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THE FORMATION, CRYSTAL AND MOLECULAR STRUCTURE OF (η^5-PENTAMETHYLCYCLOPENTADIENYL)(η^7-CYCLOHEPTATRIENYL)-TITANIUM AND (η^5-PENTAMETHYLCYCLOPENTADIENYL)-(η^8-CYCLOOCTATETRAENE)TITANIUM

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Summary

(η^5-C_5Me_5)(η^8-C_8H_8)Ti was prepared in 34% yield from a reaction between (η^5-C_5Me_5)$TiCl_3$ and $K_2C_8H_8$ in THF solution, and in 31% yield from reduction of (η^5-C_5Me_5)$TiCl_3$ in THF solution by magnesium metal in the presence of cyclooctatetraene. The latter synthesis could be extended to the synthesis of (η^5-C_5H_5)(η^8-C_8H_8)Ti in 38% yield. Reduction of (η^5-C_5Me_5)$TiCl_3$ in THF solution by metallic magnesium in the presence of cycloheptatriene produced (η^5-C_5Me_5)(η^7-C_7H_7)Ti in 68% yield. The structure of (η^5-C_5Me_5)(η^8-C_8H_8)Ti, at room temperature, was examined. This compound crystallizes in the orthorhombic space group *Pnma* with unit cell constants, *a* 9.946(7), *b* 13.597(4), *c* 11.513(9) Å and *D*(calc) 1.23 g cm^{-3} for $Z = 4$. Full matrix least-squares refinement using 915 independent observed reflections resulted in a final *R* value of 0.032. The titanium atom is located on a crystallographic mirror plane which bisects the two aromatic rings. The eight membered ring is disordered into two orientations. The average Ti–C(η^8) and Ti–C(η^5) distances are 2.34(2) and 2.338(5) Å, respectively. A low temperature (−90°C) X-ray diffraction study of (η^5-C_5Me_5)(η^7-C_7H_7)Ti resolved the disorder problem found for the C_8H_8 analogue. (η^5-C_5Me_5)(η^7-C_7H_7)Ti crystallizes in the orthorhombic space group *Pnma* with *a* 10.327(2), *b* 12.441(3), *c* 11.025(1) Å (at -90 ± 2°C) and *D*(calc) 1.29 g cm^{-3} for $Z = 4$. A final *R* value of 0.048 was obtained from full matrix least-squares refinement based on 1143 independent observed reflections. The titanium atom resides on a crystallographic mirror plane which bisects the two aromatic rings. The Ti–C(η^7) distances average 2.21(1) Å, the Ti–C(η^5) separations average 2.32(1) Å, and the Cent(η^5)–Ti–Cent(η^7) angle is 176.2°.

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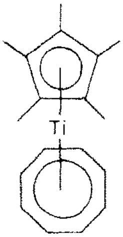
Introduction

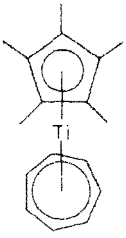
In contrast to low valent, tetra-coordinate organotitanium complexes such as $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ [1], $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$ [2], $(\eta^5\text{-}C_5H_5)_2Ti(CO)(PEt_3)$ [3], and $(\eta^5\text{-}C_5H_5)_2Ti(PF_3)_2$ [3], whose structures are pseudo-tetrahedral, organotitanium sandwich complexes which contain effectively planar organic rings are much more limited in number [4]. Two such complexes are $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ [5,6] and $(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)Ti$ [7], whose structures have been confirmed by X-ray diffraction studies [8,9]. In order to compare structural features of these organotitanium sandwich complexes with their η^5-pentamethylcyclopentadienyl analogues, we have undertaken the synthesis and X-ray structural study of $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)Ti$ (**1**) and $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)Ti$ (**2**).

Results and discussion

Both organotitanium sandwich complexes **1** and **2** could be obtained by modifications of the synthetic routes for $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ [6] and $(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)Ti$ [7]. Thus, reduction of $(\eta^5\text{-}C_5Me_5)TiCl_3$ in THF solution by metallic magnesium in the presence of cycloheptatriene gave **2** in 68% yield. Azure crystals of complex **2** were isolated by vacuum sublimation. The ^1H NMR spectrum of **2** in $CDCl_3$ consisted of 2 singlets at $\delta 1.92$ (C_5Me_5) and 5.32 (C_7H_7). The mass spectrum of **2** exhibited an intense molecular ion at m/e 274.



