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Chemistry of Trivalent Uranium Metallocenes: Electron-Transfer Reactions. Synthesis and Characterization of $[(MeC_5H_4)_3U]_2E$ (E = S, Se, Te) and the Crystal Structures of $[(MeC_5H_4)_3U]_2S$ and $(MeC_5H_4)_3UOPPh_3$

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The trivalent uranium metallocene $(MeC_5H_4)_3U{\cdot}THF$ reacts with COS, $SPPh_3$, $SePPh_3$, or $TeP(n\text{-}Bu)_3$ to form the bridging chalcogenide complexes $[(MeC_5H_4)_3U]_2E$, where E is S, Se, or Te. Crystals of $[(MeC_5H_4)_3U]_2S$ are monoclinic, $P2_1/c$, with a = 19.740 (6) Å, b = 8.302 (3) Å, c = 21.602 (4) Å, and β = 97.28 (3)° at 23 °C; for Z = 4 the calculated density is 1.920 g/cm^3. The structure was refined by full-matrix least squares to a conventional R factor of 0.053 by using 2061 data with $F^2 > 2\sigma(F^2)$. The average U–C distance is 2.77 ± 0.06 Å, the U–S distance is 2.60 (1) Å, and the U–S–U angle is 164.9 (5)°. Triphenylphosphine oxide does not behave in a similar fashion; the trivalent uranium coordination complex $(MeC_5H_4)_3UOPPh_3$ is instead isolated. Crystals of $(MeC_5H_4)_3UOPPh_3$ are monoclinic, $P2_1/n$, with a = 16.268 (3) Å, b = 17.948 (3) Å, c = 10.900 (2) Å, and β = 105.01 (2)° at 23 °C; for Z = 4 the calculated density is 1.628 g/cm^3. The structure was refined by full-matrix least squares to a conventional R factor of 0.028 [2427 data, $F^2 > 2\sigma(F^2)$]. The average U–C distance is 2.82 ± 0.04 Å, the U–O distance is 2.389 (6) Å, and the U–O–P angle is 162.8 (4)°.

Introduction

The trivalent uranium metallocene $(MeC_5H_4)_3U{\cdot}THF$ has recently been shown capable of acting as a one- or two-electron-transfer reagent toward unsaturated organic molecules.[1] In the previous paper, the reaction of trivalent uranium metallocenes with CS_2 to form the tetravalent uranium compounds $[(RC_5H_4)_3U]_2[CS_2]$ was discussed.[2] The geometry about the bridging CS_2 ligand was similar to that found in a number of transition-metal CS_2 compounds, but the C–S distances were grossly altered, suggesting complete transfer of two electrons into a C–S antibonding orbital of the coordinated carbon disulfide molecule.

The reactivity of carbonyl sulfide toward transition-metal complexes is different from that of carbon disulfide; the average CS bond dissociation energy in CS_2 is 107 kcal/mol, whereas in SCO bond dissociation energies for CO of 162 kcal/mol and for CS of 72 kcal/mol have been measured.[3] The dipolar resonance forms $^-S{-}C^+{=}O \leftrightarrow {}^-S{-}C{\equiv}O^+$ are clearly important in understanding why compounds as diverse as $Pt(PPh_3)_2$ and $(Me_5C_5)_2V$ cleave the CS bond in SCO to give $(Ph_3P)_2Pt(\mu\text{-}S)Pt(CO)(PPh_3)$[4] and $(Me_5C_5)_2V(S_2)$,[5] respectively.

The S–C bond in SCO is cleaved by $(MeC_5H_4)_3U{\cdot}THF$, giving the bridging sulfido complex $[(MeC_5H_4)_3U]_2[\mu\text{-}S]$. In order to extend this class of molecules to the congeners, i.e. $[MeC_5H_4)_3U]_2[\mu\text{-}E]$, where E is selenium or tellurium, an alternative synthetic route had to be developed. The readily available compounds $E{=}PR_3$ seemed to be likely precursors; the P=O bond dissociation energy is estimated to be 137 kcal/mol,[6] and the P=S bond energy decreases to 91 kcal/mol in $S{=}PR_3$.[7] Phosphine telluride complexes are generally unstable at room temperature with respect to formation of metallic tellurium,[8] suggesting the phosphorus–tellurium bond is rather weak.

In this paper, we describe the reaction of $(MeC_5H_4)_3U{\cdot}THF$ with SCO, $SPPh_3$, $SePPh_3$, and $TeP(n\text{-}Bu)_3$ to form the bridging chalcogenide complexes $[(MeC_5H_4)_3U]_2E$.[9] In addition, we show that $OPPh_3$ does not react in a similar fashion, instead forming the trivalent uranium coordination complex $(MeC_5H_4)_3UOPPh_3$.

