Journal of Organometallic Chemistry, 379 (1989) 259–269
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20381

Anionic tricyclopentadienyluranium(III) complexes. Crystal structure of $[Cp_3UClUCp_3][Na(18\text{-crown-}6)(THF)_2]$ ($Cp = \eta$-C_5H_5, THF = tetrahydrofuran)

Jean François LeMaréchal [a], Claude Villiers [a], Pierrette Charpin [b], Martine Nierlich [b], Monique Lance [b], Julien Vigner [b] and Michel Ephritikhine [a]*

Laboratoire de chimie de l'uranium [a] and Laboratoire de cristallographie [b], Service de Chimie Moléculaire, IRDI/DESICP/DLPC/CEA-CEN SACLAY/URA 331 CNRS, 91191 Gif sur Yvette cedex (France)

(Received June 28th, 1989)

Abstract

Sodium amalgam reduction of the complexes Cp_3UX($Cp = \eta$-C_5H_5, X = Cl, BH_4, Me, n-Bu) led to the formation of the corresponding Cp_3UX^- anions which were alternatively prepared by addition of X^- to $Cp_3U(THF)$(I). Electron transfer or ligand exchange reactions were found to occur between Cp_3UX and Cp_3UX^-, Cp_3UX or Cp_3UX^- and I. The crystal structure of $[Cp_3UClUCp_3][Na(18\text{-crown-}6)(THF)_2]$(XI) revealed the bent and symmetrical U–Cl–U bridge.

Introduction

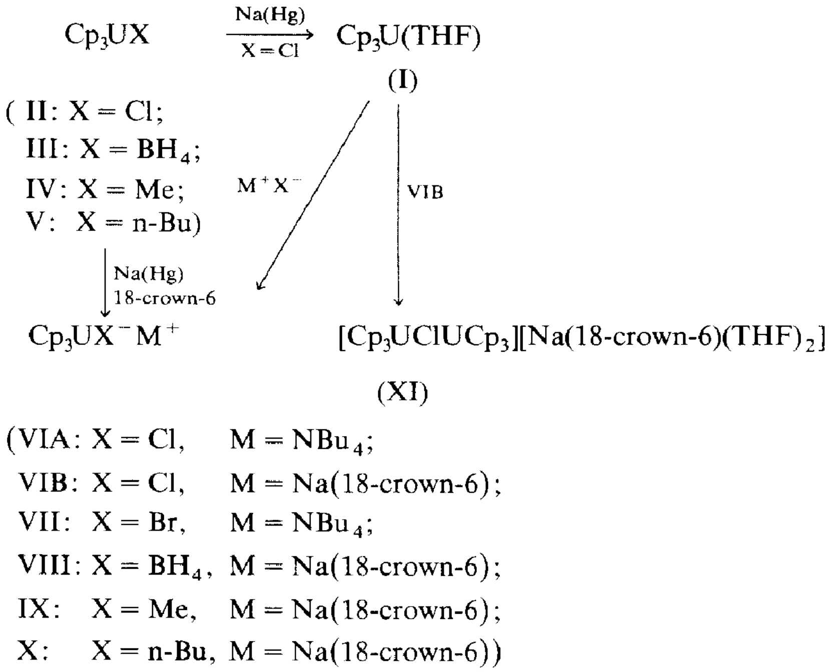
Anionic uranium(III) complexes are rare and are limited to the alkyl compounds Cp_3UXLi ($Cp = \eta$-C_5H_5, X = Me, n-Bu) [1] and a series of bis-cyclopentadienyl bis-halogeno derivatives: $(C_5Me_5)_2UCl_2Na(THF)_2$ (THF = tetrahydrofuran) [2] and salts of the $Cp_2''UXY^-$ anions ($Cp'' = \eta$-$C_5H_3(SiMe_3)_2$-1,3; X = Cl; Y = Cl or Br) [3]. We previously studied the ligand exchange reactions of the alkyl compounds Cp_3UXLi (X = Me, n-Bu) and their role in the catalytic hydrogenation of terminal olefins [4]. In order to gain further insight into their properties we wished to prepare other anionic tricyclopentadienyluranium(III) complexes. We report here new syntheses of the Cp_3UX^- anions (X = Cl, Br, BH_4, Me, n-Bu) by the sodium amalgam reduction of the Cp_3UX compounds [5] or by addition of X^- to $Cp_3U(THF)$, and describe the electron transfer and ligand exchange reactions between Cp_3UX, Cp_3UX^- and $Cp_3U(THF)$. We also describe the preparation and the crystal structure of the chloro-bridged complex $[Cp_3UClUCp_3][Na(18\text{-crown-}6)(THF)_2]$.

