ELSEVIER Journal of Organometallic Chemistry 484 (1994) 195–201

Journal of Organometallic Chemistry

Reaction of uranium tetrachloride with trimethylsilylcyclopentadiene: crystal structure of a dichloromethane adduct of $[\{U(cp)_2(\mu\text{-}Cl)\}_3(\mu_3\text{-}Cl)_2][\{U(cp)Cl_2\}_2(\mu\text{-}Cl)_3]$ (cp = η-C_5H_5)

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Received 24 March 1994

Abstract

The uranium tetrachloride reacts in dichloromethane with 1 and 3 equivalents of trimethylsilylcyclopentadiene to give $[U(cp)Cl_3]$ (**1**) and $[U(cp)_3Cl]$ (**3**) respectively (cp = η-C_5H_5). The title compound **2** was isolated from the reaction of UCl_4 with 2 equivalents of the silylated cyclopentadiene. Complex **2** is in equilibrium with **1** and **3** in refluxing dichloromethane.

Keywords: Uranium; Cyclopentadienyl; X-ray structure; Bis(cyclopentadienyl)uranium; Actinide

1. Introduction

The first organometallic compound of uranium, like the first organometallic compound of other transition metals, was made by treating the most common halide precursor, in this case UCl_4, with the sodium salt of the cyclopentadienyl anion. In this way chlorotriscyclopentadienyluranium $[U(cp)_3Cl]$ (cp = η-C_5H_5) was isolated in 1956 by Reynolds and Wilkinson [1]. The monocyclopentadienyl complexes $[U(cp)Cl_3(L)_2]$ (L = tetrahydrofuran (THF) or $(L)_2$ = dimethoxyethane) were obtained more than 15 years later by Bagnall and Edwards [2] and Zanella and coworkers [3], but dichlorobiscyclopentadienyluranium $[U(cp)_2Cl_2]$ could not be isolated [4], because of its rapid disproportionation into the monocyclopentadienyl and triscyclopentadienyl derivatives [5]. This reaction certainly involves the unstable intermediate $[U(cp)_2Cl_2(L)_2]$ (L = tetrahydrofuran or $(L)_2$ = dimethoxyethane):

$$2[U(cp)_2Cl_2(L)_2] \rightleftharpoons [U(cp)Cl_3(L)_2] + [U(cp)_3Cl] + 2L \qquad (1)$$

However, Andersen and coworkers [6] have more recently prepared the adduct of $[U(cp)_2Cl_2]$ with the chelating phosphine $Me_2PCH_2CH_2PMe_2$ (dmpe), $[U(cp)_2Cl_2(dmpe)]$, thus demonstrating that the position of the equilibrium in reaction (1) is greatly influenced by the nature of the Lewis base L. It seemed to us of interest to consider the synthesis and dynamic behaviour of the complexes $[U(cp)_{4-n}Cl_n]$ (n = 1–3) in a non-coordinating solvent and in the absence of any Lewis base. Because monocyclopentadienyl and biscyclopentadienyl complexes of the Groups 4 and 5 metals have been synthesized conveniently in dichloromethane or benzene by treatment of the parent halides with the silylated cyclopentadiene $Me_3SiC_5H_5$ (tmscp) [7], we have used this reagent for the preparation of the

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SSDI 0022-328X(94)24727-Z

desired uranium compounds. Here we describe the products isolated from the reactions of UCl_4 and various amounts of tmscp, paying special attention to the polynuclear compound $[\{U(cp)_2(\mu\text{-}Cl)\}_3(\mu_3\text{-}Cl)_2][\{U(cp)Cl_2\}_2(\mu\text{-}Cl)_3]$.

2. Results and discussion

2.1. Syntheses

Uranium tetrachloride reacts in refluxing dichloromethane for 5 days with 1 equivalent of tmscp to give the monocyclopentadienyl trichloride $[U(cp)Cl_3]$ (**1**), isolated as an orange powder with 82% yield. This compound, which is certainly polymeric in the solid state, is quite insoluble in dichloromethane or toluene but was quantitatively transformed into the known adducts $[U(cp)Cl_3(L)_2]$ (L = THF, hexamethylphosphoramide or triphenylphosphine) [8,9], by dissolution in THF or treatment with the corresponding Lewis base:

$$\mathrm{UCl_4 + tmscp \rightarrow \underset{(1)}{[U(cp)Cl_3]} + tmsCl} \tag{2}$$

Reaction (2) represents a unique route to the base free complex **1**, which could not be obtained by dissociation of THF from $[U(cp)Cl_3(THF)_2]$.

