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Notes

Synthesis of Tris(tetramethylcyclopentadienyl) Derivatives of the Actinide Metals: Molecular Structure of $[UCl(\eta\text{-}C_5Me_4H)_3]$

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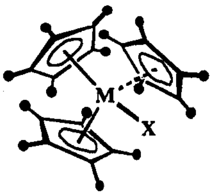
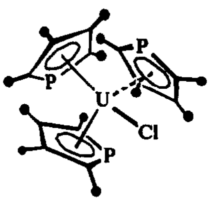
Summary: The reaction of $[Li(C_5Me_4H)]$ *with* MCl_4 *(M = U, Th) in tetrahydrofuran gives highly sterically congested tris(tetramethylcyclopentadienyl)actinide(IV) derivatives which have been characterized by variable-temperature NMR studies and, in the case of the uranium compound, by X-ray crystallography.*

There is considerable interest in the synthesis of very sterically encumbered metallocene derivatives of the f elements. For example, Evans has shown that, under suitable conditions, the permethylated compound $[Sm(\eta\text{-}C_5Me_5)_3]$ can be prepared,[1] while Schumann has recently used the tetramethylcyclopentadienyl ligand to synthesize $[M(\eta\text{-}C_5Me_4H)_3]$ (M = La, Sm).[2] For the actinide elements U and Th, neither the $[M(\eta\text{-}C_5Me_5)_3]$ nor the $[M(\eta\text{-}C_5Me_5)_3Cl]$ (1; X = *e.g.* H, Cl, Me) compounds have been synthesized,[3] despite the fact that the former, presumably trigonal,[1] complexes may be expected to be rather less sterically encumbered than tetravalent 1. In contrast, the facile synthesis $[U(\eta\text{-}C_4Me_4P)_3Cl]$ (2) has recently been reported, from which the authors concluded that the complexes $[U(\eta\text{-}C_5Me_5)_3Cl]$ are difficult to prepare because they are too electron rich.[4] Since it could be argued that tetramethylphospholyl is better compared to *tetra*methylcyclopentadienyl rather than *penta*methylcyclopentadienyl in its steric demand, we set out to prepare the complexes $[M(\eta\text{-}C_5Me_4H)_3Cl]$ (M = U, Th). Here we present the synthesis and characterization of these compounds, including variable-temperature NMR studies and the X-ray crystal structure of the uranium derivative.



1

• = Me



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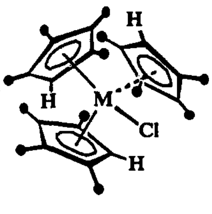

3a M = U, 3b M = Th

Results and Discussion

Chlorotris(tetramethylcyclopentadienyl)uranium (**3a**) and -thorium (**3b**) were obtained in 48% and 60% yields respectively by the reaction of 3 equiv of $Li(C_5Me_4H)$ with MCl_4 in tetrahydrofuran followed by crystallization from petroleum ether. Red **3a** and colorless **3b** are soluble in pentane and more polar solvents. They sublime with significant decomposition at 160 °C and 10^{-6} mbar.

In the ^1H NMR spectrum of paramagnetic **3a** the presence of four peaks assignable to ring methyl groups (*vide infra*) is consistent with rotation about the cyclopentadienyl–U metal bond being slow compared with the NMR time scale. As high as 363 K (above which it was not possible to obtain spectra) the same features could be discerned, indicating that the barrier to rotation is $\Delta G^* > 57$ kJ mol^{-1}.[5] In contrast, the ^1H NMR spectrum of $[U(\eta\text{-}C_4Me_4P)_3Cl]$ (**2**) at 303 K consisted of only two peaks for the methyl groups,[4] indicating that this species is in the fast exchange regime at this temperature. Lower temperature spectra were not reported, however, and so a direct comparison of the exchange barriers for **2** and **3a** is not possible at this stage.

Variable-temperature ^1H NMR spectra of diamagnetic **3b** in $[^2H_8]$toluene are shown in Figure 1. The four methyl resonances observed at 203 K coalesce at 235 K, corresponding to a value of $\Delta G^* = 48.1 \pm 0.4$ kJ mol^{-1} for rotation of the η^5 ring about the U–centroid axis. That this value is significantly less than the lower limit of that calculated for **3a** can be rationalized in terms of the larger covalent radius of thorium compared to uranium and thus greater steric crowding in isoleptic complexes of the latter. Notably, the resonance for the single C–H group of the tetramethylcyclopentadienyl rings did not shift significantly with temperature, mitigating against a fluxional process involving an η^5–η^1 ring slippage followed by rotation and recoordination.

Recrystallization of **3a** from toluene gave large red cubic crystals which were subjected to an X-ray structural

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

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(2) Schumann, H.; Glanz, M.; Hemling, H. *J. Organomet. Chem.* **1993,** *445,* C1.

(3) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981,** *103,* 6650.

(4) Gradoz, P.; Boisson, C.; Baudry, D.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1992,** 1720.

(5) Calculated using the simple Eyring equation, assuming that the outermost methyl resonances (Δν – 19 297 Hz at 263 K) are undergoing exchange at >363 K.

