of orange-brown crystalline material identified as $[(Cp^{iPr4})_2U(CN^tBu)_4][B(C_6F_5)_4]_2$ (**1**), a dicationic complex containing four isocyanide ligands and two coplanar cyclopentadienyl units (Scheme 1). In generating **1** from $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$, the uranium center became oxidized by one electron to uranium(IV), though the process by which this oxidation occurred is presently uncertain. Complex **1** was isolated after work-up in 40% yield based on $[(Et_3Si)_2(\mu-H)]$

$[\text{B}(\text{C}_6\text{F}_5)_4]$ as the limiting reagent (since the product contains two $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ions per uranium center).

Scheme 1. Syntheses of complexes **1**, **2**, and **3**.



Interestingly, upon attempts to explore the mechanism of oxidation, a different reaction outcome is observed when byproducts from the halide abstraction to form $[(\text{Cp}^{\text{iPr}4})_2\text{U}][\text{B}(\text{C}_6\text{F}_5)_4]$ were still present. The metallocene salt starting material is formed by iodide abstraction from $(\text{Cp}^{\text{iPr}4})_2\text{UI}$ using $[(\text{Et}_3\text{Si})_2(\mu\text{-H})][\text{B}(\text{C}_6\text{F}_5)_4]$, a process that generates the byproducts Et_3SiI and Et_3SiH .^{29,32} Addition of excess $t\text{BuNC}$ to crude mixtures of $[(\text{Cp}^{\text{iPr}4})_2\text{U}][\text{B}(\text{C}_6\text{F}_5)_4]$ led to isolation of dark red crystals of $[(\text{Cp}^{\text{iPr}4})_2\text{U}(\text{I})(\text{CN}^t\text{Bu})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**) in 23% yield after crystallization from diethyl ether. As observed in the formation of **1**, the uranium center in **2** became oxidized to uranium(IV) during the course of the reaction. However, **2** is monocationic, with the increase

of metal charge compensated by the abstraction of an iodide ion, presumably from the equivalent of Et₃SiI remaining in solution.[‡]

Seeking higher yielding, more rational syntheses of **1** and **2**, we attempted to prepare **2** via isocyanide addition to (Cp^{iPr4})₂UI followed by oxidation. Addition of excess ^tBuNC to hydrocarbon solutions of (Cp^{iPr4})₂UI caused a rapid color change from dark blue to dark yellow-green. The neutral mono-adduct (Cp^{iPr4})₂U(I)(CN^tBu) (**3**) was isolated as a green crystalline solid after crystallization from pentane in 85% yield. The ¹H NMR spectrum of C₆D₆ solutions of **3** exhibited a sharp (line width = 16 Hz) signal at -12.84 ppm assigned as the *tert*-butyl group of the isocyanide ligand, while the resonances for the Cp^{iPr4} ligand were very broad due to dynamic behavior we have discussed previously in related species.^{29,31}

Oxidation of *in situ* generated **3** with [Cp₂Fe][B(C₆F₅)₄] in the presence of excess ^tBuNC enabled isolation of **2** in higher yield (49%, compared to 23% via crude [(Cp^{iPr4})₂U][B(C₆F₅)₄]). Additionally, we assumed that starting from the uranium(IV) complex (Cp^{iPr4})₂UI₂, salt metathesis of either one or both of the iodide ions with [B(C₆F₅)₄]⁻ in the presence of excess ^tBuNC would generate **2** or **1**, respectively. In fact, we found that reaction between (Cp^{iPr4})₂UI₂, two equivalents of K[B(C₆F₅)₄], and excess ^tBuNC in THF exclusively led to formation of **2** in 32% isolated yield.

Single crystal X-ray crystallography confirmed the solid-state structures of **1**, **2**, and **3** (Figure 1). Obtaining diffraction data of adequate quality for **1** proved challenging; we suggest a possible explanation for this difficulty can be proposed based on the nearly spherical shape of the [(Cp^{iPr4})₂U(CN^tBu)₄]²⁺ fragment: related bulky metallocene complexes are known to yield poorly-ordered structures due to resulting small energetic differences in crystal packing effects.³³ The

large thermal ellipsoids for **1** compared to those of **2** and **3** are likely a result of disorder originating from such low preferences for specific orientations.