Not surprisingly, treatment of UCl_4 with 3 equivalents of tmscp led to the formation of $[U(cp)_3Cl]$ (**3**) with an almost quantitative yield (by NMR):

$$\mathrm{UCl_4 + 3tmscp \rightarrow \underset{(3)}{[U(cp)_3Cl]} + 3tmsCl} \tag{3}$$

this red–brown compound is soluble in dichloromethane.

More interesting was the reaction of UCl_4 with 2 equivalents of the silylated cyclopentadiene. The red solution obtained after 5 days upon cooling and concentration deposited beautiful ruby crystals. The exact nature of this new compound **2** was not known until the crystal structure was determined (see below). However, the elemental analyses were consistent with the formula $U_5(cp)_8Cl_{12}\cdot CH_2Cl$ whereas the ^1H NMR spectrum in dichloromethane exhibited two cp signals in a 3:1 ratio. These resonances were afterwards assigned to the six equivalent cp ligands of the cation $[U(cp)_6Cl_5]^+$ and the two equivalent cp ligands of the anion $[U(cp)_2Cl_7]^-$. The reaction between UCl_4 and 2 equivalents of tmscp was monitored by ^1H NMR spectroscopy and it was observed that all the tmscp was transformed into tmsCl and that approximately two molecules of **3** were formed per one molecule of **2**, assuming the latter to contain eight cp ligands. It was then possible to describe the above reaction by

$$\mathrm{7UCl_4 + 14tmscp \rightarrow \underset{(2)}{U_5(cp)_8Cl_{12}} + 2\underset{(3)}{[U(cp)_3Cl]} + 14tmsCl} \tag{4}$$

According to this equation, the yield of **2**, 44% based on UCl_4, was 62% of its maximum value. By using the stoichiometry of 8 equivalents of tmscp to 5 equivalents of UCl_4, it was expected that **2** would be the sole organouranium product ($5UCl_4 + 8\ \mathrm{tmscp} \rightarrow U_5(cp)_8Cl_{12} + 8\ \mathrm{tmsCl}$). In fact, this reaction afforded a mixture of **1**, **2** and **3** in the approximate molar ratio 3.5:1:1.5. The same mixture was obtained when **2**, or **1** and **3** (in the molar ratio 7:3) were heated in dichloromethane, thus demonstrating the equilibrium described by

$$\mathrm{\underset{(2)}{2U_5(cp)_8Cl_{12}} \rightleftharpoons 7\underset{(1)}{[U(cp)Cl_3]} + 3\underset{(3)}{[U(cp)_3Cl]}} \tag{5}$$

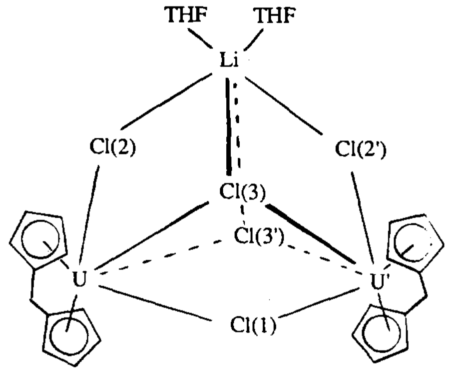
The crystals of **2** could be dissolved in THF, giving a mixture of $[U(cp)Cl_3(THF)_2]$ and $[U(cp)_3Cl]$:

$$\mathrm{\underset{(2)}{2U_5(cp)_8Cl_{12}} \xrightarrow{THF} 7\underset{(1).2THF}{[U(cp)Cl_3(THF)_2]} + 3\underset{(3)}{[U(cp)_3Cl]}} \tag{6}$$

Such ligand redistribution reactions are frequently observed in uranium chemistry. The disproportionation of the elusive $[U(cp)_2Cl_2(THF)_2]$ has already been described in Section 1. Another example is the rearrangement in THF of the borohydride complex $[U(cp)(BH_4)_3]$ into $[U(cp)_2(BH_4)_2]$ and $[U(BH_4)_4(THF)_2]$, whereas $[U(cp)(BH_4)_3]$ can be prepared in toluene from an equimolar mixture of $[U(cp)_2(BH_4)_2]$ and $[U(BH_4)_4]$ [10]. The relative stabilities of the species $[U(cp)X_3]$, $[U(cp)_2X_2]$, $[U(cp)X_3(THF)_2]$ and $[U(cp)_2X_2(THF)_2]$, where the X (BH_4 or Cl) have similar sizes, are clearly not determined by steric factors but could be accounted for by specific electronic effects of X (BH_4 is more electron-donating than Cl) [11].

