The Nature of Bis(cyclopentadienyl)uranium Dichloride and Cyclopentadienyluranium Trichloride in Solution and in the Solid State

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Abstract: The composition of the compound "$(C_5H_5)_2UCl_2$", prepared from uranium tetrachloride and thallium cyclopentadienide in DME (1,2-dimethoxyethane), has been investigated in the solid state by infrared spectroscopy and X-ray powder diffraction, and in solution by electronic and ^1H NMR spectroscopy. All results indicate that $(C_5H_5)_2UCl_2$ is a mixture of the known compounds $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3(DME)$. The structure of this latter species is proposed to be mer pseudooctahedral on the basis of solution NMR studies (which also show it to be stereochemically dynamic) and by analogy to the related complex, $(CH_3C_5H_4)UCl_3(THF)_2$, the solid-state molecular structure of which has been determined using single-crystal X-ray diffraction techniques. This compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a cell of dimensions $a = 10.481$ (2) Å, $b = 12.981$ (2) Å, $c = 13.834$ (2) Å, and $\beta = 105.86$ (1)°. Least-squares refinement of the 181 variables led to a value for the conventional R index (on F) of 0.058 for 3698 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 60.4°$ and $I > 3\sigma(I)$. The coordination geometry about the uranium ion is approximately mer octahedral with the η^5-$CH_3C_5H_4$ and one coordinated THF occupying trans axial positions, and the other THF and three chlorine atoms occupying equatorial positions. The U–C(cyclopentadienyl), U–Cl, and U–O distances average 2.720 (14), 2.623 (3), and 2.450 (8) Å, respectively. The principal distortion of the coordination geometry from octahedral is a 0.47-Å displacement of the uranium atom out of the equatorial plane toward the cyclopentadienyl ring. It is found that the THF ligands of $(C_5H_5)UCl_3(THF)_2$ are readily displaced by nitrogenous bases such as 2,2′-bipyridyl and 1,10-phenanthroline.

Marked differences in the thermal stabilities as well as other chemical properties of $(\eta^5\text{-}C_5H_5)_3MR$[5] and MR_4[6] derivatives where M is uranium or thorium suggest an important role for coordinative saturation in controlling organoactinide[7] reaction patterns. A logical device to achieve intermediate degrees of coordinative saturation (and hopefully complexes better suited for catalytic and stoichiometric chemistry) would be to reduce the number of pentahaptocyclopentadienyl ligands from three.[8] For uranium, the complexes $(C_5H_5)_2UCl_2$[9] and $(C_5H_5)UCl_3(DME)$[10] (DME = 1,2-dimethoxyethane), which were reported several years ago, appear to be ideal precursors for a wealth of new organoactinides. Both species were prepared by the reaction of thallium cyclopentadienide with various ratios of uranium tetrachloride in DME (eq 1 and 2).

$$2Tl(C_5H_5) + UCl_4 \xrightarrow{DME} (C_5H_5)_2UCl_2 + 2TlCl \quad (1)$$

$$Tl(C_5H_5) + UCl_4 \xrightarrow{DME} (C_5H_5)UCl_3(DME) + TlCl \quad (2)$$

Since $(C_5H_5)_2UCl_2$ is closely analogous to $(C_5H_5)_2MCl_2$, compounds (M = Ti, Zr, V, Nb, Mo, etc.) which are cornerstones for much early transition metal organometallic chemistry,[11] we initiated chemical investigations of this compound. As we have already communicated,[12] it soon became apparent to us that $(C_5H_5)_2UCl_2$ had been misformulated, and, based upon CW ^1H NMR, infrared, and chemical evidence, we proposed that $(C_5H_5)_2UCl_2$ was actually a mixture of $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3(DME)$.[12] At approximately the same time as our communication, another article appeared,[13] also casting doubt upon the original formulation, and suggesting on the basis of infrared and electronic spectroscopy as well as magnetic measurements that $(C_5H_5)_2UCl_2$ was actually an acid–base adduct between $(C_5H_5)_3UCl$ and UCl_4, i.e., $[(C_5H_5)_3U]_2UCl_6$, in which the central uranium(IV) ion was in an approximately octahedral environment. The exact role of the dimethoxyethane in this formulation was left undefined; however, the presence of $(C_5H_5)_3UCl$ units was clearly recognized. In regard to the monocyclopentadienyl derivative $(C_5H_5)UCl_3(DME)$, chemical and ^1H NMR studies of the related species $(C_5H_5)UCl_3(THF)_2$[14a] (THF = tetrahydrofuran) have added credence to its existence. Subsequent studies have also provided further evidence for the lability of $(C_5H_5)_2UX_2$ species and have expanded the variety of known $(C_5H_5)UCl_3L_2$ molecules (L = an oxygen-donating Lewis base).[14b] They have not, however, provided further information on the constitution of $(C_5H_5)_2UCl_2$, and questions about $(C_5H_5)UCl_3(DME)$ as basic as structure and molecularity remain.

In this article we present a complete discussion of our studies of the nature of $(C_5H_5)_2UCl_2$ and $(C_5H_5)ucl_3(DME)$. Our approach includes chemical experimentation as well as X-ray powder diffraction, electronic, infrared, and ^1H NMR spectroscopy. In regard to the latter measurements, Fourier transform techniques are shown to provide important solution structural and dynamic information on these rather insoluble compounds. We also present here the molecular structure of $(CH_3C_5H_4)UCl_3(THF)_2$, determined by X-ray diffraction.[15] On the basis of these studies we conclude that "$(C_5H_5)_2UCL_2$" is largely if not exclusively a mixture of $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3(DME)$. Judging from our NMR data as well as from the solid-state structure of $(CH_3C_5H_4)UCl_3(THF)_2$, $(C_5H_5)UCl_3(DME)$ is a bona fide compound having a monomeric structure with pseudooctahedral coordination about the U(IV) ion. We also show that the $(C_5H_5)UCl_3$ species can form complexes with the bidentate nitrogenous bases 2,2′-bipyridyl and 1,10-phenanthroline.

Experimental Section

The preparation and handling of all organoactinides were necessarily carried out in an atmosphere of prepurified nitrogen, with rigorous exclusion of air and moisture. Sample manipulations were by Schlenk methods or in a glovebox. All solvents were thoroughly dried and deoxygenated in a manner appropriate to each, and were distilled under nitrogen immediately prior to use. Elemental analyses were performed by Bernhardt Analytical Laboratory, Schwarzkopf Analytical Laboratory, or Galbraith Analytical Laboratory. The reagents

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UCl_4,[16] $UCl_4(DME)_2$,[17] $Tl(C_5H_5)$,[18] $Tl(CH_3C_5H_4)$,[18] and $(C_5H_5)_3UCl$[19] were prepared and purified by the literature procedures.

Physical Measurements. Infrared spectra were recorded with Beckman IR-5, IR-9, or Perkin-Elmer 267 spectrophotometers and calibrated with polystyrene. Mulls were prepared in a glovebox with dry, degassed Nujol. Solution electronic spectra were recorded in matched Schlenk-type quartz cells on a Cary 17D spectrophotometer. The solutions were prepared under nitrogen in Schlenk apparatus, and transferred to the cells by syringe. Nuclear magnetic resonance spectra were recorded on Perkin-Elmer R-20B (CW 60 MHz) and Varian CFT-20 (FT 80 MHz) instruments. CD_2Cl_2 was dried by storing over P_2O_5 under a nitrogen atmosphere for at least 1 week prior to use. Deuterated aromatic solvents were dried by similar treatment with Na/K alloy. Trap-to-trap distillation followed by several cycles of freeze-thaw degassing were used to remove the final traces of gases from these solvents. X-ray powder diffraction patterns were recorded photographically on a Picker 6147 X-ray diffractometer using Ni-filtered Cu Kα radiation. Samples were sealed in 0.5-mm glass capillaries under nitrogen and were rotated during exposure to ensure average random orientation of the crystallites.

