Inorganica Chimica Acta, 10 (1974) 239–252

Invited Review

Advances in the Organometallic Chemistry of Uranium(IV)

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Received February 21, 1974

Contents

1. Introduction

The organometallic chemistry of actinides is a relatively recent area of research. The first organometallic compound of a 5f element, a cyclopentadienyluranium complex, was reported in 1956 and other analogous derivatives have been synthesized and characterized in the following years. A rapid expansion in the knowledge of this branch of chemistry is occurred in the more recent years with the discovery of novel types of organometallic compounds, such as cyclooctatetraenyluranium and tetrallyluranium and, successively, with some uranium–carbon σ-bonded complexes. Some reviews,[1,2] already published, cover in part these contributions.

The main interest in these compounds is twofold: firstly to clarify their structures, the nature of the metal–carbon bond and the possibility of the participation of f electrons in the metal–ligand bond; secondly to investigate their possible use in catalytic reactions. This last aspect is only on the early stage, but seems promising also taking in account the large and increasing availability of depleted uranium.

Purpose of this article is to review the research contributions, with particular emphasis on the more recent results, covering both the aforesaid aspects.

Some unpublished data derived from our own experience in this field are included.

2. Complexes with π Ligands

A. Cyclopentadienyl Derivatives

The first cyclopentadienyl derivative was reported by Reynolds and Wilkinson[3] in 1956. The reaction of UCl_4 with sodium cyclopentadienide in the mole ratio 1:2.8 gave in high yield a dark-red crystalline compound of the formula $C_{15}H_{15}UCl$. It is thermally stable up to 300° C, insoluble in light petroleum and benzene, soluble in tetrahydrofuran and pyridine, slight soluble in carbon disulphide and chloroform with some decomposition. The formation of a "sandwich bonded" π-cyclopentadienyl derivative, was suggested on the basis of chemical and physical properties of $C_{15}H_{15}UCl$. The tetrahydrofuran solution of the compound is only weakly conducting, but its reaction with $AgClO_4$ indicates that the chlorine is ionically bonded. Some attempts to react UCl_3 with NaCp in tetrahydrofuran solution gave a very instable red compound in a few percent yield, which composition was approximately $U(C_5H_5)_3$. This compound was later reported by Kanellakopulos *et al.*[4] starting either from highly reactive U^0 and UCp_4 or from UCl_3 with KC_5H_5.

Similar attempts to react UCl_3 in tetrahydrofuran were carried out also by Ter Haar and Dubeck,[5] obtaining tricyclopentadienyluranium butoxide instead of the expected UCp_3.

Clearly an oxidation–reduction process takes place in which THF is cleaved and reduced to the butoxide anion and U^{+3} is oxidized to U^{+4}.

The butoxide was then obtained by more efficient method starting from UCl_4:

$$UCl_4 + NaOR \rightarrow NaCl + [UCl_3OR] \quad (1)$$

$$[UCl_3OR] + 3\ NaC_5H_5 \rightarrow U(C_5H_5)_3OR + 3\ NaCl \quad (2)$$

The compound is extremely air-sensitive, it is soluble to some extent in organic solvents, and very soluble in tetrahydrofuran. The proposed molecular formula, $U(C_5H_5)_3OR$, is supported by the evolution of one equivalent of 1-butanol when decomposed with methanolic HCl.

Magnetic susceptibility measurements on the solid show the presence of two unpaired electrons (μ = 2.68 BM). Using the same method also $U(C_5H_5)_3OCH_3$ was prepared, as well as the corresponding thorium derivative.

Starting from Cp_3UCl and NaOR in refluxing benzene for 1–3 days some Cp_3UOR complexes were reported also by Van Ammon.[6] In particular the methoxy, ethoxy, i-propoxy, n-butoxy and t-butoxy derivatives were prepared in good yield.

The suggested structure of $(\pi\text{-}C_5H_5)_3UCl$ has been verified by X-ray analysis.[7] The crystal data are the following: monoclinic, space group $P2_1/n$; $a = 8.26$, $b = 12.50$, $c = 13.81$ Å and $\beta = 90.6°$; Z = 4; calcd. density 2.184 g cm^{-3}. The cyclopentadienyl rings and the chlorine atom form a somewhat distorted tetrahedron about uranium atom, with the following mean bond distances: U–Cl = 2.559(16) Å; U–C = 2.74 Å (individual values ranging from 2.68 to 2.82 Å), Figure 1. U–Cl single bonds have been interpreted by the Authors having slightly over 50% of ionic character, while 2.55 pairs of electrons would take part in the π bonding between the uranium and the cyclopentadienyl ring.

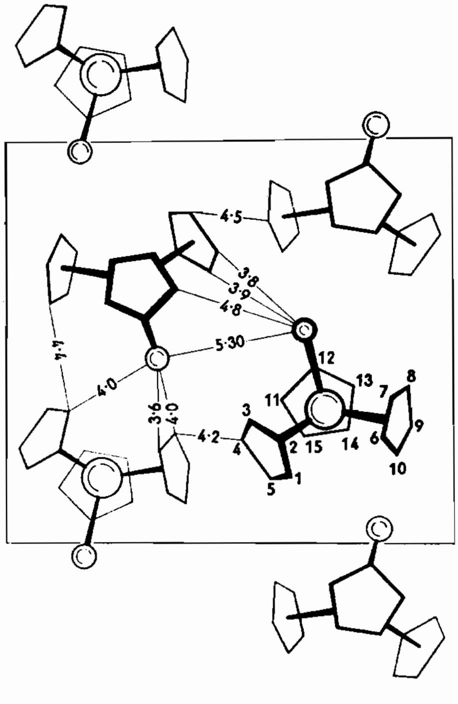


Figure 1. The structure of $U(\pi\text{-}C_5H_5)_3Cl$ viewed down the axis (from Wong, Yen and Lee,[7] by courtesy of *Acta Crystallographica*).

Vapour pressures of $U(C_5H_5)_3Cl$ and other tricyclopentadienyls of Pr and Nd were measured by the effusion method.[8] The enthalpy of sublimation of tricyclopentadienyluranium chloride was found to be 27.7 Kcal/mol. Tetracyclopentadienyluranium was first prepared by Fischer[9] starting from anhydrous UCl_4 and an excess of KC_5H_5 in benzene for many hours:

$$UCl_4 + 4\ KC_5H_5 \xrightarrow[KC_5H_5]{C_6H_6} U(C_5H_5)_4 + 4\ KCl \qquad (3)$$

The product was isolated in low yield by extraction for long time with n-heptane.

Better syntheses of both Cp_3UCl and Cp_4U were later performed[10] employing TlCp and NaCp respectively:

$$UCl_4 + 3\ TlC_5H_5 \xrightarrow{THF} U(C_5H_5)_3Cl + 3\ TlCl \qquad (90\%\ \text{yield})\ (4)$$

$$UCl_4 + NaC_5H_5\ (\text{excess}) \xrightarrow{THF} U(C_5H_5)_4 + 4\ NaCl \qquad (20\%\ \text{yield})\ (5)$$

$U(C_5H_5)_3F$ is obtained in good yield (> 90%) by heating $U(C_5H_5)_3Br$ with sodium fluoride and the base, $U(C_5H_5)_3OH$, can be synthesized in the same way employing sodium hydroxide.[2] All the UCp_3X (X = Cl, Br, I) derivatives can be also prepared by treating UCp_4 with chlorine, bromine or iodine.[2] Fischer *et al.*[11] have found that UCp_3F is dimeric through fluorine bridges. The Lewis acid character of UCp_3F towards bases (THF, pyridine) is also been investigated.[11]

The synthesis of tricyclopentadienyluranium tetrahydroborate, UCp_3BH_4, was obtained[10] by reacting UCp_3Cl with $NaBH_4$ in THF at room temperature. The NaCl and the excess of $NaBH_4$ were removed by filtration and red–orange crystals of UCp_3BH_4 were collected by sublimation at 170° C and 10^{-4} mm (95% yield).

All the cyclopentadienyl derivatives, UCp_3Cl, UCp_4, UCp_3BH_4 were characterized by mass spectra as well as visible and infrared spectra.

