Crystal Structure of Triindenylsamarium[1a]

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Abstract: The crystal structure of triindenylsamarium has been determined from three-dimensional X-ray data measured by counter methods. $Sm(C_9H_7)_3$ crystallizes in the orthorhombic space group *Pbca* with cell dimensions $a = 15.568$ (3), $b = 31.348$ (8), and $c = 8.265$ (2) Å, and $\rho_{calcd} = 1.63$ g cm^{-3} for $Z = 8$. Least-squares refinement gave a conventional *R* factor of 0.07 for 1791 observed reflections. In the monomeric molecule the samarium atom is symmetrically bonded to the five-membered ring portion of the indenyl systems with an average samarium–carbon bond distance of 2.75 Å. The placement of the indenyl moieties is such that the angles among normals from the samarium atom to the plane of the rings are close to 120°. However, there is no evidence for preferential bonding of the samarium atom to the electron-rich C-1 position on the indenyl groups.

The nature of the metal–carbon interaction in complexes of the lanthanide and actinide elements has been the subject of many recent investigations.[2,3] Streitwieser and coworkers have postulated f orbital participation in the metal–ligand bond in the dicyclooctatetraenylactinides on the basis of chemical behavior,[4] nuclear magnetic resonance contact shift studies,[5,6] and structural investigations.[7-9] In contrast, the cyclooctatetraenyllanthanides appear to be substantially ionic.[10] For the cyclopentadienides Nugent, *et al.*, have estimated[11] the covalency of the organometallic bonds to be less than 5%. However, Tsutsui and Gysling have found evidence for a covalent bonding mode in the related tetrahydrofuran adduct of triindenylsamarium.[12]

X-Ray structural data have been published on three cyclopentadienyl-based lanthanide and actinide element compounds. In $U(C_5H_5)_3Cl$[13] and $U(C_9H_7)_3Cl$[14] the five-membered rings are coordinated in a pentahapto fashion, and the overall geometry at the uranium atom is essentially tetrahedral. The structure of tricyclopentadienylsamarium, on the other hand, is reported to be a complex polymeric arrangement which involves as many as four different types of samarium–carbon bonds.[15] The crystal structure of triindenylsamarium was undertaken to clarify the role of the samarium atom in an environment of five-membered ring systems.

Experimental Section

1. Sample Preparation. The synthesis of triindenylsamarium was accomplished by the addition of samarium trichloride to a benzene solution of diindenylmagnesium at 50°. The mixture became blood-red immediately, and filtration followed by slow evaporation of the solvent produced the deep red, air-sensitive crystalline product. For the X-ray diffraction study a triangular chip was chosen with a maximum dimension of 0.58 mm and a minimum thickness of 0.04 mm. The crystal was sealed under argon in a thin-walled glass capillary tube.

2. Data Collection. Preliminary precession X-ray photographs showed the orthorhombic symmetry and uniquely defined the space group as *Pbca* by the systematic absences: $hk0$, $h = 2n + 1$; $h0l, l = 2n + 1$; $0kl, k = 2n + 1$.

For the measurement of intensities the crystal was mounted on a computer-controlled Picker X-ray diffractometer. Copper Kα (Ni filtered) radiation was selected to avoid overlap problems which could arise from having a long *b* axis. All reflections out to $2\theta = 120°$ were measured by the θ–2θ scanning technique. The background was counted at the ends of each scan, and the values were averaged. The length of the 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; there was no net change in the reference intensity during the course of the data collection.

Twelve reflections with 2θ values greater than 87° were carefully centered in the detector and their setting angles used in a least-squares refinement of the cell dimensions.

3. Calculations. The lattice parameters at 23° are $a = 15.568$ (3), $b = 31.348$ (8), and $c = 8.265$ (2) Å. A density of 1.63 g cm^{-3} is calculated for eight molecules per unit cell.