Results and Discussion

Addition of an excess of SCO or 1 molar equiv of $SPPh_3$ to an ether solution of $(MeC_5H_4)_3U{\cdot}THF$ gives red needles of $[(MeC_5H_4)_3U]_2[\mu\text{-}S]$. The ^1H and ^{13}C NMR spectra contain only one type of MeC_5H_4 resonance, and the line width in the ^1H NMR spectrum suggets the molecule is based on tetravalent uranium (see Experimental Section for details).[2] The related selenium and tellurium complexes $[(MeC_5H_4)_3U]_2[\mu\text{-}E]$, where E is Se or Te, can be prepared by the reaction of $SePPh_3$ or $TeP\text{-}n\text{-}Bu_3$ with $(MeC_5H_4)_3U{\cdot}THF$ and have similar NMR spectra.

Table I. Magnetic Susceptibility of $[(MeC_5H_4)_3U]_2[\mu\text{-}X]$

compd	μ_{eff},$^{a-c}$ μ_B	T, K	Θ, K	χ_m	ref
X = S	2.93	100–300	–84.5	2.15	this work
X = Se	2.85	110–300	–72.2	2.03	this work
X = Te	3.02	120–300	–11.8	2.29	this work
X = CS_2	3.01	120–300	–12.5	2.26	2
X = PhNCO	2.87	110–300	–89.5	2.06	1

[a] Magnetic moment as calculated from the slope of $\chi_m(\text{cor})^{-1}$ vs. T (K) where $\chi_m(\text{cor})^{-1} = [T - \Theta]\chi_m^{-1}$. [b] The data were recorded at a magnetic field strength of 40 kG. No field dependence was observed when some data were recorded at 5 kG. [c] Per uranium.

Magnetic susceptibility data of the compounds $[(MeC_5H_4)_3U]_2[\mu\text{-}X]$, where X is S, Se, Te, CS_2, or PhNCO, are listed in Table I, and a representative curve is shown in Figure 1. The plots of χ_m^{-1} as a function of T (K) are similar in shape to those of other $Cp_3U^{IV}X$ compounds, where X is an anionic ligand.[9] The apparent lack of coupling between the paramagnetic centers will be discussed below.

The synthesis of the series of chalcogenide-bridged complexes allows us to assign the U–E–U stretching frequencies by inspection of the infrared spectra. Only one absorption appears to be different in the U–S and U–Se compounds at 355 and 215 cm^{-1}, respectively. The U–Te–U stretch would be expected to be <200 cm^{-1}, outside our current spectroscopic capabilities. These frequencies are in agreement with the limited number of M–E–M assignments that have been made.[10] The observation of a single stretching frequency in the IR spectrum is consistent with a linear or nearly

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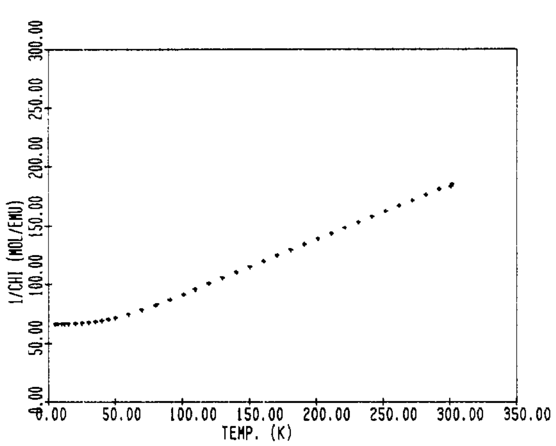

Figure 1. Plot of $\chi_m(\mathrm{cor})^{-1}$ vs. T (K) for $[(\mathrm{MeC_5H_4})_3\mathrm{U}]_2[\mu\text{-Te}]$.

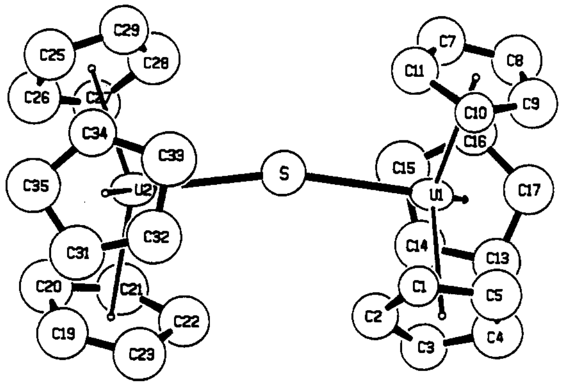

Figure 2. ORTEP drawing of $[(\mathrm{CH_3C_5H_4})_3\mathrm{U}]_2[\mu\text{-S}]$. Due to the severe thermal motion of the Cp rings the methyl groups were not found. The thermal ellipsoids are at the 50% probability level.