The mass spectra of UCp_4 show that the first Cp ligand is readily removed, but the remaining are progressively difficult to strip off. In the UCp_3Cl, the ionic U–Cl bond is more stable than the covalent U–C bond, therefore $UCp_{x-1}Cl^+$ ions are formed, where x = 3,2 or 1. The fragmentation of UCp_3BH_4 is unusual because the most intense peak corresponds to UCp_2^+ ion, resulting from the loss of two substituents instead of one. This agrees with a stronger U–C bond than the U–BH_4 bond, at least under the mass spectrometer conditions.

In the C–H stretching region of the i.r. spectra, UCp_3Cl gives rise to only an asymmetric band (3068 cm^{-1}), while UCp_3BH_4 and UCp_4 show, in addition, a symmetric stretching band (2925 cm^{-1}). The absence of a symmetric band may indicate predominantly π U–Cp bonding in UCp_3Cl, the metal–Cp ring bonds in UCp_4 and UCp_3BH_4 may possess some degree of σ character. As far as band positions of the BH_4 ligand in UCp_3BH_4 are concerned, they are comparable with those reported for $ZrCp_2(BH_4)_2$[12] (double-hydrogen bridged structure). The mass spectra of UCp_4 and several cyclopentadienyluranium halides are also reported by Müller[13] and the fragmentation discussed. Ionization energies of the complexes, appearance potentials of the fragment ions and dissociation energies of the ions are given.

The ^1H NMR spectra of several tricyclopentadienyluranium derivatives have recently been reported (Table I).[6,11,14,15] The spectra present a unique signal for the cyclopentadiene ring, showing the equivalence of all the ring protons. The reported values vary noticeably depending on the type of the other substituent. The origin of such paramagnetic shifts (dipolar or contact) is firstly discussed by Van Ammon *et al.*[16] In the case of UCp_4, the total shift was attributed exclusively to contact interactions and the hyperfine interaction constant (A = –0.131 gauss) was obtained employing the Mc Connell equation,[17] then the spin density for each carbon atom of the ring was calculated. This value would lead to a spin delocalization over the four Cp ligands of 24%.

The temperature dependence of the paramagnetic shifts of UCp_4 and UCp_3BH_4 was also studied between 165° and 248° K.[18] It was observed, in the case of UCp_3BH_4, a pronounced non linearity for Cp and BH_4 protons of the reciprocal of the chemical shift versus T. The Authors confirm their initial view that the dipolar contribution is not important in determining the paramagnetic shift in UCp_4, as suggested differently by Siddal *et al.*[19]

In fact, if the compound were perfectly tetrahedral, g factor would be isotropic and there could be no dipolar shift. The replacement of one Cp ligand in UCp_4 by BH_4 group, produces a larger g factor anisotropy and therefore a dipolar contribution to total shift of BH_4 group is not excluded. However, a dipolar contribution to total shift, calculated from average geometric factor, must be negative causing a low field shift. The experimental large upfield shift of BH_4 is thus due to genuine spin transfer.

Burns[20] has very recently completed a structure determination of $U(C_5H_5)_4$ by single crystal X-ray diffraction. The four Cp rings surrounding tetrahedrically the U atom are identical by crystallographic symmetry (Figure 2), and the distances from the centre of the rings to the metal is 2.55 Å.

The average U–C distance, 2.807(25) Å, is not in agreement with the mean value of 2.73 Å assigned[21] to this bond for π-carbocyclic ligands of charge –1, on the basis of the values observed in UCp_3Cl and $U(C_5H_4CH_2C_6H_5)_3Cl$; this difference could be probably accounted for by the perturbing effect of the chlorine atom in the latter compound (see later).

Magnetic susceptibility of some U^{IV} cyclopentadienyl derivatives has been also reported.[22]

The complexing properties of $U(C_5H_5)_3F$ have been previously reported.[11] Novel and remarkably stable adducts[23] of the type $(C_5H_5)_3UF \cdot M(C_5H_5)_3$, where

TABLE I. Properties and Nmr Data of Some Cyclopentadienyl Uranium Complexes.

Compound	Colour	Sublim. Temp. °C	Yield %	M.p. °C	Ring Shift[a] (ppm)	Other Shifts (ppm)	Solvent	References
UCp_4	red	200	6–99	dec. 250	+20.36	–	C_6H_6[b]	2, 9, 10, 16
UCp_3Cl	dark-green	120–130	80	260	+ 9.6	–	C_6D_6	3, 7, 10
UCp_3Br	dark-green	160	80	–	+ 9.8	–	C_6D_6	11, 15
UCp_3I	brown	170	80	–	+10.4	–	C_6D_6	11, 15
UCp_3F	green	170	80	–	+12.6	–	C_6D_6	11, 15
$UCp_3O–CH_3$	green	120	74	299–302	+24.3	–45.4	C_6D_6[b]	5, 6
$UCp_3O–C_2H_5$	green	120	–	210–213	+25.6	–51.8(OCH_2) – 9.6(CH_3)	C_6D_6[b]	2, 6
$UCp_3O–i\text{-}C_3H_7$	green	130	90	200	+25.8	–54.7(OC=) –10.6(CH_3)	C_6D_6[b]	6
$UCp_3O–n\text{-}C_4H_9$	green	120	15–83	150	+25.1	–50.6(OCH_2) – 9.8(CH_2) – 1.7(CH_2) + 2.6(CH_3)	C_6D_6[b]	5, 6
$UCp_3O–t\text{-}C_4H_9$	green	120–130	78	–	+26.6	–12.4(CH_3)	C_6D_6[b]	6
UCp_3BH_4	dark-red	170	95	–	+13.77	+67.2	C_6D_6[b]	2, 10, 15

[a] + = upfield shift with respect to internal standard.

[b] Shift from benzene.

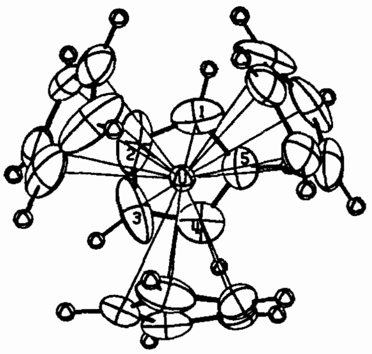


Figure 2. The tetrahedral tetracyclopentadienyluranium molecule (from Burns,[20] by courtesy of the *American Chemical Society*).

M = U, Yb are obtained confirming the exceptionally high basicity of the fluorine derivative. The adducts were prepared by mixing at room temperature UCp_3F with $YbCp_3$ or $UCp_3 \cdot THF$, according to the following reactions:

$$U(C_5H_5)_3F + (C_5H_5)_3Yb \xrightarrow[25°C]{C_6H_6} [(C_5H_5)_3UF \cdot Yb(C_5H_5)_3] \quad (6)$$

$$U(C_5H_5)_3F + U(C_5H_5)_3 \cdot THF \xrightarrow[25°C]{C_6H_6} [(C_5H_5)_3UF \cdot U(C_5H_5)_3] + THF \quad (7)$$

Both the adducts are pyrophoric in the air, not soluble in benzene or tetrahydrofuran and are not sublimable under high vacuum. Their infrared spectra show bands at 432 and 423 cm^{-1}, characteristic for $U \cdots F \cdots M$ group, remarkably shifted when compared with the starting UCp_3F.

In Table I some properties and NMR data of the compounds till now reported are summarized.

