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Some Aspects of the Coordination and Organometallic Chemistry of Thorium and Uranium ($\mathrm{M^{III}}$, $\mathrm{M^{IV}}$, $\mathrm{U^{V}}$) in +3 and +4 Oxidation States*

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Abstract

We report on the synthesis of novel hydrocarbon-soluble crystalline complexes of thorium and uranium (M), using bulky ligands {such as η-$\bar{\mathrm{C}}_5\mathrm{H_3(SiMe_3)_2}$-1,3 ($\bar{\mathrm{C}}\mathrm{p}''$), $\bar{\mathrm{O}}\mathrm{C_6H_2R_2}$-2,6-R′-4 ($\bar{\mathrm{O}}\mathrm{Ar}^{\mathrm{R'}}_{\mathrm{R}}$), $\bar{\mathrm{N}}\mathrm{(SiMe_3)_2}$ ($\bar{\mathrm{N}}''$), $\overset{2-}{\mathrm{N}}\mathrm{(SiMe_3)}$ ($\overset{2-}{\mathrm{N}}{}'$), or $\bar{\mathrm{S}}\mathrm{C_6H_2Bu^t_3}$-2,4,6 ($\bar{\mathrm{S}}\mathrm{Ar}$)}, to provide the required lipophilicity.

The new compounds have been fully characterized and features of structural interest concern results derived from single crystal X-ray diffraction and/or variable temperature NMR spectroscopy.

Complexes discussed include the following (a)–(d):

(a) $\mathrm{M^{IV}}$ cyclopentadienyls: $[\mathrm{MCp''X_2}]$ (X = Cl, Br, I, $\mathrm{BH_4}$, $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2Ph}$, or $\mathrm{OAr^{H}_{Me}}$), $[\{\mathrm{MCp''_2}(\mu\text{-O})\}_2]$, $[\mathrm{MCp''_2(Cl)X}]$ (X = $\mathrm{NMe_2}$, N″, $\mathrm{OAr^{H}_{Pr^i}}$, $\mathrm{OAr^{H}_{Ph}}$, or SAr), $[\{\mathrm{UCp''_2}(\mu\text{-F})(\mu\text{-BF_4})\}_2]$ and $[\mathrm{ThCp''_3Cl}]$;

(b) Other $\mathrm{M^{IV}}$ derivatives: $[\mathrm{MCl(OAr^{H}_{Bu^t})_3}]$, $[\{\mathrm{UX_2(OAr^{H}_{Bu^t})_2}\}_n]$ (X = Cl or $\mathrm{NEt_2}$], $[\mathrm{U(NEt_2)X_3}]$ (X = $\mathrm{OAr^{H}_{Bu^t}}$ or $\mathrm{OAr^{H}_{Pr^i}}$) and $[\mathrm{Li(thf)_4}][\mathrm{M(OAr^{H}_{Pr^i})_5}]$;

(c) $\mathrm{M^{III}}$ derivatives: $[\{\mathrm{UCp''_2}(\mu\text{-X})\}_2]$ (X = Cl or Br), $[\{\mathrm{UCp''_2X}\}_n]$ (X = F, I, $\mathrm{OAr^{H}_{Ph}}$, or $\mathrm{BH_4}$), $[\mathrm{UCp''_2(X)L}]$ (X, L = Cl or $\mathrm{BH_4}$ or $\mathrm{OAr^{H}_{Pr^i}}$, thf; Cl, tmeda; Cl, pmdeta; or $\mathrm{BH_4}$, thf) and $[\mathrm{UCp''_2X_2}]^-$ ($\mathrm{X_2 = Cl_2}$ or ClBr); $[\mathrm{UCp''_2}(\mu\text{-X})_2\mathrm{Li(LL)}]$ (X, $\mathrm{L_2}$ = Cl or Br, $\mathrm{(thf)_2}$; Cl, tmeda or pmdeta), $[\mathrm{UCp''_2}(\mu\text{-Cl})_2\mathrm{Na(tmeda)}]$, and $[\mathrm{ThCp''_3}]$;

(d) The $\mathrm{U^V}$ complex: $[\mathrm{UCp''_2(Cl)(N')}]$.

Introduction

We have for some time been interested in preparing novel hydrocarbon-soluble crystalline complexes of thorium and uranium (M). To this end our strategy has been to use bulky ligands such as η-$\bar{\mathrm{C}}_5\mathrm{H_3(SiMe_3)_2}$-1,3 (referred to as $\bar{\mathrm{C}}\mathrm{p}''$), $\bar{\mathrm{O}}\mathrm{C_6H_2R_2}$-2,6-R′-4 ($\bar{\mathrm{O}}\mathrm{Ar}^{\mathrm{R'}}_{\mathrm{R}}$), $\bar{\mathrm{N}}\mathrm{(SiMe_3)_2}$ ($\bar{\mathrm{N}}''$), or $\bar{\mathrm{S}}\mathrm{C_6H_2Bu^t_3}$-2,4,6 ($\bar{\mathrm{S}}\mathrm{Ar}$). As a consequence, the derived complexes have been either monomers or dimers, and many of them have also proved to be volatile.

