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Facile Syntheses of Unsolvated UI_3 and Tetramethylcyclopentadienyl Uranium Halides

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In the course of comparing the reaction chemistry of $(C_5Me_5)_3U$, **1**, and its slightly less crowded analogue $(C_5Me_4H)_3U$, **2**, new syntheses of UI_3, $(C_5Me_4H)_3U$, $(C_5Me_4H)_3UCl$, **3**, and $(C_5Me_5)_3UCl$, **4**, have been developed. Additionally, $(C_5Me_4H)_3UI$, **5**, and $(C_5Me_4H)_2UCl_2$, **6**, have been identified for the first time. A facile synthesis of unsolvated UI_3 is reported that proceeds in high yield with inexpensive equipment from iodine and hot uranium turnings. Both UI_3 and $UI_3(THF)_4$ react with KC_5Me_4H in toluene to make unsolvated $(C_5Me_4H)_3U$ in higher yield than in previous reports that involve reduction of tetravalent $(C_5Me_4H)_3UCl$, **3**. A more atom-efficient synthesis of complex **3** is also reported that proceeds from reduction of *t*-BuCl, PhCl, or $HgCl_2$ by **2**. Similarly, $(C_5Me_4H)_3U$ reacts with PhI or HgI_2 to generate $(C_5Me_4H)_3UI$. These studies also provided a basis to improve the synthesis of $(C_5Me_5)_3UCl$ from **1** by employing *t*-BuCl or $HgCl_2$ as the halide source. Like $(C_5Me_5)_3UCl$, the $(C_5Me_4H)_3UCl$ complex reacts with $HgCl_2$ to form $(C_5Me_4H)_2$ and $(C_5Me_4H)_2UCl_2$, **6**, but unlike $(C_5Me_5)_3UX$ (X = Cl or I), the less substituted $(C_5Me_4H)_3UX$ complexes do not reduce *t*-BuCl or PhX. The synthesis of **6** from $(C_5Me_4H)MgCl{\cdot}THF$ and UCl_4 is also included.

Introduction

Historically, the chemistry of U(IV) has been more heavily studied than that of U(III).[1-5] One practical reason for this difference is that the tetravalent chloride, UCl_4, is a more useful precursor than the corresponding trivalent compound, UCl_3.[6-12] One of the breakthroughs in U(III) chemistry was the discovery of a convenient synthesis of $UI_3(THF)_4$.[13,14] This precursor can be prepared from amalgamated uranium and iodine in THF[13-15] and is currently a starting material for many U(III) syntheses.[8,16-27]

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In some investigations, however, unsolvated UI_3 is preferred. For example, Cloke and Hitchcock needed unsolvated UI_3 for the synthesis of an unsolvated pentalene complex, $(C_5Me_5)U[C_{10}H_4(1,4\text{-}i\text{-}Pr_3Si)_2]$, that showed interesting reaction chemistry with dinitrogen.[28] Unsolvated UI_3 would also be preferred in systems in which U(III) complexes ring-open THF.[29] Indeed, the formation of oily green residues presumed to arise from THF ring opening complicates the synthesis of $UI_3(THF)_4$ from amalgamated uranium turnings and iodine, and the reaction must be carried out below 10 °C.[14] Previously, unsolvated UI_3 has been prepared by reduction of UI_4 with Zn at 870 K in sealed silica vessels.[30,31] Recently, Cloke and Hitchcock showed that UI_3 could be prepared at 370 °C from U turnings and HgI_2, eq 1, in a manner similar to the synthesis of LnI_3 described by Corbett.[32]

$$2U + 3HgI_2 \rightarrow 2UI_3 + 3Hg \tag{1}$$

We report here that unsolvated UI_3 can be made directly from uranium and iodine without the use of mercury in any form. This preparation uses the method recently employed to make highly reactive divalent lanthanide diiodides by direct reaction of the elements.[33−39] Not only is this route mercury-free, but it can be carried out in a few hours with rather inexpensive equipment. In addition, solvation of UI_3 to form the popular trivalent starting material $UI_3(THF)_4$ proceeds smoothly. The route to $UI_3(THF)_4$ reported here is more efficient than previously reported syntheses[13−15] both in terms of overall yield and in terms of uranium waste generated.

This alternative synthesis of UI_3 was developed as part of our examination of the reaction chemistry of $(C_5Me_5)_3U$, **1**,[29,40−45] vis-à-vis the slightly less crowded complex $(C_5Me_4H)_3U$, **2**.[46,47] Although both complexes crystallize with a trigonal arrangement of cyclopentadienyl ring centroids around the metal, **1** has slightly longer U−C bond distances than **2**, which apparently leads to different chemistry. Hence, both **1** and **2** form CO adducts,[43,46,47] but $(C_5Me_5)_3U(CO)$[43] retains its trigonal arrangement of cyclopentadienyl rings, whereas $(C_5Me_4H)_3U(CO)$ becomes more tetrahedral.[46,47] In addition, complex **1** displays several types of reactions not reported for **2**: sterically induced reduction reactions via a $C_5Me_5{}^{1-}/C_5Me_5$ redox couple,[41] formation of an isolable end-on dinitrogen complex,[29] ring opening of THF,[29] and cyclopentadienyl displacement reactions via ionic salt metathesis.[45]

Samples of $(C_5Me_4H)_3U$ for these comparative $(C_5Me_5)^{1-}$ versus $(C_5Me_4H)^{1-}$ studies were originally prepared by $Na(C_{10}H_8)$ reduction of $(C_5Me_4H)_3UCl$, a precursor that requires a multistep synthesis.[46,47] To obtain $(C_5Me_4H)_3U$ faster and in a more uranium-efficient method, a synthetic route from UI_3 has been developed. Exploration of the reactivity of $(C_5Me_4H)_3U$ with alkyl and aryl halides for comparison with $(C_5Me_5)_3U$ reactions has led to a more atom-efficient synthesis of $(C_5Me_4H)_3UCl$,[46−48] **3**, the former precursor of $(C_5Me_4H)_3U$, as well as the first synthesis and structural characterization of $(C_5Me_4H)_3UI$, **5**. These studies also resulted in the isolation of $(C_5Me_4H)_2UCl_2$, **6**, the analogue of a valuable starting material in pentamethylcyclopentadienyl uranium chemistry, namely $(C_5Me_5)_2UCl_2$.[1−5,49−51]