Table II. Positional Parameters in $[(\mathrm{CH_3C_5H_4})_3\mathrm{U}]_2\mathrm{S}$

atom	x	y	z
U(1)	0.34938 (6)	−0.03890 (17)	0.13625 (5)
U(2)	0.18714 (6)	0.04473 (17)	0.30270 (6)
S	0.2549 (9)	−0.0064 (12)	0.2084 (5)
C(1)	0.4177 (16)	0.227 (4)	0.1874 (14)
C(2)	0.4107 (17)	0.113 (4)	0.2333 (5)
C(3)	0.4536 (17)	−0.018 (4)	0.2275 (15)
C(4)	0.4853 (19)	0.017 (4)	0.1756 (6)
C(5)	0.4638 (18)	0.164 (4)	0.1496 (17)
C(7)	0.2487 (17)	0.017 (4)	0.0412 (16)
C(8)	0.3013 (17)	−0.034 (5)	0.0099 (17)
C(9)	0.3454 (19)	0.093 (4)	0.0209 (17)
C(10)	0.3253 (15)	0.221 (4)	0.0558 (14)
C(11)	0.2611 (16)	0.170 (4)	0.0683 (17)
C(13)	0.4214 (18)	−0.325 (5)	0.1471 (16)
C(14)	0.3671 (18)	−0.343 (5)	0.1824 (17)
C(15)	0.3020 (19)	−0.353 (6)	0.1482 (17)
C(16)	0.3172 (17)	−0.341 (4)	0.0866 (16)
C(17)	0.3873 (17)	−0.332 (5)	0.0872 (16)
C(19)	0.2485 (19)	−0.001 (5)	0.4269 (18)
C(20)	0.2015 (19)	−0.128 (5)	0.4136 (19)
C(21)	0.2418 (20)	−0.206 (5)	0.3741 (19)
C(22)	0.3007 (19)	−0.137 (5)	0.3546 (17)
C(23)	0.3047 (19)	−0.003 (5)	0.3945 (18)
C(25)	0.0472 (19)	0.045 (5)	0.2737 (16)
C(26)	0.0634 (20)	−0.090 (4)	0.3113 (19)
C(27)	0.0967 (19)	−0.212 (4)	0.2831 (17)
C(28)	0.0982 (20)	−0.156 (4)	0.2228 (17)
C(29)	0.0680 (18)	−0.003 (4)	0.2184 (16)
C(31)	0.2129 (20)	0.334 (5)	0.3612 (19)
C(32)	0.2438 (20)	0.343 (5)	0.3073 (19)
C(33)	0.1976 (20)	0.356 (6)	0.2540 (17)
C(34)	0.1377 (18)	0.356 (5)	0.2828 (17)
C(35)	0.1422 (20)	0.348 (5)	0.3475 (18)

Table III. Distances (Å) and Angles (deg) in $[(\mathrm{CH_3C_5H_4})_3\mathrm{U}]_2\mathrm{S}$

U(1)–S(1)	2.59 (1)	U(2)–S(2)	2.61 (1)
U(1)–C(1)	2.75 (4)	U(2)–C(19)	2.83 (4)
U(1)–C(2)	2.61 (4)	U(2)–C(20)	2.77 (4)
U(1)–C(3)	2.67 (4)	U(2)–C(21)	2.73 (4)
U(1)–C(4)	2.75 (4)	U(2)–C(22)	2.82 (4)
U(1)–C(5)	2.81 (4)	U(2)–C(23)	2.88 (4)
U(1)–C(7)	2.71 (4)	U(2)–C(25)	2.76 (4)
U(1)–C(8)	2.77 (4)	U(2)–C(26)	2.71 (4)
U(1)–C(9)	2.71 (4)	U(2)–C(27)	2.78 (4)
U(1)–C(10)	2.77 (3)	U(2)–C(28)	2.84 (4)
U(1)–C(11)	2.75 (4)	U(2)–C(29)	2.81 (4)
U(1)–C(13)	2.76 (4)	U(2)–C(31)	2.73 (5)
U(1)–C(14)	2.72 (4)	U(2)–C(32)	2.71 (5)
U(1)–C(15)	2.79 (5)	U(2)–C(33)	2.81 (5)
U(1)–C(16)	2.77 (4)	U(2)–C(34)	2.78 (4)
U(1)–C(17)	2.79 (4)	U(2)–C(35)	2.88 (4)
U(1)–Cp(1)[a]	2.44	U(2)–Cp(4)	2.54
U(1)–Cp(2)	2.48	U(2)–Cp(5)	2.51
U(1)–Cp(3)	2.50	U(2)–Cp(6)	2.52
av U–Cp	2.50 (4)	av U–C(ring)	2.77 (6)
Cp(1)–U(1)–Cp(2)	116.5	Cp(2)–U(1)–S	101.7
Cp(1)–U(1)–Cp(3)	116.0	Cp(3)–U(1)–S	101.5
Cp(2)–U(1)–Cp(3)	115.1	Cp(4)–U(2)–S	103.3
Cp(4)–U(2)–Cp(5)	117.4	Cp(5)–U(2)–S	100.0
Cp(4)–U(2)–Cp(6)	114.2	Cp(6)–U(2)–S	102.7
Cp(5)–U(2)–Cp(6)	115.8	U(1)–S–U(2)	164.9 (4)
Cp(1)–U(1)–S	102.4		

[a] Cp(1)–Cp(6) are cyclopentadienyl ring of atoms C(1)–C(5), C(7)–C(11), C(13)–C(17), C(19)–C(23), C(25)–C(29), and C(31)–C(35), respectively.

linear U–E–U skeleton found for the sulfur compound as shown by X-ray crystallography.