Synthesis of "$(C_5H_5)_2UCl_2$" in 1,2-Dimethoxyethane.[9] To 4.14 g (10.9 mmol) of UCl_4 in 250 mL of DME was added over a period of 1 h with rapid stirring 5.88 g (21.8 mmol) of $Tl(C_5H_5)$. The solution became a cloudy olive color immediately upon the addition of the first portion of $Tl(C_5H_5)$. After stirring for 24 h, the solution was suction filtered and the dimethoxyethane was removed in vacuo. The Nujol mull infrared spectrum of the resulting green-brown solid was in good agreement with the spectrum reported for $(C_5H_5)_2UCl_2$.[9] Sublimation of a portion of the crude reaction product at 140 °C (10^{-3} Torr) yielded a reddish-brown, microcrystalline solid identified by its infrared and NMR spectra as $(\eta^5\text{-}C_5H_5)_3UCl$.[19] Another portion of crude reaction product was Soxhlet extracted with hexane for 2 days at reduced pressure and room temperature (to avoid possible thermal decomposition). The reddish-brown solid which was extracted was identified as $(C_5H_5)_3UCl$ by its infrared and NMR spectra.[19] The same sample which had been extracted with hexane was then extracted for 5 days with benzene under reduced pressure. The product of the benzene extraction was also identified as $(C_5H_5)_3UCl$ by infrared and NMR spectroscopy.[19]

Synthesis of "$(C_5H_5)_2UCl_2$" in Toluene. To 5.53 g (14.53 mmol) of UCl_4 in 300 mL of toluene was added over a period of 1.5 h, 7.82 g (29.0 mmol) of $Tl(C_5H_5)$. After stirring for 24 h the reaction mixture was suction filtered and the green filtration residue was washed with 30 mL of toluene. It was noted that the washings were colorless. The toluene was next removed from the red-brown filtrate in vacuo, to yield a dark brown solid. This was identified as $(C_5H_5)_3UCl$ by its infrared and NMR spectra.[19]

Cyclopentadienyluranium(IV) Trichloride, Dimethoxyethane Adduct, $(C_5H_5)UCl_3(DME)$ (1).[10] This compound was prepared in ca. 90% yield from UCl_4 and $Tl(C_5H_5)$ in DME. The spectral properties were identical with those reported previously.[10]

Cyclopentadienyluranium(IV) Trichloride, Bis(tetrahydrofuran) Adduct, $(C_5H_5)UCl_3(THF)_2$. This complex was obtained in ca. 80% yield from UCl_4 and $Tl(C_5H_5)$ in THF. The spectral properties were identical with those reported in the literature.[14]

Methylcyclopentadienyluranium(IV) Trichloride Bis(tetrahydrofuran) Adduct, $(CH_3C_5H_4)UCl_3(THF)_2$ (2). To 1.34 g (3.53 mmol) of UCl_4 in 150 mL of THF was added 1.00 g (3.53 mmol) of $Tl(CH_3C_5H_4)$ with stirring. The solution, initially a dull dark green, gradually became a very bright green, and stirring was stopped after about 15 h. The solution was then suction filtered, and the solvent was removed in vacuo. The bright green solid was then washed with several portions of diethyl ether and dried in vacuo. The product is air sensitive, although not nearly as much as the analogous DME adduct.

Anal. Calcd for $C_{14}H_{23}UO_2Cl_3$: C, 29.62; H, 4.08. Found: C, 28.18; H, 4.26.

Complete infrared data (Nujol mull): 1491 sh, 1345 m, 1340 sh, 1313 w, 1293 w, 1246 m, 1189 w, 1168 w, 1134 w, 1064 w, 1048 w, sh, 1032 m, 994 s, 947 m, 916 m, 839 s, br, 825 sh, 804 s, 794 s, 662 m cm^{-1}.

Cyclopentadienyluranium(IV) Trichloride, 2,2′-Bipyridyl Adduct, $CpUCl_3(bpy)$. A slight excess of 2,2′-bipyridyl (0.30 g, 1.92 mmol) dissolved in 10 mL of THF was slowly added to a stirred solution of $CpUCl_3(THF)_2$ (1.00 g, 1.81 mmol) in 30 mL of THF. The tan-orange precipitate, which formed immediately, was stirred for 0.5 h and then filtered, washed with several 20-mL portions of THF, and dried in vacuo.

Anal. Calcd for $C_{15}H_{13}Cl_3N_2U$: C, 31.85; H, 2.32. Found: C, 31.92; H, 2.44.

Complete infrared data (Nujol mull): 3084 sh, 3058 sh, 1714 w, 1630 m, 1619 m, 1603 sh, 1599 s, 1586 s, 1572 m, 1526 ms, 1494 m, 1437 sh, 1319 ms, 1306 m, 1274 m, 1246 w, 1237 w, 1215 m, 1173 m, 1168 m, 1153 m, 1096 w, 1085 m, 1064 m, 1039 w, 1015 m, 1008 m, 990 m, 910 s, 869 m, 822 m, 793 m, 763 s, 756 s, 739 m, 728 m, 717 m, 643 w, 638 m, 623 w, 620 w, 603 w cm^{-1}.

Stirring this compound with excess bipyridyl in THF for another day resulted in isolation of material of composition intermediate between that for a mono- and bisbipyridyl adduct, indicating that some additional bipyridyl could be incorporated.

Anal. Calcd for $C_{15}H_{13}Cl_3N_2U$: C, 31.85; H, 2.32; N, 4.95. Calcd for $C_{25}H_{21}Cl_3N_4U$: C, 41.60; H, 2.93; N, 7.76. Found: C, 34.33; H, 2.86; N, 5.65.

Cyclopentadienyluranium(IV) Trichloride Bis(1,10-phenanthroline) Adduct $(C_5H_5)UCl_3(phen)_2$. Addition of 1.00 g (1.81 mmol) of $CpUCl_3(THF)_2$ in 40 mL of THF to excess anhydrous phenanthroline (1.30 g, 7.21 mmol) in THF with stirring resulted in immediate precipitation of a tan powder. After stirring overnight, the product was filtered, washed with several 20-mL portions of THF, and dried in vacuo.

Anal. Calcd for $C_{29}H_{21}Cl_3N_4U$: C, 45.24; H, 2.75; N, 7.28; Cl, 13.81. Found: C, 44.24; H, 2.66; N, 7.15; Cl, 13.03.

Complete infrared data (Nujol mull): 3080 sh, 3046 sh, 1627 m, 1615 m, 1595 m, 1575 m, 1541 m, 1521 m, 1496 m, 1422 s, 1345 m, 1311 w, 1284 w, 1235 w, 1216 m, 1210 w, 1186 w, 1137 m, 1102 m, 1052 w, 1033 w, 984 w, 971 m, 965 m, 912 m, 877 w, 858 m, 843 s, 841 sh, 797 w, 770 m, 722 s, 716 s, 633 m cm^{-1}.

X-ray Crystallographic Study[20] of $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$ (2). Single crystals of $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$ (**2**), obtained by slow diffusion of pentane into a concentrated THF solution at −15 °C, were suitable for X-ray studies when sealed under nitrogen in thin-walled glass capillaries. They are monoclinic, space group $P2_1/n$ (a special setting of $P2_1/c\text{-}C_{2h}^5$, no. 14),[21] with $a = 10.481$ (2) Å, $b = 12.981$ (2) Å, $c = 13.834$ (2) Å, $\beta = 105.86$ (1)°, and $Z = 4$ at 20 °C. Intensity measurements were made on a Syntex $P\bar{1}$ autodiffractometer using 1°-wide ω scans and graphite-monochromated Mo $K\bar{\alpha}$ radiation for a crystal shaped like a rectangular prism with principal faces of the form $10\bar{1}$, $01\bar{1}$, and 011 and dimensions of 0.78 × 0.63 × 0.41 mm. A total of 5376 independent reflections having $2\theta \leq 60.4°$ (the equivalent of 1.3 limiting Cu $K\bar{\alpha}$ spheres) were measured in four concentric shells of increasing 2θ. A scanning rate of 3°/min was employed for the scan between ω settings 0.50° respectively above and below the calculated $K\bar{\alpha}$ doublet value ($\lambda_{K\bar{\alpha}} = 0.710\,69$ Å) for those reflections having $0° < 2\theta_{MoK\bar{\alpha}} \leq 43°$; scanning rates of 2.4 and 2.0°/min were used for reflections having $43° < 2\theta_{MoK\bar{\alpha}} \leq 48.3°$ and $48.3° < 2\theta_{MoK\bar{\alpha}} \leq 60.4°$, respectively. Each of these 1° scans was divided into 19 equal (time) intervals and those 15 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-half the total time used for the net scan ($^{15}/_{19}$ of the total scan time), were measured at ω settings 1° above and below the calculated $K\bar{\alpha}$ doublet value for each reflection. The data were corrected for absorption (with[22] $\mu_{MoK\bar{\alpha}} = 11.68\ mm^{-1}$, the transmission factors ranged from 0.007 to 0.061) before applying Lorentz and polarization corrections.