Experimental Section

General Experimental. The complexes described here are extremely air- and moisture-sensitive. The syntheses and manipulations of these compounds were conducted with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. Except where noted, all glovebox manipulations were carried out in an argon-filled glovebox that was free of coordinating solvents. THF, benzene, toluene, and hexanes were saturated with Ar and passed through a GlassContour column.[52] Benzene-d_6 (Cambridge Isotope Laboratories) was distilled over a NaK alloy and benzophenone. $C_5Me_4H_2$ (Aldrich) was distilled at 140 °C as a colorless liquid and dried over Type 4 activated molecular sieves. PhCl, PhI, and *t*-BuCl (Aldrich) were dried over Type 4 activated molecular sieves. Benzene-d_6, $C_5Me_4H_2$, PhCl, PhI, and *t*-BuCl were all

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degassed by three freeze−pump−thaw cycles. $KN(SiMe_3)_2$ (Aldrich) was crystallized from toluene and washed with hexane before use. $HgCl_2$ and HgI_2 (Aldrich) were dried under vacuum (2×10^{-5} Torr). *i*-PrMgCl (Aldrich) was obtained as a 2 M solution in diethyl ether and used as received. Uranium turnings, submerged in mineral oil (Manufacturing Science Corporation, Oak Ridge, Tennessee) were cut with tin snips into small pieces to ensure uniform heating. *Caution: uranium turnings can spark!* To remove the mineral oil, the turnings were washed with hexane followed by acetone and then H_2O. The turnings were then cleaned according to the literature procedures.[14] $(C_5Me_5)_3U$[53] and UCl_4[6] were prepared as previously described. NMR experiments were conducted with Bruker 400 or 500 MHz spectrometers. IR samples were analyzed as thin films from benzene using an ASI ReactIR1000.[54] Elemental analyses were provided by Analytische Laboratorien, Lindlar, Germany.

KC_5Me_4H. A solution of $C_5Me_4H_2$ (0.98 g, 0.008 mmol) in toluene (10 mL) was added to a solution of $KN(SiMe_3)_2$ (1.955 g, 0.010 mmol) in toluene (10 mL). The reaction mixture was stirred for 12 h, the solution was centrifuged, and the insoluble yellow/white solids were washed with toluene until all of the yellow contaminant was removed. White KC_5Me_5H (1.183 g, 92%) was obtained after drying under a vacuum.

$(C_5Me_4H)MgCl{\cdot}THF$. A solution of $C_5Me_4H_2$ (629 mg, 5.2 mmol) in toluene (50 mL) was cannulated into a Schlenk flask equipped with a condenser containing gelatinous *i*-PrMgCl made by removal of the solvent from *i*-PrMgCl (2.6 mL, 5.2 mmol) in diethyl ether. The reaction mixture was lowered into an oil bath at 100 °C, and white solids immediately precipitated. After 4 h, the flask was cooled to room temperature and the solvent was removed under a vacuum. THF was added to the flask in a glovebox, and the THF insoluble solids were removed by centrifugation. The solvent was removed from the slightly yellow THF solution by rotary evaporation, leaving a pale yellow solid. The solid was washed once with toluene, and $(C_5Me_4H)MgCl{\cdot}THF$ (995 mg, 76%) was isolated as a white solid after being dried under a vacuum. ^1H NMR (C_6D_6): δ 5.7 (s, 1H, $C_5Me_5\mathit{H}$), 3.6 (s, 4H, THF), 2.3 (s, 6H, $C_5\mathit{Me}_5H$), 2.1 (s, 6H, $C_5\mathit{Me}_4H$), 1.3 (t, br, 4H, THF).

$(C_5Me_4H)_2$. In a flask wrapped in aluminum foil, $HgCl_2$ (34 mg, 0.125 mmol) and KC_5Me_4H (41 mg, 0.226 mmol) were stirred in toluene (10 mL) for 12 h. A pale yellow solution was separated from a yellow insoluble oil, a white precipitate, and a small amount of Hg metal. The solvent was removed from the pale yellow solution by rotary evaporation, and $(C_5Me_4H)_2$ was isolated as a white waxy solid (30 mg, 99%). ^1H NMR: δ 6.10 (s), 6.01 (s), 5.97 (s), 5.83 (d), 5.69 (d), 1.99 (s), 1.89 (s), 1.82 (d), 1.80 (d), 1.80 (s), 1.78 (s), 1.73(d), 1.69 (t), 1.66 (s,br), 1.63 (s,br), 1.60 (t), 1.59 (m), 1.57 (s,br), 1.51 (s,br), 1.21 (s), 1.18 (d), 1.16 (s), 1.15 (s), 1.13 (d), 1.11 (s). GC−MS *m*/*z*: 242.3.

UI_3. UI_3 was prepared in an apparatus comprised of simple 20 mL Schlenk tubes whose necks were typically 10 cm long. These Schlenk tubes were connected by pieces of Tygon tubing, 5 cm in length, whose openings were controlled by surgical clamps as shown in Figure 1. This provided a flexible apparatus that allowed a grease-free addition of solids to the hot reaction tube. The uranium turnings, cleaned as described above, were transferred into the Schlenk tube labeled flask #1. Flask #1, the Tygon tube to which it was attached, and its surgical clamp had all been preweighed. Flask #1 was attached to a Schlenk line with Tygon tubing, and the turnings were dried under a vacuum. The flask was filled with argon, the Tygon tubing was clamped shut with its surgical clamp, and the assembly was detached from the Schlenk line and weighed (1.350 g of U, 0.0056 mol).

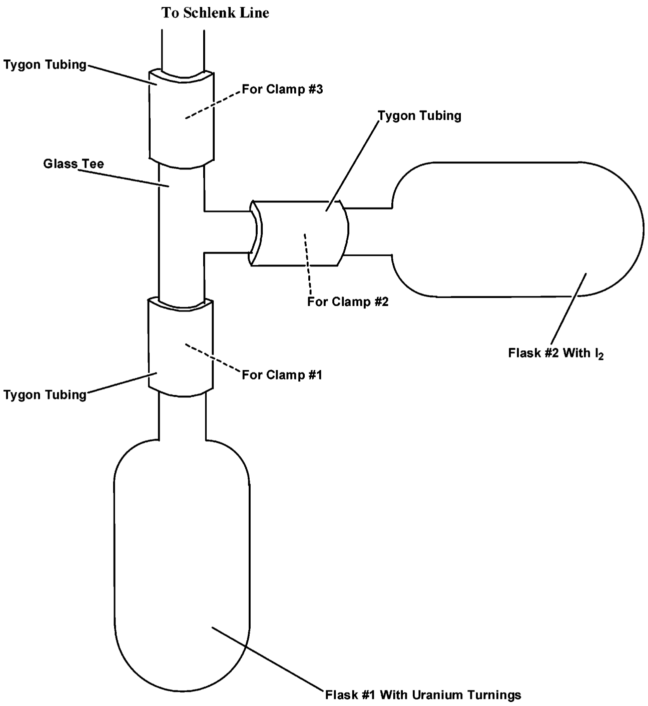

Figure 1. Apparatus used to make the UI_3.