0022-328X/89/$03.50

Results and discussion

Syntheses of the Cp_3UX^- anions

The neutral tricyclopentadienyluranium(III) compound $Cp_3U(THF)$ (I) was isolated in 70% yield from the reaction at 20 °C of Cp_3UCl (II) with a slight excess of sodium amalgam in tetrahydrofuran (Scheme 1). This air sensitive brown complex was characterized by its ^1H NMR spectrum (Table 1) and by an X-ray diffraction study [6], and was found to be identical to that prepared by treating UCl_3 with KCp [7] or by reducing II with sodium naphthalenide [8]. However, in contrast to a previous report [9], I was not the product obtained by reduction of II with sodium hydride [5].



Scheme 1

Table 1

^1H NMR spectral data for the complexes [a]

Compounds	Cp signals [b]	Other signals
$Cp_3U(THF)$ (I)	−15.24	−13.52 (s, 4H, β-THF); −30.55 (s, 4H, α-THF)
$[Cp_3UCl][NBu_4]$ (VIA)	−13.94	0.74, 0.33 and −0.27 (m, 8H + 20H + 8H, Bu)
$[Cp_3UCl][Na(18\text{-crown-}6)]$ (VIB)	−13.95	3.03 (s, 24H, 18-crown-6)
$[Cp_3UBr][NBu_4]$ (VII)	−14.10	0.94, 0.45 and 0.09 (m, 8H + 20H + 8H, Bu)
$[Cp_3UBH_4][Na(18\text{-crown-}6)]$ (VIII)	−13.27	+14.50 (q, 78, 4H, BH_4); 3.40 (s, 24H, 18-crown-6)
$[Cp_3UMe][Na(18\text{-crown-}6)]$ (IX)	−14.24	−93.6 (br, 90, 3H, CH_3); 3.43 (s, 24H, 18-crown-6)
$[Cp_3UBu][Na(18\text{-crown-}6)]$ (X)	−13.93	3.41 (s, 24H, 18-crown-6); −4.43 (t, 7, 3H, CH_3); −6.73 (m, 2H, γ-CH_2); −8.43 (m, 2H β-CH_2); −91 (br, 90, 2H, α-CH_2)

[a] In THF-d_8 except I in toluene-d_8. δ relative to TMS, (multiplicity, J or half height width in Hz, intensity, assignment). [b] The signals ($\Delta\nu_{1/2}$ 12–15 Hz) integrate for 15H.

Table 2

Elemental analyses

Compound	Analyses (found (calcd.) (%))			
	C	H	Cl, Br or B	Na or N
$[Cp_3UCl][NBu_4]$ (VIA)	52.10	7.04	5.22	1.93
	(52.36)	(7.18)	(5.00)	(1.97)
$[Cp_3UCl][Na(18\text{-crown-}6)]$ (VIB)	42.79	5.05	4.71	3.00
	(42.89)	(5.20)	(4.69)	(3.04)
$[Cp_3UBr][NBu_4]$ (VII)	49.01	6.66	10.55	1.79
	(49.28)	(6.76)	(10.58)	(1.85)
$[Cp_3UBH_4][Na(18\text{-crown-}6)]$ (VIII)	43.78	5.71	1.45	3.02
	(44.09)	(5.89)	(1.47)	(3.12)
$[Cp_3UClUCp_3][Na(18\text{-crown-}6)(THF)_2]$ (IX) [a]	44.76	5.10	2.63	1.72
	(45.03)	(5.29)	(2.65)	(1.72)

[a] U 35.95 (35.70)%.

