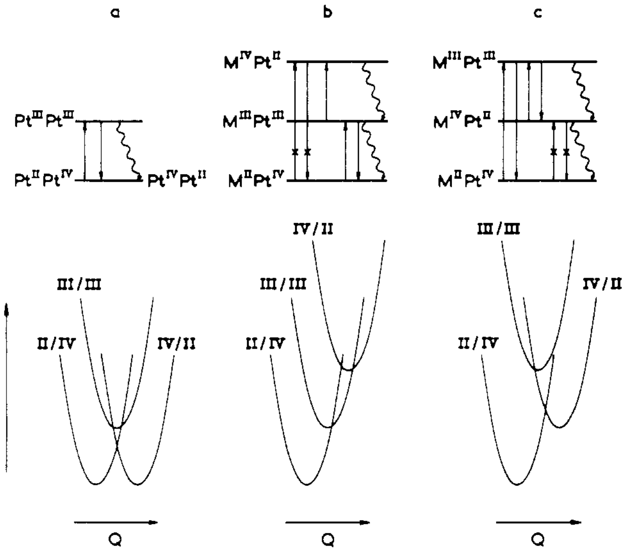

Figure 9. Representation of the relative energy levels and possible electronic transitions in linear-chain M^{II}/M^{IV} complexes.

ν_n is another Raman-active (though unassigned) mode at 223 or 279 cm^{-1}, are observed.

There is a 0.7-cm^{-1} drop in the wavenumber of ν_1 of the bromide on changing the exciting line from 520.8 to 647.1 nm. This dispersion of ν_1 with change in exciting line is characteristic of halogen-bridged mixed-valence complexes of platinum[19] and palladium.[20] A plot of the logarithm of the intensity of the ν_1 fundamental and its overtones vs. scattered photon wavenumber appears to show a discontinuity at ca. 18 300 cm^{-1}, cf. earlier discussion of the behavior of the analogous chloride.

The resonance Raman spectrum of the iodide-bridged complex has a weak, four-membered progression in ν_1 (130 cm^{-1}, Table V). The progression members give rise to asymmetric bands with more than one component, and thus there is no justification in attempting to calculate ω_1 and x_{11}.

Conclusion

The present project has led to the isolation and the spectral characterization of Ni^{II}/Pt^{IV} halogen-bridged chain complexes, directly analogous to the Pt^{II}/Pt^{IV}, Pd^{II}/Pd^{IV}, and Pd^{II}/Pt^{IV} ones already characterized. The energetics of the M^{II}/M^{IV} complexes are usually represented as in Figure 9a; the degenerate ground states M^{II}/M^{IV} and M^{IV}/M^{II} are interconvertible via the symmetric excited state M^{III}/M^{III} by successive one-electron transfers and are accompanied by suitable displacement of the halogen atom along the halogen-metal coordinate, Q_1 (the mode giving rise to the long resonance Raman progressions). The halogen would be expected to the centrally placed in the M^{III}/M^{III} state for the pure metal complexes, but not for the mixed-metal analogues. Three possible cases can be envisaged for the energetics of the mixed-metal complexes (cf. Figure 9). The first case (Figure 9a) corresponds to that in which both M^{II}/Pt^{IV} and M^{IV}/Pt^{II} (M = Ni, Pd) have the same energy. This is highly unlikely for M = Pd, Ni; indeed, for all mixed-metal complexes studied in this project and elsewhere, M^{II}/Pt^{IV} is established to be the ground state. Of the two remaining cases (Figure 9b,c) our expectation is that the situation is best represented by Figure 9c, the actual population of the M^{IV}/Pt^{II} state being effectively zero.

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Registry No. $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$, 84076-61-9; $[Ni(en)_2][Pt(en)_2Br_2][ClO_4]_4$, 84076-62-0; $[Ni(en)_2][Pt(en)_2I_2][ClO_4]_4$, 101695-47-0; $[Ni(en)_2][Pt(en)_2{}^{35}Cl_2][ClO_4]_4$, 101695-49-2; $[Ni(en)_2][Pt(en)_2{}^{35}Cl^{37}Cl][ClO_4]_4$, 101695-51-6; $[Ni(en)_2][Pt(en)_2{}^{37}Cl_2][ClO_4]_4$, 101695-53-8.

