Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Activation and reduction of diethylether by low valent uranium: formation of the trimetallic, mixed valence uranium oxo species $[U(Cp^R)(\mu\text{-}I)_2]_3(\mu^3\text{-}O)$ ($Cp^R = C_5Me_5$, C_5Me_4H, $C_5H_4SiMe_3$)

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GENERAL EXPERIMENTAL

Glassware was oven-dried then flame-dried under reduced pressure prior to use.

All air sensitive compounds were manipulated under an inert atmosphere of oxygen-free argon (passed through gas purifier) using standard Schlenk techniques or under an atmosphere of dinitrogen provided by a glove box.

Schlenk line manipulations involved the use of flame-dried glassware. Glassware was evacuated and purged with dry argon three times prior to use.

Glove box manipulations were carried out in a MBraun glove box under an atmosphere of catalytically dried and deoxygenated dinitrogen.

UI_3 was prepared via a modification of the literature method reported by Corbett. Pentamethylcyclopentadiene (Cp*), tetramethylcyclopentadiene (Cp^{Me4H}), trimethlsilylcyclopentadiene (Cp'), and the potassium salts thereof, were prepared according to literature procedures.

NMR samples were made up in the dry box and sample tubes were sealed in *vacuo*.

Diethyl ether was pre-dried over sodium wire, distilled from sodium/potassium alloy, degassed and stored under argon over a thin potassium film.

C_6D_6 was dried over molten potassium and then vacuum transferred for storage under nitrogen in the glove box prior to use.

Magnetic measurements were performed by Professor Andrew Harrison at the University of Edinburgh on a Quantum Designs SQUID magnetometer.

EXPERIMENTAL PROCEDURES

Synthesis of uranium triiodide (UI_3)

Uranium turnings were treated with concentrated nitric acid then washed with de-ionised water to give them a silver metallic finish. The turnings were then washed with methanol followed by acetone and dried in *vacuo*. A thick-walled ampoule with two constriction points was then charged with the dry uranium turnings (2.28g, 9.58×10^{-3} mol) and HgI_2 (8.71g, 19.16×10^{-3} mol). The ampoule was then evacuated to 10^{-6} mbar, sealed under vacuum at the first constriction point and fully immersed vertically in a tube furnace at 315 ^{o}C for 3 days. The furnace was then placed in a horizontal position with the empty end of the ampoule protruding from the furnace to allow Hg and unreacted HgI_2 to condense and sublime out respectively. This was left for a further 2 days at 315 ^{o}C. The sealed tube was taken into the glove box and snapped at the constriction; the UI_3 was collected and ground up with a mortar and pestle. The purple powder was transferred to a tantalum boat, which was placed in a sublimation tube. The tube was evacuated to 10^{-6} mbar and heated in a furnace to 200 ^{o}C for 2 hours, 300 ^{o}C for 1 hour and 400 ^{o}C for 30 minutes to remove any remaining Hg and HgI_2. The purple solid in the tantalum boat was then collected and stored under dinitrogen in the glovebox (5.63g, 9.09 mmol, 95% yield).

$[UCp^*I_2]_3O$ (1): UI_3 (0.619g, 1×10^{-3} mol) and Cp*K (0.174g, 1×10^{-3} mol) were placed into an ampoule and cooled to -78 ^{o}C. Pre-cooled (to -78 ^{o}C) Et_2O (40ml) was added and the reaction was left stirring for 16 hours. A dark green solution with a creamy white precipitate resulted and was filtered from insolubles through pre-dried Celite on a glass frit. The solvent was reduced in volume by 50% and the solution cooled to -50 ^{o}C. After a 48h period tiny dark green needles resulted. These were washed with cold Et_2O and collected (0.48g, 0.25 mmol 76% yield). **^{1}H NMR** (C_6D_6) δ : 20.49 (s, 45H, C**H**$_3$-Cp*). **^{13}C NMR** (C_6D_6) 298K δ : 65.9 (br s, Cp* 'ring'), 15.5 (s, CH_3-Cp*). **MS (EI)** *m/z* : 1897 [24%, M^+], 1725 [M^+ - Cp*], 1143 [M^+ - (UCp^*I_3)]. **Elemental analysis**: Anal. Calc. for $C_{30}H_{45}I_6OU_3$: C, 18.99; H, 2.39. Found C, 18.92; H, 2.41.

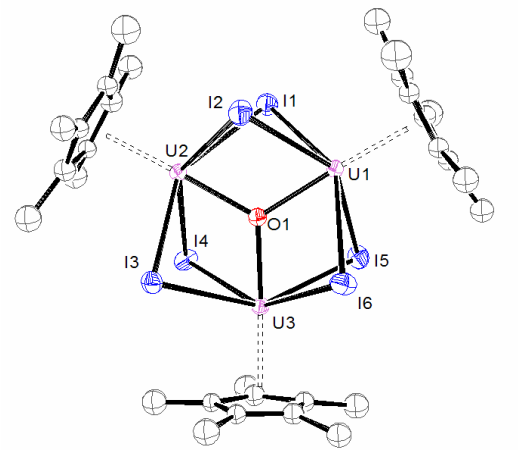
[UCp'I_2]$_3$O (2): UI_3 (0.619g, 1x10^{-3} mol) and Cp'K (0.176g, 1x10^{-3} mol) were placed into an ampoule and cooled to -78 ^oC. Pre-cooled to (-78 ^oC) Et_2O (40ml) was added and the reaction was left stirring for 24 hours. A green solution with a white precipitate resulted and was filtered from insolubles through pre-dried Celite on a glass frit. The solvent was reduced in volume by 50% and the solution cooled to -50 ^oC. After a 72h period dark green needles resulted. These were washed with cold Et_2O and collected (0.51g, 81% yield). **^{1}H NMR** (C_6D_6) δ : 3.23 (s, 6H, CH 'ring'), 1.06 (s, 6H, CH 'ring'), -3.07 (br s, 27H, $SiMe_3$ 'ring'). Numbering system for Cp' starts at the adjacent carbon to $SiMe_3$ group being 1. **^{13}C NMR** (C_6D_6) 298K δ : 118.42 (s, C^1'ring'), 78.94 (s, $C^{2,5}$ 'ring'), 61.84 (s, $C^{3,4}$ 'ring'). **MS (EI)** *m/z* : 1902 [17%, M^+], 1147 [M^+ - (UCp'I_3)]. **Elemental analysis**: Anal. Calc. for $C_{24}H_{27}I_6Si_3U_3O$: C, 15.15; H, 2.07. Found C, 15.02; H, 1.96.