Similar Na(Hg) reduction of Cp_3UBH_4 (III), Cp_3UMe (IV) and Cp_3UBu (V) readily afforded the corresponding Cp_3UX^- anions in quantitative yield. The latter were stable in tetrahydrofuran, and after addition of 18-crown-6 ether, the red compounds $[Cp_3UX][Na(18\text{-crown-}6)]$ (VIII: $X = BH_4$; IX: X = Me; X: X = n-Bu) crystallized from a THF/pentane mixture. These borohydride and alkyl anions were also synthesized in quantitative yield by treatment of I with one equivalent of $LiBH_4$ (but not KBH_4 which is poorly soluble in THF) or alkyllithium, respectively.

The Cp_3UCl^- anion was previously observed by NMR spectroscopy after electrolysis of II in a saturated THF solution of NBu_4PF_6, but was not extracted from the supporting electrolyte [10]. Complex I did not react with NaCl, but the compounds $[Cp_3UX][NBu_4]$ (IVA: X = Cl; VII: X = Br) were readily formed by addition of the more soluble ammonium salts NBu_4X. These results suggested that the Cp_3UCl^- anion would be isolated from the Na(Hg) reduction of II, providing that NaCl did not separate out, and in the presence of 1 equivalent of 18-crown-6 ether, this reaction did, indeed, give the crystalline compound $[Cp_3UCl][Na(18\text{-crown-}6)]$ (VIB), in 55% yield.

Electron transfer and ligand exchange reactions

The dynamic properties of mixtures of Cp_3UX/Cp_3UX^-, $Cp_3UX/Cp_3U(THF)$ and $Cp_3UX^-/Cp_3U(THF)$ were studied by NMR spectroscopy; the results are presented in Table 3.

The ^1H NMR spectra of mixtures of the Cp_3UX and Cp_3UX^- entities (X = halogen, BH_4, alkyl) in THF-d_8 exhibited at 30 °C single averaged resonances corresponding to the Cp and X ligands of the U^{IV} and U^{III} complexes. Coalescence of the Cp signal occurred at about −70 °C and at −90 °C, spin saturation transfer [11] was observed between the two separate broad peaks, revealing the occurrence of the rapid and reversible electron transfer reaction (eq. 1). The reaction was also studied by cyclic voltammetry [10,12].

$$Cp_3UX \underset{-e}{\overset{+e}{\rightleftharpoons}} Cp_3UX^- \qquad (1)$$

Table 3

Ligand exchange and electron transfer reactions between Cp_3UX^-, Cp_3UX and $Cp_3U(THF)$. NMR data [a]

X	$Cp_3UX^-/Cp_3U(THF)$ (in THF-d_8)	$Cp_3UX/Cp_3U(THF)$	Cp_3UX^-/Cp_3UX (in THF-d_8)
Cl	Rapid equilibrium Spectrum identical to that of XI (see text) revealing the equilibrium: $Cp_3UCl^- + Cp_3U(THF) \rightleftharpoons Cp_3UClUCp_3^-$	Rapid equilibrium in toluene δ(Cp) −8.5 (average resonance) δ(THF) −3.0; −6.9 Rapid equilibrium in THF δ(Cp) −8.8	Rapid equilibrium δ(Cp) −8.5 (average resonance)
BH_4	Rapid equilibrium δ(Cp) −14.1 (average resonance) $\delta(BH_4)$ 13.7 (broad) (instead of a quartet at +14.5 ppm in VIII)	Rapid equilibrium in toluene δ(Cp) −10.1 (average resonance) δ(THF) −11.6; −26.2 $\delta(BH_4)$ −58.1 Rapid equilibrium in THF δ(Cp) −10.0 $\delta(BH_4)$ −56.2	Rapid equilibrium δ(Cp) −10.1 $\delta(BH_4)$ −23 (average resonances)
Me	Rapid equilibrium δ(Cp) −14.7 (average resonance) coalescence at −60 °C δ(Me) −115 (instead of −93 in IX)	Rapid equilibrium in toluene δ(Cp) −7.4 (average resonance) δ(THF) −12.0; −28.4 δ(Me) −190 Slower equilibrium in THF Spin saturation transfer observed between the two broad Cp signals at −2.8 and −15.2 ppm	Rapid equilibrium δ(Cp) −8.5 δ(Me) −145 (average resonances)
n-Bu	Rapid equilibrium δ(Cp) −14.5 (average resonance) coalescence at 0 °C the butyl protons signals remained unchanged.	No equilibrium	Rapid equilibrium δ(Cp) −10.9 average resonances were also observed for the butyl protons signals

