ORGANOMETALLICS

Synthesis and characterization of (pentamethylcyclopentadienyl)uranium tris(allyl) complexes

Teddy H. Cymbaluk, Richard D. Ernst, and Victor W. Day

Organometallics, **1983**, 2 (8), 963-969• DOI: 10.1021/om50002a004 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street
N.W., Washington, DC 20036

Organometallics **1983,** *2,* 963-969

Synthesis and Characterization of (Pentamethylcyclopentadienyl)uranium Tris(allyl) Complexes

Teddy H. Cymbaluk,[1a] Richard D. Ernst,*[1a] and Victor W. Day*[1b,2]

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588, and Crystalytics Company, Lincoln, Nebraska 68501

Received August 16, 1982

The synthesis and characterization of the stable π-allylic complexes of formula $(C_5(CH_3)_5)U(allyl)_3$ are described (allyl = C_3H_5, 2-$CH_3C_3H_4$). Characterization methods include infrared and proton NMR spectroscopy, quantitative hydrolysis, elemental analysis, and single-crystal X-ray diffraction. Proton NMR spectra reveal that the syn and anti allyl protons are equivalent at and somewhat below room temperature. X-ray diffraction data for the 2-methylallyl compound confirm the essentially symmetric π-allyl structure. The space group is $P2_1/c$—C^5_{2h} with unit cell parameters of $a = 9.154$ (1) Å, $b = 29.523$ (6) Å, $c = 8.630$ (1) Å, and $\beta = 115.19$ (1)°. The overall geometry may be described as being based on a pseudotetrahedral ligand arrangement (with respect to their center of masses) with two of the allyl groups adopting a "downward" orientation (their 2-methyl groups being pointed away from the pentamethylcyclopentadienyl group), while the other allyl group adopts a "sideways" orientation. These orientations seem to result from packing forces within a given molecule. The U-C distances averaged 2.79 (1) Å to the pentamethylcyclopentadienyl ligand, 2.66 (1) Å to the terminal carbon atoms of the allyl ligands, and 2.80 (1) Å to the central carbon atoms of the allyl ligands. These distances and various "fold" and "tilt" parameters of the allyl ligands differ somewhat from values generally observed in transition-metal systems yet are far from approaching the extreme exemplified by many metal-ylide complexes.

Introduction

Transition-metal complexes containing allylic ligands have long been known for their activity in a truly wide variety of stoichiometric and catalytic chemical transformations.[3] It should come as no surprise that their high chemical activity has led to many more intensive studies, including X-ray investigations of their solid-state structures.[4] It has only been much more recently that allyl complexes of lanthanide and actinide metals have been reported, such as $(\eta^5\text{-}C_5H_5)_2Ln(\eta^3\text{-}C_3H_5)$, $Ln(\eta^3\text{-}C_3H_5)_4^-$, $(\eta^5\text{-}C_5H_5)_3U(\eta^1\text{-}C_3H_5)$, $U(\eta^3\text{-}C_3H_5)_4$, $U(\eta^3\text{-}C_3H_5)_3X$, and $U(\eta^3\text{-}C_3H_5)_2Cl_2$.[5-10] Some of these compounds have already been shown to possess a rich chemistry. For example, the $U(\eta^3\text{-}C_3H_5)_3X$ complexes stereospecifically bring about cis-1,4-polymerization of butadiene, yielding a product with highly desirable physical properties.[11] It would seem, then, that information concerning the structural nature of lanthanide-allyl or actinide-allyl linkages should be very valuable, not only with regard to the catalytic nature of these complexes but also in order to help provide a general understanding of the bonding in lanthanide or actinide allyls as compared to their much better known transition-metal counterparts. In particular, such studies would prove useful in determining the effect that ionic character has in the general bonding of a metal π-allyl. Unfortunately, however, no structural information has been available to aid in obtaining such an understanding or comparisons, other than one apparently severely disordered structure report dealing with $[U(\eta^3\text{-}C_3H_5)_2(i\text{-}OC_3H_7)_2]_2$.[12] To some extent this lack of data may be due to the low thermal stability of a number of these compounds. In this paper we report the synthesis and characterization of the relatively stable π-allyl complexes $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}C_3H_5)_3$ and $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}C_4H_7)_3$ (C_4H_7 = 2-methylallyl), including an X-ray structural study of the latter complex. This study provides the first accurate examination of the structural nature of an actinide-allyl bond and allows some initial speculations to be made concerning the bonding interactions present.

Experimental Section

All operations involving organometallics were necessarily carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glovebox. All solvents were thoroughly dried in a manner appropriate to each and were distilled under nitrogen immediately prior to use. UCl_4,[13] C_3H_5MgBr,[14] 2-C_4H_7MgCl,[15] $C_5(CH_3)_5H$,[16] and $LiC_5(CH_3)_5$[16] were prepared according to published procedures. n-C_4H_9Li was standardized according to the procedure of Eppley and Dixon.[17] Solid Grignard reagents were isolated by removal of ether solvent in vacuo until a dry product resulted. Grignard reagent purities were estimated by gas evolution on hydrolysis. Magnetic susceptibilities were determined by the Evans method,[18] and elemental analyses were performed by Galbraith Laboratories.

---

(1) (a) University of Utah. (b) University of Nebraska and Crystalytics Co.

(2) Camille and Henry Dreyfus Teacher-Scholar.

(3) Stone, F. G. A.; West, R., Eds. *Adv. Organomet. Chem.* **1979**, *17*.

(4) (a) Clarke, H. J. *J. Organomet. Chem.* **1974**, *80*, 155. (b) Kaduk, J. A.; Poulos, A. T.; Ibers, J. A. *Ibid.* **1977**, *127*, 245. (c) Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *100*, 4107.

(5) Tsutsui, M.; Ely, N. *J. Am. Chem. Soc.* **1975**, *97*, 3551.

(6) Mazzei, A. In "Organometallics of the f-Elements"; Marks, T. J., Fischer, R. D., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1979.

(7) (a) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529. (b) Halstead, G. W.; Baker, E. C.; Raymond, K. N. *Ibid.* **1975**, *97*, 3049.

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

(9) Lugli, G.; Mazzei, A.; Poggio, S. *Makromol. Chem.* **1974**, *175*, 2021.

(10) Poggio, S.; Lugli, G.; Mazzei, A., Ger. Offen. 2257787, 1973; *Chem. Abstr.* 1973, *79*, 5259h.

(11) Bruzzone, M.; Mazzei, A.; Guiliani, G. *Rubber Chem. Tech.* **1974**, *47*, 1175.

