

90% *d* and *l* isomers it is possible that some of the isomers converted to the *meso* isomer between the preparation of the solution and the EXAFS measurement. Since these isomers exist in equilibrium in solution and both *racemic* and *meso* forms crystallize from the same solution, care must be taken in analyzing and interpreting results using techniques such as EXAFS where bulk samples are used.

This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the US Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

References

BAILEY, M. F. & MAXWELL, I. E. (1966). *J. Chem. Soc. Chem. Commun.* pp. 908–910.

BAILEY, M. F. & MAXWELL, I. E. (1972). *J. Chem. Soc. Dalton Trans.* pp. 938–944.

BERMAN, H. M., BERNSTEIN, F. C., BERNSTEIN, H. J., KOETZLE, T. F. & WILLIAMS, G. J. B. (1976). *CRYSNET Manual*. Informal Report BNL 21714. Brookhaven National Laboratory, New York, USA.

FURENLID, L. R., RENNER, M. W., SZALDA, D. J. & FUJITA, E. (1991). *J. Am. Chem. Soc.* **113**, 883–892.

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

SHEDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

TAIT, A. M. & BUSCH, D. H. (1978). *Inorganic Syntheses*, Vol. XVIII, pp. 2–6. New York: John Wiley.

Acta Cryst. (1992). **C48**, 1771–1773

Structure of a Permethylcyclopentadienyl- μ -tetramethylcyclopentadienylmethylen Scandium Dimer

BY SHARAD HAJELA, WILLIAM P. SCHAEFER AND JOHN E. BERCAW

Division of Chemistry and Chemical Engineering† and The Beckman Institute, Mail Code 139-74, California Institute of Technology, Pasadena, California 91125, USA

(Received 26 December 1991; accepted 11 February 1992)

Abstract. Bis(η^5 -pentamethylcyclopentadienyl)-bis[μ -2,3,4,5-tetramethyl-1-methylene-ScC^I:Sc(η^5)-cyclopentadienyl]-disc scandium(III), [Sc₂(C₁₀H₁₅)₂-(C₁₀H₁₄)₂], M_r = 628.90, triclinic, $P\bar{1}$, a = 8.641 (5), b = 9.478 (2), c = 12.338 (5) Å, α = 75.58 (3), β = 80.39 (4), γ = 63.75 (3)°, V = 875.8 (7) Å³, Z = 1, D_x = 1.19 g cm⁻³, λ (Mo $K\alpha$) = 0.71073 Å, μ = 4.11 cm⁻¹, $F(000)$ = 340, room temperature, R (on F) = 0.046 for 2241 reflections with $F_o^2 > 3\sigma(F_o^2)$. Two bis(pentamethylcyclopentadienyl)scandium molecules are joined across a center of symmetry. One of the Cp* methyl groups has lost an H atom and that methylene group bonds to the symmetry-related Sc atom: Sc—C₆' = 2.282 (5) Å. Other aspects of the bis-Cp*Sc geometry are normal.

Introduction. Alkyl and hydride derivatives of permethylscandocene are of interest both for their C—H bond-activation chemistry (Thompson, Baxter, Bulls, Burger, Nolan, Santarsiero, Schaefer & Bercaw, 1987) and as model systems for Ziegler–Natta catalysis (Burger, Thompson, Cotter & Bercaw, 1990). A notable feature of these complexes is their ability to activate the primary C—H bonds of mol-

ecules such as CH₄, CH₃CH₂CH₃, Si(CH₃)₄ and P(CH₃)₃ (Thompson *et al.*, 1987). During the course of some recent mechanistic studies, we have observed that the cyclopentylmethyl derivative, Cp₂*ScCH₂-(cyclo-C₅H₈) [Cp* = η^5 -C₅(CH₃)₅], slowly and cleanly decomposes in cyclohexane to give methylcyclopentane and a yellow crystalline precipitate. The ¹H NMR spectrum of the yellow product is consistent with a compound containing one Cp* and one (η^5 , η^1)-C₅(CH₃)₄CH₂, the latter arising *via* metallation of a Cp* ligand (*i.e.* a ‘tuck-in’ complex). This same tuck-in complex has been previously obtained from thermolysis of Cp₂*ScCH₃ (Thompson *et al.*, 1987); however, the solid product obtained previously was not crystalline and was postulated to be oligomeric based on its solubility properties. We report herein the structure of the complex which crystallizes as the dimer, [Cp*Sc{ μ -(η^5 , η^1)-C₅(CH₃)₄CH₂}]₂, when allowed to form slowly at room temperature.

