The Nature of the Scandium–Carbon Bond. II. Crystal and Molecular Structure of Tricyclopentadienylscandium[1]

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Abstract: The first evidence for a degree of covalency in a scandium–carbon bond is provided by the crystal structure of tricyclopentadienylscandium. $Sc(C_5H_5)_3$ crystallizes in the orthorhombic space group $Pbc2_1$ with cell dimensions $a = 12.881$ (5), $b = 8.954$ (4), $c = 9.925$ (4) Å, and $\rho_{calcd} = 1.41$ g cm^{-3} for $Z = 4$. Least-squares refinement of three-dimensional X-ray data measured by counter methods gave a conventional R factor of 0.041 for 1013 observed reflections. The structure consists of $Sc(C_5H_5)_2$ units bridged together by the remaining cyclopentadienyl groups. The environment of the scandium atom is such that two rings are coordinated in a pentahapto fashion and two rings are associated through essentially only one carbon atom. For the *monohapto*cyclopentadienyl groups, the angles made by the scandium–carbon bonds with the plane of the rings are 61 and 73°. The relation of the structure of $Sc(C_5H_5)_3$ to that of $Sm(C_5H_5)_3$ is described.

At present the organometallic chemistry of scandium is a relatively unexplored area. Only tricyclopentadienylscandium,[2] triphenyl- and tri(phenylethynyl)-scandium,[3] and dicyclopentadienylscandium chloride and derivatives[4] have been synthesized. Although several studies[1,5,6] of the physical and chemical properties of these and related lanthanide compounds have been carried out over the years, the nature of the scandium–carbon linkage is still very much subject to debate.

Birmingham and Wilkinson[2] first predicted the bonding in $Sc(C_5H_5)_3$ to be purely ionic on the basis of chemical reactivity and solubility measurements. More recently, Nugent, *et al.*,[7] have determined from absorption and uv-excited emission spectra that the per cent covalent character in the tricyclopentadienyllanthanides is not greater than 2.5%. In opposition to this view stands the work of Wong, Lee, and Lee[8] on the crystal structure of $Sm(C_5H_5)_3$. Even though their calculation (from the observed bond lengths) of only 37% partial ionic character in the samarium–carbon bonds is at best questionable, the fact that the cyclopentadienyl rings have a definite preferred orientation may be interpreted as structural evidence for some covalency in the metal–carbon bonds. It has been pointed out[9] that in view of the smaller ionic radius of Sc^{3+} relative to Sm^{3+}, $Sc(C_5H_5)_3$ may be expected to exhibit considerable covalent character.

We wish to report the first direct evidence for a degree of covalency in the scandium–carbon bond, the crystal structure of tricyclopentadienylscandium.

Experimental Section

Tricyclopentadienylscandium was prepared by the sealed-tube reaction of dicyclopentadienylmagnesium with scandium trifluoride.[10] Single crystals of $Sc(C_5H_5)_3$ were grown by sublimation and sealed in thin-walled glass capillaries. Preliminary unit cell parameters were determined by precession (Cu Kα) photographs. The crystal system is orthorhombic. Systematic absences allow the space group to be $Pbcm$ or $Pbc2_1$. The lattice parameters as determined from a least-squares refinement of $(\sin \theta/\lambda)^2$ values for 12 reflections are $a = 12.881(5)$ Å, $b = 8.954$ (4) Å, $c = 9.925$ (4) Å, $V = 1145$ Å^3. The calculated density is 1.41 g cm^{-3} for $Z = 4$. Data were taken on an Enraf–Nonius CAD-4 diffractometer with Ni-filtered copper radiation. The crystal, a rod of dimensions 0.12 × 0.15 × 0.70 mm, was aligned on the diffractometer, such that the rod axis was coincident with the φ axis of the diffractometer.