Using standard Schlenk methods under Ar, the U-containing flask #1 was attached to the glass tee that was connected to the Schlenk line as depicted in Figure 1. An inert atmosphere was established in the apparatus. Under a strong flow of argon, flask #2 was replaced with a glass stopper while it was quickly charged with finely ground I_2 (1.848 g, 0.0784 mol). Flask #2 was then reattached to the apparatus in place of the glass stopper. By using clamp #2 to oscillate between dynamic and static vacuum, the iodide was cooled with a liquid-nitrogen bath and degassed by three freeze−pump−thaw cycles.

With clamp #2 closed and the iodine flask #2 under a static vacuum, clamp #1 was removed, exposing the U turnings to a dynamic vacuum. The turnings were heated with a natural gas/oxygen torch, taking care to keep the temperature below the melting point of the glass while the vacuum gauge on the Schlenk line was used to monitor the uranium for outgassing. The uranium turnings both outgassed and blackened upon heating. When no further outgassing was observed, clamps #1 and #3 were closed while the uranium containing vessel, flask #1, was kept hot. Clamp #2 was opened, a small amount of I_2 was shaken into the tee, and clamp #2 was closed. Clamp #1 was quickly opened and closed so that only small portions of I_2 fell into flask #1. The contents of the tube glowed red, and heating continued. *Caution: It is important that a high temperature is maintained in the bottom of flask #1 and that the I_2 addition is slow. If the flask is not hot enough or too much I_2 is added at one time, the I_2 will sublime in the top of the flask rather than react. This can cause increased pressure that ruptures the apparatus at the weakest point, the Tygon tube connection to the tee.*

Iodine was added repeatedly in small portions as described above. When all of the I_2 was added and the glowing in the reaction tube had stopped, heating ceased and flask #1 was slowly cooled to room temperature. The flask containing the UI_3 and unreacted uranium

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metal was lowered into a liquid-nitrogen bath, and the vessel was exposed to a dynamic vacuum by removing clamps #1 and #3. The pressure change was monitored to determine if noncondensable gases were present. Clamp #3 was subsequently closed and clamp #2 was opened, isolating the entire apparatus under a static vacuum. The iodine-containing tube was gently heated with the torch, and any remaining I_2 was sublimed under a vacuum into flask #1. Clamps #2 and #1 were closed, and flask #1 was slowly warmed to room temperature. Flask #1 was heated until its contents seemed to melt. After it appeared that all of the I_2 had reacted and there was no further glowing in flask #1, the flask was cooled to room temperature and sealed under a vacuum. The flask was then lowered into a liquid-nitrogen bath, and the UI_3 was knocked off of the walls of the flask by carefully tapping the cold flask with a rubber hose. The tube was brought into an argon-filled glovebox that was free of coordinating solvents and broken open. UI_3 was isolated as a dark purple powder (3.084 g, 89%; based on uranium). Anal. Calcd for UI_3: U, 38.5; I, 61.5. Found: U, 38.8; I, 61.3. In the event that the reaction does not go to completion, uranium metal will be present in excess. The UI_3 can be easily separated from any unreacted residual metal as the THF solvate, $UI_3(THF)_4$, by extraction with THF.

$(C_5Me_4H)_3U$, 1, from UI_3. Toluene (15 mL) was added to an intimate mixture of KC_5Me_4H (28.9 mg, 0.180 mmol) and UI_3 (34.9 mg, 0.056 mmol) and stirred for 24 h. White and black solids were removed from the green-brown solution by centrifugation. Upon removal of the solvent by rotary evaporation, the previously characterized $(C_5Me_4H)_3U$[46,47] (24 mg, 71%) was isolated as a green-brown powder. The ^1H NMR spectrum and the unit cell parameters obtained from crystals grown in toluene at −35 °C matched literature values.[46,47]

$(C_5Me_4H)_3U$, 1, from $UI_3(THF)_4$. In a nitrogen-filled glovebox that contained coordinating solvents, $UI_3(THF)_4$ was prepared by dissolving UI_3 in THF followed by centrifugation and then removal of the solvent by rotary evaporation. A purple suspension of $UI_3(THF)_4$ (472 mg, 0.520 mmol) in toluene (10 mL) was added to KC_5Me_4H (250 mg, 1.560 mmol). The mixture was stirred for 12 h, and the color slowly changed to green-brown. White insoluble solids were removed by centrifugation, and the previously characterized $(C_5Me_4H)_3U$ (288 mg, 92%), identified by ^1H NMR spectroscopy, was isolated as a green-brown powder upon removal of the solvent by rotary evaporation. Crystals obtained from saturated solutions of $(C_5Me_4H)_3U$ in toluene at −35 °C had identical unit cell parameters as those in the literature.[46,47]

$(C_5Me_4H)_3UCl$, 3, from *t*-BuCl. *t*-BuCl (7.6 μL, 0.068 mmol) was added to $(C_5Me_4H)_3U$ (41 mg, 0.068 mmol) in toluene (10 mL). The solution immediately changed to red. After the solution had been stirred for 12 h, the solvent and any organic products that had formed during the reaction were removed by rotary evaporation, and $(C_5Me_4H)_3UCl$[46−48] was isolated as a red powder (48 mg, 100%). The ^1H NMR spectrum in toluene-d_8 matched literature values.[46−48] ^1H NMR (C_6D_6): δ 33.6 (s, 9H, C_5Me_4H), −10.9 (s, 9H, C_5Me_4H), 9.7 (s, 9H, C_5Me_4H), −1.9 (s, 3H, C_5Me_4H), −34.9 (s, 9H, C_5Me_4H).

$(C_5Me_4H)_3UCl$, 3, from $HgCl_2$. A solution of $(C_5Me_4H)_3U$ (46 mg, 0.077 mmol) in toluene (7 mL) was added to $HgCl_2$ (10 mg, 0.037 mmol) in a flask that had been wrapped with tape to exclude light. After the solution had been stirred for 12 h, gray insoluble solids were removed by centrifugation and the solvent was removed by rotary evaporation. $(C_5Me_4H)_3UCl$[46−48] was isolated as a red powder (48 mg, 98% yield).

