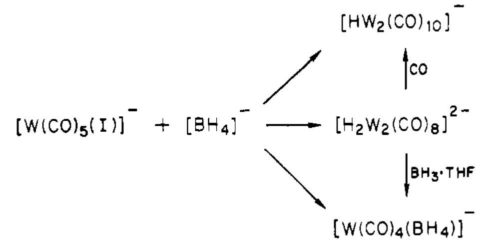

Previous work[3,11] had shown that both $[HW_2(CO)_{10}]^-$ and $[H_2W_2(CO)_8]^{2-}$ can also be produced from the direct reaction of $W(CO)_6$ and $[BH_4]^-$, but yields of $[H_2W_2(CO)_8]^{2-}$ were small. In the reaction of $[W(CO)_5(I)]^-$ with $[BH_4]^-$, the role of the cation is crucial in determining the relative yields of the three anions: When the $[(Ph_3P)_2N]^+$ cation is used exclusively, a large amount of $[H_2W_2(CO)_8]^{2-}$ is produced, but when a mixed $[(Ph_3P)_2N]^+/Na^+$ system is used, little or no $[H_2W_2(CO)_8]^{2-}$ is isolated. Apparently, it is the precipitation of the insoluble $[(Ph_3P)_2N]^+{}_2[H_2W_2(CO)_8]^{2-}$ from THF that provides the driving force of the reaction.

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Registry No. $[(Ph_3P)_2N]_2{}^+[H_2W_2(CO)_8]^{2-}$, 81293-88-1; $[(Ph_3P)_2N]^+[W(CO)_5(I)]^-$, 81315-55-1; $[(Ph_3P)_2N]^+[W(CO)_4(BH_4)]^-$, 81293-90-5; $W(CO)_6$, 14040-11-0; $[(Ph_3P)_2N]^+[BH_4]^-$, 65013-26-5; $BH_3 \cdot THF$, 14044-65-6.

Supplementary Material Available: A listing of the squared structure factor amplitudes for the neutron diffraction analysis (28 pages). Ordering information is given on any current masthead page.

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Reinvestigation of the Reaction of *tert*-Butyllithium with Uranium Tetrachloride: Formation of Catalytically Active Uranium(III) Hydride Complexes

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The reaction of UCl_4 with t-C_4H_9Li in alkane solvents has been reinvestigated in detail by quantitative collection and identification of gaseous products and by spectral, analytical, and chemical characterization of the solid uranium products. Treatment of UCl_4 with 4 equiv of t-C_4H_9Li generates 1.5–1.8 equiv of 2-methylpropane and 2-methylpropene in a 2.5–3 to 1 ratio and a solid U(III) hydride product which readily dissolves in tetrahydrofuran (THF). As much as 1.7 equiv of the starting alkyllithium reagent can be recovered unreacted in this reaction, and hence the primary features of the reaction can be reproduced by using only 2 equiv of t-C_4H_9Li. Reaction of 1 equiv of t-C_4H_9Li with UCl_4 forms a U(III) product free of hydride. The reaction of n-C_4H_9Li with UCl_4 is similar. Detailed analysis of alkane/alkene ratios of gaseous products suggests that these systems abstract hydrogen from the alkane solvent possibly through a low-valent uranium center. The U(III) hydride product of these reactions is catalytically active in alkyne and alkene hydrogenation reactions conducted under mild conditions.

One of the more controversial reactions in organoactinide chemistry is the reaction of alkyllithium reagents with uranium tetrachloride (reaction 1). Since binary alkyl complexes are

$$UCl_4 + xRLi \rightarrow UR_x + xLiCl \qquad (1)$$

of central importance to the organometallic chemistry of any metal, and since for uranium there was the additional interest of utilizing such species in gaseous diffusion processes for isotope separation, it is not surprising that research on this synthetic approach to uranium alkyls dates back to efforts in the 1940s by Gilman and co-workers.[3] Neither those attempts nor others subsequently reported[4,5] were successful in providing a stable, characterizable homoleptic uranium alkyl.

In 1974, Marks and Seyam[6] described the reaction of alkyllithium reagents with uranium tetrachloride according to eq 2, where R = isopropyl, *n*-butyl, *tert*-butyl, methyl, 2-*cis*-2-butenyl, 2-*trans*-2-butenyl, and neopentyl.

$$UCl_4 + 4RLi \xrightarrow[\text{ether}]{\text{alkane or}} [UR_4] \rightarrow \text{products} + U \qquad (2)$$

For R = isopropyl, *n*-butyl, and *tert*-butyl, the "products" of reaction 2 were found to be the alkane and alkene appropriate for β-hydrogen elimination as exemplified for R = *n*-butyl in eq 3 and R = *t*-Bu in eq 4. The yield of butane plus butene was

$$UCl_4 + 4n\text{-}C_4H_9Li \xrightarrow{\text{hexane}} [U(n\text{-}C_4H_9)_4] \xrightarrow{120\text{ h}} 1.96CH_3CH_2CH_2CH_3 + 1.84CH_3CH_2CH{=}CH_2 + U \qquad (3)$$

$$UCl_4 + 4t\text{-}C_4H_9Li \xrightarrow{\text{pentane}} [U(t\text{-}C_4H_9)_4] \xrightarrow{96\text{ h}} 3.08(CH_3)_3CH + 0.88(CH_3)_2C{=}CH_2 + U \qquad (4)$$

reported to be 95% for the *n*-butyl reaction and 99% for the *tert*-butyl reaction based upon the amount of lithium reagent used (4 equiv). These results were taken as evidence that coordinatively unsaturated U(IV) alkyls readily decompose via β-hydrogen elimination. Although it was acknowledged in the original paper[6] that the excess of alkane over alkene in eq 4 suggested that another mechanism may be operative, in subsequent discussions only β-hydrogen elimination was mentioned.[7-14] For example, in a discussion[7] of uranium

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(1) Camille and Henry Dreyfus Teacher-Scholar.

(2) NSF Undergraduate Research Program Participant.

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alkyls, [U(n-Bu)$_4$] was described as follows: "the thermally unstable complex undergoes extensive (essentially quantitative) β elimination, as do all other tetraalkyls where β-hydrogens are present". Numerous discussions of this β-hydrogen elimination chemistry of homoleptic alkylactinide complexes are now in the literature.[7-15]

The stoichiometries of the above reactions were subsequently disputed by Sigurdson and Wilkinson,[16] who presented evidence for the synthesis of more highly coordinated species, UR_6^{2-}, according to eq 5 (R = methyl, (trimethylsilyl)methyl,

$$\mathrm{UCl_4 + 6RLi \xrightarrow{Et_2O} [Li(OEt_2)_4]_2[UR_6] + 4LiCl} \tag{5}$$

phenyl, and 2-[(dimethylamino)methyl]phenyl). The reaction of 4 equiv of CH_3Li with UCl_4, a synthesis conducted in accordance with Marks' conditions,[6] was reported to yield 50% unreacted UCl_4 and a 45% yield of $[Li(OEt_2)_4]_2[U(CH_3)_6]$. This work also was challenged subsequently.[11,17]

Since uranium favors high coordination numbers,[18,19] since ligand redistribution reactions are common in organouranium chemistry,[20] and since organouranium reactions are known in which the stoichiometric product is not favored compared to a more highly coordinated alternative,[21,22] the formation of complexes with coordination number greater than four in reaction 2 is certainly plausible. Indeed, Marks originally stated[6] and subsequently has emphasized[11,12] that "a discrete four-connected, monomeric geometry" for the product of reaction 2 was only claimed as "reasonable" and it was not possible to "rigorously exclude halide and solvent coordination".