The diffracted intensities were collected by the ω–2θ scan technique with a takeoff angle of 1.5°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.8° min^{-1}. Background counts were collected for 25% of the total scan time at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where $A = 0.9°$ and $B = 0.45°$. Aperture settings were determined in a like manner with $A = 3$ mm and $B = 3$ mm. The crystal-to-source and crystal-to-detector distances were 21.6 and 20.8 cm, respectively. The lower level and upper level discriminators of the pulse height analyzer were set to obtain a 95% window centered on the Cu Kα peak. As a check on the stability of the diffractometer and the crystal, one reflection, the (121), was measured at 30-min intervals during data collection. No significant variation in the reference intensity was noticed.

The standard deviations of the intensities, σ_I, were estimated from the formula

$$\sigma_I = \{[C_N + (T_c/2T_B)^2(B_1 + B_2)] + (0.03)^2[C_N + (T_c/2T_B)^2(B_1 + B_2)]^2\}^{1/2}$$

where C_N is the counts collected during scan time T_c and B_1 and B_2 are background intensities, each collected during the background time T_B. Two symmetry related octants were measured out to $2\theta = 100°$ and one octant to $2\theta = 150°$. A total of 1620 reflections were collected of which 1013 were unique and had intensities greater than background.

The intensities were then corrected for Lorentz, polarization, and absorption[11] effects ($\mu = 53.4$ cm^{-1}). The calculated transmission factors ranged from 0.38 to 0.51.

Fourier calculations were made with the ALFF program.[12] The

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Table I. Final Fractional Coordinates and Thermal Parameters[a,b] for Tricyclopentadienylscandium

Atom	*x/a*	*y/b*	*z/c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sc	0.2514 (1)	0.4617 (1)	0.2400 (1)	0.0023 (1)	0.0056 (1)	0.0047 (1)	−0.0001 (1)	0.0004 (1)	−0.0004 (1)
C1	0.4367 (4)	0.4632 (7)	0.1568 (7)	0.0025 (3)	0.0105 (7)	0.0100 (8)	−0.0004 (4)	0.0005 (4)	0.0004 (7)
C2	0.4379 (5)	0.5172 (9)	0.2862 (9)	0.0047 (4)	0.0204 (14)	0.0133 (10)	−0.0050 (6)	−0.0035 (5)	0.0071 (10)
C3	0.3853 (6)	0.6501 (9)	0.2937 (9)	0.0062 (5)	0.0166 (12)	0.0144 (9)	−0.0061 (6)	0.0035 (5)	−0.0074 (9)
C4	0.3495 (5)	0.6809 (6)	0.1616 (9)	0.0056 (4)	0.0069 (6)	0.0150 (9)	−0.0010 (4)	0.0025 (5)	−0.0011 (7)
C5	0.3826 (4)	0.5647 (6)	0.0792 (6)	0.0039 (3)	0.0117 (8)	0.0073 (6)	−0.0017 (4)	0.0011 (3)	0.0004 (5)
C6	0.1359 (4)	0.5495 (7)	0.4227 (7)	0.0047 (4)	0.0119 (7)	0.0086 (6)	0.0015 (5)	0.0010 (5)	−0.0014 (9)
C7	0.0819 (4)	0.4362 (6)	0.3551 (7)	0.0029 (3)	0.0105 (7)	0.0089 (7)	0.0016 (4)	0.0012 (4)	0.0011 (6)
C8	0.0571 (4)	0.4868 (6)	0.2197 (8)	0.0030 (2)	0.0105 (6)	0.0065 (7)	0.0010 (3)	0.0005 (4)	0.0005 (6)
C9	0.0982 (4)	0.6321 (6)	0.2110 (6)	0.0053 (3)	0.0090 (9)	0.0082 (7)	0.0030 (4)	0.0011 (4)	0.0009 (7)
C10	0.1446 (4)	0.6697 (7)	0.3362 (8)	0.0056 (3)	0.0094 (8)	0.0127 (7)	0.0010 (4)	0.0018 (4)	−0.0045 (6)
C11	0.2047 (4)	0.2057 (5)	0.5453 (5)	0.0045 (3)	0.0081 (8)	0.0046 (8)	−0.0006 (4)	−0.0004 (4)	0.0013 (7)
C12	0.2934 (3)	0.2770 (5)	0.4887 (6)	0.0037 (4)	0.0080 (6)	0.0072 (6)	0.0005 (3)	−0.0008 (3)	0.0032 (4)
C13	0.3121 (4)	0.2167 (5)	0.3627 (5)	0.0055 (3)	0.0102 (9)	0.0050 (8)	0.0008 (4)	0.0006 (5)	0.0027 (7)
C14	0.2343 (4)	0.1061 (5)	0.3388 (5)	0.0068 (4)	0.0086 (6)	0.0056 (5)	0.0002 (4)	−0.0010 (4)	0.0008 (5)
C15	0.1689 (4)	0.1025 (6)	0.4466 (5)	0.0049 (3)	0.0102 (7)	0.0049 (5)	−0.0010 (3)	−0.0009 (3)	0.0014 (4)
H(C1)	0.4693	0.3718	0.1226	*c*					
H(C2)	0.4712	0.4710	0.3624						
H(C3)	0.3747	0.7161	0.3719						
H(C4)	0.3075	0.7646	0.1287						
H(C5)	0.3700	0.5554	−0.0143						
H(C6)	0.1631	0.5442	0.5160						
H(C7)	0.0605	0.3409	0.3919						
H(C8)	0.0236	0.4323	0.1471						
H(C9)	0.0956	0.6974	0.1330						
H(C10)	0.1770	0.7669	0.3551						
H(C11)	0.1756	0.2246	0.6305						
H(C12)	0.3313	0.3547	0.5331						
H(C13)	0.3649	0.2478	0.2997						
H(C14)	0.2295	0.0432	0.2620						
H(C15)	0.1141	0.0390	0.4551						