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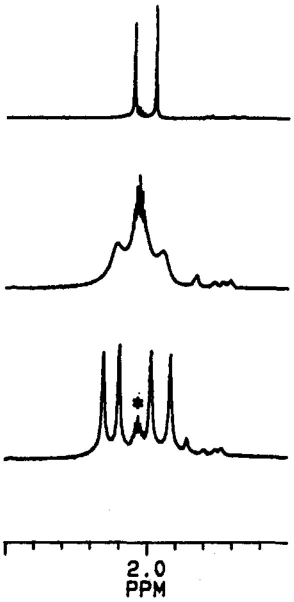

Figure 1. Variable-temperature ^1H NMR spectra in the methyl region of **3b** in [$^2H_8$]toluene (from top to bottom): 298, 233, and 213 K. The multiplet marked with an asterisk is due to residual protio solvent.

Table 1. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of [U(η-C_5Me_4H)$_3$Cl]

	x	y	z	U_{eq}[a] (Å^2)
U	0.02408(2)	0.02408(2)	0.02408(2)	0.02868(3)
Cl	0.09519(14)	0.09519(14)	0.09519(14)	0.0476(4)
C(1)	−0.0876(5)	0.0093(5)	0.0763(6)	0.047(7)
C(2)	−0.0593(5)	0.0571(6)	0.1138(5)	0.041(6)
C(3)	−0.0625(5)	0.1122(5)	0.0779(6)	0.043(6)
C(4)	−0.0898(5)	0.0981(5)	0.0189(5)	0.038(6)
C(5)	−0.1055(5)	0.0337(5)	0.0189(5)	0.046(6)
C(6)	−0.0415(6)	0.0516(6)	0.1829(6)	0.064(8)
C(7)	−0.0435(6)	0.1759(6)	0.1006(6)	0.057(8)
C(8)	−0.1133(6)	0.1488(6)	−0.0257(6)	0.064(7)
C(9)	−0.1435(6)	0.0010(6)	−0.0307(7)	0.064(8)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected Bond Lengths and Angles for [U(η-C_5Me_4H)$_3$Cl]

	Bond Lengths (Å)		
U–Cp[a]	2.520	U–C(5)	2.786(10)
U–Cl	2.637	C(1)–C(2)	1.44(2)
U–C(1)	2.658(11)	C(1)–C(5)	1.39(2)
U–C(2)	2.715(11)	C(2)–C(3)	1.41(2)
U–C(3)	2.886(12)	C(3)–C(4)	1.42(2)
U–C(4)	2.911(10)	C(4)–C(5)	1.42(2)
	Bond Angles (deg)		
Cp–U–Cp′	117.9	Cp–U–Cl	98.4

[a] Cp is the centroid of the C(1)–C(5) ring.

analysis. Tables 1–3 list experimental and structural data. The molecular structure of **3a** (Figure 2) is similar to that of [U(η-C_4Me_4P)$_3$Cl] (**2**),[4] particularly because in both structures the U–Cl vector lies on a crystallographic 3-fold axis. The U–C(Cp) lengths in **3a** (average 2.79 Å) are similar to those in a variety of bis(pentamethylcyclopentadienyl)uranium complexes (2.75 Å)[6] and somewhat shorter than those in **2** (average 2.90 Å). In **2** the three ring centroids and the phosphorus atoms lie in the same plane, while in **3a** C(1) lies out of the plane containing the three ring centroids by 0.55 Å. The carbon atoms of the methyl groups in **3a** are displaced out of the planes of their respective cyclopentadienyl rings by *ca.* 0.20 Å away from U(1), while in **2** three of the four methyl groups lie in the plane.

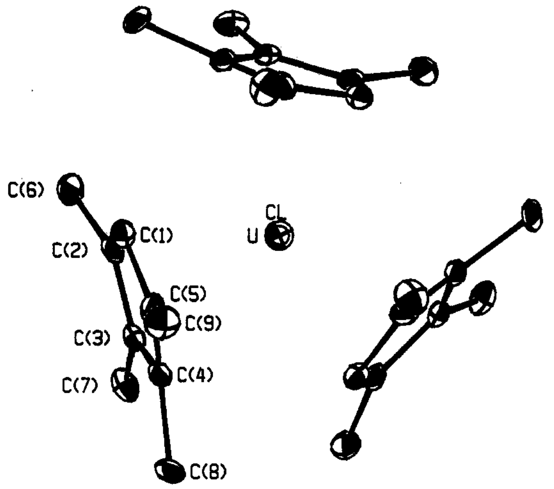

Figure 2. ORTEP[11] drawing of the molecular structure of **3a**.