(12) Brunelli, M.; Perego, G.; Lugli, G.; Mazzei, A. *J. Chem. Soc. Dalton Trans.* **1979**, 861.

(13) Hermann, J. A.; Suttle, J. F. *Inorg. Synth.* **1947**, *5*, 143.

(14) Brummitt, O.; Budewitz, E. P.; Chudd, C. C. *Org. Synth.* **1956**, *36*, 60.

(15) Benson, R. E.; McKusick, B. C. "Organic Syntheses"; Wiley: New York, 1963; Coll. Vol. IV, p 1746.

(16) (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Inorg. Synth.*, in press. (b) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

(17) Eppley, R. L.; Dixon, J. A. *J. Organomet. Chem.* **1967**, *8*, 1976.

(18) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

0276-7333/83/2302-0963$01.50/0

Spectroscopic Studies. Infrared spectra were recorded with a Perkin-Elmer Model 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol and calibrated with polystyrene. Nuclear magnetic resonance spectra were recorded on Varian FT-80 and SC-300 spectrometers.

(Pentamethylcyclopentadienyl)uranium Tris(2-methylallyl), $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}2\text{-}C_4H_7)_3$. A solution of 2.11 g (5.58 mmol) of UCl_4 in 30 mL of THF was added by dropping funnel to 5.58 mmol of $LiC_5(CH_3)_5$ in 30 mL of THF under nitrogen at −78 °C. The resulting greenish solution was allowed to warm to room temperature, and a color change to brick red was observed after about 2 h of stirring. The solution was stirred an additional 8 h to ensure complete reaction, and the THF was removed in vacuo. At this point the orange product, $(\eta^5\text{-}C_5(CH_3)_5)UCl_3(THF)_2$,[19] was removed by extraction with benzene and filtered under nitrogen by using a coarse frit. Most of the benzene solvent was then removed in vacuo, and the extracted $(\eta^5\text{-}C_5(CH_3)_5)UCl_3(THF)_2$ was taken up in a moderate volume of THF or ether.

The 2-methylallyl compound was prepared by the addition of 44.6 mmol (an excess) of solid C_4H_7MgCl to the $(\eta^5\text{-}C_5(CH_3)_5)UCl_3(THF)_2$ in 40 mL of THF or ether at −78 °C under a positive flow of nitrogen. An immediate color change to red-brown was observed. After the solution was warmed slowly to room temperature, stirring was continued for an additional hour, after which the solvent was removed in vacuo and the product was isolated in good yield by pentane extraction, filtration on a coarse frit under nitrogen, and crystallization at −20 °C. The compounds seems to exhibit inconsistent stability at room temperature. Out of a group of nearly identical single crystals, some inevitably do not diffract, and after the crystals were left standing for several days, some decomposition is noted, as evidenced by the compounds incomplete dissolution in organic solvents. This property may be responsible for the inability to obtain satisfactory analytical data even for single crystal samples.

Anal. Calcd for $C_{22}H_{36}U$: C, 49.06; H, 6.74. Found: C, 46.73; H, 6.46.

Complete infrared data (Nujol mull): 3075 (w, sh), 3050 (w, sh), 1511 (w, sh), 1492 (m, sh), 1426 (ms, sh), 1323 (w), 1076 (w, br), 1027 (m), 954 (w, br), 890 (w), 805 (vs), 750 (m), 729 (m) cm^{-1}.

(Pentamethylcyclopentadienyl)uranium Tris(allyl), $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}C_3H_5)_3$. The unsubstituted allyl compound was prepared by a procedure similar to that used for the methyl substituted compound. To 5.51 mmol of $LiC_5(CH_3)_5$ in 30 mL of THF under nitrogen at −78 °C was added a solution of 2.09 g (5.51 mmol) of UCl_4 in 30 mL of THF. After 8 h of stirring at room temperature, the brick-red solution was cooled to −78 °C and 44.1 mmol (an excess) of solid C_3H_5MgBr was added under a positive flow of nitrogen. Although reaction appeared immediate, the mixture was allowed to stir for 10 h to ensure complete reaction. The resulting dark solution was filtered by using a coarse frit under nitrogen and the solvent removed in vacuo. Although not as soluble as the corresponding substituted analogue, the compound could be extracted with several portions of pentane, filtered under nitrogen by using a coarse frit, and isolated in somewhat low yield by crystallization at −20 °C. The stability of this compound at room temperature is lower than that of the 2-methylallyl analogue, and therefore has not allowed even for approximate analytical data.

Complete infrared data (Nujol mull): 1425 (sh), 1320 (w), 1080 (w, br), 1030 (ms), 952 (w), 890 (w), 805 (s), 750 (m), 730 (m) cm^{-1}.

X-ray Diffraction Study of $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}2\text{-}C_4H_7)_3$. Well-formed single crystals of either $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-allyl})_3$ compound could be grown by slow cooling of concentrated solutions in hydrocarbon solvents. Crystals of the 2-methylallyl complex were mounted and sealed in thin-wall glass capillaries under nitrogen. A combination of precession and Weissenberg photographs together with standard Nicolet $P\bar{1}$ diffractometer software programs were used in the determination of the space group and unit-cell data. The compound crystallized in space group $P2_1/c\text{—}C^5_{2h}$ (No, 14),[20] with a = 9.154 (1) Å, b = 29.523 (6) Å, c = 8.630 (1) Å, β = 115.19 (1)°, and V = 2110.5 Å^3, as determined at 20 °C by least-squares refinement of 15 centered reflections having $2\theta > 25°$. Intensity measurements were made on a computer-controlled four-circle Nicolet autodiffractometer using 1° wide ω scans and graphite-monochromated Mo $K\bar{\alpha}$ radiation (λ = 0.71073 Å). Several attempts at data collection were initially unsuccessful as either the crystals did not diffract (though appearing identical with others that did diffract) or they appeared to decompose significantly in the X-ray beam (ca. 15%/day), as evidenced by a steady decrease in standard intensities. Eventually a rather large crystal of dimensions 0.31 × 0.31 × 1.13 mm was chosen for data collection, which was then carried out rapidly to avoid possible decomposition. Similar instability during room-temperature data collection was reported for $[(\eta^3\text{-}C_3H_5)_2U(i\text{-}OC_3H_7)_2]_2$.[12] For the above crystal a nominally 1.5-mm diameter collimator was used while data was collected in two concentric shells of 2θ out to 43° and 55° at respective scan rates of 6°/min and 4°/min.