The knowledge of the organometallic chemistry of U(IV) containing both cyclopentadienyl and halide groups is not only confined to compounds of Cp_3UX type. In fact, dicyclopentadienyluranium dichloride, UCp_2Cl_2, was prepared by Zanella *et al.*,[24] by reaction of UCl_4 with cyclopentadienylthallium (mole ratio 1:2) in dimethoxyethane. The green–brown solid obtained is soluble in THF and acetone. Attempts to crystallize or to sublime the crude product have been unsuccessful. The infrared spectra of the compound show both the asymmetric band at 3104 cm^{-1} and the symmetric one at 2927 cm^{-1}, indicating the presence of centrally bonded Cp ligands. The magnetic susceptibility suggests the existence of two unpaired electrons. Cyclopentadienyluranium trichloride was also reported by the same research group.[25] It was obtained as dimethoxyethane adduct, $UCpCl_3 \cdot DME$, by treatment of UCl_4 with TlCp in DME at room temperature for several hours. The green solution was filtered to remove TlCl and the solvent evaporated in vacuum. The green solid was insoluble in hydrocarbon solvent, but soluble in THF. Attempts to sublimation led to decomposition. IR spectrum of $UCpCl_3 \cdot DME$ is very similar to that of $UCl_4 \cdot 2DME$, instead the visible spectra of both compounds differ considerably below 500 nm. The μ_{eff} of the prepared compound, calculated using the spin only formula, is 2.59 BM, very similar to the value found for Cp_2UCl_2.

B. Indenyl and Substituted Cyclopentadienyl Derivatives

To add more knowledge about the type of bonding from the metal to the pentagonal ring, not completely solved by the structure of $U(C_5H_5)_3Cl$, indenyl complexes of the actinide elements were synthesized and studied by X-ray diffraction. Thus, the synthesis of triindenyluranium chloride and analogous thorium derivative was achieved by Laubereau,[26] following the general reaction

$$MCl_4 + 3\,KC_9H_7 \rightarrow M(C_9H_7)_3Cl + 3\,KCl; \quad M = U, Th \quad (8)$$

Pure products were obtained only if the reactants were added in a molar ratio 1:3. When an excess of KC_9H_7 was employed, not well defined products were obtained. Mass spectrometry of some of these products shows that predominantly $U(C_9H_7)_2Cl_2$ and $Th(C_9H_7)_4$ are formed. $U(C_9H_7)_3Cl$ is very air sensitive, its thermal stability is high showing no appreciable changes up to 300° C. Both uranium and thorium derivatives are soluble in tetrahydrofuran, slightly soluble in n-pentane and benzene. The characterization of $U(C_9H_7)_3Cl$ was made by mass spectrometry, NMR, infrared studies and X-ray structural determination. The fragmentation pattern confirms the formulation given; a comparison with the mass spectra of tricyclopentadienyluranium chloride shows strongly enhanced tendency to give off the first indenyl ligand. Similar to UCp_3Cl, the ion $U(C_9H_7)_2Cl^+$ appears as the strongest mass peak.

Owing to the low solubility of $U(C_9H_7)_3Cl$ in benzene, as well as broadering of the signals attributed to paramagnetism, a complete analysis by NMR could not be made. The NMR spectra of both uranium and thorium derivatives are comparatively simple and seem to indicate that only one type of indenyl ligand and one type of ligand–to–metal bond is present in the dissolved compounds. Each spectrum shows two sets of signals, one belonging to the protons of the C_6 ring and the other to the protons of the C_5 ring.

Evidence for aromatic character in the C_5 ring comes from infrared spectra. A localized metal–ligand σ bond is excluded in favour of covalent π-type bond. Support for this conclusion is found also in the ultraviolet spectra.

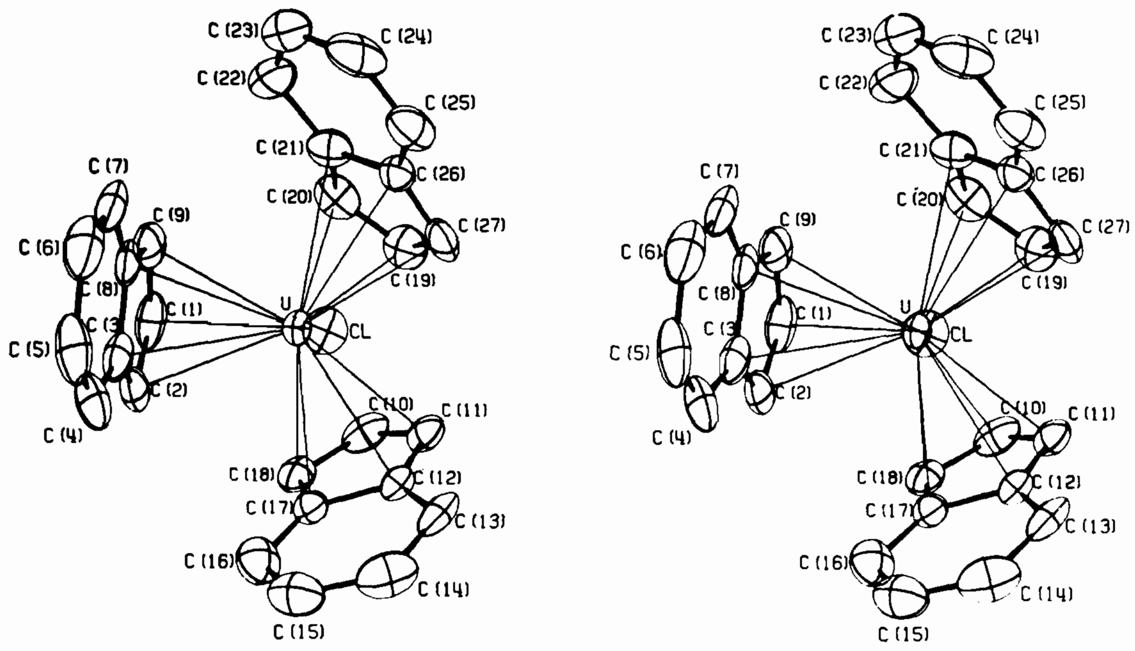


Figure 3. Stereoscopic view of one molecule of $U(C_9H_7)_3Cl$ (from Burns and Laubereau,[27] by courtesy of the *American Chemical Society*).

The crystal structure of $U(C_9H_7)_3Cl$ has been solved and refined to an R index of 0.047 by Burns and Laubereau.[27] The crystal data are: orthorhombic, space group $P2_12_12_1$; $a = 8.576$, $b = 14.24$, $c = 16.73$ Å; Z = 4; calculated density 2.01 g cm^{-3}. The chlorine atom and the five-membered rings of three indenyl moieties are arranged tetrahedrically about the uranium atom (Figure 3). The U–C distances fall in the range 2.67 to 2.89 Å, close to the range of 2.68 ÷ 2.82 Å found in the structure of UCp_3Cl, but greater than the value of 2.647 Å observed in sandwich-bonded uranocene (see later). The U–Cl distance is 2.593(3) Å which is comparable to that of 2.559(16) found in UCp_3Cl. The high similarity between the structures of the former compound and of $U(C_9H_7)_3Cl$, suggest a π interaction of the indenyl ligands with the uranium. In this structure three carbon atoms of 5-membered ring are closer to the metal (U–C < 2.77 Å) so that a possible 1,2,3-*trihapto*indenyl bonding might be suggested, instead of *pentahapto*indenyl bonding.

The ambiguity between a *penta* or *trihapto* bonding seems to be solved by the recently work of Leong *et al.*,[21] who prepared and solved the crystal structure of tris(benzylcyclopentadienyl)uranium chloride, $U(C_5H_4CH_2C_6H_5)_3Cl$. This substituted tricyclopentadienyl uranium chloride was synthesized by the thallous method[10] in dimethoxyethane and purified by extraction with cyclohexane and finally by recrystallization from heptane–toluene. Its crystal data are: monoclinic, $P2_1/n$, $a = 11.133$, $b = 16.275$, $c = 16.367$ Å; $\beta = 100.45$; Z = 4; calcd. density 1.68 g cm^{-3}. This structure provide the proof of the symmetrical *pentahapto* bonding in cyclopentadienyl complexes of the actinides. The chlorine and the 5-membered rings of the three benzylcyclopentadienyl moieties are arranged in an approximate tetrahedron about the metal atom (Figure 4).

U–Cl distance of 2.627 Å differs slightly from the reported values of 2.593 Å for $U(C_9H_7)_3Cl$ and 2.559 Å for UCp_3Cl. The average U–C distance for all three rings is 2.733 Å. The Authors, on the basis of detailed considerations, proposed the following linear relationship: U^{IV}–C distance = 2.81 + 0.0815q, where q is the charge of π-carbocyclic ligands. This gives the values of 2.81, 2.73 and 2.65 for benzyl (q = 0), cyclopentadienyl (q = 1) and indenyl (q = 2) ligands respectively. However, it must be remark that this relation has been set up on the basis of complexes with chlorine atom as ligand.