The uranium atom was located from a Patterson synthesis; the 19 remaining nonhydrogen atoms appeared in a single difference Fourier synthesis based on refined parameters for the U atom [$R_1 = 0.229$ for 1812 independent reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$]. Isotropic unit-weighted full-matrix least-squares refinement for the 20 nonhydrogen atoms gave R_1 (unweighted, based on F) = 0.084 and R_2 (weighted) = 0.092; anisotropic refinement converged to $R_1 = 0.055$ and $R_2 = 0.066$ for 1812 reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann[23] and an anomalous dispersion correction to the scattering factors of the uranium and chlorine atoms.[24]

Atomic positions were then calculated for all hydrogen atoms (except those of the methyl substituent on the methylcyclopentadienyl ligand) assuming idealized sp^2 or sp^3 geometry and a C–H bond length of 0.95 Å. The final cycles of empirically weighted full-matrix least-squares refinement, in which the structural parameters for all

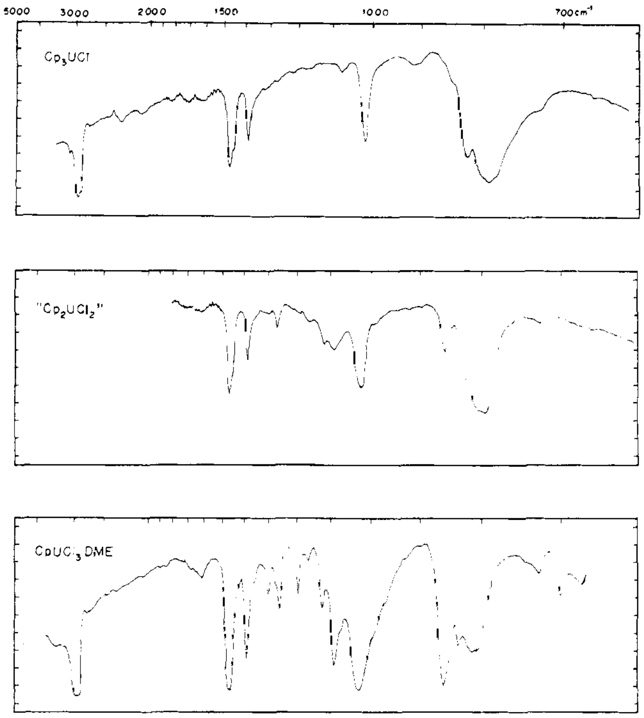


Figure 1. Solid-state infrared spectra of $(C_5H_5)_3UCl$, $(C_5H_5)_2UCl_2$, and $(C_5H_5)UCl_3$(1,2-dimethoxyethane) as Nujol mulls.

nonhydrogen atoms were varied, but those for isotropic ($B = 7.0$ Å^2) nonmethyl hydrogen atoms were not, converged to $R_1 = 0.058$ and $R_2 = 0.057$ for 3698 independent reflections having $2\theta_{MoK\bar{\alpha}} \leq 60.4°$ and $I > 3\sigma(I)$.

In addition to those programs previously described,[25] the absorption correction was performed on an IBM 360/65 computer using the program AGNOST, which is a general absorption program from J. A. Iber's laboratory that employs numerical methods.

Results and Discussion

$(C_5H_5)_2UCl_2$. The synthesis of $(C_5H_5)_2UCl_2$ by the literature procedure[9] (eq 1) yields a green-brown solid. In our hands, extraction of this product at room temperature with hexane or benzene yields as the only soluble component $(C_5H_5)_3UCl$, which was identified by infrared spectroscopy and by the characteristic isotropically shifted[5a,7a] (owing to the paramagnetism of U(IV)) resonance in the ^{1}H NMR at τ 13.4 (C_6D_6).[19] Sublimation of the green-brown solid under high vacuum at 140 °C yields only $(C_5H_5)_3UCl$.

Figure 1 presents the solid-state infrared spectra of $(C_5H_5)_3UCl$, $(C_5H_5)_2UCl_2$, and $(C_5H_5)UCl_3$(DME). The latter material can be prepared by the reaction of eq 2, and, as will be seen, is a well-defined compound. The infrared spectrum of $(C_5H_5)_2UCl_2$ is remarkably similar to a combination of the spectra of $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3$(DME). Indeed, a Nujol mull prepared from a mixture of $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3$(DME) exhibits a spectrum identical with that of $(C_5H_5)_2UCl_2$. The transitions at 780 and 1015 cm^{-1} are characteristic of (η^5-C_5H_5)U functionalities[5a] and can be assigned (under C_{5v} local symmetry) to $A_1 + E_1$ C–H out-of-plane wagging and E_1 C–H in-plane wagging modes, respectively.[5b,26] The absorptions at 1290, 1249, 1188, 1116, 1084, 1025 (in part), and 860 cm^{-1} are assignable to coordinated 1,2-dimethoxyethane.[17] Further information on the nature of $(C_5H_5)_2UCl_2$ in the solid state is provided by X-ray powder diffraction measurements. Table I contains a tabulation of the observed powder pattern lines for $(C_5H_5)_3UCl$, $(C_5H_5)_2UCl_2$, and $(C_5H_5UCl_3)$ (DME). The values listed are those directly measured from the film in millimeters, which correspond to degrees 4θ for Cu $K\bar{\alpha}$ radiation (λ = 1.541 78 Å). Again, an unmistakable relationship is obvious. The $(C_5H_5)_2UCl_2$ lines correspond perfectly in position and relative intensity with those of $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3$(DME), with no extra lines present. For $2\theta >$ ca. 27° ($4\theta > 54$ mm), precise measurement of lines was not possible owing to extensive overlap. However, it was clear by visual comparison that the higher angle patterns were following precisely the same relationship. The two most prominent high-angle lines in $(C_5H_5)_2UCl_2$ are included and compare favorably with those observed in the two known compounds (Table I). Comparison of the $(C_5H_5)_2UCl_2$ pattern with those of UCl_4 and $UCl_4(DME)_2$ revealed that the latter two compounds were absent.

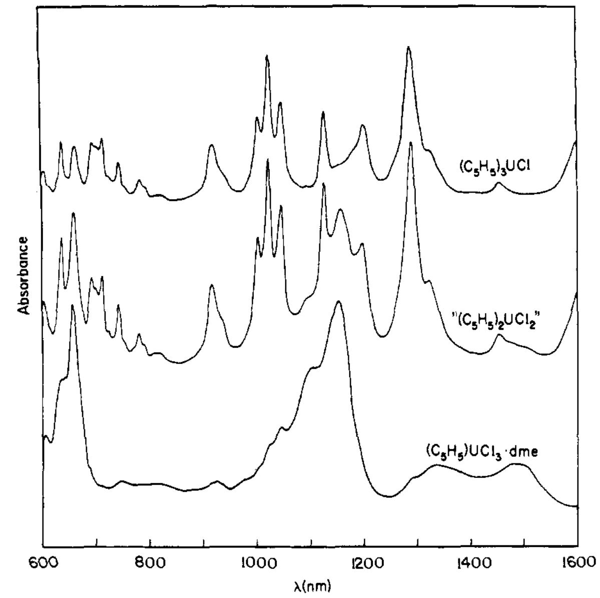


Figure 2. Electronic spectra of $(C_5H_5)_3UCl$, $(C_5H_5)_2UCl_2$, and $(C_5H_5)UCl_3$(DME) as solutions in 1,2-dimethoxyethane. The concentrations of the solutions are the same; however, the spectrum of (C_5H_5)-UCl_3(DME) has been vertically expanded by a factor of 2 for clarity.