Experimental. A parallelepiped, 0.4 × 0.2 × 0.05 mm, crystal was used for data collection on a CAD-4 diffractometer with ω scans. 25 reflections with 24 < 2θ < 28° were used for determination of the unit cell. No absorption correction was applied to the data

† Contribution No. 8551.

Table 1. Final refined positional ($\times 10^4$), equivalent isotropic displacement ($\text{\AA}^2 \times 10^4$) and isotropic displacement (\AA^2) parameters

$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$; H atoms refined with isotropic displacement parameters, B .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} or <i>B</i>
Sc	3717 (.8)	1165 (.7)	3300 (.5)	300 (1)
C1	3923 (4)	2104 (3)	4991 (2)	301 (7)
C2	3513 (4)	3428 (3)	4061 (2)	344 (7)
C3	1831 (4)	3845 (3)	3769 (3)	377 (8)
C4	1223 (4)	2744 (4)	4459 (3)	394 (8)
C5	2516 (4)	1685 (3)	5216 (2)	331 (7)
C6	5429 (4)	1412 (4)	5718 (3)	340 (7)
C7	4619 (5)	4333 (4)	3583 (3)	495 (9)
C8	706 (5)	5401 (4)	3035 (3)	611 (11)
C9	-558 (4)	2824 (5)	4496 (3)	611 (11)
C10	2290 (4)	480 (4)	6200 (3)	466 (8)
C11	3154 (4)	217 (4)	1759 (2)	397 (8)
C12	2251 (4)	1905 (4)	1524 (2)	410 (8)
C13	3485 (4)	2559 (4)	1263 (2)	414 (8)
C14	5129 (4)	1276 (4)	1334 (2)	435 (9)
C15	4929 (4)	-173 (4)	1624 (2)	408 (9)
C16	2318 (5)	-943 (5)	2048 (3)	625 (10)
C17	332 (5)	2804 (4)	1391 (3)	616 (10)
C18	3157 (5)	4283 (4)	740 (3)	647 (11)
C19	6805 (5)	1458 (5)	1009 (3)	713 (12)
C20	6366 (5)	-1823 (4)	1620 (3)	653 (11)
H6A	6294 (36)	1604 (32)	5299 (23)	2.7 (7)
H6B	5132 (33)	2166 (32)	6200 (22)	2.8 (6)

Table 2. Selected bond distances (Å) and angles (°)

Cp^* represents the centroid of the five ring atoms.

Sc—C6'	2.282 (5)	C6'— Sc— Cp* ¹	107.9
Sc—Cp* ¹	2.181	C6'— Sc— Cp* ²	108.6
Sc—Cp* ²	2.212	Cp* ¹ — Sc— Cp* ²	141.6
C6—C1	1.507 (4)	C6— C1— C2	127.9 (3)
C6—H6A	0.90 (3)	C6— C1— C5	124.7 (3)
C6—H6B	0.96 (3)	H6A—C6—C1	107.3 (19)
		H6B—C6—C1	104.8 (17)
		H6B—C6—H6A	98.1 (20)