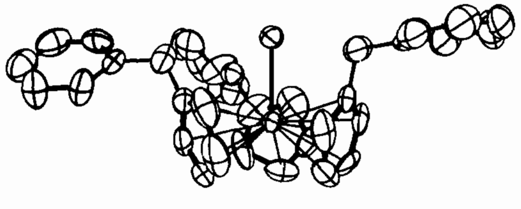


Figure 4. The $U(C_5H_4CH_2C_6H_5)_3Cl$ molecule viewed perpendicular to the U–Cl bond (from Leong, Hodgson and Raymond,[21] by courtesy of the *American Chemical Society*).

C. Cyclooctatetraenyl and Substituted Cyclooctatetraenyl Derivatives

A novel type of organometallic derivative of uranium is biscyclooctatetraenyluranium (uranocene) reported by Streitwieser and Müller–Westerhoff.[28] It was obtained by reacting cyclooctatetraene dianion with UCl_4 in dry tetrahydrofuran at –30° C. After addition of degassed water the green crystals were filtered and extracted with benzene. The compound ignites to air, but it is stable to water, acetic acid and aqueous sodium hydroxide. A sandwich structure of ferrocene type was firstly postulated on the basis of its mass spectrum, with planar eight-membered rings above and below the central uranium atom. Later, this structure was confirmed in a preliminary report, by a single crystal ray diffraction analysis.[29] It is a π sandwich compound with a molecular symmetry of D_{8h} as shown in Figure 5. A refinement of this structure as well as the structure of the thorium analog $Th(C_8H_8)_2$, was more recently reported by the same research group.[30]

The crystal data are: monoclinic, space group $P2_1/n$; a = 7.08(3), b = 8.710(3), c = 10.631 Å and β = 98.75(3) Å; calculated density 2.29 g cm^{-3}. In $U(C_8H_8)_2$ the uranium carbon bonds are equal within experimental error and average 2.647(4) Å. The mean ring–to–ring distance along the molecular axis is 3.847(10) Å, that is the distance from the metal to the center of the dianion ring is 1.924 Å. The cyclooctatetraene dianions in both compounds, $U(C_8H_8)_2$ and $Th(C_8H_8)_2$, are planar with an average C–C bond lengths of 1.392 and 1.386 Å respectively. The planarity of the ring and the mean bond lengths and angles demonstrate the aromatic nature of the 10-π-electrons dianion rings in these structures.

A more direct synthesis of $U(C_8H_8)_2$ was achieved from uranium metal with cyclooctatetraene.[31] The reaction is carried out in a sealed tube, employing particularly reactive uranium formed from the decomposition of uranium hydride.[32] The highest yield (57%) was obtained using an excess of uranium at 150° C for 2.5 hr. The product may be isolated by sublimation and recognized by the characteristic set of bands in the 600–700 nm region.

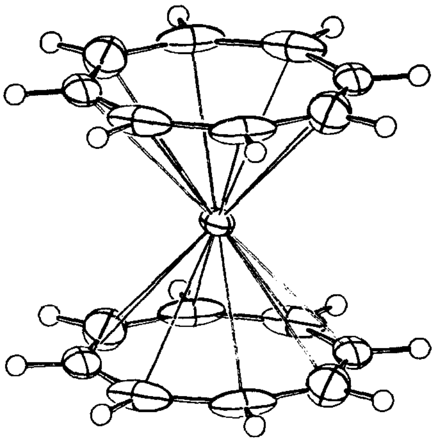


Figure 5. A perspective drawing of $U(C_8H_8)_2$ (from Zalkin and Raymond,[29] by courtesy of the *American Chemical Society*).

The reaction seems catalyzed by traces of mercury. Treatment of the same pyrophoric uranium with cyclopentadiene under the same conditions failed to produce UCp_3 or UCp_4.

We also[33] have obtained $U(COT)_2$ in high yield from a very reactive metal. In fact, some attempts to prepare pure tetralkyluranium derivatives, UR_4, by reacting UCl_4 with butyllithium in molar ratio 1:4 were unsuccessful, always obtaining a black precipitate containing pyrophoric uranium metal. Treating this mixture with cyclooctatetraene, $U(COT)_2$ was easily formed and was isolated by benzene extraction. The same black precipitate was also obtained by the reaction of UCl_4 with lithium metal (1:4) and analogously $U(COT)_2$ was recovered by the addition of cyclooctatetraene. The NMR spectrum of $U(COT)_2$ shows an upfield single signal according to structural and mass data.[34] A linear behaviour of the chemical shift with the reciprocal of the temperature is observed. On the basis of both structural and magnetic data the contact and dipolar contribution to the paramagnetic shift are calculated.

An approach to the solution of the question of f orbitals covalency was made by Streitwieser *et al.* with the synthesis and characterization of a methyl substituted uranocene,[35] bis(1,3,5,7-tetramethylcyclooctatetraene)uranium(IV) and the neptunium(IV) analog. The tetramethyluranocene has similar properties to the $U(COT)_2$ except for greater solubility in organic solvents. The proton magnetic resonance spectrum of both uranium and neptunium derivatives shows two peaks with an intensity 3:1 assigned to the methyl and ring protons respectively. The temperature dependence of ring proton shifts is practically the same for both complexes, only the linewidth in the case of $Np(TMCOT)_2$ is much pronounced (~ 300 Hz for the methyl, ~ 2000 Hz for the ring protons). The paramagnetic shifts referred to uncomplexed diamagnetic $(tetramethylcyclooctatetraene)^{-2}$ are also reported. On the basis of the known structure[29] of $U(COT)_2$ and an extrapolated structure for $Np(TMCOT)_2$, the dipolar shift is calculated for both complexes. This dipolar shift is greater for the methyl than the ring protons, but of the same sign. On the contrary, the contact shifts calculated from the difference (total shift = contact shift–dipolar shift) result of opposite sign, positive for the ring protons and negative for the methyl. This finding, in the Author opinion, suggests that the spin density in the ligand is principally in π MO's. Moreover, the high magnitude of the delocalized spin density implies a high degree of covalency and suggests the involvement of f orbitals in such covalency. A plausible mechanism suggested is a charge transfer from a filled ligand π MO's to vacant f orbitals; this would involve a positive spin density as observed.

The crystal and molecular structure of the bis(1,3,5,7-tetramethylcyclooctatetraenyl)uranium has been determined by Hodgson *et al.*[36,37] The crystal data are: monoclinic space group $P2_1/c$; a = 20.224(5); b = 12.066(3); c = 17.467(6) Å; β = 101.57(2) Å; Z = 8; calcd. density 1.74 g cm^{-3}. There are two crystallographically independent molecules in the unit cell, corresponding to two rotomeric conformations; one having the methyl groups approximately eclipsed, the other approximately staggered (Figure 6).

Another relevant feature is that all the methyl groups are bent inward toward the central metal from the plane of cyclooctatetraene ring. The angle of this bent ranges from 0.82° to 6.45°, averaging 4.1°. The Authors suggest two possible explanations: the first is the increasing of directionality for overlap between the π orbital of the $C_8H_8^{-2}$ ring and metal orbital; the second is a slight polarization of the ligand electron density toward the metal and, more important, the contraction in volume (but not in total electron charge) of the electron density on the side of the ring adjacent to the metal ion.

