Some Oxygen-donor Complexes of Cyclopentadienyluranium(IV) Halides

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The oxygen-donor complexes $[U(cp)X_3L_2]$ [cp = η-C_5H_5, X = Cl or Br, L = $Me_3CCONMe_2$ (dmpva) or PPh_3O], $[U(cp)Cl_3L_2]$ [L = $MeCONMe_2$ (dma)], and $[\{U(cp)X_3L\}_2]$ [X = Cl or Br, L = $Ph_2(O)PCH_2CH_2P(O)Ph_2$ (dppoe)] have been prepared. Products of composition '$U(cp)_2Cl_2{\cdot}dma$,' '$U(cp)_2X_2{\cdot}dmpva$,' and '$U(cp)_2X_2(PPh_3O)_2$' (X = Cl or Br) obtained from $[U(cp)X_3L_2]$ have been shown to be disproportionation mixtures which include $[U(cp)_3X]$ and free ligand, whereas $[\{U(cp)_2X_2(dppoe)\}_2]$ (X = Cl or Br) do not appear to disproportionate to an appreciable extent. The lability of the cp ligand has been utilised to prepare $[U(cp)Cl_3(PPh_3O)_2]$ from $[U(cp)_3Cl]$ and $[UCl_4(PPh_3O)_2]$ in the presence of PPh_3O. The complexes $[U(mcp)Cl_3(thf)_2]$, $[U(cp)(mcp)_2Cl]$, and $[U(cp)Br_3(thf)_2]$ have also been prepared (mcp = η-methylcyclopentadienyl, thf = tetrahydrofuran). Infrared and u.v.–visible (solution and reflectance) spectra are reported.

COMPLEXES of composition $U(cp)_2Cl_2$ [1] and $U(cp)Cl_3{\cdot}xL$ [$x = 1$, L = dimethoxyethane (dme); [2] $x = 2$, L = tetrahydrofuran (thf)[3]; cp = η-cyclopentadienyl] have been reported; the first has been shown [4] to be more correctly formulated as $[\{U(cp)_3Cl\}_2(UCl_4)(dme)_2]$ when prepared from dme solution, and evidence for the existence of analogous species in thf solution was also obtained. Very little is known about the behaviour of the solvated $U(cp)Cl_3$ species, although in one instance [3] it appears to behave chemically as its formulation would suggest. It was therefore of interest to prepare oxygen-donor complexes of $U(cp)Cl_3$ and $U(cp)Br_3$ as starting materials for the attempted preparation of complexes of $U(cp)_2X_2$ in the expectation that with strongly bound

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and/or bulky ligands the disproportionation to $U(cp)_3X$ and other products might be inhibited, as is the case with uranium(IV) complexes derived from[5] C_5H_4–$[CH_2]_n$–C_5H_4.

RESULTS AND DISCUSSION

Complexes of $U(cp)X_3$ ($X = Cl$ *or* Br).—The green phosphine oxide complexes $[U(cp)X_3(PPh_3O)_2]$ and $[\{U(cp)X_3(dppoe)\}_2]$ [dppoe = $Ph_2(O)PCH_2CH_2P(O)Ph_2$] and the amide complex $[U(cp)Br_3(dmpva)_2]$ (dmpva = $Me_3CCONMe_2$) were obtained by adding the ligand to a solution of $[U(cp)X_3(thf)_2]$ in thf; this procedure yielded unidentifiable products with $MeCONMe_2$ (dma) or dimethyl sulphoxide (dmso) ($X = Cl$), but the dma and dmpva complexes ($X = Cl$) were easily obtained by reaction of the corresponding uranium tetrachloride complex with Tl(cp) in thf. This procedure with $[UBr_4(dmpva)_2]$ and $[UBr_4(PPh_3O)_2]$, however, yielded a mixture which included $[U(cp)_3Br]$.