Table I. Positional Parameters for the Atoms of $(\eta^5\text{-}C_5Me_5)U(\eta^3\text{-}C_4H_7)_3$

atom	x	y	z
U	0.03829 (4)	0.12824 (1)	0.29625 (5)
CP(1)	0.3571 (13)	0.10010 (42)	0.4948 (15)
CP(2)	0.3012 (14)	0.07394 (39)	0.3489 (15)
CP(3)	0.2845 (14)	0.10279 (42)	0.2097 (15)
CP(4)	0.3321 (14)	0.14727 (44)	0.2814 (21)
CP(5)	0.3730 (15)	0.14556 (43)	0.4561 (17)
CM(1)	0.4194 (17)	0.08175 (61)	0.6787 (16)
CM(2)	0.2787 (19)	0.02312 (45)	0.3364 (22)
CM(3)	0.2484 (20)	0.08878 (66)	0.0275 (17)
CM(4)	0.3660 (20)	0.18783 (61)	0.1881 (27)
CM(5)	0.4439 (19)	0.18433 (54)	0.5818 (26)
CA(1)	0.0064 (17)	0.07322 (42)	0.5231 (17)
CA(2)	−0.0470 (16)	0.11417 (53)	0.5657 (15)
CA(3)	0.0471 (22)	0.15288 (55)	0.5931 (19)
CA(4)	−0.2149 (19)	0.11620 (70)	0.5550 (22)
CB(1)	0.0390 (25)	0.21846 (42)	0.3036 (27)
CB(2)	−0.0825 (17)	0.21120 (41)	0.1325 (21)
CB(3)	−0.0518 (20)	0.18282 (45)	0.0203 (19)
CB(4)	−0.2506 (19)	0.22833 (51)	0.0881 (26)
CC(1)	−0.2853 (15)	0.11467 (49)	0.1340 (18)
CC(2)	−0.2273 (15)	0.07214 (43)	0.1165 (16)
CC(3)	−0.1077 (17)	0.06780 (49)	0.0591 (18)
CC(4)	−0.2819 (22)	0.03005 (55)	0.1764 (24)

Each scan was divided into 19 equiangular intervals, and those 13 contiguous intervals having the highest single accumulated count at their midpoint were used to calculate the net intensity for the scan. Background counts were taken at 1° above and 1° below the calculated $K\bar{\alpha}$ doublet location such that the total background time equalled half the net scan time. The intensities of six standard reflections were periodically monitored throughout data collection and for this crystal did not show a noticeable decline in intensity. A total of 4849 independent reflections were collected, of which 3014 independent ones had intensities judged above background ($I > 3\sigma(I)$) and were used in subsequent calculations. An empirical absorption correction was applied based on psi scan data. The function minimized in full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, with empirical weights assigned by the method of Cruickshank.[21] The atomic scattering factors and the anomalous dispersion terms for uranium were taken from recent tabulations.[22]

The location of the uranium atom was determined from a Patterson map. Refinement of this atom anisotropically led to R = 0.112. A difference Fourier map then revealed all 22 carbon atoms which were included in subsequent calculations, eventually leading to R = 0.042 and R_w = 0.049 in fully anisotropic refinement. No attempt was made to find or include hydrogen atoms in the structure. A final difference Fourier map revealed no

---

(19) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* 1982, *104*, 4692.

(20) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 99.

(21) (a) The weighting function[21b] $w = 5.33 - 7.84\cdot10^{-2}|F_o| + 6.05\cdot10^{-4}|F_o|^2 - 9.29\cdot10^{-7}|F_o|^3$, $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. (b) Cruikshank, D. W. J. In "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; pp 187–196.

(22) Cromer, D. T.; Waber, J. T. in "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

Table III. Selected Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}C_4H_7)_3$

Bond Distances

U-CA(1)	2.654 (14)	U-CP(1)	2.808 (12)	CA(1)-CA(2)	1.41 (2)	CP(1)-CP(2)	1.38 (2)
U-CA(2)	2.781 (14)	U-CP(2)	2.763 (13)	CA(2)-CA(3)	1.39 (2)	CP(2)-CP(3)	1.43 (2)
U-CA(3)	2.631 (16)	U-CP(3)	2.763 (14)	CB(1)-CB(2)	1.44 (3)	CP(3)-CP(4)	1.44 (2)
U-CB(1)	2.664 (12)	U-CP(4)	2.803 (15)	CB(2)-CB(3)	1.40 (2)	CP(4)-CP(5)	1.39 (2)
U-CB(2)	2.809 (13)	U-CP(5)	2.820 (15)	CC(1)-CC(2)	1.40 (2)	CP(5)-CP(1)	1.41 (2)
U-CB(3)	2.698 (15)	U-CP	2.522 (6)	CC(2)-CC(3)	1.39 (2)	CP(1)-CM(1)	1.54 (2)
U-CC(1)	2.713 (15)	U-CMA	2.480 (10)	CA(2)-CA(4)	1.50 (3)	CP(2)-CM(2)	1.51 (2)
U-CC(2)	2.802 (14)	U-CMB	2.511 (8)	CB(2)-CB(4)	1.51 (3)	CP(3)-CM(3)	1.52 (2)
U-CC(3)	2.614 (14)	U-CMC	2.503 (7)	CC(2)-CC(4)	1.51 (2)	CP(4)-CM(4)	1.55 (2)
						CP(5)-CM(5)	1.52 (2)

Bond Angles

CP-U-CMA	108.6 (2)	CB(1)-CB(2)-CB(4)	118.2 (15)	CM(1)-CP(1)-CP(2)	125.2 (12)
CP-U-CMB	106.2 (3)	CB(3)-CB(2)-CB(4)	120.7 (15)	CM(1)-CP(1)-CP(5)	123.4 (12)
CP-U-CMC	128.5 (3)	CC(1)-CC(2)-CC(3)	121.1 (13)	CM(2)-CP(2)-CP(1)	127.5 (12)
CMA-U-CMB	120.5 (4)	CC(1)-CC(2)-CC(4)	120.4 (13)	CM(2)-CP(2)-CP(3)	124.7 (12)
CMA-U-CMC	95.1 (3)	CC(3)-CC(2)-CC(4)	118.2 (13)	CM(3)-CP(3)-CP(2)	127.4 (12)
CMB-U-CMC	99.2 (3)	CP(1)-CP(2)-CP(3)	107.4 (11)	CM(3)-CP(3)-CP(4)	125.9 (13)
CA(1)-CA(2)-CA(3)	119.4 (14)	CP(2)-CP(3)-CP(4)	106.2 (11)	CM(4)-CP(4)-CP(3)	125.1 (14)
CA(1)-CA(2)-CA(4)	118.5 (14)	CP(3)-CP(4)-CP(5)	109.0 (12)	CM(4)-CP(4)-CP(5)	124.8 (14)
CA(3)-CA(2)-CA(4)	121.5 (14)	CP(4)-CP(5)-CP(1)	106.5 (12)	CM(5)-CP(5)-CP(4)	125.6 (13)
CB(1)-CB(2)-CB(3)	120.4 (15)	CP(5)-CP(1)-CP(2)	110.8 (11)	CM(5)-CP(5)-CP(1)	127.3 (13)

significant peaks away from the uranium atom location. The positional parameters obtained from the final cycle of least-squares refinement are presented in Table I, along with their estimated standard deviations. The atomic thermal parameters (Table II) and the final values of $10|F_o|$ and $10|F_c|$ for the observed reflections are available as supplementary material (see final paragraph regarding such material). No unusual intermolecular contacts were observed.