[a] 30 °C. The chemical shifts correspond to equimolar mixtures for all systems but [IV]/[I] = 1.5 and [X]/[V] = 2.3

Electron transfer through a bridging chlorine atom has been previously proposed to account for the symmetrical exchange reaction (eq. 2) observed between $Cp_3U(THF)$ and Cp_3UCl [13].

$$Cp^{\star}_3U(THF) + Cp_3UX \rightleftharpoons Cp^{\star}_3UX + Cp_3U(THF) \qquad (2)$$

The same reaction was found to occur in the case of $X = BH_4$, CH_3, but no exchange was observed between I and Cp_3UBu. The rapid equilibrium (eq. 2) was demonstrated by the NMR spectra of mixtures of Cp_3UX (X = Cl, BH_4, CH_3) and I in toluene: at 30 °C, a single averaged resonance corresponding to the Cp ligand was observed, whereas two broad signals were visible at lower temperature; the peaks corresponding to the X groups remained practically unchanged. The results are in agreement with the relative abilities of the borohydride and alkyl groups to bridge two metallic centers [14,15]. Formation of the intermediate Cp_3UXUCp_3 species would be less favoured in THF, and reaction 2 was effectively slowed down in this solvent.

Exchange of ligands was found to occur between I and the Cp_3UX^- anions (X = halogen, BH_4, Me, Bu) (eq. 3)

$$Cp^{\star}_3U(THF) + Cp_3UX^- \rightleftharpoons Cp^{\star}_3UX^- + Cp_3U(THF) \qquad (3)$$

At 30 °C, the NMR spectra of each mixture in THF-d_8 showed a single resonance corresponding to the Cp ligand and, except in the case of $X = Cl$, at lower temperature, two broad peaks were observed. However, some interesting facts emerged concerning the chemical shifts of the Cp an X signals. Those of the methyl and borohydride ligands were found at -115 and $+13.7$ ppm, respectively, instead at -93.6 and $+14.5$ ppm as expected for the Cp_3UX^- anions. The spectrum of an equimolar mixture of I and the chloride derivative VI (0.145 *M* in THF-d_8) exhibited a Cp signal at -16.40 ppm, whereas those of the components were at -15.24 and -13.94, respectively; this signal was progressively shifted downfield after successive dilutions, and for a concentration of 0.04 *M* it was at -14.42 ppm, which is the average value of the Cp resonances of I and VI. These observations suggested the presence of $Cp_3UXUCp_3^-$ species, which are in equilibrium with Cp_3UX^- and $Cp_3U(THF)$, and would be intermediates in the ligand exchange reaction (eq. 3). The chloro-bridged $Cp_3UClUCp_3^-$ anion was isolated.

Synthesis and crystal structure of [$Cp_3UClUCp_3$][Na(18-crown-6)(THF)$_2$] (XI)

Complex XI was prepared by crystallization of an equimolar mixture of I and VIB from THF/pentane; it was also obtained by slow diffusion of pentane into a saturated solution of VIB in tetrahydrofuran.