In the i.r. spectra of these complexes (Table 1) the shifts observed for ν(P=O) were of the same order as those observed[6] for $[UCl_4(PPh_3O)_2]$; in the case of the dppoe complexes, this feature is split to a greater extent than is observed for the free ligand. The shifts observed for ν(C=O) in the amide complexes were somewhat larger than those reported[7,8] for the corresponding tetrahalogeno-complexes. The characteristic cp vibration appeared in the ranges 1 012—1 015 and 786—795 cm^{-1}; ν(U–Cl) was assigned to the strong features which appeared in the range 232—240 cm^{-1} in the chloro-complexes and which were absent in the spectra of the corresponding bromides, while the weaker features which appeared at slightly higher frequency (260—268 cm^{-1}, chlorides; 249—266 cm^{-1}, bromides) were assigned to the metal–ring modes (Table 1). In the i.r. spectra of the corresponding UCl_4 complexes ν(U–Cl) appears as a strong feature at 255—267 cm^{-1} [UCl_4L; L = 2dmpva (267), $2PPh_3O$ (265), dppoe (265), and 2.5 dma (255 cm^{-1})] so that the assignments should be regarded as tentative.

TABLE 1

Infrared spectra (cm^{-1}) of the complexes

Complex	ν(X=O) [a]	Δν(X=O) [a]	ν(U–Cl)	ν(U–C_5H_5) [b]
$[UCl_4(dma)_{2.5}]$ [7]	1 618s	29	256vs	
$[U(cp)Cl_3(dma)_2]$	1 615s	30	237vs	264s
' $U(cp)_2Cl_2(dma)$ '	1 600s			
$[UCl_4(dmpva)_2]$	1 584s	46	267vs	
$[U(cp)Cl_3(dmpva)_2]$	1 567s	63	232vs	260m
' $U(cp)_2Cl_2(dmpva)$ '	1 565s	65		
$[UBr_4(dmpva)_2]$	1 584s	46		
$[U(cp)Br_3(dmpva)_2]$	1 570s	60		252w
' $U(cp)_2Br_2(dmpva)$ '	1 565s	65		
$[UCl_4(PPh_3O)_2]$	1 045s	150	265vs	
$[U(cp)Cl_3(PPh_3O)_2]$	1 065s	130	235vs	260vs
' $U(cp)_2Cl_2(PPh_3O)$ '	1 065s	130		
$[UBr_4(PPh_3O)_2]$	1 030s	165		
$[U(cp)Br_3(PPh_3O)_2]$	1 060s	135		255s
' $U(cp)_2Br_2(PPh_3O)$ '	1 050s	145		
$[\{UCl_4(dppoe)\}_2]$ [c]	1 030s, 1 052s	150, 138	265vs	
$[\{U(cp)Cl_3(dppoe)\}_2]$	1 065, 1 090s	115, 100	232s	260m
$[\{U(cp)_2Cl_2(dppoe)\}_2]$	1 060, 1 080s	120, 110		
$[\{U(cp)Br_3(dppoe)\}_2]$	1 060, 1 090s	120, 100		249w
$[\{U(cp)_2Br_2(dppoe)\}_2]$	1 070, 1 105	110, 85		255s
$[U(cp)_3Cl]$			268vs(?)	241s(?)
$[U(cp)_3Br]$				245s
$[U(cp)Cl_3(thf)_2]$			240s	268m
$[U(cp)Br_3(thf)_2]$				266w

[a] X = C (amide) or P (phosphine oxide). [b] Metal–ring mode. [c] ν(P=O) of free ligand at 1 190 and 1 180 cm^{-1}.

The i.r. spectrum of $[U(mcp)Cl_3(thf)_2]$ (mcp = methylcyclopentadienyl) was similar to that of $[U(cp)Cl_3(thf)_2]$; the U–Cl and U-ring vibrations appeared together as a broad feature centred at *ca.* 263 cm^{-1}, as compared with 240s and 260 (sh) cm^{-1} in the spectrum of $[U(cp)(mcp)_2Cl]$; in both cases, features at 340—345 and 845 cm^{-1}, absent in the spectrum of $[U(cp)Cl_3(thf)_2]$, were assigned to CH_3 modes.