(1)



(2)

Complex **1** was readily produced from a reaction between $(\eta^5\text{-}C_5Me_5)TiCl_3$ and $K_2C_8H_8$ [7] in THF solution. The product was obtained by vacuum sublimation in 34% yield, as green paramagnetic crystals. A more convenient synthesis of **1** was subsequently developed involving reduction of $(\eta^5\text{-}C_5Me_5)TiCl_3$ in THF solution by metallic magnesium in the presence of cyclooctatetraene. Following vacuum sublimation, **1** could be obtained in 31% yield by this method. The mass spectrum of **1** contained an intense molecular ion at m/e 287.

In an analogous manner, we found that the parent compound $(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)Ti$ could also be produced in 38% yield from the reduction of $(\eta^5\text{-}C_5H_5)TiCl_3$ in THF solution by magnesium in the presence of cyclooctatetraene. This method thus represents a useful alternative synthesis of $(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)Ti$ in addition to the original literature procedures involving $K_2C_8H_8$ [7].

The molecular structure and atom labelling scheme for complex **1** in one of its two orientations are presented in Fig. 1. Bond distances and angles are given in Tab. 1. Complex **1** resides on a crystallographic mirror plane containing the Ti atom and bisecting both aromatic rings. The C_5 ring is ordered but the C_8 ring shows two

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) FOR $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)Ti$ (1)

Ti–C(1)a	2.35(1)	Ti–C(2)a	2.331(7)
Ti–C(3)a	2.297(7)	Ti–C(4)a	2.326(7)
Ti–C(5)a	2.38(1)	Ti–C(1)b	2.341(6)
Ti–C(2)b	2.351(7)	Ti–C(3)b	2.325(7)
Ti–C(4)b	2.349(7)	Ti–C(6)	2.333(4)
Ti–C(7)	2.338(3)	Ti–C(8)	2.343(3)
Cent(a)–Ti	1.43	Cent(b)–Ti	1.46
Cent(3)–Ti	2.01		
Cent(a)–Ti–Cent(3)	179.1	Cent(b)–Ti–Cent(3)	179.0

different orientations about the mirror plane, one with C(1)a and C(5)a on the mirror plane another with the mirror plane bisecting the C(1)b–C(1)b′ and C(4)b–C(4)b′ bonds. Much of the possible discussion on this structure has been eliminated by this disorder, but direct comparisons with similar structures can still be made.

$(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)Ti$ (**1**) has a sandwich structure similar to its unsubstituted analogue $(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)Ti$ [9]. The centroid(η^5)–Ti–centroid(η^8) angle in **1** is 179° for both C_8 ring orientations. Despite the larger size of the pentamethylcyclopentadienyl ligand, the average Ti–C(η^5) distance (2.338(5) Å) and Ti–Cent(η^5)

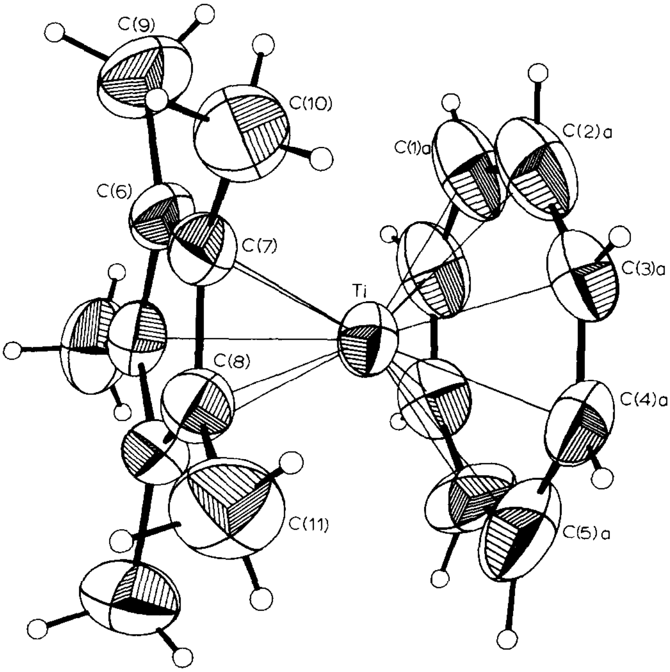


Fig. 1. Molecular structure and atom labelling scheme for $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)Ti$ (1) with the nonhydrogen atoms represented by their 50% probability ellipsoids for thermal motion. The C_8H_8 orientation with two carbon atoms on the mirror plane is represented.

