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Synthesis of monocyclopentadienyl uranium alkoxides by alcoholysis of triscyclopentadienyl uranium chlorides

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Abstract

$(RC_5H_4)_3UCl(R = H,Me)$ react with two equivalents of alcohol $R'OH(R' = Et, Pr^n, Pr^i, Bu^n, Bu^t)$ to give the corresponding $(RC_5H_4)U(OR')_2Cl$ compounds. The alkoxides $(RC_5H_4)_{4-n}U(OR')_n$ $(n = 1-3)$ are intermediates in this reaction.

Introduction

Monocyclopentadienyl compounds of transition metals are less numerous than the corresponding Cp_2M derivatives ($Cp = \eta\text{-}C_5H_5$); they generally exhibit a lower thermal stability and show a higher reactivity. In many cases, they are prepared from the more readily available biscyclopentadienyl compounds, either through redistribution reactions or by displacement of a single Cp group; in particular, Jonas et al. have developed the synthesis of reactive organometallic compounds via the degradation of metallocenes under mild conditions [1].

Stable monocyclopentadienyl uranium complexes are rare and are essentially limited to the $CpUX_3L_2$ derivatives (X = Br, Cl; L = oxygen or nitrogen ligand) [2,3] $CpU(BH_4)_3$ [4] and $CpUCl(acac)_2(OPPh_3)$ (acac = MeCOCHCOMe) [5]. On the other hand, it has been shown that with a few exceptions [6–8], the biscyclopentadienyl actinide derivatives undergo disproportionation [3]. In contrast, since the preparation of Cp_3UCl(I) [9], a large series of triscyclopentadienyl compounds have been synthesized [10]. It seemed to us of interest to prepare monocyclopentadienyl complexes from I and its ring substituted analogues. We report here a convenient synthesis of the $(RC_5H_4)U(OR')_2Cl$ compounds ($R = H$, Me; $R' =$ Et, Pr^n, Pr^i, Bu^n, Bu^t) involving alcoholysis of the corresponding triscyclopenta-

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dienyl uranium chloride. We also present results which shed light on the mechanism of these reactions.

Results and discussion

Synthesis

The triscyclopentadienyl uranium chlorides $(RC_5H_4)_3UCl$ (I: R = H; II: R = Me) reacted at 80 °C with 2 equivalents of n-butyl alcohol in THF (THF = tetrahydrofuran) to give the mixed chloride-alkoxide complexes III and IV, according to Eq. 1:

$$(RC_5H_4)_3UCl + 2R'OH \rightarrow (RC_5H_4)U(OR')_2Cl + 2RC_5H_5 \qquad (1)$$

$$\begin{array}{ll} & (\mathrm{III}: R = H,\ R' = Bu^n; \\ (\mathrm{I}: R = H; & \mathrm{IV}: R = Me, R' = Bu^n; \\ \ \mathrm{II}: R = Me) & \mathrm{V}: R = H,\ \ R' = Pr^i; \\ & \mathrm{VI}: R = Me, R' = Pr^i) \end{array}$$

Formation of III and IV was almost quantitative (by NMR); however, these compounds, like most of the metal alkoxides, are very soluble in organic solvents and were isolated as microcrystalline green powders in 35 and 50% yield, respectively, after crystallisation from cold pentane. Compound III was also obtained in 80% yield (by NMR) by treatment of $CpUCl_3(THF)_2$ [2,3] with 2 equivalents of sodium butoxide in THF.

Similar reactions of I and II with isopropyl alcohol gave the isopropoxide derivatives V and VI; complete transformation of the initial chlorides required 12 h, rather than the 4 h needed in the case of their reaction with the primary alcohol. Treatment of I and II with ethyl, n-propyl, or t-butyl alcohol led to the formation of the corresponding $(RC_5H_4)U(OR')_2Cl$ products (R = H, Me; $R' = Et, Pr^n, Bu^t$), which were characterized only by their ^1H NMR spectra (Table 1). Not surprisingly, the triscyclopentadienyl uranium butoxide Cp_3UOBu^n (VII), when treated with 2 equivalents of butyl alcohol, was quantitatively transformed into the oily brown trisalkoxide $CpU(OBu)_3$ (VIII). Compound VIII was also formed by reaction of $CpUCl_3(THF)_2$ with 3 equivalents of NaOBu (NMR experiment).

These complexes, which are the first examples of monocyclopentadienyl uranium alkoxides, are expected to have a polymeric structure in solution [11,12]. The molecular weight of III was determined by osmometry in pyridine, and found to be 2400. This value would correspond to the formula $\{CpU(OBu)_2Cl\}_5$ or $\{CpU(OBu)_2Cl(pyridine)\}_4$; the same degree of association was observed for the uranium tetraalkoxides [12].

