Synthesis, Chemistry, and Spectroscopy of Some Tris(*pentahapto*cyclopentadienyl)uranium(IV) Alkyl and Aryl Compounds

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Abstract: The systematic high yield syntheses of a number of $(h^5\text{-}C_5H_5)_3UR$ compounds from $(h^5\text{-}C_5H_5)_3UCl$ and the corresponding RLi or RMgX reagents are reported. The new compounds have been characterized by chemical and magnetochemical means and by vibrational and nmr spectroscopy. The allyl compound has a ground state *monohapto*allyl geometry and is fluxional. In the isopropyl compound restricted rotation is observed about the U–R bond, indicating considerable crowding of ligands around the central metal. Analysis of the isotropic nmr chemical shifts indicates the contribution of large contact shifts; the mechanism of spin distribution involves negative spin density at the α-carbon atom of the alkyl or aryl group and is qualitatively in accord with SCF INDO molecular orbital calculations. The U–C bond is susceptible to attack by protonic solvents and, hence, is somewhat ionic. Most of the new compounds exhibit surprisingly high thermal stability, the general order of stability determined by kinetic studies in toluene solution being primary > secondary > tertiary. In the thermolysis, β elimination of olefin does not occur to any major extent, but intramolecular abstraction of hydrogen from a cyclopentadienyl ring occurs yielding RH; this takes place with essentially complete retention of stereochemical configuration at the α carbon atom of R. A homolytic U–C bond scission producing a highly constrained caged radical pair, or a concerted elimination of RH, explains these observations.

In comparison with the great flowering which has occurred over the past 20 years in transition metal organometallic chemistry, the organometallic chemistry of the actinides has been largely ignored. Part of this was no doubt due to the early observation[3] that, "simple organometallic derivatives such as $U(CH_3)_4$, if they existed at all, were extremely unstable."[3a] Aside from reports of *pentahapto*cyclopentadienyl compounds of uranium[4] and thorium,[5] interest in organoactinide chemistry did not fully awaken until the recent synthesis of the novel molecule "uranocene."[6] It is now becoming apparent that the actinides have a rich and varied organometallic chemistry.[7] We recently communicated[8] that organouranium chemistry is by no means limited to π complexes[7] and that we had prepared the first stable and well-defined alkyl and aryl complexes.[9] These uranium compounds possess a number of interesting and informative properties upon which we elaborate, in detail, in the present paper.[10] Some insight into the chemical and physiochemical nature of the uranium to carbon σ bond emerges, as do a number of aspects of the solution structural chemistry and of the magnetic properties of $(h^5\text{-}C_5H_5)_3UR$ molecules.

Experimental Section

The preparation and handling of all organoactinides was necessarily carried out in an atmosphere of prepurified nitrogen or argon, with rigorous exclusion of air and moisture. Sample manipulation was by Schlenk methods or a glove box. All solvents were thoroughly dried in a manner appropriate to each and were distilled under nitrogen immediately prior to use. Melting points were determined in sealed, nitrogen-filled capillaries and are uncorrected. Microanalyses were performed by either Schwarzkopf or Dornis and Kolbe microanalytical laboratories. The reagent, $(C_5H_5)_3UCl$, was prepared by the literature procedure.[11] We present here several syntheses of uranium alkyls, which are representative of the methods employed.

Tris(*pentahapto*cyclopentadienyl)(*n*-butyl)uranium. To 1.0 g (2.1 mmol) of $(C_5H_5)_3UCl$ suspended in 60 ml of diethyl ether at −78° was added 1.37 ml (2.2 mmol) of commercial butyllithium in hexane. The solution became dark red almost immediately. The reaction mixture was allowed to warm to room temperature and was stirred for 5 min, and the ether was then removed *in vacuo*. The dark residue was extracted with 30 ml of toluene, and the extract was filtered under nitrogen. The filtration residue was washed with 10 ml of toluene, and the combined toluene extracts were evaporated. The resulting dark red-brown solution was next recrystallized from 30 ml of diethyl ether at −20° to yield 0.88 g (85%) of dark red crystals of $(C_5H_5)_3UC_4H_9$, mp 130° dec. The crystals smoke upon exposure to air. *Anal.* Calcd for $C_{19}H_{24}U$: C, 46.55; H, 4.94; mol wt, 490. Found: C, 46.57; H, 5.06; mol wt, 512 (cryoscopic in benzene). Ir data (cm^{-1}): 1016 (s), 807 (s, sh), 780 (vs), 726 (w), 665 (w).

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(10) The analogous thorium compounds will be discussed elsewhere: T. J. Marks and W. A. Wachter, manuscript in preparation.

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Tris(*pentahapto*cyclopentadienyl)(neopentyl)uranium. To 1.2 g (2.6 mmol) of $(C_5H_5)_3UCl$ suspended in 100 ml of diethyl ether at $-78°$, was added 7.0 ml (4.6 mmol) of neopentyllithium[12] in pentane. The reaction mixture was allowed to warm to room temperature with stirring and was maintained at this temperature for 5 min. Next the ether was evaporated and the residue was extracted with 50- and 10-ml portions of toluene. The extracts were filtered and evaporated. The dark red-brown residue was next recrystallized from a mixture of 40 ml of diethyl ether and 30 ml of pentane to yield 1.0 g (82%) of dark red-brown $(C_5H_5)_3UCH_2C(CH_3)_3$. An analytical sample was obtained by crystallization from a saturated toluene solution at $-20°$. Dark red crystals were obtained, mp 148° dec; these smoke upon exposure to air. *Anal.* Calcd for $C_{20}H_{26}U$: C, 47.65; H, 5.20; mol wt, 504. Found: C, 47.64; H, 5.18; mol wt, 510 (cryoscopic in benzene). Ir data (cm^{-1}): 1255 (m), 1160 (w), 1090 (m), 1010 (s), 780 (vs), 720 (m).

Tris(*pentahapto*cyclopentadienyl)(pentafluorophenyl)uranium. To 1.72 mmol of C_6F_5Li (prepared from C_6F_5H and butyllithium[13]) in 50 ml of diethyl ether at $-60°$, was added 0.805 g (1.72 mmol) of $(C_5H_5)_3UCl$. The mixture was stirred for 2.5 hr at $-60°$ and was then allowed to warm to room temperature. After 1 hr, the ether was evaporated and the residue extracted with 30- and 10-ml portions of toluene. The combined extracts were filtered and evaporated to *ca.* 8 ml under high vacuum. Then 15 ml of *n*-hexane was added and the mixture was cooled overnight at $-20°$. The resulting solid was washed with hexane and again recrystallized from toluene–hexane to yield 0.78 g (76%) of dark-brown microcrystalline $(C_5H_5)_3UC_6F_5$, mp 144° dec. *Anal.* Calcd for $C_{21}H_{15}F_5U$: C, 42.03; H, 2.50; mol wt, 600. Found: C, 41.71; H, 2.63; mol wt, 600 (mass spectrometric). Ir data (cm^{-1}): 1628 (w), 1540 (vw), 1500 (w), 1415 (m), 1315 (w), 1248 (w), 1075 (w), 1063 (w), 1050 (m), 1030 (w), 1015 (m), 945 (s), 835 (w), 739 (vs, br), 726 (m, br).

Tris(*pentahapto*cyclopentadienyl)(allyl)uranium. To 3.2 g (6.8 mmol) of $(C_5H_5)_3UCl$ in 80 ml of ether at $-70°$, was added 10 ml (23 mmol) of commercial allylmagnesium chloride in THF. After 5 hr, the mixture was warmed to 0° and stirred for 12 hr. Next, the solvent was evaporated and the residue was extracted with 50 ml of toluene. The filtered toluene extract was evaporated to 25 ml, 25 ml of hexane was added, and the mixture was cooled slowly to $-78°$. After 4 hr, the resulting dark brown solid was washed with hexane and dried. Recrystallization from toluene–hexane was repeated to yield 2.6 g (79%) of dark brown $(C_5H_5)_3UC_3H_5$, mp 155° dec. The microcrystalline solid inflames upon exposure to air. *Anal.* Calcd for $C_{18}H_{20}U$: C, 45.57; H, 4.25. Found: C, 45.63; H, 3.78. Ir data (cm^{-1}): 1630 (w), 1588 (s), 1300 (w), 1190 (m), 1065 (m), 1015 (vs), 984 (w), 955 (m), 935 (s), 786 (vs, br), 665 (w).

Tris(*pentahapto*cyclopentadienyl)(*cis*-2-butenyl)uranium and Tris(*pentahapto*cyclopentadienyl)(*trans*-2-butenyl)uranium. These compounds were prepared by the above procedure, using *cis*- and *trans*-2-butenyllithium.[14,15] *cis*- and *trans*-2-bromo-2-butene were available commercially (Chemical Samples Co.). The uranium alkyls were recrystallized several times from toluene–hexane mixtures. Hydrolysis of the cis and trans compounds with degassed water produced (glpc) *cis*- (91 ± 2%) and *trans*-2-butene (98 ± 2%), respectively. Pmr spectra indicated an identical isomeric purity. *Anal.* Calcd for *cis*-$C_{19}H_{22}U$: C, 46.75; H, 4.54. Found: C, 46.71; H, 4.62. Ir data (cm^{-1}): 1656 (s), 1560 (m), 1216 (w), 1200 (w), 1090 (s), 1070 (s), 1012 (vs), 785 (vs), 732 (sh), 675 (w). *Anal.* Calcd for *trans*-$C_{19}H_{22}U$: C, 46.75; H, 4.54. Found: C, 46.52; H, 4.66. Ir data (cm^{-1}): 1710 (m), 1667 (s), 1655 (s), 1575 (w), 1562 (w), 1264 (w), 1168 (m), 1105 (w), 1069 (w), 1018 (vs), 785 (vs), 732 (sh), 665 (w).