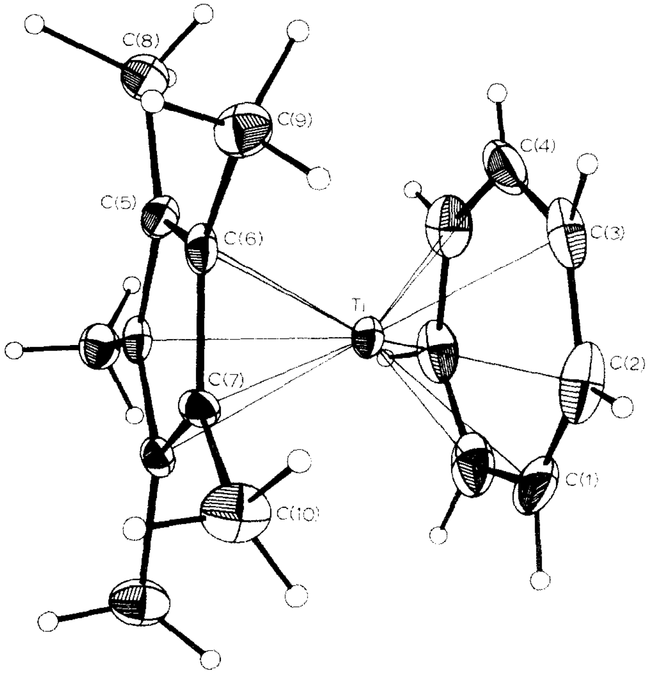


Fig. 2. Molecular structure and atom labelling scheme for (η^5-C_5Me_5)(η^7-C_7H_7)Ti (**2**).

separation (2.01 Å) are less than the corresponding Ti–C_5 ring distances in (η^5-C_5H_5)(η^8-C_8H_8)Ti of 2.353 Å and 2.030 Å [9], respectively. This perhaps reflects the electron-donating ability of the methyl groups and thus the electron rich nature of the C_5Me_5 ligand. The five membered ring in **1** exhibits a slight tilt with Ti–C(η^5) distances ranging from 2.333(4) for Ti–C(6) to 2.343(3) Å for Ti–C(8). Although these distances are within 3σ of being identical, a similar trend was observed in (η^5-C_5H_5)(η^8-C_8H_8)Ti. The five-membered ring in **1** is planar to within 0.003 Å.

The two cyclooctatetraene orientations in **1** show deviations in planarity up to 0.1 Å. The Ti–C(η^8) distances average 2.34(2) Å and exhibit a large range from 2.297(7) to 2.38(1) Å, possibly due to the disorder problem. If the shortening of the Ti–C(η^5) bond lengths in **1** compared to (η^5-C_5H_5)(η^8-C_8H_8)Ti is significant, one might expect a corresponding increase in the Ti–C(η^8) separations. A Ti–C(η^8) average value of 2.323 Å was observed in (η^5-C_5H_5)(η^8-C_8H_8)Ti. Other Ti–C(η^8) bond lengths include the 2.350(8) Å found in [(η^8-C_8H_8)Ti]$_2$(η^4,η^4-C_8H_8) [10], the 2.290(4) Å observed for (η^8-C_8H_8)Ti[$(C_2H_5)_2C_2B_4H_4$] [11], and a Ti–C(η^8) value of 2.32(2) Å reported for (η^8-C_8H_8)(η^4-C_8H_8)Ti [12].