$(C_5Me_4H)_3UCl$, 3, from C_6H_5Cl. C_6H_5Cl (1.3 μL, 0.013 mmol) was added to a solution of $(C_5Me_4H)_3U$ (7.7 mg, 0.013 mmol) in C_6D_6 (1 mL) in an NMR tube. A color change to red occurred upon addition of the aryl halide, and the ^1H NMR spectrum indicated quantitative formation of the previously characterized $(C_5Me_4H)_3UCl$[46−48] as well as resonances consistent with $(C_6H_5)_2$. $(C_5Me_4H)_3UCl$ shows no sign of reactivity with an additional equivalent of C_6H_5Cl after 12 h at 65 °C or after 24 h in neat C_6H_5Cl at room temperature.

$(C_5Me_4H)_3UI$, 5, from HgI_2. As described above for the synthesis of **3** from $HgCl_2$, $(C_5Me_4H)_3U$ (87.3 mg, 0.145 mmol) was reacted with HgI_2 (32 mg, 0.070 mmol) in toluene (10 mL) to form a red solution. $(C_5Me_4H)_3UI$ (91 mg, 88%) was isolated as a red powder. X-ray quality crystals of $(C_5Me_4H)_3UI$ were obtained from saturated solutions in toluene at −35 °C. ^1H NMR (C_6H_6, 298 K): δ 37.9 (s, 9H, C_5Me_4H), 16.5 (s, 9H, C_5Me_4H), 13.2 (s, 9H, C_5Me_4H), −7.9 (s, 3H, C_5Me_4H), −36.3 (s, 9H, C_5Me_5H). IR (thin film from C_6H_6): 2961m, 2922m, 2856m, 1602w, 1451w, 1413w, 1382w, 1262s, 1089s, 1019s, 864m, 799s, 698m, 675m cm^{-1}. Anal. Calcd for $C_{27}H_{39}UI$: C, 44.53; H, 5.36; U, 32.69; I, 17.43. Found: C, 43.77; H, 5.32; U, 33.46; I, 17.94.

$(C_5Me_4H)_3UI$, 5, from C_6H_5I. As described above for the synthesis of **3** from C_6H_5Cl, C_6H_5I (2.0 μL, 0.018 mmol) was reacted with $(C_5Me_4H)_3U$ (11.0 mg, 0.018 mmol) in C_6D_6 (1 mL) to form a red solution. After 2 h, the ^1H NMR spectrum indicated quantitative conversion to $(C_5Me_4H)_3UI$ as well as resonances consistent with $(C_6H_5)_2$. $(C_5Me_4H)_3UI$ shows no sign of reactivity with an additional equivalent of C_6H_5I, even after 12 h at 65 °C, and is stable in neat C_6H_5I.

$(C_5Me_4H)_2UCl_2$, 6, from $HgCl_2$. A solution of $(C_5Me_4H)_3UCl$ (12 mg, 0.019) in toluene (2 mL) was added to $HgCl_2$ (3 mg, 0.010 mmol) in a flask that had been wrapped with tape to exclude light. After the reaction was stirred for 12 h, a gray solid was removed by centrifugation. The solvent was removed by rotary evaporation, leaving a red powder that was subsequently washed with $(Me_3Si)_2O$. The red washings were discarded, the red powder was dried under a vacuum, and $(C_5Me_4H)_2UCl_2$ (9 mg, 82%) was isolated. A common contaminant in this reaction is unreacted $(C_5Me_4H)_3UCl$. X-ray quality crystals of $(C_5Me_4H)_2UCl_2$ readily form overnight from hot toluene solutions slowly cooled to −35 °C. ^1H NMR (C_6D_6, 298 K): δ 47.0 (s, 12H, C_5Me_5H), −16.4 (s, 12H, C_5Me_5H), −55.1(s, 2H, C_5Me_4H). IR (thin film from C_6H_6): 2961m, 2926m, 2856m, 1586vw, 1382w, 1258s, 1089s, 1019s, 864w, 795s, 698w cm^{-1}. Anal. Calcd for $C_{18}H_{26}Cl_2U$: C, 39.21; H, 4.71; Cl, 12.86; U, 43.17. Found: C, 39.12; H, 4.69; Cl, 12.69; U, 43.02. When this reaction was followed by ^1H NMR spectroscopy, resonances consistent with $(C_5Me_4H)_2$ were observed.

$(C_5Me_4H)_2UCl_2$, 6, from $(C_5Me_4H)MgCl{\cdot}THF$. In a nitrogen-filled glovebox that contained coordinating solvents, toluene (50 mL) was added to a Schlenk flask that contained an intimate mixture of $(C_5Me_4H)MgCl{\cdot}THF$ (8.601 g, 0.034 mol) and UCl_4 (6.352 g, 0.017 mol). The Schlenk flask was equipped with a condenser, attached to a Schlenk line, and heated at 100 °C. The mixture immediately turned cherry red. After 48 h, the solvent was removed under a vacuum, the reaction flask was brought into an argon-filled glovebox, and benzene (125 mL) was added. A white insoluble solid was removed from the red solution by filtration. The extraction process was repeated (three times), the extracted fractions were combined into a Schlenk flask, and the flask was attached to a vacuum line. The solvent was removed under a vacuum to give $(C_5Me_4H)_2UCl_2$ (7.118 g, 78%) as a red solid.

$(C_5Me_5)_3UCl$, 4, from *t*-BuCl. As described above for the synthesis of **3** from *t*-BuCl, $(C_5Me_5)_3U$ (150 mg, 0.233 mmol) was reacted with *t*-BuCl (28 μL, 0.244) to form a red solution. After

Table 1. Crystal Data and Structure Refinement for $(C_5Me_4H)_3UI$, **5**, and $(C_5Me_4H)_2UCl_2$, **6**

	5	**6**
empirical formula	$C_{27}H_{39}IU$	$C_{18}H_{26}Cl_2U$
fw	728.51	551.32
cryst syst	cubic	orthorhombic
space group	*I*$\bar{4}$3*d*	*Cmcm*
a (Å)	21.4984(10)	17.7866(16)
b (Å)	21.4984(10)	6.7022(6)
c (Å)	21.4984(10)	15.6540(14)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
vol(Å^3)	9936.2(8)	1866.1(3)
Z	16	4
λ(Å)	0.710 73	0.710 73
density$_{calcd}$ (mg/m^3)	1.948	1.962
abs coeff	7.788 mm^{-1}	8.977 mm^{-1}
GOF on F^2	1.163	1.136
R^a [$I > 2\sigma(I)$]: R1	0.0184	0.0121
R^b (all data): wR2	0.0467	0.0292

the solution was stirred for 3 h, the previously characterized $(C_5Me_5)_3UCl$[42] was isolated as a red powder (143 mg, 90%).

