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Synthesis of new Alkyl and Aryl σ-Bonded Uranium(IV) Derivatives

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The synthesis of some alkyl and aryl uranium (IV) derivatives of type $U(\pi\text{-}C_5H_5)_3R$ *is reported. They are obtained from* Cp_3UCl *and Li-R* ($R = CH_3$, $n\text{-}C_4H_9$, C_6H_5, $CH_2\text{-}C_6H_5$) *or RMgBr* ($R = CH_2\text{-}p\text{-}C_6H_4\text{-}CH_3$) *in tetrahydrofuran. Their NMR and infrared spectra, as well as their chemical hydrolyses are in agreement with σ-bonded alkyl or aryl groups. Thermal stability in the solid state is remarkably high for all compounds.*

Introduction

The organometallic chemistry of Uranium (IV) was limited until very recently to the cyclopentadienyl derivatives, such as $(\pi\text{-}C_5H_5)_3UCl$[1] and $(\pi\text{-}C_5H_5)_4U$.[2] Recently, a new type of organouranium compound, bis (cyclooctatetraene) uranium was reported, for which a sandwich structure was postulated[3] and subsequently established by x-ray crystallography.[4]

Some progress in the field of organometallic chemistry of actinides has been made with the synthesis of allyl derivatives of uranium, such as $(\pi\text{-allyl})_4U$[5] and $(\pi\text{-methallyl})_4U$.[6] We established the existence of the first σ-aryl bond to uranium (IV) with the synthesis and characterisation of tris(cyclopentadienyl) phenyl uranium, $U(C_5H_5)_3C_6H_5$.

A preliminary accout[6] of this work appeared in 1970, and was reported in a review article.[7]

Work on uranium carbon σ-bonds was extended to include σ-alkyl derivatives of the same class and reference to this work was made at an international and aryl derivatives of uranium (IV), urged us to publish our own result in detail.

Experimental Section

Unless otherwise stated, all operations and reactions were carried out under an atmosphere of prepurified argon. Solvents were dehydrated following the standard procedures.

Material. $(C_5H_5)_3UCl$ was prepared from UCl_4 and NaC_5H_5, or preferably by reaction between UCl_4 and Tl C_5H_5 in tetrahydrofuran.[10] The latter was prepared according to Meister[11] and Cotton.[12] $LiCH_3$ was obtained from LiC_2H_5 and CH_3J as reported in the literature.[13]

Measurements. Infrared spectra were recorded with a Perkin-Elmer model 225 grating instrument using CsJ windows for the 600-200 cm^{-1} region.

The PMR spectra were measured with a Varian H-100 spectrometer with extended sweep. Samples were dissolved in toluene - *d8* and sealed *in vacuo*. Chemical shifts above ~150 ppm were recorded in HR mode.

Preparation of U $(\pi\text{-}C_5H_5)_3C_6H_5$. A solution of 27.4 mmole of phenyllithium in 100 ml of diethylether was added very slowly at −30°C to a stirred solution of 16.7 g (17.4 mmole) of Cp_3 UCl in 100 ml of tetrahydrofuran. After half pheniyllithium had been added, a bulky green-yellow precipitate appeared and progressively increased as the reaction proceded. The mixture was warmed to room temperature, filtered, and the solid residue was washed with diethylether and dried *in vacuo*. Toluene (100 ml) was added to ness *in vacuo* and the solid residue analysed without further purification.

The yellow-green product is soluble in benzene, slightly soluble in tetrahydrofuran and cyclopentane, decomposed by pyridine. It is stable up to 150°C without melting.

Anal. calcd. for $C_{21}H_{20}U$: C, 49.4; H, 3.9; U, 46.7. Found: C, 48.95; H, 4.25; U. 46.14.

Following the same procedure just described, U (π-

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$C_5H_5)_3C_6D_5$ was obtained starting from Li C_6D_5 (prepared from C_6D_5Br) and Cp_3UCl. The compound is more soluble in tetrahydrofuran than the not deuterated one

Reaction of $U(\pi\text{-}C_5H_5)_3C_6H_5$ with methanol. The derivative (0.358 g) was treated with methanol (3 ml) at room temperature in an appartus sealed *in vacuo.*

The liquid products were removed and analysed by gas chromatography giving 96% of the expected amount of benzene.