Tris(*pentahapto*cyclopentadienyl-d_5)(*n*-butyl)uranium. Cyclopentadiene-d_6 was prepared by the method of McLean, *et al.*,[16] and was converted by standard procedures into C_5D_5Tl, $(C_5D_5)_3UCl$, and finally $(C_5D_5)_3U(n\text{-}C_4H_9)$. Pmr integration of cyclopentadienyl *vs.* alkyl protons showed the material to be 95 ± 2% deuterated in the cyclopentadienyl rings.[17]

Spectroscopic Measurements. Infrared spectra were recorded on Beckman IR-5 or IR-9 spectrometers and were calibrated with polystyrene film. Nujol mulls were prepared in a nitogen-filled glove box, with dry, degassed Nujol. Several scans were made of each spectrum to note any decomposition peaks which might be growing in; routinely, mulled samples were deliberately exposed to air, to ascertain the effect on spectra.

Nuclear magnetic resonance spectra were recorded on Varian T-60, Perkin-Elmer R-20B (60 MHz) and Bruker HFX-90 (90 MHz) instruments. The latter instrument was modified for 15 kHz (actually found to be 14,565.4 Hz) field modulation; chemical shifts were calibrated by measuring the frequency separation from the internal locking signal with a Hewlett-Packard 5216A electronic counter. In cases where resonances were greater than 15 kHz from the locking signal, spectra were recorded under unlocked, field-sweep (1.0 or 10.0 μG/sec) conditions and were calibrated by measuring the distance to the signal from a modulation band on the recorded spectrum and on spectra with known chemical shifts. The peak separation in TMS–$CHCl_3$ mixtures varied by no greater than 2% over the course of a number of scans, indicating high spectrometer stability. Variable temperature studies were accomplished with the calibrated, Bruker B-ST 100/700 temperature control unit. Sample solutions were examined under nitrogen in sample tubes capped with serum stoppers. ^{19}F spectra were also recorded on the Bruker instrument.

Mass spectra were recorded on a CEC 21-104 instrument at low ionizing voltage. Organometallics were studied by the direct inlet technique. Deuterium incorporation was measured with the appropriate precautions.[18] We thank Mr. M. Cooper and Dr. L. A. Raphelian for assistance.

Line shape analyses of dynamic systems were performed by computer simulation, using a local version of the program EXCNMR,[19] originally written by Professor G. M. Whitesides of M.I.T. Arrhenius plots were computer-fitted by the method of least squares and standard deviations reported are derived from the fitting procedure.

Thermolysis Studies. For studying the relative rates of thermal decomposition, solutions of the organouranium compounds in toluene were prepared with rigorous exclusion of air, filtered, freeze–thaw degassed several times, and sealed in nmr tubes under high vacuum (10^{-3} mm).[20] The nmr tubes had been cleaned with soap and water, rinsed with dilute ammonia and distilled water, and then dried in an oven. Additionally, the sample tubes were evacuated and flamed on a vacuum line prior to filling. The sample solutions were maintained in a constant temperature bath at 72.0 ± 0.2 or 97.0 ± 0.2° and were removed periodically and quenched in cold water; the decrease in intensity of the C_5H_5 resonance relative to the toluene CH_3 resonance was followed by integration of the pmr spectrum. Each integral was the average of at least three scans. First-order kinetic data were analyzed by standard methods,[21] employing a computer program written by Mr. J. Bartmess of this department. Standard deviations reported are derived from least-squares fitting of the data.

Product analysis studies were performed by weighing the organometallics into tared, nitrogen-filled, serum-capped nmr tubes, injecting degassed solvent (toluene or toluene-d_8[22]) *via* syringe, and decomposing the solutions in an oil bath. The end of the thermolysis was evidenced by completed precipitation of brown solid, leaving an essentially colorless toluene solution. The gases above the solutions were investigated by removing measured volumes with a gas syringe and subjecting them to gas chromatographic analysis on a Barber–Colman Series 5000 instrument using a $^1/_8$ in. × 8 ft Porapak Q-S column at 96–110° (flame ionization detection). Calibration of the yield was achieved by chromatographing control samples prepared in serum-capped nmr tubes from toluene and known amounts of hydrocarbon gases. Several runs in ampoules

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(22) The deuterium content was stated to be greater than 99% by the manufacturer (Diaprep). Pmr showed protons to be distributed in a ratio of *ca.* 5:3 between the ring and the methyl group.

sealed with Teflon needle valves gave the same result. Solutions of several of the thermolyzed organoactinides were short-path trap-to-trap distilled and were analyzed with the above gas chromatograph on a 1/4 in. × 6 ft Apiezon L on Chromosorb P column at 80°. We thank Mrs. L. Kao for helpful advice.

The deuterium content of the hydrocarbons above the thermolysis solutions was determined by removing samples from the nmr tubes with a gas syringe and injecting them into the mass spectrometer (see previous section). Known mixtures of undeuterated hydrocarbons served as a control.

Magnetic Measurements. Solution magnetic susceptibilities were determined in benzene on the R20-B nmr spectrometer using the Evans method.[23] Peak separations were calibrated with a frequency counter. Solid-state measurements were performed in sealed Teflon capsules on a Faraday balance calibrated with $HgCo(SCN)_4$; temperatures were calibrated with a thermocouple. In all cases, appropriate diamagnetic corrections were applied.

Results and Discussion

Synthesis and Characterization. The new organouranium compounds could be synthesized by the reactions

$$(C_5H_5)_3UCl + RLi \longrightarrow (C_5H_5)_3UR + LiCl \qquad (1)$$

$$(C_5H_5)_3UCl + RMgX \longrightarrow \underset{\text{I}}{(C_5H_5)_3UR} + MgXCl \qquad (2)$$

Ia, R = CH_3
Ib, R = n-C_4H_9
Ic, R = allyl
Id, R = neopentyl
Ie, R = C_6F_5
If, R = i-C_3H_7
Ig, R = t-C_4H_9
Ih, R = *cis*-2-butenyl
Ii, R = *trans*-2-butenyl
Ij, R = C_6H_5
Ik, R = vinyl

Work-up procedures involved extraction and recrystallization; yields were generally high (70–80%). The products are pyrophoric, darkly colored crystalline and microcrystalline solids, soluble in ethereal and aromatic solvents, but only sparingly soluble in aliphatic hydrocarbons. All compounds can be stored at room temperature for days under nitrogen without noticeable thermal decomposition. In toluene solution, only compounds Ie and Ig show appreciable decomposition (evidenced by precipitation of brown solid) during the course of a day at room temperature. Indeed, most of these uranium organometallics seem indefinitely stable under these conditions.

Infrared data indicate that the cyclopentadienyl rings in all molecules are bonded in a pentahapto configuration.[24] Proton nmr data (Table I) are also consistent with this conclusion. That the alkyl groups are bound directly to the uranium atom is suggested by the largest isotropic chemical shifts (*vide infra*) even observed for a uranium(IV) organometallic. Also, addition of methanol to solutions of the $(C_5H_5)_3UR$ compounds instantly produces $(C_5H_5)_3UOCH_3$[25] (detected by nmr) and the hydrocarbon RH (detected by glpc). Besides indicating that the uranium-to-carbon bond possesses

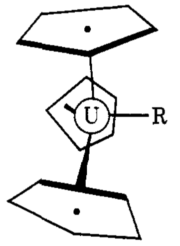
$$(C_5H_5)_3UR + CH_3OH \longrightarrow (C_5H_5)_3UOCH_3 + RH \qquad (3)$$

considerable ionic character, this reaction is further confirmation of the existence of a metal–carbon σ bond. Thus, the approximately C_{3v} structure, A, found for $(h^5\text{-}C_5H_5)_3UC_2C_6H_5$,[26a] $(h^5\text{-}C_5H_5)_3UCl$,[26b] $(h^5\text{-}C_9H_7)_3UCl$,[26c] and $(h^5\text{-}C_6H_5CH_2C_5H_4)_3UCl$[26d] is reasonable. As will be seen below, various dynamic molecular processes, as revealed by the variable temperature pmr spectra, are also explicable in terms of this proposed structure.