X-ray Data Collection, Structure Determination, and Refinement. $(C_5Me_4H)_3UI$, 5. A dark red/ruby color crystal of approximate dimensions 0.16 × 0.22 × 0.24 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[55] program package was used for determination of the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[56] and SADABS[57] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[58] program. The diffraction symmetry was 4/*mmm*, and the systematic absences were consistent with the tetragonal space group *I*$\bar{4}$3*d*, which was later determined to be correct.

The structure was solved using the uranium coordinates from the isomorphous uranium chloride complex and refined on F^2 by full-matrix least-squares techniques (see Table 1 for crystallographic data and structure refinement). The analytical scattering factors[59] for neutral atoms were used throughout the analysis. Hydrogen atom H(5) was located from a difference Fourier map and refined (x, y, z and U_{iso}). The methyl hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0467 and GOF = 1.163 for 92 variables refined against 2074 data points. As a comparison for refinement on F, R1 = 0.0184 for those 1885 data points with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.[60]

$(C_5Me_4H)_2UCl_2$, 6. A red crystal of approximate dimensions 0.08 × 0.14 × 0.24 mm was handled as described above for **5**. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Cmcm*, which was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques (see Table 1). The analytical scattering factors[59] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference Fourier map and refined (x, y, z and U_{iso}). At convergence, wR2 = 0.0292 and GOF = 1.136 for 80 variables refined against 1184 data points (0.76 Å resolution). As a comparison for refinement on F, R1 = 0.0121 for those 1166 data points with $I > 2.0\sigma(I)$.

Results

Synthesis of UI_3. Unsolvated UI_3 can be made directly from uranium turnings and iodine according to eq 2 in a three-component apparatus, as shown in Figure 1.

$$2U + 3I_2 \rightarrow 2UI_3 \qquad (2)$$

Short lengths of Tygon tubing whose openings are controlled by surgical pinch clamps provide a flexible arrangement in which solid iodine can be slowly transferred, in a grease-free environment, to a hot reaction vessel that contains the uranium. Small amounts of iodine are added repeatedly to the uranium turnings, which are heated with a torch. An amber glow emanates from the reaction vessel as the uranium is oxidized by iodine. The method generates multigram quantities of unsolvated UI_3 in high yield in powder form from a procedure that can be completed within hours.

Synthesis of $(C_5Me_4H)_3U$, 2. $(C_5Me_4H)_3U$ can be prepared directly from unsolvated UI_3, eq 3, or from the THF solvate $UI_3(THF)_4$, eq 4, in high yield.

$$UI_3 + 3KC_5Me_4H \xrightarrow[\text{toluene}]{} \underset{\mathbf{2}}{(C_5Me_4H)_3U} + 3KI \qquad (3)$$

$$UI_3(THF)_4 + 3KC_5Me_4H \xrightarrow[\text{toluene}]{} \underset{\mathbf{2}}{(C_5Me_4H)_3U} + 3KI + 4THF \qquad (4)$$

In the past, **2** was synthesized by reduction of $(C_5Me_4H)_3UCl$ with sodium naphthalenide in THF.[46,47] $(C_5Me_4H)_3UCl$ was, in turn, made from MC_5Me_4H (M = K[46,47] or Li[48]) and UCl_4, which was obtained from hexachloropropene and uranium oxides.[6−8] A representative multistep synthesis is shown in Scheme 1. The new routes to complex **2**, eqs 3 and 4, are advantageous over the previous syntheses, Scheme 1, because $(C_5Me_4H)_3U$ can be made more directly and in higher yield. In addition, **2** can be made with rigorous exclusion of coordinating solvents, like THF, if desirable, eq 3.

Synthesis of $(C_5Me_4H)_3UCl$, 3, and $(C_5Me_5)_3UCl$, 4. Both $(C_5Me_4H)_3U$ and $(C_5Me_5)_3U$ react with alkyl, aryl, and mercuric chlorides to form the corresponding tris(cyclopentadienyl) uranium chlorides, eq 5 and 6 (R = Me or H; R′ = Ph or *t*-Bu). In the $(C_5Me_4R)_3U$ reaction with PhCl, the $(C_5Me_4R)_3UCl$ complex is formed quantitatively. The major organic product identified by ^1H NMR spectroscopy was

Scheme 1

$$U_3O_8 + \text{excess } C_3Cl_6 \longrightarrow UCl_4$$

$$UCl_4 + 3MC_5Me_4H \longrightarrow (C_5Me_4H)_3UCl + 3\,MCl$$

$$(C_5Me_4H)_3UCl + NaC_8H_{10} \longrightarrow \underset{\mathbf{2}}{(C_5Me_4H)_3U} + NaCl + C_8H_{10}$$

M = Li or Na

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(55) *SMART Software User's Guide*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

(56) *SAINT Software User's Guide*, version 6.0; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

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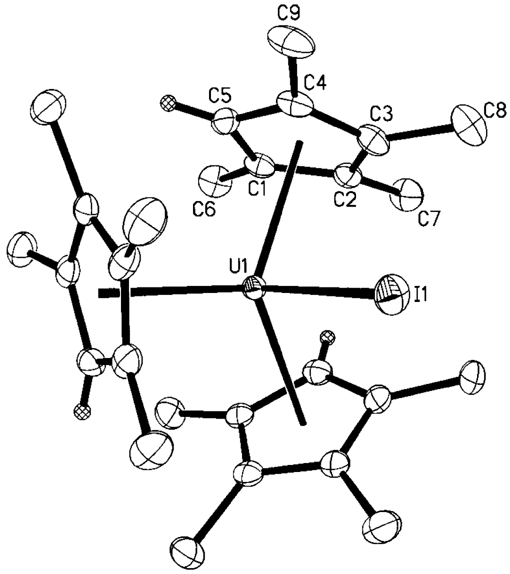
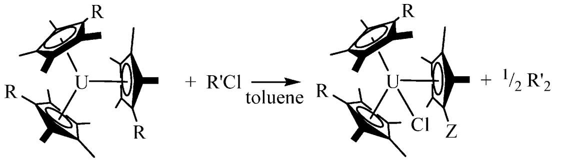
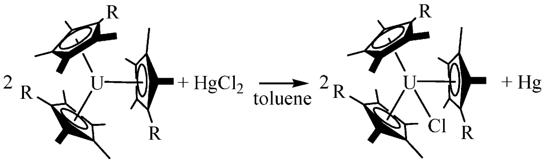


Figure 2. Thermal ellipsoid plot of $(C_5Me_4H)_3UI$, **5**, drawn at the 50% probability level.

biphenyl.[42,61,62] To obtain pure $(C_5Me_4R)_3UCl$, the organic byproducts must be separated in an extraction step that results in decreased yields. Hence, when compared to PhCl, the $HgCl_2$ or *t*-BuCl reagents are superior in the synthesis of $(C_5Me_4R)_3UCl$ complexes because the Hg and volatile organic byproducts, respectively, can be easily separated.