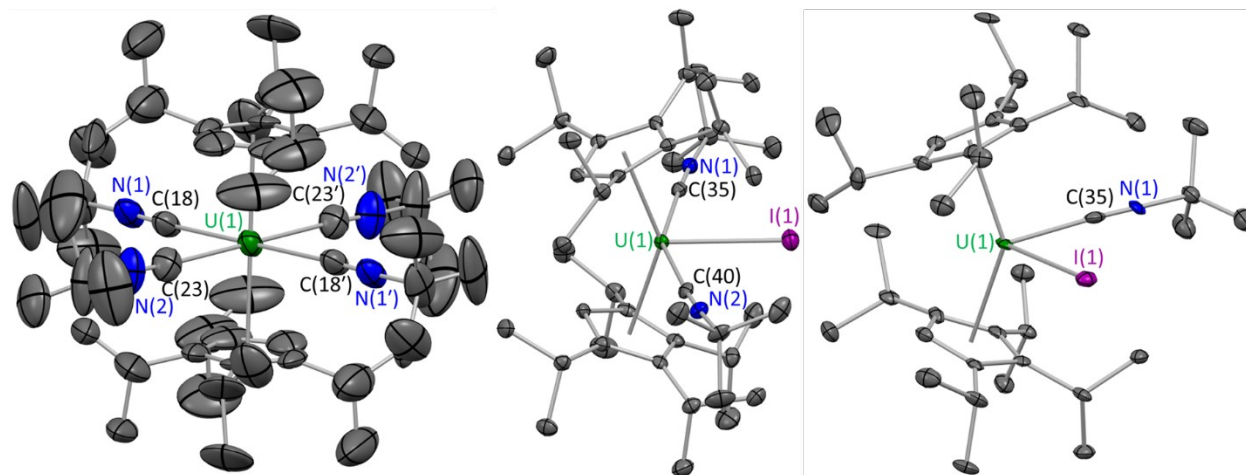


Figure 1. X-ray crystal structures of $[(\text{Cp}^{\text{iPr}4})_2\text{U}(\text{CN}^t\text{Bu})_4][\text{B}(\text{C}_6\text{F}_5)_4]_2$ (**1**, left), $[(\text{Cp}^{\text{iPr}4})_2\text{U}(\text{I})(\text{CN}^t\text{Bu})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**, middle), and $(\text{Cp}^{\text{iPr}4})_2\text{U}(\text{I})(\text{CN}^t\text{Bu})$ (**3**, right) with 50% probability ellipsoids. Hydrogen atoms and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ counteranions are omitted for clarity. Selected structural metrics are listed in Table 1.

Focusing on the Cp(cent)–U–Cp(cent) angles, **2** and **3** display similar bent metallocene geometries with values of 142.19(5) and 143.0(1)°, respectively. However, in **1**, the $[(\text{Cp}^{\text{iPr}4})_2\text{U}(\text{CN}^t\text{Bu})_4]^{2+}$ units crystallize in space group $P\bar{1}$ with the uranium atom on an inversion center, meaning a 180° Cp(cent)–U–Cp(cent) angle is crystallographically imposed. Linear actinide metallocenes are extremely rare but were first observed by Ephritikhine and coworkers in the uranium(IV) dicationic $[\text{Cp}^*_2\text{U}(\text{NCMe})_5]^{2+}$ fragment.^{34–38} In the linear metallocene uranium(IV) and thorium(IV) species $[\text{Cp}^*_2\text{U}(\text{NCMe})_5]^{2+}$, $[\text{Cp}^*_2\text{U}(\text{CN})_5]^{3-}$, and $[\text{Cp}^*_2\text{Th}(\text{NCR})_5]^{2+}$ (R = Me, Ph), this geometry is promoted by saturation of the equatorial girdle

with donor ligands,^{34–37} as appears to be the case in **1** as well. However, a very different type of uranium metallocene, the neutral, divalent complex (Cp^{iPr5})₂U, was recently isolated and also found to display a linear metallocene geometry.^{38,§}