Complex **2** was also formed when UCl_4 was treated with **3**. However, this reaction does not constitute a convenient synthesis of **2**, because of apparent passivation of the solid uranium tetrachloride.

Reactions which could lead to the formation of the biscyclopentadienyl compound $[U(cp)_2Cl_2]$, namely treatment of $[U(cp)_3Cl]$ with 1 equivalent of $[U(cp)Cl_3]$ or with 0.5 equivalent of UCl_4, gave mixtures of **2** and unreacted $[U(cp)_3Cl]$. All attempted preparations of $[U(cp)_2Cl_2]$ in non-coordinating solvents and in the absence of Lewis base thus afforded the very stable complex **2**. Even though its formation is difficult to explain mechanistically, it should be noted that **2** could come from the combination of various species: $3[U(cp)_3Cl] + 7[U(cp)Cl_3]$ (Eq. (5)), $8[U(cp)_3Cl] + 7UCl_4$, but also $4[U(cp)_2Cl_2] + UCl_4$ or $3[U(cp)_2Cl_2] + 2[U(cp)Cl_3]$. The crystal structure (see below) actually suggested that **2** would be the result of a chloride abstraction from $[U(cp)_2Cl_2]$ to genetic $[U(cp)Cl_3]$, giving the ion pair $[U_3(cp)_6Cl_5]^+$ and $[U_2(cp)_2Cl_7]^-$. It is also noteworthy that the ring-bridged cyclopentadienyl



Scheme 1. Structure of $[U_2\{(C_5H_4)_2CH_2\}_2Cl_5Li(THF)_2]$.

compounds $[U\{(C_5H_4)_2E\}Cl_2]$ (E=CH_2, Me_2Si or $CH_2CH_2CH_2$) which are stable towards ligand redistribution have been isolated in the form of LiCl adducts, such as $[U_2\{(C_5H_4)_2CH_2\}_2Cl_5Li(THF)_2]$, the structure of which is represented in Scheme 1 [12]. From these considerations, one could believe that the base-free complex $[U(cp)_2Cl_2]$, once synthesized, would instaneously form the salt $[\{U(cp)_2(\mu\text{-}Cl)\}_3(\mu_3\text{-}Cl)_2]Cl$.

2.2. *Crystal structure of* $[\{U(cp)_2(\mu\text{-}Cl)\}_3(\mu_3\text{-}Cl)_2]$-$[\{U(cp)Cl_2\}_2(\mu\text{-}Cl)_3] \cdot 2CH_2Cl_2$

The crystallographic data for compound **2** are given in Tables 1–3. The structure is composed of discrete cation–anion pairs; the cation $[\{U(cp)_2(\mu\text{-}Cl)\}_3(\mu_3\text{-}Cl)_2]^+$ is shown in Fig. 1. Although this trinuclear fragment has approximately idealized D_{3h} symmetry, the only crystallographically imposed element of symmetry in the C_2 axis passing through U(2) and Cl(11). The two pseudomirror planes defined by U(1), Cl(22), Cl(22^i), Cl(12^i) (or U(1^i), Cl(22), Cl(22^i), Cl(12)) and U(2), Cl(22), Cl(22^i) and Cl(11) respectively form a dihedral angle of 60.25(1)° and are perpendicular to the planar ring composed of the three uranium and three μ_2-Cl atoms to within $\pm 0.01(1)$ Å. The pseudothreefold axis Cl(22)–Cl(22^i) is orthogonal to the $(U\text{–}Cl)_3$ ring, the opposite μ_3-Cl atoms being equidistant from this plane at 1.52(1) Å. The geometry of the six-membered ring is quite different from that found in the uranium(III) compound $[\{U(C_5Me_5)_2(\mu\text{-}Cl)\}_3]$ [13]. In this, the U–μ_2-Cl bond distances, the U–μ_2-Cl–U and μ_2-Cl–U–μ_2-Cl angles average 2.90(2) Å, 155(3) and 84(2)° respectively whereas, in the cation of **2**, the corresponding values are 2.79(2) Å, 101.0(1) and 139.2(9)°. These distinct parameters are obviously due to the different oxidation state and coordination of uranium (tetrahedral and octahedral) in the two complexes. The environment of each metal in the trinuclear cation of **2** is very similar to that encountered in the mononuclear complex $[Th(cp)_2Cl_2(dmpe)]$ [6], in which the P atoms would be replaced by the μ_3-Cl atoms (Scheme 2).