By collecting data on complex **2** at low temperature, −90°C, the disorder problem observed in **1** was avoided. The molecular structure and atom labelling scheme for **2** are given in Fig. 2, bond distances and angles are given in Tab. 2. Again the titanium atom resides on a crystallographic mirror plane which bisects both aromatic rings. (Compounds **1** and **2** are nearly isostructural as can be seen by their coordinates in Tab. 4 and 5.) The carbon atom of the five membered ring (C(5)) and of the seven membered ring (C(1)) on the mirror are *trans* to one another. This situation is opposite to the conformation found for (η^5-C_5H_5)(η^7-C_7H_7)Ti [8]

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) FOR $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)Ti$ (**2**) [a]

Ti-C(1)	2.195(5)	Ti-C(2)	2.205(3)
Ti-C(3)	2.211(3)	Ti-C(4)	2.218(3)
Ti-C(5)	2.315(4)	Ti-C(6)	2.319(3)
Ti-C(7)	2.335(2)	C(1)-C(2)	1.419(4)
C(2)-C(3)	1.421(5)	C(3)-C(4)	1.397(5)
C(4)-C(4)′	1.449(7)	C(5)-C(6)	1.417(4)
C(5)-C(8)	1.499(6)	C(6)-C(7)	1.426(4)
C(6)-C(9)	1.506(4)	C(7)-C(10)	1.491(4)
C(7)-C(7)′	1.433(5)	Cent(1)-Ti	1.49
Cent(2)-Ti	1.98		
C(1)-C(2)-C(3)	128.2(3)	C(2)-C(1)-C(2)′	128.6(6)
C(2)-C(3)-C(4)	129.4(3)	C(3)-C(4)-C(4)′	128.1(2)
C(6)-C(5)-C(8)	125.7(2)	C(5)-C(6)-C(7)	108.0(2)
C(5)-C(6)-C(9)	126.2(3)	C(7)-C(6)-C(9)	125.7(2)
C(6)-C(5)-C(6)′	108.5(4)	C(6)-C(7)-C(10)	126.7(2)
C(6)-C(7)-C(7)′	107.7(2)	C(7)′-C(7)-C(10)	125.5(2)
Cent(1)-Ti-Cent(2)	176.2		

[a] Primed atoms are related to those in Tab. 5 by the crystallographic mirror plane.

and $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)V$ [13] in which the carbon atoms on the mirror were eclipsed.

The relative strength of the Ti–C_7H_7 interaction has previously been observed in $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ [8], and $(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_7H_6PPh_2)Mo(CO)_5 \cdot C_6H_5CH_3$ [14] where short Ti–C(η^7) separations of 2.194 and 2.203 Å were found. In $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)V$ a larger average V–C(η^7) bond length of 2.25 Å was observed [13] despite the 0.1 Å difference in the metallic radius of titanium versus vanadium. These experimental results and the crystal structure of $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Cr$ [16] are in accord with theoretical calculations that indicate the M–C_7H_7 bond strength decreases in the order Ti, V, Cr [16].

The new electronic and steric environment created by the C_5Me_5 moiety in **2** does not greatly affect the overall structure. The pentamethylcyclopentadienyl ligand in **2** is tilted slightly, Ti–C(η^5) range; 2.315(4) for C(5) to 2.334(2) Å for C(7)) as observed in **1** and both of the unsubstituted sandwich compound analogues. The average Ti–C(η^5) separation of 2.32(1) in **2** is identical to the 2.321 Å found for $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ [8]. The Ti–C(η^7) bond lengths in **2** (2.21(1) Å) are only slightly larger than the 2.194 Å found in the unsubstituted analogue, again perhaps due to the introduction of the electron-rich pentamethylcyclopentadienyl. A similar cooperative effect was found in $(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_7H_6PPh_2)Mo(CO)_5 \cdot C_6H_5CH_3$ [14], where the Ti–C(η^5) bond lengths (2.305 Å) were shorter and the Ti–C(η^7) separation (2.203 Å) longer than in $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$.

In compound **2** the five-membered ring is planar to within 0.004 Å, the seven-membered ring to within 0.007 Å. The cent(η^5)–Ti–cent(η^7) angle is 176.2° similar to the 177.8° value observed in $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ [8].

One other interesting point regarding the structure of **1** and **2** involves the deviations of the ring substituents from the plane defined by the ring atoms. The bending of ring substituents out of the carbon plane has been attributed to π