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Chemistry of Trivalent Uranium Metallocenes: Electron-Transfer Reactions with Carbon Disulfide. Formation of $[(RC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$

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The trivalent uranium metallocenes $(MeC_5H_4)_3U{\cdot}THF$ and $(Me_3SiC_5H_4)_3U$ react with CS_2 to form the binuclear U(IV) complexes $[(RC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$ (**1**, R = Me; **2**, R = $SiMe_3$). Crystals of **1** are monoclinic, $P2_1/n$, with a = 14.127 (4) Å, b = 14.182 (4) Å, c = 8.123 (2) Å, and β = 92.36 (3)° at 23 °C; for $Z = 2$ the calculated density is 2.097 g/cm^3. The structure was refined by full-matrix least-squares to a conventional R factor of 0.025, for 1402 data with $F^2 > 2\sigma(F^2)$. The central carbon atom of the complex is disordered across a center of symmetry. The geometry about the CS_2 ligand (U-S = 2.973 (3) Å and U-C = 2.53 (2) Å), as well as NMR and susceptibility data, is consistent with two full one-electron transfers into the CS_2. There is no measurable magnetic interaction between the paramagnetic ions to 5 K.

Introduction

The transition-metal coordination chemistry of heteroallenes (CS_2, SCO, and CO_2) has been extensively studied since the first report of an η^2-CS_2 complex,[1] relative to activating these linear, 16-electron molecules for further reaction chemistry.[2] Though the insertion of carbon dioxide into actinide-carbon σ bonds[3] and the insertion of CO_2 or CS_2 into f-element amide bonds has been developed,[4] no example of a heteroallene acting as a coordinating ligand to an actinide metal center has been described.

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Table I. Chemical Shifts and Line Widths of Cyclopentadienyl Proton Resonances in Tri-, Tetra-, and Pentavalent Uranium Compounds of the Type $(RC_5H_4)_3UX$[a]

compd	chem shift ($\nu_{1/2}$)			ref
	α-CH[a]	β-CH	Me or $SiMe_3$	
$(MeC_5H_4)_3U{\cdot}THF$ (27.5 °C)	−11.6 (20)	−14.4 (20)	−15.6 (10)	this work
$(MeC_5H_4)_3UOPPh_3$ (32 °C)	−12.4 (25)	−15.0 (20)	−11.4 (6)	8
$(Me_3SiC_5H_4)_3U$ (28 °C)	9.20 (78)	−19.2 (70)	−18.7 (10)	this work
$[(MeC_5H_4)_3U]_2[PhNCO]$ (29 °C)	12.6	−7.68	−3.14	5
	4.39	−18.6	−21.7	
$[(MeC_5H_4)_3U]_2[CS_2]$ (21 °C)	2.40	−10.0	0.19	this work
	−1.75	−22.0	−19.2	
$[(Me_3SiC_5H_4)_3U]_2[CS_2]$ (33 °C)	5.22	−5.39	1.33	this work
	4.09 (75)	−19.2 (75)	−12.7	
$[(MeC_5H_4)_3U]_2S$ (32 °C)	−8.88	−13.4	−9.09	8
$[(MeC_5H_4)_3U]_2Se$ (31 °C)	−8.69	−14.5	−8.31	8
$[(MeC_5H_4)_3U]_2Te$ (31 °C)	−9.73	−11.8	−8.03	8
$(MeC_5H_4)_3U{=}NPh$ (32 °C)	−3.39 (45)	−10.8 (45)	3.67 (20)	5
$(MeC_5H_4)_3U{=}NSiMe_3$ (36 °C)	−1.96 (37)	−10.4 (29)	3.03 (10)	5

[a] The chemical shift is given in δ and the width at half-height in Hz for C_6D_6 or C_7D_8 solutions. The chemical shift of the AA′ and BB′ protons in the AA′BB′X spin system is arbitrarily assigned as $\delta_A < \delta_B$. All absorptions are single resonances since the rapid electronic relaxation times obliterate the spin–spin couplings. The width of the U(IV) resonances range from 0.5 to 5 Hz, except for one type of $Me_3SiC_5H_4$ ring in $[(Me_3SiC_5H_4)_3U]_2[CS_2]$. The line width is probably due to some type of dynamic site-exchange process (see text).

Trivalent organouranium complexes have been shown to undergo one- and two-electron transfers into organic molecules.[5] We decided to extent this strategy by using heteroallenes in the hopes of inducing carbon–carbon bond formation.[6] In this paper we describe the molecules $[(RC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$, where R is Me or Me_3Si, which might be viewed as tight-ion-pair complexes of CS_2^{2-}.