[UCp^{Me4H}I_2]$_3$O (3): UI_3 (0.619g, 1x10^{-3} mol) and Cp^{Me4H}K (0.160g, 1x10^{-3} mol) were placed into an ampoule and cooled to -78 ^oC. Pre-cooled to (-78 ^oC) Et_2O (40ml) was added and the reaction was left stirring for 18 hours. A dark green solution with a creamy white precipitate resulted and was filtered from insolubles through pre-dried Celite on a glass frit. The solvent was reduced in volume by 50% and the solution cooled to -50 ^oC. After a 48h period a dark green solid resulted. The solid was isolated, washed with cold Et_2O and dried in *vacuo* (0.36g, 58% yield). **^{1}H NMR** (C_6D_6) δ : 20.69 (br s, 18H, CH_3), 17.84 (br s, 18H, CH_3), C-H on ring was not locatable due to the highly paramagnetic nature of the metal.

Numbering system for Cp^{Me4H} starts at the ring carbon adjacent to the proton as 1.

^{13}C NMR (C_6D_6) 298K δ : 176.9 (s, C^1 'ring'), 65.1 65.0 (s, $C^{2,5}$ $C^{3,4}$ 'ring'), 14.9 (s, CH_3 x 4). **MS (EI)** *m/z* : 1856 [24%, M^+]. **Elemental analysis:** Anal. Calc. for $C_{27}H_{36}I_6OU_3$: C, 17.48; H, 2.12. Found C, 17.51; H, 2.15.

CRYSTALLOGRAPHIC DATA



$[UCp^*I_2]_3O$ (1)

Table 1. Crystal data and structure refinement [O{UI2Cp*}3].

Identification code	jan703	
Empirical formula	C30 H45 I6 O U3	
Formula weight	1897.15	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (No.14)	
Unit cell dimensions	a = 24.5979(5) Å	α= 90°.
	b = 21.5504(4) Å	β= 109.891(1)°.
	c = 16.6282(3) Å	γ = 90°.
Volume	8288.7(3) $Å^3$	
Z	8	
Density (calculated)	3.04 Mg/m^3	
Absorption coefficient	16.19 mm^{-1}	
F(000)	6616	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
Theta range for data collection	3.72 to 24.67°.	
Index ranges	-9<=h<=28, 0<=k<=25, -19<=l<=19	
Reflections collected	55482	
Independent reflections	13374 [R(int) = 0.092]	

Reflections with I>2sigma(I)	11825
Completeness to theta = 24.67°	95.0 %
Tmax. and Tmin.	0.317and 0.223
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13374 / 0 / 442
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.048, wR2 = 0.113
R indices (all data)	R1 = 0.058, wR2 = 0.119
Largest diff. peak and hole	2.26 and -2.55 e.$Å^{-3}$

The crystal is twinned; matrix (1 0 1 0 –1 0 0 0 –1) , ratio 0.457

The U and I atoms are anisotropic; other atoms are isotropic.

Data collection KappaCCD , Program package WinGX , Abs correction MULTISCAN

Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Bond lengths [Å] and angles [°] for jan703.

U(1)-O(1)	2.234(12)
U(1)-M(1)	2.44(2)
U(1)-C(1)	2.69(2)
U(1)-C(2)	2.715(18)
U(1)-C(5)	2.718(19)
U(1)-C(3)	2.748(18)
U(1)-C(4)	2.791(18)
U(1)-I(2)	3.1772(15)
U(1)-I(6)	3.1979(15)
U(1)-I(1)	3.2143(15)
U(1)-I(5)	3.2260(16)
U(2)-O(1)	2.228(12)
U(2)-M(2)	2.44(2)
U(2)-C(13)	2.705(18)
U(2)-C(14)	2.721(18)
U(2)-C(12)	2.73(2)
U(2)-C(11)	2.746(18)
U(2)-C(15)	2.76(2)

U(2)-I(1)	3.1794(15)
U(2)-I(4)	3.1821(16)
U(2)-I(3)	3.1904(15)
U(2)-I(2)	3.2576(15)
U(3)-O(1)	2.192(13)
U(3)-M(3)	2.47(2)
U(3)-C(21)	2.708(19)
U(3)-C(22)	2.717(19)
U(3)-C(25)	2.727(17)
U(3)-C(24)	2.75(2)
U(3)-C(23)	2.763(18)
U(3)-I(5)	3.1539(15)
U(3)-I(4)	3.1744(15)
U(3)-I(6)	3.1809(15)
U(3)-I(3)	3.1826(15)
U(1B)-O(1B)	2.192(13)
U(1B)-M(1B)	2.46(2)
U(1B)-C(4B)	2.70(2)
U(1B)-C(5B)	2.73(2)
U(1B)-C(3B)	2.74(2)
U(1B)-C(1B)	2.748(18)
U(1B)-C(2B)	2.761(19)
U(1B)-I(2B)	3.1698(16)
U(1B)-I(5B)	3.1849(16)
U(1B)-I(6B)	3.2112(15)
U(1B)-I(1B)	3.2238(16)
U(2B)-O(1B)	2.268(13)
U(2B)-M(2B)	2.46(2)
U(2B)-C(14B)	2.679(19)
U(2B)-C(15B)	2.72(2)
U(2B)-C(13B)	2.725(19)
U(2B)-C(11B)	2.760(19)
U(2B)-C(12B)	2.78(2)
U(2B)-I(3B)	3.1652(15)
U(2B)-I(1B)	3.2040(16)