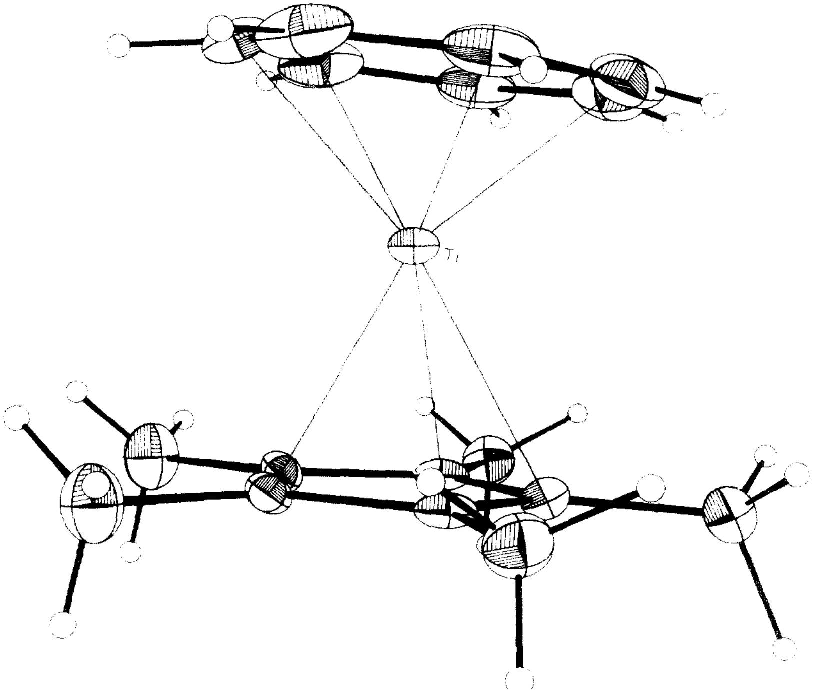


Fig. 3. Side view of **2**.

interactions and a reorientation of the ring for better metal overlap [17]. The results indicated a bending toward the metal for C_nH_n where $n > 5$ and away from the metal for $n < 5$. Theoretical calculations on a Ti(η^8-C_8H_8) fragment have yielded an optimal bending angle of 13° toward the metal for the ring hydrogens [17]. Despite a rather large range, the C_8 hydrogen atoms in **1** bend an average of 9° out of the C_8 plane toward the titanium. An average of 10° was found for complex **2**. The methyl groups have much smaller deviations and they bend away from the metal, −3° in **1** and −1° in **2**. These results and the lack of any great steric interactions, as indicated in the bond lengths and angles, would seem to agree with the idea that the crossover point between deviations toward and away from the metal occurs at C_nH_n, $n = 5$. The bending of the ring substituents can be seen in a side view of **2** presented in Fig. 3. In both **1** and **2**, two hydrogens of each methyl group are directed toward the metal and one hydrogen is directed away.

Experimental section

All reactions and manipulations were conducted under a prepurified argon atmosphere using Schlenk techniques. Gases and solvents were purified as described previously [18]. (η^5-C_5H_5)$TiCl_3$ [19] and (η^5-C_5Me_5)$TiCl_3$ [20] were prepared by literature methods. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA 01003. ^1H NMR spectra were recorded on a Varian A-60 spectrometer and are referenced to external tetramethylsilane.

(η^5-Pentamethylcyclopentadienyl)(η^8-cyclooctatetraene)titanium (1)

Method A. To (η^5-C_5Me_5)$TiCl_3$ (3.71 g, 12.8 mmol) in 200 ml of THF was added dropwise, with stirring, a solution of $K_2C_8H_8$ (15.3 mmol) in THF over a 30 min period. Following the addition, the reaction mixture was stirred at room temperature for 90 min, then heated to reflux for 15 min. The solvent was removed under reduced pressure, and the residue was sublimed at 120°C/0.2 Torr to give the product as green crystals (1.21 g, 34%). Anal. Found: C, 75.54; H, 7.93. $C_{18}H_{23}Ti$ calcd.: C, 75.26; H, 8.07%.

Method B. A solution of (η^5-C_5Me_5)$TiCl_3$ (1.1 g, 3.8 mmol) in 35 ml of THF was added dropwise with stirring to a solution of cyclooctatetraene (1.12 g, 10.7 mmol) in 30 ml of THF and magnesium turnings (0.41 g, 16.5 mmol) over a period of 45 min. After 24 h at room temperature, the solvent was removed under reduced pressure, and the residue was sublimed at 100°C/10^{-3} Torr (0.33 g, 31%).