Our publications in this area have dealt with (i) hydrocarbon-soluble, crystalline, four-coordinate chloro(aryloxide)s, dialkylamido(aryloxide)s, and di[bis(trimethylsilyl)cyclopentadienyl]s of $\mathrm{Th^{IV}}$ and $\mathrm{U^{IV}}$ [including the X-ray crystal structure of diethylamidotris(2,6-di-t-butylphenoxo)uranium(IV) [1]]; (ii) synthesis, chemical behaviour and structure (crystal and solution) of a fluorouranocene(IV) tetrafluoroborate, including the X-ray crystal structure of $[\{\mathrm{UCp''_2}(\mu\text{-BF_4})(\mu\text{-F})\}_2]$ [2]; (iii) the synthesis and characterization (including the X-ray structure) of $[\mathrm{Th(Cp'')_3}]$ [3]; and (iv) a complete series of uranocene(III) halides $[\{\mathrm{UCp''_2X}\}_2]$ [X = F, Cl, Br, or I], including the X-ray structure of the chloride and bromide (n = 2 for X = μ-Cl or μ-Br) [4].

Our work on the $\bar{\mathrm{C}}\mathrm{p}''$ ligand may be seen as complementary to the work of others using the ligand η-$\bar{\mathrm{C}}_5\mathrm{Me_5}$ ($\bar{\mathrm{C}}\mathrm{p}^*$) [5]. It has become evident that the $\bar{\mathrm{C}}\mathrm{p}''$ ligand is more sterically demanding than the $\bar{\mathrm{C}}\mathrm{p}^*$ counterpart. For example, in the series of uranocene(III) chlorides, the $\bar{\mathrm{C}}\mathrm{p}''$ complex is a dimer $[\{\mathrm{UCp''_2}(\mu\text{-Cl})\}_2]$ [4], whereas the $\bar{\mathrm{C}}\mathrm{p}^*$ analogue is a trimer $[\{\mathrm{UCp^*_2}(\mu\text{-Cl})\}_3]$ [6]. A further example to illustrate the same problem relates to the structures of the thallium(I) complexes: $[\mathrm{Tl}(\mu\text{-}\eta\text{:}\eta'\text{-Cp''})]_6$ [7] and $[\mathrm{Tl}(\mu\text{-}\eta,\eta'\text{-Cp^*})]_\infty$ [8].

Results

Metallocene(IV) Derivatives

X-ray structural data have been obtained for three of the uranocene(IV) halides and the isoelec-

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tronic tetrahydridoborate $[UCp''_2X_2]$ (X = Cl, Br, I, or BH_4). Similar results are also available on two of the corresponding thorium compounds $[ThCp''_2X'_2]$ (X′ = Cl or BH_4). Such structures are exemplified in Figs. 1 and 2. The compounds were made from MCl_4 and $2LiCp''$ for the chloride [1]; $[UCp''_2Cl_2]$ was converted into the corresponding heavier halide by treatment with BX_3 (X = Br or I). The BH_4^- complexes were made from $[UCp''_2Cl_2]$ and $Na[BH_4]$.

A number of further derivatives were made from $[UCp''_2Cl_2]$: $[MCp''X_2]$ (X = CH_2SiMe_3, CH_2Ph, or OAr^{H}_{Me}), $[\{MCp''_2(\mu\text{-}O)\}_2]$, $[MCp''_2(Cl)X]$ (X =

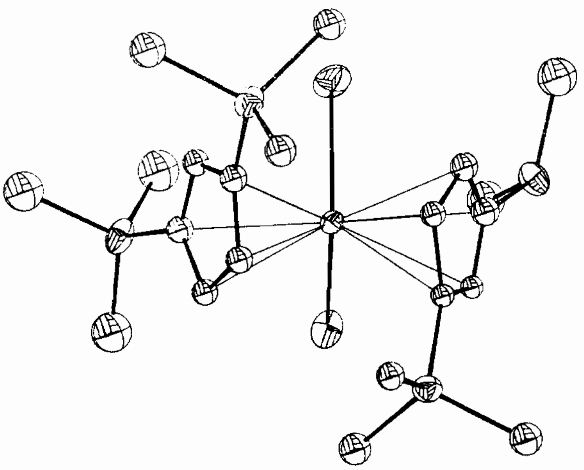


Fig. 1. X-ray structure of $[UCp''_2I_2]$. Bond distance (Å): U–I, 2.953(2); U–Cp, 2.71(1). Bond angle (°): I(1)–U–I(2), 105.40(8).

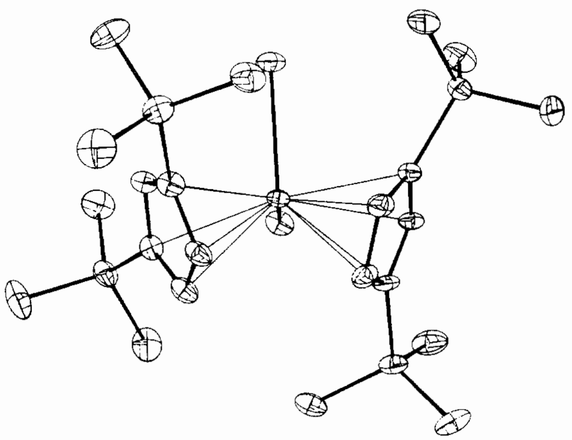


Fig. 2. X-ray structure of $[UCp''_2Br_2]$. Bond distance (Å): U–Br, 2.734(1); U–Cp, 2.71(1). Bond angle (°): Br–U–Br′, 94.60(4).