An ORTEP diagram of $[(\mathrm{MeC_5H_4})_3\mathrm{U}]_2[\mu\text{-S}]$ is shown in Figure 2. Positional parameters are given in Table II, some bond lengths and bond angles are given in Table III, and crystal data are given in Table IV. The averaged U–C(ring) distance of 2.71 ± 0.06 Å and the averaged ring centroid–uranium–ring centroid angle, 116 (2)°, are in the range expected for $\mathrm{Cp_3U^{IV}X}$ compounds.[1,11] The most important structural features of the complex are the slightly bent U–S–U angle of 164.9 (4)° and the average U–S distance of 2.60 (1) Å. The two independent U–S distances are statistically equivalent.

There are very few examples of compounds with a single sulfur atom bridging two transition-metal centers. Within this group, there are two distinct structural classes. The first class contains nearly linear M–S–M angles (ranging from 159 to 180°) with M–S distances that are shorter than expected for a M–S single bond.[12] These trends are rationalized by suggesting that the sulfide group can act as a π-donor and perhaps as a π-acceptor ligand toward the transition-metal center.[13] The compounds $(\mathrm{Ph_3P})_2\mathrm{Pt(S)Pt(PPh_3)CO}$,[14a] $[(\mathrm{salen})\mathrm{Fe}]_2\mathrm{S}$,[14b] and $[\mathrm{CpW(CO)_3}]_2\mathrm{S}$[14c] constitute the second class of M–S–M compounds, with M–S–M angles of 73.1 (4), 121.8 (1), and 127.0(2)° respectively. The tungsten compound is particularly important, as both $[\mathrm{CpCr(CO)_2}]_2\mathrm{S}$[12b,d] and $\mathrm{K_6[(CN)_6Mo]_2S}$[12c] contain the nearly linear M–S–M angles and short M–S bonds, while the bent W compound has a W–S bond length typical of a single bond, implying that linearity and short M–S distances are manifestations of the same bonding mechanism.

The U–S bond distance in $[(\mathrm{MeC_5H_4})_3\mathrm{U}]_2\mathrm{S}$, 2.60 (1) Å, is the shortest U–S bond reported. A number of mono and dithio-

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Table IV. Crystallographic Experimental Details

	$[(CH_3C_5H_4)_3U]_2S$	$(CH_3C_5H_4)_3$-$UOPPh_3$
a, Å	19.740 (6)	16.268 (3)
b, Å	8.302 (3)	17.948 (3)
c, Å	21.602 (4)	10.900 (2)
β, deg	97.28 (3)	105.01 (2)
cryst syst; space group	monoclinic; $P2_1/c$	monoclinic; $P2_1/n$
V, Å^3	3512	3074
d_{calcd}, g/cm^3	1.920	1.628
Z	4	4
temp, °C	23	23
empirical formula	$C_{36}H_{42}SU_2$	$C_{36}H_{36}OPU$
mol wt	1014.9	753.69
color	red	brown
wavelengths (for Kα_1, Kα_2), Å	0.709 30, 0.713 59	0.709 30, 0.713 59
cryst size, mm	0.12 × 0.16 × 0.31	0.13 × 0.16 × 0.26
μ, cm^{-1}	88.7	50.8
range abs cor	1.62–2.06	1.71–2.17
cryst decay, %	3	1
limits 2θ, deg	4–45	4–45
scan width, deg	1.50 + 0.693(tan θ)	1.80 + 0.693(tan θ)
range *hkl*	−21 to +21,0 to 8,−23 to +23	−17 to 17,0 to 19,−11 to 11
no. of stds; freq of stds	3; 250	3; 250
no. of reflcns	9204	8075
no. of unique reflcns	4609	4048
R_{int}^{b}	0.043	0.048
no. of nonzero weighted data	2061 ($F^2 > 2\sigma$)	2427 ($F^2 > 2\sigma$)
p^c	0.04	0.02
no. of params	148	352
R^d (nonzero weighted data)	0.053	0.028
R_w^{e}	0.068	0.025
goodness of fit^f	2.14	1.16
max shift/esd	0.08	0.03
max residuals, e/Å^3	3.4	1.08
min residual, e/Å^3	−1.9	−1.06

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 37 reflections (20° $< 2\theta <$ 33°) for the $OPPh_3$ complex, and 23 reflections (20° $< 2\theta <$ 31°) for the S complex. [b] R_{int} is the agreement factor between equivalent or multiply measured reflections $= \sum[I(hkl) - I(hkl)_{av}]/\sum I(hkl)_{av}$. [c] For the least squares, the assigned weights on the data are $1.0/\sigma(F)^2$ and were derived from $\sigma(F^2) = [S^2 + pF^2]$, where S^2 is the variance due to counting statistics and p is assigned a value that adjusts the weights of the stronger reflections to be more in line with the rest of the data. [d] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [f] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o is the number of observations and n_v is the number of variables.