Table I. X-ray Powder Diffraction Data (degrees 4θ, 1° ≈ 1 mm Film Separation) for $(C_5H_5)_3UCl$, $(C_5H_5)_2UCl_2$, and (C_5H_5)-UCl_3(DME)[a]

$(C_5H_5)_3UCl$	$(C_5H_5)_2UCl_2$	$(C_5H_5)UCl_3$(DME)
	19.1 m	19.1 m
	23.3 m	23.4 s
25.8 s	25.8 s	26.3 m
	27.7 m	27.8 s
28.7 s	28.8 s	
31.0 s	31.0 m	30.2 m, 31.7 m
	33.2 m	33.0 m
36.4 w	36.4 w	
	38.5 w	38.4 m
	40.2 w	39.9 m
41.2 vw	41.3 vw	
43.3 w, 44.3 w	43.9 mw	
46.6 w	46.4 w	
47.9 m	48.1 mw	
50.6 vw	50.8 vw	
53.6 w, 54.4 w	53.8 w	
	73.6 mw	73.7 m
76.5 m	76.5 mw	76.3 m

[a] s = strong; m = medium; w = weak.

The composition of $(C_5H_5)_2UCl_2$ was also examined in solution. Figure 2 compares the electronic spectra of $(C_5H_5)_3UCl$, $(C_5H_5)_2UCl_2$, and $(C_5H_5)UCl_3$(DME) in the energy region characterized predominantly by f–f transitions.[27] The band pattern observed in this area is a sensitive function of the strength and symmetry of the ligand field.[14b,27,28] The

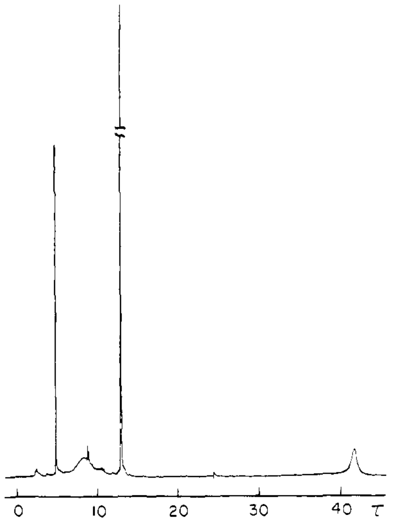


Figure 3. ^1H NMR spectrum (FT, 80 MHz) of a solution of $(C_5H_5)_2UCl_2$ in CD_2Cl_2. The sharp resonance at τ 4.7 is due to $CHDCl_2$.

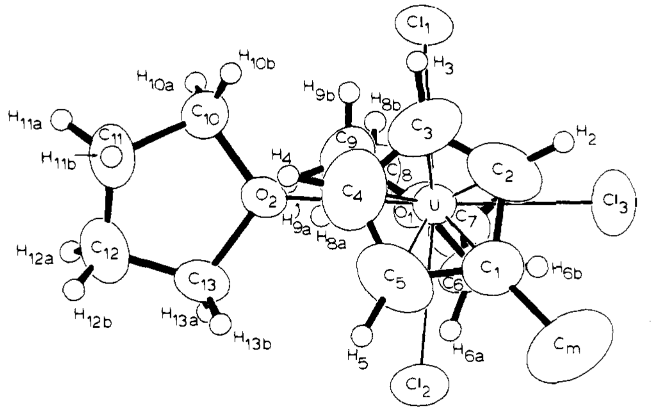


Figure 4. Perspective ORTEP drawing of the $(\eta^5\text{-}CH_3C_5H_4)UCl_3(OC_4H_8)_2$ molecule, **2**, as observed in the solid state. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Hydrogen atoms (except those of the methyl substituent on the methylcyclopentadienyl ligand) are represented at their idealized positions by arbitrarily small spheres which are in no way representative of their true thermal motion. This view is perpendicular to the mean plane of the methylcyclopentadienyl ligand skeleton.

spectra of $(C_5H_5)_3UCl$[28b] and $(C_5H_5)UCl_3(DME)$[10] are in good agreement with those reported in the literature. As can be readily seen, the pattern exhibited by $(C_5H_5)_2UCl_2$ is a superposition of the other two spectra. The electronic spectrum of $(C_5H_5)_2UCl_2$ in benzene is essentially identical with that of $(C_5H_5)_3UCl$. In accord with this, we find $(C_5H_5)UCl_3(DME)$ to be virtually insoluble in benzene. The 80-MHz Fourier transform ^1H NMR spectrum of $(C_5H_5)_2UCl_2$ in C_6D_6 exhibits only resonances attributable to $(C_5H_5)_3UCl$ (singlet, τ 12.4) and traces of 1,2-dimethoxyethane. In CD_2Cl_2 at room temperature, the spectrum shown in Figure 3 is observed for $(C_5H_5)_2UCl_2$. The resonance at τ 12.7 is due to $(C_5H_5)_3UCl$; it will be seen that the resonances at τ 8.0 and 41.5 are characteristic of $(C_5H_5)UCl_3(DME)$. Thus, the simplest interpretation of all data in both the solid state and in solution is that $(C_5H_5)_2UCl_2$ is actually a mixture of the known compounds $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3(DME)$.

The structural and chemical nature of $(C_5H_5)UCl_3(DME)$ was next of interest, both because it represented what was possibly the most coordinatively unsaturated (monocyclopentadienyl) member of the $(C_5H_5)_{4-n}UCl_n$ series and because it might provide some information concerning the instability of $(C_5H_5)_2UCl_2$. Efforts to grow single crystals of $(C_5H_5)UCl_3(DME)$ (**1**) or $(CH_3C_5H_4)UCl_3(DME)$ suitable for solid-state structural studies were unsuccessful. It was, however, possible to obtain excellent crystals of the related compound $(CH_3C_5H_4)UCl_3(THF)_2$ (**2**), and an X-ray diffraction study was undertaken. It will be seen in a following section that the solution NMR spectra of **1** can be readily interpreted in terms of a molecular structure similar to that of **2**.

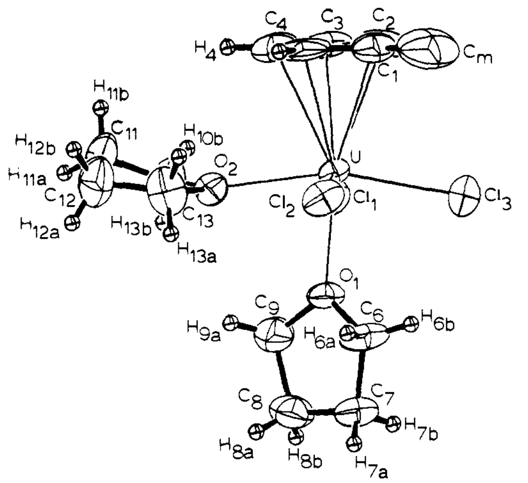


Figure 5. View of the $(\eta^5\text{-}CH_3C_5H_4)UCl_3(OC_4H_8)_2$ molecule, **2**, which is 90° away from that of Figure 4.

Table II. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $(\eta^5\text{-}CH_3\ C_5H_4)UCl_3(OC_4H_8)_2$[a]

atom type[b]	fractional coordinates		
	10^4x	10^4y	10^4z
Cl_1	1390 (3)	2842 (3)	−3187 (2)
Cl_2	1595 (3)	1016 (3)	147 (2)
Cl_3	2327 (4)	3742 (3)	−541 (3)
O_1	3293 (7)	1526 (7)	−1399 (5)
O_2	598 (8)	518 (6)	−2414 (6)
C_1	−941 (13)	2862 (13)	−755 (12)
C_2	−1019 (15)	3464 (15)	−1595 (16)
C_3	−1381 (13)	2930 (17)	−2424 (12)
C_4	−1622 (15)	1949 (19)	−2206 (19)
C_5	−1345 (13)	1891 (15)	−1169 (18)
C_6	4343 (11)	1533 (16)	−478 (9)
C_7	5627 (12)	1320 (13)	−801 (11)
C_8	5179 (15)	739 (16)	−1745 (13)
C_9	3655 (14)	930 (14)	−2154 (12)
C_{10}	126 (16)	403 (12)	−3504 (10)
C_{11}	−727 (17)	−568 (13)	−3630 (13)
C_{12}	−221 (20)	−1198 (13)	−2746 (15)
C_{13}	422 (19)	−475 (11)	−1944 (11)
C_m	−528 (22)	3189 (24)	367 (17)
	10^5x =	10^5y =	10^5z =
U	10 542 (3)	21 479 (3)	−14 920 (3)

[a] Numbers in parentheses are the estimated standard deviations in the last significant figure. [b] Atoms are labeled in agreement with Figures 4 and 5; C_m denotes the carbon atom for the methyl substituent of the η^5-methylcyclopentadienyl ligand.