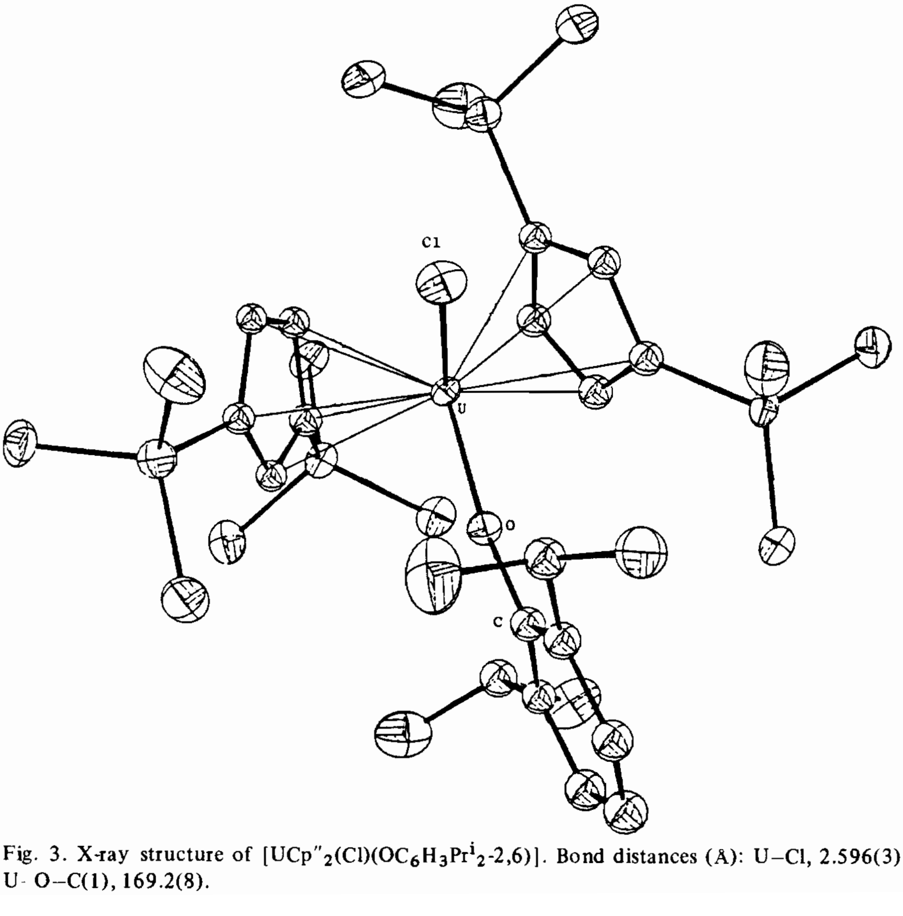


Fig. 3. X-ray structure of $[UCp''_2(Cl)(OC_6H_3Pr^i_2\text{-}2,6)]$. Bond distances (Å): U–Cl, 2.596(3); U–O, 2.061(8). Bond angle (°): U–O–C(1), 169.2(8).

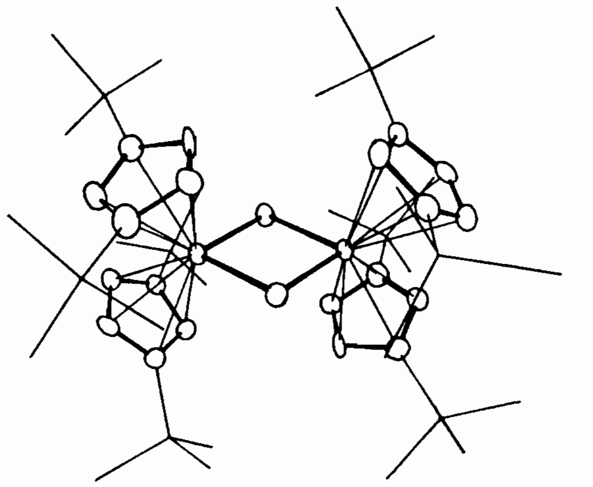


Fig. 4. X-ray structure of $[\{\mathrm{UCp''_2(\mu\text{-}O)}\}_2]$. Bond distances (Å): U–O$_{\mathrm{av}}$, 2.123(8); U–C(Cp″)$_{\mathrm{av}}$, 2.77(4); U–Cent$_{\mathrm{av}}$, 2.496. Bond angles (°): O–U–O′, 74.7; O′–U–Cent(1), 114.1; O′–U–Cent(2), 109.5; O–U–Cent(2), 109.4.

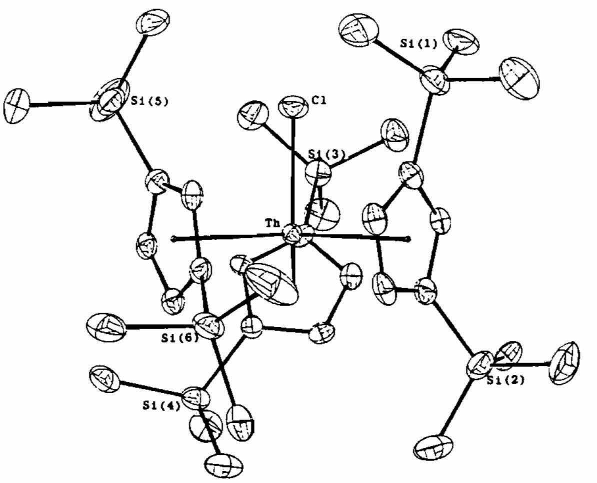


Fig. 5. X-ray structure of $[\mathrm{ThCp''_3Cl}]$ (see Table II).