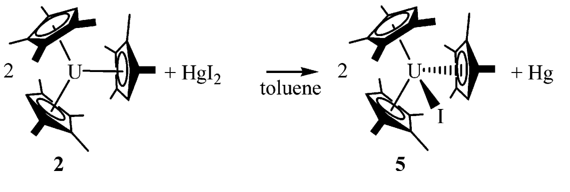


(5)



(6)

Synthesis of $(C_5Me_4H)_3UI$, 5. $(C_5Me_4H)_3U$ reacts with HgI_2 according to eq 7 to form $(C_5Me_4H)_3UI$, **5**, which, to our knowledge, has not been previously identified in the literature. Like $(C_5Me_4H)_3UCl$, it can also be prepared from PhI and $(C_5Me_4H)_3U$.



(7)

To confirm the identity of **5**, it was characterized by X-ray diffraction, Figure 2. The ^1H NMR spectrum of **5** in benzene-d_6 contains four methyl resonances at $\delta = 37.9$, 16.5, 13.2, and −36.3 ppm, which is consistent with the ^1H NMR spectra of the structurally similar $(C_5Me_4H)_3UCl$ and $(C_5Me_4H)_3UL$ (L = CO[46,47] and THF[29]) complexes. For example, the ^1H NMR spectrum of $(C_5Me_4H)_3UCl$ has four methyl resonances at $\delta = 33.6$, 10.9, 9.7, and −34.9 ppm. In contrast, the ^1H NMR spectrum of the parent molecule, $(C_5Me_4H)_3U$, displays only two methyl resonances.[46,47]

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_4H)_3UI$, **5**, and $(C_5Me_4H)_2UCl_2$, **6**

Complex **5**		Complex **6**	
U(1)−I(1)	3.0338(5)	U(1)−Cl(1)	2.5909(7)
U(1)−C(1)	2.767(4)	U(1)−C(1)	2.646(3)
U(1)−C(2)	2.901(4)	U(1)−C(2)	2.6861(18)
U(1)−C(3)	2.882(4)	U(1)−C(3)	2.7470(19)
U(1)−C(4)	2.755(4)		
U(1)−C(5)	2.669(4)	Cl(1)−U(1)−Cl(1A)	99.79(3)
U(1)−Cnt	2.524	U(1)−Cnt	2.418
Cnt−U(2)−Cnt	117.5	Cnt−U(1)−Cnt	133.1
Cnt−U(1)−I(1)	99.2	Cnt−U(1)−Cl(1)	104.8

Complex **5** is stable at 70 °C in C_6D_6 and does not react with coordinating solvents such as THF or ether. It is also stable in neat PhI.

Structure of $(C_5Me_4H)_3UI$, 5. $(C_5Me_4H)_3UI$ is isomorphous with the chloride analogue $(C_5Me_4H)_3UCl$.[48] The 99.2° (ring centroid)−U−I and 117.5° (ring centroid)−U−(ring centroid) angles in **3** give it a distorted-tetrahedral geometry similar to that found in $(C_5Me_4H)_3UCl$[48] and other crystallographically characterized $(C_5Me_4H)_3UL$ (L = CO,[46,47] CNC_6H_4-*p*-OMe,[47] or THF[29]) complexes (Table 2). Complex **5** cannot be compared with the pentamethyl analogue $(C_5Me_5)_3UI$[42] because this reactive species has not yet been characterized by X-ray diffraction. $(C_5Me_4H)_3UI$ is structurally different from crystallographically characterized $(C_5Me_5)_3U(CO)$,[43] $(C_5Me_5)_3U(N_2)$,[29] $(C_5Me_5)_3UF$,[42] $(C_5Me_5)_3UCl$,[42] and $(C_5Me_5)_3ThH$[63] complexes whose ring centroids maintain a trigonal arrangement around the metal center with 120° (ring centroid)−An−(ring centroid) angles. The fourth ligand in each case is located on the 3-fold axis perpendicular to the trigonal plane with a 90° (ring centroid)−An−(fourth ligand) angle.

The 2.52 Å U−(ring centroid) distance in **5** is similar to those in the trivalent $(C_5Me_4H)_3U$ parent molecule, 2.523 Å, as well as those in the tetravalent $(C_5Me_4H)_3UCl$ complex, 2.520 Å. The five unique $U-C(C_5Me_4H)$ distances in **5** span a wide range, 2.699(4)−2.901(4) Å, and are very similar to those of $(C_5Me_4H)_3UCl$, 2.658(11)−2.911(10) Å.[48] The shortest $U-C(C_5Me_4H)$ distance involves the H-substituted C(5) ring carbon, whereas the longest $U-C(C_5Me_4H)$ distances involve the C(2) and C(3) carbons, which are furthest from C(5). The longest $U-C(C_5Me_4H)$ bond distances in **5** are similar to those in the sterically crowded $(C_5Me_5)_3UCl$ complex, 2.780(6)−2.899(9) Å. The shorter distances are similar to those in less crowded complexes, for example, the 2.69(2)−2.78(3) Å $U-C(C_5H_5)$ lengths in $(C_5H_5)_3UI$.[64] The 3.0338(5) Å U−I distance in **5** is similar

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(61) Finke, R. G.; Hirose, Y.; Gaughan, G. *J. Chem. Soc., Chem. Commun.* **1981**, 232.