Many other substituted uranocenes, in addition to the tetramethyl derivative, have been synthesized and characterized. Streitwieser[38] reported the derivatives of the following cyclooctatetraenes: ethyl, n-butyl, vinyl, phenyl, cyclopropyl. 1,1'-Diethyl and 1,1'-di-n-butyl uranocene have also been prepared by Karraker.[39]

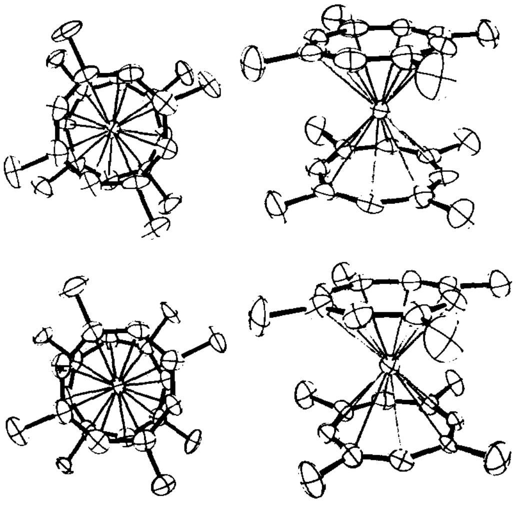


Figure 6. The two crystallographically independent molecules A and B in the crystal structure of $U(C_8H_4(CH_3)_4)_2$ (from Hodgson and Raymond,[37] by courtesy of the *American Chemical Society*).

The general preparation was the same used also for $U(COT)_2$, that is starting from the substituted cyclooctatetraene dianion and UCl_4 in tetrahydrofuran. The yield is generally high, namely 92% for the ethyl, 90% for the n-butyl, 87% for the phenyl, 97% for the vinyl, 88% for cyclopropyl and 53% for the tetramethyl derivative. All the substituted complexes are much more soluble in organic solvents than uranocene. The solids are less sensitive to oxygen, in particular the phenyl derivative is stable in air for several minutes. Spectral data as far as visible, infrared, mass and nmr are concerned, are reported in Table II, in comparison with the simple uranocene.

The alkyl substituted uranocenes show bathochromic shifts in the visible spectrum interpreted as charge-transfer transitions and this agrees with the formulation of uranocene as an f orbital metallocene.

Only slight changes in the infrared absorption bands are observed in the substituted compounds in addition to the absorptions due to the substituent.

TABLE II. Spectral Data on Uranocene and Substituted Uranocenes, $U(R\text{–}COT)_2$ (from Streitwieser and Harmon,[38] by Courtesy of the *American Chemical Society*).

R	Visible spectrum,[a] nm ($\epsilon \times 10^{-3}$)
H	616 (1.8), 643 (0.72), 661 (0.41), 671 (0.12)
C_2H_5	619 (1.5), 644 (0.54), 666 (0.36), 682 (0.30)
n-C_4H_9	622 (1.6), 651 (0.60), 671 (0.37), 681 (0.23)
C_6H_5	625 (1.1), 652 (0.45), 671 (0.30), 684 (0.19)
$CH{=}CH_2$	617 (1.1), 645 (0.33), 664 (0.20)
c-C_3H_5	619 (1.5), 647 (0.52), 662 (0.37), 683 (0.16)
1,3,5,7-$(CH_3)_4$	650 (0.90), 689 (0.47), 704 (0.44), 718 (0.33)

R	Infrared spectrum, cm^{-1} (Nujol mull)
H	1320 w, 1260 w, 900 m, 780 w, 775 w, 745 m, 700 s
C_2H_5	1321 w, 1247 m, 940 m, 900 m, 720 s, 682 m
n-C_4H_9	1320 w, 1245 m, 941 m, 907 m, 727 s, 684 m
C_6H_5	1590 w, 1330 w, 1254 m, 925 w, 765 w, 750 w, 725 s, 700 s
$CH{=}CH_2$	1615 w, 1333 w, 1296 w, 1256 m, 987 m, 935 m, 750 m, 722 s
c-C_3H_5	1322 w, 1260 m, 798 m, 720 m, 710 m
1,3,5,7-$(CH_3)_4$	1250 m, 907 m, 836 m, 728 s

R	Mass spectrum, *m/e* of major identifiable peaks
H	446 $(C_8H_8)_2U^+$, 342 $(C_8H_8)U^+$, 104 $(C_8H_8)^+$
C_2H_5	502 $(EtC_8H_7)_2U^+$, 446 $(C_8H_8)_2U^+$, 370 $(EtC_8H_7)U^+$
n-C_4H_9	558 $(BuC_8H_7)_2U^+$, 515 $(BuC_8H_7)(C_8H_7CH_2)U^+$, 502 $(BuC_8H_7)(C_8H_8)U^+$, 446 $(C_8H_8)_2U^+$, 398 $(BuC_8H_7)U^+$
C_6H_5	598 $(C_6H_5C_8H_7)_2U^+$, 521 $(C_6H_5C_8H_7)(C_8H_7)U^+$, 446 $(C_8H_8)_2U^+$, 418 $(C_6H_5C_8H_7)U^+$, 180 $(C_6H_5C_8H_7)^+$
$CH{=}CH_2$	498 $(C_{10}H_{10})_2U^+$, 446 $(C_8H_8)_2U^+$, 368 $(C_{10}H_{10})U^+$, 130 $(C_{10}H_{10})^+$
c-C_3H_5	526 $(C_{11}H_{12})_2U^+$, 485 $(C_{11}H_{12})(C_8H_7)U^+$, 446 $(C_8H_8)_2U^+$, 382 $(C_{11}H_{12})U^+$
1,3,5,7-$(CH_3)_4$	558 $(C_{12}H_{16})_2U^+$, 398 $(C_{12}H_{16})U^+$, 160 $(C_{12}H_{16})^+$

R	Solvent	Nmr spectrum, δ[b] at 34°
H	THF[c]	−35.2
C_2H_5	THF	0.2 (CH_3), −16.3 (CH_2), −31.8, −33.3, −35.0, −38.1
n-C_4H_9	C_6D_6	1.23 (CH_2), 0.54 (CH_3), −25.9 (CH_2), −32.0, −33.5, −35.6, −39.2
$CH{=}CH_2$	C_6D_6	−8.7 (quartet), −10.4 (d), −13.6 (d), −33.4 (d), −35.1, −37.2
1,3,5,7-$(CH_3)_4$	THF	−3.8, −34.5

[a] Spectra taken in THF. [b] Referenced to TMS with minus sign indicating upfield. [c] At 29°.

All of the compounds, except octamethyluranocene, give a relevant mass peak corresponding to $U(C_8H_8)_2^+$ coming from the stripping off of the side chain.

The NMR spectra are consistent with the already discussed interpretations based on consistent dipolar contribution and a contact term derived from spin density in the π MO of the ligand. The chemical reactivity of these substituted uranocenes was also investigated. Some attempts to prepare mixed sandwich complexes, for example starting from 1,1′-diethyluranocene and 1,1′-dibutyluranocene, were unsuccessful showing the covalent nature of the ring–metal bonding in uranocene. Substituted uranocenes are stable to the hydrogenation: only 1,1′-divinyluranocene is readily hydrogenated on the substituent groups to yield diethyluranocene.

D. Allyl Derivatives

Considerable progress in the field of organometallic chemistry of the actinides has been made with the synthesis of the first allyl derivative of uranium: tetra (allyl)uranium.[40] The compound was obtained from the reaction of UCl_4 with allyl Grignard at low temperature, according to the equation

$$UCl_4 + 4C_3H_5MgBr \rightarrow U(C_3H_5)_4 + 4\ MgBrCl \qquad (9)$$

The isolated crystalline dark-red complex burns spontaneously in the air, but it is stable under inert atmosphere at low temperature (< −20° C).

Preliminary characterization has been made by infrared spectroscopy and magnetic susceptibility.

The more definite bands at 1220, 1000, 810, 750 and 580 cm^{-1} have been reasonably attributed to the modes of vibration of a π-allylic group. No double stretching frequencies, which could be ascribed to a σ-allyl structure, were observed in the $1650 \div 1600$ cm^{-1} range.

The magnetic moment of the compound is calculated to be 2.6 BM, very similar to what was found for UCp_3Cl and UCp_4, supporting the idea of a similarity in the type of bonding. Also $U(2\text{-methylallyl})_4$ was prepared in the same way from methallylmagnesium chloride.[41] The definite proof of the suggested π-allyl structure of these compounds comes from NMR spectra. A preliminary account[42] on this subject shows that the large chemical shifts observed are significantly affected by a pseudo-contact mechanism. More complete date on the proton magnetic resonance on both $U(allyl)_4$ and $U(2\text{-methylallyl})_4$ are recently presented.[43] Both spectra show patterns indicating equivalent, symmetrically bonded π-allyl groups with no sign of exchange between *syn* and *anti* protons. The chemical shifts of $U(allyl)_4$ and $U(2\text{-methallyl})_4$ are reported in Table III.