[a] Standard deviations in parentheses refer to last digit quoted. [b] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Isotropic thermal parameters for hydrogen atoms taken as 4.0 Å².

full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[13] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Ibers[14] for Sc, C, and H. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE program.[15] Crystal structure illustrations were obtained with the program ORTEP.[16]

Solution and Refinement of the Structure. Preliminary density calculations indicated the presence of four molecules of $Sc(C_5H_5)_3$ in the unit cell. This was interpreted to mean that the scandium atom must lie on special positions in space group *Pbcm* or in general positions in the acentric $Pbc2_1$. The Patterson map clearly showed the presence of the metal atoms on or near $Z = {}^1/_4, {}^3/_4$, the location of the mirror planes in *Pbcm*. A structure factor calculation based on the centric space group yielded an *R* factor of 38%, but the corresponding Fourier map was complex. Several attempts at positioning cyclopentadienyl carbon atoms with both ordered and disordered models did not improve the *R* factor to below 33%. At this point the structure solution was sought in the acentric space group $Pbc2_1$. Fourier maps phased on the scandium atom quickly revealed the coordinates of several carbon atoms, and two electron density maps preceded by partial least-squares refinement showed all the nonhydrogen atoms in the asymmetric unit. The final positions of the carbon atoms clearly show that the molecular grouping cannot contain the mirror plane demanded by space group *Pbcm*. Although the standard acentric space group is $Pca2_1$, the structure reported here is based on $Pbc2_1$ to emphasize the similarity with tricyclopentadienylsamarium. Subsequent isotropic refinement led to $R_1 = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|] \times 100 = 9.6\%$. Anisotropic refinement lowered R_1 to 7.1%. The inclusion of hydrogen atom contributions at calculated positions 0.95 Å from the corresponding carbon atoms followed by further anisotropic refinement of all nonhydrogen atoms led to a final $R_1 = 4.1\%$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(wF_o)^2]^{1/2} \times 100 = 4.3\%$, where $w = 1/\sigma^2$. Unobserved reflections and two reflections, the (200) and (111), which appeared to suffer from extinction, were not included. The largest parameter shifts in the final cycle or refinement were less than 0.02 of their estimated standard deviations. A final difference Fourier map showed no feature greater than 0.4 e/A³. The standard deviation of an observation of unit weight was 2.39. No systematic variation of $w(|F_o| - |F_c|)^2$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was observed. The final values of the positional and thermal parameters are given in Table I.[17]

Discussion

The most striking feature of the structure of tricyclopentadienylscandium is the existence of both bridging and terminal cyclopentadienyl groups (Figure 1). Each scandium atom is thus coordinated to two $C_5H_5^-$ ions in a pentahapto fashion and to two others through essentially only one carbon atom. The result is a polymeric arrangement of two symmetry related chains of $Sc(C_5H_5)_3$ units.