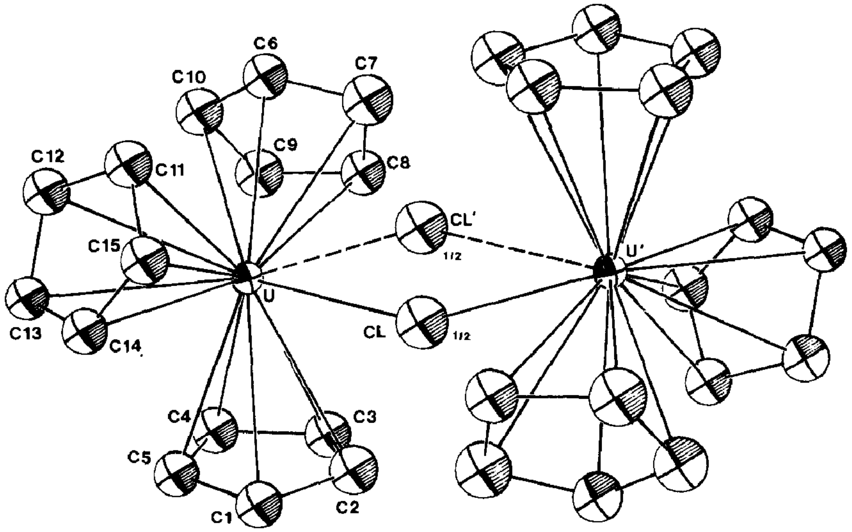


Fig. 1. ORTEP drawing of the $Cp_3UClUCp_3^-$ anion. Primed atoms are related by the inversion centre. The Cl atom is disordered and occupies statistically two positions symmetrical with respect to the inversion centre.

Table 4

Selected bond distances (Å) and angles (°)

Anion			
U–Cl	2.82(2)	U–Cl–U′	156.5(7)
U′–Cl [a]	2.79(2)	Cp1–U–Cp2	117(3)
U–Cp1 [b]	2.50(4)	Cp1–U–Cp3	116(3)
U–Cp2	2.53(3)	Cp2–U–Cp3	117(3)
U–Cp3	2.54(3)	Cp1–U–Cl	91(3)
		Cp2–U–Cl	110(3)
		Cp3–U–Cl	101(3)
		Cp1–U–Cl′	111(3)
		Cp2–U–Cl′	89(3)
		Cp3–U–Cl′	101(3)
Cation			
Na–O(20)	2.81(5)	O(23)–Na–O(20)	61(1)
Na–O(23)	2.72(4)	O(20)–Na–O(26)	58(1)
Na–O(26)	2.73(4)	O(30)–Na–O(60)	62(1)
Na–O(30)	2.87(6)	O(60)–Na–O(36)	55(1)
Na–O(36)	2.86(4)	O(23)–Na–O(100)	94(1)
Na–O(60)	2.81(4)	O(20)–Na–O(100)	88(1)
Na–O(100)	2.38(2)	O(26)–Na–O(100)	91.2(9)
		O(30)–Na–O(100)	93(1)
		O(36)–Na–O(100)	84(1)
		O(60)–Na–O(100)	101(1)

[a] Primed atom is related by the centre of symmetry. [b] Cp denotes the centroid of the cyclopentadienyl ring.

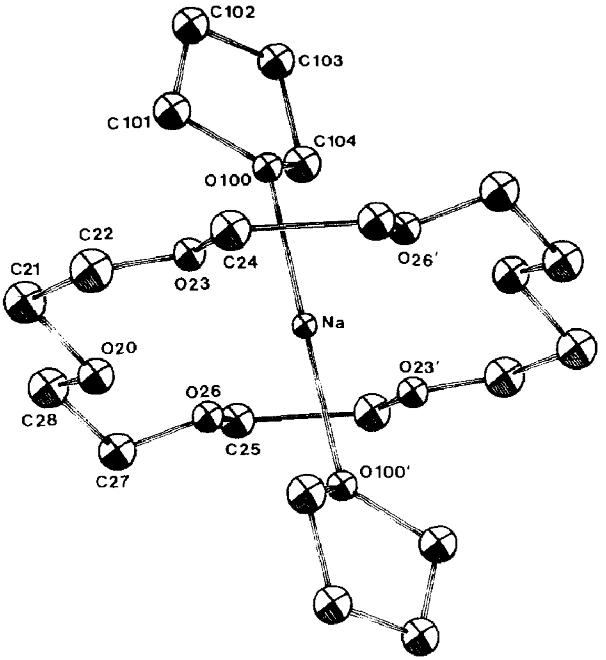


Fig. 2. ORTEP drawing of the Na(18-crown-6)(THF)$_2^+$ cation. Primed atoms are related by the inversion centre. Only one configuration of the disordered crown ether is shown (see text).