Reaction mechanism

We noted that the initial reaction between I and the alcohol always gave the triscyclopentadienyl uranium alkoxide Cp_3UOR [13], which was observed by NMR spectroscopy after 15 min at 20 °C. Subsequent alcoholysis of this alkoxide would then give the biscyclopentadineyl derivative $Cp_2U(OR)_2$, which, as shown by Zanella et al. [8], undergoes rapid disproportionation into $CpU(OR)_3$ and Cp_3UOR, except when bulky alkoxide groups ($R = Bu^t$) are present. We found that $Cp_2U(OBu^t)_2$ and $CpU(OBu^t)_3$ are transiently formed during the slow reaction of I

Table 1

NMR spectra for the complexes [a]

Compound	Cp ligands	Alkoxide ligands
$CpU(OBu^n)_2Cl$(III)	−50.50(15)	22.83(25, 6H), 48.32(35, 4H), 79.59(50,4H), 178.3(210, 4H)
$Cp'U(OBu^n)_2Cl$(IV)	−21.71(10), −36.94(10) −58.17(20)	22.78(25, 6H), 47.76(35, 4H) 78.90(50, 4H), 174.9(375, 4H)
$CpU(OPr^i)_2Cl$(V)	−49.61(15)	71.06(70, 12H), 175.4(175, 2H)
$Cp'U(OPr^i)_2Cl$(VI)	−26.79(20), −28.90(10) −60.81(20)	70.74(90, 12H), 175.6(225, 2H)
$CpU(OEt)_2Cl$	−49.88(20)	75.82(35, 6H), 179.0(115, 4H)
$Cp'U(OEt)_2Cl$	−18.26(30), −39.05(7) −55.37(70)	74.88(100, 6H), 177.2(190, 4H)
$CpU(OPr^n)_2Cl$	−50.82(15)	44.18(40, 6H), 80.32(80, 4H) 179.2(350, 4H)
$Cp'U(OPr^n)_2Cl$	−21.10(20), −36.70(20) −57.08(25)	42.30(60, 6H), 77.80(80, 4H) 174.8(450, 4H)
$CpU(OBu^t)_2Cl$	−45.87(20)	57.90(130, 18H)
$Cp'U(OBu^t)_2Cl$	−24.35(10), −22.73(40) −60.98(15)	58.96(105, 18H)
$CpU(OBu^n)_3$(VIII)	−33.32(20)	5.85(45, 9H),9.79(60, 6H) 16.86(155, 6H), 44.39(400, 6H)

[a] In THF-d_8 at 30 °C. δ relative to TMS (half height width in Hz, intensity). Cp signals integrate for 5H; the three peaks corresponding to the Cp′ ($Cp' = MeC_5H_4$) ligand, in the given order, integrate respectively for 3,2 and 2 H.

with Bu^tOH; these two compounds were independently obtained by treatment of $Cp_2U(NEt_2)_2$ with t-butyl alcohol [8,14*].

These facts led us to suggest the mechanism represented by equations (2)–(5):

$$2Cp_3UCl + 2ROH \rightleftarrows 2Cp_3UOR + 2HCl \quad (2)$$

$$2Cp_3UOR + 2ROH \rightarrow 2Cp_2U(OR)_2 + 2CpH \quad (3)$$

$$2Cp_2U(OR)_2 \rightarrow CpU(OR)_3 + Cp_3UOR \quad (4)$$

$$CpU(OR)_3 + HCl \rightarrow CpU(OR)_2Cl + ROH \quad (5)$$

Reactions (3) and (4) adequately account for the synthesis of VIII by alcoholysis of VII. That reaction (2) is reversible was shown by treatment of VII with HBr, in form of triphenylphosphonium bromide [15], which gave Cp_3UBr [16]. The feasibility of reaction (5) was similarly demonstrated by formation of the bromide analogue of III, $CpU(OBu)_2Br$, from an equimolecular mixture of VIII and PPh_3HBr.

Experimental

General methods

Microanalyses and molecular weight determination were carried out by the Analytical Laboratories at Engelskirchen (FRG). The ^1H NMR spectra were recorded on a Bruker W60 (FT) instrument. Deuterated solvents were dried over

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* A reference number with an asterisk indicates a note in the list of references.

Table 2

Elemental analyses [a]

Compound	Analyses (found (calcd.) (%))			
	C	H	Cl	U
$CpU(OBu^n)_2Cl$ (III)	32.16	4.68	7.10	48.95
	(32.20)	(4.75)	(7.33)	(49.12)
$Cp'U(OBu^n)_2Cl$ (IV)	33.88	4.92	7.17	47.50
	(33.70)	(5.01)	(7.12)	(47.74)
$CpU(OPr^i)_2Cl$ (V)	28.73	4.01	7.95	51.90
	(28.92)	(4.16)	(7.78)	(52.14)
$Cp'U(OPr^i)_2Cl$ (VI)	30.42	4.36	7.70	50.30
	(30.60)	(4.46)	(7.54)	(50.58)
$CpU(OBu^n)_3$ (VIII)	38.91	6.12		45.80
	(39.10)	(6.13)		(45.59)

[a] Cp′ means MeC_5H_4.

