A Series of Bis(η-cyclopentadienyl)uranium(III) Dichloro-bridged-alkali-metal and Dihalogenobis(η-cyclopentadienyl)uranate(III) Complexes: Single-crystal *X*-Ray Structure Determination of $[UCp''_2(\mu\text{-}Cl)_2Li(pmdeta)]$ and $[PPh_4][UCp''_2Cl_2]$ $[Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$, pmdeta = $(Me_2NCH_2CH_2)_2NMe]$†

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Reduction of $[UCp''_2Cl_2]$ with either $LiBu^n$ or Na–Hg in presence of the appropriate ligand L yields $[UCp''_2(\mu\text{-}Cl)_2M(L)_n]$ [M = Li or Na, L_n = $(thf)_2$ or tmeda: or M = Li and L_n = pmdeta (**5**)], while addition of LiX in thf or $[PPh_4]X$ in PhMe to $[\{UCp''_2(\mu\text{-}Cl)\}_2]$ gives $[UCp''_2(\mu\text{-}Cl)(\mu\text{-}X)Li(thf)_2]$ or $[PPh_4][UCp''_2(Cl)X]$ [X = Cl (**7**) or Br]; *X*-ray and ^1H n.m.r. data on complexes (**5**) and (**7**) are compared with those for three other bis(η-cyclopentadienyl)-uranium(III or IV) or -uranate(III) chlorides having 2 $\bar{C}p''$s and 2 $\bar{C}l$s around U[Cp″ = $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$; thf = OC_4H_8, tmeda = $(Me_2NCH_2)_2$; pmdeta = $(Me_2NCH_2CH_2)_2NMe$)].

The only previously well characterised bis(η-cyclopentadienyl)-uranium(III) or -uranate(III) halides have been the monometallic neutral complexes $[\{U(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)\}_3]$,[1] $[U(\eta\text{-}C_5Me_5)_2(Cl)L]$ (L = thf or py; thf = tetrahydrofuran, py = pyridine),[1] and $[\{UCp''_2(\mu\text{-}X)\}_n]$ [Cp″ = $\eta\text{-}C_5H_3\text{-}(SiMe_3)_2\text{-}1,3$, $n = 2$ for X = Cl or Br, or not determined for n = F or I].[2]

We now report on a range of bis(η-cyclopentadienyl)uranium(III) chloro-bridged-alkali-metal and dihalogenbis(η-cyclopentadienyl) uranate(III) complexes: $[UCp''_2(\mu\text{-}Cl)_2M(thf)_2]$ [M = Li (**1**) or Na (**2**)], $[UCp''_2(\mu\text{-}Cl)_2M(tmeda)]$ [M = Li (**3**) or Na (**4**), tmeda = $(Me_2NCH_2)_2$], $[UCp''_2(\mu\text{-}Cl)_2Li(pmdeta)]$ (**5**) [pmdeta = $(Me_2NCH_2CH_2)_2NMe$], $[UCp''_2(\mu\text{-}Br)(\mu\text{-}Cl)Li(thf)_2]$ (**6**), and $[PPh_4][UCp''_2(Cl)X]$ [X = Cl (**7**) or Br (**8**)].

Compounds (**1**)—(**5**) were prepared by reduction of $[UCp''_2Cl_2]$ (**9**)[3] with n-butyl-lithium or sodium amalgam, in the presence of the appropriate neutral ligand, Scheme 1. Addition of LiCl or LiBr to $[\{UCp''_2(\mu\text{-}Cl)\}_2]$ (**10**)[2] in thf yielded $[UCp''_2(\mu\text{-}Cl)(\mu\text{-}X)Li(thf)_2]$ [X = Cl (**1**) or Br (**6**)].

Complexes (**1**)—(**8**) are thermally stable as evident from their high m.p.s; only (**1**), (**2**), and (**6**) decomposed upon melting in a sealed capillary, probably due to elimination of thf. Sublimation of $[UCp''_2(\mu\text{-}Cl)_2Li(thf)_2]$ (**1**) at 245 °C gave the volatile monometallic complex (**10**).