Table V. Positional Parameters in $(CH_3C_5H_4)_3UOP(C_6H_5)_3$

atom	*x*	*y*	*z*
U	0.24958 (2)	0.06736 (2)	0.04502 (3)
P	0.22138 (14)	0.18911 (14)	−0.25260 (23)
O	0.2293 (4)	0.1301 (3)	−0.1539 (6)
C(1)	0.1555 (9)	0.0315 (7)	0.3207 (13)
C(2)	0.1463 (8)	0.0880 (6)	0.2115 (13)
C(3)	0.0887 (7)	0.0876 (7)	0.0913 (15)
C(4)	0.1024 (8)	0.1533 (9)	0.0273 (11)
C(5)	0.1668 (8)	0.1938 (6)	0.1052 (13)
C(6)	0.1928 (7)	0.1544 (8)	0.2181 (11)
C(7)	0.2978 (8)	−0.1323 (6)	0.1892 (11)
C(8)	0.2511 (9)	−0.0920 (5)	0.0627 (11)
C(9)	0.1655 (7)	−0.0712 (7)	0.0248 (10)
C(10)	0.1461 (6)	−0.0427 (5)	−0.0977 (11)
C(11)	0.2205 (8)	−0.0459 (5)	−0.1412 (10)
C(12)	0.2854 (6)	−0.0759 (6)	−0.0406 (11)
C(13)	0.3904 (8)	0.2392 (7)	0.2266 (12)
C(14)	0.3947 (6)	0.1588 (7)	0.1787 (12)
C(15)	0.4119 (6)	0.1380 (8)	0.0640 (13)
C(16)	0.4237 (6)	0.0615 (10)	0.0643 (16)
C(17)	0.4139 (8)	0.0314 (8)	0.1786 (18)
C(18)	0.3922 (7)	0.0924 (9)	0.2498 (11)
C(19)	0.3139 (5)	0.1898 (5)	−0.3132 (8)
C(20)	0.3430 (6)	0.2521 (5)	−0.3635 (9)
C(21)	0.4147 (6)	0.2481 (6)	−0.4093 (10)
C(22)	0.4563 (6)	0.1827 (7)	−0.4073 (10)
C(23)	0.4291 (7)	0.1196 (6)	−0.3576 (10)
C(24)	0.3570 (6)	0.1232 (6)	−0.3111 (9)
C(25)	0.1312 (5)	0.1712 (5)	−0.3847 (8)
C(26)	0.0738 (6)	0.1163 (6)	−0.3743 (9)
C(27)	0.0035 (7)	0.1028 (6)	−0.4769 (12)
C(28)	−0.0075 (7)	0.1441 (7)	−0.5887 (11)
C(29)	0.0493 (7)	0.1980 (7)	−0.5984 (10)
C(30)	0.1198 (6)	0.2121 (6)	−0.4946 (10)
C(31)	0.2060 (5)	0.2798 (5)	−0.1926 (8)
C(32)	0.1305 (6)	0.3166 (6)	−0.2221 (9)
C(33)	0.1187 (7)	0.3827 (7)	−0.1655 (11)
C(34)	0.1851 (7)	0.4118 (5)	−0.0736 (10)
C(35)	0.2629 (7)	0.3767 (6)	−0.0419 (10)
C(36)	0.2741 (6)	0.3106 (5)	−0.1015 (9)

carbamate uranyl complexes, binary and ternary sulfide complexes, and a uranyl η^2-disulfide complex are reported with U–S distances from 2.69 to 2.95 Å.[15] Only one other $(MeC_5H_4)_3U$–S–R (R = ($\eta^{\cdot}$CS)U$(MeC_5H_4)_3)^2$ compound has been structurally characterized, and the U–S distance (2.792 (3) Å) and bent U–S–R angle (112.4 (7)°) support the π-bonding explanation for the bridging-sulfido geometry.

There are a number of structurally characterized U(IV) and U(V) compounds with alkoxo,[16] amido,[17] or imido[18] ligands containing nearly linear (alkoxo, imido) or planar (amido) geometries that have been attributed to some type of M–L π bonding (the difference between the U–S distance here and the U–O distance in the uranium alkoxide complex $(MeC_5H_4)_3U$–O–R (R = $(MeC_5H_4)_3U$ (η^2-NC–)^1, 0.49 Å, is close to the 0.4-Å[19] value predicted with radius summation arguments[11]), but an extension of this concept to second-row elements on the basis of one structurally characterized example is not warranted at this time. A more complete set of bond lengths is needed before we can address this question in a meaningful way.