NMe$_2$, N″, $\mathrm{OAr^{H}_{Pr^i}}$, $\mathrm{OAr^{H}_{Ph}}$, or SAr), or $[\{\mathrm{UCp''_2(\mu\text{-}F)(\mu\text{-}BF_4)}\}_2]$ [2]. These were obtained by appropriate metathetical reaction, e.g., using $\mathrm{2Li(OAr^{H}_{Me})}$ for the bis(mesityloxo) complex.

Among the features of interest are the following.

(i) The X-ray structures of several of the complexes have been determined, as exemplified by $[\mathrm{UCp''_2Cl(OAr^{H}_{Pr^i})}]$ in Fig. 3.

(ii) A number of compounds have shown interesting variable temperature NMR behaviour. For example, in the complex [UCp″$_2$(Cl)SAr] there is evidence for restricted rotation about both the U⤺Cp″ and the S⤺Ar bonds.

(iii) A bis-μ-oxo complex has been X-ray authenticated (Fig. 4) and shows an exceptionally short U• • •U distance.

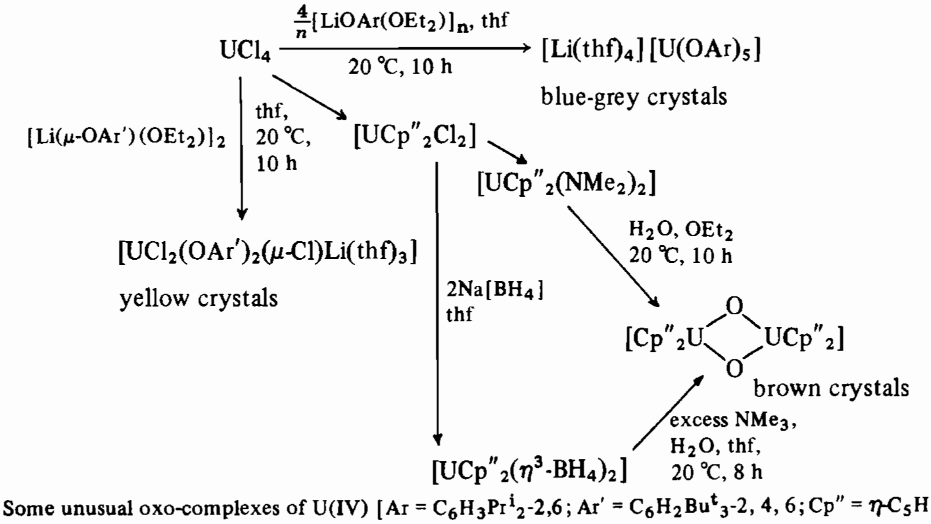
(iv) The compound [ThCp″$_3$Cl] appears to be the first X-ray authenticated tris(cyclopentadienyl)thorium(IV) complex (see Fig. 5).

Some Aryloxo Complexes Free From Cyclopentadienyl Ligands in Metal Oxidation State +4

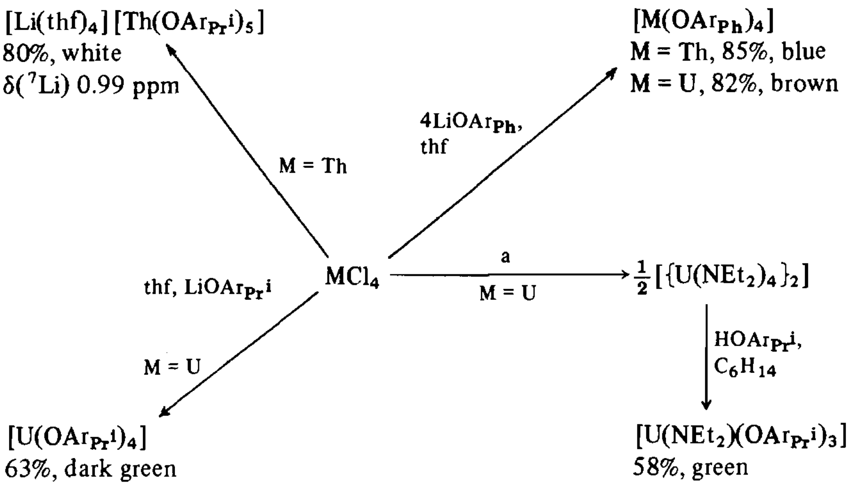
Representative results are summarized in Schemes 1 and 2. The features of interest include either the formation of low coordination number (C.N.) metal complexes (in the limit C.N. = 4), the isolation of 5-coordinate-metal species, and the identification of complexes having a single μ-Cl$^-$ between uranium and lithium. X-ray data are available, as indicated in Schemes 1 and 2, for some of the compounds; selected structural results are summarized in Figs. 6 and 7.