The U–I bond length in **3** is roughly 0.08 Å longer than that of **2**, roughly equivalent to the expected difference in effective ionic radii between the respective uranium centers (Table 1).^{§§} In contrast, the average U–C_{isocyanide} distance of **2** (2.599(4) Å) is essentially equivalent to the U–C_{isocyanide} distance of 2.602(8) Å in **3**. Moreover, the average U–C_{isocyanide} bond length of 2.643(8) Å in **1** is longer than those of **2** and **3** despite the higher charge state of the complex ion in **1**. Similarly, the U–Cp(cent) distance in **1** (2.565(3) Å) is longer than those of **2** and **3** (2.495(2) and 2.532(3) Å, respectively). These results are consistent with the explanation that strong donation from the isocyanide ligands significantly compensates for the buildup of positive charge on the uranium center that would otherwise be expected as oxidation state and complex ion charge increase (see discussion of ν_{NC} values below). Greater steric pressure from the presence of four ^tBuNC ligands in **1** also likely contributes to longer U–C_{isocyanide} and U–Cp(cent) distances. The shorter average U–Cp(cent) distance in **2** versus in **3** is consistent with the higher oxidation state and complex ion positive charge in **2** with only one additional ^tBuNC not causing a large amount of steric pressure.

Table 1. Selected Distances (Å) and Angles (°) for **1**, **2** and **3**.

Complex	U–C _{isocyanide}	U–Cp(cent)	Cp(cent)–U–Cp(cent)	U–I
1	2.635(9), 2.650(7)	2.565(3)	180	—
2	2.584(4), 2.613(4)	2.494(2), 2.495(2)	142.19(5)	2.9903(4)
3	2.602(8)	2.518(3), 2.546(3)	143.0(1)	3.0691(6)

The IR spectra of **1**, **2**, and **3** each displayed a single strong, sharp ν_{NC} band at 2176, 2182, and 2166 cm^{-1} , respectively, all higher than the frequency for free $t\text{-BuNC}$ (2134 cm^{-1}).^{39,40} An increase in ν_{NC} is typically observed for isocyanides upon coordination to electropositive metal ions that do not participate in significant π -backbonding interactions.^{41–43} Nonetheless, uranium(III) complexes $(\text{Cp}^{\text{R}})_3\text{U}$ (Cp^{R} = substituted cyclopentadienyl) have been shown to undergo back-donation to the isocyanide π^* orbitals in their respective adducts, with ν_{NC} values of 2127 and 2140 cm^{-1} reported for $(\text{C}_5\text{Me}_4\text{H})_3\text{U}(\text{CN}^t\text{Bu})$ and $(1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3)_3\text{U}(\text{CN}^t\text{Bu})$, respectively, compared to a ν_{NC} value of 2178 cm^{-1} in $(1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3)_3\text{La}(\text{CN}^t\text{Bu})$, in which no π -backbonding is expected.^{43,44}

The ν_{NC} value of **3** (2166 cm^{-1}) is larger than the abovementioned $(\text{Cp}^{\text{R}})_3\text{U}(\text{CN}^t\text{Bu})$ species as well as that of the uranium(III) complex $[\text{Cp}^*_2\text{U}(\text{CN}^t\text{Bu})(\mu\text{-CN})]_3$ (2143 cm^{-1}),⁴⁵ suggesting minimal or insignificant π -backbonding in **3**. The uranium(IV) cation $[\text{Cp}^*_2\text{U}(\text{NMe}_2)(\text{CN}^t\text{Bu})_2][\text{BPh}_4]$ has a similar ν_{NC} value (2181 cm^{-1}) to that of closely related cation **2**,⁴⁶ while the neutral uranium(IV) and uranium(V) complexes $\text{Cp}^*_2\text{U}(\text{CN}^t\text{Bu})(\eta^2\text{-N}^t\text{BuC}=\text{PPh})$ and $(\text{Cp}^*)(\eta^8\text{-C}_8\text{H}_6\text{-1,4-(Si}^i\text{Pr}_3)_2)\text{U}(\text{O})(\text{CN}^t\text{Bu})$ display ν_{NC} values of 2171 and 2179 cm^{-1} , respectively.^{40,47} Although a higher ν_{NC} might be expected for dicationic **1** relative to **2** on the basis of complex ion charge, the increased number of strongly donating isocyanide ligands in **1** would be expected to have the opposite effect, and the different geometry of the Cp^{iPr_4} ligands is a further complicating factor; the net result is a slightly lower ν_{NC} value in **1**.