Minimally, there appears to be agreement that a tetravalent uranium complex involving at least four alkyl groups is formed in these reactions. Certainly, there is agreement that the alkyluranium products are thermally unstable. The thermal decomposition (eq 2) is reported by Marks to generate uranium metal,[6,8,10] and this result has been used subsequently for synthetic purposes. The decomposition of mixtures of UCl_4 and 4 equiv of RLi has been used by Streitwieser and Miller[23] as a source of a "colloidal suspension of uranium" and by Cernia and Mazzei[24] as a source of "pyrophoric uranium metal" for the direct synthesis of uranocenes from 1,3,5,7-cyclooctatetraenes (reaction 6).

$$\mathrm{UCl_4 + 4RLi \xrightarrow{room\ temp} [U] \xrightarrow{C_8H_8} U(C_8H_8)_2} \tag{6}$$

In conjunction with our investigations of low-valent f-element chemistry[25-29] and the chemistry of *tert*-butyl f-element complexes,[30-32] we have investigated the reaction of $t\text{-}C_4H_9Li$ with UCl_4 on a preparative scale. Initially, we were interested in using the reaction of 4 equiv of $t\text{-}C_4H_9Li$ with UCl_4 in an alkane solvent as a source of metallic uranium.[6,23,24] Prior to using the black reaction product synthetically, we isolated this material by filtration and examined its solubility in several solvents. We found that the precipitate immediately formed an intensely colored purple solution in THF, a result quite unexpected based on the former formulation[6,8,10] of this material as a mixture of uranium metal and LiCl (eq 2). Equally surprising was the fact that the alkane filtrate, obtained when we first isolated the black reaction product by filtration, was highly reactive and apparently contained significant quantities of unreacted $t\text{-}C_4H_9Li$. Characterization of the purple THF solution by far-infrared, near-infrared, and visible spectroscopy (vide infra) further suggested that this reaction was more complex than eq 2 and that a detailed investigation would be needed to better understand this interesting system.

Although we agree with previous workers that this system is complex and not readily amenable to definitive characterization, we present here new evidence that this reaction can proceed in a manner which is substantially different from that previously assumed.[6] In our hands we find that (1) the net reaction of UCl_4 with $t\text{-}C_4H_9Li$ in alkanes involves approximately 2 equiv of $t\text{-}C_4H_9Li$ only, (2) the reaction product contains primarily uranium(III), (3) a hydride is present in the reaction product, and (4) the reaction product functions as a heterogeneous catalyst for the hydrogenation of unsaturated hydrocarbons.

Results

General Procedure. As a mixture of $t\text{-}C_4H_9Li$ and UCl_4 in alkane is warmed to room temperature from −78 °C over several hours, a reaction occurs which generates a transient brown color and ultimately a black precipitate along with 2-methylpropane and 2-methylpropene, as previously reported.[6] We have studied this reaction in several ways: by monitoring the gases evolved during the reaction, by filtering the reaction mixture and analyzing the alkane filtrate by hydrolysis, and by characterizing the black precipitate by hydrolysis, elemental analysis, spectroscopy, and reaction chemistry. The reactions were conducted by two general methods. For those experiments in which quantitative data on gas evolution were obtained, the reactions were carried out in a specially constructed vacuum-tight reactor (described in the Experimental Section) which could be directly attached to a Toepler pump. With this reactor, the previously used[6] septum/syringe techniques and their inherent limitations could be avoided in the quantitative collection of the gases produced both during the re-

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Table I. Gaseous Products of *n*-RLi/UCl_4 Reactions and Hydrolytic Decompositions

		C_4 hydrocarbons evolved during reacn		alkane formed by hydrolysis of filtrate[a,b]	gases formed by deuterolysis of black insoluble products	
R	*n*	amt[a,b]	alkane/alkene ratio		HD[a]	D_2[a]
t-C_4H_9	4	1.5–1.8	(2.5–3)/1	1–1.7	0.75–0.95	0.63–0.68
t-C_4H_9	2	1.3–1.33[c]	(1.5–2)/1	0.09	0.25–0.40	0.50–0.56
t-C_4H_9	1	0.75	1.4/1	0	0	0.45
n-C_4H_9	4	1.6	1.2/1	2.1	0.65	0.63

[a] Amounts given in equiv/equiv of uranium. [b] The total amount of C_4 hydrocarbons analyzed was always greater than 75% of the starting amount. [c] 2,2,3,3-Tetramethylbutane [0.1 equiv (0.2 equiv of C_4)] was found when the liquid phase was analyzed.

action and upon subsequent hydrolysis. Octane rather than pentane was used as a solvent to facilitate quantitative separation of 2-methylpropane and 2-methylpropene by Toepler pump. For those experiments in which gases were not collected, reactions were carried out in pentane in Schlenk vessels and the products were isolated for further study in a glovebox. Since sublimed, crystalline *t*-C_4H_9Li was used in these reactions, septum/syringe techniques again could be avoided. The UCl_4/*t*-C_4H_9Li system was studied in a variety of stoichiometries as described in the following sections.

4-Equiv Reactions. A. Low Temperature. The reaction of *t*-C_4H_9Li with UCl_4 was examined at −78 °C to determine if any reaction occurred at low temperature, i.e., to determine if a uranium alkyl of any kind was formed at −78 °C. Accordingly, 4 equiv of *t*-C_4H_9Li was added to UCl_4 in pentane at −78 °C and stirred for 15 h at this temperature. The reaction was quickly vacuum filtered, and the green precipitate was washed with chilled pentane (−78 °C). The solvent was removed from the colorless pentane solution, octane was added, and the solution was hydrolyzed to form 95% of the 2-methylpropane expected from 4 equiv of *t*-C_4H_9Li. The green solids were dissolved in THF, spectrophotometrically analyzed, and found to contain >99% of the uranium initially used. Hence, *t*-C_4H_9Li does not react with UCl_4 at −78 °C to form a uranium alkyl which decomposes at a higher temperature. Instead, the reaction observed as such a solution warms to ~−50 °C is the initial reaction of *t*-C_4H_9Li with UCl_4.

B. Room Temperature. In a typical reaction, 4 equiv of *t*-C_4H_9Li was added to UCl_4 in octane at −196 °C. The frozen mixture was allowed to melt in a −45 °C slush bath over several hours, and then the reaction was warmed to room temperature. The mixture was stirred for 5–6 days, a reaction time which is 1–2 days in excess of that originally reported.[6,33] After the gas collection reactor was attached to a Toepler pump, the 2-methylpropane and 2-methylpropene evolved in this reaction were collected and analyzed by GC. As shown in Table I, alkane to alkene ratios of 2.5–3/1 were observed in qualitative agreement with the literature ratio of 77%/22% = 3.5 shown in eq 4.[6] However, the total amount of C_4 hydrocarbons evolved was only 1.5–1.8 equiv compared to the expected and previously reported 4 equiv.[6,7,34,35]

After the evolved gases were collected and analyzed, a high-vacuum filtration apparatus was attached to the gas collection reactor and the octane solution was separated from the black reaction product by filtration. Hydrolytic decomposition of the light yellow octane filtrate produced 1–1.7[37] equiv of 2-methylpropane (Table I), indicating that a substantial amount of unreacted *t*-C_4H_9Li had remained in the octane. Analogous pentane solutions, similarly obtained from 4-equiv reactions in which evolved gases were not collected, produced comparable amounts of 2-methylpropane upon hydrolysis. Further evidence that unreacted *t*-C_4H_9Li was present in the alkane filtrates was obtained by removing the alkane from these solutions. Substantial amounts of a yellow oil were obtained and found by infrared spectroscopy to contain primarily *t*-C_4H_9Li.

The black solids remaining in the gas collection reactor were analyzed by condensing D_2O into the reactor and collecting the volatile products by Toepler pump. The condensable gases consisted of trace amounts of 2-methylpropane and about 0.1 equiv of 2-methylpropene. The component of the black solids, which contained the 2-methylpropene precursor could apparently be separated from the main black product, since in reactions in which the black solids were isolated in a glovebox and washed with diethyl ether a brown solution was obtained which formed comparable amounts of 2-methylpropene upon hydrolysis.

The noncondensable gases formed by deuterolysis of the black solids in the gas collection reactor consisted of HD and D_2. For each equivalent of uranium in the system, approximately 0.75–0.96 equiv of HD and 0.63–0.65 equiv of D_2 were formed. Color changes accompanied these deuterolyses. First, the black precipitate changed to a purple color, and subsequently, at a slower rate, a clear green solution was formed. Deuterolysis of the black reaction products which were obtained from reactions conducted in Schlenk flasks, and which were isolated in a glovebox, gave similar yields of D_2 (0.5–0.66 equiv/equiv of uranium) but rather less HD (0.3 equiv). The fact that only 0.65 equiv of D_2 was formed/equiv of uranium suggested that deuterolysis did not involve a uranium metal to U(IV) conversion, which would have liberated 2 equiv of

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(33) This reaction time was originally chosen because it exceeds the originally reported reaction time.[6] In some cases, after product gases were collected at the end of 5–6 days, the reactions were allowed to run an additional 3–4 days. Gaseous products were collected daily during the additional reaction time but amounted to less than 0.05 equiv of C_4 hydrocarbons.