Results and Discussion

Addition of carbon disulfide to solutions of $(MeC_5H_4)_3U{\cdot}THF$ or $(Me_3SiC_5H_4)_3U$ results in the immediate formation of the red complexes $[(RC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$. The substituted cyclopentadienyl compounds were used for solubility reasons since the cyclopentadienyl analogues are much less soluble in common organic solvents. The ^1H NMR spectra of the carbon disulfide complexes show two equal intensity, chemically inequivalent types of RC_5H_4 groups that do not undergo site exchange to 80 °C. The line widths and chemical shifts of the ^1H NMR absorptions (see Table I) suggest that the uranium centers are tetravalent. We have made the empirical observation that the line widths of the resonances due to the cyclopentadienyl ligands bound to a U(IV) center, an f^2 ion, are narrow ($\nu_{1/2}$ on the order of 0.5–4 Hz at room temperature), whereas the line widths of the resonances of cyclopentadienyl groups bonded to U(III) or U(V) are broader ($\nu_{1/2}$ varying from 20 to 80 Hz). The line width and chemical shift data are shown for some complexes in Table I. We have found these guidelines to be useful as a preliminary diagnostic handle for the oxidation state, though there are exceptions. In particular, the line widths for two of the ring C–H protons in $[(Me_3SiC_5H_4)_3U]_2[CS_2]$ are broad and two are narrow. The broad set of resonances can most reasonably be attributed to a $(Me_3SiC_5H_4)_3U$ group with inequivalent $Me_3SiC_5H_4$ sites undergoing a dynamic site exchange process with a rate constant comparable to the NMR time scale. Below −50 °C, these resonances are broadened into the baseline; at room temperature, $\nu_{1/2}$ = 75 Hz, and at 50 °C, $\nu_{1/2}$ = 30 Hz. The limiting slow-exchange spectrum was not observed at −90 °C (90 MHz); nonequivalent Cp resonances have been observed in a related compound, $Cp_3\overline{UN(R){=}C}(R)$.[7a]

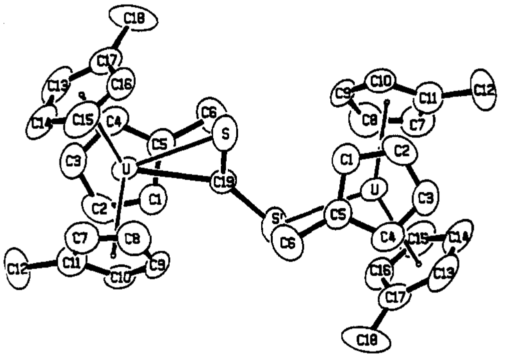

Figure 1. ORTEP diagram of $[(CH_3C_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$. C(19) is disordered across the center of symmetry (50% probability ellipsoids).

The product stoichiometry was shown to be $[(RC_5H_4)_3U]_2[CS_2]$ by elemental analysis. Therefore the inequivalent sets of RC_5H_4 resonances could indicate that the product is structurally similar to $[(MeC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}PhNCO]$[5]. This suggests that a two-electron reduction of carbon disulfide to CS_2^{2-} has occurred.

Comparison of the infrared spectrum of $(Me_3SiC_5H_4)_3U$ and $[(Me_3SiC_5H_4)_3U]_2[CS_2]$ suggests that three absorptions at 995 w, 809 w, and 645 m cm^{-1} are associated with the CS_2 group. We cannot assign these frequencies with certainty, but in η^2-CS_2 complexes the out of plane C=S stretching mode occurs at 653–632 cm^{-1}.[9a] In bridging carbon disulfide complexes with an η^2,η^1-CS_2 group, the C–S absorptions occur at 1175–1113 and 745–715 cm^{-1}.[9b,c] Since the asymmetric stretching frequency in free carbon disulfide occurs at 1533 cm^{-1},[9d] the significant lowering in energy of the C–S stretching frequency and, presumably, of the bond order in the uranium compound is consistent with the suggested electron transfer. We have been unable to assign the infrared absorptions due to CS_2 in $[(MeC_5H_4)_3U]_2[CS_2]$ with confidence.

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Table II. Positional Parameters in $[(CH_3C_5H_4)_3U]_2[CS_2]$