Synthetic and Spectroscopic Results and Discussion

The first reported π-allyl derivative of an actinide was the formally eight-coordinate $U(\eta^3\text{-}C_3H_5)_4$,[8] which decomposes above ca. −20 °C. As uranium(IV) organometallics tend to be most stable when a formal coordination number of ten is attained,[23] our attempts to prepare a stable uranium π-allyl focused on ways in which a higher coodination number could be reached. The addition of the bidentate ligand, 2,2′-bipyridine, to $U(\eta^3\text{-}C_3H_5)_4$ at −20 °C was first attempted with the goal of isolating a stable, ten-coordinate (2,2′-bipyridyl)$U(\eta^3\text{-}C_3H_5)_4$ complex. However, this reaction instead led to incorporation of three bipyridyl ligands in an isomeric mixture of rather unusual formulation.[24] Subsequent attempts centered on the preparation of the formally nine-coordinate complex $(\eta^5\text{-}C_5H_5)U(\eta^3\text{-allyl})_3$ from $(\eta^5\text{-}C_5H_5)UCl_3(THF)_2$.[25] While these attempts (particularly for a 2-methylallyl ligand) did lead to a product of higher thermal stability compared to $U(\eta^3\text{-}C_3H_5)_4$, decomposition still took place around 0–10 °C. Ultimately, we found that the proper balance of ligand size necessary to lead to stability yet not bringing about isomerization to a σ-bound linkage (e.g., $(\eta^5\text{-}C_5H_5)_3U(\eta^1\text{-}C_3H_5)$ and $(\eta^5\text{-}C_5H_5)_3U(\eta^1\text{-}2\text{-}C_4H_7)$)[7] could be attained by utilizing the bulkier $(\eta^5\text{-}C_5(CH_3)_5)UCl_3(THF)_2$[19] as starting material for the preparation of $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-allyl})_3$ complexes (allyl = C_3H_5, 2-$CH_3C_3H_4$) as in eq 1. The resulting

$$(\eta^5\text{-}C_5(CH_3)_5)UCl_3(THF)_2 + 3(\text{allyl})MgX \xrightarrow{THF} (\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-allyl})_3 + 3MgClX \quad (1)$$

$$X = Br, Cl$$

products are very air-sensitive but somewhat stable at room temperature, and soluble in hydrocarbon and other organic solvents. The infrared spectra of the two $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-allyl})_3$ complexes indicated the presence of π (η^3), rather than σ (η^1), allyl ligands. In particular, no band was observed in the region 1600–1640 cm^{-1}, which would have been indicative of a localized olefinic carbon–carbon double bond present in a σ-allyl complex. Elemental analysis (see Experimental Section) and quantitative hydrolysis[26] provided further support for the above formulations, although the carbon analyses were noticeably low, probably due in major part to slow decomposition, although incomplete combustion may also contribute. Proton NMR spectra (Figure 1) are also indicative of the presence of π-allyl ligands. Near room temperature each compound displays three peaks possessing relative intensities of 15:12:3 and 15:12:9 for the allyl and methyallyl complexes, respectively. These are observed at δ 0.6, −24.8, and −12.7 for $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}C_3H_5)_3$ at −51 °C and δ 1.4, −24.3, and −11.7 for $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}2\text{-}C_4H_7)_3$ at 43 °C, respectively. Thus, the syn and anti substituents on the allyl C(1) and C(3) sites are all equivalent at (and even somewhat below) room temperature through a facile fluxional process.

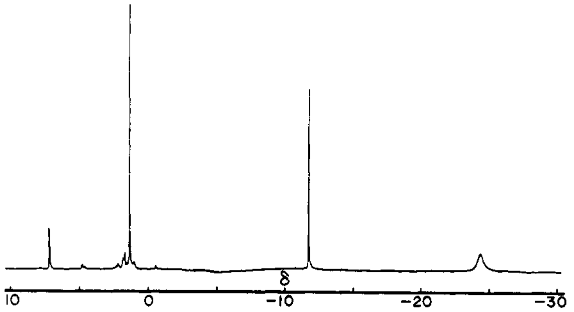


Figure 1. Proton NMR spectrum for $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}2\text{-}C_4H_7)_3$ (C_6D_6 solvent, C_6D_5H internal standard). The peak at δ 7.23 is due to the C_6D_5H resonance. The relative integrations for the other three resonances are 15:9:12.

Crystallographic Results and Discussion

General Molecular Structure. A perspective view of an individual $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}2\text{-}C_4H_7)_3$ molecule is

---

(23) Baker, E. C.; Halstead, G. W.; Raymond, K. N. *Struct. Bonding (Berlin)* **1976**, *25*, 23.

(24) Vanderhooft, J. C.; Ernst, R. D. *J. Organomet. Chem.* **1982**, 233, 313.

(25) Ernst, R. D.; Kennelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656.

(26) Hydrolysis of 0.100 g (0.186 mmol) of $(C_5(CH_3)_5)U(C_4H_7)_3$ led to evolution of 0.573 mmol of isobutene (3.08 mmol of isobutene/mmol of complex).

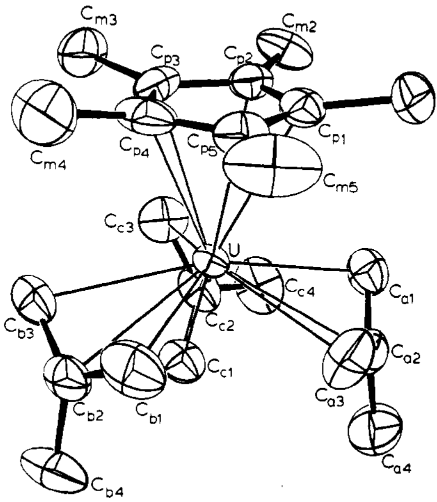


Figure 2. Perspective view and numbering scheme of an individual (η^5-$C_5(CH_3)_5$)U(η^3-2-C_4H_7)$_3$ molecule. The 50% probability vibrational ellipsoids are shown.