Table I. Nuclear Magnetic Resonance Data for $(h^5\text{-}C_5H_5)_3UR$ Compounds[a–c]

Compound	
Ia	+10.0 (15 H, s), +202.0 (3 H, s)
Ib	+10.3 (15 H, s), +18.7 (3 H, t, J = 7 Hz), +27.6 (2, H, m, J = 7 Hz), +33.6 (2 H, m, J = 7 Hz), +200.0 (2 H, m, J = 7 Hz)
Ic	+10.0 (15 H, s), +38.2 (1 H, quint, J = 11 Hz), +126.0 (4 H, br)
	−90° +13.1 (15 H), +41.0 (1 H), +57.5 (1 H), +60.9 (1 H), +344 (2 H)
Id	+11.6 (15 H, s), +22.1 (9 H, s), +192.0 (2 H, s)
Ie	+10.9 (15 H, s)
	+88.7 (2 F), +99.1 (2 F), +115.5 (1 F)
If	+10.9 (15 H, s), +19.3 (6 H, d, J = 7 Hz), +190.0 (1 H, sept, J = 7 Hz)
Ig	+11.4 (15 H, s), +23.2 (9 H, s)
Ih	+10.6 (15 H, s), +19.8 (3 H, s), +22.6 (1 H, quart, J = 6 Hz), +42.3 (3 H, d, J = 6 Hz)
Ii	+10.7 (15 H, s), −23.5 (1 H, quart, J = 7 Hz), +33.0 (3 H, d, J = 7 Hz), +33.6 (3 H, s)
Ij	+10.6 (15 H, s), +6.0 (1 H, t, J = 7 Hz),[d] +15.0 (2, H, t, J = 7 Hz), +24.2 (2 H, d, J = 7 Hz)
Ik	+9.3 (15 H, s), −24.4 (1 H, dd, J = 16.5 Hz), +17.0 (1 H, dd, J = 20.5 Hz), +163.6 (1 H, dd, J = 16.2 Hz)

[a] Pmr data in ppm relative to internal benzene, (+) indicating shift to high field. ^{19}F data in ppm to high field of internal $C_6H_5CF_3$. [b] All data at +25° except where indicated. [c] Key: s = singlet; d = doublet; t = triplet; quart = quartet; quint = quintet; sept = septet; m = multiplet; br = broad. [d] Assignment verified by spin decoupling.



A

Magnetic Data. Table II presents solution magnetic susceptibilities for several of the new alkyl and aryl

Table II. Magnetic Data for $(C_5H_5)_3UR$ Compounds

Solution[a] compound	Solvent	$\chi_M \times 10^6$, cgs
$(C_5H_5)_3UCl$	THF	2890[b]
$(C_5H_5)_3UCl$	Benzene	3000
Ib	Benzene	2945
If	Benzene	2934
Ii	Benzene	3032
Ij	Benzene	2869

Solid-state compound	Temp range, °K	C	θ, °K	μ_{eff}, BM
$(C_5H_5)_3UCl$	90–313	1.48	150	3.44[b,c]
	2.56–90	TIP[d]		
Ib	150–300	1.41	180	3.36[e]

[a] All data at 308°K except the first. Estimated error is ±3%. [b] Reference 4a, 305°K, by Guoy method. [c] Reference 28. [d] Temperature independent paramagnetism. [e] This work. Estimated error is ±3%.

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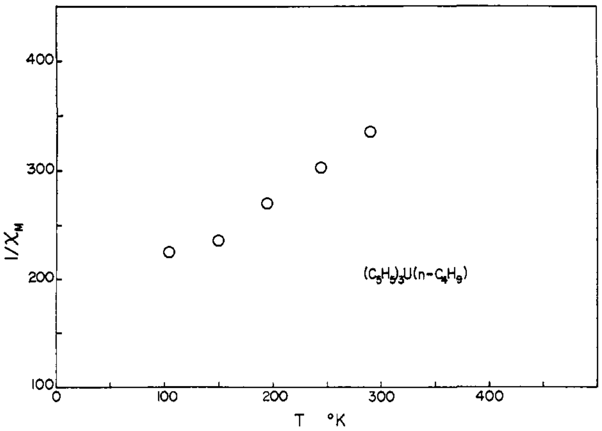

Figure 1. Solid-state magnetic data for $(C_5H_5)_3U(n\text{-}C_4H_9)$ as a function of temperature.

compounds. The values are in the range expected for U(IV) compounds with two unpaired electrons[7,27] and are near those found for the closest analog, $(C_5H_5)_3UCl$.[28] Figure 1 illustrates the temperature dependence of the magnetic susceptibility of $(C_5H_5)_3U(n\text{-}C_4H_9)$ in the solid state down to 105°K, showing a region of near Curie–Weiss behavior. Measurements at lower temperatures[29] confirm that χ approaches temperature independence below 100°K, reminiscent of $(C_5H_5)_3UCl$,[28] and indicative of a nonmagnetic ground state. The value of μ_{eff} calculated from the Curie–Weiss expression $\chi = C/(T + \theta)$ is given in Table II. The foregoing observations and the rather large magnitude of the Weiss constant suggest that μ_{eff} is not particularly meaningful. Similar temperature-dependent magnetic behavior and magnetic moments were observed for a series of *trans*-L_2UX_4 compounds[30] and were shown to be a sensitive function of the ligand field strength of L, since the degree of tetragonal distortion controlled the relative contribution of first- and second-order Zeeman effects.[30] Without more exact structural data[31,32] in the present case and further measurements on related compounds, all that can be said is that any difference in behavior between $(C_5H_5)_3UCl$ and $(C_5H_5)_3UR$ probably reflects a difference in the ligand field strength of Cl^- and R^- and that the fact that the calculated μ_{eff} is close to the free ion f^2 value (3.58 BM)[33] does not necessarily mean that the crystal field splitting is appreciably less than kT.

Nmr Spectroscopy. Contact and Dipolar Shifts. As noted already, the pmr spectra of the compounds synthesized in this study exhibit very large displacements of resonances from diamagnetic positions and very narrow line shapes in the absence of chemical exchange.[34] The former phenomenon is common for paramagnetic systems,[35] though the latter is restricted to molecules with short electron spin relaxation times[36] such as certain transition metal complexes,[36c] and numerous lanthanide and actinide[35f] complexes. In the latter two series, very strong spin–orbit coupling no doubt plays an important role in determining electronic relaxation times.[36b] Large paramagnetic chemical shift displacements reflect, in general, both contact and dipolar (pseudocontact) contributions. The former term reflects the disposition of unpaired spin density (5f electron in the present case) through the ligand system and has been of considerable recent interest in attempting to understand bonding and covalency in organoactinide molecules.[7,37] If it is assumed[38] that J is a good quantum number (*i.e.*, the crystal field splitting is much less than the separation between states) then the contact shift for nucleus i can be expressed as[31]

$$\frac{\Delta H_i^{\text{con}}}{H} = -\frac{A_i(g_J - 1)\chi}{Ng_J\beta g_N\beta_N} \qquad (4)$$

where A_i is the electron–nuclear hyperfine coupling constant, χ is the magnetic susceptibility, g_J the Landé g factor, and the other terms have their usual meaning.[39–41] An important consequence of the form of these equations is that for a given mechanism of spin distribution, transition metal complexes (where orbital angular momentum is partially or totally quenched) and uranium(IV) complexes ($g_J < 1$) should exhibit contact shifts in opposite directions.[37a,b,38,41]

In its most general form, the dipolar shift can be expressed as[42]

$$\frac{\Delta H_i^{\text{dip}}}{H} = -D\left\langle\frac{3\cos^2\theta_i - 1}{r_i^3}\right\rangle - D' \times \left\langle\frac{\sin^2\theta\cos 2\Omega_i}{r_i^3}\right\rangle \qquad (5)$$

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(27) (a) G. A. Candela, C, A. Hutchison, Jr., and W. B. Lewis, *J. Chem. Phys.*, **30**, 246 (1959); (b) C. A. Hutchison, Jr., and G. A. Candela, *ibid.*, **27**, 707 (1957).

(28) D. G, Karraker and J. A. Stone, *Inorg. Chem.*, 11, 1742 (1972).

(29) D. G. Karraker, private communication. We are grateful to Dr. Karraker for these measurements.

(30) B. C. Lane and L. M. Venanzi, *Inorg. Chim. Acta*, **3**, 239 (1969).

(31) Even under ideal C_{3v} symmetry the $J = 4$ manifold (arising from $^3H_4$) splits into three singly and three doubly degenerate levels.[32]

(32) G. G. Wybourne, "Spectroscopic Properties of Rare Earths," Interscience, New York, N. Y., 1965, Chapter 6.

(33) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, Chapters 10 and 13.

(34) For example, in $(C_5H_5)_3UCH(CH_3)_2$, it is possible to resolve all seven lines of the methine proton septet ($J \approx 7$ Hz) even though it resonates 190 ppm above benzene.

(35) (a) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, 1, 103 (1965); (b) E. DeBoer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967); (c) R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969); (d) D. R. Eaton in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience, New York, N. Y., 1968, p 462; (e) G. A. Webb, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **3**, 211 (1970); (f) R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, 11, 675 (1972).

(36) (a) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, Chapter 8; (b) H. J. Keller, *NMR (Nucl. Magn. Resonance)*, **2**, 53 (1970); (c) G. N. LaMar, *J. Amer. Chem. Soc.*, **87**, 3567 (1965); (d) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961); (e) H. Sternlicht, *ibid.*, **42**, 2250 (1966).

(37) (a) A. Streitweiser, Jr., D. Dempf, G. N. LaMar, D. G. Karraker, and N. Edelstein, *J. Amer. Chem. Soc.*, **93**, 7343 (1971); (b) N. Edelstein, G. N. LaMar, F. Mares, and A. Streitweiser, Jr., *Chem. Phys. Lett.*, **8**, 399 (1971); (c) R. von Ammon, B. Kazellakopulos, and R. D. Fischer, *ibid.*, **4**, 553 (1970); (d) R. von Ammon, B. Kanellakopulos, and R. D. Fischer, *ibid.*, **2**, 513 (1968); (e) N. Paladino, G. Lugli, U. Pedretti, M. Brunelli, and G. Giacemetti, *Chem. Phys. Lett.*, **5**, 15 (1970).