An alternative interpretation of the nearly linear sulfido geometry is that if the bonding in this complex is primarily electrostatic, the U–S–U angle may be due to the repulsive interaction between the two $(MeC_5H_4)_3U$ groups. From this model, a bent geometry containing stereochemically active lone pairs on the bridging atom would be predicted for the bridging Se or Te compounds, where the increased U–E distance reduces the repulsive interaction between the cyclopentadienyl groups on the uranium atoms. The model also predicts a linear U–O–U arrangement, since the radius of O is 0.4 Å[19] shorter than S and

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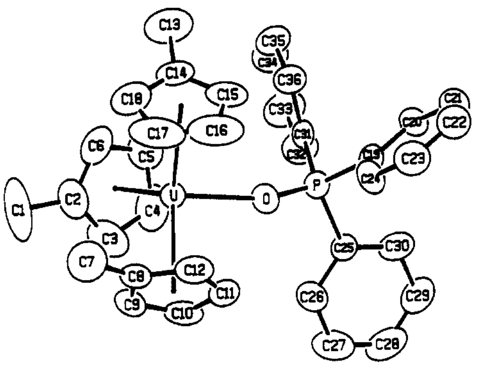

Figure 3. ORTEP drawing of $(MeC_5H_4)_3UOPPH_3$. The thermal ellipsoids are at the 50% probability level.

the ligand–ligand repulsions must therefore increase on bending. It has not yet been possible to grow acceptable single crystals of the Se or Te complex, but this is being pursued.

There is no observed magnetic interaction between the two uranium centers to 5 K (Table I). The χ_m^{-1} curves are of the same form as those found for Cp_3UX systems[9] and $[Cp_3U]_2[X]$ where X is CS_2 or PhNCO. The curves follow Curie–Weiss behavior from ca. 100 to 300 K. Below 100 K the slope of the curve changes due to depopulation of excited crystal field states. Below ca. 10 K, the susceptibility becomes temperature-independent. The values for μ_{eff} are in the range of those reported for other Cp_3UX compounds, but without knowing the energies or wave functions of the ground or excited states, it is impossible to rigorously interpret the data.

In an attempt to synthesize the bridging oxide complex, we allowed $(MeC_5H_4)_3U·THF$ to react with Ph_3PO, but instead the simple coordination complex $(MeC_5H_4)_3UOPPh_3$ was isolated. This reactivity pattern was previously reported in the low-valent f-metal complex $(C_5Me_5)_2SmOPPh_3(thf)$.[20] An ORTEP diagram is shown in Figure 3, positional parameters are given in Table V, some bond lengths and angles are given in Table VI, and crystal data is given in Table IV. The complex is pseudotetrahedral, with an average ring centroid–uranium–ring centroid angle of 117°. The averaged U–C distance is 2.82 ± 0.04 Å, the U–ring centroid distance is 2.56 ± 0.02 Å, the U–O distance is 2.389 (6) Å, and the U–O–P angle is 162.8 (4)°. The U–C distance is similar to those in other Cp_3UL complexes,[21] and the uranium oxygen distance, while slightly longer than the U–O distance found in U(IV),[22] U(V),[23] and U(VI)[24] $OPPh_3$ complexes, is reasonable considering the large coordination number (10) and low oxidation state (III) of the metal. The nearly linear U–O–P angle has been observed in all but one U–$OPPh_3$ complex.[22a]

Table VI. Selected Distances (Å) and Angles (deg) in $(MeC_5H_4)_3UOPPh_3$

U–O	2.389 (6)	U–C(15)	2.888 (10)
U–C(2)	2.798 (10)	U–C(16)	2.788 (10)
U–C(3)	2.815 (9)	U–C(17)	2.769 (11)
U–C(4)	2.812 (10)	U–C(18)	2.808 (11)
U–C(5)	2.802 (11)	U–Cp(1)[a]	2.538 (7)
U–C(6)	2.784 (10)	U–Cp(2)	2.564 (6)
U–C(8)	2.867 (8)	U–Cp(3)	2.563 (8)
U–C(9)	2.819 (11)	P–O	1.492 (6)
U–C(10)	2.793 (9)	P–C(19)	1.794 (9)
U–C(11)	2.824 (9)	P–C(25)	1.799 (8)
U–C(12)	2.847 (10)	P–C(31)	1.796 (9)
U–C(14)	2.935 (9)	av U–C	2.82 ± 0.04
O–U–Cp(1)	99.3	O–P–C(19)	110.3 (4)
O–U–Cp(2)	98.7	O–P–C(25)	110.5 (4)
O–U–Cp(3)	100.7	O–P–C(31)	112.0 (4)
Cp(1)–U–Cp(2)	117.4	C(19)–P–C(25)	107.2 (4)
Cp(1)–U–Cp(3)	117.6	C(19)–P–C(31)	109.7 (4)
Cp(2)–U–Cp(3)	116.9	C(25)–P–C(31)	107.0 (4)
U–O–P	162.8 (4)		

[a] Cp(1)–Cp(3) represent the centers of atom groups C(2)–C(6), C(8)–C(12) and C(14)–C(18), respectively.

As to mechanism, using SPR_3 as an example, we would suggest as a working hypothesis that coordination to the metal center followed by single-electron transfer gives $Cp_3U^{IV}[S–PR_3]^-$. Coordination of a second molecule of Cp_3U to the lone pair of electrons on sulfur followed by another single-electron transfer gives $[Cp_3U]_2[S]$ and PR_3. This mechanistic speculation accounts for the inability of $OPPh_3$ to act as a source of O^{2-} since its first reduction potential is −2.5 V[25a] and the oxidation potential of $(MeC_5H_4)_3U$ is estimated to be ca. −1.5 V.[25b] Further, the irreversible reduction potentials (two-electron process) of $SPPh_3$ and $SePPh_3$ are −2.7 and −2.7 V, respectively.[25c] All of the values are relative to SCE.