The reflectance spectra of the solid oxygen-donor complexes exhibit strong features in the range 1 000—1 300 nm at 1 104—1 140 ($X = Cl$) and 1 080—1 160 nm (Br) (Table 2) which may indicate a low-symmetry high-co-ordination-number (⩾8) environment for the U^{IV}; these strong features appear also in the solution spectra of these complexes, with an additional feature at 1 178—1 195 ($X = Cl$) or 1 166—1 189 nm (Br) which suggests the presence of a second solution species, in which the uranium atom is certainly in a high-co-ordination-number (⩾8) environment. Such an environment could be achieved by formation of a chloride-bridged dimer, and the molecular weight of $[U(cp)Cl_3(thf)_2]$ in dichloromethane (649) is higher than that expected for a monomer (553); the value also appears to increase with time, indicating an appreciable degree of association; however, the spectra are more useful as a means of checking whether disproportionation to $[U(cp)_3Cl]$ has occurred since this complex exhibits six features in this range (Table 2).

TABLE 2

Principal features (1 000—1 300 nm) of the u.v.–visible spectra of $U(cp)X_3$ complexes and $U(cp)_3X$

	Solution in thf	Solid reflectance
$[U(cp)Cl_3(thf)_2]$	1 153s, 1 188m	1 140s
$[U(cp)Br_3(thf)_2]$	1 144s, 1 166s	1 130s, 1 160s
$[U(cp)Cl_3(PPh_3O)_2]$	1 111s, 1 178m	1 104s
$[U(cp)Br_3(PPh_3O)_2]$	1 096s	1 099s
$[\{U(cp)Cl_3(dppoe)\}_2]$	1 116s, 1 184m	1 116s
$[\{U(cp)Br_3(dppoe)\}_2]$	1 094s	1 080m
$[U(cp)Cl_3(dma)_2]$	1 126s, 1 185m	1 115s
$[U(cp)Cl_3(dmpva)_2]$	1 158s, 1 195m	
$[U(cp)Br_3(dmpva)_2]$	1 154s, 1 189m	1 144m
$[U(cp)_3Cl]$	1 004m, 1 025s, 1 045m, 1 127m, 1 205m, 1 290s	1 036s, 1 139m, 1 199m, 1 295s
$[U(cp)_3Br]$	1 011m, 1 029s, 1 044m, 1 126m, 1 207m, 1 292s	1 021s, 1 112m, 1 182m, 1 276s

Relative intensities: m = medium, s = strong.

Halide-replacement Reactions.—Replacement of chloride by other groups was first attempted. The re-

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action of $[U(cp)Cl_3(thf)_2]$ with sodium alkoxides in thf did not yield $U(cp)(OR)_3$ owing to oxidation to U^V [possibly to $U(OR)_5$]. The reaction of $[U(cp)Cl_3(thf)_2]$ with the stoicheiometric quantities of Tl(mcp) and Tl(cp) yielded, respectively, brown sublimable $[U(cp)(mcp)_2Cl]$ and khaki '$U(cp)Cl_2 \cdot thf$,' the latter behaving as a mixture of disproportionation products, as previously reported.[4] However, it was observed that slow evaporation of the supernatant from this last reaction, or from the reaction of UCl_4 with 2 mol of Tl(cp), first yielded crystals of bright green $[U(cp)Cl_3(thf)_2]$, and then, on further evaporation, brown sublimable $[U(cp)_3Cl]$, when the solvent had previously been rigorously dried. With less carefully dried solvent a green precipitate was obtained in which the atomic ratio U : Cl was 1 : 3.5; this is evidently a hydrolysis product.

The appearance of $[U(cp)Cl_3(thf)_2]$ as one of the disproportionation products suggests that in thf solution there may be an equilibrium of the form (1), even

$$2[U(cp)_3]_2[UCl_6] \overset{thf}{\rightleftharpoons} 3[U(cp)Cl_3(thf)_2] + 3[U(cp)_3Cl] \quad (1)$$

though the presence of $[U(cp)Cl_3(thf)_2]$ could not be detected spectrophotometrically. Conductimetric titration of '$U(cp)_2Cl_2(thf)$' against $PPh_3(CH_2C_6H_4)Cl$ in thf shows a clear end-point after the addition of 0.6 equivalents of chloride, and analysis of the pale green precipitate showed it to be the solvated hexachlorouranate(IV) salt, confirming earlier observations.[4] Evidently, removal of the $[UCl_6]^{2-}$ anion (or UCl_4 if the formulation is $[\{U(cp)_3Cl\}_2] \cdot UCl_4 \cdot solvent$) by precipitation shifts the equilibrium to the left, whereas slow evaporation of the solvent shifts it to the right owing to the relatively low solubility in thf of $[U(cp)Cl_3(thf)_2]$ as compared with that of $[U(cp)_3Cl]$.

