oxygen to the metal ion with some π bonding M→CN with the cyanide ions. Multiple bonding to the bridging oxygen decreases the Re–O distance significantly below that for a single bond. On the basis of the small range of Re–O distances and the relative shortness of the bridged (single) Re–O bond compared with (single) Re–C distances we are of the opinion that all of the Re–O bonds seen here and in the other compounds in Table VI are stronger than single bonds and that none reaches pure triple-bond characteristics.

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The Crystal Structure of Triindenyluranium Chloride[1]

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The crystal structure of triindenyluranium chloride, $U(C_9H_7)_3Cl$, was determined from single-crystal X-ray diffraction data by use of Patterson and Fourier techniques and refined by the method of least squares to an R index of 0.047. The orthorhombic unit cell has $a = 8.576$ Å, $b = 14.24$ Å, $c = 16.73$ Å; the space group is $P2_12_12_1$; and $Z = 4$. In each molecule of the structure a uranium atom is bonded almost symmetrically to the carbon atoms of the five-membered ring of each of three planar indenyl ring systems at distances of 2.67–2.89 Å and to one chloride ion at 2.593 Å, in a tetrahedral array. Some types of bonding which are consistent with the observed molecular structure are discussed.

Introduction

A report on the preparation of triindenyluranium chloride,[3] $(C_9H_7)_3UCl$, raises the question of the type of bonding between the metal and the five-membered rings in this compound. While the similar cyclopentadienyl complexes with trivalent lanthanides and actinides are generally regarded as ionic,[4] there is evidence for a higher degree of covalency in organometallic complexes of the tetravalent actinides. Several compounds of uranium(IV) which have been described as having covalent bonding to some extent are $(C_5H_5)_3UCl$,[5] $(C_5H_5)_4U$,[6] $(C_3H_5)_4U$ (C_3H_5 = allyl),[7] and $(C_8H_8)_2U$ (C_8H_8 = cyclooctatetraenyl).[8] Structural investigation[9] of $(C_8H_8)_2U$ showed the existence of a π-sandwich complex similar to the well-known $(C_5H_5)_2Fe$, ferrocene.[10] For the case of $(C_5H_5)_3UCl$ an approximate determination,[11] in which individual carbon atoms were not located, showed the chlorine atom and the five-membered rings to be in a tetrahedral array about the uranium atom. This structure is consistent with either covalent or electrostatic attraction. The chemical evidence[5] for $(C_5H_5)_3UCl$ favors covalent bonding between the rings and uranium and ionic bonding between the chlorine and uranium.

Recently the structure of triindenylsamarium, $(C_9H_7)_3Sm$, was reported;[12] in it the metal is symmetrically bonded to the five-membered rings of three indenyl ring systems in a trigonal array. In contrast a covalent σ-type metal to carbon bond was proposed for $(C_9H_7)_3Sm \cdot THF$, based on nmr evidence.[13] No other lanthanide or actinide indenyl complexes have been reported, but the transition metal complexes $(C_9H_7)_2Fe$[14] and $(C_9H_7)_2Ru$[15] were both shown to have the sandwich-bond geometry.

The determination of the structure of triindenyluranium chloride, to be discussed here, was undertaken to provide accurate details from which the bonding possibilities can be considered. The naming of the compound which we use is not meant to imply any particular degree of covalency.

Experimental Section

The Sample.—The synthesis of triindenyluranium chloride is described elsewhere.[3] The compound crystallizes in the form of irregular polyhedra which are deep reddish brown and very reactive with moisture and air. For the X-ray diffraction study a crystal was chosen which had no well-defined faces but was approximately a prolate ellipsoid with major and minor axes of length 0.25 and 0.22 mm, respectively. It was sealed under vacuum in a thin-walled glass capillary tube.