Conclusions

Addition of $t\text{BuNC}$ to $[(\text{Cp}^{\text{iPr}_4})_2\text{U}][\text{B}(\text{C}_6\text{F}_5)_4]$ produced uranium(IV) complexes as the only isolable products. When iodide sources present after generation of the metallocenium salt were washed away, the dicationic complex $[(\text{Cp}^{\text{iPr}_4})_2\text{U}(\text{CN}^t\text{Bu})_4][\text{B}(\text{C}_6\text{F}_5)_4]_2$ (**1**) was isolated. However, addition of $t\text{BuNC}$ to crude $[(\text{Cp}^{\text{iPr}_4})_2\text{U}][\text{B}(\text{C}_6\text{F}_5)_4]$ yielded the monocationic complex $[(\text{Cp}^{\text{iPr}_4})_2\text{U}(\text{I})(\text{CN}^t\text{Bu})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**). Addition of $t\text{BuNC}$ to solutions of $(\text{Cp}^{\text{iPr}_4})_2\text{UI}$ led to mono-adduct formation without a change in oxidation state, yielding $(\text{Cp}^{\text{iPr}_4})_2\text{U}(\text{I})(\text{CN}^t\text{Bu})$ (**3**). X-ray crystallography and infrared spectroscopy revealed effects of having a large number of strongly donating isocyanide ligands in **1**, most notably resulting in a rare linear metallocene geometry.

Experimental Section

General Considerations: Unless otherwise noted, all reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or argon or in an MBraun inert atmosphere glove box under an atmosphere of nitrogen. Glassware and Celite[®] were stored in an oven at *ca.* 150 °C for at least 3 h prior to use. Molecular sieves (4 Å) were activated by heating to 200 °C overnight under vacuum prior to storage in a glove box. NMR spectra were recorded at room temperature unless noted otherwise on Bruker AV-300, AVB-400, AVQ-400, AV-500, or AV-600 spectrometers. ¹H NMR chemical shifts (δ) are given relative to residual solvent peaks and are recorded in units of parts per million (ppm). Default (0.3 Hz) line broadening functions were applied to ¹H NMR spectra unless stated otherwise. FT-IR samples were prepared as Nujol mulls pressed between KBr plates, with data collected with a Nicolet iS10 FT-IR spectrometer. Elemental analyses were determined at the Microanalytical Facility at the College of Chemistry, University of California, Berkeley.

Materials: Diethyl ether, *n*-hexane, *n*-pentane, and THF were purified by passage through columns of activated alumina and degassed by sparging with nitrogen. C₆D₆ was vacuum transferred from a flask containing sodium/benzophenone and stored over molecular sieves. (Cp^{iPr4})₂UI,²⁹ (Cp^{iPr4})₂UI₂,²⁹ and [(Et₃Si)₂(μ-H)][B(C₆F₅)₄]³² were synthesized according to literature procedures. [Cp₂Fe][B(C₆F₅)₄] was synthesized by using K[B(C₆F₅)₄] in place of [NH₄][PF₆] in the literature procedure for [Cp₂Fe][PF₆].^{48,49} K[B(C₆F₅)₄] was generously donated by Boulder Scientific Company. All other chemicals were purchased from commercial sources and used as received.