U(2B)-I(2B)	3.2377(15)
U(2B)-I(4B)	3.2398(16)
U(3B)-O(1B)	2.200(15)
U(3B)-M(3B)	2.46(6)
U(3B)-C(24B)	2.70(2)
U(3B)-C(25B)	2.701(19)
U(3B)-C(21B)	2.713(19)
U(3B)-C(23B)	2.739(19)
U(3B)-C(22B)	2.752(18)
U(3B)-I(5B)	3.1654(14)
U(3B)-I(6B)	3.1666(15)
U(3B)-I(4B)	3.1714(14)
U(3B)-I(3B)	3.1806(14)
C(1)-C(5)	1.40(3)
C(1)-C(2)	1.46(3)
C(1)-C(6)	1.49(3)
C(2)-C(3)	1.41(3)
C(2)-C(7)	1.53(3)
C(3)-C(4)	1.45(3)
C(3)-C(8)	1.50(3)
C(4)-C(5)	1.42(3)
C(4)-C(9)	1.45(3)
C(5)-C(10)	1.56(3)
C(11)-C(12)	1.35(3)
C(11)-C(15)	1.49(3)
C(11)-C(16)	1.54(3)
C(12)-C(13)	1.40(3)
C(12)-C(17)	1.52(3)
C(13)-C(14)	1.43(3)
C(13)-C(18)	1.50(3)
C(14)-C(15)	1.44(3)
C(14)-C(19)	1.51(3)
C(15)-C(20)	1.47(3)
C(21)-C(22)	1.38(3)
C(21)-C(25)	1.43(3)

C(21)-C(26)	1.51(3)
C(22)-C(23)	1.43(3)
C(22)-C(27)	1.54(3)
C(23)-C(24)	1.41(3)
C(23)-C(28)	1.51(3)
C(24)-C(25)	1.44(3)
C(24)-C(29)	1.59(3)
C(25)-C(30)	1.47(3)
C(1B)-C(2B)	1.43(3)
C(1B)-C(5B)	1.44(3)
C(1B)-C(6B)	1.49(3)
C(2B)-C(3B)	1.38(3)
C(2B)-C(7B)	1.50(3)
C(3B)-C(4B)	1.42(3)
C(3B)-C(8B)	1.54(3)
C(4B)-C(5B)	1.38(3)
C(4B)-C(9B)	1.55(3)
C(5B)-C(10B)	1.51(3)
C(11B)-C(12B)	1.40(3)
C(11B)-C(15B)	1.41(3)
C(11B)-C(16B)	1.56(3)
C(12B)-C(13B)	1.40(3)
C(12B)-C(17B)	1.54(3)
C(13B)-C(14B)	1.37(3)
C(13B)-C(18B)	1.52(3)
C(14B)-C(15B)	1.45(3)
C(14B)-C(19B)	1.55(3)
C(15B)-C(20B)	1.53(3)
C(21B)-C(25B)	1.42(3)
C(21B)-C(22B)	1.45(3)
C(21B)-C(26B)	1.51(3)
C(22B)-C(23B)	1.40(3)
C(22B)-C(27B)	1.48(3)
C(23B)-C(24B)	1.39(3)
C(23B)-C(28B)	1.52(3)

C(24B)-C(25B)	1.41(3)
C(24B)-C(29B)	1.54(3)
C(25B)-C(30B)	1.53(3)
O(1)-U(1)-M(1)	176.7(5)
O(1)-U(1)-I(2)	74.2(3)
M(1)-U(1)-I(2)	109.0(4)
O(1)-U(1)-I(6)	73.2(3)
M(1)-U(1)-I(6)	105.8(4)
I(2)-U(1)-I(6)	91.66(4)
O(1)-U(1)-I(1)	72.9(3)
M(1)-U(1)-I(1)	107.9(4)
I(2)-U(1)-I(1)	80.92(4)
I(6)-U(1)-I(1)	146.11(4)
O(1)-U(1)-I(5)	71.8(3)
M(1)-U(1)-I(5)	105.0(4)
I(2)-U(1)-I(5)	146.02(4)
I(6)-U(1)-I(5)	79.81(4)
I(1)-U(1)-I(5)	88.07(4)
O(1)-U(2)-M(2)	178.0(3)
O(1)-U(2)-I(1)	73.7(3)
M(2)-U(2)-I(1)	108.0(3)
O(1)-U(2)-I(4)	73.7(3)
M(2)-U(2)-I(4)	105.1(4)
I(1)-U(2)-I(4)	90.41(4)
O(1)-U(2)-I(3)	72.1(3)
M(2)-U(2)-I(3)	106.2(4)
I(1)-U(2)-I(3)	145.81(4)
I(4)-U(2)-I(3)	81.47(4)
O(1)-U(2)-I(2)	72.6(3)
M(2)-U(2)-I(2)	108.6(4)
I(1)-U(2)-I(2)	80.22(4)
I(4)-U(2)-I(2)	146.32(4)
I(3)-U(2)-I(2)	88.33(4)
O(1)-U(3)-M(3)	177.7(3)