Preparation of $U(\pi\text{-}C_5H_5)_3CH_2\text{-}C_6H_5$. A solution of 12.6 mmole of benzyl lithium complexed with tetramethylethylendiamine in 90 ml diethyl ether was slowly added with stirring at –30°C to a solution of 5.92 g (12.6 mmole) of Cp_3 UCl in 60 ml of tetrahydrofuran.

The mixture was gently warmed to room temperature and the solvents removed in vacuum. The residue was extracted with benzene at 50°C under a partial vacuum (~100 mm Hg). Dark violet needles were obtained, soluble in aromatic solvents, tetrahydrofuran, insoluble in diethyl ether and aliphatic solvents. The yield was about 20% of recrystallized product. The compound melts at 200°C with decomposition.

Anal. calcd. for $C_{22}H_{22}U$: C, 50.40; H, 4.00; U, 45.80
Found.: C, 50.31; H, 4.50; U, 45.40.

The product, by treatment with methanol at room temperature yielded toluene (94% yield) by gas-chromatography.

Preparation of $U(\pi\text{-}C_5H_5)_3CH_2$ - $p\text{-}C_6H_4\text{-}CH_3$. A solution of 9.35 mmole of $ClMgCH_2pC_6H_4CH_3$ in 50 ml of diethylether was slowly droped at –30°C into a stirred solution of 4.4 g (9.35 mmole) of Cp_3UCl in 50 ml tetrahydrofuran.

The temperature was progressively increased to room temperature and the solvents removed *in vacuo.* Then 150 ml of benzene were added to the residue and the mixture was filtered. Dioxane (5 ml) was added to the clear benzene solution, which was filtered. By recrystallization from toluene the compound was obtained (30% yield) as dark violet crystals.

Anal. calcd. for $C_{23}H_{24}U$: C, 51.3; H, 4.46; U, 44.2
Found. C, 50.9; H, 4.50; U, 43.10.

Preparation of $U(\pi\text{-}C_5H_5)_3CH_3$. A solution of 12.0 mmole of methyl lithium in 60 ml of anhydrous diethylether was slowly dropped into a stirred solution of 5,58 g (11.9 mmole) of Cp_3UCl in 70 ml of tetrahydrofuran cooled at –30°C.

The mixture was stirred for an hour, while the temperature was progressively rised to room temperature. The solvents were then removed *in vacuo* and the solid residue extracted with three 50 ml portions of benzene. The extracts were filtered and evaporated to dryness *in vacuo.* Some attempts to recrystallize the pale- yellow powder obtained (63% yield) were unsuccessful.

Anal. calcd. for $C_{16}H_{18}U$: C, 42.9, H, 4.02; U, 53.1
Found.: C, 42.5; H, 4.11; U, 48.9.

Preparation of $U(\pi\text{-}C_5H_5)_3n\text{-}C_4H_9$. Buthyllithium (15,7 mmole) in diethylether was dropped at 0°C into a stirred solution of 7.17 g (15.3 mmole) of Cp_3 UCl in 100 ml of tetrahydrofuran. After stirring for 1 hour at room temperature, the solvent was removed *in vacuo* and the crude residue was then extracted with three 40 ml portions of benzene. The solvent was removed from the collected extracts at reduced pressure. The brown residue was dissolved in 150 ml of hexane at 50°C and recrystallization was achieved by cooling the filtered solution at 0°C. Large dark-brown crystals were formed, which were collected by filtration and dried *in vacuo* (50% yield).

The compound melts (dec.) at 176-178°C.

Anal. calcd. for $C_{19}H_{24}U$; C, 46.50; H, 4.90; U, 48.60
Found.: C, 45.90; H, 4.50; U, 47.50.

Decomposition of $U(\pi C_5H_5)_3n\text{-}C_4H_9$ with water. The compound was treated with acqueous H_2SO_4 in a gas-volumetric equipment. The gaseous products were analyzed by mass-spectrometry and found to consist of cyclopentadiene (58.5%) and butane (41.5%), the latter corresponding to a substantially quantitative yield.