(34) It is conceivable that the percentages reported as yields by Marks and Seyam[6] are really the percentages of gaseous products observed rather than the percentages of stoichiometrically expected amount of gaseous products as claimed in the paper. For reactions run to completion, the total yields of gaseous products reported are very high. The *lowest* total percentage found was 96.4%. In three cases, 100% yields were reported including one reaction in which the gaseous products were methane and ethane. Given the inherent limitations of their analytical methods which involved sampling the gases over solutions in septum capped vessels, the total reported yields seem too high to represent stoichiometric amounts of alkane and alkene detected. Nevertheless, in a subsequent article,[7] the yields were reported as "essentially quantitative".

(35) Professor Marks has informed us that the success of a RLi/UCl_4 reaction is dependent on the prior treatment of UCl_4 and has suggested that our UCl_4 crystallite size and stirring methods for this heterogeneous reaction may prevent "complete" reaction. In Marks' original paper[6] commercial UCl_4 was finely pulverized and dried with $SOCl_2$ before use. We have been dissatisfied with the purity of commercal UCl_4 and prefer to make our UCl_4 from the oxide using hexachloropropene.[36] Hence, our study differs from Marks' study in this regard. However, our UCl_4 was characterized by complexometric analysis prior to use, was used as a powder of less than 100 mesh, and was found to react every time to form a black precipitate as described by Marks in NMR tube experiments.[6] We also find that the first equivalent of *t*-C_4H_9Li quantitatively converts all of the U(IV) to U(III) (vide infra); hence unreacted UCl_4 is not present after the reaction of the first equivalent of *t*-C_4H_9Li.

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D_2/equiv of uranium, but rather the conversion of U(III) or some U(II) species to U(IV). The formation of HD in the deuterolysis reaction indicates the presence of a hydride in the UCl_4/t-C_4H_9Li reaction product. The fact that smaller amounts of HD are sometimes obtained from samples manipulated in the glovebox suggests that the hydridic component of this product decomposes with prolonged storage or handling.

In summary, the reaction of 4 equiv of t-C_4H_9Li with UCl_4 in alkanes generates a total amount of 2-methylpropane and 2-methylpropene which never exceeds 2 equiv. Most of the remaining 2 equiv of t-C_4H_9Li originally added is found unreacted in the alkane filtrate. Deuterolysis of the black reaction product indicates that the uranium has been reduced to a lower valent state, but not to uranium metal, and that a hydride moiety is present.

2-Equiv Reactions. Since it appeared that only 2 equiv of t-C_4H_9Li was actually reacting with UCl_4, some 2-equiv reactions were examined. As expected, the results are similar (Table I).

When reaction mixtures containing 2 equiv of t-C_4H_9Li/equiv of UCl_4 in octane (or pentane) were allowed to warm from −78 °C to room temperature, the initially green suspensions turned brown and ultimately black. After several days of stirring at room temperature, approximately 1.3 equiv of 2-methylpropane and 2-methylpropene were isolated in ratios of 1.5–2/1. Longer reaction times favored higher alkane to alkene ratios, suggesting the possibility that the initially formed 2-methylpropene was being hydrogenated in the course of the reaction. In one 2-equiv reaction, the octane solvent also was examined for organic decomposition products and 0.1 equiv of the *tert*-butyl dimer, 2,2,3,3-tetramethylbutane, was found (none was present in the original octane solvent). Filtration of the 2-equiv reactions after 6 days gave alkane solutions, which upon hydrolysis formed only trace amounts of 2-methylpropane as expected. Deuterolysis of the black solids obtained after filtration produced 0.25–0.40 equiv of HD and 0.50–0.56 equiv of D_2/equiv of uranium. In one case, the deuterolytic decomposition of the reaction product was analyzed in two stages defined by the color changes which accompany this reaction (as well as the hydrolytic decomposition of the 4-equiv product; vide supra). D_2O was condensed onto the black reaction product at −196 °C. Upon being warmed to room temperature, the mixture turned purple and evolved 0.53 equiv of gas/equiv of uranium. The gas analyzed as 60% HD and 40% D_2. After standing overnight, the mixture had turned green and an additional 0.4 equiv of gas was collected. This second volume of gas analyzed as 20% HD and 80% D_2. The total yield of HD and D_2 was 0.40 and 0.53 equiv, respectively. These results are consistent with a scheme involving the fast reaction of a hydride with D_2O to form HD and a slower oxidation of purple U(III) to green U(IV) with generation of D_2. Overall, the results of the 2-equiv reactions are in qualitative agreement with the 4-equiv reactions.

1-Equiv Reactions. A reaction involving equimolar amounts of t-C_4H_9Li and UCl_4 in octane was carried out in a Schlenk flask with a procedure analogous to that outlined above. Like the other reactions, the original green suspension changed to a darker color. After 6 days, however, the suspension was observed to be redder than the products of 2- or 4-equiv reactions. After filtration, a red-purple solid was obtained. The octane filtrate was hydrolyzed giving only traces of 2-methylpropane, again as expected. In contrast to the black products obtained from 2- and 4-equiv reactions, however, the red-purple solid isolated from this reaction formed *no* HD but only D_2 (0.45 equiv/equiv of uranium) upon deuterolysis. Consistent with this result, treatment of the red-purple precipitate with CH_3I formed no CH_4, whereas a black reaction product formed from excess t-C_4H_9Li and UCl_4 reacted with CH_3I to form around 0.7 equiv of CH_4/equiv of uranium. Hence, the hydride-containing material in these products appears to be associated with the action of a *second equivalent* of t-C_4H_9Li on UCl_4.

A 1-equiv reaction was also run in the gas collection reactor. After 2 days, 0.75 equiv of C_4 hydrocarbons was collected (Table I) with a 2-methylpropane to 2-methylpropene ratio of approximately 1.4/1. Subsequently, an additional 3 equiv of t-C_4H_9Li was added to this reaction and gas evolution monitored. A total of 1.8 equiv of C_4 hydrocarbons was collected and shown by analysis to have an alkane/alkene ratio of 1.5. Deuterolysis of the octane filtrate at the end of the reaction generated 1.8 equiv of 2-methylpropane, formed from the unreacted t-C_4H_9Li. Hence, the overall results of this 4-equiv reaction, in which the first equivalent of t-C_4H_9Li was added separately, were consistent with 4-equiv reactions in which the 4 equiv were added all at once. One difference between these reactions was the alkane/alkene ratio: reactions unperturbed by intermittent gas collection contained larger amounts of 2-methylpropane. This was another indication that hydrogenation of the alkene may occur under the reaction conditions.

Analysis of Solid Products. In addition to the deuterolytic experiments discussed above, the solids obtained from the reaction of t-C_4H_9Li with UCl_4 were characterized by far-infrared spectroscopy, elemental analysis, and solubility studies. Marks and Seyam had previously examined the far-infrared spectra of the solid residues of the 4/1 RLi/UCl_4 reactions "in several instances" and had observed an absorbance at 250 cm^{-1}, but only in "partially decomposed samples".[6] This was assigned to a U(IV)–Cl stretch, suggesting that some chloride coordination persisted during the decomposition. For fully decomposed samples, the far-infrared region was said to be featureless. We find that the solid products obtained from 1-, 2- or 4-equiv of t-C_4H_9Li/equiv of UCl_4 reactions run for at least 4 days show featureless infrared spectra except for a broad, poorly defined band at 310 cm^{-1} in the far-infrared region. We are uncertain how to assign this band, but it seems too high to be attributed to U(III)–Cl[38] or U(IV)–Cl stretches. In the case of a 4-equiv t-C_4H_9Li reaction interrupted after 1 day, the isolated solid also showed a broad band centered at 240 cm^{-1}. Interruption of a 1-equiv reaction after 1 day also gave a solid which exhibited an absorption at 240 cm^{-1}, but in this case the 310-cm^{-1} band was barely visible, appearing only as a very weak shoulder. Since the optical spectrum of this latter sample in THF exhibited no U(IV) absorptions and only U(III) bands, the 240-cm^{-1} absorption may arise from a U(III) intermediate rather than from unreacted UCl_4.