The stereochemistry of the thorium complex, in which the two cp are in relative *cis* positions, being *trans* to the chelating phosphine, has been rationalized on the bases of Keppert rules (the ligands with the shortest metal ligand distances occupy the less sterically crowded sites *trans* to the bidentate ligand [14]). In the uranium compound $[U_2\{(C_5H_4)_2CH_2\}_2Cl_5Li(THF)_2]$ in Scheme 1, the angles Cl(1)–U–Cl(2) and Cl(3)–U–Cl(3') are 68.9(3) and 146.3(4)° respectively. Like the trinuclear uranium complexes $[U_3(E)(E'_{^tBu})_{10}]$ (E = O [15] or S [16]), the cation of **2** has a structure which results from the cofacial fusion of three distorted octahedra sharing a common edge. The average U–Cl bond lengths (⟨U–μ_2-Cl⟩, 2.79(2) Å; ⟨U–μ_3-Cl⟩, 2.91(2) Å) are as expected for bridging U–Cl bonds [12,13,17] and the geometry of the cp ligands is unexceptional.

An ORTEP drawing [18] of the dinuclear anion $[\{U(cp)Cl_2\}_2(\mu\text{-}Cl)_3]^-$ is shown in Fig. 2. The line passing through Cl(31) and the middle of the U(3)–U(3^{ii}) segment is a C_2 axis of symmetry. The plane defined by U(3), U(3^{ii}) and Cl(31) is a pseudomirror plane, orthogonal to the other pseudomirror plane which contains the three bridging chlorine atoms. The

Table 1
Selected bond distances (Å) and angles (°) with estimated standard deviations for **2**. $2CH_2Cl_2$

The cation $[\{U(cp)_2(\mu\text{-}Cl)\}_3(\mu_3\text{-}Cl)_2]^+$			
Bond lengths			
U(1)–Cl(11)	2.812(7)	U(1)–Cl(12)	2.766(7)
U(1)–Cl(22)	2.920(6)	U(2)–Cl(12)	2.778(6)
U(2)–Cl(22)	2.894(6)	⟨U(1)–C⟩	2.70(2)
⟨U(2)–C⟩	2.73(3)	U(1)–1[a]	2.462(6)
U(1)–2[a]	2.429(7)	U(2)–3[a]	2.467(6)
Bond angles			
Cl(11)–U(1)–Cl(12)	138.6(2)	Cl(12)–U(2)–Cl(12^i)	139.9(3)
1–U(1)–2	115.2(2)	3–U(2)–3^i	115.6(6)
U(1)–Cl(11)–U(1^i)	101.1(3)	U(1)–Cl(12)–U(2)	100.9(2)
U(1)–Cl(22)–U(1^i)	96.1(2)	U(1)–Cl(22)–U(2)	94.7(2)
Cl(22)–U(1)–Cl(22^i)	62.9(2)	Cl(22)–U(2)–Cl(22^i)	63.5(2)
The anion $[\{U(cp)Cl_2\}_2(\mu\text{-}Cl)_3]^-$			
Bond lengths			
U(3)–Cl(31)	2.758(8)	U(3)–Cl(32)	2.817(7)
U(3)–Cl(33)	2.576(8)	U(3)–Cl(34)	2.570(7)
⟨U(3)–C⟩	2.67(2)	U(3)–4[a]	2.423(7)
Bond angles			
Cl(31)–U(3)–4	173.0(2)	Cl(31)–U(3)–Cl(32)	74.1(2)
Cl(32)–U(3)–Cl(32^{ii})	74.6(2)	Cl(33)–U(3)–Cl(34)	97.0(3)
U(3)–Cl(31)–U(3^{ii})	93.0(3)	U(3)–Cl(32)–U(3^{ii})	90.8(2)

Symmetry codes: (i) $1+(\frac{1}{2}-x)$, y, $1+(\frac{1}{2}-z)$; (ii) $1+(\frac{1}{2}-x)$, y, $\frac{1}{2}-z$

[a] 1, 2, 3 and 4 are the centroids of the cyclopentadienyl rings C(10)–C(14), C(15)–C(19), C(20)–C(24) and C(30)–C(34) respectively.