Organometallic Complexes of Uranium and Thorium in Oxidation State +3 [and a Note on a U(V) Complex]

The syntheses of the four uranocene(III) halides are summarized in Scheme 3. At this time, X-ray results are only available for two of the compounds,



Scheme 1. Some unusual oxo-complexes of U(IV) [Ar = $\mathrm{C_6H_3Pr^i_2}$-2,6; Ar′ = $\mathrm{C_6H_2Bu^t_3}$-2, 4, 6; Cp″ = η-$\mathrm{C_5H_3(SiMe_3)_2}$].



Scheme 2. Some low C.N. aryloxides of Th(IV) and U(IV) $[\mathrm{OAr_X} = \mathrm{OC_6H_3X_2}\text{-}2,6]$. [a]Taken from ref. 10.

the chloride and the bromide, as illustrated in Fig. 8. Most of these data have been briefly published [4].

Various other uranocene(III) chlorides have been made in which the uranium is invariably 4-coordinate, taking each cyclopentadienyl ligand as occupying only a single coordination site. A diagram indicating their interconversion is shown in Scheme 4. Several alternative routes to uranocene(III) compounds are

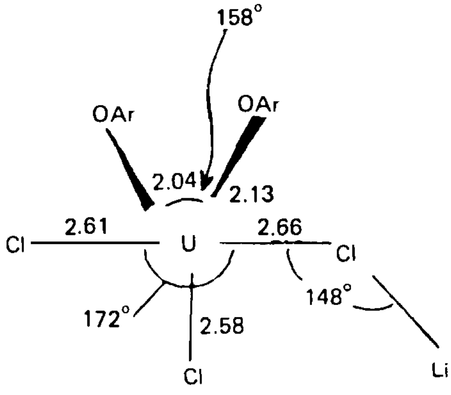


Fig. 6. X-ray structure of $[\mathrm{U(OAr^{Bu^t}_{Bu^t})_2Cl_2(\mu\text{-}Cl)Li(thf)_3}]$.

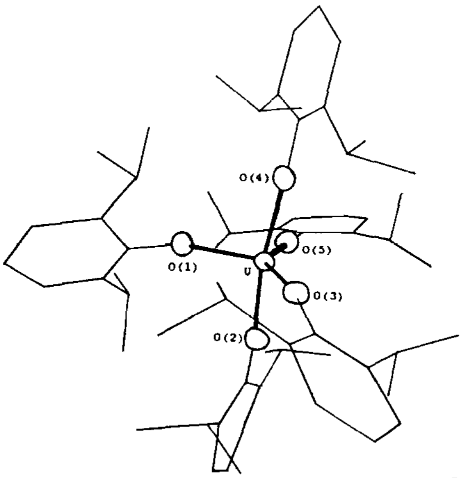
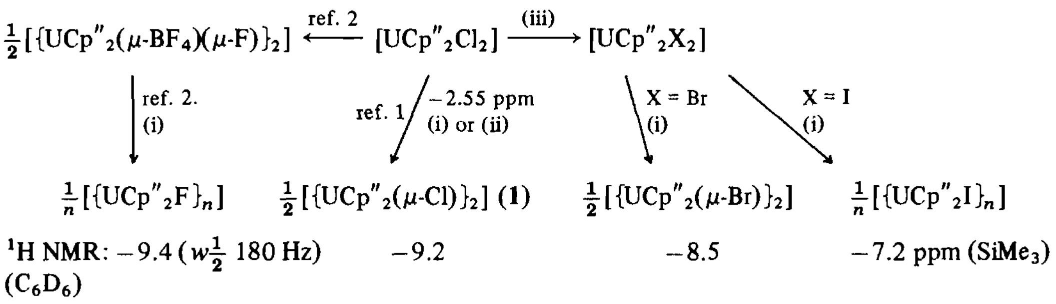


Fig. 7. X-ray structure of $[\mathrm{Li(thf)_4}][\mathrm{U(OAr^{H}_{Pr^i})_5}]$. Bond distances (Å): U–O(1), 2.15(1); U–O(2), 2.17(2); U–O(3), 2.19(2); U–O(4), 2.17(2); U–O(5), 2.16(2); Li–O(thf)$_{\mathrm{av}}$, 1.94(8). Bond angles (°): O(1)–U–O(3), 107.2(7); O(1)–U–O(4), 94.6(6); O(3)–U–O(4), 88.9(6); O(2)–U–O(5), 88.0(6); O(4)–U–O(5), 88.3(6); O(1)–U–O(2), 94.8(6); O(2)–U–O(3), 88.4(6); O(2)–U–O(4), 170.6(6); O(1)–U–O(5), 113.0(6); O(3)–U–O(5), 139.8(6), O–Li–O'$_{\mathrm{av}}$, ~109.



Scheme 3. Synthesis of uranocene(III) halides, $\mathrm{UCp''_2X}$ [4]. (i) Na–Hg, PhMe, 20 °C, 12 h; (ii) $\mathrm{LiBu^n}$, $\mathrm{C_6H_{14}}$, 20 °C, 12 h; (iii) $\mathrm{BX_3}$.