atom	x	y	z
U	0.36112 (3)	0.17785 (3)	0.00793 (4)
S	0.40461 (23)	−0.00546 (23)	−0.0891 (4)
C(1)	0.4394 (8)	0.1586 (8)	0.3247 (12)
C(2)	0.3996 (10)	0.2499 (9)	0.3150 (13)
C(3)	0.3016 (9)	0.2423 (9)	0.3021 (13)
C(4)	0.2811 (8)	0.1458 (10)	0.3094 (13)
C(5)	0.3643 (8)	0.0925 (8)	0.3262 (13)
C(6)	0.3733 (9)	−0.0133 (8)	0.3545 (14)
C(7)	0.4181 (9)	0.3148 (11)	−0.2030 (16)
C(8)	0.4708 (10)	0.2383 (11)	−0.2347 (16)
C(9)	0.5358 (8)	0.2259 (9)	−0.1034 (17)
C(10)	0.5184 (8)	0.2929 (9)	0.0137 (16)
C(11)	0.4443 (8)	0.3506 (8)	−0.0450 (16)
C(12)	0.4034 (10)	0.4398 (9)	0.0358 (21)
C(13)	0.1658 (8)	0.2006 (10)	−0.0253 (15)
C(14)	0.2034 (8)	0.2594 (11)	−0.1404 (18)
C(15)	0.2398 (9)	0.2009 (11)	−0.2607 (16)
C(16)	0.2256 (8)	0.1069 (11)	−0.2185 (16)
C(17)	0.1776 (8)	0.1046 (10)	−0.0661 (16)
C(18)	0.1431 (10)	0.0175 (11)	0.0226 (18)
C(19)	0.4766 (13)	0.0419 (15)	0.0159 (23)

Table III. Bond Lengths (Å) and Angles (deg) in $[(CH_3C_5H_4)_3U]_2[CS_2]$[a]

U–S	2.792 (3)	U–C(14)	2.745 (11)
U–C(19)	2.525 (19)	U–C(15)	2.738 (11)
U–C(1)	2.772 (10)	U–C(16)	2.787 (11)
U–C(2)	2.730 (10)	U–C(17)	2.834 (11)
U–C(3)	2.724 (11)	S–C(19)	1.464 (19)
U–C(4)	2.776 (11)	S′–C(19)	1.831 (19)
U–C(5)	2.853 (11)	S–S′	3.010 (7)
U–C(7)	2.733 (12)	U–Cp(1)[b]	2.50
U–C(8)	2.696 (11)	U–Cp(2)	2.47
U–C(9)	2.749 (10)	U–Cp(3)	2.51
U–C(10)	2.755 (11)	av U–Cp	2.49 (2)
U–C(11)	2.759 (11)	av U–C(ring)	2.76 (4)
U–C(13)	2.780 (12)		
Cp(1)–U–Cp(2)	116.6	Cp(2)–U–S	107.5
Cp(1)–U–Cp(3)	115.4	Cp(3)–U–S	92.8
Cp(2)–U–Cp(3)	114.0	U–C(19)–S	84.4 (9)
Cp(1)–U–C(19)	90.8	U–C(19)–S′	143.8 (11)
Cp(2)–U–C(19)	92.4	S–C(19)–S	131.7 (13)
Cp(3)–U–C(19)	124.3	C(19)–S–U	112.4 (7)
Cp(1)–U–S	107.2		

[a] Primed atom at 1 − x, −y, −z. [b] Cp(1)–Cp(3) are cyclopentadienyl rings of atoms C(1)–C(5), C(7)–C(11), and C(13)–C(17), respectively.

Table IV. Crystallographic Experimental Details for $[(CH_3C_5H_4)_3U]_2[CS_2]$

a, Å	14.127 (4)
b, Å	14.182 (4)
c, Å	8.123 (2)
β, deg	92.36 (3)
cryst syst; space group	monoclinic; $P2_1/n$
V, Å^3	1626
d_{calcd}, g/cm^3	2.097
Z	2
temp, °C	23
empirical formula	$C_{37}H_{42}S_2U_2$
mol wt	1026.9
color	red
wavelengths (for Kα_1, Kα_2), Å	0.709 30, 0.713 59
cryst size, mm	0.09 × 0.09 × 0.18
μ, cm^{-1}	95.76
range abs cor	1.97–2.25
cryst decay, %	3
limits, 2θ, deg	4–45
scan width, deg	1.70 + 0.693(tan θ)
range hkl	−15 to +15,0 to +15,−8 to 8
no. of stds; freq of stds	3; 250
no. of reflcns	4333
no. of unique reflcns	2171
R_{int}[b]	0.036
no. of nonzero weighted data	1402 ($F^2 > 2\sigma$)
p[c]	0.03
extinction k[d]	1.40 × 10^{-8}
no. of params	237
R[e] (nonzero weighted data)	0.025
R_w[f]	0.025
goodness of fit[g]	1.04
max shift/esd	0.02
max residual e/Å^3	1.3
min residual, e/Å^3	−1.1