Results and Discussion

All the compounds reported in this paper were obtained by the following reactions:

$$U(C_5H_5)_3Cl + LiR \xrightarrow{THF} U(C_5H_5)_3R + LiCl \qquad (1)$$

$R = CH_3$, $n\text{—}C_4H_9$, $\text{—}C_6H_5$, $\text{—}CH_2\text{—}C_6H_5$

$$U(C_5H_5)_3Cl + RMgBr \xrightarrow{THF} U(C_5H_5)_3R + MgBrCl \qquad (2)$$

$R = \text{—}CH_2\text{—}p\text{—}C_6H_4\text{—}CH_3$

The products are moderately soluble in aromatic hydrocarbons and tetrahydrofuran. The thermal stability in the solid state is remarkably high since most of these compounds can be heated without decomposition at 150°C.

The presence of uranium-carbon bond in these compounds is chemically evidenced by the typical reaction with methanol:

$$U(C_5H_5)_3R + R\text{—}OH \rightarrow R\text{—}H + U(C_5H_5)_3OR \qquad (3)$$

In the case of the phenyl, benzyl and n-butyl derivatives the amount of R-H produced was determined and found to be substantially quantitative.

Reaction (3) was also reported by Marks and Seyam.[9]

However, in all derivatives we have found substantial amounts of cyclopentadiene; this suggests that, under our reaction conditions, alcoholysis of the cyclopentadienyl groups also takes place:

$$U(C_5H_5)_3OR + R\text{—}OH \rightarrow C_5H_6 + U(OR)_4 \ (*)$$

The mass spectrum of the phenyl derivative shows

(*) Confirmed by IR spectrum in the case of hydrolysis of $Cp_3U\text{-}CH_2\text{-}C_6H_5$.

Table I. PMR data at room temperature for Cp_3UR in toluene d_8 [a].

A)

Compounds	$H_{C_5H_5}$	H_{CH_3}(***) H_{CH_2}	H_{CH_2}	H_{CH_2}(**)	H_{CH_3}(**)
Cp_3UCH_3	9.88s(*)	206±2s			
$Cp_3UC_4H_9$	10.33s	194±2t(*)	33.46m(*)	27.64m(*)	18.76t

B)

Compounds	$H_{C_5H_5}$	H_{CH_2}(***)	H_{ortho}(**)	H_{meta}(**)	H_{para}(**)	H_{CH_3}
Cp_3UPh	9.77s		23.65d	14.50	6.16t	
Cp_3UCH_2-Ph	9.90s	213±2s	29.37d(*)	4.65t	10.12t	
Cp_3UCH_2-Ph-CH_3	9.95s	214±2s	29.41d	5.62d		3.62s

[a] The chemical shifts are in ppm upfield with respect to benzene as internal standard. (*) s = singlet, d = doublet, t = triplet, m = multiplet, unresolved for CH_2 in $Cp_3UC_4H_9$. (**) Coupling constants, J_{vic} = 8 Hz $J_{o/m}$ = $J_{m/p}$ = 8 Hz. (***) CH_2 shift has been measured in HR mode.