Solid-State Molecular Structure of $(CH_3C_5H_4)UCl_3(THF)_2$ (2). Final atomic coordinates and anisotropic thermal parameters for nonhydrogen atoms of crystalline $(\eta^5\text{-}CH_3C_5H_4)UCl_3(OC_4H_8)_2$ are presented in Tables II and III, respectively; calculated positions for hydrogen atoms are presented in Table IV.[20] Models seen in perspective of the contents of the asymmetric unit specified by the atomic coordinates of Tables II and IV are illustrated in Figures 4 and 5; each nonhydrogen atom is represented by an ellipsoid having the shape, orientation, and relative size consistent with the thermal parameters listed in Table III (hydrogen atoms are represented by arbitrarily small

Table V. Bond Distances and Polyhedral Edge Lengths in the Coordination Group of $(\eta^5\text{-}CH_3C_5H_4)UCl_3(OC_4H_8)_2$^{a}

type^b	length, Å	av^c	type^b	length, Å	av^c
U-Cl$_1$	2.625 (3)		Cl$_1$···Cl$_3$	3.710 (5)	3.754 (5, 44, 44, 2)
U-Cl$_2$	2.631 (3)	2.623 (3, 6, 9, 3)	Cl$_2$···Cl$_3$	3.797 (5)	
U-Cl$_3$	2.614 (4)				
			Cl$_1$···O$_1$	3.212 (9)	
			Cl$_2$···O$_1$	3.204 (8)	
U-O$_1$	2.451 (7)	2.450 (8, 1, 1, 2)	Cl$_3$···O$_1$	3.371 (9)	3.327 (8, 96, 144, 5)
U-O$_2$	2.449 (8)		Cl$_1$···O$_2$	3.379 (8)	
			Cl$_2$···O$_2$	3.471 (8)	
U-C$_1$	2.726 (13)		O$_1$···O$_2$	3.081 (11)	
U-C$_2$	2.737 (14)				
U-C$_3$	2.723 (13)	2.720 (14, 11, 28, 5)			
U-C$_4$	2.720 (16)		Cl$_1$···Cp^d	3.965	
U-C$_5$	2.692 (12)		Cl$_2$···Cp^d	3.914	3.936
			Cl$_3$···Cp^d	3.930	
U-Cp^d	2.459		O$_2$-Cp^d	3.684	

[a] Numbers in parentheses are the estimated standard deviations in the last significant figure. [b] Atoms are labeled in agreement with Figures 4 and 5. [c] The figures in parentheses following each averaged value are the root mean square value of the estimated standard deviation for an individual datum, the mean deviation, the maximum deviation, and the number of individual measurements which are included in the average value. [d] Cp denotes the center of gravity for the five carbon atoms which comprise the ring of the η^5-bonded methylcyclopentadienyl ligand.

Table VI. Bond Angles Subtended at the U(IV) Atom in the Coordination Group of $(\eta^5\text{-}CH_3C_5H_4)UCl_3(OC_4H_8)_2$^{a}

type^b	angle, deg	type^b	angle, deg
Cl$_1$UCl$_3$	90.2 (1)	Cl$_1$UCl$_2$	155.8 (1)
Cl$_2$UCl$_3$	92.8 (1)	Cl$_3$UO$_2$	161.1 (2)
Cl$_1$UO$_2$	83.4 (2)	O$_1$UCp^c	175.0
Cl$_2$UO$_2$	86.1 (2)		
		C$_1$UC$_2$	29.4 (5)
Cl$_1$UO$_1$	78.4 (2)	C$_2$UC$_3$	27.7 (6)
Cl$_2$UO$_1$	78.1 (2)	C$_3$UC$_4$	28.7 (6)
Cl$_3$UO$_1$	83.4 (2)	C$_4$UC$_5$	29.7 (6)
O$_2$UO$_1$	77.9 (3)	C$_5$UC$_1$	30.0 (6)
Cl$_1$UCp^c	102.4	C$_1$UC$_3$	48.3 (5)
Cl$_2$UCp^c	100.5	C$_2$UC$_4$	46.8 (6)
Cl$_3$UCp^c	101.5	C$_3$UC$_5$	47.8 (5)
O$_2$UCp^c	97.3	C$_4$UC$_1$	49.3 (5)
		C$_5$UC$_2$	47.3 (5)

[a] Numbers in parentheses are the estimated standard deviations in the last significant figure. [b] Atoms are labeled in agreement with Figures 4 and 5. [c] Cp denotes the center of gravity for the five carbon atoms which comprise the ring of the η^5-bonded methylcyclopentadienyl ligand.

spheres for purposes of clarity). Bond distances and polyhedral edge lengths in the coordination group are given with their estimated standard deviations in Table V; bond angles subtended at the U(IV) atom are given in Table VI. Bond lengths and angles involving nonhydrogen ligand atoms are given with estimated standard deviations in Table VII; least-squares mean planes and atomic displacements therefrom are given for structurally significant groups of atoms along with selected dihedral angles in Table VIII.

The structure analysis reveals that the crystal is composed of discrete monomeric $(\eta^5\text{-}CH_3C_5H_4)UCl_3(OC_4H_8)_2$ molecules in which each uranium(IV) ion is coordinated to three chloride ions, two tetrahydrofuran (THF) oxygen atoms, and a pentahapto-bonded methylcyclopentadienyl ligand. Although the uranium atom in this complex would have a formal coordination number of eight if the η^5-bonded ring is considered to occupy three coordination sites, the data in Table VI for interligand bond angles subtended at the uranium atom indicate a pseudooctahedral geometry with the bulky $CH_3C_5H_4$ ligand occupying a single coordination site. If viewed in terms of a pseudooctahedral geometry, the structure of $(CH_3C_5H_4)UCl_3(THF)_2$ is seen to represent a mer-octahedral configuration with cis THF ligands; such a coordination polyhedron would have a maximum possible symmetry of $C_s(m)$. Examination of the data in Tables V–VIII indicates that the coordination polyhedron does approximate rather closely this maximum symmetry with U, Cl$_3$, O$_1$, O$_2$, and the center of gravity for the five-membered ring of the $CH_3C_5H_4$ ligand (hereafter designated Cp) determining the pseudo-mirror plane. An accurate characterization of the coordination geometry about U will be aided by the establishment of a Cartesian coordinate system with its origin at the uranium atom and its positive z axis collinear with the vector from U to Cp. The xz plane would ideally contain U, Cp, Cl$_3$, O$_1$, and O$_2$, and the yz plane would ideally contain U, Cp, Cl$_1$, Cl$_2$, and O$_1$; each of these five atom groups are individually coplanar to within 0.10 Å and their least-squares mean planes (Table VIII) intersect in a dihedral angle of 89.9°. The least-squares mean planes of these two five-atom groupings intersect that of the planar (to within 0.01 Å) six-atom $CH_3C_5H_4$ ligand skeleton (Table VIII) in dihedral angles of 88.2 and 86.7°, respectively.