(38) (a) M. P. Eastman, H. G. Hecht, and W. B. Lewis, *J. Chem. Phys.*, **54**, 4141 (1972); (b) W. B. Lewis, S. W. Rabideau, N. H. Krikorian, and W. G. Witteman, *Phys. Rev.*, **170**, 455 (1968).

(39) The further assumption (which is probably only valid for the lanthanides[38,40]), that the separation between the crystal field levels is less than kT, leads to the more familiar[40,41] expression

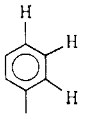
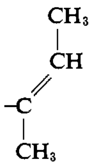
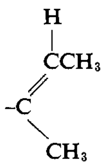
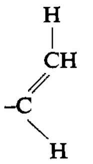
$$\frac{\Delta H_i^{\text{con}}}{H} = -\frac{A_i(g_J - 1)g_J\beta J(J + 1)}{3g_N\beta_N kT} \qquad \text{(i)}$$

(40) W. B. Lewis, J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **36**, 694 (1962).

(41) I. M. Walker, L. Rosenthal, and M. S. Quereshi, *Inorg. Chem.*, **10**, 2463 (1971).

(42) (a) W. DeW. Horrocks, Jr., and J. P. Sipe, III, *Science*, 177, 994 (1972); (b) W. DeW. Horrocks, Jr., and E. S. Greenberg, *Inorg. Chem.*, **10**, 2190 (1971).

Table III. Isotropic Nmr Shift Data for $(C_5H_5)_3UR$ Compounds

R	Geometric factors, Å^{-3} U–C equals 2.3 Å	2.5 Å	2.7 Å	Exptl $\Delta H^{con} + \Delta H^{dip}$, ppm	Calcd ΔH^{dip}, ppm U–C equals[a] 2.3 Å	2.5 Å	Calcd ΔH^{con}, ppm U–C equals[a] 2.3 Å	2.5 Å	INDO/2 a_i, G
$-CH_3$	0.0709	0.0599	0.0511	+196	+163.3	+133.8	+32.7	+62.2	−9.1
$-C(CH_3)_3$	0.0183	0.0182	0.0172	+15.1	+42.0	+40.6	−26.9	−25.5	+20.8
	0.0086	0.0078	0.0071	+6.1	+19.8	+17.5	−13.7	−11.4	+3.9
	0.0101	0.0100	0.0085	+15.0	+23.2	+22.4	−8.2	−7.4	+6.1
	0.0208	0.0207	0.0206	+24.0	*+47.9*	*+46.3*	*−23.9*	*−22.3*	+18.7
 CH_3	−0.0044	−0.0011	−0.0008	+25.2	−10.3	−2.4	+35.5	+27.6	−4.0
CH	0.0238	0.0212	0.0208	−25.0	*+55.7*	*+47.2*	*−80.7*	*+72.2*	+60.6
CH_3	0.0183	0.0183	0.0176	+25.6	+42.8	+40.7	−17.2	−15.1	+15.8
 H	0.0224	0.0216	0.0215	+21.0	+51.2	+48.2	−30.2	−27.2	+20.8
CCH_3	0.0112	0.0108	0.0100	+34.3	+25.8	+24.1	+8.5	+10.2	−2.6
CH_3	0.0183	0.0183	0.0176	+12.0	+42.0	+40.6	−30.0	−28.6	+15.8
 H	0.0219	0.0219	0.0215	+15.5	+50.3	+49.1	−34.8	−33.6	+21.2
CH	0.0239	0.0212	0.0208	−26.1	+55.1	+47.2	−81.2	−73.3	+55.1
H	0.0647	0.0554	0.0474	+162	+148.7	+124.1	+13.3	+37.9	+17.1
C_5H_5		−0.797[b]		+9.0	−19.1		+28		−4.8

[a] Italicized numbers are not independent parameters. [b] Calculated by the method of ref 23 using structural data of ref 26a.

where

$$D = \frac{1}{3N}[\chi^z - {}^1/_2(\chi^x + \chi^y)] \quad (6)$$

$$D' = \frac{1}{2N}[\chi^x - \chi^y] \quad (7)$$

and r, θ, and Ω are spherical polar coordinates; the χ's are principal molecular susceptibilities. For molecules with threefold or higher symmetry axes, $D' = 0$.

The relative contribution of ΔH^{con} and ΔH^{dip} to an observed chemical shift is of great interest. Magnetically anisotropic rare earth systems are commonly analyzed by assuming axial molecular symmetry[43] and attempting to fit experimental shift ratios for various sites on the molecule to the calculated "geometric factor" ratios $(3 \cos^2 \theta - 1)/r^3$ for these sites. In cases where dipolar shifts predominate, small deviations from exact agreement can be assigned to contact shifts. For the complexes $(C_5H_5)_3UOR$[25,44] such was the case, with deviations only detected in protons closest to the oxygen. These deviations were ascribed to contact shifts.

Geometric factors were calculated for the axially symmetric and more rigid $(C_5H_5)_3UR$ molecules assuming axial symmetry along the U–R bond in all cases. Low-temperature pmr data presented for the isopropyl compound in the next section indicate this assumption is only approximately valid for nonaxial molecules. The $(C_5H_5)_3U$ geometry was taken from crystallographic data for similar molecules.[26] The U–C(R) distance, which is 2.32 (2) Å for R = $-C{\equiv}CC_6H_5$,[26a] is probably nearer to or in excess of 2.4 Å for most of the compounds in this study.[45] The U–C(R) distance was varied from 2.3 to 2.7 Å for the geometric factor calculations. As can be seen in Table III, qualitative results are not critically sensitive to this quantity. Bond distance and angle data for alkyl and aryl groups were obtained from standard sources.[46] Geometric factors for protons in freely rotating methyl groups were calculated for the conformation which molecular models suggested was the most stable; single proton geometric factors generally varied less than 15% within a given methyl group. The average of these values was taken to be the geometric factor for the group. Results are compared in Table III with estimated isotropic shifts from the diamagnetic[10] resonance position. The most striking feature is that the agreement (*i.e.*, proportionality) is so poor. The relative constancy of the C_5H_5 resonances indicates that, assuming the contact shift for C_5H_5 protons remains approximately invariant, there are no great fluctuations in molecular magnetic anisotropy throughout the series. That these deviations from a purely dipolar fit are due to substantial contact shifts is most evident in the case of the vinylic compounds. No pseudocontact interaction could produce downfield shifts. Indeed, reference to Table III indicates that the downfield contact shift was large enough to overcome a sizable upfield dipolar shift.

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[43] Which is not always strictly valid.[42a]

[44] R. von Ammon, R. D. Fischer, and B. Kanellakopulos, *Chem. Ber.*, **105**, 45 (1972).

[45] (a) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970), and references therein; (b) W. A. Spofford, P. D. Garfagna, and E. L. Amma, *Inorg. Chem.*, **6**, 1553 (1967); errata, *ibid.*, **7**, 2677 (1968).

[46] "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **18**, No. m665 (1965).

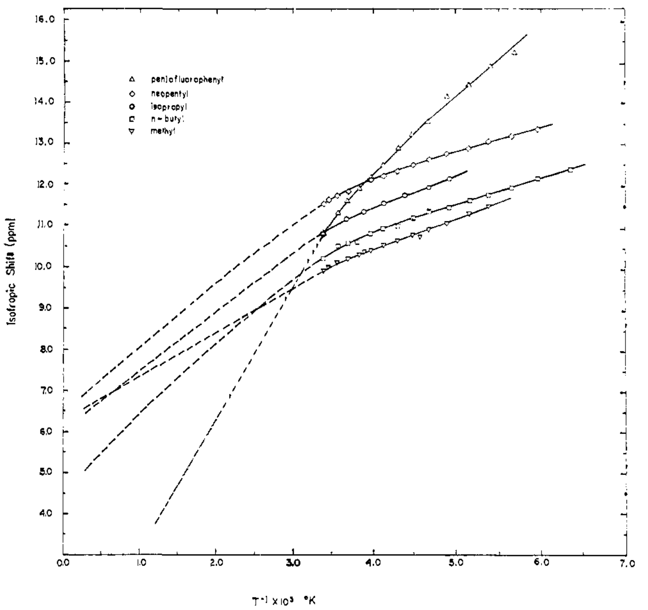

Figure 2. Measured isotropic chemical shifts of C_5H_5 protons for some $(C_5H_5)_3UR$ compounds in solution as a function of temperature.

