A Complete Series of Uranocene(III) Halides [{UCp″$_2$X}$_n$] [X = F, Cl, Br, or I; Cp″ = η-C$_5$H$_3$(SiMe$_3$)$_2$]; Single-crystal *X*-Ray Structure Determinations of the Chloride and Bromide (*n* = 2 for X$^-$ = μ-Cl$^-$ or μ-Br$^-$)†

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Reduction of [UCp″$_2$X$_2$] [Cp″ = η-C$_5$H$_3$(SiMe$_3$)$_2$; X = Cl, Br, or I] or [{UCp″$_2$(μ-BF$_4$)(μ-F)}$_2$] with Na/Hg in toluene yields the lipophilic (and n.m.r. characterisable) compounds [{UCp″$_2$X}$_n$] (X = F, Cl, Br, or I), which are versatile precursors to uranocene (III or IV) compounds; *X*-ray data on the chloro- and bromo-derivatives reveal them to be the first uranocene(III) halide dimers (*i.e.*, *n* = 2, with μ-X$^-$).

We report on a complete series of uranocene(III) halides [{UCp″$_2$X}$_n$] [X = F (**1**), Cl (**2**), Br (**3**), or I (**4**); Cp″ = η-C$_5$H$_3$(SiMe$_3$)$_2$-1,3]. Fluorides, bromides, and iodides were previously unknown in organouranium(III) chemistry.

X-Ray data on the isostructural chloride (**2**) and bromide (**3**) show them to be dimers in the crystal, having a pair of bridging halide ligands (Figure 1).‡ By contrast, the only other known uranocene(III) chloride. [{UCp*$_2$(μ-Cl)}$_3$] (**5**) (Cp* =

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‡ *Crystal data* for [{UCp″$_2$(μ-Cl)}$_2$] (**2**) and in parentheses, for [{UCp″$_2$(μ-Br)}$_2$] (**3**) $C_{44}H_{84}Cl_2Si_8U_2$ ($C_{44}H_{84}Br_2Si_8U_2$), M = 1384.72 (1473.73), space group $P\bar{1}$ ($P\bar{1}$), a = 10.622(5) [10.786(6)], b = 11.815(5) [11.607(6)], c = 13.304(5) [13.227(7)] Å, α = 109.30(4) [73.79(8)], β = 99.56(4) [83.83(8)], γ = 95.67(4) [77.91(6)]°, U = 1532.6 (1552.6) Å^3, Z = 1 (1), D_c = 1.50 (1.58) g cm^{-3}, F(000) = 678 (714).

The structures of complexes (**2**) and (**3**) were solved by routine heavy atom methods and refined to (i) R = 0.040, R' = 0.049 for 2818 observed reflections for (**2**); and (ii) R = 0.103, R' = 0.122 for 1148 observed reflections for (**3**), measured on a CAD-4 diffractometer with Mo-K_α radiation. Attempts to gain a lower R factor for (**3**) have failed owing to the small size of the crystal and its poor scattering properties. Details of the data collection process have previously been given.[8] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

