

Ligand exchange reactions of the alkyluranium(III) complexes $(\eta^5\text{-C}_5\text{H}_5)_3\text{URLi}$

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(Received April 21st, 1987)

Abstract

The Cp_3URLi compounds ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{R} = \text{Me}, \text{n-Bu}, \text{n-Pent}$) have been synthesized by reaction of $\text{Cp}_3\text{U}(\text{THF})$ with 1 equivalent of RLi . Exchange of the R alkyl occurs on treatment with alkylolithium reagents or in hydrogenolysis in the presence of a terminal olefin. These reactions presumably involve the Cp_3U and Cp_2UR species which are in equilibrium with the Cp_3URLi complexes.

Introduction

The alkyluranium(IV) compounds, especially the $(\eta^5\text{-C}_5\text{Me}_5)_2\text{UR}_2$ and $(\eta^5\text{-C}_5\text{H}_5)_3\text{UR}$ derivatives, have been extensively studied [1]. The $(\eta^5\text{-C}_5\text{H}_5)_3\text{URLi}$ anionic products (I) are unique examples of alkyl complexes of uranium(III) [2,3]; it seemed to us that it would be of interest to study their reactivity and to determine the eventual influence of the electronic charge and the metal oxidation state. We present here a discussion of the results relating to the new synthesis, dynamic behaviour in solution, and ligand exchange reactions of the complexes I [4].

Results

Synthesis and NMR spectra of the Cp_3URLi complexes. The alkyluranium(III) compounds Cp_3URLi (I) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; a, $\text{R} = \text{Me}$; b, $\text{R} = \text{n-Bu}$) were synthesized as previously reported [2 *], by reduction of the corresponding uranium(IV) derivatives Cp_3UR with an excess of methyl- or butyl-lithium. They were also prepared in quantitative yield by treatment of $\text{Cp}_3\text{U}(\text{THF})$ (II) ($\text{THF} = \text{tetrahydrofuran}$) [5],

* This and other references marked with asterisks indicate notes occurring in the list of references.

with 1 equivalent of RLi (eq. 1). No reaction was observed between II and an excess of CpLi.



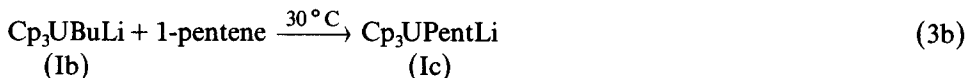
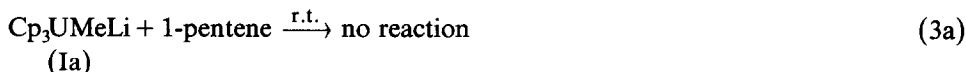
(a, R = Me; b, R = n-Bu; c, R = n-Pent)

Equilibrium mixtures of Ia and Ib or Ic were obtained when the complexes were treated with the appropriate alkyllithium reagent (eq. 2).

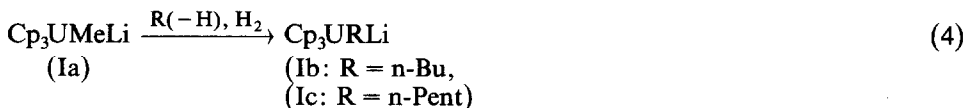


Some interesting facts were revealed by the ^1H NMR spectra of Ia in the presence of II and CpLi in THF. Irradiation of the Cp signal of II or CpLi caused a decrease in intensity of the signal of the cyclopentadienyl ligand of Ia. The signal of II was not affected when the signal of CpLi was irradiated.

Reactions of the Cp₃URLi complexes with hydrogen and/or terminal olefin. No reaction between Ia and 1-pentene was observed during 12 months at room temperature. However, Ib reacted with the terminal olefin (1-pentene/Ib 26) to give the n-pentyl derivative Ic in 30% yield in 7 days at 30 °C (eq. 3).