Reaction of the oxygen-donor complexes $[U(cp)X_3L_2]$ (X = Cl or Br, L = dmpva or PPh_3O; X = Cl, L = dma; X = Br, L = thf) with the stoicheiometric quantity of Tl(cp) in thf yielded green-brown products of composition '$U(cp)_2X_2 \cdot yL$' (y = 1, L = dma, dmpva, or thf; y = 2, L = PPh_3O), but the electronic spectra of these products as solutions in thf and as solids showed clearly that the main component was $[U(cp)_3X]$ (see Table 1). The presence of the $[UX_6]^{2-}$ anion could not be detected in these spectra, but bands due to this anion would, of course, be of low intensity because of its centre of symmetry. Additional bands at 1 154—1 156s nm and 1 187—1 193m nm appeared in the spectra of these products (X = Cl) in thf solution, but not in dichloromethane solutions; these indicate the presence of a high-co-ordination-number uranium(IV) species and are consistent with either highly solvated uranium UCl_4 or $U(cp)Cl_3$ species. In the i.r. spectra of these products, ν(C=O) and ν(P=O) are closer to the frequencies observed for $[U(cp)X_3L_2]$ (L = dmpva or PPh_3O) than for $[UX_4L_2]$ (X = Cl or Br), whereas ν(C=O) for the dma complex (X = Cl) is consistent with both that for $[UCl_4(dma)_{2.5}]$ and for $[U(cp)Cl_3(dma)_2]$. All attempts to prepare complexes of $[U(cp)_3Cl]$ with any of these ligands were unsuccessful, so that these results could indicate that the disproportionation products are simple mixtures of $[U(cp)_3Cl]$ and $[U(cp)Cl_3L_2]$.

The addition of PPh_3O to a thf or dichloromethane solution of '$U(cp)_2Cl_2(thf)$' or '$U(cp)_2Cl_2(dmpva)$' yielded crystals of the sparingly soluble $[U(cp)Cl_3(PPh_3O)_2]$, and the last complex was also obtained when a mixture of $[U(cp)_3Cl]$, $[UCl_4(PPh_3O)_2]$, and PPh_3O in dry thf or dichloromethane was stirred overnight; the u.v.–visible spectrum of the supernatant indicated the presence of small amounts of both starting material and final product, which suggests an equilibrium of the form (2).

$$[U(cp)_3Cl] + 2[UCl_4(PPh_3O)_2] + 2PPh_3O \rightleftharpoons 3[U(cp)Cl_3(PPh_3O)_2] \quad (2)$$

A similar equilibrium appears to be established in the corresponding dmpva complex system, in which the species present were identified by spectrophotometry, but from which $[U(cp)Cl_3(dmpva)_2]$ was not isolated owing to its high solubility as compared with the analogous PPh_3O complex.

The stability towards disproportionation of the previously reported pyrazol-1-ylborate complex,[3] $[U(cp)Cl_2\{HB(pz)_3\}]$ (pz = $C_3H_3N_2$), is almost certainly the result of the bond-breaking step required in the rearrangement of the complex which contains a multidentate ligand, as compared with the easier cp ring exchange, which could occur by a simple $\pi \longrightarrow \sigma \longrightarrow \pi$ process, so leading to ready disproportionation of '$U(cp)_2Cl_2$' type species. In order to investigate this, $U(cp)X_3$ and $U(cp)_2X_2$ complexes containing dppoe were prepared; the 'bite' of the ligand is somewhat too large for it to chelate to a single uranium atom, therefore one would expect the ligand to bridge two uranium atoms, so preventing the close approach necessary for a cp ring-exchange process to operate in the disproportionation. The complexes formed with this ligand are probably dimeric {$[U(cp)Cl_3(dppoe)]$ in dichloromethane, M 1 078; the dimer requires M 1 679} and are so written. The complexes $[\{U(cp)X_3(dppoe)\}_2]$ exhibit the same electronic spectra in thf as $[U(cp)X_3(PPh_3O)_2]$ discussed earlier (Table 2); the products of composition $[U(cp)_2X_2(dppoe)]_2$, prepared from the former, have too low a solubility in thf for their spectra to be recorded, but their spectra in dichloromethane exhibit bands at 1 151s and 1 127w nm (X = Cl) and at 1 145s and 1 114m nm (X = Br), together with weak features assigned to small amounts of $[U(cp)_3X]$, so that these complexes appear to be genuine. Both of the $[\{U(cp)_2X_2(PPh_3O)\}_2]$ are very much more air and moisture sensitive than any of the $U(cp)X_3$ complexes.