Data Collection.—Precession X-ray photographs showed the orthorhombic symmetry, gave preliminary unit cell dimensions, and indicated the probable space group $P2_12_12_1$ by the pattern of systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. For measurement of intensities the crystal was mounted on a computer-controlled Picker X-ray diffractometer which was equipped with a scintillation counter. Molybdenum Kα (Nb filtered) X-rays were employed at a takeoff angle of 2° and all independent reflections out to $2\theta = 55°$ were measured by θ–2θ scanning. The background was counted at the ends of each scan and the values were averaged. The length of scan ranged from 1° at the lower to 1.3° at the upper limit. The detector aperture was 3 mm. A reference reflection was measured once each hour; it usually varied by less than 2%

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] Supported by the Bundesministerium für wissenschaftliche Forschung, Bonn, Federal Republic of Germany.

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TABLE I

POSITIONAL AND THERMAL PARAMETERS[a] FOR $U(C_9H_7)_3Cl$

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
U	0.03411 (4)	0.26643 (2)	0.23992 (3)	60.3 (4)	24.7 (2)	22.7 (1)	2.7 (3)	−1.2 (2)	0.1 (1)
Cl	0.0292 (3)	0.4485 (2)	0.2377 (2)	118 (4)	26 (1)	33 (1)	0 (2)	−2 (2)	0 (1)
C(1)	0.2864 (12)	0.1519 (8)	0.2457 (9)	71 (15)	41 (6)	66 (7)	24 (7)	−7 (10)	5 (7)
C(2)	0.3220 (14)	0.2125 (10)	0.1805 (7)	59 (16)	50 (10)	40 (5)	17 (10)	7 (7)	−1 (5)
C(3)	0.3601 (15)	0.2998 (9)	0.2127 (7)	69 (18)	48 (8)	39 (5)	21 (10)	−15 (7)	−7 (5)
C(4)	0.4085 (15)	0.3880 (10)	0.1751 (8)	72 (18)	56 (9)	57 (6)	−24 (11)	14 (8)	0 (6)
C(5)	0.4430 (14)	0.4613 (10)	0.2209 (9)	58 (17)	54 (8)	64 (7)	−30 (10)	9 (9)	−11 (6)
C(6)	0.4270 (16)	0.4571 (11)	0.3058 (9)	87 (22)	62 (9)	65 (8)	15 (12)	−23 (9)	−24 (7)
C(7)	0.3766 (14)	0.3771 (9)	0.3452 (7)	59 (17)	39 (7)	50 (6)	6 (9)	−23 (8)	−9 (5)
C(8)	0.3437 (13)	0.2987 (9)	0.2967 (7)	37 (15)	49 (8)	39 (5)	14 (9)	−5 (7)	−1 (5)
C(9)	0.2935 (15)	0.2039 (10)	0.3181 (8)	67 (18)	45 (9)	41 (6)	15 (10)	−2 (8)	7 (5)
C(10)	−0.1271 (17)	0.1545 (9)	0.1375 (7)	154 (25)	41 (7)	31 (5)	−26 (12)	−27 (9)	−5 (5)
C(11)	−0.2200 (13)	0.2360 (9)	0.1408 (6)	101 (17)	40 (6)	26 (4)	−15 (10)	−16 (6)	5 (5)
C(12)	−0.1402 (14)	0.3094 (9)	0.0981 (6)	73 (18)	46 (7)	22 (4)	−3 (10)	−10 (7)	−2 (4)
C(13)	−0.1865 (15)	0.4026 (9)	0.0787 (6)	137 (21)	44 (7)	29 (4)	−7 (10)	−40 (8)	4 (4)
C(14)	−0.0772 (19)	0.4542 (9)	0.0305 (7)	230 (34)	38 (7)	30 (5)	−4 (12)	−16 (10)	2 (5)
C(15)	0.0657 (18)	0.4170 (10)	0.0100 (7)	192 (31)	57 (9)	31 (5)	−15 (3)	−3 (9)	2 (5)
C(16)	0.1144 (17)	0.3291 (9)	0.0311 (7)	147 (24)	42 (8)	36 (5)	6 (11)	2 (9)	−7 (5)
C(17)	0.0082 (12)	0.2723 (9)	0.0736 (5)	83 (19)	39 (6)	20 (3)	7 (9)	−4 (5)	−4 (4)
C(18)	0.0125 (15)	0.1757 (8)	0.0982 (6)	124 (24)	43 (7)	21 (4)	4 (10)	−13 (8)	−10 (4)
C(19)	−0.1959 (17)	0.1805 (10)	0.3190 (9)	111 (22)	56 (10)	42 (6)	−34 (12)	8 (10)	3 (6)
C(20)	−0.0656 (17)	0.1642 (8)	0.3679 (7)	155 (27)	31 (6)	37 (5)	−12 (10)	21 (9)	9 (4)
C(21)	−0.0307 (16)	0.2488 (8)	0.4086 (5)	150 (19)	36 (8)	24 (3)	−11 (12)	10 (8)	8 (3)
C(22)	0.0850 (16)	0.2702 (11)	0.4699 (6)	183 (25)	81 (10)	27 (4)	13 (16)	−14 (8)	−6 (6)
C(23)	0.0779 (17)	0.3598 (11)	0.5020 (7)	168 (27)	74 (10)	28 (5)	13 (14)	−9 (8)	−5 (5)
C(24)	−0.0266 (21)	0.4275 (9)	0.4741 (7)	257 (33)	39 (7)	32 (5)	23 (15)	28 (11)	−10 (4)
C(25)	−0.1296 (16)	0.4114 (9)	0.4139 (6)	159 (24)	47 (8)	26 (4)	19 (12)	14 (8)	−2 (5)
C(26)	−0.1339 (16)	0.3202 (8)	0.3818 (6)	96 (20)	42 (7)	21 (4)	16 (9)	9 (7)	5 (4)
C(27)	−0.2354 (14)	0.2789 (10)	0.3215 (7)	91 (18)	49 (9)	32 (5)	4 (10)	29 (7)	5 (5)