collection; $(\sin\theta/\lambda)_{\max} = 0.59 \text{ \AA}^{-1}$; h from -10 to 10, k from -11 to 11, l from -14 to 14. Three standard reflections (300, 023, 030) showed no variations greater than expected from counting statistics. 6239 reflections were measured, of which 3068 were independent; goodness of fit for merging was 0.98; R_{int} for 2682 reflections with exactly two observations was 0.032. All reflections were used in solution and refinement of the structure. The Sc-atom position was determined from a Patterson map and the C atoms were all found in a subsequent Fourier map. H atoms were placed at idealized positions based on difference maps calculated in their expected planes (C—H = 0.95 Å). H atoms on C6 were found in a three-dimensional difference map and their positions and isotropic displacement parameters were refined, but all other H-atom parameters were fixed. Positional and anisotropic displacement parameters of the Sc and C atoms, plus the C6 H-atom parameters and a scale factor were refined. For all 2856 reflections with $F_o^2 > 0$, R (on F) = 0.062, wR (on F^2) = 0.010, $S = 2.19$ for 3068 reflections and 198 parameters. Weights were calculated as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged

data by propagation of e.s.d. plus another additional term, $(0.014\bar{I})^2$. Maximum shift/e.s.d. in the final cycle was 0.02. Maximum and minimum heights in final difference Fourier map were 0.40 and $-0.35 \text{ e } \text{\AA}^{-3}$, respectively. Atomic scattering factors were obtained from Cromer & Waber (1974), and the dispersion correction for Sc from Cromer (1974). Computer programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEP* (Johnson, 1976). Final refined parameters of the atoms are given in Table 1* with selected distances and angles in Table 2. Fig. 1 shows a

* Lists of assigned H-atom parameters, anisotropic displacement parameters, complete distances and angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55184 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0622]

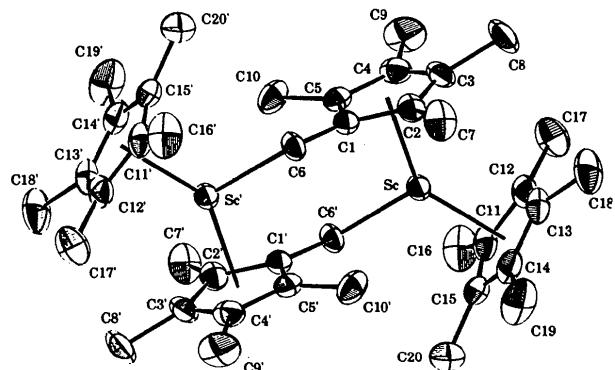


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the dimer with 50% probability ellipsoids showing the numbering system. H atoms are not shown.

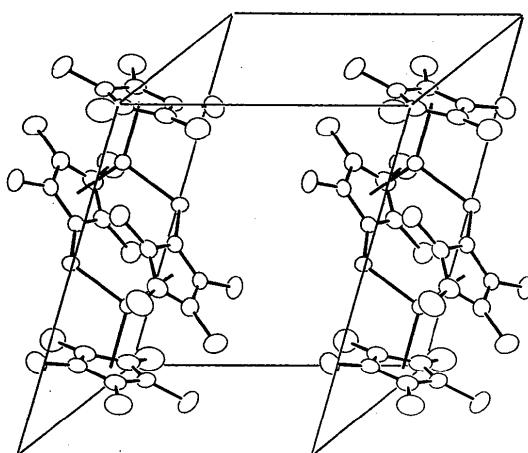


Fig. 2. An *ORTEPII* (Johnson, 1976) packing drawing showing the contents of a unit cell, with the unit cell outlined. Atoms are shown as 50% probability ellipsoids; H atoms are not shown.

labeled drawing of the dimer; crystal packing is shown in Fig. 2.

Discussion. The dimer is joined across an inversion center by an (η^5, η^1)-Cp* group which bridges the two symmetry-related Sc atoms. The η^1 -methylene (C6) has been formed as the result of C—H activation of a Cp* methyl group. A somewhat surprising result is that, in all other regards, the bonding is very similar to that determined for Cp₂ScCH₃ (Thompson *et al.*, 1987). The (η^5, η^1)-ring remains planar with a maximum deviation of only 0.22 Å from the least-squares plane calculated for C1 through C10. The geometry about C6 is essentially tetrahedral; the angles C1—C6—Sc', C1—C6—H6A, C1—C6—H6B and H6A—C6—H6B are 118.9, 107.3, 104.8 and 98.1°, respectively, giving an average value of 107.3 (8.6)°. The H6A—C6—H6B angle is slightly compressed (98.1°) while the C1—C6—Sc' angle is somewhat opened (118.9°). The Sc'—H6A and Sc'—H6B distances are 2.76 (3) and 2.79 (3) Å indicating that there is no agostic interaction for the α -H atoms with the Sc center. The Cp*—Sc—Cp* angle (141.8°) is approximately the same as for Cp₂

ScCH₃ (144.7°) suggesting that formal replacement of a methyl ligand with a bulkier (η^5, η^1)-Cp* group as the alkyl does not significantly perturb the Sc—Cp* bonding.

