*Journal of Organometallic Chemistry*, 393 (1990) 339–342
Elsevier Sequoia S.A., Lausanne
JOM 21026

# Oxidative addition of organic halides to $(\eta\text{-}C_5H_5)_3U(THF)$ (THF = tetrahydrofuran). A convenient new synthesis of triscyclopentadienyl uranium(IV) hydrocarbyl complexes

**Claude Villiers and Michel Ephritikhine**

*Service de Chimie Moléculaire, IRDI/DESICP/DLPC/CEA-CEN Saclay, CNRS URA 331, 91191 Gif sur Yvette Cédex (France)*

(Received March 13th, 1990)

## Abstract

$Cp_3U(THF)$ ($Cp = \eta\text{-}C_5H_5$; 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 $(\eta\text{-}C_5Me_5)_2UCl(THF)$ [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 $Cp_3U(THF)$ (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 $Cp_3U(THF)$ with organic halides*

The triscyclopentadienyl uranium(III) compound $Cp_3U(THF)$ (I) when treated at room temperature in tetrahydrofuran with $CH_3I$, n-$C_4H_9X$ (X = Cl, Br, I), i-$C_3H_7Cl$, $C_6H_5CH_2Cl$ and $CH_2{=}CHCH_2Cl$ was totally converted into an equimolecular

0022-328X/90/$03.50

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

$$\underset{(I)}{Cp_3U(THF)} + 0.5\ RX \rightarrow 0.5\ \underset{(II)}{Cp_3UX} + 0.5\ \underset{(III)}{Cp_3UR} \qquad (1)$$

When 0.5 equivalent of organic halide was used, an unidentified intermediate, the proportion of which never exceeded 5%, was sometimes detected (by NMR, $\delta Cp = -12.4$ 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 $Cp_3UR + RCl \rightarrow Cp_3UCl + RR$ ($R = C_6H_5CH_2$ or $CH_2{=}CHCH_2$) 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 ($(C_6H_5)_3CCl$, $tC_4H_9Br$) gave only $Cp_3UX$, the corresponding $Cp_3UR$ derivatives being unstable [3]. The phenyl halides $C_6H_5X$ (X = Br, I) also reacted in THF with I (0.05 *M* each) to give a mixture of II (50%) and $Cp_3UC_6H_5$ (37%) and an unidentified product ($\delta Cp = -6.7$ 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 $n\text{-}C_4H_9Cl$ and reacted with 1 equivalent of phenyl chloride (0.05 *M*, $t_{1/2} = 3$ h) to give an equimolecular mixture of II and $Cp_3UC_6H_5$. 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 $Cp_3UCH_2CH_2CH{=}CH_2$, 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.

$$Cp_3U(THF) \rightleftarrows Cp_3U + THF \qquad (2)$$

$$Cp_3U + RX \rightarrow Cp_3UX + R\cdot \qquad (3)$$

$$Cp_3U + R\cdot \rightarrow Cp_3UR \qquad (4)$$

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 $Cp_3U(THF)$ can readily be obtained by the Na(Hg) reduction of $Cp_3UCl$ (IIa), and in view of the above results we though that it might be possible to isolate the U(IV) alkyl complexes $Cp_3UR$(III) from the reaction of IIa with RX in the presence of sodium amalgam (Eq. 5).

$$\underset{(IIa)}{Cp_3UCl} + RX + 2Na(Hg) \rightarrow \underset{(III)}{Cp_3UR} + NaCl + NaX \qquad (5)$$

$(RX = CH_3I, nC_4H_9Br, iC_3H_7Cl, CH_2=CHCH_2CH_2Br,$

$CH_2=CHCH_2Cl, C_6H_5CH_2Cl)$

This procedure does, in fact, provide a convenient synthesis of compounds III, which are usually prepared by treatment of IIa 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 $Cp_3U(THF)$ from $Cp_3UCl$ is faster than the $Cp_3UR \rightarrow Cp_3UR^-$ reduction, and in the reaction shown in Eq. 5 no $U^{III}$ alkyl anion is formed because the organic halide reacts rapidly with $Cp_3U(THF)$.

The new compound $Cp_3UCH_2CH_2CH=CH_2$ was synthesized on a preparative scale and isolated as red crystals in 90% yield. $Cp_3UCH_2C_6H_5$ was similarly obtained in 87% yield (compared with the 20% yield from treatment of IIa with benzyllithium [9]). Reaction 5 is also applicable to the synthesis of binuclear complexes: brown crystals of $Cp_3U(CH_2)_4UCp_3$ 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 $\delta$ 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 $Cp_3U(THF)$ [6] were prepared by published methods.