Complete elemental analysis of the black solids produced in a 4-equiv reaction indicated a Li/U ratio of approximately 2/1, consistent with approximately 2 equiv only of t-C_4H_9Li being involved in the reaction. Specifically, after alkane and ether wash, this sample had an analysis consistent with the stoichiometry 2/1/0.25 LiCl/UCl_2H/Et_2O. Anal. Calcd: U, 57.60; Cl, 34.31; Li, 3.36; C, 2.90; H, 0.85; O, 0.97. Found: U, 57.34; Cl, 34.59; Li, 3.50; C, 2.94; H, 0.67, O, 0.96, by difference. This formula is also consistent with the presence of U(III) and 1 equiv of hydride in the sample. (Note that deuterolysis formed up to 0.95 equiv of HD/equiv uranium (Table I).)

The solid products isolated from all of the reactions were insoluble in hydrocarbon solvents and sparingly (<5%) soluble in diethyl ether but rapidly dissolved (>90%) in THF to form intense purple solutions. The near-infrared–visible spectrum of these solutions clearly showed the presence of U(III). The

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(38) Barnard, R.; Bullock, J. I.; Gellatly, B. J.; Larkworthy, L. F. *J. Chem. Soc., Dalton Trans.* **1972**, 1932–1938.

spectra are almost identical with the spectrum of $UCl_3(THF)_x$ shown in a paper by Moody and Odom[39] (see Experimental Section). The purple solid obtained by removing THF from the solution under high vacuum at room temperature had an infrared spectrum containing absorptions at 1040 and 890 cm^{-1}, indicating coordinated THF.[32] Consistent with this, spectrophotometric analysis of the uranium content in the purple solid indicated it had decreased from ca. 57% (vide supra) to 44%. Deuterolysis of the purple solids obtained after THF extraction generated HD and D_2 in a ratio similar to that found for *t*-C_4H_9Li/UCl_4 reaction products prior to THF extraction.

Reaction of *n*-C_4H_9Li with UCl_4. The reaction between *n*-C_4H_9Li and UCl_4 was briefly studied to determine whether or not the above results were limited only to *t*-C_4H_9Li. Hence, in the greaseless gas collection reactor described previously, UCl_4 and 4 equiv of *n*-C_4H_9Li were mixed at −78 °C in octane and allowed to warm to room temperature. During this period the green suspension turned black. After 6 days at room temperature, 1.6 equiv of C_4 hydrocarbons had evolved, comprised of butane and 1-butene in a ratio of 1.2/1 (Table I). The mixture was filtered to give a brown octane filtrate and black solids. Upon hydrolysis the filtrate evolved 2.1 equiv of butane.

The solid black reaction product exhibited a far-infrared absorption at 310 cm^{-1} as was found in the *t*-C_4H_9Li/UCl_4 products. The *n*-C_4H_9Li/UCl_4 product also displayed similar solubility; it was insoluble in hydrocarbons and diethyl ether but dissolved rapidly in THF to form a deep purple solution. The near-infrared visible spectrum of this solution again showed the presence of U(III), comparing well with the published spectrum of $UCl_3(THF)_x$.[39] Deuterolysis of the solids formed 0.65 equiv of HD and 0.63 equiv of D_2 (Table I). As in the *t*-C_4H_9Li reaction, a small amount of alkane, 0.1 equiv of *n*-butane, was also generated by deuterolysis of the solids.

Therefore, the essential features of the *t*-C_4H_9Li/UCl_4 system are reproduced with *n*-C_4H_9Li/UCl_4: approximately *2* equiv of the alkyllithium reagent was consumed under the analogous conditions employed and the solid products obtained showed hydridic character and appeared to contain U(III).

Discussion

General Data. It is clear that the reactions of *t*-C_4H_9Li and *n*-C_4H_9Li with UCl_4 in our hands[35] do not occur as originally written in ref 6, i.e., by formation of thermally unstable $U(C_4H_9)_4$ species at low temperatures which, upon warming to room temperature, decompose to form 4 equiv of C_4 hydrocarbons and uranium metal.

First, our reaction does not require 4 equiv of RLi, as evidenced by the recovery of almost 2 equiv of unreacted *t*-C_4H_9Li or *n*-C_4H_9Li at the end of the reaction. The main features of the reaction can be reproduced with only 2 equiv of *t*-C_4H_9Li and elemental analysis of the solid products indicates a 2/1 lithium to uranium ratio. Quantitative collection of the gaseous decomposition products yielded slightly less than 2 equiv of C_4 hydrocarbons, consistent with the fact that the reaction involves essentially 2 rather than 4 equiv of RLi.

Second, the solid product obtained after the reaction has proceeded for 5–6 days is not uranium metal but rather is substantially U(III) and contains significant amounts of hydride. All of the uranium appears to be reduced to the +3 state even after reaction of 1 equiv of RLi, but the appearance of hydride is associated only with the reaction of a second equivalent. The presence of U(III) is demonstrated by the deuterolysis reactions of the solid products obtained from 1-, 2-, or 4-equiv reactions, which yield 0.45–0.65 equiv of D_2/equiv of uranium accompanied by the appropriate color changes (eq 7). In contrast, 2 equiv of D_2 would be expected

$$\underset{\text{purple}}{U^{3+}} + D_2O \rightarrow \underset{\text{green}}{U^{4+}} + OD^- + {}^1/_2D_2 \qquad (7)$$

if the product contained uranium only as the metal. In addition, these reaction products readily dissolve in THF to form purple solutions whose near-infrared visible spectra are characteristic of U(III).[40] The presence of hydride is confirmed by the formation of HD upon deuterolysis of 2- or 4-equiv products and by the formation of CH_4 when these products are treated with CH_3I.[43]

These data illustrate the gross characteristics of this RLi/UCl_4 system and can be rationalized to some extent by a series of simple homogeneous reactions well-established in organometallic chemistry. Given the complexity and heterogeneity of this reaction system, however, the obtainable data allow us to present only a reasonable explanation for the observed results rather than a definitive mechanism.

The formation of U(III) upon reaction of *1 equiv* of RLi with UCl_4 may result from direct reduction of UCl_4 by electron transfer (eq 8; this and the following reactions are written

$$UCl_4 + RLi \rightarrow UCl_3 + LiCl + R\cdot \qquad (8)^{44}$$

stoichiometrically and are not necessarily meant to imply that free UCl_3 is present[44]). The resulting alkyl radical would form alkane, R–H, and alkene, R(–H), by disproportionation, and R–R by dimerization. For *tert*-butyl radicals in solution, a disproportionation to dimerization ratio of 7.2[46] has been reported. This ratio is consistent with the observed excess of C_4 hydrocarbon products (80%) compared to the 2,2,3,3-tetramethylbutane found.[47]

The data obtained from the *n*-C_4H_9Li reaction do not match the reaction sequence in eq 8 as well as those obtained from the *t*-C_4H_9Li reaction. *n*-Butyl radicals have disproportionation/dimerization ratios of 0.13–0.14.[46] Hence, if the first equivalent of *n*-C_4H_9Li reacts to form *n*-butyl radicals in a process analogous to eq 8, only about 0.1 equiv of C_4 hydrocarbons should be generated. With allowance for quantitative reaction of the second equivalent, a maximum of 1.1 equiv of C_4 products would be expected. In fact, 1.6 equiv of C_4 hydrocarbons are found in the *n*-C_4H_9Li reaction, suggesting a

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(39) Moody, D. C.; Odom, J. D. *J. Inorg. Nucl. Chem.* **1979**, *41*, 533–535.