Experimental Section

All operations were done under nitrogen. Microanalyses were performed by the microanalytical laboratory of this department. The ^1H and ^{13}C NMR spectra were measured at 89.56 and 22.50 MHz, respectively, on a JEOL-FX90Q instrument. Chemical shifts are reported in δ relative to tetramethylsilane with positive values to high frequency. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 580 instrument. Mass spectra were obtained on a AEI-MS-12 machine equipped with a direct inlet using electron ionization. Magnetic susceptibility measurements were performed as previously described.[26]

$[(MeC_5H_4)_3U]_2S$. (a) From SCO. A solution of $(CH_3C_5H_4)_3U·THF$[1] (1.0 g, 0.0018 mol) in ether (50 mL), was exposed to vacuum until the ether began to reflux. An atmosphere of carbonyl sulfide was then introduced, yielding an immediate red precipitate. After the mixture was stirred for 10 min, the volatile material was removed under reduced pressure. The residue was extracted with a toluene/hexane mixture (20 mL/10 mL, 15 mL/15 mL, 15 mL/5 mL), the combined extracts were filtered, and the filtrate was cooled to −20 °C. The dark red needles were collected and dried under reduced pressure in 23% yield (0.40 g); mp 274.5–275.5 °C. Anal. Calcd. for $C_{36}H_{42}U_2S$: C, 44.0; H, 4.31; S, 3.26. Found: C, 44.4; H, 4.41; S, 3.10. IR: 1240 w, 1170 w, 1047 w, 1035 m, 973 w, 930 w, 888 w, 847 m, 795 w, 768 s, 727 m, 693 w, 604 m, 470 w, 358 s, 330 w, 236 s cm^{-1}. ^1H NMR (C_6D_6, 32 °C): −8.88 (2 H), −9.09 (3 H), −13.41 (2 H). The line width at half-height varies from 0.5 to 4 Hz in all the U(IV) species described in this paper. ^{13}C NMR (C_6D_6, 34 °C): 203.82, 201.09, 199.73, −34.05.

(b) From $SPPh_3$. A solution of $(CH_3C_5H_4)_3U·THF$ (0.91 g, 1.7 mmol) in diethyl ether (20 mL) was added to a suspension of $SP(C_6H_5)_3$ (0.51 g, 1.7 mmol) in diethyl ether (10 mL). The red mixture was stirred for 1 h, and the diethyl ether was removed under reduced pressure. The red residue was extracted with toluene (25 mL), the resulting mixture was filtered, and the filtrate was cooled to −20 °C. The dark red needles were shown to be the sulfide by the melting point and IR and ^1H NMR spectroscopy.

$[(MeC_5H_4)_3U]_2Se$. Triphenylphosphine selenide[27] (0.77 g, 0.0023 mol) in toluene (10 mL) was added to $(CH_3C_5H_4)_3U·THF$ (1.4 g, 0.0026 mol)

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dissolved in toluene (40 mL). The red suspension was stirred for 1 h, and the suspension was filtered. The residue was dissolved in toluene (7 mL), the filtrates were combined, and cooling (−20 °C), yielded red needles (0.25 g, 18%), mp 240–241 °C. The mother liquor was concentrated to 20 mL, and cooling (−20 °C), afforded a second crop of crystals (0.27 g, 20%). Anal. Calcd. for $C_{36}H_{42}U_2Se$: C, 42.0; H, 4.11. Found: C, 41.3; H, 3.90. The mass spectrum gave a M^+ peak at *m/e* 1030. IR: 1980 w, br, 1490 w, 1240 w, 1045 w, 1035 m, 975 w, 928 w, 888 w, 845 m, 770 s, 725 m, 693 w, 605 m, 590 w, 470 w, 327 m, 238 m, 216 s cm^{-1}. ^{1}H NMR (C_6D_6, 31 °C): −8.31 (3 H), −8.69 (2 H), −14.50 (2 H). ^{13}C NMR (C_6D_6, 32 °C): 214.6, 207.6, 205.9, −33.34.