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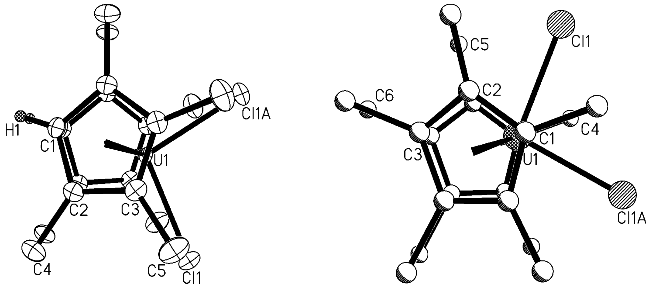
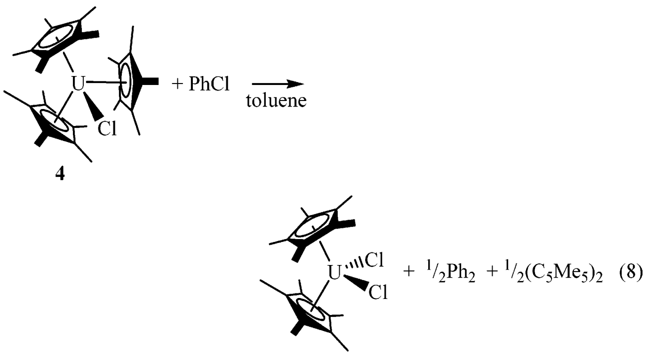
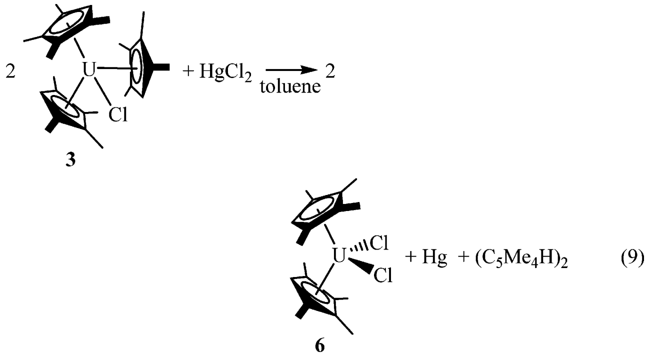


Figure 3. Left: Thermal ellipsoid plot of $(C_5Me_4H)_2UCl_2$, **6**, drawn at the 50% probability level. Right: Ball-and-stick representation of $(C_5Me_5)_2UCl_2$.[35]

to the 3.059(2) Å distance in $(C_9H_7)_3UI$[65] and the 3.041(1) Å distance in $(C_5H_5)_3UI$.[64]

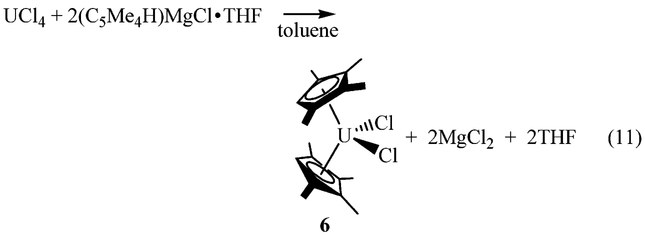
Synthesis of $(C_5Me_4R)_2UCl_2$, 6. In contrast to $(C_5Me_5)_3UCl$, which reacts with PhCl via sterically induced reduction to make $(C_5Me_5)_2UCl_2$,[51] eq 8, PhCl is unreactive with the less substituted $(C_5Me_4H)_3UCl$ complex and can be used as a solvent. However, the $(C_5Me_4H)_3UCl$ complex does react with $HgCl_2$ to form $(C_5Me_4H)_2UCl_2$, eq 9 and Figure 3, a compound that has never before been synthesized to our knowledge. The reaction in eq 9 generates black solids and $(C_5Me_4H)_2$, which can be removed from $(C_5Me_4H)_2UCl_2$ by extraction with $(Me_3Si)_2O$. $(C_5Me_4H)_2$ was identified by comparing its ^1H NMR spectra and GC−MS data with that of a sample independently synthesized as shown in eq 10. The ^1H NMR spectra indicate that multiple isomers of $(C_5Me_4H)_2$ are generated in both eqs 9 and 10.





$$HgCl_2 + 2KC_5Me_4H \xrightarrow[\text{toluene}]{} (C_5Me_4H)_2 + Hg + 2KCl \tag{10}$$

Like other dichlorouranium metallocenes,[49−51,66] $(C_5Me_4H)_2UCl_2$ can also be made from cyclopentadienyl magnesium salts. Thus, UCl_4 reacts with $(C_5Me_4H)MgCl{\cdot}THF$ to form **6**, eq 11.



Structure of $(C_5Me_4H)_2UCl_2$, 6. The structure of $(C_5Me_4H)_2UCl_2$ can be compared with those of $(C_5Me_5)_2UCl_2$,[51] **7**; $[(1,3\text{-}Me_3Si)_2C_5H_3]_2UCl_2$,[66,67] **8**; $[(1,3\text{-}t\text{-}Bu)_2C_5H_3]_2UCl_2$,[66] **9**; and $[(1,2\text{-}t\text{-}Bu)_2C_5H_3]_2UCl_2$, **10**.[68] The U−(ring centroid) distance in **6** is 2.42 Å compared to 2.47, 2.44, 2.49, and 2.43 Å for **7**−**10**, respectively. The three unique U−C(C_5Me_4H) bond lengths in **6** are 2.646(3), 2.6861(18), and 2.7470(19) Å, and they average 2.69(5) Å. In comparison, **7**−**10** have U−C bond distances that average 2.72(2), 2.72(1), 2.77(5), and 2.71(7) Å, respectively.

The (ring centroid)−U−(ring centroid) angle in **6** is 133.1° compared to 132°, 124.85°, 128.1°, and 123.3° in **7**−**10**, respectively. The cyclopentadienyl rings in **6** are eclipsed similar to those in $(C_5Me_5)_2UCl_2$ and $[(1,2\text{-}t\text{-}Bu)_2C_5H_3]_2UCl_2$ and in contrast to the structures of $[(1,3\text{-}Me_3Si)_2C_5H_3]_2UCl_2$ and $[(1,3\text{-}t\text{-}Bu)_2C_5H_3]_2UCl_2$.[51,66−68] Although **6** and **7** have eclipsed rings, they differ in the orientation of the rings to the $[UCl_2]^{2+}$ units. As shown in Figure 3, the methyl groups eclipse both of the chlorides in **6**, whereas the methyl groups in **7** are staggered with respect to the chlorides. This allows the H-substituted carbon atoms, C(1) and C(1A), to be in the most congested part of the metallocene substructure; C(1) and C(1A) lie opposite the metallocene wedge and in the plane defined by the ring centroids and the uranium ion. This ring orientation is similar to that observed in rotationally constrained metallocenes, such as in $[Me_2Si(C_5Me_4)_2]UCl_2{\cdot}2LiCl{\cdot}4(Et_2O)$.[69]