(40) It is conceivable that if the black reaction product is uranium metal, the purple U(III) solution could be generated by the uranium metal rapidly attacking THF to form a soluble U(III) complex of the THF fragments. Although unlikely, this possibility was tested by the following experiment: THF was condensed onto the black reaction product of a 4-equiv reaction in an evacuated vessel, the purple solution was stirred for several days, and the presence of volatile THF decomposition products was checked by Toepler pump. Neither ethene[41] nor any other organics reportedly formed in metal decompositions of THF[42] was observed. No evidence of the $^-OCH{=}CH_2$ anion[41] was found in the infrared spectra of the purple material.

(41) Bates, R. B.; Kroposki, L. M.; Potter, D. F. *J. Org. Chem.* **1972**, *37*, 560–562.

(42) Sobota, P.; Pluzinski, T.; Jezowska-Trzebiatowska, B. *J. Organomet. Chem.* **1980**, *185*, 69–74.

(43) After this manuscript was originally submitted, further evidence for the existence of U(III) hydride complexes was presented by T. J. Marks and V. W. Day, who described a (bis(dimethylphosphino)ethane)uranium(III) hydride complex at the 15th Rare Earth Research Conference, Rolla, MO, June 1981.

(44) Given the high solubility of these uranium products in THF (cf. the low solubility of UCl_3[38,45]), double salt formulations such as Li_nUCl_{3+n} may be more appropriate. Double salts of U(III) are known.[38]

(45) Barnard, R.; Bullock, J. I.; Gellatly, B. J.; Larkworthy, L. F. *J. Chem. Soc., Dalton Trans.* **1973**, 604–607.

(46) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395–4404.

(47) The formation of R–R, although generally taken as an indication of radical involvement, could also result from a reductive elimination step which generates UCl_2 (vide infra).

$$UCl_4 \xrightarrow[-2LiCl]{2RLi} UCl_2R_2 \rightarrow R_2 + UCl_2$$

This alternative cannot be ruled out but would be a minor reaction pathway at best considering the small amount of R–R observed.

reaction other than eq 8 may be operative.

An alternative reaction sequence for the reaction of the first equivalent of RLi with UCl_4 is (a) metathesis to form an alkyl complex (eq 9), (b) β-hydrogen elimination to form a U(IV) hydride (eq 10), and (c) subsequent reductive elimination of H_2 or RH to form U(III) (eq 11 and 12).

$$UCl_4 + RLi \rightarrow UCl_3R + LiCl \qquad (9)^{48}$$

$$UCl_3R \rightarrow UCl_3H + R(-H) \qquad (10)^{48}$$

$$2UCl_3H \rightarrow 2UCl_3 + H_2 \qquad (11)^{48}$$

$$UCl_3H + UCl_3R \rightarrow 2UCl_3 + RH \qquad (12)^{48}$$

It is interesting to note that the reduction of U(IV) by an alkyllithium to form U(III) has already been reported in the literature. Hence, t-C_4H_9Li has been shown to reduce the U(IV) organometallic $(C_5Me_5)_2UCl_2$ to a U(III) species: $[(C_5Me_5)_2UCl]_3$.[49] Unfortunately, no mention was made of the gaseous products of the reaction and it is uncertain whether this reaction involves reduction by electron transfer and radical formation (eq 8) or β-hydrogen elimination and subsequent decomposition of a chloro–uranium(IV) hydride species.

Our data on the C_4H_9Li/UCl_4 systems do not allow us to distinguish easily between the two pathways to U(III) described above. Indeed, it is possible that one mechanism is predominant for t-C_4H_9Li and the other for n-C_4H_9Li. Since t-C_4H_9Li is a stronger reducing agent,[50] the electron-transfer reaction (eq 8) may be favored in that case and the alternative reaction sequence may be more important for n-C_4H_9Li. Precedent for both possibilities exists in the literature as demonstrated by the following examples. *tert*-Butyllithium reduction of the organolanthanide complex $[(C_5H_5)_2YbCl]_2$ offers evidence in support of eq 8.[32] The trivalent ytterbium complex is rapidly reduced by t-C_4H_9Li at −78 °C to form the divalent $(C_5H_5)_2Yb(THF)$.[29] 2-Methylpropane and 2-methylpropene are formed in a 2.4/1 ratio which is close to that observed in the t-C_4H_9Li/UCl_4 reactions. The rapidity of the ytterbium reaction, compared to similar β-hydrogen elimination reactions of lutetium[32] and erbium, in which the hydride is isolated,[51] suggests that the reduction is occurring by electron transfer (analogous to eq 8) rather than by β-hydrogen elimination to form an Yb(III)–H which decomposes to Yb(II)[29] (analogous to eq 9–12).

Precedent for the formation of U(III) by decomposition of a U(IV)–H (eq 11) has been presented in two studies. The uranium(IV) hydride $[(C_5Me_5)_2UH_2]_2$ is observed to lose 1 equiv of H_2 at room temperature.[52] The uranium(IV) chlorohydride $[(C_5Me_5)_2UClH]_2$ presumed to form when $[(C_5Me_5)_2UH_2]_2$ and $[(C_5Me_5)_2UCl_2]_2$ are mixed, decomposes to form the trivalent $[(C_5Me_5)_2UCl]_3$.[49] Another example of an f-element hydride which decomposes with reduction when a lower valent state is accessible is the apparent instability of the intermediate $(CH_3C_5H_4)_2YbH$ (formed by hydrogenolysis of $[(CH_3C_5H_4)_2YbCH_3]_2$) with respect to $(CH_3C_5H_4)_2Yb$.[29]

In any case, it is clear that in the present system, the first equivalent of RLi generates U(III) quantitatively, and that in the 2- and 4-equiv reactions, the subsequent alkylation chemistry involves uranium in the +3 oxidation state. Metathesis (eq 13) followed by β-hydrogen elimination from the uranium(III) alkyl (eq 14) gives a uranium(III) hydride product in qualitative agreement with our data.

$$UCl_3 + RLi \rightarrow UCl_2R + LiCl \qquad (13)^{48}$$

$$UCl_2R \rightarrow UCl_2H + R(-H) \qquad (14)^{48}$$

Regardless of what simple rationale may account for the gross characteristics of these RLi/UCl_4 systems, it should be emphasized that these are heterogeneous reactions in which several reaction mechanisms can operate simultaneously. For instance, as noted previously,[48] the presence of LiCl in these reactions could lead to double salt addition products such as $LiUCl_4$, Li_2UCl_4R, and Li_2UCl_4H in addition to or instead of UCl_3, UCl_2R, and UCl_2H. Indeed, our detailed observations suggest that reactions 8–14 are too simple to completely describe these UCl_4/RLi systems. The observed alkane/alkene ratios are particularly informative in this regard. Reaction of 1 equiv of RLi by either reaction 8 or reactions 9–12 followed by reaction of a second equivalent via reaction 13 and 14 should yield an excess of alkene over alkane. This is contrary to the observed ratios (Table I) in which alkane predominates. Although we have shown (vide infra) that the hydride products of these reactions have hydrogenation capability, for the 2-equiv reactions, the above mechanisms do not provide enough "hydrogen" to account for the alkane/alkene ratios observed. Specifically, reaction of the first equivalent of RLi (via eq 8 or eq 9–12) should lead to a 1:1 alkane to alkene ratio.[53] Reaction of the second equivalent according to eq 13 and 14 should form exclusively alkene along with an equivalent amount of hydride. Even if all the uranium(III) hydride formed in reaction 14 were consumed in alkene hydrogenation, only half of the alkene could be hydrogenated. This would also give a 1/1 alkane to alkene ratio. Since 0.25–0.95 equiv of hydride is found in the final products of these reactions, the uranium(III) hydride is clearly not fully consumed in hydrogenation of the alkene. Hence, the hydrogen necessary to achieve the observed excess of alkane over alkene must arise elsewhere.

Possible sources of the "extra" hydrogen are suggested by our observation that higher alkane/alkene ratios are associated with 4-equiv (i.e., "excess" RLi) reactions and with reactions involving longer uninterrupted stirring times. These data suggest that the excess alkyllithium reagent and/or the solvent could be the "hydrogen" source. Both possibilities are supported by the detailed stoichiometries observed in these reactions.

In 4-equiv reactions, we generally recover less than a full 2 equiv of unreacted RLi (Table I). In addition, 4-equiv reactions generally provide more hydride in the final product. This suggests that an additional pathway involving RLi operates and hence some portion of the "excess" RLi in 4-equiv reactions functions as the source of hydride.