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 25 reflections (20° < 2θ < 31°). [b] R_{int} is the agreement factor between equivalent or multiply measured reflections $R_{int} = \sum[I(hkl) - I(hkl)_{av}]/\sum I(hkl)_{av}$. [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] Simple extinction correction has the form $(F_o)_{cor} = (1 + kI)F_o$, where I is the uncorrected intensity and F_o is the observed amplitude. [e] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [f] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [g] 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. Bond Lengths and Angles in η^2- and η^2,η^1-CS_2 Complexes

compd	type	Δ,[a] Å	α_1,[b] deg	α_2,[b] deg	ref
$(Ph_3P)_2Pd(CS_2)$	η^2	0.02	140		18a
$HC(CH_2PPh_2)_3Ni(CS_2)$	η^2	0.02	136		2e
$Cp_2V(CS_2)$	η^2	0.05	138		18b
$Fe(CO)(PMe_3)(PPh_3)(CS_2)$	η^2	0.06	139		18d
$HC(CH_2PPh_2)_3Co(CS_2)$	η^2	0.06	134		18e
$CpCo(PMe_3)(CS_2)$	η^2	0.08	141		18f
$Cp_2Nb(CS_2)(allyl)$	η^2	0.15	137		18g
$(Ph_3P)_2Pt(CS_2)$	η^2	0.18	136		15
$Fe(CO)_2(PMe_2Ph)_2(CS_2)Mn(CO)_2Cp$	η^2,η^1	0.02	140	120	18c
$[Ph\text{-}t\text{-}Bu_2PPt(CS_2)]_2$	η^2,η^1	0.02	133	108	9c
$HC(CH_2PPh_3)_2Co(CS_2)Cr(CO)_5$	η^2,η^1	0.03	136	113	18e
$[Ph_3PNi(CS_2)]_2$	η^2,η^1	−0.05	137	145	9b
$[(MeC_5H_4)_3U]_2(CS_2)$	η^2,η^1	−0.37	132	112	this work

[a] Δ is $l_2 - l_1$. [b] See text.

The magnetic susceptibility of $[(MeC_5H_4)_3U]_2[CS_2]$ from 4 to 300 K is field-independent (5–40 kG) and the slope of $\chi_m(cor)^{-1}$ vs. T (K) is very similar to those that have been observed in related Cp_3UX[10] complexes. The χ_m^{-1} vs. T (K) curve follows Curie–Weiss behavior from 120 to 300 K with $\theta = -12.5$ K, $C = 2.26$, and $\mu_{eff} = 4.25\ \mu_B$/molecule (3.01 μ_B/uranium) where $\chi_m = C_m(T - \theta)^{-1}$; below 120 K the curve flattens, and below 35 K χ_m is temperature-independent. The shape of the magnetic susceptibility curve suggests that there is no measurable interaction of the f-electrons on the uranium atoms across the CS_2 ligand to 5 K.

An ORTEP idagram of $[(MeC_5H_4)_3U]_2[CS_2]$ is shown in Figure 1. The 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 carbon atom of the carbon disulfide ligand, C(19), is disordered across the center of symmetry, and the structure was refined with an occupancy factor of 0.5. The center of symmetry renders the $(MeC_5H_4)_3U$ groups crystallographically indistinguishable. The averaged U–C(ring) distance is 2.76 (4) Å, the averaged U–(ring centroid) distance is 2.49 Å, and the averaged ring centroid–uranium–ring centroid angle is 115°. These values are in the range for trivalent[11] or tetravalent[5,8,12] uranium metallocenes of the type Cp_3UL, Cp_3UX, or

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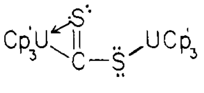
$Cp_3U(\eta^2\text{-}LX)$, where L is a neutral ligand and X is an anionic group.

The most important feature of the crystal structure is the geometry of the coordinated carbon disulfide. The carbon disulfide molecule bridges the two uranium atoms, with one C–S fragment coordinated in an η^2 fashion and the remaining sulfur atom coordinated to the second uranium atom in an η^1 fashion. Only a few examples of this type of coordination have been described; see Table V. The center of symmetry makes the two U–S distances identical at 2.792 (3) Å. There are few U–S distances in related compounds available for comparison. The U–S distance in $(MeC_5H_4)_3U$(tetrahydrothiophene)[11b] is 2.986 (5) Å, in $[(MeC_5H_4)_3U]_2[\mu\text{-}S]$ it is 2.60 (1) Å[8], and the U–S distances in some uranyl and mineral[13] structures range from 2.69 to 2.93 Å in oxidation states and coordination numbers that range from III to VI and 6 to 12, respectively. The U–C(19) bond length of 2.53 (2) Å is in the region found for the U–C σ bonds in Cp_3UCH_2Ph,[14a] $Cp_3U\text{-}n\text{-}Bu$,[14a] and $Cp_3UCH_2C(Me){=}CH_2$[14b] of 2.51 (2), 2.43 (2), and 2.48 (3) Å, respectively.