For the purpose of correcting for absorption, the crystal was described by eight bounding planes which were derived from the coordinates of corners measured with a microscope. Calculated transmission factors were then obtained with the ORABS computer program.[16] A large variation in these factors, 0.04 to 0.43, resulted from the relatively high linear absorption coefficient, 201 cm^{-1}, and the plate-like morphology of the sample. Indeed the systematic errors which may arise from this source should be considered when evaluating the significance of interatomic distances and the shapes of thermal ellipsoids. Intensities were normalized by comparison with the values of the reference reflection interpolated between measurements, corrected for absorption, and

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[1] (a) Presented in part before the American Crystallographic Association Meeting, Columbia, S. C., Jan 31–Feb 4, 1971. (b) ORAU Research Participant, Summer 1969; address correspondence to this author at The University of Alabama. (c) Oak Ridge National Laboratory.

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Table I.

Atom	x/a	y/b	z/c	$10^4\beta_{11}$[a]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Sm	0.2064 (1)	0.3833 (1)	0.3513 (2)	34 (0)	6 (0)	102 (1)	−1 (0)	3 (0)	−1 (0)
C(1)	0.1269 (7)	0.4037 (4)	0.6343 (14)	46 (6)	13 (2)	177 (24)	6 (2)	24 (10)	−7 (4)
C(2)	0.1431 (8)	0.3590 (3)	0.6394 (16)	47 (6)	10 (2)	136 (23)	−2 (2)	0 (11)	−5 (4)
C(3)	0.2317 (7)	0.3529 (3)	0.6580 (16)	39 (6)	11 (2)	146 (24)	−2 (3)	5 (9)	6 (6)
C(4)	0.2817 (7)	0.3153 (3)	0.6721 (14)	61 (6)	11 (1)	138 (24)	1 (2)	−19 (10)	6 (4)
C(5)	0.3683 (8)	0.3200 (4)	0.6792 (17)	68 (7)	15 (2)	277 (36)	10 (3)	−38 (13)	−3 (4)
C(6)	0.4075 (7)	0.3593 (5)	0.6757 (18)	39 (6)	29 (3)	257 (36)	3 (3)	−20 (11)	4 (9)
C(7)	0.3631 (8)	0.3974 (4)	0.6640 (16)	60 (7)	21 (2)	165 (27)	−8 (3)	−8 (12)	−6 (6)
C(8)	0.2720 (8)	0.3949 (4)	0.6570 (15)	60 (6)	10 (1)	111 (22)	−1 (3)	−10 (10)	−5 (7)
C(9)	0.2064 (7)	0.4249 (3)	0.6443 (15)	75 (5)	10 (2)	143 (24)	2 (2)	14 (9)	0 (4)
C(10)	0.3288 (6)	0.4343 (6)	0.2008 (16)	36 (5)	12 (1)	214 (32)	−1 (2)	22 (9)	−6 (5)
C(11)	0.2904 (7)	0.4600 (3)	0.3195 (13)	45 (5)	11 (1)	149 (24)	−4 (2)	−7 (10)	−2 (4)
C(12)	0.2000 (8)	0.4670 (3)	0.2738 (13)	58 (6)	8 (1)	111 (21)	−5 (3)	6 (10)	10 (4)
C(13)	0.1325 (8)	0.4894 (3)	0.3501 (18)	70 (7)	8 (1)	279 (31)	0 (3)	−16 (14)	2 (6)
C(14)	0.0515 (9)	0.4869 (4)	0.2807 (16)	71 (8)	10 (1)	230 (36)	8 (3)	−12 (13)	−2 (5)
C(15)	0.0383 (8)	0.4649 (4)	0.1370 (20)	52 (6)	13 (2)	306 (40)	−3 (3)	−14 (14)	36 (7)
C(16)	0.1013 (8)	0.4437 (4)	0.0587 (14)	62 (7)	13 (1)	102 (22)	2 (3)	−7 (10)	6 (5)
C(17)	0.1862 (6)	0.4453 (3)	0.1245 (16)	40 (6)	9 (1)	208 (30)	−2 (2)	0 (9)	14 (5)
C(18)	0.2650 (7)	0.4253 (3)	0.0752 (15)	52 (6)	11 (1)	153 (24)	−3 (2)	8 (10)	14 (5)
C(19)	0.2389 (8)	0.3244 (4)	0.1147 (13)	49 (6)	11 (1)	189 (25)	−4 (2)	17 (9)	−15 (6)
C(20)	0.1526 (8)	0.3390 (3)	0.0934 (13)	58 (7)	9 (1)	178 (26)	2 (3)	−26 (10)	1 (5)
C(21)	0.1017 (7)	0.3215 (3)	0.2168 (18)	36 (6)	7 (1)	191 (25)	3 (2)	−9 (12)	0 (5)
C(22)	0.0135 (7)	0.3230 (4)	0.2566 (15)	50 (6)	15 (1)	173 (24)	7 (2)	−28 (11)	−10 (6)
C(23)	−0.0196 (8)	0.2992 (4)	0.3758 (16)	37 (6)	15 (2)	243 (35)	−2 (2)	−3 (11)	3 (5)
C(24)	0.0352 (7)	0.2722 (4)	0.4633 (16)	63 (7)	15 (1)	222 (32)	−11 (3)	20 (13)	−1 (5)
C(25)	0.1210 (8)	0.2697 (5)	0.4409 (14)	46 (6)	11 (1)	224 (32)	−1 (3)	−23 (12)	5 (4)
C(26)	0.1557 (8)	0.2957 (4)	0.3167 (16)	50 (6)	8 (2)	167 (25)	0 (3)	−6 (10)	−4 (5)
C(27)	0.2431 (9)	0.2998 (4)	0.2562 (20)	47 (6)	10 (2)	135 (24)	−1 (3)	6 (10)	−3 (5)
HC(1)	0.0688 (60)	0.0819 (33)	0.1349 (120)	[b]					
HC(2)	0.0996 (60)	0.1673 (32)	0.1105 (121)						
HC(4)	0.2407 (63)	0.2083 (32)	0.1615 (136)						
HC(5)	0.3992 (68)	0.2078 (35)	0.1749 (139)						
HC(6)	0.4619 (59)	0.1422 (34)	0.1665 (117)						
HC(7)	0.3828 (61)	0.0718 (33)	0.1771 (118)						
HC(9)	0.1971 (58)	0.0468 (33)	0.1397 (124)						
HC(10)	0.3858 (60)	0.4299 (33)	0.2088 (118)						
HC(11)	0.3203 (58)	0.4697 (33)	0.4211 (137)						
HC(13)	0.1399 (56)	0.5044 (33)	0.4512 (134)						
HC(14)	−0.0034 (62)	0.5057 (34)	0.3205 (124)						
HC(15)	−0.0117 (58)	0.4676 (33)	0.0869 (131)						
HC(16)	0.0861 (56)	0.4252 (33)	−0.0286 (126)						
HC(18)	0.2733 (59)	0.4054 (33)	−0.0020 (121)						
HC(19)	0.3008 (58)	0.3266 (32)	0.0610 (132)						
HC(20)	0.1397 (56)	0.3543 (34)	0.0080 (123)						
HC(22)	−0.0159 (60)	0.3377 (32)	0.1907 (119)						
HC(23)	−0.0870 (59)	0.2957 (34)	0.3833 (124)						
HC(24)	0.0128 (55)	0.2572 (34)	0.5403 (135)						
HC(25)	0.1632 (55)	0.2391 (33)	0.4801 (123)						
HC(27)	0.3059 (60)	0.2847 (33)	0.3196 (122)						

[a] Thermal parameters are for the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic B values of 4.0 were used for all hydrogen atoms.

converted to squared structure amplitudes. The amplitudes were then averaged for equivalent reflections.

A Patterson map was calculated and interpreted to yield the position of the samarium atom. Subsequent Fourier and difference Fourier maps revealed the location of all 27 carbon atoms in the asymmetric unit.

The positional and anisotropic thermal parameters of the 28 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 $\Sigma w(F_o^2 - F_c^2)^2$, where F_o is the observed, and F_c is the calculated structure factor. The weight, w, of an observation was taken as $1/\sigma^2(F^2)$, and the variance, $\sigma^2(F_o^2)$, was estimated from counting statistics plus a contribution of 0.03 of the intensity for possible systematic errors. Intensities measured to be less than background were not included in the refinement process.

Atomic scattering factors for Sm, C, and H were taken from Cromer and Waber,[18] and the scattering by samarium was corrected for the real and imaginary components of anomalous dispersion using Cromer's table.[19]

A difference Fourier computed during the later stages of refinement revealed peaks near the expected positions for the ring hydrogen atoms. Inclusion of the coordinates of the peaks into the refinement reduced the R index significantly. For the 1791 observed reflections the final value of the index $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ was 0.070 and the standard deviation of an observation of unit weight was 1.60. A final difference Fourier map showed no peak larger than 0.6 e/Å^3. The refined positional and thermal parameters are given in Table I, and the observed and calculated structure amplitudes are available elsewhere.[20] The bond distances and angles were calculated with the program ORFFE.[21]

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(17) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(18) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(19) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(20) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1830. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

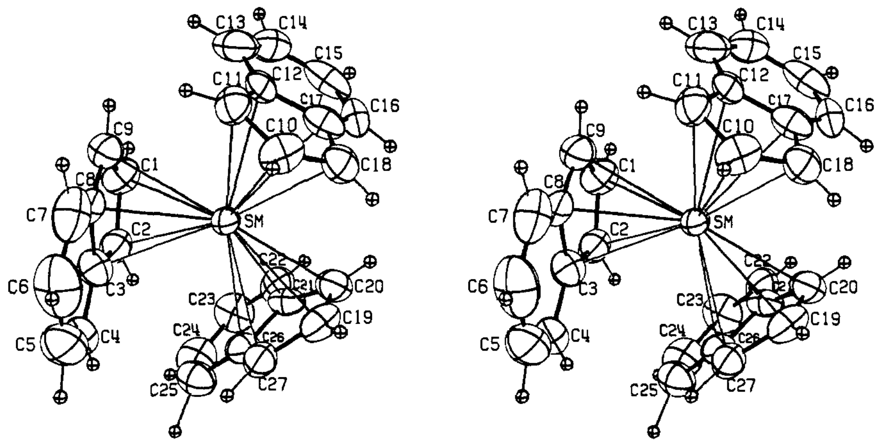

Figure 1. Stereoscopic drawing of one molecule of $Sm(C_9H_7)_3$ with atoms represented by thermal ellipsoids.

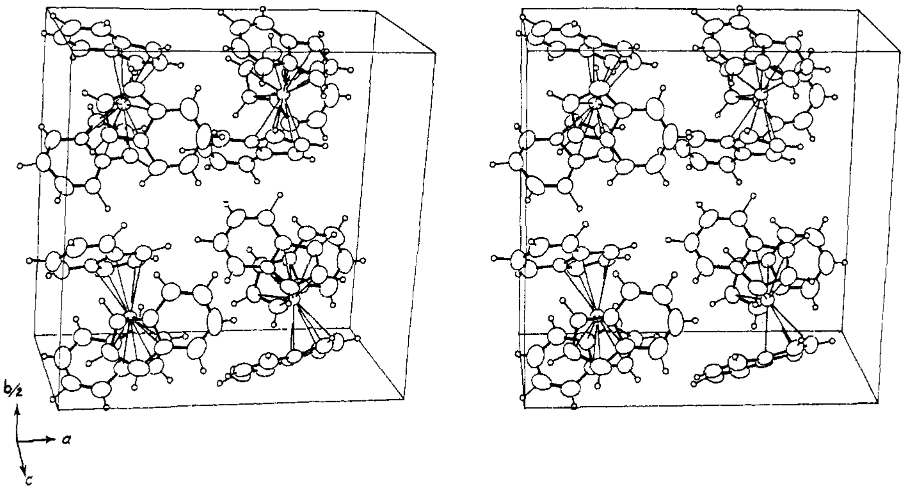

Figure 2. Stereoscopic drawing showing the packing of $Sm(C_9H_7)_3$ molecules in half the unit cell.

Discussion

The structure of triindenylsamarium is illustrated by Figure 1, which shows one molecule, including the physically reasonable thermal motions represented by their 50% probability ellipsoids,[22] and by Figure 2, which shows the packing in the unit cell. The five-membered rings of the three indenyl groups are found in an almost trigonal configuration about the samarium atom. This is shown by the angles among normals from the samarium atom to the least-squares planes of the five-membered ring portions of indenyl groups A, B, and C (Figure 3): A-Sm-B, 120°; A-Sm-C, 121°; B-Sm-C, 116°.

The samarium atom is bonded in a pentahapto fashion to the five-membered ring portion of the indenyl systems with an average samarium-carbon separation of 2.75 Å (Table II). The distances of the samarium atom from the planes of rings A, B, and C are 2.45, 2.44, and 2.48 Å, respectively. For the entire nine-carbon indenyl framework, the results of least-squares plane calculations are shown in Table III. The fact that rings B and C exhibit significant deviations from planarity is probably a steric rather than an electronic effect; the five-membered portions of B and C are planar to within 0.03 Å.

Table II. Samarium to Ring–Carbon Distances (Å)

Ring A		Ring B		Ring C	
Sm–C(1)	2.73 (1)	Sm–C(10)	2.73 (1)	Sm–C(19)	2.74 (1)
Sm–C(2)	2.69 (1)	Sm–C(11)	2.75 (1)	Sm–C(20)	2.68 (1)
Sm–C(3)	2.74 (1)	Sm–C(12)	2.70 (1)	Sm–C(21)	2.77 (1)
Sm–C(8)	2.75 (1)	Sm–C(17)	2.72 (1)	Sm–C(26)	2.87 (1)
Sm–C(9)	2.75 (1)	Sm–C(18)	2.79 (1)	Sm–C(27)	2.79 (1)

Nonbonded Intramolecular Carbon–Carbon Distances (Å)

Ring A–ring B		Ring A–ring C		Ring B–ring C	
C(9)–C(11)	3.19	C(2)–C(25)	3.27	C(18)–C(19)	3.21
C(9)–C(12)	3.34	C(2)–C(26)	3.33	C(18)–C(20)	3.23
C(9)–C(13)	3.37	C(4)–C(25)	3.46	C(17)–C(20)	3.38
C(8)–C(11)	3.47	C(2)–C(24)	3.52	C(16)–C(20)	3.39
C(1)–C(13)	3.57	C(4)–C(27)	3.53	C(10)–C(19)	3.76

Figure 3 shows the bond lengths and angles in the three indenyl rings. The average carbon–carbon bond distance in the six-membered rings is 1.40 Å and in the five-membered rings, 1.42 Å. These values are well within the range expected for fully conjugated systems of this type,[23] and no significance is placed on the ob-

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(21) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFEE, A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(22) 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.

(23) N. C. Webb and R. E. Marsh, *Acta Crystallogr.*, **22**, 382 (1967).

Table III. Weighted Least-Squares Planes

Plane	Equation of plane[a]
A	$0.0676X - 0.0423Y - 0.9968Z + 5.6282 = 0$
B	$0.2331X + 0.8249Y - 0.5150Z - 11.6109 = 0$
C	$-0.1621X - 0.7695Y - 0.6178Z + 9.0906 = 0$

Deviation of Atoms from Planes (Å)

Atom	Plane A	Atom	Plane B	Atom	Plane C
C(1)	0.00[b]	C(10)	−0.06	C(19)	0.07
C(2)	0.04	C(11)	−0.02	C(20)	0.05
C(3)	−0.01	C(12)	0.03	C(21)	−0.03
C(4)	−0.03	C(13)	−0.03	C(22)	−0.05
C(5)	0.00	C(14)	0.04	C(23)	0.00
C(6)	0.02	C(15)	−0.03	C(24)	0.07
C(7)	0.02	C(16)	−0.02	C(25)	0.03
C(8)	−0.02	C(17)	0.05	C(26)	−0.06
C(9)	−0.02	C(18)	0.03	C(27)	−0.07
Sm	2.45	Sm	−2.44	Sm	−2.48

[a] The weight of each atom was inversely proportional to the mean variance of the positional parameters of that atom. [b] The standard deviation for the distance of each carbon atom from the plane is 0.01 Å.

served variation. The carbon–hydrogen bond lengths range from 0.84 to 1.21 Å. The standard deviation associated with the bond lengths is approximately 0.10 Å.

Tsutsui and Gysling[12] have postulated a covalent bonding mode for the related THF adduct, $Sm(C_9H_7)_3 \cdot OC_4H_8$, on the basis of nuclear magnetic resonance experiments. In THF-d_8 they found an ABX pattern for the protons of the five-membered ring similar to that reported for the covalent compound $(\pi\text{-}C_5H_5)Fe(CO)_2$-(1-indenyl).[24] However, in the structure of the unsolvated $Sm(C_9H_7)_3$ one can find scant evidence to bear out the idea that enhanced electron density at the C-1 position[25] should promote covalent bonding to the samarium atom. Furthermore, the shorter bonds between the samarium atom and the carbon atoms in the 1,2,3 ring positions of the indenyl groups do not necessarily lend support to a model involving 1,2,3-*trihapto*indenyl coordination. This observation may be interpreted as, in fact, a lengthening of the bonds of the samarium atom to the carbon atoms in the 8,9 ring positions because of steric interactions between the six-membered ring portions of indenyl moieties. Although the coordination appears most reasonably viewed in terms of 1,2,3,8,9-*pentahapto*indenyl groups, the structure does not afford a basis for the assessment of the degree of covalency in the metal–carbon linkage. It should be noted, however, that the structure of $Sm(C_9H_7)_3 \cdot OC_4H_8$ could be quite different from that of the unsolvated species.

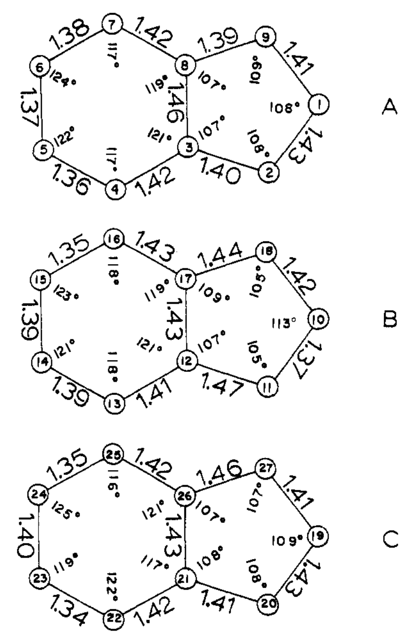

Figure 3. Bond distances and angles in the three indenyl rings.

The average samarium–carbon bond distance (2.75 Å) may be compared with the scandium–carbon length (2.48 Å) found in $[Sc(C_5H_5)_2Cl]_2$[26] where the cyclopentadienyl groups also show pentahapto coordination. The difference in the ionic radii[27] of Sm^{3+} (0.96 Å) and Sc^{3+} (0.68 Å) is within 0.01 Å of the difference in the corresponding metal–carbon distances.

Acknowledgment. This research was sponsored in part by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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