The temperature dependence of the chemical shifts of the two compounds shows the following feature: (i) the plots of δ versus 1/T are approximately linear, but give non-zero intercepts which are very far from expected diamagnetic limit calculated from similar diamagnetic compounds. In the case of the CH_2-*syn* protons the shift appears to be almost independent from the temperature; (ii) going from $U(allyl)_4$ to $U(2\text{-methylallyl})_4$ the CH_3 protons are shifted markedly to low field respect to the allyl proton.

The analysis of the non-Curie behaviour of the temperature dependence of the signals is made using the Kurland–Mc Garvey equations and the contact and dipolar terms are calculated by using the comparison between methylated compound and non-methylated analog.

E. π-Arene Complex of Uranium–Aluminium Chloride

Even though not strictly pertinent with the subject of this article, which mainly deals with U(IV) organometallic complexes, it is interesting to mention a unique example of π-arene derivative, that is $(C_6H_6)UCl_3 \cdot 3AlCl_3$.[44] The interest of this compound lies also in the comparison of its crystallographic data (for ex. U–C and U–Cl bond lengths, *etc.*), with that already

TABLE III. Chemical Shifts of $U(allyl)_4$ and $U(2\text{-methylallyl})_4$ as a Function of T.[a]

Compound	°K	H_{syn}	$H_{methine}$	H_{anti}	CH_3
$U(allyl)_4$	∞[b]	19.83	−5	22.3	–
	248	18.72	28.74	53.8	–
	213	18.70	35.3	59.8	–
	183	18.33	40.9	66.1	–
$U(2\text{-methylallyl})_4$	∞	22.31	–	20.49	3.96
	241	18.24	–	53.28	18.08
	224	17.99	–	56.06	19.19
	209	17.61	–	58.70	20.23
	193	17.92	–	61.40	21.61

[a] The signals are upfield with respect to the internal standard. [b] From extrapolation to 1/T = 0.

reported for cyclopentadiene and cyclooctatetraene uranium derivatives.

The new complex is obtained by reacting UCl_4, $AlCl_3$ and powdered aluminium in anhydrous benzene. The mixture was refluxed for several hours and the brown suspension filtered. By cooling to room temperature and very slowly (2–3 days) big black crystals appeared. The compound was repeatedly crystallized from benzene. Chemical analyses agree with the crude formula $C_6H_6Cl_{12}Al_3U$. It is practically insoluble in all common organic solvents; polar solvents (THF) decompose the complex giving $AlCl_3 \cdot$base, UCl_3 and benzene.

The crystal and molecular structure of the complex was investigated by single crystal X-ray method. The crystal data are: triclinic, space group $P\bar{1}$; $a = 9.47$; $b = 10.81$; $c = 16.79$ Å; $\alpha = 98.7°$; $\beta = 86.5°$; $\gamma = 122.9°$; $Z = 2$; calculated density = 1.914 g cm^{-3}.

In Figure 7 two projections of the molecule, one parallel, the other perpendicular to the mean plane of benzene, are given. The structure is made up of an uranium atom which coordinates three $AlCl_4$ tetrahedra, through U–Cl–Al bridge bonds and a benzene ring.

The mean U–C distance of 2.91(5) Å is significantly large even though compared with the values found, for this bond, in all the other π-carbocyclic complexes (with chlorine atom as ligand) of U(IV), whose ionic radius is smaller (about 0.1 Å[21]) than that of U(III). This is in agreement with a zero charge which is assigned to the benzene molecule.

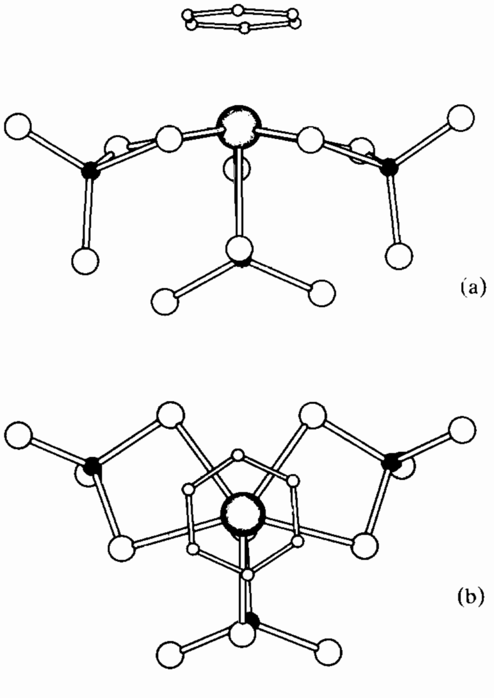


Figure 7. Projections of the molecule of $C_6H_6 \cdot UCl_3 \cdot 3AlCl_3$ in the plane of the benzene ring, b); and in a plane perpendicular, a) (from Cesari *et al.*[44]).

3. Complexes with σ Ligands

The preparation of the first alkyl and aryl derivatives of uranium(IV) was achieved in our laboratories.[45]

A preliminary account of this work, concerning particularly the synthesis and characterization of tris (cyclopentadienyl)phenyluranium, $U(C_5H_5)_3C_6H_5$, was presented in 1970[41] and reference to this work was made also in a review article by Calderazzo.[46]

Work on uranium carbon bonds was extended by us to include σ-alkyl derivatives of the same class, Cp_3UR, and the obtained results were presented in part at an international Symposium.[47] More detailed data were reported later[48] regarding the synthesis and characterization of some Cp_3UR and, namely, $U(C_5H_5)_3C_6H_5$, $U(C_5H_5)_3CH_2C_6H_5$, $U(C_5H_5)_3CH_2\text{-}p\text{-}C_6H_4CH_3$, $U(C_5H_5)_3CH_3$, $U(C_5H_5)_3\text{n-}C_4H_9$.

All the compounds were obtained by the following reactions:

$$U(C_5H_5)_3Cl + LiR \xrightarrow{THF} U(C_5H_5)_3R + LiCl \quad (11)$$

where R = methyl, n-butyl, phenyl, benzyl

$$U(C_5H_5)_3Cl + RMgBr \xrightarrow{THF} U(C_5H_5)_3R + MgClBr \quad (12)$$

where r = xylyl

The compounds are moderately soluble in organic solvents and thermally stable in the solid state.

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

$$U(C_5H_5)_3R + CH_3OH \rightarrow R\text{–}H + U(C_5H_5)_3OCH_3 \quad (13)$$

However, substantial amount of cyclopentadiene was found in this reaction, suggesting that alcoholysis of cyclopentadienyl groups also takes place

$$Cp_3UOR + R\text{–}OH \rightarrow C_5H_6 + U(OR)_4 \quad (14)$$

The mass spectrum of the phenyl derivative showed 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 the C_5H_6 fragment. Further unequivocal evidence for the presence of the uranium carbon bond comes from the NMR measurements (Table IV).