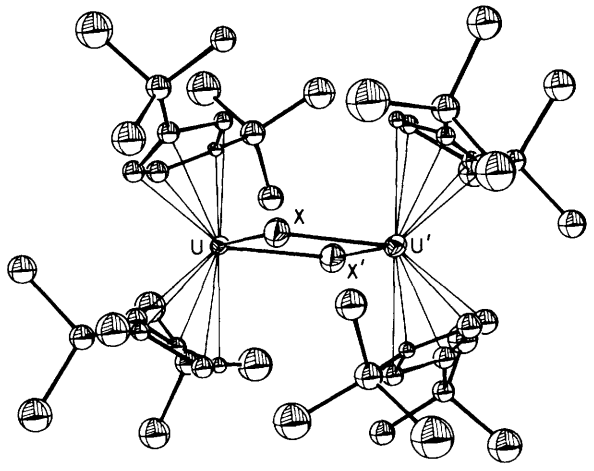
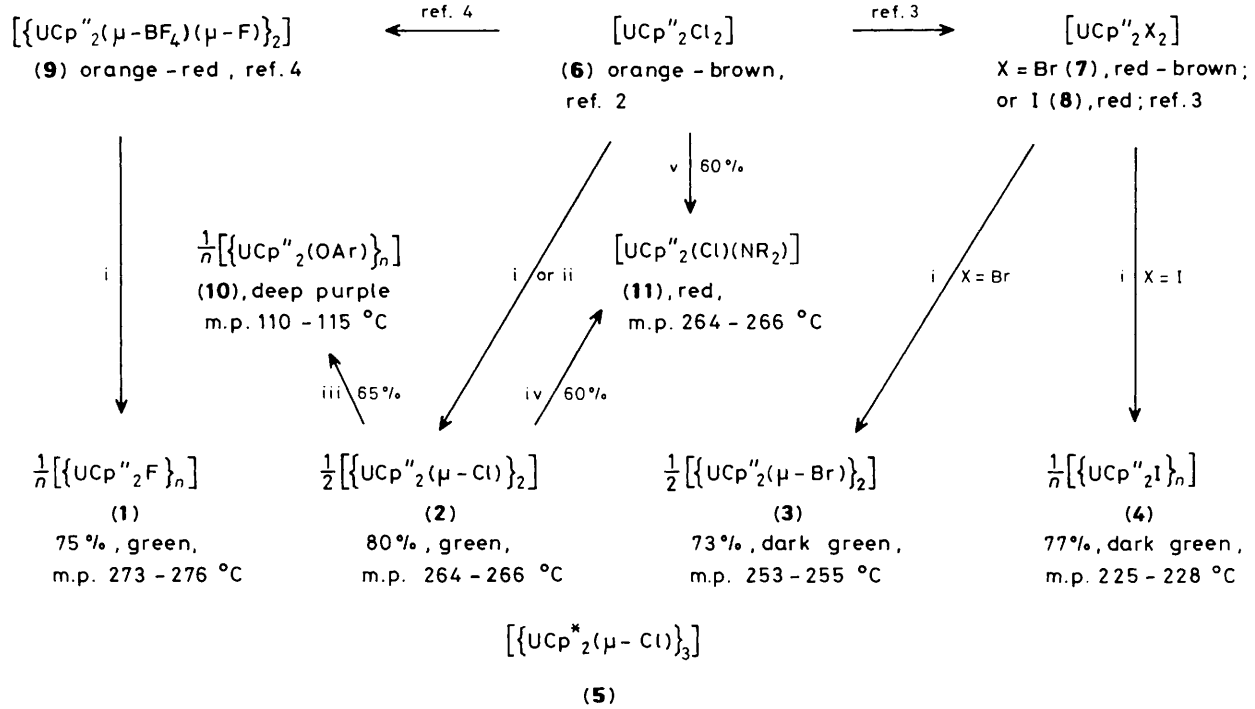


Figure 1. The molecular structure, and atom labelling scheme, for [{UCp″$_2$(μ-Cl)}$_2$] (**2**); the bromide (**3**) is isostructural. Relevant dimensions are [data for the bromide (**3**) in parentheses]: U · · · U′ 4.357(1) [4.335(5)], U–X 2.818(4) [2.94(1)], U–X′ 2.802(4) [2.93(1)], U–Cen(1) 2.496 [2.000], U–Cen(2) 2.494 [2.000], U–Cp″(1) aver. 2.79(2) [2.74(8)], U–Cp″(2) aver. 2.78(2) [2.76(8)] Å; X–U–X′ 78.5(1) [84.8(3)], U–X–U′ 101.5 [95.4(3)], X–U–Cen(1) 107.2 [100.0], Cen(1)–U–Cen(2) 130.8 [100.0]°. [Cen(1) and Cen(2) are the centroids of the cyclopentadienyl rings.]



Scheme 1. *Abbreviations:* Cp″ = η-$C_5H_3(SiMe_3)_2$; Ar = $C_6H_3Pr^i_2$-2,6; R = $SiMe_3$. *Reagents and conditions:* i, Na/Hg, PhMe, *ca.* 20 °C, *ca.* 12 h; ii, $LiBu^n$, n-C_6H_{14}, *ca.* 20 °C, *ca.* 12 h; iii, LiOAr, n-C_6H_{14}, 24 h, *ca.* 20 °C; iv, $Sn(NR_2)_2$, tetrahydrofuran (thf), 72 h, *ca.* 20 °C; v, $LiNR_2$-(OEt_2), thf, 24 h, *ca.* 20 °C. *Identification procedures:* crystals of compounds (**1**)—(**4**), (**10**), and (**11**) were obtained from n-C_6H_{14} at −30 °C, and were characterised by microanalysis, ^1H n.m.r. spectroscopy, and, in the case of the halides (**2**) and (**3**) (Figure 1), by *X*-ray diffraction.