(η^5-Cyclopentadienyl)(η^8-cyclooctatetraene)titanium

The procedure was identical to Method B as described above, employing cyclooctatetraene (1.48 g, 14.3 mmol) in 15 ml of THF, magnesium turnings (0.53 g, 22.7 mmol), and (η^5-C_5H_5)$TiCl_3$ (1.20 g, 5.47 mmol) in 100 ml of THF. The product was obtained as green crystals by vacuum sublimation (0.45 g, 38%).

(η^5-Pentamethylcyclopentadienyl)(η^7-cycloheptatrienyl)titanium (2)

(η^5-C_5Me_5)$TiCl_3$ (5.68 g, 19.6 mmol) in 80 ml THF was added dropwise with stirring to cycloheptatriene (3.0 ml, 29.0 mmol) in 25 ml of THF and magnesium turnings (1.9 g, 78 mmol) over a period of 1 h. The reaction mixture was stirred at room temperature for 24 h, after which time the solvent was removed under reduced pressure. Sublimation of the dark residue at 125°C/10^{-4} Torr gave the product as azure crystals (3.66 g, 68%). Anal. Found: C, 74.34; H, 8.12; Ti, 17.2. $C_{17}H_{22}Ti$ calcd.: C, 74.45; H, 8.09; Ti, 17.47%.

X-ray data collection, structure determination, and refinement for (η^5-C_5Me_5)(η^8-C_8H_8)Ti (1)

Single crystals of the air sensitive compound were sealed under N_2 in thin walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 19°$) accurately centered on the diffractometer are given in Tab. 3. The space group was determined to be either centric, *Pnma* or acentric, $Pn2_1a$ by the systematic absences. The correct choice, as discussed below, was determined to be the centrosymmetric *Pnma*.

Data were collected on an Enraf–Nonius CAD-4 diffractometer by the θ–2θ scan technique. A summary of data collection parameters is given in Tab. 3. The intensities were corrected for Lorentz and polarization effects, but not for absorption (μ 5.58 cm^{-1}).

Calculations were carried out with the SHELX system of computer programs. Neutral atom scattering factors for Ti, C and H were taken from reference [21] and the scattering from titanium was corrected for the real and imaginary components of anomalous dispersion [21].

The position of the titanium atom was revealed by the inspection of a Patterson map to be either on a mirror plane in *Pnma* or a general position in $Pn2_1a$. Statistical methods indicated that the space group was centrosymmetric and *Pnma*

TABLE 3

CRYSTAL DATA AND SUMMARY OF INTENSITY DATA COLLECTION AND STRUCTURE REFINEMENT

	$(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)Ti$ (**1**)	$(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)Ti$ (**2**)
Mol. wt.	287.3	274.3
Space group	*Pnma*	*Pnma*
Temperature	23 ± 1°C	-90 ± 2°C
Cell constants (Å)		
a	9.946(7)	10.327(2)
b	13.597(4)	12.441(3)
c	11.513(9)	11.025(1)
Cell vol. ($Å^3$)	1557.0	1416.5
Molecules/unit cell	4	4
ρ(calcd.) ($g\ cm^{-3}$)	1.23	1.29
μ(calcd.) (cm^{-1})	5.58	51.3
Radiation	Mo-K_α (λ 0.71073 Å)	Cu-K_α (λ 1.54178 Å)
Max. crystal dimensions, (mm)	$0.42 \times 0.52 \times 0.60$	$0.35 \times 0.55 \times 0.75$
Scan width	$0.80 + 0.20\tan\theta$	$0.80 + 0.20\tan\theta$
Standard reflections	(600) (040) (008)	(531) (022) (140)
Decay of standards	±2%	−0.3%
Reflections measured	1642	1143
2θ-range	$1.0 \leq 2\theta \leq 50°$	$3.0 \leq 2\theta \leq 115.0°$
Reflections collected	915	944
No. of parameters varied	127	124
GOF	0.79	0.78
R	0.032	0.048
R_w	0.034	0.083

was therefore taken as the initial choice. A difference Fourier map phased on the titanium atom position readily revealed the unique carbon atoms of the pentamethylcyclopentadienyl ligand. The cyclooctatetraene moiety was found to be disordered about the mirror in two orientations, one with two carbon atoms of the ring on the mirror and another with the mirror bisecting two of the C–C bonds. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | =$ 0.112. Because of the disorder problem, a detailed investigation of the acentric space group $Pn2_1a$ was carried out. High correlations between atoms related by the mirror, a higher *R* value, and the continued presence of the disorder in the C_8H_8 ring, indicated the correct space group to be the original choice of *Pnma*. The hydrogen atoms of the C_8H_8 ring were placed at calculated positions 0.95 Å from the bonded carbon atom. The methyl hydrogen atoms were located with the aid of a difference Fourier map. Hydrogen positional parameters were refined for a few least-squares cycles of refinement. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of *R* 0.032 and R_w 0.034. A final difference Fourier showed no feature greater than 0.3 $e^-/Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Tab. 4 [22].