[a] Thermal parameters are for the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

from one measurement to the next but its value changed by 4% in one case. There was no net change in the reference intensity during the course of the data collection.

Twelve reflections with $2\theta \approx 45°$ were carefully centered in the detector and their setting angles used in a least-squares refinement of the unit cell dimensions. The wavelength of Mo Kα was taken to be 0.70926 Å.

Calculations.—Corrections for absorption were calculated with the ORABS computer program,[16] which was modified by C. K. Johnson to handle an ellipsoidal crystal. The linear absorption coefficients for $U(C_9H_7)_3Cl$ is 98.4 cm^{-1}, and the calculated transmission factors ranged from 0.22 to 0.24. Intensities were normalized by comparison to the values of the reference reflection interpolated between measurements, corrected for absorption, and converted to squared structure amplitudes.

A Patterson map was calculated and interpreted to yield the positions of the uranium and chlorine atoms. Subsequent difference Fourier maps revealed the locations of the 27 carbon atoms of the asymmetric unit.

The positions and anisotropic thermal parameters of the 29 nonhydrogen atoms and one scale factor were refined by the method of least squares. For these computations a modification of the full-matrix computer program of Busing, Martin, and Levy[17] was used. The function minimized was $\Sigma w(F^2 - F_o^2)^2$, where F_o is the observed structure factor and F is the calculated structure factor corrected for extinction using Coppens and Hamilton's formulation[18] of the Zachariasen approximation.[19] Accordingly F is defined by $F^2 = F_k^2 y$, where F_k is the scaled calculated structure factor and $y = (1 - g\gamma F_c^2)^{-1/2}$. In this expression γ is a quantity which depends on the mean path length, the polarization factor, the wavelength, and the cell volume; and g is the isotropic extinction parameter, which was varied in the least-squares refinement. F_c is the unscaled absolute calculated structure factor. The weight, w, of an observation was taken as $1/\sigma^2(F_o^2)$, and the variance, $\sigma^2(F_o^2)$, was estimated from counting statistics plus a contribution of 3% of the intensity for possible systematic errors. Intensities measured to be less than background were set equal to zero.

Atomic scattering factors for U^{4+}, Cl^-, and C were taken from Cromer and Waber,[20] and the scattering by uranium was corrected for the real and imaginary components of anomalous dispersion using Cromer's table.[21] As a test for the absolute configuration, the sign of $\Delta f''$ was changed and then $\Delta f''$ was adjusted in the refinement. Initially the R index increased significantly. Then, on varying the $\Delta f''$, it returned to its original sign and reached a final value of −9.5 (4) electrons (theoretical value −9.19). Thus the correct absolute configuration is given by the positional parameters in Table I.

For all 2685 reflections the index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.047, and the standard deviation of an observation of unit weight was 1.30. The refined positional and thermal parameters are given in Table I, and the observed (corrected for extinction with refined g of 0.86 (3)) and calculated structure amplitudes on an absolute scale are available elsewhere.[22]

After this refinement was completed, a difference Fourier map was calculated in an attempt to find the hydrogen atoms. Some peaks appeared at or near the expected positions, but not all the hydrogen atoms could be located. Moreover, calculation of structure factors with hydrogen atoms in assumed reasonable positions did not reduce the R index significantly. Thus the hydrogen atoms were not included in further calculations.

From the final parameters bond distances and angles of interest were calculated with the program ORFFE.[23]

Results and Discussion

The orthorhombic unit cell has the following dimensions at 23°: $a = 8.576$ (2) Å, $b = 14.238$ (5) Å, and $c = 16.725$ (5) Å, with least-squares standard errors in

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[16] D. J. Wehe, W. R. Busing, and H. A. Levy, "ORABS, A Fortran Program for Calculating Single-Crystal Absorption Corrections," Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

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[19] W. H. Zachariasen, *ibid.*, **23**, 558 (1967).

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[22] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[23] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

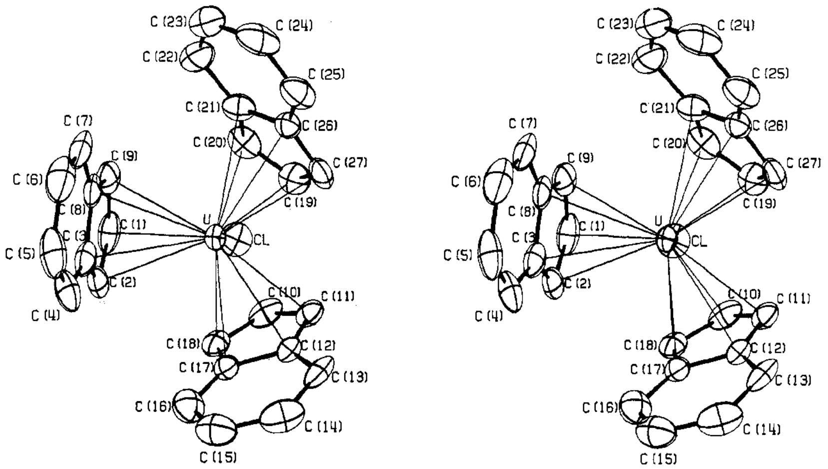

Figure 1.—Stereoscopic view of one molecule of U(C$_9$H$_7$)$_3$Cl. Atoms are depicted by 50% probability thermal ellipsoids.

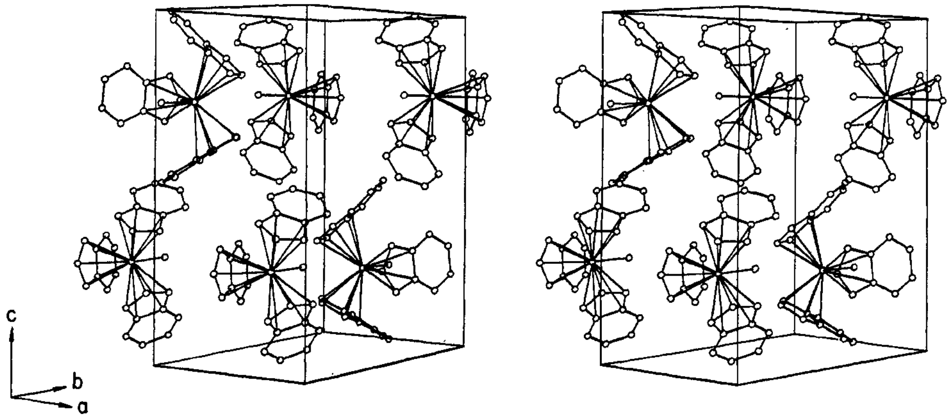

Figure 2.—Stereoscopic view of the contents of one and a half unit cells of U(C$_9$H$_7$)$_3$Cl to show packing of molecules.

parentheses. A density of 2.01 g cm^{-3} is calculated for 4 molecules per unit cell.