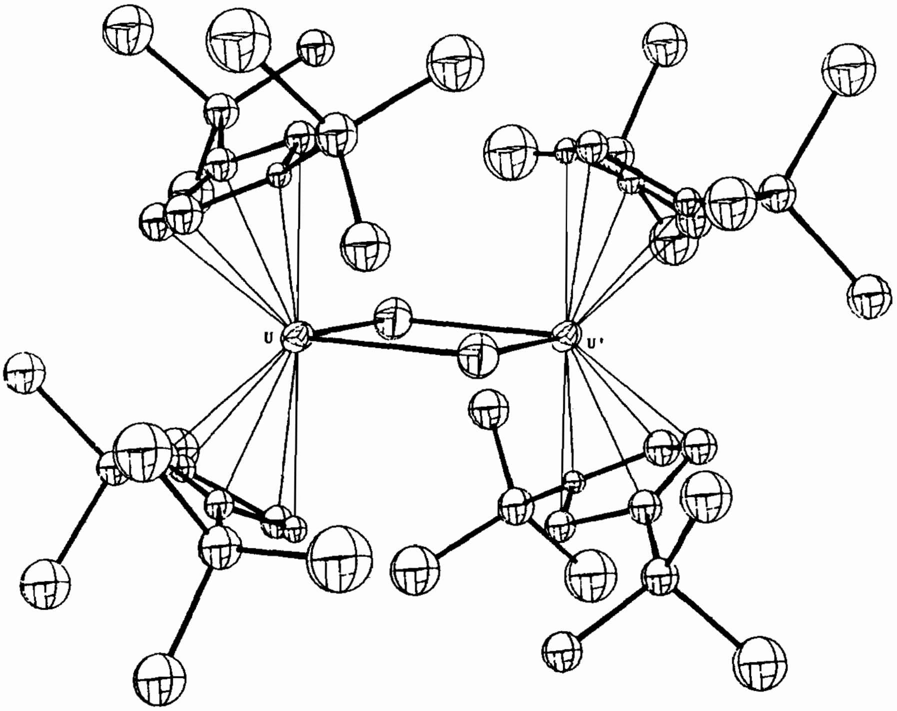
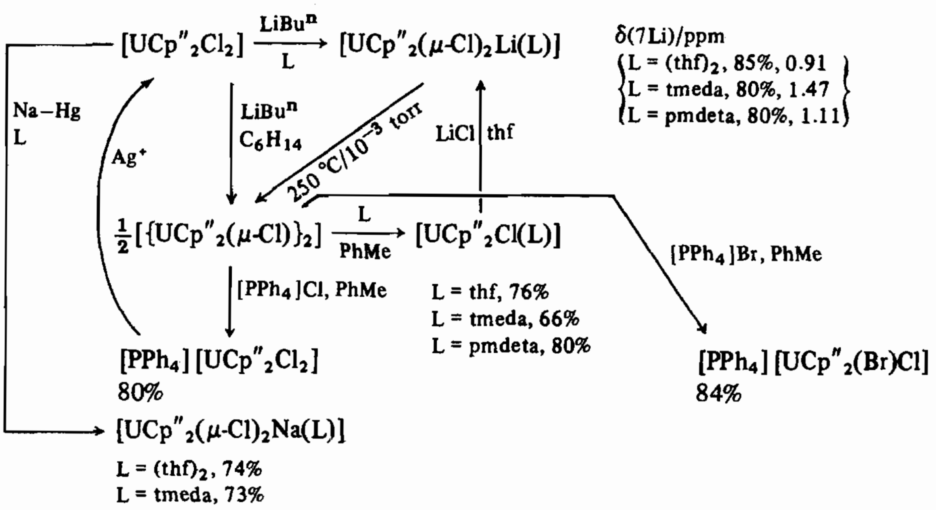
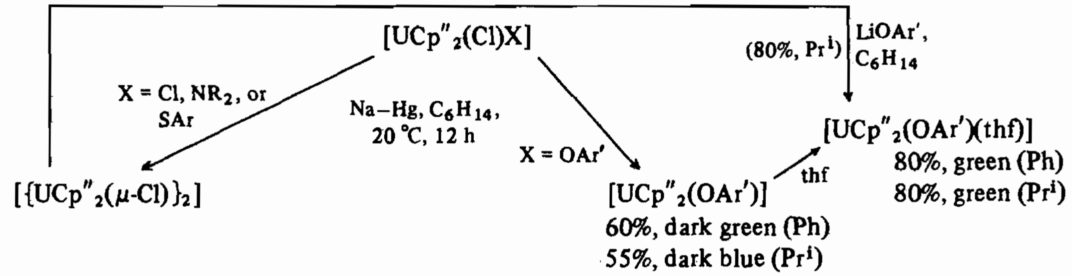


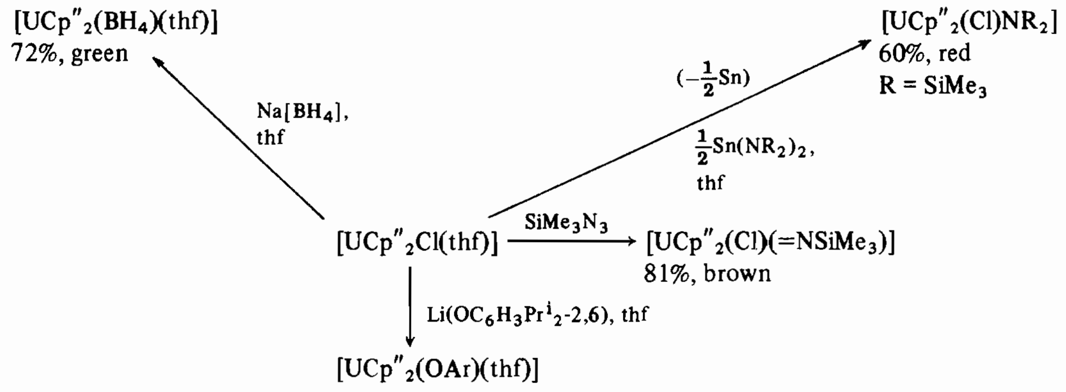
Fig. 8. X-ray structures of $[\{UCp''_2(\mu\text{-}X)\}_2]$ (X = Cl or Br) [4] (see Table I for X = Cl).