The protons of α-alkyl groups are characterized by very large chemical shifts, ranging from 194 ppm (from benzene) for the α-CH_2 of $UCp_3\text{n-}C_4H_9$ to 213 ppm

TABLE IV. Proton Magnetic Resonance Data for Some $(h^5\text{-}C_5H_5)_3UR$ Compounds.[a]

R	Solvent	$H_{C_5H_5}$	H_{C_1}[b]	H_{C_2}	H_{C_3}	H_{C_4}	Ref.
Methyl	Toluene-d_8	9.88(15H,s)	206(3H,s)				48, 51
n-Butyl	Toluene-d_8	10.3 (15H,s)	194(2H,m)	33.4(2H,m, J = 8Hz)	27.6(2H,m, J = 8Hz)	18.7(3H,t, J = 8Hz)	48, 51
t-Butyl	–	11.4 (15H,s)		23.2(9H,s)			51
i-Propyl	–	10.9 (15H,s)	190(1H, sept., J = 7Hz)	19.3(6H,d, J = 7Hz)			51
Neopentyl	–	11.6 (15H,s)	192(2H,s)	22.1(9H,s)			51
Vinyl	–	9.3 (15H,s)	163.6(1H, dd, J = 16Hz)	17.0(1H,dd, J = 20.5Hz) –24.4(1H, dd, J = 16.5Hz)			51
Allyl	–	10.0 (15H,s)	126(4H,br)	38.2(1H,quint, J = 11Hz)			51
Allyl (–90°C)	–	13.1 (15H,s)	344(2H)	41(1H)	57.5(1H) 60.9(1H)		51
Cis-2-Butenyl	–	10.6 (15H,s)		19.8(3H,s) 22.6(1H,quart, J = 6Hz)	42.3(3H,d, J = 6Hz)		51
Trans-2-Butenyl	–	10.7 (15H,s)		33.0(3H,d, J = 7Hz) –23.5(1H,quart., J = 7Hz)	33.6(3H,s)		51

R	Solvent	$H_{C_5H_5}$	H_{C_1}	H_{ortho}	H_{metha}	H_{para}	$H_{p\text{-}CH_3}$	Ref.
Phenyl	Toluene-d_8	9.77(15H,s)		23.6 (2H, d, J = 8Hz)	14.5(2H, t, J = 8Hz)	6.1 (1H, t, J = 8Hz)		48, 51
p-Tolyl	THF	3.98(15H,s)		18.5(2H,d, J∼8Hz)	9.65(2H,d, J∼8Hz)		15.13(3H,s)	52
Phenyl-acetylide[c]	THF	4.27(15H,s)		9.65(2H,d, J∼8Hz)	4.24(t)	–4.65(1H,t, J∼8Hz)		52
	Benzene	9.98(15H,s)		14.7 (2H,d, J∼8Hz)	9.65(2H,t, J∼8Hz)			52
Benzyl	Toluene-d_8	9.90(15H,s)	213(2H,s)	29.37(2H,d, J∼8Hz)	4.6 (2H,t, J∼8Hz)	10.12(1H,t, J∼8Hz)		48
p-Xylyl	Toluene-d_8	9.95(15H,s)	214(2H,s)	29.4 (2H,d, J∼8Hz)	5.62(2H,d, J∼8Hz)		3.6(3H,s)	48

[a] PMR data in ppm relative to internal benzene: the positive values are upfield; the negative downfield respect to internal standard. [b] Chemical shifts measured in unlocked conditions. [c] Chemical shifts referred to the upfield THF resonance.
s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

for the methylene group of $UCp_3CH_2C_6H_5$. A discussion on the origin of such shifts in terms of contact and dipolar couplings will be reported elsewhere.[48a] The protons of the cyclopentadienyl groups give rise to one signal at ~ 10 ppm.

Also infrared spectra show the presence of *pentahapto*-cyclopentadienyl rings (characteristic bands at 3080, 1435, 1010, 790 and 780 cm^{-1}). 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.

Some contributions on the same subject came also, independently, from other research groups.

Gebala and Tsutsui[49] prepared tricyclopentadienylphenyluranium by reaction of Cp_3UCl with phenyllithium. Marks and Seyan[50] reported in a preliminary paper a series of Cp_3UR derivatives obtained by the same reactions (11) and (12).

Successively other new compounds have been prepared by the latter Authors[51] and characterized by chemical and physical means.

The synthesized complexes belong to the general formula Cp_3UR, where R is: CH_3; n-C_4H_9; allyl; neopentyl; C_6F_5; i-C_3H_7; t-C_4H_9; *cis*-2-butenyl; *trans*-2-butenyl; C_6H_5; vinyl.

Generally the products are darkly coloured crystalline solids, soluble in aromatic solvents, sparingly soluble in aliphatic hydrocarbons. They can be stored under nitrogen without decomposition.

Infrared data indicate that the cyclopentadienyl rings are bonded in a *pentahapto* configuration.

A summary of NMR data are reported in Table IV. All compounds exhibit very large chemical shifts characteristic for paramagnetic systems and agree with our data. The dipolar and contact terms are also reported showing that both terms are equally important, but opposite in direction. The allyl derivative is fluxional at room temperature, showing a typically A_4X pattern; at low temperature (179° K) it became a *monohapto*allyl with a characteristic A_2BCD spectrum.

The NMR results are interpreted satisfactorily by an interconversion mechanism. Furthermore, from NMR spectra of the isopropyl derivative a restricted rotation about uranium–carbon bond is observed.

After their initial communication, Gebala and Tsutsui reported the synthesis of $(\pi\text{-}C_5H_5)_3UC_6H_5$, $(\pi\text{-}C_5H_5)_3UC_6H_4CH_3$ and $(\pi\text{-}C_5H_5)_3UC_8H_5$ (phenylacetylide).[52] All three compounds are extremely air sensitive and reactive with water. Hydrolysis of $Cp_3UC_6H_5$ results in the release of benzene (~ 90%). Their thermal stability is high.

The reported chemical shifts of the *ortho* and *meta* protons of the phenyl derivative are correct, but the value for the *para* proton does not agree with that reported by other Authors.[48,51] In fact, according with the data reported by Marks and Seyan, we have observed for the same compound a chemical shift very different, as verified by spin-decoupling experiment.

An X-ray study on a single crystal of tricyclopentadienyl phenylethynyluranium was carried out by Atwood *et al.*[53] The σ nature of the bond between the phenylacetylide group and the U atom is shown in Figure 8.

The uranium–carbon σ bond length is 2.33(2)Å, while the uranium–π-C_5H_5 carbon lengths average is 2.68 Å. Thus the σ-bond is at least 0.3 Å shorter than any of the reported values.

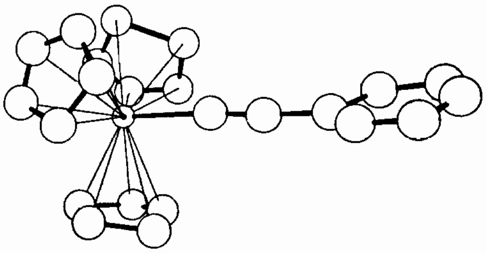


Figure 8. Structure of tricyclopentadienylphenylethynyluranium (from Atwood *et al.*[53] by courtesy of the *Chemical Society*).

4. Complexes with Various Ligands: Some Recent Aspects

It is beyond the scope of this article to review the coordination chemistry of uranium(IV), which generally is well known from long time and many articles and reviews have been published.[54] In the more recent years some papers appeared on novel compounds with oxygen and nitrogen donor ligands,[55] with quadridentate ligands such as $U(Salen)_2$ and phosphine ligands,[56] with N,N-diethyldithiocarbamate[57] and formate.[58] Also crystal structures have been reported for the acetylacetonatouranium(IV)[59] and related compounds.[60]

We would like to report some very recent aspects of the research carried out in our and other laboratories, some of which not yet published, more strictly related to the organometallic chemistry of uranium(IV).

These researches may be also the basis of new advances in this field, as far as both the synthesis and characterization of new complexes are concerned, as well as the investigation of their catalytic properties.

Since 1963 Herzog and Oberender[61] reported the synthesis of an uranium complex with 2,2′-dipyridyl, tetrakis-2,2′-dipyridyluranium. It was obtained by the reaction:

$$UCl_4 + 4\ Lidipy \rightarrow U(dipy)_4 + 4\ LiCl \qquad (15)$$

employing either Li_2dipy in THF or Lidipy in dioxane. This procedure was recently repeated by us, obtaining the same results. The isolated compound was studied by infrared spectroscopy and its crystalline and molecular structure was determined by means of X-ray analysis.[62]

The meaningful frequencies of the infrared spectrum are 1580 (m), 1570 (m), 1557 (m), 1515 (m), 1503 (m), 1420 (m), 1395 (m), 1325 (m), 1145 (s), 935 (s) cm^{-1} a complex multiplet in the range $600 \div 800\ cm^{-1}$ and a very weak absorption in the $200 \div 600\ cm^{-1}$ range. The characteristic feature of the spectrum, when compared with that of Li_2dipy agrees with the hypothesis of a partially ionic uranium–dipyridyl bond.