The structure of triindenyluranium chloride is illustrated by Figure 1, which shows one molecule, including the physically reasonable thermal motions depicted by their 50% probability ellipsoids,[24] and by Figure 2, which shows the contents of the unit cell. It is seen that the chlorine and the five-membered rings of three indenyl moieties are arranged tetrahedrally about the uranium atom. The extent to which this arrangement approximates a regular tetrahedron is shown by the following angles among normals to planes A, B, and C and the U–Cl bond direction: U–Cl to A, 108°; U–Cl to B, 107°; U–Cl to C, 105°; A to B, 112°; A to C, 120°; B to C, 105°. The designations A, B, and C are defined by reference to Figures 1 and 3.

The uranium atom is bonded to the carbon atoms of the five-membered rings of three indenyl ring systems at distances (Table II) ranging from 2.67 to 2.89 Å. The closest C–U approach, in each case, is to the three nonbridging atoms of the five-membered rings. The distances from the uranium atom to the centroids of rings A, B, and C are 2.51, 2.49, and 2.49 Å, respectively.

TABLE II

URANIUM TO RING DISTANCES (Å)

Ring A		Ring B		Ring C	
U–C(1)	2.71 (1)	U–C(18)	2.71 (1)	U–C(19)	2.67 (1)
U–C(9)	2.73 (1)	U–C(10)	2.72 (1)	U–C(27)	2.69 (1)
U–C(2)	2.77 (1)	U–C(11)	2.77 (1)	U–C(20)	2.73 (1)
U–C(8)	2.86 (1)	U–C(17)	2.79 (1)	U–C(26)	2.88 (1)
U–C(3)	2.87 (1)	U–C(12)	2.87 (1)	U–C(21)	2.89 (1)

The nine-carbon indenyl ring systems are planar within experimental error. Equations for the least-squares best planes, in which x, y, and z are fractional crystal coordinates, are as follows: (A) $8.17x - 4.10y + 1.36z = 2.01$, average deviation 0.02 Å; (B) $3.49x + 4.51y + 1.43z = 2.28$, average deviation 0.04 Å; (C) $-5.62x - 3.73y + 1.18z = 4.12$, average deviation 0.04 Å.

Bond lengths and angles within the indenyl rings are given in Figure 3. The least-squares standard deviation is 0.02 Å for each of the C–C bonds and 1.2° for the angles. The average C–C distance in the six-membered rings is 1.41 Å and in the five-membered rings is 1.43 Å. These values are within the range expected for five- and six-membered conjugated ring systems. The accuracy of the determination of carbon positions is not great enough to allow us to ascribe significance to the variations found.

The U–Cl bond length is 2.593 (3) Å and is comparable to that in (C$_5$H$_5$)$_3$UCl which is 2.559 (16) Å. Other, nonbonded, contacts between the Cl atom and the C atoms of various rings are listed in Table III. Since the normal van der Waals distance[25] between a Cl atom and an aromatic ring is about 3.5 Å, there appear to be

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[24] C. K. Johnson "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965, p 70.

[25] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 237.

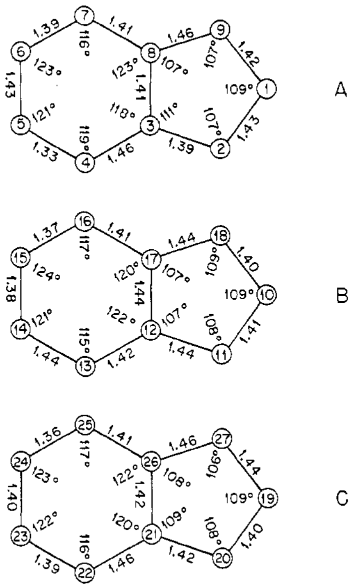

Figure 3.—Bond distances and angles in the three indenyl moieties.