O(1)-U(3)-I(5)	73.8(3)
M(3)-U(3)-I(5)	108.3(4)
O(1)-U(3)-I(4)	74.3(3)
M(3)-U(3)-I(4)	104.6(4)
I(5)-U(3)-I(4)	89.34(4)
O(1)-U(3)-I(6)	74.1(3)
M(3)-U(3)-I(6)	107.0(4)
I(5)-U(3)-I(6)	81.16(4)
I(4)-U(3)-I(6)	148.37(5)
O(1)-U(3)-I(3)	72.7(3)
M(3)-U(3)-I(3)	105.3(4)
I(5)-U(3)-I(3)	146.46(5)
I(4)-U(3)-I(3)	81.71(4)
I(6)-U(3)-I(3)	89.71(4)
O(1B)-U(1B)-M(1B)	178.1(4)
O(1B)-U(1B)-I(2B)	73.2(4)
M(1B)-U(1B)-I(2B)	107.7(4)
O(1B)-U(1B)-I(5B)	73.5(4)
M(1B)-U(1B)-I(5B)	104.7(4)
I(2B)-U(1B)-I(5B)	93.57(4)
O(1B)-U(1B)-I(6B)	73.4(4)
M(1B)-U(1B)-I(6B)	105.8(3)
I(2B)-U(1B)-I(6B)	146.45(4)
I(5B)-U(1B)-I(6B)	79.25(4)
O(1B)-U(1B)-I(1B)	74.7(4)
M(1B)-U(1B)-I(1B)	107.1(4)
I(2B)-U(1B)-I(1B)	80.51(4)
I(5B)-U(1B)-I(1B)	147.97(4)
I(6B)-U(1B)-I(1B)	88.44(4)
O(1B)-U(2B)-M(2B)	175.6(4)
O(1B)-U(2B)-I(3B)	73.6(4)
M(2B)-U(2B)-I(3B)	104.4(4)
O(1B)-U(2B)-I(1B)	74.3(4)
M(2B)-U(2B)-I(1B)	109.8(4)
I(3B)-U(2B)-I(1B)	88.53(4)

O(1B)-U(2B)-I(2B)	70.9(4)
M(2B)-U(2B)-I(2B)	111.2(4)
I(3B)-U(2B)-I(2B)	144.43(4)
I(1B)-U(2B)-I(2B)	79.79(4)
O(1B)-U(2B)-I(4B)	70.3(4)
M(2B)-U(2B)-I(4B)	105.7(4)
I(3B)-U(2B)-I(4B)	82.83(4)
I(1B)-U(2B)-I(4B)	144.56(4)
I(2B)-U(2B)-I(4B)	87.52(4)
O(1B)-U(3B)-M(3B)	177.0(4)
O(1B)-U(3B)-I(5B)	73.8(3)
M(3B)-U(3B)-I(5B)	106.3(4)
O(1B)-U(3B)-I(6B)	74.3(4)
M(3B)-U(3B)-I(6B)	108.7(4)
I(5B)-U(3B)-I(6B)	80.22(4)
O(1B)-U(3B)-I(4B)	72.5(4)
M(3B)-U(3B)-I(4B)	104.6(4)
I(5B)-U(3B)-I(4B)	91.00(4)
I(6B)-U(3B)-I(4B)	146.73(5)
O(1B)-U(3B)-I(3B)	74.0(3)
M(3B)-U(3B)-I(3B)	106.0(4)
I(5B)-U(3B)-I(3B)	147.52(5)
I(6B)-U(3B)-I(3B)	86.83(4)
I(4B)-U(3B)-I(3B)	83.68(4)
U(2)-I(1)-U(1)	74.31(3)
U(1)-I(2)-U(2)	73.74(3)
U(3)-I(3)-U(2)	73.74(3)
U(3)-I(4)-U(2)	73.97(4)
U(3)-I(5)-U(1)	73.99(3)
U(3)-I(6)-U(1)	74.01(3)
U(3)-O(1)-U(2)	119.8(5)
U(3)-O(1)-U(1)	120.3(5)
U(2)-O(1)-U(1)	119.9(6)
C(5)-C(1)-C(2)	105.3(17)
C(5)-C(1)-C(6)	130(2)

C(2)-C(1)-C(6)	124.6(19)
C(3)-C(2)-C(1)	108.4(16)
C(3)-C(2)-C(7)	122.8(16)
C(1)-C(2)-C(7)	128.6(16)
C(2)-C(3)-C(4)	108.9(16)
C(2)-C(3)-C(8)	125.7(16)
C(4)-C(3)-C(8)	124.1(17)
C(5)-C(4)-C(3)	105.3(16)
C(5)-C(4)-C(9)	125.9(18)
C(3)-C(4)-C(9)	128.3(18)
C(1)-C(5)-C(4)	112.1(17)
C(1)-C(5)-C(10)	122.8(18)
C(4)-C(5)-C(10)	125.0(17)
C(12)-C(11)-C(15)	109.9(17)
C(12)-C(11)-C(16)	128.0(18)
C(15)-C(11)-C(16)	121.4(17)
C(11)-C(12)-C(13)	108.4(17)
C(11)-C(12)-C(17)	123.9(18)
C(13)-C(12)-C(17)	127.1(18)
C(12)-C(13)-C(14)	110.3(16)
C(12)-C(13)-C(18)	125.5(18)
C(14)-C(13)-C(18)	124.0(18)
C(13)-C(14)-C(15)	106.3(16)
C(13)-C(14)-C(19)	126.6(17)
C(15)-C(14)-C(19)	127.0(17)
C(14)-C(15)-C(20)	128.5(19)
C(14)-C(15)-C(11)	105.1(17)
C(20)-C(15)-C(11)	125.7(19)
C(22)-C(21)-C(25)	108.1(16)
C(22)-C(21)-C(26)	124.8(18)
C(25)-C(21)-C(26)	126.8(17)
C(21)-C(22)-C(23)	110.2(17)
C(21)-C(22)-C(27)	125.2(17)
C(23)-C(22)-C(27)	123.5(17)
C(24)-C(23)-C(22)	106.2(17)