*X-ray data collection, structure determination, and refinement for $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)Ti$ (**2**)*

Crystals of this compound were treated as stated for **1** prior to X-ray examina-

TABLE 4

FINAL FRACTIONAL COORDINATES FOR $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)Ti$ (**1**) [a]

Atom	x/a	y/b	z/c
Ti	0.35940(8)	0.7500	0.52080(7)
C(1)a	0.306(1)	0.7500	0.7198(8)
C(2)a	0.3547(9)	0.6552(6)	0.6894(6)
C(3)a	0.4567(7)	0.6198(5)	0.6161(6)
C(4)a	0.5546(6)	0.6577(7)	0.5431(6)
C(5)a	0.597(1)	0.7500	0.495(1)
C(1)b	0.3283(8)	0.6973(5)	0.7125(5)
C(2)b	0.4041(7)	0.6257(5)	0.6575(5)
C(3)b	0.5099(6)	0.6284(5)	0.5780(6)
C(4)b	0.5838(6)	0.6964(6)	0.5170(7)
C(6)	0.1349(4)	0.7500	0.4621(3)
C(7)	0.1962(3)	0.6655(2)	0.4140(2)
C(8)	0.2954(3)	0.6979(2)	0.3349(2)
C(9)	0.0185(5)	0.7500	0.5444(5)
C(10)	0.1602(4)	0.5602(3)	0.4368(3)
C(11)	0.3789(4)	0.6329(3)	0.2583(3)
H(1)a[C(1)a]	0.241	0.750	0.758
H(2)a[C(2)a]	0.290	0.608	0.718
H(3)a[C(3)a]	0.450	0.556	0.613
H(4)a[C(4)a]	0.595	0.614	0.490
H(5)a[C(5)a]	0.658	0.750	0.414
H(1)b[C(1)b]	0.249	0.670	0.754
H(2)b[C(2)b]	0.367	0.557	0.667
H(3)b[C(3)b]	0.526	0.565	0.547
H(4)b[C(4)b]	0.648	0.678	0.468
H(6)[C(9)]	−0.072	0.750	0.513
H(7)[C(9)]	0.022	0.692	0.589
H(8)[C(10)]	0.114	0.561	0.506
H(9)[C(10)]	0.100	0.534	0.387
H(10)[C(10)]	0.228	0.512	0.434
H(11)[C(11)]	0.338	0.631	0.183
H(12)[C(11)]	0.387	0.568	0.284
H(13)[C(11)]	0.454	0.661	0.242

[a] a, b atoms correspond to the disordered C_8H_8 ligand. The disorder is 50%/50%.

tion. A preliminary data set on **2** was collected at room temperature. The C_7H_7 ring was found to be disordered. In order to resolve the disorder problem for this compound data were recollected at −90°C. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta/\lambda)^2$ values for 25 reflections ($\theta > 15°$) accurately centered on a Nicolet P3/F diffractometer are given in Tab. 3. Again the systematic absences indicated the space group to be either *Pnma* or *Pn*2_1*a*. This time solution and refinement of the structure in the centric *Pnma* with no disorder indicated this space group to be the correct choice.

Data were collected on a Nicolet diffractometer by the ω scan technique at −90°C. A summary of data collection parameters is given in Tab. 3. The intensities were corrected for Lorentz and polarization effects, and for absorption.