The average scandium–carbon bond length for the h^5-C_5H_5 rings is 2.49 Å (Table II), and the average distance of the scandium atom from the planes of the two cyclopentadienyl groups is 2.19 Å. Both of these values compare favorably with the standards reported

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(13) 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.

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(16) 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.

(17) 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-75-1488. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table II. Interatomic Distances (Å) and Angles (deg) for Tricyclopentadienylscandium

Ring A	Ring B	Ring C	Ring C′[a]
	Bond Distance		
Sc–C1 2.525 (4)	Sc–C6 2.473 (6)	Sc–C11 3.847 (4)	Sc–C11′ 2.519 (4)
Sc–C2 2.495 (5)	Sc–C7 2.474 (4)	Sc–C12 3.020 (5)	Sc–C12′ 3.329 (5)
Sc–C3 2.471 (6)	Sc–C8 2.521 (4)	Sc–C13 2.629 (4)	Sc–C13′ 4.144 (5)
Sc–C4 2.461 (5)	Sc–C9 2.511 (5)	Sc–C14 3.341 (5)	Sc–C14′ 4.032 (5)
Sc–C5 2.500 (5)	Sc–C10 2.505 (5)	Sc–C15 3.961 (4)	Sc–C15′ 3.151 (4)
C1–C2 1.372 (9)	C6–C7 1.402 (7)	C11–C12 1.425 (6)	
C2–C3 1.371 (9)	C7–C8 1.475 (7)	C12–C13 1.383 (6)	
C3–C4 1.416 (9)	C8–C9 1.408 (6)	C13–C14 1.430 (7)	
C4–C5 1.391 (7)	C9–C10 1.419 (8)	C14–C15 1.363 (6)	
C5–C1 1.381 (7)	C10–C6 1.382 (8)	C15–C11 1.423 (6)	
	Nonbonded Distance		
C8–C11 3.10 (1)	C3–C10 3.13 (1)	C4–C10 3.16 (1)	C7–C11 3.21 (1)
C2–C13 3.23 (1)	C6–C12 3.24 (1)	C1–C12′ 3.29 (1)	C4–C9 3.30 (1)
C5–C11′ 3.35 (1)	C7–C12 3.35 (1)	C5–C12′ 3.39 (1)	C14–C11′ 3.39 (1)
C5–C15′ 3.40 (1)	C1–C13 3.41 (1)	C5–C14 3.42 (1)	C6–C11 3.43 (1)
	Bond Angles		
C4–C1–C5 107.1 (5)	C7–C6–C10 107.9 (5)	C12–C11–C14 106.3 (4)	
C1–C2–C3 110.6 (6)	C6–C7–C8 109.0 (4)	C11–C12–C13 108.7 (4)	
C2–C3–C4 106.3 (5)	C7–C8–C9 105.2 (5)	C12–C13–C14 107.4 (4)	
C3–C4–C5 107.4 (5)	C8–C9–C10 108.9 (5)	C13–C14–C15 108.6 (4)	
C1–C5–C4 108.6 (5)	C6–C10–C9 109.0 (5)	C11–C15–C14 108.9 (4)	

[a] C′ is related to C by the symmetry operations (x, $^1/_2 - y$, $^1/_2 + z$), followed by a unit cell translation in z.