In an attempt to qualitatively assess the signs and magnitudes of the contact shifts in these complexes, we have undertaken unrestricted Hartree–Fock INDO/2[47] SCF molecular orbital calculations on various alkyl radicals. This method has yielded gratifying agreement between calculated and experimental a_i values[48] in a large number of organic radicals and has been employed to interpret contact shifts in a number of σ-bonded transition metal complexes with recent success.[49] Our primary concern here is to try to determine the direction of the contact shift relative to the sign of a_i and then to try qualitatively to understand the magnitudes of the contact shifts. The spin density distribution mechanism suggested[37a] for $(C_8H_8)_2U$ and $[(CH_3)_4C_8H_4]_2U$ and also discussed for a number of other actinide[39,50a] and lanthanide[40] (with less than half-filled 4f shells) inorganics (though not the only possible explanation[38,50b,c]) is one in which the ligand (R^- here) donates electron density to partially filled or empty metal orbitals (in this case either 5f or 7s, 7p 6d). Exchange interaction (Hund's rule) requires that this electron density be preferentially transferred parallel to the spin on uranium,[51] leaving unpaired spin density of the opposite spin remaining on the ligand (the α-carbon atom here). The interaction of this spin density with other nuclei on the σ-organic fragment is assumed[49] to be proportional to the a_i's,[52] the electron-nuclear hyperfine coupling constants for the various nuclei in the free organic radical. Thus, for a closely related series of compounds, the above mechanism of spin distribution should give upfield proton shifts for $a_1 < 0$ ($A_1 > 0$) and downfield shifts for $a_1 > 0$ ($A_i < 0$).[37a]

Table III presents the results of the INDO calculations on a number of the $\cdot R$ groups found in $(C_5H_5)_3UR$ molecules.[53] Some qualitative agreement is immediately evident since the only protons which experimentally exhibit a large downfield shift are those calculated to possess large, positive a_i. The protons shifted to highest field generally have negative a_i. Since many of the more subtle effects could be masked by the pseudocontact shifts, we conducted the following experiment in an attempt to separate the competing effects. It was assumed that ratio of the contact shifts for the ortho phenyl protons in Ij and the vinylic proton in Ii[54] was equal to the ratio of the calculated a_i's; it was assumed that the ratio of the dipolar shifts was given by the ratio of the geometric factors in Table III.[55] This approach yields simultaneous equations, which can be solved for the contact and dipolar shifts in Ii and Ij. Assuming dipolar shifts can be calculated for all members of the series from the proportionality of the geometric factors, it is then possible to calculate contact shifts for all members of the series, shown in Table III. The results are in surprisingly good qualitative agreement with the computed a_i's considering the level of approximation—in all cases except one, contact shifts are in the direction predicted. The only case where there is a serious discrepancy in sign or magnitude is for protons directly attached to the α-carbon atom. Possibly a different mechanism is also operative here (*e.g.*, hyperconjugative). The results of Table III are an indication that the mechanism of unpaired electron density distribution in $(C_5H_5)_3UR$ compounds is identical with that for the uranocenes. The magnitudes of the contact shifts are in accord with a high degree of covalency and could be interpreted[37a] in terms of large 5f orbital involvement.[56]

It is also of interest to compare these results for $(C_5H_5)_3UR$ compounds with those of the analogous alkoxy compounds,[44] $(C_5H_5)_3UOR$. First, it is apparent that the pseudocontact shifts are opposite in direction though nearly comparable in magnitude—replacement of R by OR has caused a reversal in sign of the magnetic anisotropy (*D* in eq 5 and 6). Secondly, our calculated value for the contact shift of C_5H_6 ring protons (*ca.* +28 ppm) is near the value calculated for the alkoxy system (+17.6 ppm).[44] Thirdly, the calculated

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[47] (a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, p 80; (b) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

[48] (a) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968). (b) Reference 45a, p 128. (c) We are designating electron–nuclear hyperfine interaction constants in paramagnetic metal complexes by A_i, in organic radicals by a_i.

[49] (a) W. DeW. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, **10**, 1835 (1971); (b) I. Morishima, K. Okada, and T. Yonezawa, *J. Amer. Chem. Soc.*, **94**, 1425 (1972); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *ibid.*, **93**, 3922 (1971), see especially ref 17a; (d) W. DeW. Horrocks, Jr., *Inorg. Chem.*, **12**, 1211 (1973).

[50] (a) W. Kolbe and N. Edelstein, *Phys. Rev., B*, **4**, 2869 (1971); (b) J. Owen and J. H. M. Thornley, *Rep. Progr. Phys.*, **29**, 675 (1966), and references therein; (c) R. E. Watson and A. J. Freeman, *Phys. Rev. Lett.*, **6**, 277 (1961).

[51] Note here that for U(IV) the spin angular momentum is quantized in the direction parallel to the external magnetic field, and this is reflected in eq 4.

[52] Hence, metal–ligand π bonding is assumed to be negligible.

[53] (a) The geometries of the radicals were those used for the geometric factor calculations. This included constraining the α-carbon in alkyl radicals to a pyramidal geometry, which results in a large decrease in the magnitudes of the α-proton a_i's.[53b,c] For rotating methyl groups, the average a_i is given. (b) S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 5596 (1970). (c) D. L. Beveridge and K. Miller, *Mol. Phys.*, **14**, 401 (1968).

[54] The documented[49] success with the phenyl radical, the clear agreement with theory for the shift direction in the vinylic system, the large calculated values of the a_i's, and the probable similarity in bonding to the uranium suggested these two radicals were the most appropriate "calibrants."

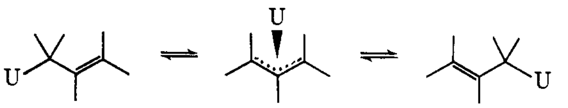
[55] We take all U–C to be 2.3 or 2.5 Å.

[56] From eq 4 and our physical data it is possible to estimate A_i's, *e.g.*, CH_3 = −1.3 MHz and t-C_4H_9 = +1.2 MHz. The accuracy of these values is probably no better than ±40%.

contact shift for the α- proton (*ca.* −28 ppm at room temperature) in the cholesteroxy derivative[44] is in reasonable agreement with a value of −20 ± 10 ppm which we estimate from an INDO calculation of a_i for the methoxyl radical[57] and the assumption that the proportionality between ΔH^{con} and a_i of Table III can be extrapolated to the alkoxy system.

Figure 2 illustrates the temperature dependence of the C_5H_5 isotropic shifts in toluene. The approximately linear behavior is commonly observed for organouranium(IV) compounds[7,37b,43] and nondiamagnetic (the diamagnetic position is estimated in this case as +1.2 ppm, from data for the thorium analogs[11]) intercepts at $T^{-1} = 0$ have also been observed.[37b]

Nmr Spectroscopy. Molecular Dynamics. The room temperature field-sweep proton nmr spectrum of $(C_5H_5)_3U$(allyl) is shown at the top of Figure 3. The pattern (see also Table I) for the allyl portion is approaching a dynamic A_4X spectrum, typically observed for fluxional metal allyls.[58] The well-resolved quintet of the X resonance again illustrates the typically narrow spectral line widths observed in these systems. As the temperature is lowered (Figure 3) the allyl resonances collapse, and finally at 179°K, the A_2BCD pattern, characteristic of a *monohapto*allyl linkage[58,59] is frozen out. The spectral changes are independent of concentration, and are completely reversible. Further support for a *monohapto*allyl geometry is derived from the observation of a weak band at 1630 cm^{-1} in the infrared spectrum. Absorptions in the 1610–1640-cm^{-1} region are commonly assigned to ν(C=C) and are usually absent in *trihapto*allyls.[58,60] A $\sigma \rightleftharpoons \pi \rightleftharpoons \sigma$ interconversion mechanism satisfactorily explains the nmr results.


(8)

Though mechanistic details are sparse for fluxional *monohapto*allyl systems[61] (the above mechanism has been proposed[61a]), several thorough studies strongly suggest that a σ-allyl intermediate is involved in the syn–anti proton exchange of a number of π-allylic complexes.[58,62] Reaction 8 portrays a case where the potential energy surface is an approximately inverted form of that for fluxional *trihapto*allyls. Taking the spectral coalescence point to be 230°K, we estimate the $\Delta G^{\ddagger}$[63] of process 8 to be 8.0 ± 1.0 kcal/mol; assuming log $A \approx 13.0$, then $E_a = 8.7$ kcal/mol. This implies that for $(C_5H_5)_3UC_3H_5$, the trihapto bonding configuration can lie no higher than *ca.* 8–9 kcal/mol in energy above the monohapto configuration. For $U(C_3H_5)_4$,[37e,64] the trihapto configuration is lowest in energy.

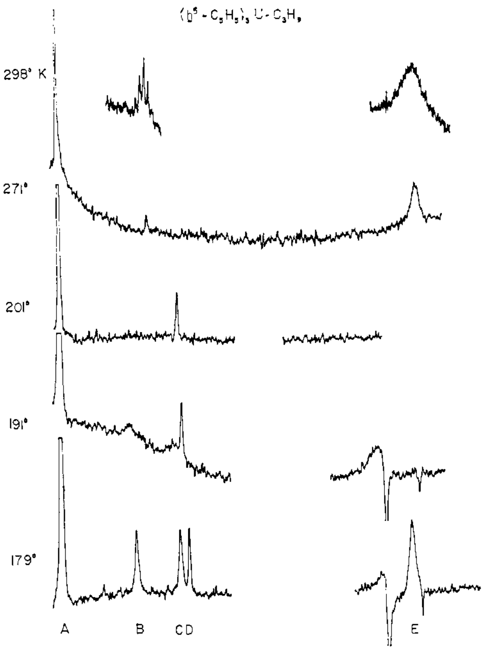
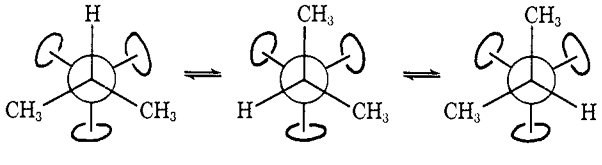


Figure 3. Field sweep pmr spectra (90 MHz) of $(C_5H_5)_3U$(allyl) in toluene-d_8. Letters identify resonances in the order given for Ic in Table I; inset resonances at the top were run at expanded scale. Dispersion bands are an artifact of 15 kHz field modulation.