Table IV. Deviations (Å) of Atoms from Best Weighted Least-Squares Planes

(a) Planes Defined by the Three Backbone Carbon Atoms of the Allyl Ligands[a]

atom	dist	atom	dist	atom	dist
CA(4)	0.20	CB(4)	0.23	CC(4)	0.14
U	2.01	U	2.05	U	1.99

atom	dist	atom	dist
(b) Plane Defined by the Cyclopentadienyl Ligand[b]			
CP(1)	0.013	CM(1)	0.252
CP(2)	−0.007	CM(2)	0.107
CP(3)	−0.002	CM(3)	0.169
CP(4)	0.009	CM(4)	0.293
CP(5)	−0.013	CM(5)	0.114
		U	−2.521
(c) Idealized Pentagonal Plane[c]			
CA(1)	−0.072	CA(3)	0.093
CB(1)	−0.065	CB(3)	0.021
CC(1)	1.963	CC(3)	0.023
		U	−0.516

[a] Equations (monoclinic coordinates): *A*, $0.650x - 6.764y + 7.320z = 3.338$; *B*, $4.922x + 23.029y - 4.475z = 3.865$; *C*, $3.009x + 1.556y + 6.156z = 0.145$. [b] Equation (monoclinic coordinates): $8.859x - 5.598y - 2.259z = 1.473$. This plane is defined by the five carbon atoms CP(1)–CP(5). [c] Equation (monoclinic coordinates): $8.821x - 4.907y - 1.905z = -1.372$. This plane is defined by CA(1), CB(1), CA(3), CB(3), and CC(3). Interplanar angles: A–B, 63.2°; A–C, 22.1°; A–CP, 74.1°; A–PP, 72.0°; B–C, 85.2°; B–CP, 71.4°; B–PP, 71.3°; C–CP, 62.3°; C–PP, 59.6°; CP–PP, 2.8°

presented in Figure 2, along with the atom numbering scheme. Hydrogen atoms were neither located nor included in the structure. Pertinent bond distances and angles are contained in Table III, and various least-squares planes are described in Table IV. The five interior carbon atoms of the pentamethylcyclopentadienyl ligand have been given the sequential designations CP(1)–CP(5), with the methyl groups receiving the analogous CM(1)–CM(5) designations. The carbon atoms of the 2-methylallyl ligands are designated as CA(1)–CA(4) for allyl group A, CB(1)–CB(4) for group B, and CC(1)–CC(4) for group C and will simply be referred to as C(1)–C(4) when average bonding parameters are being discussed. The notations CP, CMA, CMB, and CMC refer respectively to the center of masses of the pentamethylcyclopentadienyl and the three allyl ligands. These center of masses are defined only by the carbon atoms bound to the uranium atom (e.g., CP(1)–CP(5), CA(1)–CA(3), etc.).

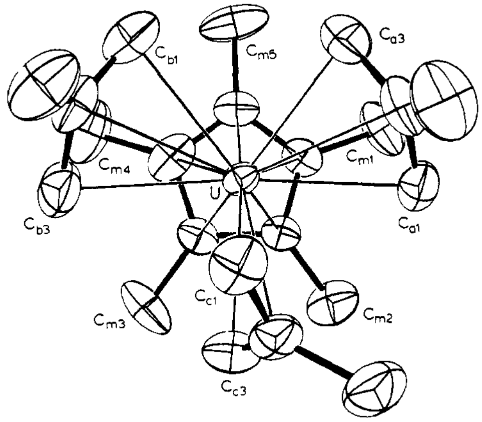


Figure 3. Perspective view of an individual (η^5-$C_5(CH_3)_5$)U(η^3-2-C_4H_7)$_3$ molecule perpendicular to the pentamethylcyclopentadienyl ligand plane. A partial numbering scheme has been included to aid the discussion in the text.

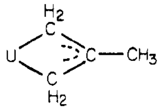
The overall disposition of ligands about the uranium atom may be regarded as distorted tetrahedral, with the bonding angles between pairs of ligand mass centers ranging from 95.1 (3) to 128.5 (3)°. However, there clearly is a great deal of distortion that primarily results from the different (sideways) orientation of allyl group C with respect to allyl groups A and B (which might be described as having a downward orientation). The distortion is such that the molecular stereochemistry is approaching that of a pentagonal bipyramid, with CP and CC(1) defining the axial sites and CA(1), CA(3), CB(1), CB(3), and CC(3) defining the equatorial plane (see Table IV). (Atom CC(1) is, however, actually located ca. 1.10 Å from the idealized axial line.) Such a configuration has been used to describe the structure of the somewhat related (η^5-C_5H_5)U[$(CH_2)_2P(C_6H_5)_2$]$_3$ ylide complex.[27] The cause of the distortion is best grasped by reference to Figure 3. It is observed that allyl groups A and B are essentially sitting atop methyl groups CM(1) and CM(4) of the pentamethylcyclopentadienyl ligand, with the result that CM(1) and CM(4) bend out of the cyclopentadienyl ligand plane in a direction away from the uranium atom more than the other methyl groups do (Table IV). This results in a reasonable packing of allyl groups A and B with respect to the $C_5(CH_3)_5$ ligand but would impose short contacts of atoms CC(2) and CC(3) with methyl groups CM(2) and CM(3) if a similar orientation of allyl group C were attempted. An "upward" orientation of allyl group C (where CC(4) is pointing between CM(2) and CM(3)) is here unattainable due to the significant extension of the methyl groups from the allyl ligand. One can speculate, however, that such an orientation might result for one of the allyl groups in the solid-state structure of the (η^5-$C_5(CH_3)_5$)U(η^3-C_3H_5)$_3$ complex. The sideways orientation of allyl group C clearly allows for a relatively effective fitting of atom CC(3) between methyl groups CM(2) and CM(3). Interestingly, in (η^5-C_5H_5)Mo(CO)$_2$(η^3-C_3H_5) spectral evidence has been provided for the existence of conformations having either the "downward" or "upward" (but not the "sideways") allyl ligand orientations.[28]

---

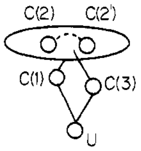
(27) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Inorg. Chem.* **1981**, *20*, 2466.