The crystal data of the complex are: triclinic, space group $P\bar{1}$; $a = 12.21, b = 15.76, c = 9.63$ Å; $\alpha = 106.1°$, $\beta = 101.7°$, $\gamma = 88.5°$; Z = 2; calcd. density 1.58 g cm^{-3}. The structure is illustrated in Figure 9. The coordination around the uranium atom is approximatively cubic, with an average U–N bond distance 2.48 ± 0.02Å. In spite of the equality of all the U–N bond lengths, two of the four ligands are structurally different from the two others. The most relevant difference lies in the angles between the mean planes of the dipyridyl groups of each pair: by referring to Figure 9 the angle between the I and II ligands is 81°, while the correspondent between the III and IV is 27°. This feature could be connected to an sp^2 hybridization of the nitrogen atoms in I and II ligands, but to an hybrid-

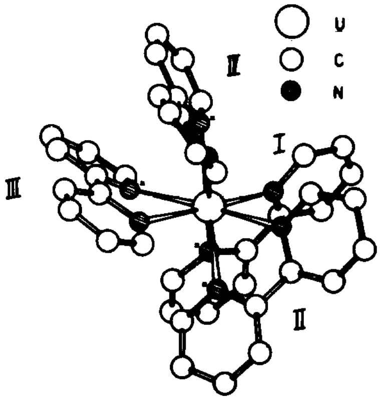


Figure 9. Molecular structure of tetra(2,2′-dipyridyl)uranium (G. Perego, G. Del Piero, A. Zazzetta and M. Cesari, data to be published).

ization close to sp^3 type in III and IV ligands. It is therefore highly probable that the last two ligands are dianions, so that the compound ought to be better considered as $U^{IV}(dipy^{-2})_2(dipy)_2$. Some attempts to prepare organometallic complexes containing more than one σ uranium–carbon bond were also carried out.[63] Among the chelating agents able to stabilize metal–carbon bonds by coordination with heteroatoms, the dibenzylethylamine was considered. The *o,o′*-dichlorodibenzylethylamine was synthesized and reacted in refluxing n-hexane with lithium sand containing 2% of sodium, in such a way to obtain the *o,o′*-dilithium derivative (yield 90%). By reacting an ethereal solution of this dilithium derivative with UCl_4 in tetrahydrofuran (molar ratio 2:1), followed by solvent evaporation and benzene extraction, a red very air sensible compound was obtained, which analyses fit well for $C_{32}H_{34}N_2U$. A comparison of infrared spectra of the isolated compound and the dibenzylethylamine shows variations of the aromatic ligand in the range $600 \div 800\ cm^{-1}$ (out of plane vibrations) and in the range $1700 \div 2000\ cm^{-1}$ (overtone modes vibrations). On this basis it is reasonable to suppose a substitution in *ortho* positions of the aromatic ring. Unfortunately, repeated attempts to prepare this uranium derivative were not always successful. Additional work is necessary to well characterize the complex, for ex. by NMR and X-ray tecniques.

The work reported by Sebin *et al.*[56] on the bis N,N′-ethylenebis(salicylideneiminato)uranium(IV), $U(Salen)_2$, was recently extended by Calderazzo *et al.* with the synthesis of mixed complexes of formula $U(Salen)X_2$. In a preliminary note the preparation of $U(Salen)Cl_2$ and its adduct with tetrahydrofuran, $U(Salen)Cl_2 \cdot 2THF$ has been reported.[64] Further details of the redistribution reaction between $U(Salen)_2$ and UCl_4 and some mixed complexes $U(Salen)X_2$ (X = Cl, N-methylsalicylideneiminato, acetylacetonato, dibenzoylmethanato and dipivaloylmethanato) are now reported.[65] The following equilibria are suggested to be operating in THF solutions:

$$U(Salen)_2 + UCl_4 \rightarrow U(Salen)_2 \cdot UCl_4 \qquad (16)$$

$$U(Salen)_2 \cdot UCl_4 \rightarrow 2\ U(Salen)Cl_2 \qquad (17)$$

Also the conjugate bases of acetylacetone (AcacH), dipivaloylmethane (DPMH) and N-methylsalicylideneimina (Me-SalH) react with the product resulting by mixing equimolar amount of $U(Salen)_2$ and UCl_4 yielding the mixed complexes:

$$U(Salen)_2 + UCl_4 + 4\ C_5H_7O_2^- \rightarrow 2\ USalen(Acac)_2 + 4\ Cl^- \qquad (18)$$

$$U(Salen)_2 + UCl_4 + 4\ C_{11}H_{19}O_2^- \rightarrow 2\ USalen(DPM)_2 + 4\ Cl^- \qquad (19)$$

$$U(Salen)_2 + UCl_4 + 4\ C_8H_8NO^- \rightarrow 2\ USalen(Me\text{-}Sal)_2 + 4\ Cl^- \qquad (20)$$

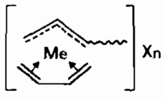
Chemical and mass-spectrometric data are presented supporting the monomeric structure of these complexes.

The interest in such type of complexes comes not only from the novelty of these redistribution reactions for uranium(IV) compounds, but also from the possibility, now under investigation, of preparing new organometallic complexes with two uranium–carbon bonds.

The synthesis of several chelates of uranium(IV) from UCl_4 in tetrahydrofuran by treatment with the organic chelating acid in the presence of ammonia is also reported from the same Authors.[66] Mass spectra of these chelates are discussed.

5. Catalytic Behaviour of Some Uranium Derivatives

The role of organometallic transition metal derivatives in homogeneous catalysis is well known and largely investigated in the last years. Among the catalytic reactions promoted by organometallic metal complexes, the stereospecific polymerization of unsaturated monomers has received particular attention reaching relevant results, not only from a theoretical point of view, but also for the development of new polymerization processes today employed industrially. Particularly for the eight group metals (for ex. cobalt and nickel) many recent finding indicate the formation of π-allylic type structure when conjugate dienes are polymerized.[67] The π-allylic bond can be generated by the action of the monomer, thus supporting the hypothesis that growth of polymer chain occurs by the insertion of monomer on the π-allylic bond between the last polymerized unit and the transition metal:



Of great importance, therefore, are the investigations on the stereospecific polymerization by simple and pure π-allyl transition metal derivatives, which can be considered as a good model (or precursor) of the active site structure. In view of this, since the discovery of tetra(π-allyl)uranium, a great deal of research work was carried out in our laboratories to investigate its catalytic behaviour in diolefins polymerization. Tetraallyluranium itself is not active in the polymerization of butadiene, giving only traces of dimerization and trimerization products. By reacting $(\pi\text{-allyl})_4U$ with anhydrous HCl (HBr, HI) we have obtained $(\pi\text{-allyl})_3UX$[68] according to the following reaction:

$$(\pi\text{-allyl})_4U + HX \rightarrow (\pi\text{-allyl})_3UX + C_3H_6 \qquad (21)$$

where X = Cl, Br, I. A preliminary characterization of these novel complexes was recently reported.[69] Trisallyluranium halides can initiate alone the stereospecific polymerization of butadiene giving 1,4-*cis* polybutadiene with an extremely high *cis* content, up to 99%, and better technological properties than that of traditional polybutadienes.[70] When a Lewis acid is added to allyluranium halogenides or to the tetraallyluranium the catalyst activity is very much improved.

π-allyluranium catalysts are also active in other diolefin polymerizations (isoprene, pentadiene, *etc.*) as well as in the polymerization of α-olefins.[70] Also diolefin copolymers, characterized by the high 1,4-*cis* content of both monomer units, can be prepared by the uranium catalysts. Studies carried out by means of H NMR spectroscopy on the isolated uranium catalysts as well as in the presence of the monomer (for ex. butadiene), now in progress in our laboratories, should help the understanding of the polymerization mechanism, today not completely solved in all aspects.

As shown previously, these researches are not only interesting from the theoretical point of view. Considering the large availability of depleted uranium, the manifold possibility of coordination of this metal and the more and more increasing knowledge on the organometallic chemistry of this element, the research on uranium based catalysts in homogeneous catalysis seems undoubtedly attractive.

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