TABLE III

CHLORINE TO CARBON DISTANCES (Å)

Ring A		Ring B		Ring C	
Cl···C(4)	3.52	Cl···C(13)	3.30	Cl···C(25)	3.29
C(3)	3.57	C(12)	3.39	C(26)	3.33
C(5)	3.57	C(14)	3.58	C(20)[a]	3.56
C(8)	3.58	C(10)[a]	3.70	C(27)	3.60
C(6)	3.60	C(17)	3.72	C(19)[a]	3.72
C(7)	3.63	C(15)	3.85	C(24)	3.99
Cl(1)[a]	3.97	C(16)	3.92	C(21)	4.06
C(2)	4.30	C(11)	4.04	C(23)	4.62
C(9)	4.37	C(18)[a]	4.26	C(22)	4.67

[a] Atomic position derived from the basic site x, y, z, by the symmetry operation $-x, {}^1/_2 + y, {}^1/_2 - z$.

some rather short distances in the case of rings B and C. Packing of molecules in the structure is shown in Figure 2. It is of interest that the U–Cl bond of one molecule is directed toward the uranium atom of an adjacent molecule; however, there is no bonding because the Cl···U distance is 4.58 Å.

Because of the U–C bond lengths found and the orientation of the indenyl moeities, we can rule out σ bonding of the uranium atom to a single carbon atom of the ring such as was found in $(\pi\text{-}C_5H_5)Fe(CO)_2$(1-indenyl).[26] (For a description of the nomenclature in which 1-indenyl is called *monohapto*indenyl, see Cotton.[27]) Other possibilities include 1,2,3-*trihapto*indenyl, 1,2,3,8,9-*pentahapto*indenyl, ionic bonding, or some combination of covalent and electrostatic interaction.[28] Possible support for some trihapto character of the arrangement is the observed shorter bonds between uranium and carbon atoms in the 1,2,3 ring positions of each indenyl moeity, but this also can be ascribed to lengthening of bonds to carbon atoms in the 8,9 positions resulting from steric interference between the chlorine atoms and the six-membered rings, especially for rings B and C. If the variation is attributed to steric causes, then the five-membered rings are essentially symmetrically bonded to the uranium atom; this would be consistent with either pentahapto covalent or ionic bonding. The U–C distances, which range from 2.67 to 2.89 Å, correspond rather closely to the U–C distance of 2.648 Å in sandwich-bonded uranocene[9] and to the range of 2.68–2.82 Å in the less accurately known structure of $(C_5H_5)_3UCl$.[11] There is, in fact, much similarity between the molecular configurations of $(C_9H_7)_3UCl$ and $(C_5H_5)_3UCl$. If this structural similarity can be taken to mean similar bonding, then the indenyl rings are bonded to the uranium atom with considerable covalent character because chemical evidence indicates covalency in $(C_5H_5)_3UCl$.[5] The tetrahedral arrangement of the ligands found with $(C_9H_7)_3UCl$ and the evidence for pentahapto character of the bonding of the aromatic ligands to the metal suggests that, in case of covalent bonding, π interaction of the indenyl ligands with the uranium $f_{x(z^2-y^2)}$, $f_{y(z^2-x^2)}$, and $f_{z(x^2-y^2)}$ orbitals should be involved.[29]

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[26] F. A. Cotton, A. Musco, and G. Yagupsky, *J. Amer. Chem. Soc.*, **89**, 6136 (1967).

[27] F. A. Cotton, *ibid.*, **90**, 6230 (1968).

[28] The numbers used here correspond to the standard organic chemical nomenclature for any indenyl ring and not to the numbering used in Table I.

[29] For the symbolism of f orbitals, see H. G. Friedman, G. R. Choppin, and D. G. Feuerbacker, *J. Chem. Educ.*, **41**, 354 (1964).