The structural analysis showed that crystals of XI are composed of discrete cation–anion pairs. The anion $Cp_3UClUCp_3^-$ is shown in Fig. 1. Selected bond distances and angles are listed in Table 4. Two Cp_3U units are bridged by a chlorine atom which is disorded between two positions symmetrical with respect to the inversion center; the U–Cl distances are 2.79(2) and 2.82(2) Å, the U–Cl–U angle value is 156.5(7)°, and the two uranium atoms are separated by 5.495(1) Å. These bonding parameters of the U^{III}–Cl–U^{III} bridge of XI are similar to those in the neutral trimeric complex $(Cp'_2UCl)_3$ [2]. The geometry of the Cp_3U fragment is unexceptional: the U–C bond lengths range from 2.72(9) to 2.87 Å (mean 2.79 Å), and the Cp (centroid)–U–Cp(centroid) angles average 117°. The structure of the $Cp_3UClUCp_3^-$ anion is somewhat similar to that of its samarium analogue in $[Cp_3SmClSmCp_3][Li(dimethoxyethane)_3]$ [16].

An ORTEP drawing [17] of the cation Na^+(18-crown-6)$(THF)_2$ is shown in Fig. 2. The hexaethyl ether molecule is disordered and only one configuration is shown; the crown ether is centrosymmetric with the sodium atom lying at the center. The environment of the Na^+ ion is a hexagonal bipyramid; the six oxygen atoms of the 18-crown-6 ether lie in the equatorial plane and the apices are occupied by the two THF ligands at 2.38(2) Å.

Experimental

General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (FRG). The ^1H NMR spectra were recorded on a Bruker W60 (FT) instrument. Deuteriated solvents were dried over Na/K alloy. The paramagnetic shifts are relative to tetramethylsilane (δ 0 ppm). The ^1H NMR spectral and analytical data are given in Tables 1 and 2.

All experiments were carried out under argon in Schlenk type glassware attached to a high vacuum line or used in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and were distilled immediately prior to use. 18-crown-6 ether (Fluka) was dried under vacuum after evaporation of a solution of it in toluene. NBu_4Cl, H_2O and NBu_4Br (Fluka) were dehydrated and dried by heating under vacuum. Cp_3UCl [18], Cp_3UMe and Cp_3U-n-Bu [19], Cp_3UBH_4 [20] were prepared by published methods.

Synthesis

$Cp_3U(THF)$ (I). A 100 ml round bottom flask was charged with Cp_3UCl (1.4 g) and 2% Na(Hg) (3.9 g) and THF (50 ml) was condensed under vacuum at −78° C. The mixture was stirred at 20° C for 48 h and the solution then decanted off and filtered, and the solvent was evaporated off to leave red-brown microcrystals of I (1.1 g, 77%) The product was identified from its crystal structure. Its NMR spectrum was identical to that of the compound prepared as described previously [7,8].

$[Cp_3UCl][NBu_4]$ (VIA). A 50 ml round bottom flask was charged with I (151 mg) and NBu_4Cl (83 mg) and THF (20 ml) was condensed under vacuum at −78° C. The mixture was stirred at 20° C for 2 h. The solution was filtered and the solvent evaporated, to leave brown microcrystals of VIA (200 mg, 93%).

[Cp$_3$UCl][Na(18-crown-6)] (VIB). A 50 ml round bottom flask was charged with Cp$_3$UCl (465 mg), 2% Na(Hg) (1.3 g) and 18-crown-6 ether (280 mg) and THF (25 ml) was condensed under vacuum at −78 °C. The mixture was stirred at 20 °C for 48 h then the solution was decanted and filtered and the solvent evaporated off. Crystallization of the residue from a mixture of THF and pentane gave red microcrystals of VIB, which were filtered off and dried under vacuum (497 mg, 81%).

[Cp$_3$UBr][NBu$_4$] (VII). This was prepared as described for VIA by using NBu$_4$Br instead of NBu$_4$Cl; yield 90%.