Table 2
Crystallographic data and experimental details for compound **2**. $2CH_2Cl_2$

Crystal data	
Formula	$C_{42}H_{44}Cl_{16}U_5$
M	2304.2
Crystal dimensions (mm)	0.65 × 0.15 × 0.08
Colour	Red
Crystal system	Monoclinic
Space group	$P2/n$
a (Å)	14.479(3)
b (Å)	11.096(2)
c (Å)	18.265(5)
β (°)	99.15(2)
V (Å^3)	2897(2)
Z	2
D_{calc} (g cm^{-3})	2.641
μ(Mo Kα) (cm^{-1})	139.83
$F(000)$	2052
Data collection	
θ limits (°)	1, 20
Scan type	ω, 2θ
Scan width	$0.8 + 0.35 \tan\theta$
Range of abs. trans.	0.942, 1.120
Range of h, k, l	− 13 to 13, 0 to 10, 0 to 17
Reflections collected	
Total	3124
Unique	2714
With $I > 3\sigma(I)$	1593
Number of parameters	199
$R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$	0.032
$R_w = [\Sigma_w \| |F_o| - |F_c| \|^2 / \Sigma_w(|F_o|)^2]^{1/2}$	0.037
Maximum residual electron density (electrons Å^{-3})	0.9

structure of the anion results from the cofacial fusion of two octahedrally coordinated [U(cp)Cl_5] units. The four chlorine atoms Cl(32), Cl(32^{ii}), Cl(33) and Cl(34) are coplanar to within ± 0.001(7) Å and constitute the equatorial basis which is parallel to the cp ring. The U atom is displaced by 0.524(1) Å from this four-atom mean plane towards the cp, as invariably observed in the complexes [U(cp)Cl_3(L)$_2$] [5,8]. As expected, the terminal U-Cl bond distances are shorter than the bridging distances, and the ligation of the cp is unexceptional.

3. Experimental details

3.1. General methods

All preparations and reactions were carried out under argon (less than 5 ppm oxygen) using standard Schlenk vessel and vacuum-line techniques, or in a glove-box. Solvents were thoroughly dried and deoxygenated by the standard methods and distilled immediately before use.

Elemental analyses were carried out by Analytische Laboratorien at Engelkirchen (Germany). The ^1H NMR spectra were recorded on a Bruker W60 (Fourier transform) instrument and referenced internally using the residual proton solvent resonances relative to tetramethylsilane ($\delta = 0$). UCl_4 [19], [U(cp)$_3$Cl] [1] and tmscp [20] were prepared according to published methods.

3.2. Reaction of UCl_4 with 1 equivalent of tmscp: synthesis of [U(cp)Cl_3] (1)

A 50 ml two-necked round bottomed flask was charged with UCl_4 (660 mg, 1.74 mmol) and was attached to another 50 ml round-bottomed flask containing tmscp (240.3 mg, 1.74 mmol). CH_2Cl_2 was condensed into the flasks (20 ml in each one) under vacuum at − 78°C. The solution of tmscp was added to the suspension of UCl_4 and the reaction mixture was heated under reflux for 5 days with vigorous stirring. The bright-orange precipitate was filtered off, washed

Table 3
Fractional atomic coordinates, thermal parameters and their estimated standard deviations for compound **2**. $2CH_2Cl_2$

Atom	x	y	z	B (Å^2)
U(1)	0.72828(7)	− 0.28480(9)	0.62962(5)	3.14(2) ^{a}
U(2)	0.750	0.0472(1)	0.750	2.64(3) ^{a}
U(3)	0.77157(7)	0.12307(9)	0.36090(5)	3.21(2) ^{a}
Cl(1)	0.574(1)	0.637(1)	0.1467(8)	18.4(5) ^{a}
Cl(2)	0.613(1)	0.590(2)	0.296(1)	20.6(7) ^{a}
Cl(11)	0.750	− 0.4459(9)	0.750	4.2(2) ^{a}
Cl(12)	0.7253(4)	− 0.0387(6)	0.6053(3)	4.0(1) ^{a}
Cl(22)	0.6446(4)	− 0.1747(5)	0.7486(3)	3.1(1) ^{a}
Cl(31)	0.750	− 0.0481(9)	0.250	4.6(2) ^{a}
Cl(32)	0.6323(4)	0.2131(7)	0.2490(3)	4.0(1) ^{a}
Cl(33)	0.9135(5)	− 0.0085(7)	0.4129(4)	6.0(2) ^{a}
Cl(34)	0.6466(5)	− 0.0060(7)	0.4091(4)	6.4(2) ^{a}
C(1)	0.605(3)	0.693(4)	0.237(2)	9 (1)
C(10)	0.544(2)	− 0.348(3)	0.621(2)	6.2(7)
C(11)	0.582(2)	− 0.438(3)	0.590(2)	7.2(8)
C(12)	0.608(2)	− 0.411(3)	0.529(2)	6.1(8)
C(13)	0.588(2)	− 0.295(3)	0.513(2)	8.3(9)
C(14)	0.546(2)	− 0.251(3)	0.573(2)	7.9(9)
C(15)	0.846(2)	− 0.441(3)	0.580(2)	7.4(8)
C(16)	0.905(2)	− 0.358(3)	0.626(2)	6.3(7)
C(17)	0.899(2)	− 0.254(3)	0.590(1)	5.6(7)
C(18)	0.837(2)	− 0.266(3)	0.526(2)	7.2(8)
C(19)	0.810(2)	− 0.387(3)	0.523(2)	6.5(8)
C(20)	0.857(2)	0.223(3)	0.702(2)	6.9(8)
C(21)	0.910(2)	0.121(3)	0.702(2)	7.3(8)
C(22)	0.943(2)	0.077(3)	0.771(1)	5.4(7)
C(23)	0.909(2)	0.159(3)	0.818(2)	5.9(7)
C(24)	0.855(2)	0.247(2)	0.776(1)	5.0(6)
C(30)	0.709(2)	0.306(3)	0.432(2)	6.0(7)
C(31)	0.777(2)	0.356(3)	0.397(2)	5.9(7)
C(32)	0.858(2)	0.312(2)	0.431(1)	5.1(7)
C(33)	0.844(2)	0.244(3)	0.485(2)	6.6(8)
C(34)	0.753(2)	0.240(3)	0.487(2)	6.5(8)

^{a} $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij} a_i a_j$.

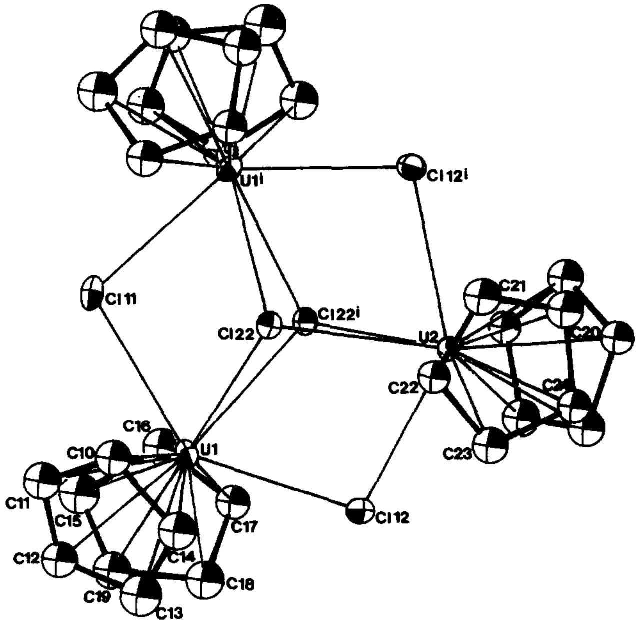


Fig. 1. Perspective view of the cation of 2. Atoms labelled by (i) are related to those unlabelled by the C_2 axis passing through U(2) and Cl(11).

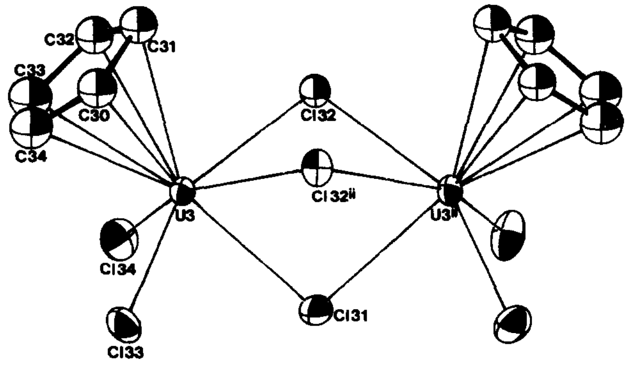


Fig. 2. Perspective view of the anion of 2. Atoms labelled by (ii) are related to those unlabelled by the C_2 axis passing through Cl(31).

with CH_2Cl_2 (2 × 10 ml) and dried under vacuum (585 mg; 82%). Anal. Found: C, 14.54; H, 1.38; Cl, 25.75. $C_5H_5Cl_3U$ calcd.: C, 14.67; H, 1.23; Cl, 25.97%.

3.3. Formation of the adducts [U(cp)$Cl_3(L)_2$] (L = THF, hexamethylphosphoramide or triphenylphosphine oxide)

(a) An NMR tube was charged with 1 (about 10 mg) in THF-d_8 (0.3 ml) and the spectrum of the green solution exhibited at 30°C a signal at 0.98 ppm ($w_{1/2}$ = 25 Hz); at −70°C, a single resonance was observed at 9.35 ppm ($w_{1/2}$ = 20 Hz). These spectra were identical with those of [U(cp)$Cl_3(THF)_2$ [9], without the signals corresponding to free THF.

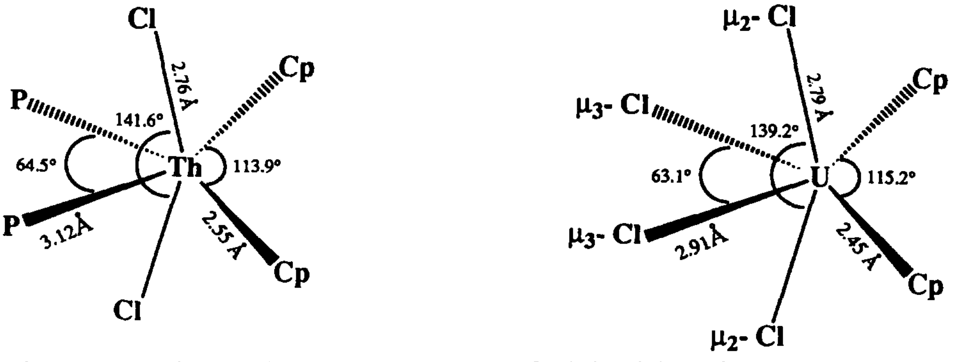
(b) An NMR tube was charged with 1 (about 10 mg) in dichloromethane-d_2 (0.3 ml) and 2 equivalents of hexamethylphosphoramide or triphenylphosphine oxide were added. The spectra of the green solutions were identical with those of the corresponding adducts [U(cp)$Cl_3(L)_2$] [9].

3.4. Reaction of UCl_4 with 3 equivalents of tmscp

An NMR tube was charged with UCl_4 (11.9 mg, 0.031 mmol) in deuterated dichloromethane (0.3 ml), and tmscp (12.9 mg, 0.094 mmol) was added via a gas-tight microsyringe. The tube was heated in an oil bath at 70°C for 2 days. The spectrum of the red–brown solution revealed the presence of [U$(cp)_3$Cl] and tmsCl in the molar ratio 1 : 3.

3.5. Reaction of UCl_4 with 2 equivalents of tmscp: synthesis of [$U_5(cp)_8Cl_{12}$] (2)

(a) A 50 ml two-necked round-bottomed flask was charged with UCl_4 (558 mg, 1.47 mmol) and was attached to another 50 ml round-bottomed flask containing tmscp (406.7 mg, 2.94 mmol). CH_2Cl_2 was condensed into the flasks (20 ml in each one) under vacuum at −78°C. The solution of tmscp was added to the suspension of UCl_4, and the reaction mixture was



Scheme 2. The metal environment in the mononuclear complex [Th$(cp)_2(Cl)_2$(dmpe)] and the trinuclear cation of 2.