The majority of the carbon disulfide complexes that have been structurally characterized are η^2-bonded $\overbrace{\mathrm{M{—}S{—}C}}\mathrm{{=}S}$; see Table V. Only a few complexes are η^2,η^1 bonded $\mathrm{M{—}}\overbrace{\mathrm{S{—}C}}\mathrm{{—}S{—}M'}$. As can be seen from the results tabulated in Table IV, α_1, the exocyclic S–C–S angle, is essentially constant in the η^2 complexes at 132–141°. The C–S–M angle, α_2, ranges from 108° to 145° in the five η^1,η^2 complexes. The C–S distance in the η^2-fragment, l_2, is longer, with one exception, than the C–S distance in the η^1 fragment, l_1. In Table IV, this shortening is expressed by $\Delta = l_2 - l_1$. In the transition-metal compounds Δ ranges from 0.02 to 0.18 Å. The bond length increase was interpreted by Mason,[15] in the complex $(Ph_3P)_2Pt(\eta^2\text{-}CS_2)$, using the model first proposed by Chatt to describe the platinum–ethylene interaction in platinum–olefin complexes.[16] The HOMO of ethylene acts as a σ donor toward the metal center, and the LUMO of ethylene acts as a π acceptor. Since charge is transferred into the LUMO, which is C–C antibonding, the carbon–carbon bond length is increased relative to ethylene. Mason[15] has analyzed the η^2-CS_2 bonding in a similar fashion. The LUMO of CS_2 in $D_{\infty h}$ symmetry transforms as $2\pi_u$.[17] Bending CS_2 to C_{2v} symmetry removes the degeneracy of the $2\pi_u$ orbitals, and the $4a_1$ is stabilized and the $2b_1$ level is little changed in energy. Population of the $4a_1$ orbital that is C–S antibonding lengthens the C–S bond. In this model, the C–S bond length relative to free CS_2 or to the uncomplexed C–S bond length is a qualitative measure of the extent of electron transfer, i.e. Δ in Table V. This trend carriers over to the bridging η^2,η^1 complexes with exception of the nickel complex in which the η^2-carbon–sulfur distance is shorter than the η^1-sulfur–carbon distance.

In the uranium complex $[(MeC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$, l_2 = 1.46 (2) Å, l_1 = 1.83 (2) Å, and Δ = –0.37 Å. The large negative value indicates that the η^2-CS distance is shorter than the η^1-SC distance, contrary to all but one example in the transition-metal series. Furthermore, the CS distance in free CS_2 is 1.559 (3) Å,[19] and the C=S and C—S distances in $p\text{-}Me_3CC_6H_4C(S)SMe$ are 1.630 (2) and 1.788 (3) Å, respectively.[20] Pauling[21] suggests that C=S and C—S distances should be 1.61 and 1.81 Å, respectively. Hence, the bonding in the uranium complex is quite different from that found in most transition-metal complexes since the latter can readily act as π donors whereas π donation from uranium(IV) to the LUMO of CS_2 is not likely. A model that accounts for the bond length and spectroscopic data is the resonance structure



in which the negative charges are localized on carbon and the η^1 sulfur atoms. In the simplest possible sence, population of the LUMO of CS_2 in C_{2v} symmetry with a pair of electrons results in reduction of the bond order to 1.

Experimental Section

All reactions were done under nitrogen. Analyses were done by the microanalytical laboratory of this department. Infrared spectra were recorded as Nujol mulls with the use of a Perkin-Elmer 580 instrument. Proton and carbon NMR spectra were measured on a JEOL FX-90Q machine in C_6D_6 or C_7D_8. The chemical shifts are expressed in δ, with positive values to high frequency of tetramethylsilane. Magnetic susceptibility studies were done as previously described.[22]