This work was supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER113431).

References

BURGER, B. J., THOMPSON, M. E., COTTER, W. D. & BERCAW, J. E. (1990). *J. Am. Chem. Soc.* **112**, 1566–1577.

CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

DUCHAMP, D. J. (1964). CRYM crystallographic computing system. *Am. Crystallogr. Assoc. Meet.*, Bozeman, Montana. Paper B14, p. 29.

JOHNSON, C. K. (1976). ORTEPII. Report ORNL-3794, third revision. Oak Ridge National Laboratory, Tennessee, USA.

THOMPSON, M. E., BAXTER, S. M., BULLS, A. R., BURGER, B. J., NOLAN, M. C., SANTARSIERO, B. D., SCHAEFER, W. P. & BERCAW, J. E. (1987). *J. Am. Chem. Soc.* **109**, 203–219.

Acta Cryst. (1992). C48, 1773–1776

A Silicon-Bridged Bis(substituted Cp) Yttrium Complex

BY RICHARD E. MARSH, WILLIAM P. SCHAEFER, E. BRYAN COUGHLIN AND JOHN E. BERCAW

Division of Chemistry and Chemical Engineering and The Beckman Institute, Mail Code 139-74, California Institute of Technology, Pasadena, California 91125, USA*

(Received 9 December 1991; accepted 11 February 1992)

Abstract. *rac*-Bis(tetrahydrofuran)lithium [bis(2-trimethylsilyl-4-*tert*-butyl- η^5 -cyclopentadienyl)dimethylsilane]dichloroyttrate, $[\text{Li}(\text{C}_4\text{H}_8\text{O})_2]\text{Y}(\text{C}_{26}\text{H}_{48}\text{Si}_3)\text{Cl}_2$, $M_r = 755.87$, triclinic, $\bar{P}\bar{I}$, $a = 13.110$ (8), $b = 17.163$ (15), $c = 20.623$ (14) Å, $\alpha = 104.02$ (7), $\beta = 99.38$ (5), $\gamma = 100.24$ (6)°, $V = 4326$ (6) Å³, $Z = 4$, $D_x = 1.16$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 15.86$ cm⁻¹, $F(000) = 1608$, room temperature, $R = 0.056$ for 6136 reflections with $F^2 > 3\sigma(F^2)$. There are two virtually identical molecules in the asymmetric unit. In each, the Y atom is tetrahedrally coordinated to a substituted Si-bridged bis(cyclopentadienyl) ligand and to two Cl ions in the cleft. The Li atom is 2.35 Å from each Cl ion, and two molecules of tetrahydrofuran are connected to the Li, completing its tetrahedral coordination.

Introduction. The Ziegler–Natta polymerization of olefins has occupied the attention of chemists for nearly four decades. Recently, the development of homogeneous transition-metal catalyst systems has afforded the possibility of mechanistic investigations into various key steps of polymer initiation, propagation and chain termination. Brintzinger and co-workers have developed a series of *ansa*-zirconocene catalysts which possess a C_2 symmetric ligand arrangement about the metal center (Roll, Brintzinger, Rieger & Zolk, 1990; Wiesenfeldt, Reinmuth, Barsties, Evertz & Brintzinger, 1989). Moreover, activation of these *ansa*-zirconocene catalysts with methylalumoxane results in production of highly isospecific polymers. Work in this laboratory has centered on the study of well defined single-component Ziegler–Natta-type catalyst systems (Piers, Shapiro, Bunel & Bercaw, 1990). We report

* Contribution No. 8539.