Scheme 4. Interconversion of uranocene(III) chlorides.



Scheme 5. Further reduction reactions of uranocene(IV) chlorides (R = $SiMe_3$; Ar = $C_6H_2Bu^t{}_3$-2,4,6; Ar' = $C_6H_3R_2$-2,6).



Scheme 6. Ligand substitution and oxidative addition reactions of $[UCp''_2Cl(thf)]$; for $[\{UCp^*_2(\mu\text{-}Cl)\}_3]$ as a volatile precursor to U(III)/U(IV) complexes, see ref. 6.

indicated in Schemes 5 and 6, which also show examples of oxidations to complexes in which the metal oxidation state is either +4 or +5. $[UCp''_2(Cl)(=NSiMe_3)]$ {for $[UCp^*_3N']$, see ref. 9}. A number of these compounds have been X-ray characterized (see Figs. 9–11).

Chemistry Derived From a Homoleptic π-Complex of Thorium(III)

We have already published a preliminary communication on the synthesis of $[Th(\eta\text{-}Cp'')_3]$ [3]. Some further data, both on this compound and on other derivatives, as well as $[Th(\eta\text{-}C_8H_8)_2]$, are shown in Scheme 7. A diagram showing the X-ray structure of $[Th(\eta\text{-}Cp'')_3]$ is shown in Fig. 12 [3].

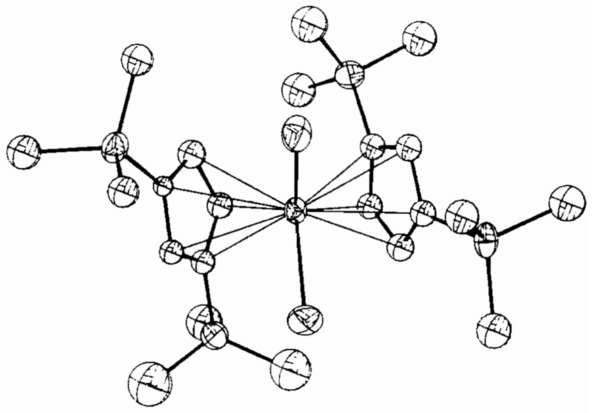


Fig. 10. X-ray structure of the anion $[UCp''_2Cl_2]^-$.

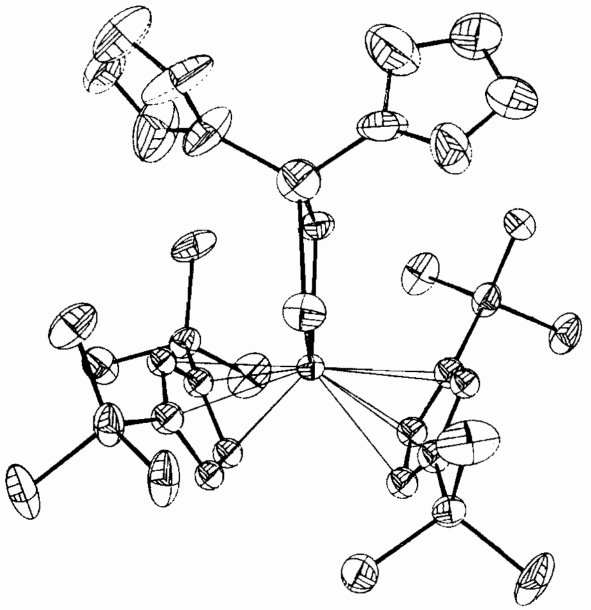


Fig. 9. X-ray structure of $[UCp''_2(\mu\text{-}Cl)_2Li(thf)_2]$. Bond distances (Å): U–Cl, 2.729(6); U–Co, 2.78(2); Cl–Li, 2.46(6). Bond angles (°): Cl(1)–Li–Cl(2), 82.83(2); U–Cl(2)–Li, 91(1); U–Cl(1)–Li, 92(1); Cl(1)–Li–Cl(2), 94(2).