[[Cp$_3$UBH$_4$][Na(18-crown-6)] (VIII). (a) A 50 ml round bottom flask was charged with Cp$_3$UBH$_4$ (450 mg), 2% Na(Hg) (1.22 g) and 18-crown-6 ether (280 mg) and THF (30 ml) was condensed under vacuum at −78 °C. The mixture was stirred at 20 °C for 1 h, then the solution was decanted and filtered, and the solvent was evaporated off. Crystallization of the residue from a mixture of THF and ethyl-ether gave red microcrystals of VIII, which were filtered off, washed with pentane (3 × 5 ml), and dried under vacuum (620 mg, 84%).

(b) An NMR tube was charged with I (8 mg) and LiBH$_4$ (2 mg) and THF-d_8 (0,4 ml) was condensed in. The NMR spectrum at 30 °C showed a signal at −13.45 ppm corresponding to the Cp ligand of the Cp$_3$UBH$_4^-$ anion and a quartet (δ −0.67; 82 Hz) attributed to exchanging borohydrides. This signal was resolved at −80 °C into a quartet corresponding to free LiBH$_4$, (δ −0.60; 80 Hz) and a broad signal (δ 12.40; $w_{1/2}$ 350 Hz; relative intensity 4H) corresponding to the borohydride ligand.

[Cp$_3$UMe][Na(18-crown-6)] (IX) and [Cp$_3$UnBu][Na(18-crown-6)] (X). A 50 ml round bottom flask was charged with Cp$_3$UMe (225 mg), 2% Na(Hg) (650 mg) and 18-crown-6 ether (140 mg) and THF (20 ml) was condensed in under vacuum at −78 °C. The mixture was stirred at 20 °C for 3 h, then the solvent was decanted and filtered, and the solvent was evaporated off. Crystallization of the residue from a mixture of THF and pentane gave red microcrystals of IX, which were filtered off, washed with pentane, and dried under vacuum (280 mg, 76%). The product was identified from its NMR spectrum [4]. The same procedure using Cp$_3$UnBu instead of Cp$_3$UMe, gave crystals of X in 82% yield.

Cp$_3$UMe$^-$ and Cp$_3$UBu$^-$ were respectively prepared in quantitative yield (NMR experiments) by adding 1 equivalent of MeLi or BuLi (1.6 *M* solution in ether or hexane respectively) to a solution of I (3 mg) in THF-d_8 (0.4 ml).

[Cp$_3$UClUCp$_3$][Na(18-crown-6)(THF)$_2$] (XI). A 50 ml round bottom flask was charged with I (252 mg) and VIB (379 mg) and THF (20 ml) was condensed in under vacuum at −78 °C. Addition of pentane (15 ml) gave, within a few minutes, red microcrystals of XI, which were filtered off, washed with pentane (3 × 5 ml), and dried under vacuum (410 mg, 60%; the yield is very dependent on the quantities of THF and pentane used for the crystallization).

X-ray analysis of XI

An irregular shaped single crystal was placed in a thin-walled Lindeman glass tube in an inert-atmosphere glovebox, and the capillary was mounted on an Enraf Nonius CAD4 automatic diffractometer. Cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8° and 12°. Empirical absorption correction using DIFABS[21] was applied. After

Table 5

Crystal data and experimental details.

Crystal Data	
Cryst. dimensions (mm)	0.500 × 0.200 × 0.150
color	red-brown
crystal system	triclinic
space group	$P\bar{1}$
a(Å)	8.778(6)
b(Å)	11.315(2)
c(Å)	13.647(3)
α(°)	77.03(2)
β(°)	85.28(5)
γ(°)	85.45(4)
V(Å^3)	1313.8(6)
Z	1
D_{calc}(g cm^{-3})	1.685
μ(Mo-K_α) (cm^{-1})	59.41
Data collection	
θ limits (°)	1,22
Scan type	$\omega/2\theta$
monochromator	graphite
reflections measured	
h	−9,0
k	−11,11
l	−14,14
Reflections collected	
total	3615
unique	2957
with $I > 3\sigma(I)$	1742
$R(F) = \Sigma(F_0) - (F_c)/\Sigma(F_0)$	0.064
$R_w(F^2) = [\Sigma w(\lvert F_0 \rvert - \lvert F_c \rvert)^2/\Sigma w(F_0)^2]^{1/2}$	0.071
with $w = 1/(\sigma F_0^2)$ and $\sigma F_0^2 = [(\sigma I)^2 + (pF^2)^2]^{1/2}$ ($p = 0.04$)	