(28) (a) Davison, A.; Rode, W. C. *Inorg. Chem.* **1966**, *6*, 2124. (b) Faller, J. W.; Chen, C.-C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361.

The observed geometry of the complex seems to provide some insight into various molecular reorientation processes that clearly must be occurring in solution. The ^1H NMR spectra, for example, indicate all three allyl ligands to be equivalent at room temperature on the NMR timescale. Because of the essentially "keyed" interaction of the allyl ligands with the pentamethylcyclopentadienyl methyl groups (Figure 3), a "cartwheel" or "turnstile" rotation of this ligand would quite easily, perhaps almost inevitably, bring about equivalence of these ligands. The equivalence of the syn and anti substituents on the terminally bound allyl carbon atoms could probably be brought about by a rocking motion of an allyl ligand while in the sideways orientation (such as group C in Figure 2; of course, a $\pi \rightarrow \sigma$ isomerization must also be considered). This would seemingly require little other molecular reorientation as the CMC–U–CMA and CMC–U–CMB angles are fairly similar at 95.1 (3) and 99.2 (3)°, respectively. The postulated intermediate, of course, would involve the allyl group forming a more ylide-like attachment to the uranium atom, as in I, wherein the uranium atom lies in the allyl ligand plane.[29] The accessibility of intermediate I naturally depends heavily on the extent of interaction between the uranium atom and CC(2). In this regard, the nature of the disorder (depicted as II) present in the structure of $[\eta^3\text{-}C_3H_5)_2U(i\text{-}OC_3H_7)_2]_2$[12] might arise from a relatively low bonding interaction between uranium(IV) and the central carbon atom of an allyl ligand.



I



II

Bonding of Ligands. The pentamethylcyclopentadienyl ligand is bound in the usual fashion with average[30] U–C and C–C bond distances of 2.79 (1) and 1.41 (2) Å, respectively. As can be seen from Table IV, the atoms CP(1)–CP(5) are planar within experimental error, and their methyl substituents are located out of the pentamethylcyclopentadienyl ligand plane in the direction away from the uranium atom by an average of 0.19 Å, corresponding to a bend of 7.1 (6)°. The average separation of adjacent methyl groups on the pentamethylcyclopentadienyl ligand is 3.183 (12) Å. These parameters are comparable to those observed in other bis(pentamethylcyclopentadienyl)uranium derivatives.[31]

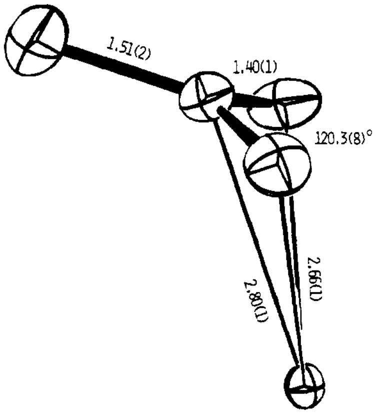
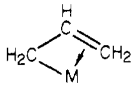


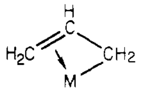
Figure 4. Side-on view of the bonding of a single π-allyl ligand to the uranium metal atom. Distances are given in angstroms.

The bonding description of the uranium–allyl linkages is naturally of greatest interest. Figure 4 presents a side-on view of a single such (clearly symmetric π-allyl) attachment. The average delocalized C–C bond distance of 1.40 (1) Å is quite comparable to values observed in a great number of transition-metal allyl complexes (ca. 1.35–1.45 Å).[4] Furthermore, the C(1)–C(2)–C(3) angles average 120.3 (8)°, again quite comparable to values observed for transition-metal systems (ca. 115–130°).[4] The data in Table IV indicate that the methyl substituents on the allyl group are displaced out of the allyl plane *toward* the uranium atom by an average of 0.19 Å, corresponding to an average bend of 7.3 (11)°. This is again much like most transition-metal systems where a similar bending of a 2-substituent generally takes place up to ca. 12° (e.g., $(\eta^3\text{-}2\text{-}C_4H_7)_2Ni$, 12°),[4a] although bending away from the metal is sometimes also observed. Whether the bending in the present case represents any electronic preferences or simply just packing forces is not evident.

Perhaps most informative are the various U–C(allyl) bond distances. In transition-metal allyl systems, the metal–carbon distance is nearly always shortest for the carbon atom(s) in the 2-position,[4] even though it is the 1- and 3-positions that formally share the negative charge. This would suggest a reasonable contribution of the olefin–metal interaction depicted in resonance hybrids IIIa,b.



IIIa



IIIb

In the case of a more ionic actinide metal such as uranium, for which olefin complexes are nearly unknown (note $(\eta^6\text{-}C_6H_6)U(AlCl_4)_3$),[32] one could readily predict less involvement of the formally uncharged central carbon atom in the bonding and thus one might expect to see more ylide character in the complex (such as in I). Indeed, the fact that the U–C(2) distances average 2.80 (1) Å compared to the average U–C(1,3) distances of 2.66 (1) Å clearly indicates a significant change in the nature of the bonding, particularly less involvement of the neutral central carbon atom.[33] (Note, however, that the U–C(2) distances are

---

(29) It is interesting to speculate that such π-allyl to ylide interconversions may be responsible for some of the catalytic behavior in such systems, in addition to the more commonly invoked π-allyl to σ-allyl isomerizations.

(30) When average values are quoted, the associated number in parentheses is the standard deviation of the mean.

(31) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170.

(32) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1971**, *5*, 439.

(33) (a) A similar situation may exist in the d^1 $(\eta^5\text{-}C_5H_5)_2Ti(\eta^3\text{-}1,2\text{-}$dimethylallyl) compound,[33b] where an average Ti–C(1,3) bond distance of 2.34 (2) Å was observed as compared to a Ti–C(2) bond distance of 2.43 (3) Å. Such a trend was not obvious, however, in recent d^0 zirconium(IV) allyl structures.[33c] It should also be noted that even though the allyl C(2) atom is generally closest to a transition metal, various molecular orbital calculations indicate that the metal–C bond order is actually less for the C(2) atom.[33d,e] Thus, factors besides bond strength may be at least partly responsible for the relative metal–carbon distances in allyl complexes. (b) Helmholdt, R. B.; Jellinek, F.; Martin, H. A.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1263. (c) Brauer, D. J.; Krüger, C. *Organometallics* **1982**, *1*, 204, 207. (d) Clarke, H. L. *J. Organomet. Chem.* **1974**, *80*, 369. (e) Bohm, M. C.; Gleiter, R. *Chem. Phys.* **1982**, *64*, 183.