Examination of models together with mechanistic questions pertaining to the thermolysis of $(C_5H_5)_3UR$ compounds (*vide infra*) suggested to us that considerable steric crowding of groups must occur about the uranium atom. Figure 4 illustrates the pmr spectrum of $(C_5H_5)_3U$(isopropyl) in the C_5H_5 region as a function of temperature. This spectral behavior is independent of concentration and solvent; it is completely reversible. Throughout the spectral range, the line shape of the isopropyl methyl resonance remains unchanged. We interpret this behavior in terms of restricted rotation about the U–C bond, which is best viewed *via* Newman projections, where rotation of the



(9)

h^5-C_5H_5 rings about their fivefold axes, a process known to have a low barrier,[65] remains rapid. Line shape analysis *via* computer simulation (Figure 4) yields the activation parameters, $E_a = 10.5 \pm 0.5$ kcal/mol and log $A = 14.7 \pm 0.6$. This process was not sufficiently slow to observe for other compounds in

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(57) We calculate an average value for the three protons of +18 G.

(58) (a) K. Vrieze and P. W. N. M. van Leeuwen, *Progr. Inorg. Chem.*, **14**, 1 (1971), and references therein; (b) M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 46; (c) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966); (d) F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968); (e) J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc. A*, 423 (1967).

(59) (a) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 71 (1965); (b) H. E. Zieger and J. D. Roberts, *J. Org. Chem.*, **34**, 2826 (1969).

(60) (a) G. Davidson, *Organometal. Chem. Rev., Sect. A*, **8**, 303 (1972); (b) G. Davidson and D. C. Andrews, *J. Chem. Soc., Dalton Trans.*, 126 (1972); (c) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).

(61) (a) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discuss. Faraday Soc.*, **34**, 185 (1962); (b) K. H. Thiele and J. Köhler, *J. Organometal. Chem.*, 7, 365 (1967); (c) K. H. Thiele, G. Engelhardt, J. Köhler, and M. Arnsted, *ibid.*, **9**, 385 (1967). Also see the discussion of diallylzinc in ref 58c.

(62) (a) J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, **93**, 2642 (1971), and references therein; (b) J. K. Krieger, J. M. Deutch, and G. M. Whitesides, *Inorg. Chem.*, **12**, 1535 (1973); (c) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 1339 (1969).

(63) (a) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970). (b) $1/\tau = (kT/h)e^{-\Delta G^{\ddagger}/RT}$ and $\tau_0 = 2/\pi\Delta\nu$.

(64) G. Lugli, W. Marconi, A. Mazzei, N. Paladino, and U. Pedretti, *Inorg. Chim. Acta*, **3**, 253 (1969).

(65) (a) L. N. Mulay and A. Attalla, *J. Amer. Chem. Soc.*, **85**, 702 (1963); (b) R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, **5**, 470 (1966).

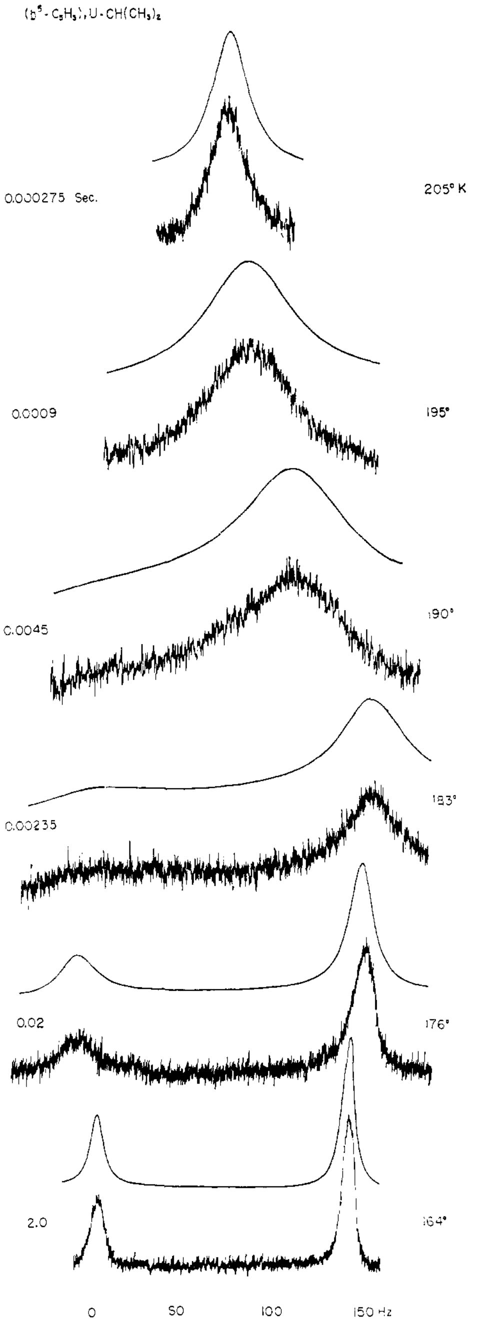

Figure 4. Pmr spectra (90 MHz) in the C_5H_5 region of $(C_5H_5)_3U$-(isopropyl) as a solution in dimethyl ether–toluene. Computer generated spectra are for the mean preexchange lifetimes of the low field resonance.

which the carbon σ-bonded to uranium contained two different groups[66] or in which this carbon was sp^2 hybridized. The chemical shift difference imparted in the cyclopentadienyl resonances as a consequence of the nonaxiality is most likely dipolar in origin and amounts to *ca.* 10% of the ring dipolar shift.

Mixtures of two different $(C_5H_5)_3UR$ compounds invariably exhibited two discrete C_5H_5 resonances up to +140 °C in toluene, even for highly concentrated solutions. Thus, rapid exchange of alkyl groups between metals, which is a common process in main group organometallic chemistry,[67] is not observed in these uranium complexes.

Chemistry. Thermal Stability. Remarkable that it might be that such a variety of σ-bonded uranium organometallics should even exist,[3] it also became apparent in the early stages of this investigation that these compounds possessed very high (compared with other metalloorganic systems) thermal stability. Those factors determining the stability of metal–carbon bonds have long been of interest in organometallic chemistry[68] and much effort has been expended in studying the mechanism of thermolysis for both main group[69] and transition metal[70–76] organometallics. However, those factors determining the stability of uranium-to-carbon σ bonds have remained unexplored. The most securely established mechanisms for the decomposition of metal alkyls are the homolytic scission (free radical) (eq 10) and the β elimination (eq 11) sometimes followed by (12). In a number of cases it appears that reaction 10

$$MR \longrightarrow M\cdot + \cdot R \tag{10}$$

$$MCH_2CH_2R \longrightarrow MH + CH_2{=}CHR \tag{11}$$

$$MH + MCH_2CH_2R \longrightarrow 2M + CH_3CH_2R \tag{12}$$

may take place only when (11) is thwarted, *e.g.*, in neopentyl and similar compounds[70a,77] and then only at a considerably higher cost in energy. Reaction sequence 11 and 12 is evidenced by nearly comparable quantities of alkane and alkene as the major organic decomposition products. Reaction 10 would be expected to yield some olefin and alkane (*via* radical disproportionation[78]) but also large quantities of the radical recombination product RR plus additional RH from solvent molecule hydrogen abstraction.[79]

Product analysis revealed that thermal decomposition of the $(C_5H_5)_3UR$ compounds in toluene solution produced nearly quantitative yields of the alkane RH (Table IV) and only traces of olefin. Small quantities of R_2 and cyclopentadiene were also detected among the

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[66] The neopentyl compound appeared to exhibit slight broadening at the lowest temperatures achieved.

[67] N. S. Ham and T. Mole, *Progr. Nucl. Magn. Resonance Spectrosc.*, **4**, 91 (1969).

[68] (a) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, 7, 157 (1968); (b) P. M. Treichel and F. G. A. Stone, *ibid.*, 1, 143 (1964); (c) G. Wilkinson, *Pure Appl. Chem.*, **30**, 627 (1972); (d) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, Chapter 23-6; (e) reference 58b, Chapter 7; (f) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **705** (1959); (g) H. H. Jaffe and G. O. Doak, *J. Chem. Phys.*, **21**, 196 (1953); (h) F. A. Cotton, *Chem. Rev.*, **55**, 551 (1955).

[69] S. J. W. Price in "Comprehensive Chemical Kinetics," Vol. **4**, C. H. Bamford and C. F. H. Tipper, Ed., American Elsevier, New York, N. Y., 1972, p 197, and references therein.

[70] (a) G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 232 (1972), and references therein; (b) K. Wada, M. Tamura, and J. Kochi, *ibid.*, **92**, 6656 (1970).

[71] (a) R. P. A. Sneeden and J. H. Zeiss, *J. Organometal. Chem.*, **26**, 101 (1970), and references therein; (b) W. Kruse, *ibid.*, **42**, C39 (1972).

[72] M. Tamura and J. Kochi, *ibid.*, **29**, 111 (1971).

[73] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 3350 (1971).

[74] G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *ibid.*, **94**, 5258 (1972), and references therein.

[75] (a) H. Bürger and K. J. Neese, *J. Organometal. Chem.*, **21**, 381 (1970); (b) G. Fachinetti and C. Floriana, *J. Chem. Soc., Chem. Commun.*, 654 (1972); (c) J. Dvorak, R. J. O'Brien, and W. Santo, *Chem. Commun.*, 411 (1970); (d) G. A. Razuvaev and N. M. Latyaeva, *Organometal. Chem. Rev.*, **2**, 349 (1967), and references therein.