Although the neutral bis(η-cyclopentadienyl)uranium(III) chlorides $[\{UCp''_2(\mu\text{-}X)\}_n]$ gave well resolved ^1H and ^{13}C n.m.r. spectra, the signals for these formally f^3 complexes were significantly broader [especially those of compounds (**2**), (**9**), and (**10**), having $w_{\frac{1}{2}} \geqslant 180$ Hz] than those for their f^2 $[UCp''_2X_2]$ precursors ($w_{\frac{1}{2}} \leqslant 30$ Hz).[2] By contrast, corresponding bands in each of the four lithium-containing (f^3) complexes (**1**), (**3**), (**5**), and (**6**), and the ate complexes (**7**) and (**8**)

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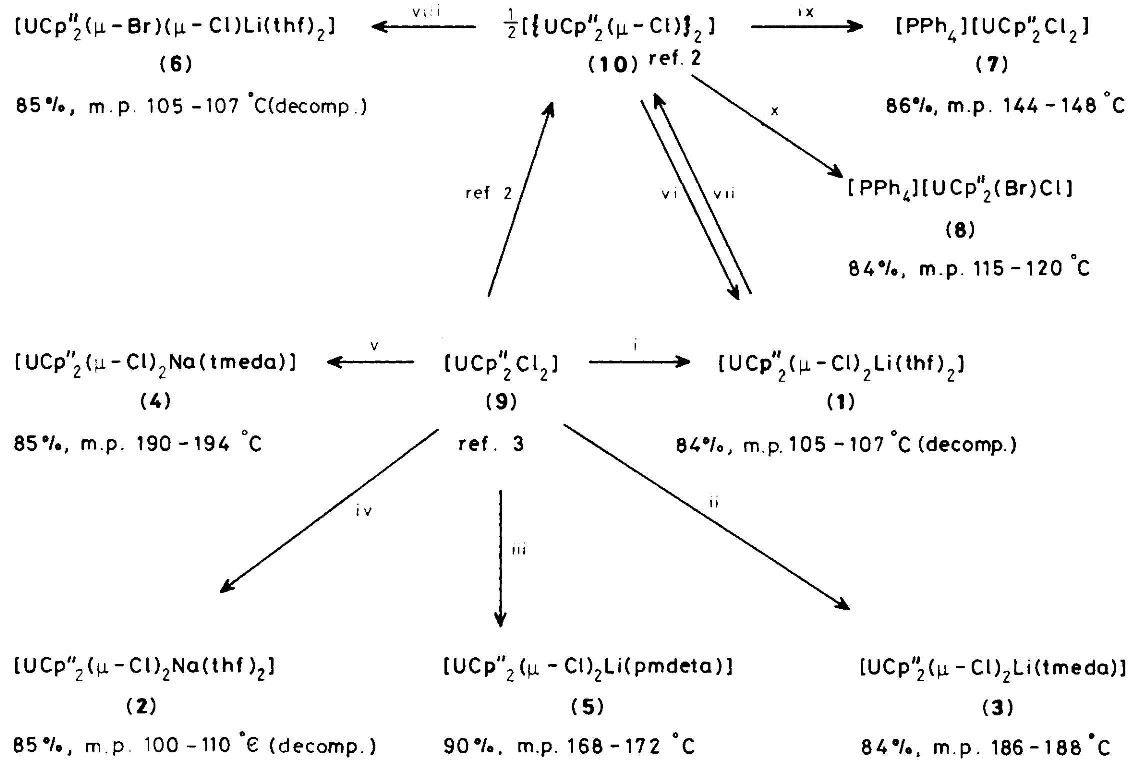
† No reprints available.

Table 1. Selected ^1H and ^7Li (rel. to aq. Li[NO_3]) n.m.r. chemical shifts (δ) for **(1)**—**(10)** in $C_6D_5CD_3$ at 305 K.

	(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**	**(8)**	**(9)**	**(10)**
Si(CH_3)$_3$	−5.0	−3.6	−5.19	−3.7	−4.2	−4.06, −4.46	−2.92	0—3	−2.55	−9.2
2-H in C_5H_3-($SiMe_3$)$_2$-1,3	37.5	33.4	35.9	32.7	24.7	45.9	25.5	31.2	87.3	
4- or 5-H in C_5H_3 ($SiMe_3$)$_2$-1,3	−33.2	−39.2	−31.3	−37.7	−26.9	−32.1, −35.4	−31.9	−31.7, −35.6	−33.4	
^7Li	0.82	—	1.47	—	−1.11	−1.96	—	—	—	—



Scheme 1. *Abbreviations*: Cp'' = η-C_5H_3($SiMe_3$)$_2$-1,3; tmeda = (Me_2NCH_2)$_2$; pmdeta = ($Me_2NCH_2CH_2$)$_2$NMe. *Reagents and conditions* (*ca.* 1 h at *ca.* 20 °C, except for vii): i, LiBu^n, thf; ii, LiBu^n, tmeda, thf; iii, LiBu^n, pmdeta, thf; iv, Na–Hg, thf; v, Na–Hg, tmeda, thf; vi, LiCl, thf; vii, 245 °C, 10^{-2} Torr, *ca.* 3 h; viii, LiBr, thf; ix, [PPh_4]Cl, PhMe; x, [PPh_4]Br, PhMe. *Identification procedures*: green crystals of compounds **(1)**—**(8)** were obtained from n-C_6H_{14} at *ca.* −30 °C, and were characterised by microanalysis, ^1H (and ^7Li, where appropriate) n.m.r. spectroscopy, (Table 1) and, in the case of **(1)** (ref. 11) **(5)** (Figure 1), and **(7)** (Figure 2) by *X*-ray diffraction.