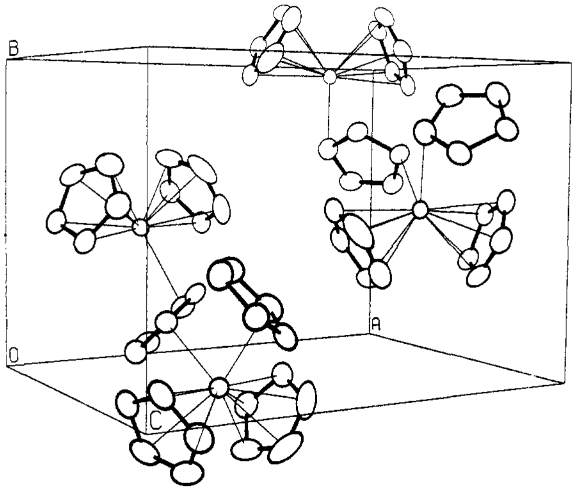

Figure 1. Structure and unit cell packing of tricyclopentadienylscandium. The atoms are displayed as the 50% probability ellipsoids for thermal motion.

Table III. Comparison of Metal–Cyclopentadienyl Carbon Bond Distances

Compound[a]	M–π-C	(Sc–C) − (M–C)	r(Sc) − r(M)[b]	Ref
$Sc(C_5H_5)_3$	2.49			
$[(C_5H_5)_2ScCl]_2$	2.48			1
$C_5H_5TiCl(ONC_9H_6)_2$	2.41	0.08	0.15	*c*, 18
$(C_5H_5)_2Ti(C_6H_5)_2$	2.31	0.18	0.15	*d*
$C_5H_5V(CO)_4$	2.28	0.20	0.28	*e*, 18
$C_5H_5Cr(NO)_2NCO$	2.20	0.28	0.34	*f*
$C_5H_5Mn(CO)_3$	2.17	0.31	0.35	*g*
$Fe(C_5H_5)_2$	2.04	0.44	0.36	*h*
$C_5H_5Co(CH_3C_2CH_3)_2CO$	2.07	0.41	0.37	*i*
$Ni(C_5H_5)_2$	2.20	0.28	0.38	*j*

[a] Representative compounds have been chosen. [b] Metallic radii as given in L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 403. [c] J. D. Matthews and A. G. Swallow, *Chem. Commun.*, 882 (1969). [d] V. Kocman, J. C. Rucklidge, R. J. O'Brien, and W. Santo, *ibid.*, 1340 (1971). [e] J. B. Wilford, A. Whitla, and H. M. Powell, *J. Organometal. Chem.*, **8**, 495 (1967). [f] M. A. Busch, G. A. Sim, G. R. Knox, M. Ahmad, and C. G. Robertson, *Chem. Commun.*, 74 (1969). [g] A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **18**, 118 (1963). [h] J. D. Dunitz, L. E. Orgel, and A. Rich, *ibid.*, **9**, 373 (1956). [i] L. F. Dahl and D. J. Smith, *J. Amer. Chem. Soc.*, **83**, 752 (1961). [j] L. Hedberg and K. Hedberg, *J. Chem. Phys.*, **53**, 1228 (1970).

for $[(C_5H_5)_2ScCl]_2$:[1] 2.48 and 2.17 Å, respectively. The data in Table III indicate that the scandium–carbon distance fits in well with the general trend found among first-row transition metal π-cyclopentadienyl complexes. As Stucky has pointed out,[18] the only metal–carbon bond lengths which are significantly shorter than one would predict on the basis of metallic radii are those found with iron and cobalt.

For each ring the results of least-squares best-plane calculations are shown in Table IV. The fact that ring C is in an environment quite different from that of rings A and B does not affect the planarity of the group; the maximum deviation in any case is 0.01 Å from the plane.

Figure 2 shows the bond lengths and angles in the three cyclopentadienyl moieties. The average carbon–carbon bond distance of 1.40 Å is well within the expected range.[19] It should be noted that the bridging $C_5H_5^-$ group does not differ significantly from the terminal groups with respect to either bond distances or angles and, within the group itself, no unusual variations are found.

Table II shows that the scandium atom is bonded equally to all five carbon atoms of ring A and of ring B. On the other hand, the association with rings C and C′ appears to be of a fundamentally different nature. The Sc–C13 bond is 0.15 Å longer than the average found in A and B, and the bond makes an angle of 73° with the

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[18] C. Johnson, J. Toney, and G. D. Stucky, *J. Organometal. Chem.*, **40**, C11 (1972).

[19] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley-Interscience, New York, N. Y., 1966, p 768.