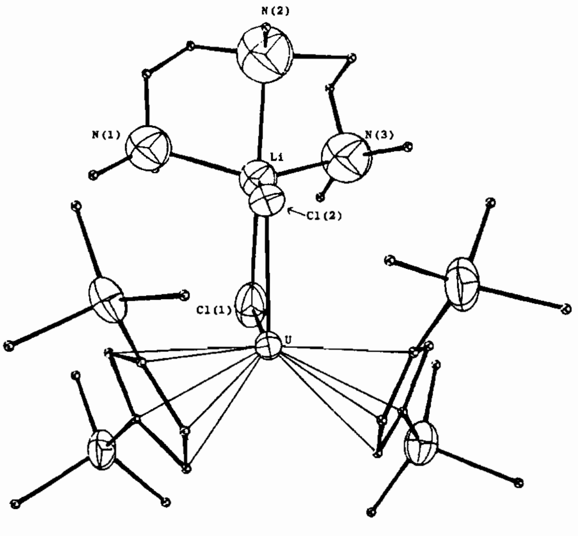
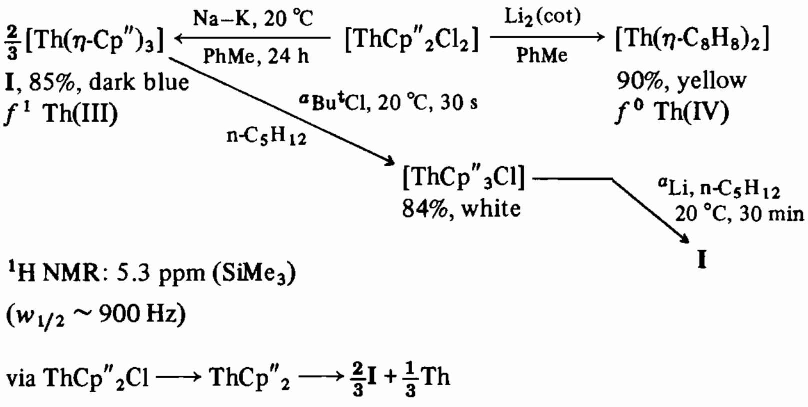


Fig. 11. X-ray structure of $[UCp''_2(\mu\text{-}Cl)_2Li(pmdeta)]$. Bond distances (Å): U–Cl(1), 2.69(2); U–Cl(2), 2.72(1); Li–Cl(1), 2.52(4); U–Cen(1), 2.58; U–Cen(2), 2.51; Li–Cl(2), 2.51(4). Bond angles (°): U–Cl(1)–Li, 92(1); U–Cl(2)–Li, 91(1).



Scheme 7. Homoleptic π-complexes of thorium.

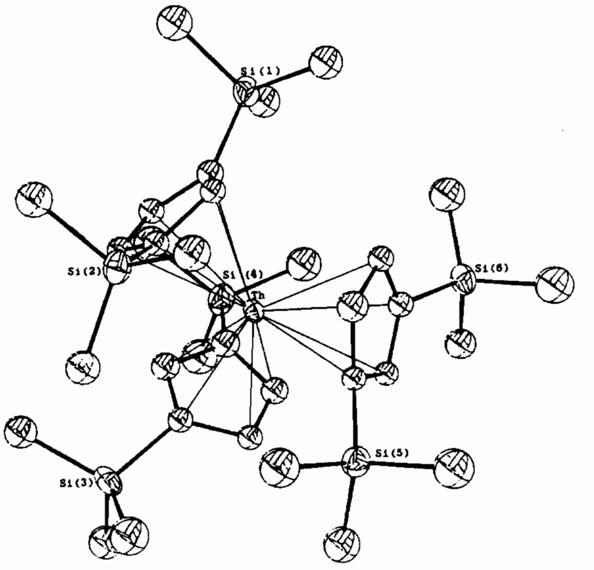


Fig. 12. X-ray structure of [Th(η-Cp″)$_3$] [3]. Bond distances (Å): Th–Cp, 2.80(2); Th–Cent, 2.51. Bond angle (°): Cent–Th–Cent, 120.

Some Comparative X-ray Data for Uranocene and Thoracene Derivatives

From the above discussion, it will be clear that X-ray data are now available for various uranocene chlorides and for a series of cyclopentadienylthorium derivatives. Some U–Cl bond distances are summarized in Table I, and selected parameters for three cyclopentadienylthorium compounds are in Table II.

TABLE I. U–Cl Bond Lengths for some Uranocene Chlorides

Oxidation state	Complex	Bond length (Å)
+4	[UCp″$_2$Cl$_2$]	2.579(2)
	[UCp″$_2$Cl(OC$_6$H$_3$Pr$^i_2$-2,6)]	2.596(3)
+3	[UCp″$_2$Cl$_2$]$^-$	2.667(8)
	[{UCp″$_2$(μ-Cl)}$_2$]	2.801(4)^a
	[UCp″$_2$(μ-Cl)$_2$Li(thf)$_2$]^b	2.729(6)
	[UCp″$_2$(μ-Cl)$_2$Li(pmdeta)]^b	2.70(4)

[a] From ref. 4. [b] Abbreviations: thf = tetrahydrofuran, pmdeta = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine.

Acknowledgements

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TABLE II. Selected Structural Parameters for some Bis(1,3-trimethylsilyl)cyclopentadienylthorium Complexes

Bond length (Å) or angle (°)	Complex		
	[ThCp″$_2$Cl$_2$]	[ThCp″$_3$]	[ThCp″$_3$Cl]
Th–Cl	2.632(2)		2.651(2)
Th–C(av)	2.78(1)	2.81(2)	2.83(1)
Th–Cent	2.506	2.509–2.519	2.562–2.568
Cent–Th–Cent′	124.36	118.86–121.11	116.65–117.65
Cent–Th–Cl	106.01, 110.44		99.54–100.84

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