[(Cp^{iPr4})₂U(CN^tBu)₄][B(C₆F₅)₄]₂ (**1**). Hexane (1.5 mL) was added to a mixture of (Cp^{iPr4})₂UI (40 mg, 0.048 mmol, 1.0 equiv) and [(Et₃Si)₂(μ-H)][B(C₆F₅)₄] (45 mg, 0.049 mmol, 1.0 equiv), and the resulting suspension was stirred vigorously for 1 h at room temperature. The solution was then decanted, and the blue solid was washed with 3 × 1 mL of hexane to remove any remaining Et₃SiI, Et₃SiH, and (Cp^{iPr4})₂UI. The crude [(Cp^{iPr4})₂U][B(C₆F₅)₄] was extracted into 16 mL of ether and filtered through Celite to yield a dark blue solution. A solution of ^tBuNC (27 μL, 0.24 mmol, 5.0 equiv) in 1 mL of ether was added by pipette with stirring at room temperature, and the resulting mixture quickly turned orange and formed crystalline orange precipitate. After stirring at room temperature for an additional 20 min, volatiles were removed *in vacuo*, and the product was extracted into 1 mL of THF and filtered through Celite. Hexane (2 mL) was then layered onto the THF solution, and the resulting mixture was allowed to sit undisturbed at -40 °C overnight, resulting in the formation of a red oil. The solution was decanted, and the oil was

dried *in vacuo*. Ether (2 mL) was then added to the crude product, and the mixture was swirled for several seconds before sitting undisturbed at room temperature, causing the material to dissolve initially then rapidly form crystalline solid. The mixture was allowed to sit for an additional 24 h at room temperature, then the solution was decanted. The product was isolated as orange-brown crystals, washed with 2 × 1 mL ether, and dried *in vacuo* (24 mg, 0.0099 mmol, 40% yield (based on [(Et₃Si)₂(μ-H)][B(C₆F₅)₄] as the limiting reagent)). X-ray quality crystals of **1** were grown from ether/THF (~20:1 ratio) at room temperature. IR: 2176 (s, ν_{CN}). Anal. Calcd. (%) for C₁₀₂H₉₄B₂F₄₀N₄U (**1**): C, 51.14; H, 3.96; N, 2.34. Found: C, 51.13; H, 4.04; N, 2.55.

[(Cp^{iPr4})₂U(I)(CN^{Bu})₂][B(C₆F₅)₄] (**2**). *Method A*. A solution of ^tBuNC (12 μL, 0.10 mmol, 2.2 equiv) in 1 mL of ether was added to a solution of (Cp^{iPr4})₂UI (39 mg, 0.047 mmol, 1.0 equiv) in 1 mL of ether at room temperature with stirring. After stirring the resulting green solution for an additional minute, [Cp₂Fe][B(C₆F₅)₄] (42 mg, 0.048 mmol, 1.0 equiv) was added to the reaction mixture as a solid with stirring, quickly resulting in a dark red suspension. The reaction mixture was stirred for an additional 20 min at room temperature, then volatiles were removed *in vacuo*. The crude solid was washed with 4 × 1 mL of hexane to remove Cp₂Fe and was dried again *in vacuo*. The product was extracted into 1 mL of THF and filtered through Celite. Hexane (2 mL) was layered on top, and the resulting mixture was allowed to sit undisturbed at -40 °C. The product was isolated as dark red crystals, washed with 1 mL of hexane, and dried *in vacuo* (38 mg, 0.023 mmol, 49% yield). X-ray quality crystals of **2** were grown from ether at room temperature. IR: 2182 (s, ν_{CN}). Anal. Calcd. (%) for C₆₈H₇₆BF₂₀IN₂U (**2**): C, 48.70; H, 4.57; N, 1.67. Found: C, 48.87; H, 4.63; N, 1.80.

Method B. Hexane (1.5 mL) was added to a mixture of $(\text{Cp}^{\text{iPr}_4})_2\text{UI}$ (30 mg, 0.036 mmol, 1.0 equiv) and $[(\text{Et}_3\text{Si})_2(\mu\text{-H})][\text{B}(\text{C}_6\text{F}_5)_4]$ (36 mg, 0.039 mmol, 1.1 equiv), and the resulting suspension was stirred vigorously for 4 h at room temperature. Dark blue solids rapidly precipitated, and the solution gradually changed from dark blue to dark yellow-green. Next, $t\text{BuNC}$ (21 μL , 0.18 mmol, 5.0 equiv) was added to the reaction mixture by pipette, resulting in a rapid color change to an orange solution with concomitant formation of a red-orange oily solid. The suspension was stirred for an additional hour at room temperature, then the solution was decanted, and the oily solid was washed with 3×1 mL of hexane before drying *in vacuo*. The solid was extracted into 2 mL of ether, filtered through Celite, concentrated to a volume of 0.5 mL, and cooled to -40 °C. The product was isolated as dark red crystals, washed with 1 mL of hexane, and dried *in vacuo* (14 mg, 0.0082 mmol, 23% yield). The IR spectrum of **2** prepared by this method was identical to that isolated by Method A above.