C(24)-C(23)-C(28)	124.3(18)
C(22)-C(23)-C(28)	128.7(18)
C(23)-C(24)-C(25)	109.0(17)
C(23)-C(24)-C(29)	126.0(19)
C(25)-C(24)-C(29)	124.7(17)
C(21)-C(25)-C(24)	106.4(15)
C(21)-C(25)-C(30)	128.4(17)
C(24)-C(25)-C(30)	125.0(18)
U(2B)-I(1B)-U(1B)	73.98(4)
U(1B)-I(2B)-U(2B)	74.24(4)
U(2B)-I(3B)-U(3B)	74.79(3)
U(3B)-I(4B)-U(2B)	73.89(3)
U(3B)-I(5B)-U(1B)	73.72(3)
U(3B)-I(6B)-U(1B)	73.35(3)
U(1B)-O(1B)-U(3B)	120.3(6)
U(1B)-O(1B)-U(2B)	120.2(7)
U(3B)-O(1B)-U(2B)	119.2(6)
C(2B)-C(1B)-C(5B)	107.5(17)
C(2B)-C(1B)-C(6B)	126.6(18)
C(5B)-C(1B)-C(6B)	125.0(18)
C(3B)-C(2B)-C(1B)	108.3(18)
C(3B)-C(2B)-C(7B)	129.3(19)
C(1B)-C(2B)-C(7B)	121.5(17)
C(2B)-C(3B)-C(4B)	107.6(18)
C(2B)-C(3B)-C(8B)	125.8(19)
C(4B)-C(3B)-C(8B)	126.3(18)
C(5B)-C(4B)-C(3B)	110.0(18)
C(5B)-C(4B)-C(9B)	126.3(19)
C(3B)-C(4B)-C(9B)	123.7(19)
C(4B)-C(5B)-C(1B)	106.6(17)
C(4B)-C(5B)-C(10B)	128.2(18)
C(1B)-C(5B)-C(10B)	125.0(18)
C(12B)-C(11B)-C(15B)	108.5(17)
C(12B)-C(11B)-C(16B)	125.4(17)
C(15B)-C(11B)-C(16B)	125.6(18)

C(11B)-C(12B)-C(13B)	108.3(18)
C(11B)-C(12B)-C(17B)	125.6(18)
C(13B)-C(12B)-C(17B)	125.6(18)
C(14B)-C(13B)-C(12B)	108.7(18)
C(14B)-C(13B)-C(18B)	127.4(18)
C(12B)-C(13B)-C(18B)	123.6(18)
C(13B)-C(14B)-C(15B)	108.4(17)
C(13B)-C(14B)-C(19B)	129.2(18)
C(15B)-C(14B)-C(19B)	122.3(17)
C(11B)-C(15B)-C(14B)	106.1(18)
C(11B)-C(15B)-C(20B)	127.7(19)
C(14B)-C(15B)-C(20B)	126.1(18)
C(25B)-C(21B)-C(22B)	107.8(16)
C(25B)-C(21B)-C(26B)	130.2(18)
C(22B)-C(21B)-C(26B)	121.9(18)
C(23B)-C(22B)-C(21B)	106.0(16)
C(23B)-C(22B)-C(27B)	129.3(17)
C(21B)-C(22B)-C(27B)	124.1(17)
C(24B)-C(23B)-C(22B)	110.4(17)
C(24B)-C(23B)-C(28B)	122.5(18)
C(22B)-C(23B)-C(28B)	126.5(17)
C(23B)-C(24B)-C(25B)	108.0(17)
C(23B)-C(24B)-C(29B)	125.6(19)
C(25B)-C(24B)-C(29B)	124.9(18)
C(24B)-C(25B)-C(21B)	107.8(16)
C(24B)-C(25B)-C(30B)	128.3(18)
C(21B)-C(25B)-C(30B)	123.8(17)