Hydrogenolysis of Ia (20 °C, 1 atm H₂, 10 h) led to quantitative formation of II and CH₄ (characterized by MS analysis); when deuterium was used, monodeuteriomethane was obtained. Reaction of Ia with hydrogen in the presence of 1-pentene (Ia/H₂/1-pentene = 0.1/2/6) for 15 h gave the pentyl derivative Ic in quantitative yield (by NMR) and a third of the pentene was hydrogenated to n-pentane (GC analysis). The same experiment under deuterium instead of hydrogen led to Ic, which was monodeuteriated at the β position of the alkyl chain. Similarly, Ib was obtained by hydrogenolysis of Ia in the presence of 1-butene (eq. 4); this reaction also gave II.



Discussion

The trivalent uranium complexes ($\eta^5\text{-C}_5\text{H}_4\text{R}$)₃U(THF) (R = H, Me, SiMe₃) were known to react with a variety of L ligands including carbon monoxide [6] and diphenylacetylene [4], yielding the corresponding adducts ($\eta^5\text{-C}_5\text{H}_4\text{R}$)₃UL. We found that Cp₃U(THF) (II) can also, by formation of uranium to carbon σ bonds, give a series of complexes Cp₃URLi (I). Equation 1 represents a new route to

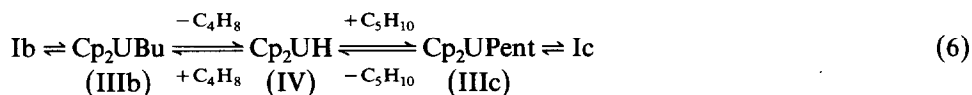
alkyluranium(III) complexes, but it is similar to the preparation of some anionic alkyl-lanthanide compounds [1,7].

Marks et al. [1,8] pointed out the rather inert nature of the complexes Cp_3UR , which do not undergo ligand exchange reactions, do not react with hydrogen, and resist β -hydride elimination. This lack of reactivity was attributed to the saturation and the congestion of the coordination sphere. In the case of compounds I, ligand exchange reactions and formation of hydrides by either β elimination or hydrogenolysis could be favoured by the rapid equilibria illustrated by eq. 5. Evidence for these equilibria was provided by spin saturation transfer [9] observed between the

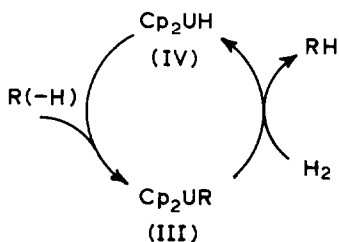


Cp ligands of I and II or CpLi in THF. Complex II is the probable intermediate in the R group substitutions brought about by RLi reagents (eq. 2) [10*]. The alternative associative mechanism [11], which would involve $\text{Cp}_3\text{UR}_2\text{Li}_2$ species, is not likely in view of the steric and electronic factors; these factors would also impede the formation of the Cp_4ULi anionic compound.

We think that the neutral, coordinatively unsaturated and sterically uncongested species III play an important role in the alkyl exchange reactions of I in the presence of a terminal olefin (eq. 3 and 4). We assume that III can undergo β elimination leading to the uranium(III) hydride (IV), which would then add to the double bond. Equation 6 illustrates the intermediates in the formation of Ic from Ib in the presence of 1-pentene (eq. 3). In agreement with this mechanism, the methyl derivative Ia, which possesses no β -hydrogen atom, does not react with 1-pentene.



A more efficient route to uranium hydrides was the hydrogenolysis of alkyl complexes I. Compound II appeared to be more stable than the plausible primary products [12] of the reaction, IV and Cp_3UHLi . Addition of these hydrides (which could be in equilibrium, by analogy with eq. 5) to a terminal olefin would give the corresponding primary alkyl complexes (eq. 4). As the latter would themselves undergo hydrogenolysis, catalytic hydrogenation of the olefin was observed; II is the inert product of this process. We imagine again that, for steric and electronic factors, the active intermediates of the catalytic cycle (Scheme 1) are species III and IV rather than the coordinatively and sterically congested I and Cp_3UHLi anions.