Calculations were carried out with the SHELX systems of computer programs. Neutral atom scattering factors for Ti, C and H were taken from ref. 21 and the

TABLE 5

FINAL FRACTIONAL COORDINATES FOR $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)Ti$ (**2**)

Atom	x/a	y/b	z/c
Ti	0.34957(6)	0.7500	0.51811(7)
C(1)	0.5618(4)	0.7500	0.5301(4)
C(2)	0.5159(3)	0.6472(3)	0.5659(3)
C(3)	0.4117(3)	0.6225(2)	0.6451(3)
C(4)	0.3283(3)	0.6917(3)	0.7072(3)
C(5)	0.1345(4)	0.7500	0.4589(4)
C(6)	0.1938(3)	0.6575(2)	0.4083(2)
C(7)	0.2900(2)	0.6924(2)	0.3243(2)
C(8)	0.0253(4)	0.7500	0.5485(4)
C(9)	0.1599(3)	0.5424(3)	0.4362(3)
C(10)	0.3736(4)	0.6228(2)	0.2469(3)
H(1)[C(1)]	0.623	0.750	0.465
H(2)[C(2)]	0.547	0.580	0.526
H(3)[C(3)]	0.379	0.547	0.647
H(4)[C(4)]	0.273	0.660	0.733
H(5)[C(8)]	−0.080	0.750	0.509
H(6)[C(8)]	0.026	0.697	0.601
H(7)[C(9)]	0.132	0.521	0.520
H(8)[C(9)]	0.101	0.518	0.382
H(9)[C(9)]	0.234	0.508	0.428
H(10)[C(10)]	0.379	0.550	0.274
H(11)[C(10)]	0.457	0.648	0.245
H(12)[C(10)]	0.326	0.617	0.179

scattering was corrected for the real and imaginary components of anomalous dispersion [21].

The position of the titanium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the titanium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.094$. The hydrogen atoms were located with the aid of a difference Fourier map and their positional parameters were varied for several least-squares refinement cycles. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of R 0.048 and R_w 0.083. A final difference Fourier showed no feature greater than 0.3 $e^-/Å^3$. The weighting scheme was based on $[(1/\sigma^2 F_o) + (1/pF_o^2)]$ where p 0.011; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Tab. 5 [22].

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Supplementary Material

Tables of thermal parameters, best planes results and calculated and observed structure factors for **1** and **2** and bond distances and angles for **1** are available. See NAPS document No. 04325 for 14 pages of supplementary material which may be ordered from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each 10 pages of material thereafter. $1.50 for microfiche postage.

References and notes

1 J.L. Atwood, K.E. Stone, H.G. Alt, D.C. Hrncir, and M.D. Rausch, J. Organomet. Chem., 132 (1977) 367.
2 D.J. Sikora, M.D. Rausch, R.D. Rogers, and J.L. Atwood, J. Am. Chem. Soc., 103 (1981) 1265.
3 B.H. Edwards, R.D. Rogers, D.J. Sikora, J.L. Atwood, and M.D. Rausch, J. Am. Chem. Soc., 105 (1983) 416.
4 M. Bottrill, P.D. Gavens, J. McMeeking in G. Wilkinson, F.G.A. Stone, and E.W. Abel, (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, New York, 1982, Vol. 3, Chapt. 22.2, p. 281.
5 H.O. van Oven and H.J. de Liefde Meijer, J. Organomet. Chem., 23 (1970) 159.
6 B. Demerseman, G. Bouquet, and M. Bigorgne, J. Organomet. Chem., 101 (1975) C24.
7 H.O. van Oven and H.J. de Liefde Meijer, J. Organomet. Chem., 19 (1969) 373.
8 J.D. Zeinstra and J.L. de Boer, J. Organomet. Chem., 54 (1973) 207.
9 P.A. Kroon and R.B. Helmholdt, J. Organomet. Chem., 25 (1970) 451.
10 H. Dierks and H. Dietrich, Acta Cryst. (1968), B24, 58.
11 R.G. Swisher, E. Sinn, and R.N. Grimes, Organometallics, 3 (1984) 599.
12 H. Dietrich and M. Soltwisch, Angew. Chem. Int. Ed. Engl., 8 (1969) 765.
13 G. Engebretson and R.E. Rundle, J. Am. Chem. Soc., 85 (1963) 481.
14 B. Demerseman, P.H. Dixneuf, J. Douglade, and R. Mercier, Inorg. Chem., 21 (1982) 3942.
15 L. Pauling, The Nature of the Chemical Bond, Cornell University Press, 1960, 3rd edn., p. 256.
16 J.D. Zeinstra, W.C. Nieuwpoort, Inorg. Chim. Acta, 30 (1978) 103 and refs. therein.
17 J.W. