

Oxidative addition of organic halides to $(\eta\text{-C}_5\text{H}_5)_3\text{U}(\text{THF})$ (THF = tetrahydrofuran). A convenient new synthesis of triscyclopentadienyl uranium(IV) hydrocarbyl complexes

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Abstract

$\text{Cp}_3\text{U}(\text{THF})$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$; THF = tetrahydrofuran) reacts with organic halides RX to give the equimolecular mixture of the Cp_3UX and Cp_3UR compounds. The features of the reaction are characteristic of an atom abstraction oxidative addition mechanism. Treatment of Cp_3UCl with RX in the presence of sodium amalgam leads to quantitative formation of the Cp_3UR complexes.

Introduction

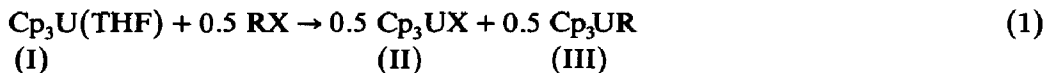
Oxidative additions of organic halides to d transition metal complexes have been extensively studied, but in organoactinide chemistry only the reactions of the uranium(III) compound $(\eta\text{-C}_5\text{Me}_5)_2\text{UCl}(\text{THF})$ [1] have been examined. More recently, oxidative addition reactions of various organolanthanide(II) systems have been reported [2]; mechanistic studies were complicated by further reactions of the initial products. We describe below the reactions of the tris-cyclopentadienyl uranium derivative $\text{Cp}_3\text{U}(\text{THF})$ (I) with some organic halides, and provide clear evidence for a halogen atom abstraction oxidative addition mechanism. We also describe a convenient new synthesis of the uranium(IV) alkyl derivatives Cp_3UR .

Results and discussion

Reactions of $\text{Cp}_3\text{U}(\text{THF})$ with organic halides

The triscyclopentadienyl uranium(III) compound $\text{Cp}_3\text{U}(\text{THF})$ (I) when treated at room temperature in tetrahydrofuran with CH_3I , $n\text{-C}_4\text{H}_9\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $i\text{-C}_3\text{H}_7\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $\text{CH}_2=\text{CHCH}_2\text{Cl}$ was totally converted into an equimolecular

mixture of Cp_3UX (II) and Cp_3UR (III), according to Eq. 1.



When 0.5 equivalent of organic halide was used, an unidentified intermediate, the proportion of which never exceeded 5%, was sometimes detected (by NMR, $\delta_{\text{Cp}} = -12.4$ ppm); it was rapidly transformed into the final products in the presence of a slight excess of RX (< 1 equiv.). Under these conditions, the Grignard type reactions $\text{Cp}_3\text{UR} + \text{RCl} \rightarrow \text{Cp}_3\text{UCl} + \text{RR}$ ($\text{R} = \text{C}_6\text{H}_5\text{CH}_2$ or $\text{CH}_2 = \text{CHCH}_2$) were found to be very slow [2].

These oxidation reactions of I proceeded quite rapidly, being complete within < 5 min, except for that with n-butyl chloride, which required 1.5 hour for completion. It was thus evident that an alkyl chloride is less reactive than the corresponding bromide and iodide, and that a primary halide is less reactive than a secondary, benzylic or allylic halide. Treatment of I with tertiary organic halides ((C₆H₅)₃CCl, tC₄H₉Br) gave only Cp₃UX, the corresponding Cp₃UR derivatives being unstable [3]. The phenyl halides C₆H₅X (X = Br, I) also reacted in THF with I (0.05 M each) to give a mixture of II (50%) and Cp₃UC₆H₅ (37%) and an unidentified product (δCp = -6.7 ppm); the reaction times were 10 min (X = I) and 6 h (X = Br).

The rates of these reactions were much higher in benzene. In this solvent, I was immediately oxidized by $n\text{-C}_4\text{H}_9\text{Cl}$ and reacted with 1 equivalent of phenyl chloride (0.05 M , $t_{1/2} = 3\text{ h}$) to give an equimolecular mixture of II and $\text{Cp}_3\text{UC}_6\text{H}_5$. This solvent dependence is clearly indicative of the need for prior dissociation of the THF ligand of I, leading to the less sterically hindered and more reactive Cp_3U species.

Treatment of I with either cyclopropyl methyl bromide or 4-bromobut-1-ene led to the immediate formation of $\text{Cp}_3\text{U}\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$, showing that alkyl radicals are involved in the reactions [4].

The observations provide good evidence for the halogen atom abstraction oxidative addition mechanism [5] depicted in Eqs. 2–4.



That the reaction rate is greatly dependent on the concentration of the coordinatively unsaturated species (Eq. 2) can be attributed to the availability of an inner sphere pathway for the U^{III} species. Such a mechanism was also suggested to account for the oxidation of some organolanthanide(II) systems [2] and $(C_5Me_5)_2UCl(THF)$ by organic halides [1]. However, in this case, it was found that not all of $R\cdot$ radical was captured by the U^{III} species (Eq. 4), and, in particular, when benzyl chloride was used, no $(C_5Me_5)_2U(Cl)(CH_2C_6H_5)$ was formed. This unusual behaviour cannot be easily explained.

Synthesis of the Cp_3UR complexes

We recently showed [6] that $\text{Cp}_3\text{U}(\text{THF})$ can readily be obtained by the $\text{Na}(\text{Hg})$ reduction of Cp_3UCl (IIa), and in view of the above results we thought that it might

be possible to isolate the U(IV) alkyl complexes $\text{Cp}_3\text{UR(III)}$ from the reaction of **Ia** with RX in the presence of sodium amalgam (Eq. 5).



($\text{RX} = \text{CH}_3\text{I}$, $\text{nC}_4\text{H}_9\text{Br}$, $\text{iC}_3\text{H}_7\text{Cl}$, $\text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{Br}$,
 $\text{CH}_2 = \text{CHCH}_2\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$)

This procedure does, in fact, provide a convenient synthesis of compounds **III**, which are usually prepared by treatment of **Ia** with the corresponding Grignard or alkyllithium reagent [3]. No alkylsodium or alkylmercury species [7] are involved in these alkylation reactions, since RX was found to be inert towards the sodium amalgam in THF at 20°C . The Cp_3UR complexes were obtained in quantitative yield (as indicated by NMR spectroscopy). The latter were reduced to the corresponding U^{III} anions Cp_3UR^- [8] when 3 equivalents of Na(Hg) were used. Formation of $\text{Cp}_3\text{U(THF)}$ from Cp_3UCl is faster than the $\text{Cp}_3\text{UR} \rightarrow \text{Cp}_3\text{UR}^-$ reduction, and in the reaction shown in Eq. 5 no U^{III} alkyl anion is formed because the organic halide reacts rapidly with $\text{Cp}_3\text{U(THF)}$.

The new compound $\text{Cp}_3\text{UCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ was synthesized on a preparative scale and isolated as red crystals in 90% yield. $\text{Cp}_3\text{UCH}_2\text{C}_6\text{H}_5$ was similarly obtained in 87% yield (compared with the 20% yield from treatment of **Ia** with benzylolithium [9]). Reaction 5 is also applicable to the synthesis of binuclear complexes: brown crystals of $\text{Cp}_3\text{U(CH}_2)_4\text{UCp}_3$ were prepared in 85% yield by using 0.5 equivalent of 1,4-dibromobutane. We are at present studying this compound and other similar bimetallic derivatives.

Experimental

General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (F.R.G.). The ^1H NMR spectra were recorded on a Bruker W60 (FT) instrument. Deuteriated solvents were dried over Na/K alloy. The chemical shifts are given as δ values relative to tetramethylsilane ($\delta = 0$).

All experiments were carried out under argon in Schlenk type glassware on a high vacuum line or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately prior to use. The organic halides (Aldrich) were distilled over CaCl_2 or MgSO_4 . Cp_3UCl [10] and $\text{Cp}_3\text{U(THF)}$ [6] were prepared by published methods.

Reactions of $\text{Cp}_3\text{U(THF)}$ with organic halides

In a typical experiment, an NMR tube was charged with $\text{Cp}_3\text{U(THF)}$ (10.1 mg), hexamethylbenzene (1.6 mg) as internal standard, and $\text{THF-}d_8$ or $\text{benzene-}d_6$ (0.4 ml). The organic halide (0.5 equiv.) was introduced with a gas-tight syringe. The products were characterized by their NMR spectra, which were identical to those of authentic samples and/or to those described in the literature (Cp_3UX in [11], and Cp_3UR in [3,9]). The yields were determined from the integrated spectra.

Reactions of Cp_3UCl with organic halides in the presence of Na(Hg)

(a) In a typical experiment, an NMR tube was charged with Cp_3UCl (9.4 mg), 2% Na(Hg) (46 mg) and $\text{THF-}d_8$ (0.4 ml). The organic halide (1 equiv.) was introduced with a gas-tight syringe. The NMR tube was immersed for 5 min in an ultrasound bath (60 W, 40 kHz). The products were characterized by their NMR spectra; the yields were determined from the relative integrals of the Cp and solvent signals.

(b) An NMR tube was charged with Cp_3UCl (14.0 mg), 2% Na(Hg) (103 mg), and $\text{THF-}d_8$ (0.4 ml). *n*-Butylbromide (3.2 μl) was introduced with a gas-tight syringe. The tube was immersed in the ultrasound bath; after 5 min, the NMR spectrum showed the formation of $\text{Cp}_3\text{UC}_4\text{H}_9$, which was reduced into the corresponding U(III) anion by further sonication (10 min).

$\text{Cp}_3\text{UCH}_2\text{C}_6\text{H}_5$

A 50 ml round bottom flask was charged with Cp_3UCl (209 mg) and 2% Na(Hg) (1027 mg); then immersed in liquid nitrogen, and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (56.5 mg) was condensed in under vacuum. THF (15 ml) was then condensed in under vacuum at -78°C . The mixture was stirred at 20°C for 3 h and the solution then decanted off and filtered, and the solvent was evaporated to leave brown crystals of $\text{Cp}_3\text{UCH}_2\text{C}_6\text{H}_5$ (204 mg, 87%). The product was identified from its ^1H NMR spectrum [9].

$\text{Cp}_3\text{UCH}_2\text{CH}_2\text{CH}=\text{CH}_2$

This was prepared as described for $\text{Cp}_3\text{UCH}_2\text{C}_6\text{H}_5$ by using 4-bromobut-1-ene instead of benzyl chloride. Yield 90%. Analysis. Found: C, 46.44; H, 4.42. $\text{C}_{19}\text{H}_{22}\text{U}$ calcd.: C, 46.72; H, 4.54%. ^1H NMR = $\delta(\text{THF-}d_8, 30^\circ\text{C})$: $-2.69(\text{s}, 15\text{H}, \text{Cp})$; $-6.85(\text{d of d}, 2.5 \text{ and } 9.1 \text{ H}, \delta\text{-CH cis to } \gamma\text{-CH})$; $-10.91(\text{d of d}, 2.5 \text{ and } 17, 1\text{H}, \delta\text{-CH trans to } \gamma\text{-CH})$; $-17.79(\text{d of d}, 9 \text{ and } 17, 1\text{H}, \gamma\text{-CH})$; $-27.45(\text{br}, 2\text{H}, \beta\text{-CH}_2)$; $-194.1(\text{br}, 2\text{H}, \alpha\text{-CH}_2)$.

$\text{Cp}_3\text{U}(\text{CH}_2)_4\text{UCp}_3$

This was prepared as described for $\text{Cp}_3\text{UCH}_2\text{C}_6\text{H}_5$ by using 1,4-dibromobutane (0.5 equiv.) instead of benzyl chloride. The less soluble product was extracted with THF ($3 \times 20 \text{ ml}$). Yield 85%. Analysis. Found: C, 43.97; H, 3.93. $\text{C}_{34}\text{H}_{38}\text{U}_2$ calcd.: C, 44.25; H, 4.15%. ^1H NMR = $\delta(\text{THF-}d_8, 30^\circ\text{C})$: $-6.65(\text{s}, 30\text{H}, \text{Cp})$; $-47.50(\text{br}, 4\text{H}, \beta\text{-CH}_2)$; $-192.65(\text{br}, 4\text{H}, \alpha\text{-CH}_2)$.

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