Scheme 1. R = n-Bu, n-Pent.

This mechanism is similar to that proposed for the hydrogenation of olefins catalysed by $(\text{Cp}'_2\text{MH})_n$ compound [13] ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$; $\text{M} = \text{Nd}, \text{U}$); in this latter case, the corresponding alkyl derivatives $\text{Cp}'_2\text{MR}$ were not observed.

Conclusions

The Cp_3URLi compounds I have been found to give hydrides either by hydrogenolysis or β elimination reactions. Substitution of alkyl groups by hydrogenolysis in the presence of olefin or by treatment with alkyllithium reagents, is novel. We think that these reactions are not determined by the metal oxidation state but are mainly influenced by the anionic character of complexes I. We have demonstrated that these stable compounds readily dissociate reversibly in solution to give the very reactive, neutral, coordinatively and sterically unsaturated species Cp_2UR (which would be solvated by THF). This dynamic behaviour is unusual for uranium complexes which, in many cases, show a tendency to increase their coordination number and to accept a more negative charge, giving intermediates which would themselves undergo further reactions and rearrangements [14]. We envisage that other anionic actinide complexes could act as "masked" and protected catalysts.

Experimental

General methods. All manipulations were carried out under reduced pressure in Schlenk type apparatus connected to a vacuum line. The glassware was constructed with greaseless Teflon taps and adaptors for connection to the vacuum line. Solutions were degassed by freeze-thaw cycles. Reactions with gases were performed within a closed system in the vacuum line; gas uptake was monitored with a manometer. THF was distilled under argon from sodium-benzophenone and THF- d_8 was dried over potassium. MeLi in diethyl ether (1.6 M, Merck), n-BuLi in hexane (1.6 M, Merck) and CpLi (Alfa) were used without purification, n-PentLi was made by treatment of pentyl-bromide with lithium. 1-Butene (Alfa) was dried over CaH_2 and 1-pentene (Jansen Chimica) was distilled from sodium. Hydrogen was dried by passage through two traps cooled in liquid nitrogen. $\text{Cp}_3\text{U}(\text{THF})$ was prepared as described in ref. 5, by treatment of Cp_3UCl [15] with NaH (Aldrich), which was itself used without purification. Solutions of $\text{Cp}_3\text{U}(\text{THF})$ in THF could be stored at room temperature for several weeks.

^1H NMR spectra were recorded on a Bruker WH 60 instrument, samples were prepared on the vacuum line, the solvent was a 1/1 mixture of THF and THF- d_8 (internal lock); yields were determined by use of C_6H_6 as internal standard. Paramagnetic chemical shifts were calculated with respect to tetramethylsilane (δ 0.00 ppm); positive values correspond to low field shifts. GC analyses were obtained on a Perkin-Elmer 3920 B gas chromatograph using a 10% SE 30 column. The mass spectra were recorded on a micromass 305 VG instrument.

Synthesis and ^1H NMR spectra of Cp_3URLi complexes I. Complexes I were prepared as described in ref. 2. A new synthesis is as follows.

Cp_3UMeLi (Ia). MeLi (0.07 ml of a 1.6 M solution in diethyl ether, 0.11 mmol) was added to a red solution of $\text{Cp}_3\text{U}(\text{THF})$ (2.35 ml of a 0.048 M solution in THF, 0.11 mmol). After 1 h at 20°C , the NMR spectrum of the red solution showed quantitative formation of Ia.