correction for Lorentz and polarization effects, 1742 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. The U atom was located from a Patterson map and the other non-hydrogen atoms were located from subsequent least-squares refinements and difference Fourier syntheses. In the final difference Fourier map, 6 residual peaks were observed near the O atoms of the crown ether, revealing positional disorder of the latter; 12 O atoms were introduced in the least squares refinement with occupation factor of 0.5. C atoms of the THF molecule were refined with relatively high thermal parameters. H atoms were not included in the refinement. All calculations were performed on a micro VAX 2 computer using the Enraf Nonius Structure Determination Package [22]. Scattering factors for neutral atoms [23] were corrected for both $\Delta F'$ and $\Delta F''$ components of anomalous dispersion. The U and Cl atoms were refined with anisotropic thermal parameters. Crystallographic data and experimental details are given in Table 5; final positional parameters are listed in Table 6. Lists of bond lengths and distances, structure factors and anisotropic thermal parameters are available from the authors.

Table 6

Positional Parameters and their estimated standard deviations

Atom	x	y	z	B(Å)^2
U	0.1673(1)	0.33712(8)	0.40535(7)	5.35(2) ^{a}
C(1)	−0.097(4)	0.214(3)	0.416(2)	10.2(8)
C(2)	−0.130(4)	0.328(3)	0.357(2)	11.3(9)
C(3)	−0.041(3)	0.326(3)	0.261(2)	10.3(8)
C(4)	0.055(3)	0.219(3)	0.277(2)	9.7(8)
C(5)	0.016(3)	0.151(2)	0.365(2)	8.6(7)
C(6)	0.415(3)	0.484(3)	0.337(2)	10.0(8)
C(7)	0.276(5)	0.571(4)	0.327(3)	15(1)
C(8)	0.224(4)	0.526(3)	0.240(2)	10.9(9)
C(9)	0.318(4)	0.427(3)	0.221(3)	12(1)
C(10)	0.447(4)	0.398(3)	0.287(3)	12(1)
C(11)	0.358(4)	0.284(3)	0.564(2)	10.6(9)
C(12)	0.417(3)	0.190(3)	0.502(2)	9.6(8)
C(13)	0.300(3)	0.115(2)	0.513(2)	8.7(7)
C(14)	0.189(3)	0.153(3)	0.576(2)	9.9(8)
C(15)	0.215(4)	0.248(3)	0.608(2)	10.7(9)
Cl	−0.052(2)	0.471(2)	0.508(2)	11.8(6) ^{a}
Na	0.500	0.000	0.000	6.9(3)
O(20)	0.212(6)	−0.094(5)	0.005(4)	14(2)
O(23)	0.416(5)	−0.066(4)	−0.167(3)	11(1)
O(26)	0.317(5)	−0.055(4)	0.174(3)	11(1)
O(30)	0.280(6)	−0.104(5)	−0.095(4)	16(2)
O(36)	0.411(5)	0.017(4)	0.202(3)	12(1)
O(60)	0.266(5)	−0.127(4)	0.123(4)	14(1)
C(21)	0.201(5)	−0.183(4)	−0.053(4)	19(2)
C(22)	0.293(6)	−0.109(5)	−0.178(4)	19(2)
C(24)	0.474(5)	−0.018(4)	−0.256(3)	16(1)
C(25)	0.643(4)	0.068(4)	−0.256(3)	14(1)
C(27)	0.177(5)	−0.087(4)	0.182(3)	16(1)
C(28)	0.153(5)	−0.147(4)	0.077(3)	18(2)
O(100)	0.376(2)	0.198(2)	−0.042(1)	10.1(5)
C(101)	0.428(7)	0.316(5)	−0.039(5)	24(2)
C(102)	0.312(6)	0.406(5)	0.932(4)	20(2)
C(103)	0.239(6)	0.347(5)	0.864(4)	24(2)
C(104)	0.317(7)	0.224(5)	0.861(4)	23(2)

^{a} $B\text{eq} = 4/3\ \Sigma_i\ \Sigma_j\ \beta_{ij}\ a_i^-\ a_j^-$.

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