Activation of hydrogen in solvent molecules could occur in the following way. A hydrogenation cycle involving the uranium(III) hydride product must include a reductive elimination step in which U(II) is formed (eq 15). The presence of some

$$UCl_2H + \text{alkene} \rightarrow UCl_2R \xrightarrow{UCl_2H} 2UCl_2 + RH \qquad (15)$$

small amount of a lower valence state of uranium in the product is indicated by the fact that the deuterolyses of 2- and 4-equiv (but *not* 1-equiv) reaction products give slightly more than the $^1/_2$ equiv of D_2 expected for a U(III) → U(IV)

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(48) The uranium species in these equations may exist as double salts formed by formal addition of LiCl[44] or LiR (cf. Wilkinson's Li_xUR_{4+x}[16]).

(49) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075–5078.

(50) Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741–5748 and references therein.

(51) Evans, W. J.; Wayda, A. L.; Bloom, I.; Coleson, K. M., "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, Georgia, March, 1981; American Chemical Society: Washington, D.C., 1981; INOR 219. Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008–2014; 2015–2017.

(52) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939–3941.

(53) Radical abstraction of hydrogen from solvent could increase the alkane to alkene ratio slightly.

oxidation. It is expected that the U(II) formed according to reaction 15 would be quite reactive[54,55] and would be capable of abstracting hydrogen from solvent to form a uranium(III) hydride, hence maintaining a hydrogenation cycle. Activation of solvent hydrogen by a U(III) center is also possible, although, at present, known reactions in which C–H is attacked in the presence of a U(III) complex are limited to C–H bonds adjacent to oxygen.[56,57]

In summary, although the main features of the UCl_4/RLi system, where R = t-C_4H_9 and n-C_4H_9, can be rationalized according to eq 8–14, this description is incomplete. Additional reaction pathways exist in these systems. It should also be noted that when UCl_4 reacts with alkyllithium reagents which are weaker reducing agents and which lack β-hydrogen atoms, and when such reactions are conducted in strongly coordinating solvents, chemistry differing from that observed here may occur.[16]

Further Reaction Chemistry. The above analysis of the UCl_4/RLi reactions based on our data indicated that the uranium in the product was not in the elemental state as was previously postulated.[6] Nevertheless, these RLi/UCl_4 reaction products had been used as the source of uranium, presumed to be the metal, in uranocene syntheses.[23,24] Finely divided uranium metal is known to react at 150 °C with 1,3,5,7-cyclooctatetraene (1,3,5,7-C_8H_8) to form uranocene[58] (eq 16),

$$2C_8H_8 + U \rightarrow U(C_8H_8)_2 \qquad (16)$$

and a similar reaction scheme had been assumed to apply when RLi/UCl_4 products were employed.[23,24] To resolve this inconsistency, we examined the reaction of the black product of a 4/1 t-C_4H_9Li/UCl_4 reaction with 1,3,5,7-C_8H_8 in an evacuated vessel so that gases could be monitored. The black product reacts with 1,3,5,7-C_8H_8 at room temperature to form $U(C_8H_8)_2$ in low yield (~5%[59]). More importantly, this reaction generates 1.7 mol of H_2 for every 1 mol of $U(C_8H_8)_2$ formed, suggesting that our synthesis occurs by a route such as reactions 17 and 18 rather than by eq 16.[60] The reaction

$$4\text{"H}^-\text{"} + 2C_8H_8 \rightarrow 2H_2 + 2C_8H_8^{2-} \qquad (17)$$

$$2C_8H_8^{2-} \xrightarrow{U^{3+}} U(C_8H_8)_2 \qquad (18)$$

of UBr_3 and UI_3 with $C_8H_8^{2-}$ previously has been shown to form uranocene[61] (reaction 18). Hence, the reported[23,24] formation of uranocene by addition of 1,3,5,7-C_8H_8 to a 4/1 RLi/UCl_4 reaction mixture (which actually contains U(III)H and approximately 2 equiv of unreacted RLi[59]) may occur by reactions 17 and 18. Furthermore, the unreacted 2 equiv of RLi may provide an additional reaction pathway. The excess RLi may reduce 1,3,5,7-C_8H_8 to $Li_2C_8H_8$ which then reacts with U(III) to form uranocene.[61] In support of this scheme, Streitwieser and Miller have recently reported[23b] that "substantially better" yields of uranocene are obtained by adding 1,3,5,7-C_8H_8 at −78 °C to the mixture of UCl_4 and n-C_4H_9Li in THF rather than by adding the 1,3,5,7-C_8H_8 to the decomposed n-C_4H_9Li/UCl_4 product at room temperature. Hence, the previously reported uranocene syntheses are not inconsistent with our results and can be explained without postulating the presence of uranium metal.

The reactivity of the black products of the 4/1 t-C_4H_9Li/UCl_4 reaction with cyclopentadiene, C_5H_6, and 3,3-dimethyl-1-butyne ($HC\equiv CC(CH_3)_3$) further supports this scheme. Hydrogen is evolved in both of these reactions, and infrared absorptions characteristic of the expected anions, $C_5H_5^-$ (1010 and 750 cm^{-1}) and $C\equiv CC(CH_3)_3^-$ (2040 cm^{-1}), are observed in the products. In comparison, uranium metal reacts with C_5H_6 only under special conditions. Finely divided uranium prepared by decomposition of uranium hydride does not react with C_5H_6 even under conditions which allow direct synthesis of uranocene.[58] Only uranium prepared by subliming mercury from U(Hg) has been reported to react with C_5H_6.[62]

The utility of the 1-equiv reaction of t-C_4H_9Li with UCl_4 as a source of U(III) was investigated by using this product to prepare $U(C_5H_5)_3$. Addition of 3 equiv of NaC_5H_5 to the purple THF solution of a 1-equiv t-C_4H_9Li/UCl_4 reaction product causes an immediate color change to red brown. After overnight stirring, the THF is removed and the product is extracted with benzene to give a 40% yield of $U(C_5H_5)_3$(THF). This synthesis is superior to previous preparations in terms of reaction/workup time and availability of starting materials.[62–64]

Catalytic Studies. The presence of hydride in the 4/1 t-C_4H_9Li/UCl_4 reaction product and the enhanced amounts of 2-methylpropane compared to 2-methylpropene in reactions stirred unperturbed for several days suggested that this system had the capacity to hydrogenate unsaturated organic molecules. Indeed, when 2-methylpropene was added to an octane slurry of the black reaction product, the alkene was converted to 2-methylpropane at a slow rate. When hydrogen was added to this system, 40% of the 2-methylpropene was converted to 2-methylpropane in 4 days.

The catalytic reactivity of the 4/1 t-C_4H_9Li/UCl_4 reaction product with 3-hexyne and 1-hexene was subsequently examined. 3-Hexyne is converted to 3-hexene and hexane in a catalytic reaction at a rate of 0.001 turnover/min. The rate for catalytic hydrogenation of 1-hexene is faster: 0.01 turnover/min. In comparison, a soluble uranium(IV) hydride has been reported to catalytically hydrogenate 1-hexene at a rate of 0.019 turnover/s.[65] $Ni_2(C_8H_{12})_2(C_6H_5C\equiv CC_6H_5)$ in toluene catalyzes the hydrogenation of 3-hexyne at a rate of 0.067 turnover/min.[66]

Conclusion

The results of our study indicate that the 4/1 RLi/UCl_4 reaction is more complex than originally thought. Although it may be possible to force 4 equiv of t-C_4H_9Li or n-C_4H_9Li to react with UCl_4 in alkane solvents by using very long reaction times (>2 weeks[33]) and forcing conditions (e.g., high temperature and special stirring methods[35]), the major reaction which occurs in this system at room temperature over a 5–6 day period involves only 2 equiv of RLi and may proceed

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(54) Divalent uranium complexes are not known: "Comprehensive Inorganic Chemistry"; Bailar, J. C., et al., Eds.; Pergamon Press: New York, 1973; Vol. 5.

(55) The U(III) → U(II) reduction potential has been estimated as −4.7 V vs. NHE: Nugent, L. J.; Baybarz, R. D.; Burnett, J. L.; Ryan, J. L. *J. Phys. Chem.* **1973**, *77*, 1528–1539.