[76] R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, **22**, 713 (1970).

[77] (a) G. Yagupsky, M. Mowat, A. Shortland, and G. Wilkinson, *Chem. Commun.*, 1369 (1970); (b) M. F. Lappert and R. Pearce, *J. Chem. Soc., Chem. Commun.*, 24 (1973).

[78] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, Chapter 20.

[79] Reference 78, Chapter 12.

Table IV. Volatile Thermolysis Products for $(C_5H_5)_3UR$ Compounds

Compd	Product	Yield[a]	% R–D_1[b]
Ib	Butane	92.0	5.0[d]
	Butene	<2.0	
	Octane	<1.0	
If	Propane	97.0	9.0[d]
	Propene	3.0	
Ig	Isobutane	96.5	6.6[d]
	Isobutene	3.0	
Ii	*trans*-2-Butene	97.0	4.2[d]
	cis-2-Butene	<2.0	
Ih	*cis*-2-Butene	100.0	
	trans-2-Butene	<2.0	
Ia	Methane	*c*	
Ic	Propene	*c*	
Id	Neopentane	*c*	
$(C_5D_5)_3UC_4H_9$	Butane	*c*	95[e]

[a] Based on starting uranium alkyl; estimated error ±2%. [b] Estimated error, ±1%. [c] Yield not measured. [d] Thermolysis in toluene-d_8. [e] Thermolysis in toluene.

volatile products. When thermolysis was performed in toluene-d_8, the alkane produced contained small amounts of RD_1 (Table IV). The uranium-containing product of all the thermolyses studied was an insoluble, pyrophoric brown powder. It consistently analyzed for $(C_{5.5}H_{10.4})U$ (after washing with hexane and drying) and exhibited absorbances in the infrared at 1260 (vw), 1205 (vw), 1010 (m), 900 (w), and 780 (vs) cm^{-1}. The mull infrared spectra for toluene and toluene-d_8 decompositions appear identical. It is clear from the infrared that this substance contains an h^5-C_5H_5 ring, but any structural proposals beyond this would be, at the present, tenuous.

Kinetic investigations were initiated to ascertain how the nature of the alkyl substituent affected the thermal stability. Rates were measured at various concentrations by following the disappearance of the $(C_5H_5)_3UR$ compounds in the nmr. The thermolysis reactions are first order in uranium alkyl (Figure 5) and rate constants, half-lives, and free energies of activation are given in Table V.[80] The data for the primary alkyls reveal the surprising fact that the *n*-butyl compound, which might be expected to undergo facile β elimination, is somewhat more stable than the neopentyl compound, which would resist β elimination. The methyl compound is more stable than either of these. It is also surprising that the pentafluorphenyl compound shows no enhancement in thermal stability.[81] Overall, it appears that the trends in stability reflect mostly whether the alkyl group is primary, secondary, or tertiary, the general order of thermal stability being primary > secondary > tertiary. The high stability of the trans 2-butenyl compound is a clear exception to this trend.

Table V. Kinetic Data for the Thermolysis of $(C_5H_5)_3UR$ Compounds in Toluene Solution

R	Concn, *M*	Temp, °C	$k \times 10^4$, hr^{-1}	$t_{1/2}$, hr	$\Delta G^{\ddagger}$, kcal/mol
t-C_4H_9	0.086	72	51,000 ± 5100	0.137	24.8
C_6F_5	0.208	72	1890 ± 50	3.86	27.0
Allyl	0.138	72	167 ± 3	40.0	28.7
i-C_3H_7	0.292	72	34.0 ± 1	201	29.8
Neo-C_5H_{11}	0.042	97	25.7 ± 0.2	270	32.2
n-C_4H_9	0.220	97	6.10 ± 0.3	1136	33.3
	0.072	97	6.17 ± 0.1	1123	33.3
CH_3	0.181	97	1.10 ± 0.1	6300	34.5
trans-2-Butenyl	0.303	97	1.03 ± 0.1	6730	34.6

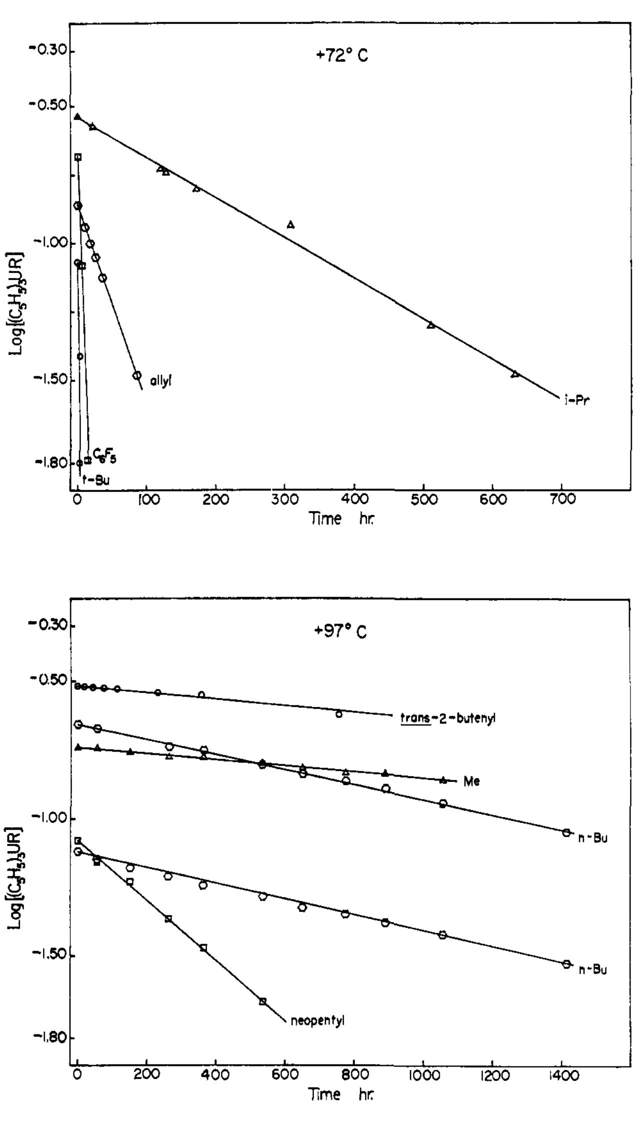

Figure 5. Kinetic plots for the thermolysis of some $(C_5H_5)_3UR$ compounds in toluene solution.

The lack of evidence from both product analysis and relative stability trends for dominant β elimination prompted further search for evidence of a homolytic scission, as opposed to an alternative such as a concerted elimination of RH. Vinyl radicals are known to undergo rapid ($k \approx 3 \times 10^7$–3×10^9 sec^{-1}) inversion

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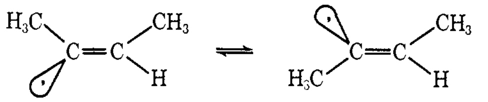
(80) Flaming of the thermolysis tubes before introducing samples was found to increase the half-lives of several of the compounds at more dilute concentrations; thus some data in ref 8 actually underestimate the stability.

(81) (a) No detectable quantities of $(C_5H_5)_3UF^{81b}$ were observed in the nmr during decomposition. This might be expected from the observation[81c] that thermolysis of $(C_5H_5)_2Ti(C_6F_5)_2$ yields $(C_5H_5)_2Ti(C_6F_5)F$, and from other fluorine transfer reactions observed on heating fluorocarbon organometallics.[68b] (b) R. D. Fischer, R. von Ammon, and B. Kanellakopulos, *J. Organometal. Chem.*, 25, 123 (1970). (c) M. Chaudhari, P. M. Treichel, and F. G. A. Stone, *ibid.*, 2, 206 (1964).

at −180°,[82] and there is strong evidence that at room temperature and above, the rate of inversion is competitive with (if not faster than) radical atom transfer from solvents or scavengers.[83]

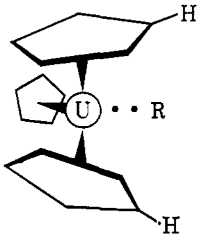
This unique mechanistic probe has been previously utilized in organocopper chemistry,[14a] and Table IV presents the results of thermolyzing the cis and trans 2-butenyl uranium compounds Ih and Ii. The free 2-butenyl radical is also expected[14a] to undergo rapid inversion, and significant inversion of configuration



(13)

would support a homolytic U–C bond scission involving free 2-butenyl radicals. However, this is not observed, and our data reveal nearly complete retention of configuration in the 2-butenes.