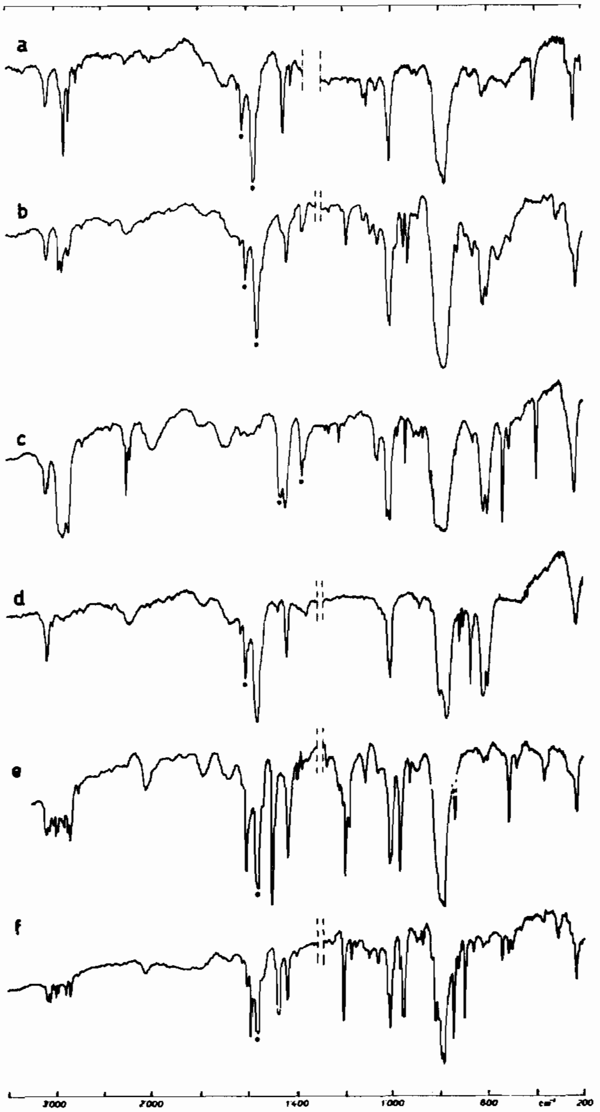

Figure 1. Infrared spectra of Cp_3UR: a, Cp_3UCH_3 in HCB and nujol; b, Cp_3Un-C_4H_9 in HCB and nujol; c, $Cp_3UC_6D_5$ in nujol; d, $Cp_3UC_6H_5$ in HCB and nujol; e, Cp_3UCH_2p-C_6H_4-CH_3 in HCB and nujol, f, Cp_3UCH_2-C_6H_5 in HCB and nujol.

(*) Absorptions of hexaclorobutadiene (HCB) or nujol.

the parent peak at m/e 510 and loss of a C_5H_6 fragment; since the same fragmentation was observed for $U(C_5H_5)_3C_6D_5$ it was concluded that a hydrogen transfer from cyclopentadienyl rings was involved in the formation of C_5H_6.

Further unequivocal evidence for the presence of the uranium carbon bond comes from the H-NMR measurementes (sce Table I). The protons of the cyclopentadienyl groups give rise to one signal at *ca.* 10 ppm upfield with respect to benzene as internal standard.

On the other hand, the protons of σ-alkyl and aryl groups are characterised by very large chemical shifts, about 200 ppm, in the case of the methyl derivative and the α-CH_2 of the other compounds.

The origin of such shifts in terms of contact and dipolar couplings will be discussed elsewhere.

When the protons are far from the paramagnetic centre, dipolar interactions are predominant and the chemical shifts are presumably mainly geometry-dependent. On the contrary, for the protons of the C_5H_5 rings and of carbons directly bonded to the central atom, the contact and dipolare effects are presumably equally important.

The infrared spectra, reported in Figure 1, show the presence of *pentahapto* - cyclopentadienyl rings, containing characteristic bands at 3080 (ν CH), 1435 (ω C-C), 1010 (δ C-H), 790 and 780 (γ CH) cm^{-1}. A doublet at 620-600 cm^{-1} is also observed, which can be ascribed to the cyclopentadienyl group, because it is not shifted by substitution with deuterium as in $Cp_3UC_6H_5/Cp_3UC_6D_5$. The origin of this doublet is still unknown.[10] In the same way the absorption at 230 cm^{-1} can be ascribed to a metal-ring vibration.

Moreover, the absence of two vibrations at ca. 2900 cm^{-1} and 1100 cm^{-1} suports the idea that metal-ring bonding is partially ionic in character.[14]

In the stretching region (see Table II), asymmetrical and symmetrical vibration of methyl and methylene groups are lower than in alkanes.[15]

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Table II. Infrared frequencies of methyl and methylene groups in $(C_5H_5)_3$ UR.

R	νCH_3 (cm^{-1}) asym.	νCH_3 (cm^{-1}) sym.	νCH_2 (cm^{-1}) asym.	νCH_2 (cm^{-1}) sym.
CH_3	2.900	2.840		
C_4H_9	2.950	2.860	2.920	2.850
CH_2-Ph			2.900	2.850
CH_2-Ph-CH_3	2.960	2.870	2.905	2.850

As far as the far infrared region is concerned, the absorption band at 400 cm^{-1} in Cp_3UCH_3 can be reasonably assigned to the metal-carbon stretching vibration.

On the other hand such band does not appear in any other derivative, for which some weak bands in the region 400-300 cm^{-1} are found.

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