$[(MeC_5H_4)_3U]_2Te$. Tri-*n*-butylphosphine telluride[8] (0.27 g, 0.000 88 mol) in diethyl ether (30 mL) was added to $(CH_3C_5H_4)_3U{\cdot}THF$ (1.02 g, 0.001 84 mol) in ether (30 mL). A precipitate formed immediately, and the solution turned dark green. The mixture was stirred for 1 h, and the volatile material was removed under reduced pressure. The residue was extracted with toluene (30 mL), the resulting mixture was filtered, and the filtrate concentrated to ca. 10 mL. Cooling (−20 °C) afforded dark green bars (0.28 g, 28%), mp 200–200.5 °C. Anal. Calcd. for $C_{36}H_{42}U_2Te$: C, 40.1; H, 3.93; Te, 11.8. Found: C, 42.1; H, 4.03; Te, 10.4. The mass spectrum showed a M^+ at *m/e* 1080. IR: 1970 w, br, 1941 w, 1240 w, 1023 s, 972 w, 930 w, 845 s, 770 s, 725 s, 692 m, 603 m, 467 m, 330 s, 240 s cm^{-1}. ^{1}H NMR (C_6D_6, 31 °C): −8.03 (3 H), −9.73 (2 H), −11.83 (3 H). ^{13}C NMR (C_6D_6, 32 °C): 236.0 (s), 227.5 (d, *J* = 167.1 Hz), 217.2 (d, *J* = 167.1), −36.39 (q, *J* = 126.0 Hz).

$(MeC_5H_4)_3UOPPh_3$. Triphenylphosphine oxide (0.17 g, 0.000 61 mol) in diethyl ether (30 mL) was added to $(CH_3C_5H_4)_3U{\cdot}THF$ (0.71 g, 0.0013 mol) in diethyl ether (30 mL). A red solid slowly formed on stirring for 2.5 h. The diethyl ether was evaporated, and the brown residue was extracted with toluene (50, 30 mL). The combined extracts were filtered, and cooling (−20 °C), afforded red crystals (0.24 g, 52% based on OPR_3), mp 238–238.5 °C. Anal. Calcd. for $C_{36}H_{36}POU$: C, 57.4; H, 4.81; P, 4.11. Found: C, 57.80; H, 4.73; P, 3.48. The compound showed a M^+ peak at *m/e* 753. IR: 1585 w, 1435 s, 1310 w, 1185 w, 1150 s, 1120 s, 1088 s, 1070 w, 1043 w, 1031 m, 1022 w, 996 w, 992 w, 942 w, 847 m, 821 m, 813 m, 765 m, 750 s, 725 s, 690 s, 610 m, 544 s, 520 w, 478 m, 445 w, 412 w, 324 m, 308 w, 294 w, 210 m cm^{-1}. ^{1}H NMR (C_6D_6, 32 °C): 5.58 (3 H), 4.90 (6 H), −2.60 (6 H), −11.42 (9 H), −12.35 (6 H), −15.01 (6 H).

X-ray Crystallography on $[(MeC_5H_4)_3U]_2[\mu\text{-}S]$. The crystals, because of their air sensitivity, were sealed inside thin-walled quartz capillaries under argon and mounted on a modified Picker FACS-1 automatic diffractometer equipped with a Mo Kα X-ray tube and a graphite monochromator. Sets of θ–2θ scan data were collected and corrected for crystal decay, absorption (analytical method),[28] and Lorentz and polarization effects. The uranium atoms were located with the use of three-dimensional Patterson maps, and subsequent least-squares refinement and electron-density maps revealed the locations of the other atoms. The structures were refined by full-matrix least squares. Only the U and S atoms were refined with anisotropic thermal parameters. The methylcyclopentadienyl rings suffered extreme thermal motion, and Fourier maps through the planes of the rings showed the electron density spread about the ring with poor resolution of the atoms. The methyl atoms were not included; all attempts to refine any of the number of small peaks observed in the difference Fourier maps that might be methyl groups, even with severe distance restraints, resulted in large and unrealistic thermal parameters. The carbon atoms in the ring were refined with isotropic thermal parameters and restrained C–C distances of 1.39 ± 0.01 Å. Atomic scattering factors of Doyle and Turner[29] were used, and anomalous dispersion corrections were applied.[30] With the exception of the ORTEP program all of the computer programs used are our own.

X-ray Crystallography on $(MeC_5H_4)_3UOPPh_3$. Crystals were sealed inside quartz capillaries because of their reactivity in the atmosphere. The structure was solved by Patterson and Fourier methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Nonmethyl hydrogen atoms were included in their calculated positions with isotropic temperature factors but not refined. A full-matrix least-squares program was used. Atomic scattering factors for all the atoms were taken from ref 32.

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Registry No. $[(MeC_5H_4)_3U]_2S$, 101630-44-8; $[(MeC_5H_4)_3U]_2Se$, 101630-45-9; $[(MeC_5H_4)_3U]_2Te$, 101652-31-7; $(CH_3C_5H_4)_3U{\cdot}THF$, 78869-46-2; $SPPh_3$, 3878-45-3; $SePPh_3$, 3878-44-2; $TeP(Bu\text{-}n)_3$, 2935-46-8; $OPPh_3$, 791-28-6; $(MeC_5H_4)_3U(OPPh_3)$, 101630-46-0; carbonyl sulfide, 463-58-1.

Supplementary Material Available: Listings of thermal parameters and additional distances for $[(MeC_5H_4)_3U]_2[\mu\text{-}S]$ and thermal parameters, hydrogen isotropic thermal parameters, least-squares planes, and additional distances and angles for $(MeC_5H_4)_3UOPPh_3$ (7 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (34 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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