$(MeC_5H_4)_3U{\cdot}THF$. Sodium methylcyclopentadienide (18.3 mL of a 1.26 M solution in tetrahydrofuran, 0.023 mol) was added to a suspension of uranium trichloride[23] [prepared from UCl_4; 2.9 g, 0.0077 mol] in tetrahydrofuran (70 mL). The brown suspension was stirred for 6 h and then the solvent was removed under reduced pressure. The residue was warmed (50–60 °C) for 1.5 h under reduced pressure to remove naphthalene. The brown solid was extracted with diethyl ether (150 mL), the extract was filtered, and the filtrate was concentrated to ca. 120 mL. Cooling to –80 °C yielded brown needles (2.1 g, 50% yield), mp 136–140 °C dec. An additional crop of brown needles can be obtained by concentrating the mother liquor to ca. 40 mL, and cooling to –80 °C. Anal. Calcd. for $C_{22}H_{29}OU$: C, 48.3; H, 5.33. Found: C, 47.9; H, 5.31. IR: 1651 w, 1596 w, 1508 w, 1260 m, 1234 w, 1210 w, 1170 w, 1032 s, 1015 s, 971 w, 954 w, 927 m, 848 w, 822 s, 779 s, 758 s, 721 s, 628 w, 615 m, 480 m, 400 w, 322 m cm^{-1}. ^1H NMR (27.5 °C): –11.62 (6 H), –13.99 (4 H), –14.39 (6 H), –15.61 (9 H), –31.06 (4 H). The second and fifth resonances shift toward the diamagnetic region of the spectrum upon addition of tetrahydrofuran. ^{13}C NMR (28 °C): 286.0 (d, J = 161 Hz), 275.1 (d, J = 161 Hz), 256.9 (s), –5.49 (t, J = 135 Hz), –84.2 (br, $\nu_{1/2}$ = 180 Hz), –90.6 (q, J = 125 Hz).

$(Me_3SiC_5H_4)_3UCl$. Potassium (trimethylsilyl)cyclopentadienide (46 mL of a 0.77 M solution in diethyl ether, 0.036 mol) was added to uranium tetrachloride (4.50 g, 0.0118 mol) dissolved in tetrahydrofuran (50 mL). The red suspension was stirred for 6 h, the volatile material was removed under reduced pressure, and the red residue was extracted with hot hexane (150 mL and then 50 mL, 55 °C). The combined extracts were filtered and then cooled to –80 °C. The red needles (7.4 g, 91%) were collected and dried under reduced pressure; mp 101–102 °C. Anal. Calcd. for $C_{24}H_{39}ClSi_3U$: C, 42.1; H, 5.79; Cl, 5.17. Found: C, 41.6; H, 5.78; Cl, 5.05. IR: 1685 w, br, 1595 w, br, 1404 w, 1309 m, 1274 s, 1195 w, 1175 s, 1079 w, 1040 s, 901 s, 875 w, 839 s, 797 s, 754 s, 720 w, 687 m, 633 m, 620 w, 416 s, 330 m, 328 w, 308 w, 262 w,

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253 w, 242 m cm^{-1}. ^{1}H NMR (21 °C): 16.4 (2 H), −5.68 (9 H), −17.2 (2 H). ^{13}C{^{1}H} NMR (21 °C): 278.2, 250.3, 228.1, −4.79.

(Me$_3$SiC$_5$H$_4$)$_3$U. To (Me$_3$SiC$_5$H$_4$)$_3$UCl (0.46 g, 0.000 67 mol) dissolved in toluene (5 mL) was added sodium amalgam (1 mL of a 1% amalgam, 0.002 52 mol). After the green solution was stirred for 4 h, the toluene was removed under reduced pressure. The residue was dissolved in pentane (5 mL), the resulting mixture was filtered, and the filtrate was cooled to −80 °C. The green crystals were collected and dried under reduced pressure. Yield was 0.22 g (51%); mp 76–76.5 °C. Anal. Calcd. for C$_{24}$H$_{39}$Si$_3$U: C, 44.4; H, 6.05. Found: C, 43.9; H, 5.78. IR: 1310 w, 1260 w, 1248 s, 1175 s, 1090 w, 973 w, 950 w, 902 s, 835 s, 783 m, 766 s, 752 m, 723 m, 690 m, 627 m, 620 m, 565 w, 470 w, 420 s, 326 m, 312 m cm^{-1}. ^{1}H NMR (28 °C): −19.2 (2 H), −18.7 (9 H), 9.2 (2 H). ^{13}C{^{1}H} NMR (28 °C): 360.9, 332.0, 314.5, −59.9. A more convenient preparation of (Me$_3$SiC$_5$H$_4$)$_3$U on a large scale is given below. *tert*-Butyllithium (7.70 mL of a 1.45 M solution in hexane, 0.0112 mol) was added to (Me$_3$SiC$_5$H$_4$)$_3$UCl (7.6 g, 0.011 mol) suspended in hexane (100 mL). The green suspension was stirred for 8 h, and the hexane was removed under reduced pressure. The residue was extracted with hexane (100 mL), the resulting mixture was filtered, and the filtrate was evaporated to dryness. The green oil will solidify on exposure to vacuum over a period of minutes to hours. The solid had the same IR and ^{1}H NMR spectrum as that reported above.