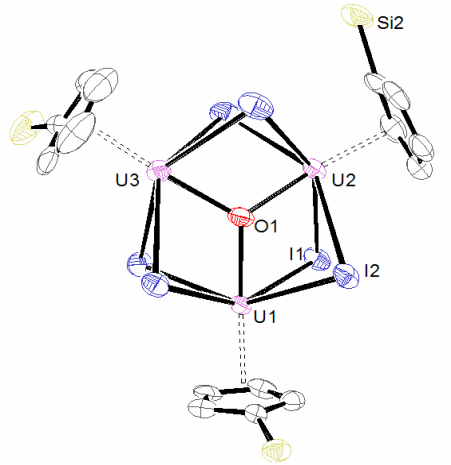
M(1),M(2),M(3) and M(1B,M(2B),M(3B) are the centroids of the Cp* rings.

```
 Least-squares planes (x,y,z in crystal coordinates) and deviations from
them
  (* indicates atom used to define plane)

 - 14.7988 (0.0058) x + 0.7728 (0.0051) y + 15.8809 (0.0015) z = 3.7217
(0.0041)

 *    0.0000 (0.0000)  U1
 *    0.0000 (0.0000)  U2
```

```
 *    0.0000 (0.0000)  U3
      0.0136 (0.0128)  O1_a

 Rms deviation of fitted atoms =   0.0000


 - 1.1317 (0.0075) x + 0.0854 (0.0057) y + 15.8798 (0.0015) z = 10.4604
(0.0020)

 Angle to previous plane (with approximate esd) = 34.42 ( 0.02 )

 *    0.0000 (0.0000)  U1B
 *    0.0000 (0.0000)  U2B
 *    0.0000 (0.0000)  U3B
     -0.0648 (0.0146)  O1B_a

 Rms deviation of fitted atoms =   0.0000


  7.6206 (0.2204) x + 19.5814 (0.0870) y + 2.6257 (0.1583) z = 12.1346
(0.0333)

 Angle to previous plane (with approximate esd) = 74.39 ( 0.60 )

 *    0.0061 (0.0122)  C1_a
 *   -0.0105 (0.0118)  C2_a
 *    0.0108 (0.0116)  C3_a
 *   -0.0067 (0.0118)  C4_a
 *    0.0004 (0.0127)  C5_a
      2.4470 (0.0082)  U1
     -0.0658 (0.0367)  C6_a
     -0.1313 (0.0340)  C7_a
     -0.2278 (0.0334)  C8_a
     -0.1883 (0.0355)  C9_a
     -0.0854 (0.0356)  C10_a

 Rms deviation of fitted atoms =   0.0079


 - 10.2497 (0.2107) x + 18.3107 (0.1127) y - 2.6955 (0.1581) z = 15.3975
(0.1334)

 Angle to previous plane (with approximate esd) = 56.46 ( 0.58 )

 *   -0.0019 (0.0126)  C11_a
 *   -0.0023 (0.0125)  C12_a
 *    0.0057 (0.0120)  C13_a
 *   -0.0067 (0.0121)  C14_a
 *    0.0052 (0.0121)  C15_a
     -2.4500 (0.0083)  U2
      0.1993 (0.0351)  C16_a
      0.1822 (0.0362)  C17_a
      0.1285 (0.0366)  C18_a
      0.0303 (0.0345)  C19_a
      0.1988 (0.0364)  C20_a
```

```
 Rms deviation of fitted atoms =   0.0047


  19.2782 (0.1600) x + 2.0667 (0.1870) y + 5.1612 (0.1672) z = 11.5105
(0.1353)

 Angle to previous plane (with approximate esd) = 63.68 ( 0.79 )

 *    0.0005 (0.0110)  C21_a
 *   -0.0015 (0.0112)  C22_a
 *    0.0019 (0.0115)  C23_a
 *   -0.0016 (0.0119)  C24_a
 *    0.0007 (0.0114)  C25_a
     -2.4522 (0.0090)  U3
      0.1371 (0.0374)  C26_a
      0.2480 (0.0346)  C27_a
      0.2149 (0.0346)  C28_a
      0.1275 (0.0382)  C29_a
      0.0814 (0.0330)  C30_a

 Rms deviation of fitted atoms =   0.0014


  12.7958 (0.2107) x + 18.3757 (0.1128) y - 2.1896 (0.1682) z = 11.7408
(0.1038)

 Angle to previous plane (with approximate esd) = 58.73 ( 0.82 )

 *   -0.0024 (0.0119)  C1B_a
 *    0.0011 (0.0123)  C2B_a
 *    0.0006 (0.0127)  C3B_a
 *   -0.0022 (0.0128)  C4B_a
 *    0.0028 (0.0124)  C5B_a
     -2.4578 (0.0085)  U1B
      0.2110 (0.0376)  C6B_a
      0.2276 (0.0355)  C7B_a
      0.1514 (0.0384)  C8B_a
      0.0545 (0.0401)  C9B_a
      0.1269 (0.0358)  C10B_a

 Rms deviation of fitted atoms =   0.0020


  9.8394 (0.2344) x - 19.7398 (0.0905) y - 2.7483 (0.1696) z = 1.1918
(0.1209)

 Angle to previous plane (with approximate esd) = 54.94 ( 0.58 )

 *   -0.0082 (0.0127)  C11B_a
 *    0.0060 (0.0123)  C12B_a
 *   -0.0013 (0.0124)  C13B_a
 *   -0.0037 (0.0126)  C14B_a
 *    0.0072 (0.0126)  C15B_a
     -2.4552 (0.0086)  U2B
      0.1402 (0.0341)  C16B_a
      0.1941 (0.0365)  C17B_a
```

```
      0.1212 (0.0352)  C18B_a
      0.0790 (0.0367)  C19B_a
      0.1192 (0.0388)  C20B_a

 Rms deviation of fitted atoms =   0.0059


  24.5653 (0.0129) x + 0.4622 (0.1980) y - 4.9180 (0.1664) z = 0.0139
(0.1197)

 Angle to previous plane (with approximate esd) = 67.77 ( 0.78 )

 *    0.0033 (0.0114)  C21B_a
 *    0.0028 (0.0110)  C22B_a
 *   -0.0079 (0.0116)  C23B_a
 *    0.0099 (0.0121)  C24B_a
 *   -0.0080 (0.0121)  C25B_a
      2.4392 (0.0092)  U3B
     -0.0747 (0.0386)  C26B_a
     -0.1591 (0.0347)  C27B_a
     -0.2174 (0.0349)  C28B_a
     -0.2507 (0.0370)  C29B_a
     -0.1163 (0.0335)  C30B_a

 Rms deviation of fitted atoms =   0.0070
```



$[UCp'I_2]_3O$ (2)

Empirical formula	C24 H39 I6 O Si3 U3
Identification code	dec705
Formula weight	1903.31
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$ (No.14)
Unit cell dimensions	a = 16.7070(3) Å α= 90°.

	b = 8.3748(1) Å	β= 102.745(1)°.
	c = 31.3762(4) Å	γ = 90°.
Volume	4281.92(11) $Å^3$	
Z	4	
Density (calculated)	2.95 Mg/m^3	
Absorption coefficient	15.75 mm^{-1}	
Crystal size	0.25 x 0.20 x 0.02 mm^3	
Theta range for data collection	3.45 to 25.97°.	
Reflections collected	61341	
Independent reflections	8349 [R(int) = 0.125]	
Reflections with I>2sigma(I)	6849	
Completeness to theta = 25.97°	99.7 %	
Data / restraints / parameters	8349 / 0 / 334	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.045, wR2 = 0.110	
R indices (all data)	R1 = 0.059, wR2 = 0.118	
Largest diff. peak and hole	2.96 and -2.54 $e.Å^{-3}$ (near U atoms)	

Table 2. Bond lengths [Å] and angles [°]

U(1)-O(1)	2.168(7)
U(1)-M(1)	2.43(1)
U(1)-C(2)	2.689(10)
U(1)-C(3)	2.697(10)
U(1)-C(5)	2.717(10)
U(1)-C(4)	2.718(10)
U(1)-C(1)	2.722(10)
U(1)-I(1)	3.1420(7)
U(1)-I(5)	3.1473(7)
U(1)-I(6)	3.1586(8)
U(1)-I(2)	3.1644(7)
U(2)-O(1)	2.156(7)
U(2)-M(2)	2.43(1)
U(2)-C(12)	2.688(11)
U(2)-C(11)	2.694(11)
U(2)-C(13)	2.701(11)
U(2)-C(10)	2.726(10)
U(2)-C(9)	2.734(10)
U(2)-I(3)	3.0973(8)
U(2)-I(1)	3.1375(8)
U(2)-I(4)	3.1486(8)
U(2)-I(2)	3.2256(8)
U(3)-O(1)	2.311(7)
U(3)-M(3)	2.44(1)
U(3)-C(20)	2.702(13)
U(3)-C(21)	2.706(12)
U(3)-C(18)	2.712(12)
U(3)-C(17)	2.726(11)
U(3)-C(19)	2.743(14)
U(3)-I(5)	3.2017(8)
U(3)-I(4)	3.2266(8)
U(3)-I(3)	3.2302(9)
U(3)-I(6)	3.2574(8)