Thermal Stability of the Complexes.—All the complexes $[U(cp)Cl_3L_2]$ became darker and ultimately blackened when heated at 483 K (10^{-2} Torr) for 5 h.* Trace amounts of sublimate, too little for analysis, were observed; this appeared to be mainly PPh_3O in the case

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

of $[U(cp)Cl_3(PPh_3O)_2]$, but in the case of $[U(cp)Cl_3(dma)_2]$ the i.r. spectrum of the sublimate was identical to that of the starting material. The i.r. spectra of the dark residues were also the same as those of the starting materials. The complex $[U(mcp)Cl_3(thf)_2]$ showed similar behaviour. The products of composition '$U(cp)_2X_2L$' (L = thf or dmpva), '$U(cp)_2Cl_2{\cdot}dma$,' and '$U(cp)_2Cl_2(PPh_3O)_2$' all yielded sublimates of $[U(cp)_3Cl]$ when heated at 450—470 K (10^{-2} Torr) for 3 h, and in the last case some free PPh_3O was found in the sublimate; the i.r. spectra of the residues left after this treatment were identical to those of the corresponding $[U(cp)Cl_3L_2]$. The complexes $[\{U(cp)_2X_2(dppoe)\}_2]$ did not yield $[U(cp)_3X]$ under similar conditions. The i.r. spectrum of $[\{U(cp)_2Cl_2(dppoe)\}_2]$ remained unchanged under these conditions, but the corresponding bromide appeared to have decomposed partially.

Table 3

Analytical results (%) [a]

Complex	U	C	H	Halogen	N
$[U(mcp)Cl_3(thf)_2]$	41.0 (42.1)	29.1 (29.7)	4.1 (3.9)	19.1 (18.8)	
$[U(cp)Br_3(thf)_2]$	34.3 (34.6)	22.6 (22.7)	3.1 (3.1)	36.0 (34.9)	
$[U(cp)(mcp)_2Cl]$	47.0 (48.4)	41.7 (41.4)	3.9 (3.9)	8.3 (7.2)	
$[U(cp)Cl_3(dma)_2]$	39.6 (40.8)	26.4 (26.7)	3.9 (3.9)	18.2 (18.3)	4.8 (4.8)
$[U(cp)Cl_3(dmpva)_2]$	35.2 (34.2)	35.2 (35.7)	5.3 (5.3)	15.6 (16.0)	3.9 (4.2)
$[U(cp)Br_3(dmpva)_2]$	29.3 (29.7)	26.4 (28.5)	4.3 (4.4)	29.9 (30.0)	4.2 (3.5)
$[U(cp)Cl_3(PPh_3O)_2]$	24.2 (24.7)	51.7 (51.0)	4.0 (3.6)	10.8 (11.0)	
$[U(cp)Br_3(PPh_3O)_2]$	21.4 (21.7)	44.6 (44.8)	3.5 (3.2)	21.8 (21.8)	
$[\{U(cp)Cl_3(dppoe)\}_2]$	27.9 (28.4)	44.4 (44.4)	3.4 (3.2)	12.1 (12.7)	
$[\{U(cp)Br_3(dppoe)\}_2]$	22.9 (24.5)	39.6 (38.2)	3.6 (3.0)	23.7 (24.7)	
$[\{U(cp)_2Cl_2(dppoe)\}_2]$ [b]	25.3 (27.4)	48.5 (49.8)	4.0 (3.7)	6.9 (8.2)	
$[\{U(cp)_2Br_2(dppoe)\}_2]$ [b]	25.4 (24.8)	43.6 (45.1)	3.5 (3.5)	17.1 (16.7)	

[a] Calculated values are given in parentheses. [b] Air and moisture sensitive; must be stored *in vacuo*.

The ^1H n.m.r. spectra of the complexes $[U(cp)Cl_3L_2]$ could not be interpreted.