Although uranium(IV) complexes with formal coordination numbers as high as 12 are known,[7d,29,30] the formally eight-coordinate $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$ molecule of the present study is a sterically crowded species. In fact, major deviations of the bond angles involving uranium from the idealized octahedral value of 90°, as well as the adoption of the observed mer configuration, can be attributed to minimization of intramolecular ligand–ligand repulsions. Even if the η^5-bonded $CH_3C_5H_4$ ring is formally considered to be a single-site ligand, it will clearly occupy the largest area on the surface of the uranium coordination sphere; likewise, if interligand contacts between noncoordinated atoms are ignored, a coordinated THF oxygen atom will occupy the smallest area on the coordination sphere.

Both the need for a reasonably isotropic distribution of coordinated atoms about the U atom and the steric constraints imposed by a disk-shaped $\eta^5\text{-}CH_3C_5H_4$ ligand will favor a uniform displacement in the negative z direction of those ligands which would ideally occupy sites in the xy plane. Thus Cl$_1$, Cl$_2$, Cl$_3$, and O$_2$ are coplanar (Table VIII) to within 0.06 Å and their least-squares mean plane is within 3.8° of being parallel to that of the $CH_3C_5H_4$ skeleton; the U atom is displaced by 0.47 Å from this four-atom mean plane toward the Cp ligand. This is quite similar to the pseudo-pentagonal-bipyramidal geometry observed in $(\eta^6\text{-}C_6H_6)U(AlCl_4)_3\cdot C_6H_6$, where the U atom is displaced[31] by ~0.5 Å from the pentagonal girdle of five chlorine atoms toward the bulky, disk-

Table VII. Bond Lengths and Angles Involving Nonhydrogen Atoms in Ligands of Crystalline $(\eta^5\text{-}CH_3C_5H_4)UCl_3(OC_4H_8)_2$[a]

bond lengths

type[b]	length, Å	av[c]	type[b]	length, Å	av[c]
O_1-C_6	1.44 (1)	1.45 (2, 2, 3, 4)	C_1-C_2	1.38 (2)	1.36 (3, 3, 6, 5)
O_1-C_9	1.43 (2)		C_1-C_5	1.40 (3)	
O_2-C_{10}	1.46 (2)		C_2-C_3	1.30 (3)	
O_2-C_{13}	1.48 (2)		C_3-C_4	1.35 (3)	
			C_4-C_5	1.39 (3)	
C_6-C_7	1.56 (2)	1.51 (2, 4, 6, 6)			
C_7-C_8	1.47 (2)		C_1-C_m	1.55 (3)	
C_8-C_9	1.56 (2)				
C_{10}-C_{11}	1.53 (2)				
C_{11}-C_{12}	1.45 (3)				
C_{12}-C_{13}	1.47 (2)				

bond angles

type[b]	angle, deg	av[c]	type[b]	angle, deg	av[c]
$C_6O_1C_9$	112 (1)	111 (1, 2, 2, 2)	UO_1C_6	122 (1)	124 (1, 1, 2, 4)
$C_{10}O_2C_{13}$	109 (1)		UO_1C_9	125 (1)	
			UO_2C_{10}	126 (1)	
			UO_2C_{13}	124 (1)	
$O_1C_6C_7$	105 (1)	106 (1, 1, 3, 8)			
$C_6C_7C_8$	105 (1)		$C_5C_1C_2$	103 (2)	108 (2, 2, 5, 5)
$C_7C_8C_9$	107 (1)		$C_1C_2C_3$	112 (2)	
$C_8C_9O_1$	106 (1)		$C_2C_3C_4$	109 (2)	
$O_2C_{10}C_{11}$	103 (1)		$C_3C_4C_5$	107 (2)	
$C_{10}C_{11}C_{12}$	108 (1)		$C_4C_5C_1$	109 (2)	
$C_{11}C_{12}C_{13}$	105 (1)				
$C_{12}C_{13}O_2$	108 (1)		$C_mC_1C_2$	128 (2)	129 (2, 1, 1, 2)
			$C_mC_1C_5$	129 (2)	

[a] Numbers in parentheses are the estimated standard deviation in the last significant figure. [b] Atoms are labeled in agreement with Figures 4 and 5; C_m denotes the carbon atom for the methyl substituent of the η^5-methylcyclopentadienyl ligand. [c] The figures in parentheses following each averaged value are the root mean square value of the estimated standard deviation for an individual datum, the mean deviation, the maximum deviation, and the number of individual measurements which are included in the average value.

shaped η^6-bonded benzene ligand. Even with this distortion from idealized octahedral geometry for **2**, several cyclopentadienyl carbon-to-chlorine intramolecular contacts are significantly less than the 3.50-Å sum of the appropriate van der Waals radii:[32] $C_2\cdots Cl_3$, 3.43 (2) Å; $C_3\cdots Cl_1$, 3.35 (1) Å; $C_5\cdots Cl_2$, 3.32 (2) Å. The 3.05 (2) Å $C_4\cdots O_2$ separation is also less than the van der Waals value.[32]

If the four coordinated atoms which would normally lie in the *xy* plane are required to be "folded down" toward the negative *z* axis, the most favorable set of ligand-ligand contacts on the coordination sphere will result when the ligand with the smallest coordinating atom occupies the polyhedral site trans to the bulky $CH_3C_5H_4$ ligand. These considerations would favor a THF ligand occupying this site to give the observed mer isomer with cis THF ligands. The $Cl_1\cdots O_1$ and $Cl_2\cdots O_1$ contacts of 3.208 (9, 4, 4, 2) Å[33] are only 0.008 Å larger than the sum of the van der Waals radii for O and Cl (1.40 and 1.80 Å, respectively).[32] If O_1 and Cl_3 were interchanged without altering the angles subtended at U to give the mer isomer with trans THF ligands, the two $Cl\cdots Cl_3$ contacts would average 3.31 Å and be significantly (0.29 Å) less than the van der Waals value.[32] This analysis is also consistent with the solid-state observation of the mer isomer with *cis*-triphenylphosphine oxide (TPPO) ligands in $(\eta^5\text{-}C_5H_5)UCl_3(TPPO)_2$.[34] It would also seem to preclude the formation of bis(cyclopentadienyl)-actinide complexes with trans (or parallel) cyclopentadienyl ligands. A nonparallel cis arrangement would clearly be favored sterically.

Should any critically short ligand-ligand contacts exist on the coordination sphere of **2**, the relative compactness of the coordinated THF oxygen atoms would (in the absence of critical contacts involving the rest of the ligand) clearly favor the alteration of idealized polyhedral parameters involving them. Thus both the $O_1\cdots O_2$ polyhedral edge and the O_1UO_2 bond angle are compressed to values of 3.081 (11) Å and 77.9 (3)°, respectively, as a result of THF oxygen atom O_2 being displaced in the pseudo-mirror plane by ~0.26 Å off the negative *z* axis toward O_1.

The presence of a methyl substituent on the cyclopentadienyl ring also appears to favor the observed mer-octahedral isomeric arrangement for **2**. With the disk-shaped cyclopentadienyl ligand being oriented perpendicular to the *z* axis, the orientations of any THF ligands in the *xy* plane will be restricted to those which are nearly parallel to that plane. This orientational restriction therefore precludes the possibility of having two THF ligands occupying cis positions in the *xy* plane since only a trans arrangement would have reasonable interligand THF H $\cdots\cdots$ H contacts. The possibility of such a trans arrangement can probably be eliminated for **2** by examining contacts between the MeCp and THF ligands. The $H_4\cdots O_2$, $H_4\cdots H_{10b}$, and $H_4\cdots H_{13b}$ contacts of 2.81, 2.59, and 3.14 Å, respectively, indicate that seriously short interligand $(CH_3C_5H_4\cdots THF)$ contacts would result if a cyclopentadienyl hydrogen atom (van der Waals radius[32] of 1.20 Å) contiguous to a THF ligand were replaced by a bulkier methyl group (van der Waals radius[32] of 2.00 Å). The most favorable orientation for the $CH_3C_5H_4$ methyl group would in fact be the one observed in the solid state for **2**—directly over the midpoint of a $Cl\cdots Cl$ polyhedral edge. This would in turn imply either a single THF ligand in the *xy* plane or the sterically improbable case where two THF ligands occupy cis polyhedral sites in this plane. Although the $C_m\cdots Cl_2$ and