Si(1)-C(8)	1.846(14)
Si(1)-C(6)	1.861(12)
Si(1)-C(1)	1.862(11)
Si(1)-C(7)	1.864(14)
Si(2)-C(14)	1.84(2)
Si(2)-C(16)	1.861(17)
Si(2)-C(9)	1.884(12)
Si(2)-C(15)	1.896(16)
Si(3)-C(24)	1.80(2)
Si(3)-C(23)	1.828(18)
Si(3)-C(17)	1.832(12)
Si(3)-C(22)	1.96(2)
C(1)-C(2)	1.419(15)
C(1)-C(5)	1.438(14)
C(2)-C(3)	1.413(14)
C(3)-C(4)	1.401(16)
C(4)-C(5)	1.397(15)
C(9)-C(13)	1.424(17)
C(9)-C(10)	1.437(16)
C(10)-C(11)	1.384(18)
C(11)-C(12)	1.381(16)
C(12)-C(13)	1.412(17)
C(17)-C(18)	1.419(17)
C(17)-C(21)	1.431(19)
C(18)-C(19)	1.335(19)
C(19)-C(20)	1.32(2)
C(20)-C(21)	1.49(2)

O(1)-U(1)-M(1)	175.1(2)
O(1)-U(1)-I(1)	73.9(2)
M(1)-U(1)-I(1)	101.2(2)
O(1)-U(1)-I(5)	75.1(2)
M(1)-U(1)-I(5)	109.7(2)
I(1)-U(1)-I(5)	149.05(2)
O(1)-U(1)-I(6)	75.5(2)

M(1)-U(1)-I(6)	104.1(2)
I(1)-U(1)-I(6)	92.59(2)
I(5)-U(1)-I(6)	79.51(2)
O(1)-U(1)-I(2)	72.4(2)
M(1)-U(1)-I(2)	108.0(2)
I(1)-U(1)-I(2)	80.39(2)
I(5)-U(1)-I(2)	90.52(2)
I(6)-U(1)-I(2)	147.89(2)
O(1)-U(2)-M(2)	174.1(2)
O(1)-U(2)-I(3)	77.1(2)
M(2)-U(2)-I(3)	105.8(2)
O(1)-U(2)-I(1)	74.2(2)
M(2)-U(2)-I(1)	102.9(2)
I(3)-U(2)-I(1)	151.24(2)
O(1)-U(2)-I(4)	74.4(2)
M(2)-U(2)-I(4)	110.9(2)
I(3)-U(2)-I(4)	82.80(2)
I(1)-U(2)-I(4)	89.32(2)
O(1)-U(2)-I(2)	71.2(2)
M(2)-U(2)-I(2)	103.4(2)
I(3)-U(2)-I(2)	91.48(2)
I(1)-U(2)-I(2)	79.51(2)
I(4)-U(2)-I(2)	145.49(2)
O(1)-U(3)-M(3)	172.6(2)
O(1)-U(3)-I(5)	72.3(2)
M(3)-U(3)-I(5)	105.7(2)
O(1)-U(3)-I(4)	71.0(2)
M(3)-U(3)-I(4)	111.4(2)
I(5)-U(3)-I(4)	142.78(2)
O(1)-U(3)-I(3)	72.4(2)
M(3)-U(3)-I(3)	100.960(19)
I(5)-U(3)-I(3)	95.54(2)
I(4)-U(3)-I(3)	79.54(2)
O(1)-U(3)-I(6)	71.8(2)
M(3)-U(3)-I(6)	115.0(2)

I(5)-U(3)-I(6)	77.265(19)
I(4)-U(3)-I(6)	85.35(2)
I(3)-U(3)-I(6)	143.98(2)
U(2)-I(1)-U(1)	74.197(17)
U(1)-I(2)-U(2)	72.697(17)
U(2)-I(3)-U(3)	74.498(18)
U(2)-I(4)-U(3)	73.869(18)
U(1)-I(5)-U(3)	75.099(17)
U(1)-I(6)-U(3)	74.169(17)
C(8)-Si(1)-C(6)	111.1(6)
C(8)-Si(1)-C(1)	108.9(6)
C(6)-Si(1)-C(1)	111.4(5)
C(8)-Si(1)-C(7)	109.9(8)
C(6)-Si(1)-C(7)	109.6(7)
C(1)-Si(1)-C(7)	105.9(5)
C(14)-Si(2)-C(16)	112.1(9)
C(14)-Si(2)-C(9)	112.9(7)
C(16)-Si(2)-C(9)	108.9(7)
C(14)-Si(2)-C(15)	107.4(9)
C(16)-Si(2)-C(15)	111.1(9)
C(9)-Si(2)-C(15)	104.2(7)
C(24)-Si(3)-C(23)	116.0(12)
C(24)-Si(3)-C(17)	112.9(7)
C(23)-Si(3)-C(17)	107.2(9)
C(24)-Si(3)-C(22)	109.6(10)
C(23)-Si(3)-C(22)	102.7(11)
C(17)-Si(3)-C(22)	107.8(7)
U(2)-O(1)-U(1)	122.3(3)
U(2)-O(1)-U(3)	118.1(3)
U(1)-O(1)-U(3)	119.5(3)
C(2)-C(1)-C(5)	104.4(9)
C(2)-C(1)-Si(1)	128.0(8)
C(5)-C(1)-Si(1)	125.5(8)
C(2)-C(1)-U(1)	73.5(6)
C(5)-C(1)-U(1)	74.5(6)