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(59) Previous syntheses[23a,24] did not give reaction conditions or yields.

(60) If the reaction between C_8H_8 and the RLi/UCl_4 product is conducted at a higher temperature, an alternative mechanism is possible in which the $U^{III}H$ decomposes to a lower oxidation state of uranium and H_2 gas. Reaction conditions previously used in this synthesis of uranocene were not reported.[23,24]

(61) Karraker, D. G.; Stone, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 6885–6888.

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without U(IV) β-hydrogen elimination. The solid product is not uranium metal but instead a uranium(III) hydride, possibly formed by β-hydrogen elimination from a uranium(III) alkyl. The main features of the system can be rationalized by a series of well-established organometallic reactions, but a detailed explanation of all the data requires several reaction sequences, as may be appropriate for a heterogeneous system. The U(III) complexes formed in this system have synthetic utility and catalytic activity as well.

Experimental Section

General Data. Since both starting materials and products of the RLi/UCl_4 reactions are highly sensitive toward oxidation and hydrolysis, rigorous exclusion of air and moisture is necessary at all times. To this end, experiments were assembled in the recirculating nitrogen atmosphere of a Vacuum/Atmospheres HE-43 Dri-Lab glovebox equipped with an additional recirculation system incorporating a cold trap for removal of solvent vapors.[67] The syntheses and subsequent manipulations of reaction products were conducted with standard Schlenk and high-vacuum techniques except that septum/syringe methods were avoided.

Solvents were rigorously dried and degassed before use. Pentane and octane were treated with H_2SO_4, washed with water, and dried over $MgSO_4$. Subsequently, pentane was heated at reflux over $LiAlH_4$ and then vacuum transferred. Octane was heated at reflux over sodium and distilled. 1-Hexyne, 3-hexyne (Chem Samples), and 1-hexene (Aldrich) were dried over activated Linde 4A molecular sieves and degassed by vacuum transfer. Dicyclopentadiene (Aldrich) was dried over CaH_2 and cracked immediately before use. Prepurified hydrogen was passed through an Oxy-Trap (Alltech Assoc.) before use.

tert-Butyllithium was purchased as a pentane solution (Aldrich) and sublimed at 70 °C (<1 torr). The use of accurately weighed amounts of this crystalline reagent precluded errors associated with reagent calibration or with decomposition arising from the use of septum/syringe techniques. Since *n*-butyllithium does not readily sublime, this reagent was used in hexane solution as purchased (Aldrich). The reagent was titrated before use.[68] UCl_4 was synthesized from UO_3 and hexachloropropene by literature methods[36] and was used as a powder of less than 100 mesh particle size.

Physical Measurements. Infrared spectra were obtained as Nujol mulls on CsI plates contained in an O-ring sealed Barnes Presslok holder with a Perkin-Elmer 283 spectrometer. Optical spectra were obtained on a Cary 14 spectrometer using 2-mm Teflon-stoppered cells. Gas chromatography was performed on a Hewlett Packard 5830A and a Varian 202 equipped with thermal conductivity detectors and a 6 × $^1/_4$ in. 5A molecular sieve column, a 20% tricresyl phosphate on 60/80 Chromosorb W/dimethyldichlorosilane column, and a saturated $AgNO_3$–ethylene glycol on Chromosorb P column. Complete elemental analyses were performed by Bernhardt Analytical Laboratories, 5250 Engelskirchen, Germany. Uranium was analyzed by dissolving weighed samples in concentrated HCl and determining the concentration spectrophotometrically with the absorption at 675 nm.

Reactions. These were generally carried out with 3 mmol (1.14 g) of UCl_4. Solid t-C_4H_9Li was accurately weighed to give 1, 2, or 4 (molar) equiv. n-C_4H_9Li was titrated as a hexane solution and the appropriate measured volume added by syringe (inside the drybox). The reactions were performed in two distinct ways, described below.

A. In Gas Collection Apparatus. Since proper analysis of this reaction requires accurate collection of the gases which are generated during the reaction (but which also may result from decomposition of the alkyllithium starting material), special care is needed in this system. Accordingly, *when quantitative gas measurements were necessary*, the Schlenk and septum/syringe techniques commonly used to manipulate air-sensitive compounds and used previously in RLi/UCl_4 studies[6,16] were *avoided* in favor of a more rigorous, specially designed greaseless high-vacuum reactor. The reactor is a 2-neck 300-mL round-bottom flask fitted as follows. One neck consists of a high-vacuum Teflon stopcock attached to a 24/40 ground-glass joint and the other neck is a vacuum-tight solvent seal joint (Fisher Porter, 15 mm). A modified Schlenk solution funnel (Kontes) was constructed with a high-vacuum Teflon stopcock at the top and a 15-mm solvent seal joint at the bottom in place of the normal ground-glass joint.

A typical reaction between UCl_4 and t-C_4H_9Li was carried out with this apparatus in the following way. Inside the glovebox, UCl_4 and octane (30 mL) were placed in the reactor along with a glass-encased magnetic stir bar. t-C_4H_9Li (1, 2, or 4 equiv) and octane (30 mL) were placed in the addition funnel. The two pieces of equipment were then joined via the 15-mm solvent seal joint and the whole assembly removed from the glovebox. On a high-vacuum line, both parts of the apparatus were carefully evacuated. The reactor was cooled to −78 °C and the t-C_4H_9Li solution slowly added to the frozen octane/UCl_4 mixture. The −78 °C bath was replaced by a −45 °C bath, and the reaction thawed over several hours. Subsequently, the −45 °C bath was removed and the reactor allowed to warm slowly to room temperature with stirring. After 4–6 days, the reactor was attached to a Toepler pump through a U-trap cooled by a −22 °C slush bath and gaseous reaction products were quantitatively collected and analyzed by GC.

A Schlenk filtration apparatus was connected to the gas collection reactor via the ground-glass joint and evacuated. The reaction mixture was then filtered to give black solids and a light yellow octane solution. The greaseless stopcock on the Schlenk filter was closed, separating the solids (which remained under vacuum) from the filtrate. The Schlenk flask containing the filtrate was detached and taken into the glovebox where the contents were transferred to a high-vacuum vessel. This vessel subsequently was attached to a high-vacuum line where vacuum-degassed H_2O was condensed onto the filtrate at −196 °C. 2-Methylpropane was quantitatively collected by Toepler pump and identified by GC.

Vacuum-degassed D_2O (5–10 mL) was condensed onto the black precipitate remaining in the evacuated filtration apparatus attached to the gas collection reactor. Gas was evolved as a purple suspension formed. Subsequently, this changed to a clear green solution. The noncondensable gaseous decomposition products were passed through a trap cooled by a −196 °C bath, quantitatively collected by Toepler pump, and identified by GC. The condensable gaseous products were passed through a trap cooled to −22 °C, collected, and analyzed.

B. In Schlenk Equipment. For experiments in which the main objective was to isolate and study the solid reaction products, it was more convenient to use conventional Schlenk equipment as opposed to the gas collection reactor described above. Accordingly, inside the drybox, UCl_4 and pentane (30 mL) were placed in a 125-mL Schlenk flask, and the appropriate amount of t-C_4H_9Li was dissolved in pentane (30 mL) in a Schlenk addition funnel. The two pieces of apparatus were connected and brought outside the box. The flask was cooled to −78 °C and the pentane solution of the alkyllithium reagent added slowly. When the addition was complete, the reaction mixture was allowed to warm slowly to room temperature. The addition funnel was removed against a stream of nitrogen and replaced by a greased ground-glass stopper. The mixture was stirred for 4–6 days at the end of which period the flask was returned to the glovebox where the mixture was filtered. The black solid thus obtained was washed free of any residual alkyllithium reagent with pentane and allowed to dry. A 1–1.25-g sample of the solid products was usually obtained from 3 mmol of UCl_4 (1.14 g). When dissolved in THF, these products formed purple solutions whose optical spectra are characteristic of U(III).[39] λ [nm (relative absorbance)]: 750 (0.40); 900 (0.90); 958 (0.53); 1095 (0.50); 1180 (0.55); 1230 (0.53).