Table 2. Selected bond lengths (Å) to U and angles (°) subtended at U for related uranocene(III or IV) chlorides.

	U–Cl	U–Cen	Cen–U–Cen	<Cen–U–Cl>	Cl–U–Cl	Ref.
(1) [UCp''$_2$(μ-Cl)$_2$-Li(thf)$_2$][a]	2.729(6), 2.730(7)	2.48, 2.50	124.1	110.6	82.6(2)	11
(5) [UCp''$_2$(μ-Cl)$_2$-Li(pmdeta)][b]	2.69(2), 2.72(1)	2.51, 2.58	123.9	110.5	84.6(5)	This work
(7) [PPh_4][UCp''$_2$Cl$_2$]	2.667(8), 2.666(8)	2.52, 2.54	125.8	107.7	96.1(3)	This work
(10) [{UCp''$_2$-(μ-Cl)}$_2$]	2.818(4), 2.802(4)	2.496, 2.494	130.8	107.2	78.5(1)	2
(9) [UCp''$_2$Cl$_2$]	2.579(2)	2.435	124.8	105.4	95.3	12

[a] Li–Cl, 2.446(6) and 2.48(6) Å; U–Cl–Li 92(1) and 91(1)°; Cl–Li–Cl 94(2)°.[11] [b] Li–N, 2.22(6), 2.35(6), and (axial) 2.41(6) Å; Li–Cl, 2.52(4) and 2.51(4) Å; U–Cl–Li 92(1) and 91(1)°; Cl–Li–Cl, 93(1)°.

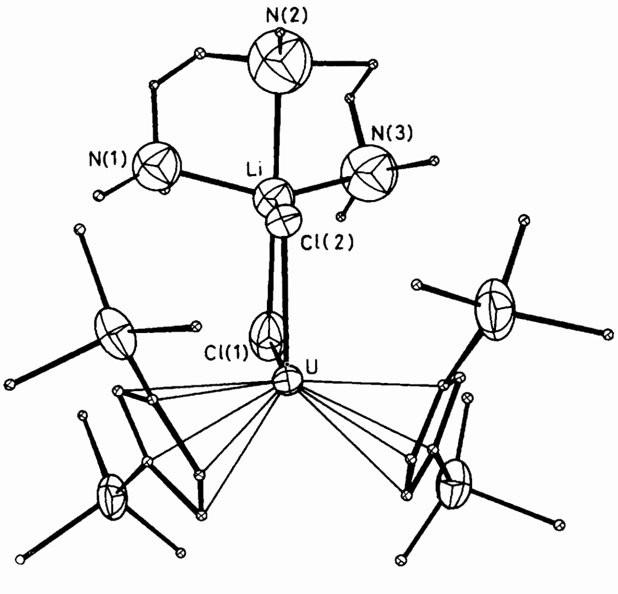


Figure 1. Structure of (**5**), $[\mathrm{UCp''_2(\mu\text{-}Cl)_2Li(pmdeta)}]$.

displayed narrow linewidths. In their ^{1}H n.m.r. spectra the bromo-chloro compounds (**6**) and (**8**) had two trimethylsilyl [incompletely resolved for (**8**)] and three cyclopentadienyl ring proton signals due to the prochirality of the uranium atom (Table 1). On the other hand, the ^{1}H n.m.r. spectra of $[\mathrm{UCp''_2(\mu\text{-}Cl)_2Na(thf)_2}]$ (**2**) and $[\mathrm{UCp''_2(\mu\text{-}Cl)_2Na(tmeda)}]$ (**4**) were extremely broad at 303 K (or up to 353 K).