η-C_5Me_5),[1] is a trimer. Hence, we infer that the $\bar{C}p''$ ligand is sterically more demanding than $\bar{C}_5Me_5$.

We have previously shown that $\bar{C}p''$ is able to stabilise the uranocene(IV) halides $[UCp''_2X_2]$ [X = Cl, Br, or I; (**6**)—(**8**), respectively].[2,3] We now find that their facile one-electron reduction yields the corresponding U^{III} halide (**2**)—(**4**), using either Na/Hg in toluene or n-butyl-lithium in n-hexane, Scheme 1. Similarly, the bridging tetrafluoroborato complex $[\{UCp''_2(\mu\text{-}BF_4)(\mu\text{-}F)\}_2]$ (**9**)[4] was employed as precursor for the uranocene(III) fluoride (**1**).

The uranocene(III) halides are versatile precursors to a wide range of uranocene(III or IV) compounds (see also ref. 1). This is illustrated in Scheme 1 by (i) a ligand substitution reaction to yield the first U^{III} aryloxide (**10**), and (ii) a surprising redox reaction, in which $Sn[N(SiMe_3)_2]_2$ behaves uncharacteristically[5] as an oxidising agent, to give the U^{IV} chloro-bis-(trimethylsilyl)amide (**11**).

The new uranocene(III) halides are readily hydrocarbon-soluble. Although they are formally f^3 complexes they give reasonably well resolved n.m.r. spectra, but the signals are considerably broader than those of their f^2 $[UCp''_2X_2]$ progenitors (*cf.* ref. 1), and are significantly shifted [*e.g.* the $SiMe_3$ ^1H signals in C_6D_6 at *ca.* 30 °C are δ −9.4 ($w_{\frac{1}{2}}$ *ca.* 180 Hz) (**1**), −9.2 (**2**), −8.5 (**3**), −7.2 (**4**), and −15.74 (sharp) (**10**); *cf.* ref. 3 −2.55 for (**5**)].

The average U–C(η-) distance of 2.78(2) Å in $[\{UCp''_2(\mu\text{-}Cl)\}_2]$ (**2**) is very nearly equivalent to the 2.77(1) Å found in $[\{UCp^*_2(\mu\text{-}Cl)\}_3]$ (**5**). However, <U–Cl> in (**2**) at 2.810(4) Å is significantly shorter than the 2.900(2) Å in (**5**).[1] This may be due to a weakened U–Cl interaction in (**5**), caused by the wide <U–Cl–U> angle of 154.9(1)°; the corresponding <U–Cl–U> angle in the dimer (**2**) is 101.5(1)°. Both the $(UCl)_2$ and $(UCl)_3$ rings of (**2**) and (**5**), respectively, are planar.

Although there are no bis(cyclopentadienyl)uranium(III) bromides in the literature for direct comparison with complex (**3**), the <U–X> bond length change in progressing from $[U^{IV}Cp''_2X_2]$ to $[\{U^{III}Cp''_2(\mu\text{-}X)\}_2]$ is similar for X = Cl as for X = Br: 2.579(2) $(U^{IV})^3 \rightarrow$ 2.81(1) Å (U^{III}) in the chlorides, and 2.734(1) $(U^{IV})^3 \rightarrow$ 2.94(2) Å (U^{III}) in the bromides.

The uranocene(III) chloride (**2**) is also isomorphous with $[\{PrCp''_2(\mu\text{-}Cl)\}_2]$, and the crystal [*a* = 10.630(5), *b* = 11.817(5); *c* = 13.293(5) Å, α = 109.30(4), β = 99.42(4), γ = 86.66(4)°] and molecular [<Pr–Cl> 2.81, <Pr–C(η-)> 2.76 Å, Cl–Pr–Cl 78, Pr–Cl–Pr 102, Cent–Pr–Cent′ 130°] parameters are almost identical.[6] Evidently the U^{III} and Pr^{III} radii are very similar.[7]

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