Table IV. Best Weighted Least-Squares Planes

Plane	
A	$0.8482X + 0.4935Y - 0.1927Z - 6.5220 = 0$
B	$0.8691X - 0.3680Y - 0.3307Z + 1.6838 = 0$
C	$-0.5811X + 0.7008Y - 0.4137Z + 2.4670 = 0$

Deviation of Atoms from Planes (Å)					
Atom	Plane A	Atom	Plane B	Atom	Plane C
C1	-0.00^b	C6	0.01	C11	-0.01
C2	0.00	C7	-0.00	C12	0.00
C3	0.00	C8	-0.00	C13	0.00
C4	-0.00	C9	0.01	C14	-0.01
C5	0.00	C10	-0.01	C15	0.01
Sc	-2.19	Sc	2.19	Sc	2.50^c

[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 and for the scandium atom, 0.04 Å. [c] The distance of the scandium atom from the plane of C′ is −2.21 Å.

plane of ring C. The Sc–C11′ bond distance is within the range of those noted for A and B, and the bond makes an angle of 61° with the plane of ring C′. A further survey of Table II and Figure 1 indicates that the interaction is through only one carbon atom. This is especially evident for C11′, where the next closest approaches to the scandium atom (C12′, C15′) differ by only 0.18 Å.

One would expect the scandium–carbon bond to make an angle of 55° with the plane of the ring if the carbon atom were sp^3 hybridized.[20,21] Unfortunately, the meaning of the observed angles (61, 73°) is probably obscured by the rather strict steric requirements obtained by placing four cyclopentadienyl groups about the scandium atom. It is possible that the geometry of the bridging C_5H_5 ion is simply the result of the minimization of the potential energy of the crystal. However, the structural parameters may perhaps be more reasonably interpreted in terms of a preferential interaction between one carbon atom and the scandium atom. To the extent to which one wishes to view a preferred orientation as an implication of covalent bond character, this represents the first experimental evidence for an appreciable amount of covalency in an organoscandium compound.

The crystal structure of tricyclopentadienylscandium also has a direct relation to the inaccurately determined structure of tricyclopentadienylsamarium[8] (Table V). The only real difference in the lattice parameters is that *b* for the samarium compound is almost twice the value for the scandium analog. Wong, Lee, and Lee[8] state that only a few very weak reflections were found for $k \neq 2n$. A careful search between layers in *k* for $Sc(C_5H_5)_3$ showed no such intensities. Further studies on $Sm(C_5H_5)_3$ and related compounds may reveal even closer similarities between the two substances.

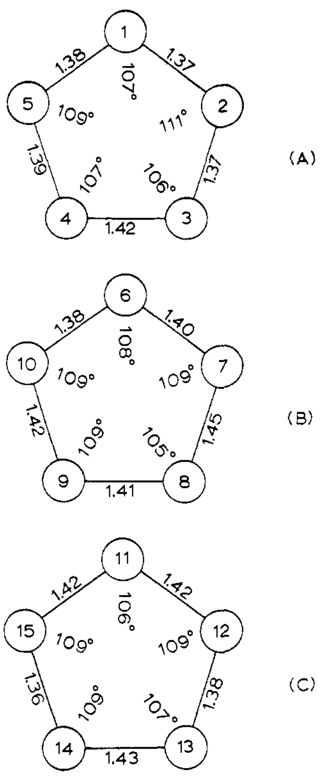

Figure 2. Bond distances and angles within the cyclopentadienyl groups for $Sc(C_5H_5)_3$.

Table V. Comparison of Crystal Data for $Sc(C_5H_5)_3$ and $Sm(C_5H_5)_3$

	$Sc(C_5H_5)_3$	$Sm(C_5H_5)_3$
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbcm* or *Pbc*2$_1$	*Pbcm* or *Pbc*2$_1$
a, Å	12.881 (5)	14.23 (2)
b, Å	8.954 (4)	17.40 (1)
c, Å	9.925 (4)	9.73 (2)
V, Å^3	1145	2295
Z	4	8
Space group selected	*Pbc*2$_1$	*Pbcm*

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