Table 3. Experimental Data for the X-ray Diffraction Study of [U(η-C_5Me_4H)$_3$Cl]

formula	$C_{27}H_{39}ClU$
fw	637.1
cryst syst	cubic
space group	*I*43d (No. 220)
cell dimens	$a = 21.414(7)$ Å
cell vol	$V = 9819.59$ Å^3
Z	16
density (calcd)	1.72 g cm^{-3}
$F(000)$	4960
λ(Mo $K\alpha$)	0.710 69
μ	63.9 cm^{-1}
temp	293 K
cryst size	0.2 × 0.2 × 0.2 mm in capillary
scan mode	θ–2θ
$2\theta_{max}$	50°
total no. of rflns measd	4681
no. of unique rflns	878
no. of significant rflns, $\lvert F^2\rvert > 2\sigma(F^2)$	540
soln	heavy-atom methods
refinement	full-matrix least squares
quantity minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
no. of variables	100
no. of obsd rflns	540
R, R'	0.022, 0.027

The cyclic voltammogram of **3a** exhibited an irreversible reduction peak at −2.35 V (relative to ferrocene–ferrocenium), indicating that the uranium center is very electron rich. Our attempts so far at the synthesis of [U(η-C_5Me_4H)$_3$] from **3a** by reduction have been unsuccessful.

In conclusion, we have prepared tris(tetramethylcyclopentadienyl)actinide complexes, where the corresponding tris(pentamethylcyclopentadienyl) compounds have eluded synthesis, and found them to be highly sterically encumbered and very electron rich.

Experimental Section

All manipulations involving air- or water-sensitive materials were carried out under an inert atmosphere of argon using standard Schlenk techniques, or in a N_2-filled drybox. NMR samples were made up in the drybox, and the sample tubes were sealed *in vacuo*. Solvents were predried over activated 5-Å

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(6) Cramer, R. E.; Roth, S.; Edelman, F.; Bruck, M. A.; Cohn, K. C.; Gilje, J. W. *Organometallics* **1989**, *8*, 1192 and references therein.

molecular sieves and then distilled over potassium (tetrahydrofuran), sodium (toluene) or sodium–potassium alloy (petroleum ether (bp 40–60 °C)) under a slow passage of nitrogen. Deuterated solvents were dried over molten potassium and distilled. NMR spectra were recorded on a Bruker AC-250 spectrometer and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ 0 ppm). Low-resolution EI mass spectra were obtained on a VG 12-253 mass spectrometer at the SERC mass spectrometry service, University College, Swansea, U.K. Elemental Analyses were performed by Canadian Microanalytical Services Ltd., Delta, BC, Canada. Cyclic voltammetry studies were performed in tetrahydrofuran saturated with tetra-*n*-butylammonium tetrafluoroborate containing ferrocene as an internal standard, using a platinum-wire working electrode and silver reference electrode. $Li(C_5Me_4H)$ was prepared by literature methods.[7]

Synthesis of Chlorotris(1,2,3,4-tetramethylcyclopentadienyl)uranium(IV). Tetrahydrofuran (50 cm^3) was added at −40 °C to a mixture of $[Li(C_5Me_4H)]$ (0.75 g) and $[UCl_4]$ (0.73 g) and the mixture stirred at ambient temperature for 16 h. Volatiles were removed under reduced pressure, and the red residue was extracted with petroleum ether (2 × 100 mL). The combined extracts were filtered and reduced in volume until the onset of crystallization followed by cooling to −30 °C. The red microcrystals of $[UCl(C_5Me_4H)_3]$ thus obtained were isolated by filtration and dried *in vacuo* (0.6 g, 48%). ^1H NMR (250 MHz, $[^2H_8]$toluene; 263 K, all signals are singlets with $w_{1/2}$ = 10–30 Hz): δ 37.73 (9H), 12.13 (9H), 10.20 (9H), −3.02 (3H), −39.46 (9H). Anal. Calcd for $C_{27}H_{39}ClU$: C, 50.90; H, 6.17. Found: C, 51.10; H, 6.12. EI-MS: m/z 635 $[M^+]$ (10%), 514 $[M - C_5Me_4H]$ (100%).

The analogous thorium derivative was prepared similarly (yield 60%). ^1H NMR (250 MHz, $[^2H_8]$toluene, 203 K): δ 5.64 (3H), 2.15 (9H), 2.10 (9H), 1.98 (9H), 1.92 (9H). ^1H NMR (250 MHz, 298 K): δ 5.61 (3H), 2.04 (18H), 1.97 (18H). Anal. Calcd for $C_{27}H_{39}ClTh$: C, 51.39; H, 6.23. Found: C, 51.38; H, 6.17. EI-MS: m/z 630 $[M - 1]$ (5%), 509 $[M - C_5Me_4H - 1]$ (100%).

Crystallography. Data were collected on an Enraf-Nonius CAD4 diffractometer. A total of 540 reflections with $I > 3\sigma(I)$ were used after correction for absorption[8] (maximum 1.12, minimum 0.90). The intensity of standard reflections did not decay significantly. Solution was by heavy-atom methods and refinement by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms using the molEN program package[9] and scattering factors.[10] H(1) was fixed in its calculated position; other H atoms were omitted.

Acknowledgment. We thank the SERC for support.

Supplementary Material Available: Tables of crystal structure determination details, all bond lengths and angles, H atom parameters, displacement parameters, and least-squares planes for **3a** (6 pages). Ordering information is given on current masthead page.

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