### *Reactions of $Cp_3U(THF)$ with organic halides*

In a typical experiment, an NMR tube was charged with $Cp_3U(THF)$ (10.1 mg), hexamethylbenzene (1.6 mg) as internal standard, and THF-$d_8$ or 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 THF-$d_8$ (0.4 ml). The organic halide (1 equiv.) was introduced with a gas-tight syringe. The NMR tube was immerged 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 THF-$d_8$ (0.4 ml). n-Butylbromide (3.2 $\mu$l) 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 $Cp_3UC_4H_9$, which was reduced into the corresponding U(III) anion by further sonication (10 min).

### *$Cp_3UCH_2C_6H_5$*

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 $C_6H_5CH_2Cl$ (56.5 mg) was condensed in under vacuum. THF (15 ml) was then condensed in under vacuum at $-78\,^\circ$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 $Cp_3UCH_2C_6H_5$ (204 mg, 87%). The product was identified from its $^1$H NMR spectrum [9].

### *$Cp_3UCH_2CH_2CH{=}CH_2$*

This was prepared as described for $Cp_3UCH_2C_6H_5$ by using 4-bromobut-1-ene instead of benzyl chloride. Yield 90%. Analysis. Found: C, 46.44; H, 4.42. $C_{19}H_{22}U$ calcd.: C, 46.72; H, 4.54%. $^1$H NMR = $\delta$(THF-$d_8$, 30 °C): $-2.69$(s, 15H, Cp); $-6.85$ (d of d, 2.5 and 9,1 H, $\delta$-CH *cis* to $\gamma$-CH); $-10.91$ (d of d, 2.5 and 17, 1H, $\delta$-CH *trans* to $\gamma$-CH); $-17.79$ (d of d, 9 and 17, 1H, $\gamma$-CH); $-27.45$ (br, 2H, $\beta$-$CH_2$); $-194.1$ (br, 2H, $\alpha$-$CH_2$).

### *$Cp_3U(CH_2)_4UCp_3$*

This was prepared as described for $Cp_3UCH_2C_6H_5$ by using 1,4-dibromobutane (0.5 equiv.) instead of benzyl chloride. The less soluble product was extracted with THF (3 × 20 ml). Yield 85%. Analysis. Found: C, 43.97; H, 3.93. $C_{34}H_{38}U_2$ calcd.: C, 44.25; H, 4.15%. $^1$H NMR = $\delta$(THF-$d_8$, 30 °C): $-6.65$ (s, 30H, Cp); $-47.50$(br, 4H, $\beta$-$CH_2$); $-192.65$ (br, 4H, $\alpha$-$CH_2$).

## References

1 R.G. Finke, Y. Hirose and G. Gaughan, J. Chem. Soc. Chem. Commun., (1981) 232; R.G. Finke, D.A. Schiraldi and Y. Hirose, J. Am. Chem. Soc., 103 (1981) 1875.

2 R.G. Finke, S.R. Keenan and P.L. Watson, Organometallics, 8 (1989) 263 and references therein.

3 T.J. Marks, A.M. Seyam and J.R. Kolb, J. Am. Chem. Soc., 95 (1973) 5529.

4 A. Effio, D. Griller, K.U. Ingold, A.L.J. Beckwith and A.K. Serelis, J. Am. Chem. Soc., 99 (1979) 250.

5 P.B. Chock and J. Halpern, J. Am. Chem. Soc., 91 (1969) 582.

6 J.F. Le Maréchal, C. Villiers, P. Charpin, M. Nierlich, M. Lance, J. Vigner and M. Ephritikhine, J. Organomet. Chem., 379 (1989) 259.

7 J.L. Wardell in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Vol. 1, p. 43 and Vol. 2, p. 863, Pergamon, Oxford, 1982.

8 L. Arnaudet, P. Charpin, G. Folcher, M. Lance, M. Nierlich and J. Vigner, Organometallics, 5 (1986) 270.

9 G. Brandi, M. Brunelli, G. Lugli and A. Mazzei, Inorg. Chim. Acta, 7 (1973) 319.

10 L.T. Reynolds and G. Wilkinson, J. Inorg. Nucl. Chem., 2 (1956) 246.

11 N.K. Sung-Yu, F.F. Hsu, C.C. Chang, G.R. Her and C.T. Chang, Inorg. Chem., 20 (1981) 2727.