quite comparable to the U–C(CP) distances.) Further, even though it is clear that there is less involvement of the central carbon atom, the overall geometry is still much closer to that of the usual allyl ligation rather than that of an ylide. Two useful (essentially alternative) geometric parameters have been noted to be of value in comparing various metal π-allyl complexes. (A third description relates to the orientation of an allyl ligand plane to a metal coordination plane.[4c]) The first is the so-called fold angle that is formed between the allyl ligand plane and the plane defined by the metal atom and the two terminal atoms (C(1) and C(3)) of the allyl group.[4a] For transition-metal complexes this angle is generally in the range of 90–115°, and a value of 180° would be indicative of an ylide structure. The second description defines a tilt angle τ that is the angle subtended about the allyl ligand center of mass by the central carbon atom and the bound metal.[4b] In most observed structures this parameter tends to range from 100 to 125°. A value of 180° would again correspond to an ylide configuration. The corresponding average values of these parameters observed in the present structure are 121.5 (9)° (being 121.1 (13), 120.7 (19), and 122.7 (13)° for the respective groups A, B, and C) and 126.0 (12)° (being 125.7 (18), 125.3 (24), and 127.1 (17)° for the respective groups A, B, and C). Thus the values observed here are at or slightly beyond the high end of values observed for transition-metal complexes yet not nearly that of an ylide complex. To what extent the observed geometric parameters reflect metal preferences rather than simply hybridization or other preferences by the allyl ligand is not yet clear. It is also important to note that even though two different orientations of the allyl ligand are observed on the coordination sphere (downward and sideways), their relative tilt and fold angles are essentially the same, which could indicate that the metal–allyl linkages are not effected by crystal packing forces. While it could be claimed that such packing forces are simply forcing a π configuration up to the point where a repulsive U–C(2) interaction becomes excessive, the nonbonded contacts observed in the structure are most severe between the ligands on a given coordination sphere. For example, the following nonbonded intramolecular contacts are observed, which are less than the sum of the van der Waals radii of carbon (1.7 Å) and/or a methyl group (2.0 Å):[34] CA(1)–CC(4) = 3.29 (2) Å; CA(1)–CC(2) = 3.24 (2) Å; CB(1)–CA(3) = 3.14 (3) Å; CC(1)–CB(3) = 3.37 (3) Å; CA(1)–CM(1) = 3.44 (2) Å; CC(3)–CM(3) = 3.44 (3) Å; CB(3)–CM(4) = 3.47 (2) Å. This would seem to suggest that the U–C(2) bond distances are perhaps actually being lengthened through intramolecular contact rather than being shortened through intermolecular contacts. Finally, it can also be observed that the intramolecular contacts are apparently starting to nudge allyl group C toward a σ-bound configuration since the U–CC(1) and U–CC(3) distances are respectively 2.713 (15) and 2.614 (14) Å. This is somewhat reminiscent of a recently described thorium benzyl complex, wherein a η^1 resonance hybrid seems to play a key role.[19]

It is important to note that both the average delocalized C–C bond distance of 1.27 (2) Å and the average C(1)–C(2)–C(3) bond angle of 145.1 (12)° found in the $[(\eta^3\text{-}C_3H_5)_2U(i\text{-}OC_3H_7)_2]_2$ structure[12] differ greatly from the values found in the present study. Reference to structure II is helpful in understanding the origin of this difference. If a disorder occurs in which the allyl ligand occupies two orientations, the apparent position of the central carbon atom will be at an intermediate site between the two actual locations. This apparent site is clearly closer to the metal than either of the actual locations, as the central atom locations of constant distance from the metal describe a semicircle (dashed on structure II). Several features should result from this distortion. First, large thermal parameters should be observed for the central carbon atom. Second, there will be an apparent shortening of the delocalized C–C bond distances, and finally the C(1)–C(2)–C(3) bond angle will appear more linear.[35] Each of these features is indeed observed in their data. However, the model of structure II indicates that the observed positions of the terminal carbon atoms will not be affected. Thus, even though the bond distance from the uranium to the central carbon atom is noticeably shorter in the disordered structure as expected from the above model (2.675 (16) Å vs. the present value of 2.80 (1) Å), the average distances to the terminal carbon atoms are quite comparable for the two structures (2.68 (1) Å vs. 2.66 (1) Å). Their observed C(1)–C(2)–C(3) angle of 145.1 (13)° has also been clearly affected by the disorder.

It is also instructive to compare the present results with those observed in the related ylide complex $(\eta^5\text{-}C_5H_5)U[(CH_2)_2P(C_6H_5)_2]_3$,[27] where the fold angles range from ca. 162 to 180° and U–C(ylide) bond distances average 2.66 (1) Å, identical with that observed in the present structure. It therefore appears that the uranium–carbon bonding is similar for the terminal carbon atoms in each of these complexes. Unfortunately, there is not a great deal of structural data that would allow similar comparisons with and for transition-metal complexes. It can be noted, however, that in $(\eta^3\text{-}2\text{-}C_4H_7)_2Ni$[36] and $[(CH_3)_2P(CH_2)_2]_4Ni_2$[37] (which contains one "terminal" ylide, actually a "phosphoallyl", per metal with two other ylide ligands serving to bridge the two metals), comparable Ni–C (terminal) bond distances of 2.018 (8) and 2.031 (3) Å, respectively, were observed. The Ni–C bond distances to the terminal carbon atoms of the bridging ylides were even shorter at 1.978 (3) Å. In $Cr_2(C_3H_5)_4$[38] and $Cr_2[(CH_2)_2P(CH_3)_2]_4$,[39] the respective Cr–C bond distances average 2.249 (3) and 2.22 (1) Å. Overall, then, metal–terminal carbon bond distances appear relatively comparable for ylide and allyl complexes whether the metal is a transition metal or actinide metal.

Despite the above discussion, the nature of interaction between the uranium atom and the central carbon atom of the allyl ligand remains most open to question. As already mentioned, the U–C(2) distances are longer than the U–C(1,3) distances, in direct opposition to most transition-metal systems. The only structural data involving an actinide bound to a neutral olefin concerns the uranium(III) arene complex $(\eta^6\text{-}C_6H_6)U(AlCl_4)_3$,[32] which possessed U–C bond distances averaging ca. 2.91 (1) Å.[40] Correcting this value for the differences in size for U(III) and U(IV) (ca. 0.13 Å)[41] leads to a predicted U(IV)–neutral carbon atom bond distance of 2.78 Å, very similar to that

---

[34] Pauling, L. "The Nature of the Chemical Bond", 3rd Ed.; Cornell University Press: Ithaca, New York, 1960; Chapter 7.