heated under reflux for 5 days, with vigorous stirring. After filtration, the volume of the red solution was reduced to 15 ml and, upon cooling to −78°C, red crystals were formed. These were filtered off, washed with CH_2Cl_2 and dried under vacuum (290 mg; 44% from UCl_4). Anal. Found: C, 22.12; H, 2.02; Cl, 22.18. $C_{41}H_{42}Cl_{14}U_5$ (1.CH_2Cl_2) calc.: C, 22.17; H, 1.90; Cl, 22.34%. ^1H NMR (dichloromethane-d_2, 30°C): δ 14.6 (10 H, br, $w_{1/2} = 100$ Hz) and 5.79 (30 H, s, $w_{1/2} = 10$ Hz).

(b) An NMR tube was charged with UCl_4 (10.5 mg, 0.028 mmol) in dichloromethane-d_2 (0.3 ml), and tmscp (7.6 mg, 0.056 mmol) was added via a microsyringe. The tube was heated in an oil bath at 70°C for 5 days. The spectrum revealed the disappearance of tmscp and the formation of **2**, **3** and tmsCl in the molar ratio 1:2:14.

3.6. Reaction of UCl_4 with 1.6 equivalents of tmscp

An NMR tube was charged with UCl_4 (11.3 mg, 0.03 mmol) in dichloromethane-d_2 (0.3 ml), and tmscp (6.5 mg, 0.047 mmol) was added via a microsyringe. After heating for 4 days in an oil bath at 70°C, a reddish solution and an orange precipitate were obtained. The spectrum of the solution showed the presence of tms-Cl, **2** and **3** in the approximate molar ratio 8:0.5:0.75. After filtration, the precipitate was dissolved in THF-d_8 and the spectrum showed only the resonance attributed to the cp of [U(cp)Cl_3(THF-d_8)$_2$].

3.7. Equilibrium between 1, 2 and 3

(a) An NMR tube was charged with **2** (12.5 mg) in dichloromethane-d_2 (0.3 ml) and tmsCl was introduced as an internal standard. After heating in an oil bath at 70°C for 4 days, an orange power of **1** was deposited and the spectrum showed that about 50% of **2** was transformed into **3** ([**3**]/[**2**] = 1.5).

(b) An NMR tube was charged with **1** (10.5 mg, 0.026 mmol) and **3** (5.2 mg, 0.011 mmol) in dichloromethane-d_2 (0.3 ml). After heating in an oil bath at 70°C for 4 days, the spectrum indicated that about 50% of **3** were transformed into **2** ([**3**]/[**2**] = 1.5).

3.8. Disproportionation of 2 in tetrahydrofuran

An NMR tube was charged with **2** (about 10 mg) in THF-d_8 (0.3 ml). The compound dissolved partially, giving a green solution and a yellow precipitate. The spectrum showed the presence of [U(cp)Cl_3(THF-d_8)$_2$] and a small quantity of **3** (about 10%). On gently heating at 40°C, the precipitate readily dissolved and the spectrum then revealed the formation of [U(cp)Cl_3(THF-d_8)$_2$] and **3** in the molar ratio 7:3.

3.9. X-ray crystal structure of $[\{U(cp)_2(\mu\text{-}Cl)\}_3(\mu_3\text{-}Cl)_2][\{U(cp)Cl_2\}_2(\mu\text{-}Cl)_3].2CH_2Cl_2$

A selected single crystal was introduced into a thin-walled Lindemann glass tube in the glove-box. Data were collected at room temperature on an Enraf–Nonius CAD 4 diffractometer equipped with a graphite monochromator ($\lambda = 0.71073$ Å). The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after each hour, a decay of 30% in 35 h was observed and was linearly corrected. The data were corrected for Lorentz, polarization effects and absorption [21]. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method on F with anisotropic thermal parameters for U and Cl atoms. The H atoms of the cp ligands were introduced at calculated positions (C–H, 0.95 Å; $B = 6$ Å^2); they were not refined but constrained to ride on their parent carbon atom. All calculations were performed on a VAX 4200 computer with the Enraf–Nonius MolEN system [22]. Analytical scattering factors for neutral atoms [23] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 2. Final positional and thermal parameters are listed in Table 3. Full lists of atomic coordinates, bond lengths, angles and thermal parameters are available from the Cambridge Crystallographic Data Centre.

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