Cp₃U-n-BuLi (Ib) and Cp₃U-n-PentLi (Ic). These compounds were prepared as described for Ia but use of n-BuLi (1.6 M solution in hexane) or n-PentLi (0.8 M solution in ether) instead of MeLi. Compounds I were characterized by their ¹H NMR spectra: δ (ppm) (60 MHz, 30 °C), Ia: -14.33 (15 H, s, Cp), -93.63 (3H, br); Ib: -4.43 (3H, t *J* 7.5 Hz), -6.73 (2H, sext, *J* 7.5 Hz), -8.43 (2H, m), -13.93 (15H, s, Cp), -91.13 (2H, m). Ic: -1.98 (3H, t *J* 7.5 Hz), -4.76 (2H, sext *J* 7.5 Hz), -7.12 (2H, m), -8.92 (2H, m), -14.77 (15 H, s, Cp), -94.83 (2H, m). The paramagnetic chemical shifts of the alkyl chain signals decrease with the distance from the metal centre.

Spin saturation transfer experiments. The NMR spectrum of a THF solution of Ia, II and CpLi in the ratio 1/2/40 was recorded. Irradiation of the cyclopentadienyl signal of Ia causes a decrease in the intensity of the signals of II (δ -21.55 ppm) and CpLi (δ 5.68 ppm) to 85 and 15%, respectively of their original values. Irradiation of the signal of II lowered the intensity (to 75% of its original value) of the Cp signal of Ia; no change in the CpLi signal was observed. The intensity of the Cp signal of Ia was lowered to 40% of its original value, when the signal of CpLi was irradiated whereas that of II was not affected. Similar results were obtained when Ib was used instead of Ia.

Reaction of Cp₃UMeLi with n-BuLi. n-BuLi (0.35 ml of a 1.6 M solution in hexane, 0.56 mmol) was added to a solution of Ia (4 ml of a 0.03 M solution in THF, 0.12 mmol). After 1 h, 50% of Ia was converted into Ib (NMR analysis).

Reaction of Cp₃U-n-PentLi with MeLi. MeLi (0.12 ml of a 1.6 M solution in diethyl ether, 0.19 mmol) was added to a solution of Ic (4 ml of a 0.013 M solution in THF, 0.05 mmol). Quantitative formation of Ia was revealed by NMR spectroscopy after 1 h.

Reaction of Cp₃UMeLi and Cp₃UBuLi with 1-pentene. 1-Pentene (0.15 ml, 1.37 mmol) was added to a solution of Ib (4 ml of a 0.013 M solution in THF, 0.05 mmol). After 7 days at 30 °C, the NMR spectrum showed that 30% of Ib had been transformed into Ic; during the same time at 20 °C, 13% of Ib were transformed into Ic. No reaction between Ia and 1-pentene was observed during 12 months at 20 °C.

Hydrogenolysis of Cp₃UMeLi. Hydrogen (3 mmol) was introduced into a 100 ml flask containing 4.4 ml of a 0.10 M solution of Ia in THF (0.44 mmol). The solution was stirred for 10 h at 20 °C. Cp₃U(THF) was formed in quantitative yield (by NMR). Mass analysis of the gas phase indicated the formation of CH₄ (CH₃D when D₂ was used instead of H₂).

Hydrogenolysis of Cp₃UMeLi in the presence of 1-butene. Hydrogen (2.70 mmol) was introduced into a 100 ml flask containing Ia (3.4 ml of a 0.027 M solution in THF; 0.091 mmol) and 1-butene (6.6 mmol). The red solution was stirred at 20 °C for 10 h. The NMR spectrum indicated the formation of Ib (40%) and II (60%). GC analysis showed that 40% of the butene had been converted into n-butane.

Hydrogenolysis of Cp₃UMeLi in the presence of 1-pentene. Hydrogen (2.05 mmol) was introduced into a 100 ml flask containing Ia (3 ml of a 0.029 M solution in THF, 0.087 mmol) and 1-pentene (0.7 ml, 6.4 mmol). The red solution was stirred for 15 h at 20 °C. Quantitative formation of Ic was revealed by NMR spectroscopy; GC analysis indicated that 30% of 1-pentene had been converted into n-pentane. The height of the NMR signal from Ic at δ -8.92 ppm was halved when D₂ was used instead of H₂.

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