Na/K alloy. The chemical shifts are relative to tetramethylsilane ($\delta = 0$). The ^1H NMR spectra and analytical data are given in Tables 1 and 2.

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. Alcohols were purchased as anhydrous from Aldrich (Pr^nOH, Pr^iOH and Bu^nOH) or dried by the usual methods. Cp_3UCl [9], $(MeC_5H_4)_3UCl$ [17], $CpUCl_3(THF)_2$ [3], Cp_3UOBu^n [13] and PPh_3HBr [15] were prepared by published methods.

Synthesis

$CpU(OBu^n)_2Cl$ (III). A 100 ml round bottom flask was charged with I (500 mg) and THF (40 ml) was condensed into it under vacuum at −78 °C. n-Butyl alcohol (215 μl) was introduced via a gas tight syringe. The mixture was stirred at 80 °C for 4 h then allowed to cool to room temperature. The green solution was filtered and the solvent evaporated off. The waxy residue was dissolved in pentane (40 ml) and after 2 h at −78 °C the solution deposited green microscrystals, which were rapidly filtered off and dried under vacuum (189 mg, 35%).

$(MeC_5H_4)U(OBu^n)_2Cl$ (IV). This was prepared as described for III, using II instead of I. 50% yield.

$CpU(OPr^i)_2Cl$ (V) and $(MeC_5H_4)U(OPr^i)_2Cl$ (VI). These complexes were prepared respectively from I and II, as described for III and IV, by using isopropyl alcohol instead of n-butyl alcohol and by heating the reaction mixture for 12 h instead of 4 h. 42 and 33% yield respectively.

Reactions of I and II with EtOH, Pr^nOH and Bu^tOH. An NMR tube was charged with I or II (ca. 20 mg) in THF d_8 (0.4 ml) and 2 equivalents of alcohol was added. After 15 min at 20 °C, the NMR spectrum showed the initial formation of Cp_3UOR (ca. 10%). The tube was heated at 80 °C for 1 h (10 h for Bu^tOH). The NMR spectral data for the products are listed in Table 1. Formation of 2 equivalents of RC_5H_5 was observed.

Bu^tOH (6 mg) was introduced into an NMR tube containing I (21 mg) in THF-d_8 (0.4 ml). After 30 min at 20 °C, the NMR spectrum showed the formation of Cp_3UOBu^t (ca. 10%). (δ: −18.73 (s, 15H, Cp) and 19.05 (s, 9H, CH_3)). The tube was heated at 80 °C for 15 h. The NMR spectrum indicated the formation of $CpU(OBu^t)_2Cl$ (ca. 80%) (Table 1) and the presence of Cp_3UOBu^t (ca. 5%), $Cp_2U(OBu^t)_2$ (ca. 5%) (δ: -22.16 (s, 10H, Cp), 12.72 (s, 18H, CH_3)) and $CpU(OBu^t)_3$ (ca. 10%) ($\delta = -42.26$ (s, 5H, Cp), 33.3 (br, $W_{1/2}$ 65, 27H, CH_3)). The NMR spectra of Cp_3UOBu^t [13] and $Cp_2U(OBu^t)_2$ [8] correspond to those reported in the literature.

$CpU(OBu^n)_3$ (VIII). A tube containing VII (40.5 mg) and BuOH (15 μl) in THF (0.7 ml) was heated at 80 °C for 3 h. The solvent was evaporated off to leave the oily brown product.

Reactions of $CpUCl_3(THF)_2$ with NaOBu. An NMR tube was charged with $CpUCl_3(THF)_2$ (6 mg) and NaOBu (2.5 mg) in THF-d_8 (0.4 ml). After 15 min at 20 °C the NMR spectrum showed the formation of III as the major product (ca. 80%) and VIII (ca. 20%). Compound VIII was formed in 80% yield when $CpUCl_3(THF)_2$ was treated with 3 equivalents of NaOBu.

Reactions of VII and VIII with PPh_3HBr. An NMR tube was charged with VII (8 mg) and PPh_3HBr (6 mg) in toluene-d_8. The NMR spectrum of the brown solution indicated the immediate formation of Cp_3UBr (δCp = 3.44).

An NMR tube was charged with VIII (prepared by addition of 2 equivalent of Bu^nOH to VII (8 mg)) and PPh_3HBr (6 mg) in THF-d_8. The NMR spectrum of the brown solution showed the immediate formation of the bromide analogue of III.δ(30 °C): 181.6 (br, 265, 4H, α-CH_2), 81.04 (br, 80,m 4H, β-CH_2), 49.22 (br, 50, 4H, γ-CH_2), 23.39 (br, 45, 6H, CH_3), -51.07 (s, 5H, Cp). Other signals corresponding to an unidentified butoxide group were also visible at δ: 209.6, 93.07, 56,44 and 26.72; their intensity is 50% of that of the butoxide signals corresponding to the cyclopentadienyl compound.

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