Si(1)-C(1)-U(1)	129.3(5)
C(3)-C(2)-C(1)	110.2(10)
C(3)-C(2)-U(1)	75.1(6)
C(1)-C(2)-U(1)	76.1(6)
C(4)-C(3)-C(2)	107.3(10)
C(4)-C(3)-U(1)	75.8(6)
C(2)-C(3)-U(1)	74.5(6)
C(5)-C(4)-C(3)	108.2(9)
C(5)-C(4)-U(1)	75.0(6)
C(3)-C(4)-U(1)	74.2(6)
C(4)-C(5)-C(1)	109.8(10)
C(4)-C(5)-U(1)	75.2(6)
C(1)-C(5)-U(1)	74.9(6)
C(13)-C(9)-C(10)	105.2(11)
C(13)-C(9)-Si(2)	126.5(9)
C(10)-C(9)-Si(2)	126.3(9)
C(13)-C(9)-U(2)	73.6(6)
C(10)-C(9)-U(2)	74.4(6)
Si(2)-C(9)-U(2)	129.6(6)
C(11)-C(10)-C(9)	108.7(10)
C(11)-C(10)-U(2)	73.9(6)
C(9)-C(10)-U(2)	75.0(6)
C(12)-C(11)-C(10)	109.6(11)
C(12)-C(11)-U(2)	74.9(7)
C(10)-C(11)-U(2)	76.5(7)
C(11)-C(12)-C(13)	107.5(11)
C(11)-C(12)-U(2)	75.4(7)
C(13)-C(12)-U(2)	75.3(7)
C(12)-C(13)-C(9)	109.0(10)
C(12)-C(13)-U(2)	74.3(6)
C(9)-C(13)-U(2)	76.1(6)
C(18)-C(17)-C(21)	103.8(12)
C(18)-C(17)-Si(3)	127.6(9)
C(21)-C(17)-Si(3)	126.8(11)
C(18)-C(17)-U(3)	74.3(7)

C(21)-C(17)-U(3)	74.0(7)
Si(3)-C(17)-U(3)	127.8(6)
C(19)-C(18)-C(17)	113.0(14)
C(19)-C(18)-U(3)	77.1(8)
C(17)-C(18)-U(3)	75.4(7)
C(20)-C(19)-C(18)	109.0(15)
C(20)-C(19)-U(3)	74.3(9)
C(18)-C(19)-U(3)	74.6(8)
C(19)-C(20)-C(21)	109.0(13)
C(19)-C(20)-U(3)	77.7(9)
C(21)-C(20)-U(3)	74.2(7)
C(17)-C(21)-C(20)	105.1(13)
C(17)-C(21)-U(3)	75.5(7)
C(20)-C(21)-U(3)	73.8(8)

M(1),M(2), and M(3) are the three ring centroids.

```
Least-squares planes (x,y,z in crystal coordinates) and deviations from
them
 (* indicates atom used to define plane)

  8.0359 (0.0019) x + 7.0501 (0.0006) y - 10.8250 (0.0039) z = 7.4167
(0.0007)

 *    0.0000 (0.0000)  U1
 *    0.0000 (0.0000)  U2
 *    0.0000 (0.0000)  U3
      0.0249 (0.0068)  O1_a
     -0.1903 (0.0006)  M1_b
      0.0622 (0.0006)  M2_b
      0.2582 (0.0007)  M3_b

 Rms deviation of fitted atoms =   0.0000


  12.4309 (0.0572) x - 2.9650 (0.0408) y + 12.1895 (0.1541) z = 8.0397
(0.0446)

 Angle to previous plane (with approximate esd) = 85.47 ( 0.27 )

 *   -0.0022 (0.0060)  C1_a
 *    0.0034 (0.0061)  C2_a
 *   -0.0032 (0.0062)  C3_a
 *    0.0018 (0.0064)  C4_a
 *    0.0002 (0.0063)  C5_a
     -2.4272 (0.0046)  U1
      0.3922 (0.0165)  Si1_a

 Rms deviation of fitted atoms =   0.0024


  8.0359 (0.0019) x + 7.0501 (0.0006) y - 10.8250 (0.0039) z = 7.4167
(0.0007)

 Angle to previous plane (with approximate esd) = 85.47 ( 0.27 )

 *    0.0000 (0.0000)  U1
 *    0.0000 (0.0000)  U2
 *    0.0000 (0.0000)  U3
      0.0249 (0.0068)  O1_a
     -0.1903 (0.0006)  M1_b
      0.0622 (0.0006)  M2_b
      0.2582 (0.0007)  M3_b

 Rms deviation of fitted atoms =   0.0000


  0.9363 (0.0961) x - 2.3765 (0.0452) y - 29.6829 (0.0575) z = 0.0939
(0.0444)

 Angle to previous plane (with approximate esd) = 88.71 ( 0.31 )

 *   -0.0044 (0.0067)  C9_a
```

```
 *    0.0044 (0.0069)  C10_a
 *   -0.0026 (0.0070)  C11_a
 *   -0.0003 (0.0069)  C12_a
 *    0.0030 (0.0068)  C13_a
     -2.4290 (0.0049)  U2
      0.3895 (0.0186)  Si2_a

 Rms deviation of fitted atoms =   0.0033


  8.0359 (0.0019) x + 7.0501 (0.0006) y - 10.8250 (0.0039) z = 7.4167
(0.0007)

 Angle to previous plane (with approximate esd) = 88.71 ( 0.31 )

 *    0.0000 (0.0000)  U1
 *    0.0000 (0.0000)  U2
 *    0.0000 (0.0000)  U3
      0.0249 (0.0068)  O1_a
     -0.1903 (0.0006)  M1_b
      0.0622 (0.0006)  M2_b
      0.2582 (0.0007)  M3_b

 Rms deviation of fitted atoms =   0.0000


 - 11.8598 (0.0799) x + 5.1911 (0.0434) y + 15.1493 (0.1747) z = 5.9661
(0.0599)

 Angle to previous plane (with approximate esd) = 84.35 ( 0.30 )

 *   -0.0011 (0.0074)  C17_a
 *   -0.0029 (0.0082)  C18_a
 *    0.0060 (0.0092)  C19_a
 *   -0.0063 (0.0089)  C20_a
 *    0.0043 (0.0078)  C21_a
     -2.4427 (0.0052)  U3
      0.3601 (0.0202)  Si3_a

 Rms deviation of fitted atoms =   0.0046
```