[35] The observed fold angles of 134.6 and 135.9° would also be similarly effected by disorder.

[36] Uttech, R.; Dietrich, H. *Z. Kristallogr.* **1965**, *122*, 60.

[37] Brauer, D. J.; Kruger, C.; Roberts, P. J.; Tsay, Y.-H. *Chem. Ber.* **1974**, *107*, 3606.

[38] Aoki, T.; Furusaki, A.; Tomiee, Y.; Ono, K.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 545.

[39] Cotton, F. A.; Hanson, B. E.; Ilsley, W. H.; Rice, G. W. *Inorg. Chem.* **1979**, *18*, 2713.

[40] An estimated standard deviation for the individual U–C bond distances was suggested as being less than 0.05 Å. This, however, seems to be significantly larger than justified as individual values ranged from 2.91 to 2.93 Å.

[41] Shannon, R. D. *Acta. Crystallogr., Sect. A* **1976**, *A32*, 751.

observed here for the U–C(2) bond distances, suggesting relatively similar bonding. It can be noted that while the $(\eta^6\text{-}C_6H_6)U(AlCl_4)_3$ complex is readily destroyed by THF, it is thermally stable to 110° (80° in vacuo),[32] suggesting a reasonably attractive interaction. Due to the contracted nature of the metal f orbitals, however, this bonding would seem to involve a predominantly donor role for the central carbon atom (and the entire allyl anion), analogous to the situation for silver(1+) olefin complexes.[42]

The above structural results shed some light on the nature of the bonding in actinide π-allyl complexes. There would seem to be a definite interaction taking place between the uranium atom and the central carbon atom of the allyl ligand, although the relative strength of this bonding is certainly open to question. A more explicit understanding of the bonding in these systems, however, will only be obtained through further chemical and physical studies.

Acknowledgment. R.D.E. wishes to express his graditude for partial support of this research from the donors of the Petroleum Research Fund, administered by the American Chemical Society, a Pennwalt Corporation Grant of Research Corp., and The University of Utah Research Committee. We wish to thank Professor Roger E. Cramer of the University of Hawaii for providing structural data in advance of publication.

Registry No. $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}2\text{-}C_4H_7)_3$, 84895-68-1; $(\eta^5\text{-}C_5(CH_3)_5)U(\eta^3\text{-}C_3H_5)_3$, 84895-69-2.

Supplementary Material Available: Table II, a listing of atomic thermal parameters, and a table of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

---

[42] (a) Quinn, H. W.; Tsai, J. H. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 217. (b) Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *43*, C7.

Crystal and Molecular Structure of *N*-(Trimethylstannyl)succinimide, an Associated, Helical Polymer

F. E. Hahn, T. S. Dory, C. L. Barnes, M. B. Hossain, D. van der Helm, and J. J. Zuckerman*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

Received September 1, 1982

N-(Trimethylstannyl)succinimide, $C_7H_{13}NO_2Sn$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.599\ (8)$ Å, $b = 14.054\ (12)$ Å, $c = 13.558\ (10)$ Å, $\beta = 110.29\ (7)°$, $V = 1894.26$ Å^3, $Z = 8$, and $\rho_{\text{calcd}} = 1.754$ g cm^{-3}. The structure was solved by Patterson and Fourier techniques from 3903 reflections measured at 138 ± 2 K on an Enraf-Nonius CAD/4 automatic diffractometer using monochromated Mo Kα radiation to a final R value of 0.045 for the 3588 reflections included in the least-squares sums ($R_w = 0.0581$). The title compound contains five-coordinated, trigonal-bipyramidal tin groups with axial -O→Sn-N units [175.1° (mean)] bound through planar succinimide rings which use only one of their carbonyl groups in coordination. This C═O bond is longer [d(C═O) = 1.227 Å (mean)] and its contiguous C—N distance is shorter [d(C—N) = 1.366 Å (mean)] than those for the noncoordinated carbonyl group [d(C═O) = 1.211 Å (mean); d(C—N) = 1.394 Å (mean)] as expected for contributions by an >N═C(—O$^-$)- form in the coordinated carbonyl. The nitrogen atom is planar [the sum of the three angles subtended at nitrogen is 359.8° (mean)], but the ∠-Sn—N—C(═O)- angles are larger than the ∠-C(═O)—N—C(═O)- [110.3° (mean)] angles. The trimethyltin unit is not perfectly planar, with the sum of the three ∠sC—Sn—C being 354.3° (mean) and the tin atom lying out of the plane determined by the three carbon atoms at 0.30 Å (mean) toward the nitrogen atom. The chains are nearly linear at the tin atom, but bent through the -O═C—N- system of the succinimide ring at ∠-Sn←O═C< [136.5 (3)°, 142.3 (4)°], -O═C—N- [123.0° (mean)], and -C—N—Sn- [121.6° (mean)] angles. The planes containing the ←O═C—N- units of the succinimide rings are turned at each tin atom by 30.18° at Sn(1) and 38.72° at Sn(2). The chains thus propagate along the *b* axis of the crystal to produce a flattened helix which completes its rotation with each fifth molecule. There are two crystallographically independent molecules per asymmetric unit, two asymmetric units per helix, and two helixes per centrosymmetric unit cell. The two helixes, being related by the center of symmetry, turn in opposite hands to produce a meso form of the solid.

Introduction

N-(Trimethylstannyl)succinimide has a number of features of potential structural interest. One is the structural consequence of the competition for the nitrogen atom lone pair among the d orbitals at tin and the double amide system of the succinimide ring. Populating the tin orbitals would lower its Lewis acid character, potentially leading to a monomeric structure containing four-coordinated tin, while delocalization of the lone pair through the five-atom O–C–N–C–O π system of the ring might allow coordination by both oxygen atoms to adjacent tins to give a rare, six-coordinated, R_3SnNO_2 system. Five-coordination in the ubiquitous, axially most-electronegative N–Sn←O configuration could lead to an *n*-meric ring association of coordinated molecules, the smallest of which would be a puckered tetramer, a situation of the type we have recently discovered in the hexameric triphenyltin(IV) diphenyl phosphate.[1] Carbonyl groups are usually weak donors toward tin, but the structures of the dimethyltin(IV) di-

---

[1] Molloy, K. C.; Nasser, F. A. K.; Barnes, C. L.; van der Helm, D.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 960.