The *X*-ray structures of $[\mathrm{UCp''_2(\mu\text{-}Cl)_2Li(pmdeta)}]$ (**5**) (Figure 1)‡ and $[\mathrm{UCp''_2Cl_2}]^-$ [the anion of (**7**)] (Figure 2)‡ are compared with those of three other bis(η-cyclopentadienyl)-uranium(III or IV) complexes having the same ligands (2 $\bar{\mathrm{C}}\mathrm{p}''$s and 2 $\bar{\mathrm{C}}\mathrm{l}$s) around U, Table 2. The heterobimetallic complex (**5**) is unusual in having a trigonal bipyramidal (tbp) environment around the Li atom, with one $\bar{\mathrm{C}}\mathrm{l}$ ligand axial and the other equatorial. Five-co-ordination in lithium chemistry has few precedents;[4] lithium glycollate monohydrate has five oxygen atoms in a tbp arrangement around Li,[5] whereas $(\mathrm{Li(NR_2)(12\text{-}crown\text{-}4)}]$ ($\mathrm{R{=}SiMe_3}$) has an apical nitrogen and four oxygen atoms completing the square pyramidal geometry about Li.[6]

Complex (**5**) has no analogue in 4f element chemistry, but heterobimetallic complexes, such as the f^3 $[\mathrm{NdCp''_2(\mu\text{-}Cl)_2Li(thf)_2}]$,[7] are known, as are the analogous dichloro-lanthanates(III), *e.g.*, $[\mathrm{AsPh_4}][\mathrm{NdCp''_2Cl_2}]$.[8]

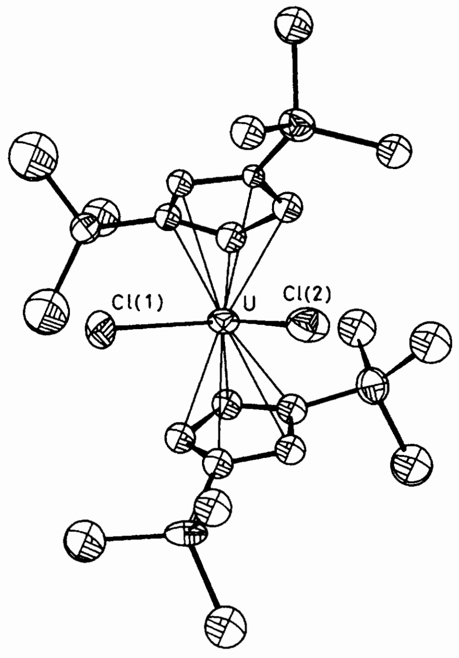


Figure 2. Structure of the anion of (**7**), $[\mathrm{UCp''_2Cl_2}]^-$.

Complexes (**1**)—(**8**) are likely to prove to be progenitors of three new classes of 5f-block metal complexes: $[\mathrm{M'Cp_2(\mu\text{-}Y)(\mu\text{-}Y')ML_2}]$, $[\mathrm{M'Cp_2(\mu\text{-}Y)(\mu\text{-}Y')ML_3}]$, or $[\mathrm{M'Cp_2(Y)Y'}]^-$, in which M represent an alkali metal, M′ a 5f metal, $\bar{\mathrm{C}}\mathrm{p}$ an η^5-cyclopentadienyl-type ligand, $\bar{\mathrm{Y}}$ and $\bar{\mathrm{Y}}'$ monodentate ligands, and L a neutral monodentate ligand (or $\mathrm{L_2}$ or $\mathrm{L_3}$ the bi- or tri-dentate equivalents); such chemistry is already well developed for 4f metals.[9]

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‡ *Crystal data*: compound (**5**), $[\mathrm{UCp''_2(\mu\text{-}Cl)_2Li(pmdeta)}]$, $\mathrm{C_{31}H_{65}Cl_2LiN_3Si_4U}$, $M = 908.10$, orthorhombic, space group $P2_12_12_1$, $a = 12.447(9)$, $b = 13.463(6)$, $c = 26.980(8)$ Å, $U = 4521.1$ Å^3, $Z = 4$, $D_c = 1.33$ g cm^{-3}. Compound (**7**), $[\mathrm{PPh_4}][\mathrm{UCp''_2Cl_2}]$, $\mathrm{C_{46}H_{62}Cl_2PSi_4U}$, $M = 1067.26$, triclinic, space group $P\bar{1}$, $a = 12.470(6)$, $b = 15.212(5)$, $c = 17.498(6)$ Å, $\alpha = 76.94(3)$, $\beta = 67.96(5)$, $\gamma = 72.93(5)°$, $U = 2915.7$ Å^3, $Z = 2$, $D_c = 1.22$ g cm^{-3}. Single crystals of each compound were mounted in Lindemann glass capillaries under argon. The structures of (**5**) and (**7**) were solved using routine heavy atom methods and refined to $R = 0.064$, $R' = 0.073$ for 1519 observed reflections for (**5**), and $R = 0.067$, $R' = 0.083$ for 2738 observed reflections for (**7**), measured on a CAD-4 diffractometer with Mo-K_α radiation. The lithium atom in (**5**) was not directly located and was geometrically generated with respect to the chlorine and nitrogen atoms. Details of the data collection process have been given previously.[10] 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.