[(MeC$_5$H$_4$)$_3$U]$_2$[CS$_2$]. Carbon disulfide (0.05 mL, 1.1 mmol) dissolved in diethyl ether (10 mL) was added to (MeC$_5$H$_4$)$_3$U·THF (0.55 g, 0.99 mmol) dissolved in diethyl ether (20 mL) at 0 °C. A red precipitate appeared within seconds, and the precipitate was stirred for 30 min. The diethyl ether was evaporated, and the red residue was dissolved in toluene (10 mL). Hexane (5 mL) was added, and the solution was filtered. Cooling the filtrate (−20 °C) yielded dark red needles in 56% yield (0.31 g); mp 235–240 °C dec. Anal. Calcd. for C$_{37}$H$_{42}$S$_2$U$_2$: C, 43.3; H, 4.12; S, 6.24. Found: C, 43.4; H, 4.15; S, 6.24. IR: 1240 w, 1230 m, 978 m, 926 w, 865 w, 848 w, 835 w, 780 s, 762 s, 721 m, 340 m, 200 m cm^{-1}. The ^{1}H NMR spectrum is listed in Table I.

[(Me$_3$SiC$_5$H$_4$)$_3$U]$_2$[CS$_2$]. Carbon disulfide (0.35 mL, 7.5 mmol) was added to (Me$_3$SiC$_5$H$_4$)$_3$U (4.4 g, 0.0067 mol) in hexane (45 mL) at −70 °C. The color changed from green to red, and a red precipitate formed within seconds of mixing. The mixture was stirred for 1 h at −70 °C then warmed to room temperature. The hexane layer was separated and cooled (−20 °C), yielding red needles (0.26 g). The residue from the hexane extraction was dissolved in toluene (20 mL), and the resulting mixture was concentrated to ca. 18 mL and filtered. The filtrate was cooled (−20 °C) to yield red needles that were identical with those isolated from hexane. The combined yield was 1.2 g, (30%); mp 154–154.5 °C. Anal. Calcd. for C$_{49}$H$_{78}$S$_2$Si$_2$U$_2$: C, 42.8; H, 5.71; S, 4.66. Found: C, 42.8; H, 5.85; S, 4.65. IR: 1309 w, 1247 w, 1172 m, 1040 m, 995 w, 900 m, 835 s, 809 w, 786 m, 769 w, 753 m, 721 w, 690 w, 645 m, 620 w, 475 w, 420 s, 318 m, 230 w, cm^{-1}. The ^{1}H NMR spectrum is listed in Table I. ^{13}C NMR (32 °C): 266.8 (d, J = 166 Hz), 260.3 (d, J = 162 Hz), 196.8 (d, br), 161.7 (d, br), 5.10 (q, J = 120 Hz), −18.5 (q, J = 120 Hz).

X-ray Crystallography of [(MeC$_5$H$_4$)$_3$U]$_2$[CS$_2$]. 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),[24] and Lorentz and polarization effects. Experimental details are shown in Table IV. The uranium atoms were located with the use of three-dimensional Patterson maps, and subsequent least-squares and electron density maps revealed the locations of the other atoms. The structure was refined by full-matrix least-squares techniques. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The C(19) atom in the CS$_2$ ligand is disordered across the center of symmetry and was assigned an occupancy factor of one-half. In spite of this disorder the thermal parameters of C(19) and atoms to which it is bonded do not show unusual anisotropy. Only the non-methyl hydrogen atoms were included, and these were refined with isotropic thermal parameters and C–H distance restraints[25] of 0.98 ± 0.02 Å. The thermal parameter of H(10) was fixed because it would not converge. Atomic scattering factors of Doyle and Turner[26] were used, and anomalous dispersion corrections were applied.[27] With the exception of the ORTEP programs all of the computer programs used are our own. A small extinction correction was applied. Details of the refinements and residuals are given in Table IV.

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Registry No. (MeC$_5$H$_4$)$_3$U·THF, 78869-46-2; (Me$_3$SiC$_5$H$_4$)$_3$UCl, 74238-52-1; (Me$_3$SiC$_5$H$_4$)$_3$U, 99708-59-5; [(MeC$_5$H$_4$)$_3$U]$_2$[CS$_2$], 101630-42-6; [(Me$_3$SiC$_5$H$_4$)$_3$U]$_2$[CS$_2$], 101652-30-6; UCl$_3$, 10025-93-1; UCl$_4$, 10026-10-5; CS$_2$, 75-15-0; sodium methylcyclopentadienide, 55562-83-9; potassium (trimethylsilyl)cyclopentadienide, 101630-43-7.

Supplementary Material Available: Listings of thermal parameters, additional C–C and C–H distances, and positional parameters for the hydrogen atoms (3 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 (9 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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