EXPERIMENTAL

All the experimental work, including the drying of solvents, preparation of starting materials, and physical measurements, was carried out as described previously.[3,8,9] The compound Tl(mcp), which is very air sensitive, was prepared in the same way as Tl(cp);[10] '$U(cp)_2Cl_2{\cdot}thf$,'[1] $[U(cp)Cl_3(thf)_2]$,[3] $[UCl_4(dma)_{2.5}]$,[7] $[UX_4(dmpva)_2]$,[8] UCl_4,[11] and UBr_4 [12] were prepared by published methods.

Preparations.— *Trichloro*(*η-methylcyclopentadienyl*)*bis*(*tetrahydrofuran*)*uranium*(IV). The compound Tl(mcp) (2.82 g, 9.60 mmol) was added to UCl_4 (3.78 g, 9.98 mmol) dissolved in thf (80 cm^3); after stirring overnight the supernatant was evaporated *in vacuo* to 5 cm^3, when the bright green *product* separated. This was washed with thf (5 cm^3) and vacuum dried (yield 70%). The complex $[U(cp)Br_3(thf)_2]$ was similarly prepared from Tl(cp) and UBr_4, except that the solution was evaporated to dryness to yield the bright green *product*.

Chloro(*η-cyclopentadienyl*)*bis*(*η-methylcyclopentadienyl*)*uranium*(IV). The compound Tl(mcp) (0.95 g, 3.34 mmol) was added to $[U(cp)Cl_3(thf)_2]$ (0.87 g, 1.57 mmol) dissolved in thf (80 cm^3); after stirring (16 h) the supernatant was evaporated to dryness *in vacuo* and the residue was heated at 393 K (10^{-3} Torr) for 4 h to eliminate Tl(mcp), after which the *product* was sublimed at 453 K (10^{-3} Torr) (yield 30%).

Trichloro(*η-cyclopentadienyl*)*bis*(NN-*dimethylacetamide*)*uranium*(IV). The compound Tl(cp) (0.35 g, 1.30 mmol) was added to a suspension of $[UCl_4(dma)_{2.5}]$ (0.77 g, 1.29 mmol) in thf (30 cm^3); the mixture was stirred overnight and the supernatant evaporated to dryness *in vacuo*. The dark green oily *residue* solidified completely on trituration with n-pentane (yield 85%). The green *complex* $[U(cp)Cl_3(dmpva)_2]$ was similarly prepared from $[UCl_4(dmpva)_2]$ (yield 70%).

Trichloro(*η-cyclopentadienyl*)*bis*(*triphenylphosphine oxide*)*uranium*(IV). Triphenylphosphine oxide (0.59 g, 2.10 mmol) in thf (10 cm^3) was added to $[U(cp)Cl_3(thf)_2]$ (0.58 g, 1.04 mmol) in thf (40 cm^3); after standing for 30 min the mixture was centrifuged and the supernatant was left to stand overnight, whereupon the brilliant green *complex* crystallised out. The product was washed with thf (2 × 5 cm^3) and vacuum dried (1 h), yield 75%. The *complexes* $[\{U(cp)Cl_3(dppoe)\}_2]$ (pale green), $[U(cp)Br_3(PPh_3O)_2]$ (green), $[U(cp)Br_3(dmpva)_2]$, and $[\{U(cp)Br_3(dppoe)\}_2]$ (both bright yellowish green) were prepared in the same way (yields 60%).

Bis{[1,2-*bis*(*diphenylphosphoryl*)*ethane*]*dichlorobis*(*η-cyclopentadienyl*)*uranium*(IV)}. The compound Tl(cp) (0.046 g, 0.171 mmol) was added to a suspension of $[\{U(cp)Cl_3(dppoe)\}_2]$ (0.276 g, 0.165 mmol) in thf (30 cm^3); after standing overnight the filtrate was evaporated to dryness *in vacuo*. The resulting oily solid was washed with n-pentane (10—15 cm^3) and vacuum dried (yield 45%, dark green). Brown $[\{U(cp)_2Br_2(dppoe)\}_2]$ was prepared in the same way (yield 50—60%). Both of these complexes are much more air and moisture sensitive than any of the $[U(cp)X_3L_2]$.

Analyses (Table 3) were obtained as described previously.[9]

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