4-Equiv Reaction. As an example of a typical 4-equiv reaction in the gas collection apparatus, UCl_4 (1.17 g, 3.09 mmol) reacted with t-C_4H_9Li (0.811 g, 12.6 mmol) in octane to form 2-methylpropane (3.52 mmol, 1.14 equiv) and 2-methylpropene (1.43 mmol, 0.46 equiv) after 5 days. Hydrolysis of the octane filtrate formed 2-methylpropane (5.23 mmol, 1.69 equiv). Deuterolysis of the solid reaction products formed 2-methylpropane (0.08 mmol, 0.03 equiv), 2-methylpropene (0.72 mmol, 0.23 equiv), HD (2.32 mmol, 0.75 equiv), and D_2 (2.10 mmol, 0.68 equiv).

Reactions of the 4/1 t-C_4H_9Li/UCl_4 Product. A. 1,3,5,7-C_8H_8. In the glovebox, a portion (0.24 g, ca. 0.60 mmol of U present) of the black reaction product obtained from the reaction of 4 equiv of t-C_4H_9Li with UCl_4 was placed in 10 mL of toluene in a 100-mL round-bottom flask equipped with a high-vacuum stopcock. The flask was removed to a high-vacuum line and evacuated. 1,3,5,7-C_8H_8 (ca. 1 mL, ca. 0.9 mmol) was vacuum transferred onto the mixture, and

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(67) This modification enabled us to handle solid *tert*-butyllithium in the glovebox without coming into contact with THF vapors. Hence, contamination of this reagent by decomposition products arising from THF cleavage[41] was avoided.

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the reaction was allowed to warm to room temperature. Bubbling was observed upon warming, and after 1 day the evolved gases were collected by Toepler pump and identified by GC as hydrogen (0.023 mmol). In the glovebox, the solids were extracted with toluene until the extract was no longer visibly green. The yield of $U(C_8H_8)_2$ was determined spectrophotometrically by using the 615-nm absorption (0.0134 mmol, 3%).

B. C_5H_6. In a reaction conducted as described above, a portion (0.335 g, ca. 0.85 mmol U present) of the solid product of a 4/1 t-C_4H_9Li/UCl_4 reaction was reacted with excess freshly distilled C_5H_6. Vigorous bubbling occurred when the reaction was warmed to room temperature. After overnight stirring, H_2 (0.14 mmol) was collected. The IR spectra of the solids exhibited bands at 1010 and 750 cm^{-1}.

C. Terminal Alkynes. Reactions of the black product of a 4/1 t-C_4H_9Li/UCl_4 reaction with 3,3-dimethyl-1-butyne and with 1-hexyne were also investigated briefly. 3,3-Dimethyl-1-butyne reacted to form a brown THF-soluble oil which exhibited an alkynide stretching absorption at 2030 cm^{-1} in the IR. Gas evolution was qualitatively monitored in a 1-hexyne reaction, and a pressure increase was observed upon reaction. The rather intractable products were not further characterized.

Reaction of the 1-Equiv Product with NaC_5H_5. Synthesis of $U(C_5H_5)_3(THF)$. UCl_4 (1.14 g, 3 mmol) was reacted with t-C_4H_9Li (0.192 g, 3 mmol) in 30 mL of hexane in a Schlenk flask as described above for Schlenk reactions. The black solid product was separated by filtration and extracted with THF to form a deep purple solution. NaC_5H_5 (0.79 g, 9 mmol) was added to the THF solution, causing an immediate color change to deep brown. The mixture was stirred overnight, the THF was removed by rotary evaporation, and the dark brown residue was extracted with benzene. Removal of solvent from this solution left a brown, free-flowing powder which was characterized by IR and ^1H NMR spectroscopy, complexometric metal analysis, and quantitative deuterolytic decomposition as $U(C_5H_5)_3(THF)$ (0.65 g, 42%).

Catalysis. A portion (0.264 g, ca. 0.67 mmol U present) of the solid black product of a 4/1 t-C_4H_9Li/UCl_4 reaction and 3-hexyne (5 mL, 44 mmol) were placed in a calibrated test tube (70.1 mL) fitted with a greaseless high-vacuum stopcock in the glovebox. The vessel was attached to a high-vacuum line, evacuated, and filled with hydrogen (1 atm). The pressure drop was monitored and the hydrogen replenished. A rate of 10^{-3} turnover/min was observed. The reaction was terminated at 15 turnovers, and the liquid products were analyzed by GC. A 3-hexene/hexane ratio of 20 was found with *cis*-3-hexene, the predominant isomer (90%). Deuterolysis of the residue after the catalysis gave 0.2 equiv of HD and 0.41 equiv of D_2/equiv of uranium.

The catalytic hydrogenation of 1-hexene to 1-hexane was similarly effected by a 4/1 t-C_4H_9Li/UCl_4 reaction product at a rate of 2.5×10^{-3} turnover/min. The reaction was terminated after 20 turnovers.

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Registry No. UCl_4, 10026-10-5; t-C_4H_9Li, 594-19-4; n-C_4H_9Li, 109-72-8; $U(C_8H_8)_2$, 11079-26-8; $U(C_5H_5)_3(THF)$, 74237-38-0.

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X-ray Evidence for C–H Bond Activation and C–C Bond Formation in the Cyclopentadienylmanganese Tricarbonyl Series: Peculiar CO Insertion, Formation, and Expansion of Alicyclic Rings in Friedel–Crafts Reactions with *tert*-Butyl Chloride

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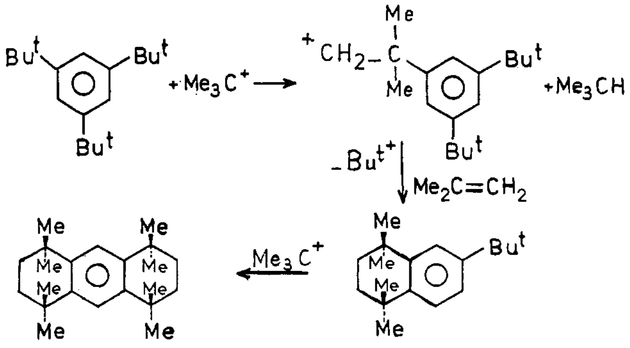
The reaction of $CpMn(CO)_3$ (CMT) with t-BuCl and $AlCl_3$ in CH_2Cl_2 gives a series of CMT complexes with one or two t-Bu substituents and/or one or two CO-t-Bu groups on the Cp ring and three complexes in which the Cp is substituted by both alicyclic rings (of various sizes) and CO-t-Bu-groups. The reaction products result from alicyclic ring formation and expansion and "CO insertion" into a Cp–t-Bu bond; but this latter process does not occur starting with t-BuCMT. Friedel–Crafts acylations of $CpMn(CO)_3$ also provide analogous mixtures of complexes, which indicates that the formation of cyclized products only occurs if the Cp ring is substituted by an acyl group. The crystal and molecular structure of one of these reaction products, the methyl ester of (6,7-($\alpha,\alpha,\delta,\delta$-tetramethylcyclohexene)cymantrenoyl)propanoic acid (**12a**, Scheme III), has been resolved. It crystallizes in the space group $P2_1/n$ with cell dimensions a = 7.996 (3) Å, b = 25.00 (1) Å, c = 10.486 (4) Å, β = 96.18 (2)°, and Z = 4. Refinement based on 1237 observed ($I \geq 3\sigma(I)$) diffractometer data converged at R = 0.059 and R_w = 0.068. Small but significant disparities are observed in $Mn–C_{Cp}$ distances.

Introduction

A peculiar side process[2] in the reaction of t-BuCl with 1,4-di- and 1,3,5-tri-*tert*-butylbenzene (and also presumably with benzene itself) is the formation of a cyclized compound outlined in Scheme I.

Scheme I



Among aromatics complexed to metal carbonyls, few are susceptible to extensive Friedel–Crafts chemistry, the cyclopentadienylmanganese tricarbonyl (cymantrene or CMT) series being one of the most reactive.[3] The above process has not been observed starting with $C_6H_6Cr(CO)_3$[4] or ferrocene.[5]

No study on such a reactivity of cymantrene has ever been noted; therefore, we intended to study its reaction with *tert*-butyl chloride under the Friedel–Crafts conditions. A very

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