The 2.5909(7) Å U−Cl distance and the 99.79(3)° Cl(1)−U−Cl(1A) angle in **6** are similar to those in **7**−**10:** 2.583(6) Å and 97.9(4)°;[51] 2.579(2) Å and 95.3(1)°;[66,67] 2.577(4) Å and 91.0(2)°;[66] and 2.591(4) Å, 2.576(4) Å, and 97.66(14)°, respectively.[68]

Discussion

Unsolvated UI_3 can be synthesized by direct reduction of iodine by uranium turnings in simple Schlenk tubes without the use of furnaces. This method offers advantages over other procedures[13−15,28,30,31] in that it provides UI_3 in high yield via a mercury-free route using inexpensive equipment within

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hours. The unsolvated UI_3 reacts in nonpolar solvents, like toluene, with KC_5Me_4H to make $(C_5Me_4H)_3U$ free of coordinating solvents. UI_3 can also be readily converted to the popular $UI_3(THF)_4$ reagent[13,14] without the formation of green oily contaminants.[13,14]

The synthesis of $(C_5Me_4H)_3U$ from UI_3 or $UI_3(THF)_4$ is an improvement over previous synthetic routes that were based on reduction of tetravalent precursors originating from UCl_4.[46−48] $(C_5Me_4H)_3U$ can subsequently be used to prepare $(C_5Me_4H)_3UCl$ in quantitative yield. This synthetic route to $(C_5Me_4H)_3UCl$ proceeds with an 82% overall yield from the uranium turnings compared to a 33% yield based on uranium in the previous synthesis from uranium oxides.[46−48]

The reductions of PhCl, *t*-BuCl, and $HgCl_2$ by $(C_5Me_4H)_3U$ to form $(C_5Me_4H)_3UCl$, eqs 6 and 7, as well as the reduction of HgI_2 and PhI by $(C_5Me_4H)_3U$ to form $(C_5Me_4H)_3UI$, eq 7, are consistent with the one-electron reduction chemistry previously observed for trivalent uranium.[61,62,70−75] $(C_5Me_4H)_3UI$ can be crystallographically characterized, whereas the sterically more-crowded pentamethyl analogue, $(C_5Me_5)_3UI$, readily decomposes to $(C_5Me_5)_2UI$ at room temperature.[42] In contrast to their $(C_5Me_5)_3UX$ analogues, the $(C_5Me_4H)_3UX$ complexes do not decompose in THF or in alkyl halides such as PhX and *t*-BuCl. This suggests that the reactivity of $(C_5Me_4R)_3UX$ (R = H, Me; X = Cl, I) complexes relates to the amount of steric crowding: the less sterically crowded complexes are more stable.

Interestingly, $(C_5Me_4H)_3UCl$ does react with $HgCl_2$ to form $(C_5Me_4H)_2UCl_2$, eq 9, in a reaction similar to the sterically induced reduction of $HgCl_2$ by $(C_5Me_5)_3UCl$ to form $(C_5Me_5)_2UCl_2$. As in the $(C_5Me_5)_3UCl$ chemistry, a cyclopentadienyl dimer is also observed as a byproduct. If the reaction in eq 9 does involve a ligand-based reduction with a $(C_5Me_4H)^{1-}/(C_5Me_4H)_2$ redox couple, it is the first example, to our knowledge, of this type of cyclopentadienyl reduction reaction in an f element complex that contains some normal metal−C(ring) bond distances. As noted above, the structure of $(C_5Me_4H)_3UCl$ has some long U−C(C_5Me_4H) bond distances, similar to those in the sterically crowded $(C_5Me_5)_3UCl$, but it also has some more conventional bond lengths. If $(C_5R_5)^{1-}/(C_5R_5)_2$ reductions can occur without having all of the M−C(ring) bonds unusually long, this would substantially increase the scope of this reaction. However, it is also possible that $(C_5Me_4H)_3UCl$ reacts with $HgCl_2$ via a ligand exchange reaction. Because KC_5Me_4H reacts with $HgCl_2$ to form $(C_5Me_4H)_2$, transmetalation between $(C_5Me_4H)_3UCl$ and $HgCl_2$ to form an unstable $(C_5Me_4H)_2Hg$ intermediate could also explain the products.

In any case, the reaction of $(C_5Me_4H)_3UCl$ with $HgCl_2$ provides a useful way to generate $(C_5Me_4H)_2UCl_2$ for the first time. Syntheses of bis(cyclopentadienyl) uranium dichloride complexes, in general, are not straightforward.[49,50,66−68] For example, $(C_5Me_5)_2UCl_2$ is not prepared simply from UCl_4 and KC_5Me_5. In practice, magnesium reagents are typically used. Because the alternative mercuric salt method, exemplified in eq 9, proceeds with complexes that contain normal bond distances, this approach may provide entrance into other (ancillary ligand)$_2UCl_2$ complexes that are not synthetically available via ionic metatheses with alkali or alkaline earth salts.

The synthetic accessibility of $(C_5Me_4H)_2UCl_2$, which can also be synthesized from $(C_5Me_4H)MgCl{\cdot}THF$ and UCl_4, provides further opportunities to compare $(C_5Me_5)^{1-}$ versus $(C_5Me_4H)^{1-}$ chemistry with uranium. These ligands clearly have different chemistry in tris(cyclopentadienyl) complexes,[29,40−45] but this may also be true with the $[(C_5Me_4R)_2U]^{2+}$ metallocenes. For example, the recent use of the $(C_5Me_4H)^{1-}$ versus $(C_5Me_5)^{1-}$ ligand has had a significant impact in early transition-metal dinitrogen chemistry.[76−79]

Conclusion

The solid-state synthesis of UI_3 described here provides a simple and inexpensive entrance into trivalent uranium chemistry. Also reported here are more atom-efficient syntheses of $(C_5Me_4H)_3U$ and $(C_5Me_4H)_3UCl$. These complexes, in turn, provide access to $(C_5Me_4H)_3UI$ and $(C_5Me_4H)_2UCl_2$, valuable precursors for further exploration of the effect of cyclopentadienyl ring substitution on uranium chemistry.

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Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, complete bond distances and angles, and a listing of observed and calculated structure factor amplitudes for compounds **5** and **6** (in PDF and CIF formats). This material is available free of charge via the Internet at http://pubs.acs.org.

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