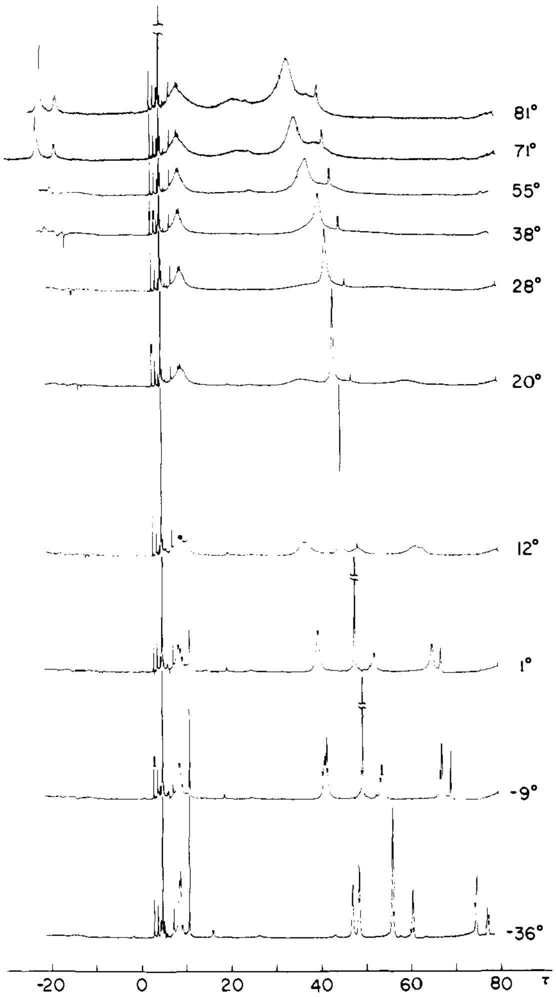


Figure 6. Variable-temperature FT 80-MHz ^1H NMR spectra of $(C_5H_5)UCl_3(DME)$ as a solution in CD_2Cl_2. The sharp signal at τ 4.7 is due to $CHDCl_2$.

$C_m \cdots Cl_3$ contacts in **2** average 3.64 (2, 2, 2, 2) Å[33] or nearly 0.16 Å less than the van der Waals value,[32] any other orientation of the $CH_3C_5H_4$ ligand would produce an even shorter $C_m \cdots Cl$ contact.

Since the average U–C distance of 2.720 (14, 11, 28, 5) Å in **2** is nearly identical with those observed in several formally ten-coordinate $(\eta^5\text{-}C_5H_5)_3UX$ complexes,[35] the present study seems to violate Raymond's suggestion[36] that Pauling's radius ratio[37] can be used to predict metal–carbon bond lengths in these species. This is probably not unexpected since Raymond's analysis[36] does not take into account ligand–ligand contacts on the coordination sphere. The average U–Cl bond of 2.623 (3, 6, 9, 3) Å in **2** is quite similar to the 2.599 (9, 2, 2, 2) Å average for U–Cl bonds in $[(C_2B_9H_{11})_2UCl_2]^{2-}$[39] as well as those observed in several formally ten-coordinate species: 2.559 (16) Å in $(\eta^5\text{-}C_5H_5)_3UCl$,[35] 2.627 (2) Å in $(\eta^5\text{-}C_5H_4CH_2C_6H_5)_3UCl$,[35b] and 2.593 (3) Å in $(\eta^5\text{-}C_9H_7)_3UCl$.[35] When cation size and coordination number differences are taken into account,[40] the average U–O (THF) bond length of 2.450 (8, 1, 1, 2) Å in **2** is quite comparable to the 2.519 (6) Å Th–O bond involving the neutral dimethylformamide ligand in nine-coordinate tetrakis(tropolonato)-*N,N'*-dimethylformamidethorium(IV).[38] There are no intermolecular contacts in **2** which are less than the appropriate sum of van der Waals radii.

Table VIII. Atomic Displacements from Selected Mean Planes of $(\eta^5\text{-}CH_3C_5H_4)UCl_3(OC_4H_8)_2$

Equations of Mean Planes[a,b]

I. methylcyclopentadienyl ligand skeleton:[c] $-0.972X + 0.228Y - 0.060Z = 1.59$

II. *xy* coordination polyhedron plane:[d] $-0.954X + 0.290Y - 0.069Z = -1.12$

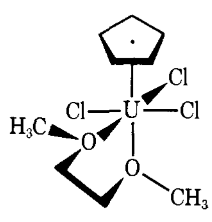
III. *xz* coordination polyhedron plane:[e] $0.194X + 0.463Y - 0.865Z = 3.34$

IV. *yz* coordination polyhedron plane:[f] $-0.225X - 0.836Y - 0.500Z = -1.61$

atom	displacement,[i] Å, from			
type[g]	plane I	plane II	plane III	plane IV
U	2.46	−0.47	0.01*	0.10*
Cl_1	3.08	0.06*	−2.55	−0.05*
Cl_2	2.87	0.06*	2.59	−0.05*
Cl_3	3.01	−0.05*	−0.04*	2.68
O_1	4.90	1.98	0.04*	0.01*
O_2	2.74	−0.06*	−0.05*	−2.31
C_1	0.00*	−2.93	0.89	0.83
C_2	−0.01*	−3.01	−0.48	0.98
C_3	0.01*	−2.95	−1.11	−0.16
C_4	0.00*	−2.88	−0.20	−1.16
C_5	0.00*	−2.86	1.05	−0.56
C_m	0.00*	−2.94	1.98	1.94
C_6	5.69	2.77	0.94	0.82
C_7	7.16	4.23	0.43	0.68
C_8	7.15	4.26	−0.29	−0.60
C_9	5.66	2.77	−0.60	−0.99
C_{10}	2.61	−0.20	−1.22	−3.18
C_{11}	2.06	−0.65	−0.61	−4.51
C_{12}	2.51	−0.15	0.74	−4.56
C_{13}	2.72	0.01	1.16	−3.16
Cp[h]	0.00	−2.93	0.03*	−0.01*

[a] *X*, *Y*, and *Z* are orthogonal coordinates in Å along **a**, **b**, and **c***, respectively, of the crystallographic coordinate system. [b] Angles (degrees) between the normals to selected pairs of planes follow: I–II, 3.75; I–III, 88.23; I–IV, 86.68; III–IV, 89.90. [c] Comprises atoms C_1, C_2, C_3, C_4, C_5, and C_m. [d] Comprises atoms Cl_1, Cl_2, Cl_3, and O_2. [e] Comprises atoms U, Cl_3, O_1, O_2, and Cp. [f] Comprises atoms U, Cl_1, Cl_2, O_1, and Cp. [g] Atoms labeled in agreement with Figures 4 and 5. [h] Cp denotes the center of gravity for the five-membered ring of the methylcyclopentadienyl ring. [i] Displacements for the atoms used to calculate the mean plane are marked with asterisks.

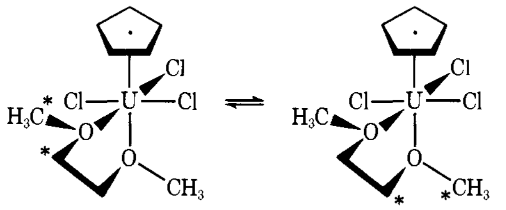
$(C_5H_5)UCl_3(DME)$. NMR Studies and Solution Structure. It was found that $(C_5H_5)UCl_3(DME)$ was not sufficiently soluble in the traditional noncoordinating solvents benzene-d_6 and toluene-d_8 for NMR studies, even using Fourier transform techniques. However, the compound was found to be sparingly soluble in CD_2Cl_2 and solutions are stable for a number of hours at room temperature or below. Figure 6 shows proton spectra of $(C_5H_5)UCl_3(DME)$. Comparison with Figure 3 reveals that the room temperature spectrum of $(C_5H_5)UCl_3(DME)$ is identical with that of $(C_5H_5)_2UCl_2$ when the sharp resonance at τ 12.7 due to $(C_5H_5)_3UCl$ is subtracted. Because of the breadth of a number of the $(C_5H_5)UCl_3(DME)$ resonances at room temperature, variable-temperature studies were undertaken. Referring to the −36 °C spectrum, diamagnetic (i.e., sharp, easily saturated) solvent ($CHDCl_2$) and organic impurity resonances are assigned in the τ 3–6 region. The slightly broadened resonance centered at $\tau \approx 8$ is attributed to 1,2-dimethoxyethane. The broadening and slight shift from the diamagnetic field position appear to reflect rapid chemical exchange with coordinated, isotropically shifted DME. Incremental addition of DME to these solutions causes the $\tau \approx 8$ resonance to increase in intensity and split into two resonances which shift slightly toward the diamagnetic resonance positions as well as decrease in line width. The resonances at τ 46.8, 48.2, 55.8, 60.2, and 74.5 are in an approximate intensity ratio of 2:3:5:2:3 and can be attributed to CH_2, CH_3, C_5H_5, CH_2, and CH_3 resonances, respectively, of the mer-octahedral isomer,