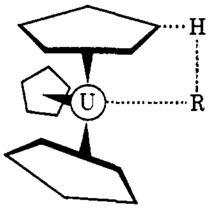
Thus, our results indicate that β elimination of olefin (reaction 11) does not occur to any major extent on thermolysis of $(C_5H_5)_3UR$ compounds but that hydrogen is transferred in an intramolecular, stereospecific fashion from the cyclopentadienyl rings, with some competition involving abstraction from solvent molecules. For deuterated solvents, some incorporation of deuterium from the solvent molecules is observed (RD_1). There is no evidence for appreciable incorporation of deuterium on the rings prior to decomposition.[84,85] These observations could be explained by homolytic U–C bond scission, leading to a caged radical pair,[86] B,



B

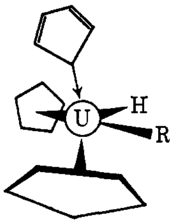
followed by rapid hydrogen abstraction. The nearly complete retention of configuration we observe for the hydrogen abstraction has never been previously observed for vinyl radical atom transfer reactions,[87] nor is such stereospecificity even observed for caged radical pair recombination reactions under normal conditions.[87] However, it is reasonable[87a] that such stereospecificity might occur if the cage were highly constrained and the reacting species close enough. The α-alkyl carbon in the $(C_5H_5)_3UR$ compounds is probably within 3 Å (assuming U–C ≈ 2.4 Å) of several of the ring hydrogens which are arrayed about the threefold molecular axis. The variable temperature nmr results for If (*vide supra*) also indicate close crowding of groups about the uranium atom. Within the context of a homolytic cleavage reaction, the deuterium incorporation in R could be explained by diffusion of a small percentage of the radicals out of the cage.[88]

It should be recognized that part of the constraint of the solvent cage could be due to persisting interaction (*e.g.*, π bonding to the butenyl radical) between members of the cage pair, such as in C. Furthermore, the



C

radical mechanism becomes indistinguishable from, if not in some cases identical with, a concerted mechanism as the radical cage becomes increasingly constrained.[89] An intramolecular mechanism, involving initial transfer of hydrogen from the ring to the uranium (D),[90] followed



D

by concerted R–H elimination[73,74] is also conceivable. Several related examples are known of alkyl group to ring transfer in $(C_5H_5)MR$ compounds. These are believed,[91] however, to be free radical in nature. Pathways B, C, and D, involving high stereochemical control during RH formation, all suffice to explain the experimental results.

The reluctance of the $(C_5H_5)_3UR$ systems to undergo β elimination may reflect partial or complete coordina-

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(82) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) R. W. Fessenden, *J. Phys. Chem.*, 71, 74 (1967); (c) P. H. Kasai and E. B. Whipple, *J. Amer. Chem. Soc.*, **89**, 1033 (1967).

(83) (a) R. M. Kopchik and J. A. Kampmeier, *ibid.*, **90**, 6733 (1968); (b) R. M. Frantazier and J. A. Kampmeier, *ibid.*, **88**, 1959, 5219 (1966); (c) L. A. Singer and N. P. Kong, *ibid.*, **88**, 5213 (1966); (d) J. A. Kampmeier and G. Chen, *ibid.*, **87**, 2608 (1965).

(84) (a) Nmr integration of (C_5H_5) *vs.* R resonances in several compounds during the course of thermolysis revealed no discrepancies in the relative intensities. To obtain 5–9% R–D *via* random, free-radical deuterium abstraction from the rings would probably require ring deuterium contents in excess of 20% since k_H/k_D ratios are typically greater than 4 for abstraction of hydrogen from hydrocarbons by alkyl radicals.[85] (b) Further support for the intramolecularity of R–H formation is derived from two additional experiments. The rate of decomposition of $(C_5H_5)_3U$(*n*-butyl) is independent of added $(C_5H_5)_3U$(*i*-propyl) and *vice versa.* Secondly, decomposition of a mixture of $(C_5D_5)_3U$(*n*-butyl) and $(C_5H_5)_3U$(isopropyl) in toluene produces exclusively butane-d_1 and propane.

(85) (a) M. Szwarc, *Chem. Soc., Spec. Publ.*, No. **16**, 94 (1962); (b) R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

(86) (a) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 352; (b) R. M. Noyes, *Progr. React. Kinet.*, 1, 129 (1961).

(87) (a) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970), and references therein; (b) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

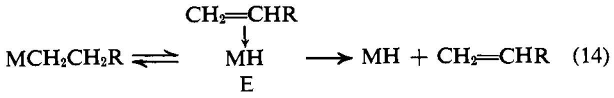
(88) (a) For the case of the 2-butenyl compounds, the amount of inverted 2-butene detected should be roughly one-half the amount of deuterium incorporated, *ca.* 2% at the most. This nears the limit of detectability. (b) So far, we have been unable to detect chemically induced dynamic nuclear polarization (CIDNP) in any of the decomposing samples. However, it is conceivable that the presence of paramagnetic U(IV) species might reduce spin–lattice relaxation times to a point where the effect was quenched.

(89) A minor, competing escape of the caged radical would then explain the deuteration results.

(90) For examples of C_5H_5 to titanium H transfer, see (a) J. E. Bercaw, R. H, Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972); (b) H. H. Brintzinger and J. E. Bercaw, *ibid.*, **92**, 6182 (1970).

(91) (a) A. N. Nesmeyanov, L. G. Makarova, N. A. Ustynyuk, and L. V. Bogatyreva, *J. Organometal. Chem.*, **46**, 105 (1972), and references therein; (b) J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4096 (1963).

tive saturation. The generally accepted scheme for transition metal systems (eq 14) requires an empty co-



$$\mathrm{MCH_2CH_2R} \rightleftharpoons \underset{\mathrm{E}}{\overset{\overset{\mathrm{CH_2{=}CHR}}{\downarrow}}{\mathrm{MH}}} \longrightarrow \mathrm{MH} + \mathrm{CH_2{=}CHR} \qquad (14)$$

ordination position, which is sometimes created by dissociation of another ligand.[92,93] Attempts in this laboratory to prepare $(C_5H_5)_3UH$ have so far been unsuccessful.

Additional Reactions. Over a period of several hours there was no evidence from pmr spectra that $(C_5H_5)_3UR$ compounds added to either acetone or CO_2 to produce the corresponding alkoxide[25] or carboxylate.[94] Thus, these uranium alkyls, though susceptible to attack by protonic reagents, appear to be poor nucleophiles.

Further studies of the chemical and structural characteristics of actinide alkyls and aryls are in progress.

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Supplementary Material Available. Analytical data and infrared data for the compounds described here will appear, at the request of the Editor, following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-5529.

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[92] (a) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972). (b) That the *trihapto*allyl configuration could be as much as 8–9 kcal/mol above the monohapto configuration in $(C_5H_5)_3U(C_3H_5)$ supports this, though the steric requirements of E may be somewhat different.

[93] Thermal decomposition of the reaction product of UCl_4 + 4*n*-C_4H_9Li in diethyl ether or hexane yields butene and butane, but only traces of octane. These products appear to arise *via* β elimination: T. J. Marks and A. M. Seyam, submitted for publication.

[94] T. J. Marks, unpublished work.

Electron Transfer through Organic Structural Units. XIV. Linear Free Energy Relationships between the Chromium(II) and Vanadium(II) Reductions of Pentaamminecobalt(III) Derivatives[1]

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Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44242. *Received February 14, 1973*

Abstract: The specific rates of reduction of 23 pentaamminecobalt(III) complexes (containing a variety of aliphatic, aromatic, and heterocyclic ligands) with V^{2+} and Cr^{2+} are compared. The Cr(II) values cover a range of 10^8 and the V(II) values a range of 3×10^3. Outer-sphere reductions (at 25° and $\mu = 1.0$) conform to the relationship $\log k_{V^{2+}} = 1.10 \log k_{Cr^{2+}} + 1.85$. The slope near unity, like that observed for the corresponding Cr^{2+}–Eu^{2+} comparison, is in accord with Marcus's model. Values of $k_{V^{2+}}$ for the more rapidly reduced carboxylato complexes lie below 20 M^{-1} sec^{-1}, indicating that these are inner-sphere reductions with specific rates limited by the rate of ligand substitution in $V(H_2O)_6{}^{2+}$. Rates for the more slowly reacting carboxylato complexes, which are known to react with Cr^{2+} with transfer of the carboxylato group, fit the equation $\log k_{V^{2+}} = 0.40 \log k_{Cr^{2+}} + 0.22$. The latter linear free energy relationship, the first to be applied to redox series in which the bridging ligand is varied, is taken as an indication that the oxidants in this rate range oxidize V^{2+} *via* the inner-sphere mechanism. Several kinetic acidity patterns are common to the two reductants, and, when difference in such patterns arise, they are in accord with the substitution-related upper limit for inner-sphere reductions by V^{2+}; this limit generally masks accelerative chelating effects unless the chelating species is a major Co(III) component. Values of $\log k_{V^{2+}}$ for the aliphatic complexes are linear functions of Taft's steric substituent parameters, indicating that rates are related to the severity of nonbonded interaction between the side chain and the reducing center. Reductions, by V^{2+} (but not by Cr^{2+}), of the complexes of 2,4- and 2,5-pyridinedicarboxylic acid are autocatalytic, and the free dicarboxylic acids catalyze the outer-sphere V^{2+} reductions of $(NH_3)_6Co^{3+}$, $(NH_3)_5pyCo^{3+}$, and $(NH_3)_5(DMF)Co^{3+}$. These catalytic phenomena provide additional examples of rapid reduction of Co(III) by pyridine-derived radicals, formed, in the present case, by one-electron reduction of the free ligand with V^{2+}. The high specific rates for the catalyzed reductions ensure that the initial step is an outer-sphere one, and the observed inhibition of catalysis by V^{3+} points to the reversibility of this step.

Linear free energy relationships[2a] have been found to correlate reactivity patterns for electron transfer reactions in a number of instances where two or more reducing centers react, *via* outer-sphere mechanisms, with the same series of oxidants[2b] and have been ap-

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(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) (a) For a broad survey of this area, see P. R. Wells, "Linear Free Energy Relationships," Academic Press, London, 1968. (b) The application of linear free energy relationships to outer-sphere redox reactions has been briefly but critically reviewed by D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, 94, 394 (1972).