Method C. A solution of $t\text{BuNC}$ (16 μL , 0.14 mmol, 10 equiv) in 2 mL of THF was added by pipette to a dark red-orange solution of $(\text{Cp}^{\text{iPr}_4})_2\text{UI}_2$ (14 mg, 0.014 mmol, 1.0 equiv) and $\text{K}[\text{B}(\text{C}_6\text{F}_5)_4]$ (23 mg, 0.032 mmol, 2.2 equiv) in 1 mL of THF at room temperature with stirring. No color change was observed for the reaction mixture, but after 48 h of stirring at room temperature, volatiles were removed, and the crude material was triturated with 1 mL of hexane. The product was extracted with 3 mL of ether, filtered through Celite, concentrated to a volume of 0.5 mL, and cooled to -40 °C. The product was isolated as dark red crystals and dried *in vacuo* (7.8 mg, 0.0047 mmol, 32% yield). The IR spectrum of **2** prepared by this method was identical to that isolated by Method A above.

(Cp^{iPr4})₂U(I)(CN^tBu) (3). A solution of ^tBuNC (22 μL, 0.19 mmol, 5.0 equiv) in 0.5 mL of hexane was added by pipette to a stirring solution of (Cp^{iPr4})₂UI (32 mg, 0.039 mmol, 1.0 equiv) in 1 mL of hexane at room temperature. The reaction quickly changed from dark blue to dark yellow-green and was stirred for an additional 5 min at room temperature. Volatiles were removed *in vacuo*, then the product was extracted into 2 mL of pentane, filtered through Celite, concentrated to a volume of 0.5 mL, and cooled to −40 °C. The product was isolated as green crystals and dried *in vacuo* (30 mg, 0.033 mmol, 85% yield). X-ray quality crystals of **3** were grown from pentane at −40 °C. ¹H NMR (400 MHz, C₆D₆): δ 21.19 (broad), 16.53 (very broad), 12.63 (broad), 10.84 (broad), 4.37 (very broad), 0.23 (broad), −12.84 (s, CNC(CH₃)₃), −32.88 (broad), −42.57 (very broad), −59.47 (very broad). Assignments of numbers of hydrogen atoms were not possible due to the intrinsically broad nature of the signals (except for the ^tBu group, which was much sharper with a line width (FWHM) of 16 Hz) and the related difficulty of correcting the spectrum's baseline. IR: 2166 cm^{−1} (s, ν_{CN}). Anal. Calcd. (%) for C₃₉H₆₇INU (**3**): C, 51.20; H, 7.38; N, 1.53. Found: C, 51.22; H, 7.29; N, 1.46.

Conflicts of Interest

There are no conflicts to declare.

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Notes and References

†Electronic supplementary information (ESI) available: ¹H NMR spectrum of **3** and X-ray crystallography procedures and data tables. CCDC 2006480–2006482.

‡It is possible that traces of (Cp^{iPr4})₂UI may remain in solution and could also act as a source of iodide.

§While also quite rare, linear metallocenes with divalent lanthanides have been observed (see H. Sitzmann, T. Dezember, O. Schmitt, F. Weber, G. Wolmershäuser and M. Ruck, *Z. Anorg. Allg. Chem.*, 2000, **626**, 2241 and C. A. Gould, K. R. McClain, J. M. Yu, T. J. Groshens, F. Furche, B. G. Harvey and J. R. Long, *J. Am. Chem. Soc.*, 2019, **141**, 12967.)

§§Using 6-coordinate U(III) and 7-coordinate U(IV) to approximate both the change in oxidation state and coordination number between **2** and **3**, a difference of 0.075 Å is predicted (see R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, **32**, 751.)

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