A

A. This ligand arrangement is analogous to the $(CH_3C_5H_4)UCl_3(THF)_2$ molecular structure, and, as will be seen, the observed site exchange processes are in accord with this assignment. The additional resonances at $\tau \approx 11.0$ and 78.0 arise from small amounts of $UCl_4(DME)_2$,[17] present as a contaminant.[41] As the temperature is raised, two kinds of phenomena are observed: shifts in the line positions and exchange-related collapse and coalescence of the signals.

The temperature dependence of NMR resonance positions in paramagnetic organoactinides reflects the temperature-dependent changes in populations of the electronic energy levels.[42] A rigorous theoretical description of how this will affect contact (hyperfine) and pseudocontact (dipolar) contributions to the isotropic shifts in the present case is not possible with the information at hand. Empirically, however, it is generally observed that ligand proton chemical shifts of low-symmetry U(IV) complexes exhibit approximate Curie behavior in the temperature range presently under discussion.[5a,28b,42,43] That is, plots of the isotropic shift vs. $1/T$ (K) are nearly linear. Analysis of the chemical shift vs. $1/T$ data for the $(C_5H_5)UCl_3(DME)$ solutions in CD_2Cl_2 also produced linear plots. The importance of such a relationship is that it allows prediction of the resonance positions of exchanging sites at temperatures above the coalescence point. As the temperature is increased from −36 °C, the resonances assigned to the coordinated DME CH_3 and CH_2 protons of structure A begin to broaden (Figure 6). In the initial stages of the exchange process, neither the C_5H_5 resonance nor the $\tau \approx 78.0$ resonance displays detectable broadening; there may be some broadening of the DME signal at $\tau \approx 8$. By 12 °C, the CH_3, CH_2 and τ 8 (DME) resonances are substantially broadened. Raising the temperature produces further collapse and coalescence of the CH_3, CH_2 lines, further broadening of the τ 8 DME resonance, and broadening of the C_5H_5 signal. These changes are reversible upon lowering the temperature; however, above 60 °C, signals to low field of τ −10 grow in irreversibly. These are assigned to thermal decomposition products. If the observed broadening in the pairs of CH_3 and CH_2 resonances is due predominantly to mutual exchange within the instantaneous structure identified at −36 °C, e.g., eq 3, then the fast exchange, coalesced resonance positions should be at the average of the low-temperature positions after correction for the temperature dependence of the isotropic shifts. Extrapolation of the shift vs. $1/T$ graph to 71 °C yields CH_3 resonance positions at τ 26.4 and 51.9, or a predicted, averaged resonance at τ 39.2. This result can be favorably compared to the position of the emerging peak to the high-field side of the C_5H_5 signal (τ 39.4). A similar procedure for the CH_2 resonance yields 71 °C positions of τ 27.9 and 40.4, and an average of τ 34.2. This anticipated value is too near the C_5H_5 signal at τ 34.6 for complete resolution, but can explain the apparent asymmetry of the latter line shape. These results show that the high-temperature DME resonance positions are consistent with the structural/dynamic model of eq 3. The eventual broadening of the C_5H_5 resonance indicates the presence of an additional dynamic process at higher temperatures. Efforts to carry out accurate supplementary studies of line shapes as a function of concentration and added quantities of DME were frustrated by the extreme insolubility and sensitivity of $(C_5H_5)UCl_3(DME)$.



(3)

The ^1H NMR spectra of $(C_5H_5)UCl_3(THF)_2$ and $(CH_3C_5H_4)UCl_3(THF)_2$ were also examined. These exhibited broad, complex, temperature-dependent spectra suggestive of the presence of a number of species in dynamic equilibrium. This result is consistent with molecular weight measurements.[14]

Coordination Chemistry of $(C_5H_5)UCl_3$. It is known that $(C_5H_5)UCl_3$ forms adducts with a variety of oxygen donor ligands in addition to THF and DME. These ligands include phosphine oxides, amides, and dimethyl sulfoxide.[14b,34] It was of interest to also probe the tendency of $(C_5H_5)UCl_3$ to bind nitrogenous ligands. Thus, it was found that $(C_5H_5)UCl_3(THF)_2$ reacts with 2,2′-bipyridyl and 1,10-phenanthroline according to the equations

$$(C_5H_5)UCl_3(THF)_2 + 2,2'\text{-bpy} \rightarrow (C_5H_5)UCl_3(2,2'\text{-bpy}) + 2THF \qquad (4)$$

$$(C_5H_5)UCl_3(THF)_2 + \text{excess } 2,2'\text{-bpy} \rightarrow (C_5H_5)UCl_3(2,2'\text{-bpy})_{\sim 1.3} + 2THF \qquad (5)$$

$$(C_5H_5)UCl_3(THF)_2 + \text{excess } 1,10\text{-phen} \rightarrow (C_5H_5)UCl_3(1,10\text{-phen})_2 + 2THF \qquad (6)$$

The products of these reactions are rather insoluble. We presume the product of eq 5 to be a mixture. Whether greater than one 2,2′-bipyridyl or 1,10-phenanthroline moiety is actually accommodated within the uranium ion coordination sphere (with or without chloride ion displacement) or whether one ligand is simply held in the lattice remains to be determined. These compounds were not sufficiently soluble for NMR spectroscopy. The complex $CH_2(C_5H_4)_2UCl_2(2,2'\text{-bpy})$ is known to contain a bidentate 2,2′-bipyridyl moiety.[8a,b,15]

Conclusions

The results of this study indicate that, in both solution and in the solid state, $(C_5H_5)_2UCl_2$ prepared via the route of eq 1 is predominantly, if not exclusively, a mixture of the known compounds $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3(DME)$. Based upon solution NMR studies and analogy to the diffraction-determined molecular structure of $(CH_3C_5H_4)UCl_3(THF)_2$, it is proposed that $(C_5H_5)UCl_3(DME)$ is a monomeric complex with a pseudooctahedral coordination geometry. Those factors which stabilize various $(C_5H_5)_2UX_2$ species with respect to ligand redistribution appear to involve the bulk and possibly charge donor power of the X ligand. Thus, uranium(IV) bis(cyclopentadienyls) are relatively stable for X = $^-N(C_2H_5)_2$,[44] various thiolates,[44] $^-S_2CN(C_2H_5)_2$,[44] acetylacetonate,[45] and BH_4^-.[46] The stability reflects, among other factors, the tendency of these ligands to saturate the uranium coordination sphere. Alternative approaches to stabilize bis(cyclopentadienyl) compounds include linking the cyclopentadienyl rings together, e.g., $A(C_5H_4)_2$ complexes,[8a,b] or increasing their bulk. The latter device involves indenyl,[8c] pentamethylcyclopentadienyl,[8d,e] and ethyltetramethylcyclopentadienyl[8f] ligands. Initial chemical studies[8a,d,e] reveal such compounds to have a far richer and more diverse chemistry than the highly saturated $(C_5H_5)_3MX$ complexes.

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Supplementary Material Available: A listing of anisotropic thermal parameters for nonhydrogen atoms (Table III), calculated fractional atomic coordinates for hydrogen atoms (Table IV), a detailed Experimental Section for the X-ray crystallographic study of (η^5-$CH_3C_5H_4$)$UCl_3(THF)_2$, and a table of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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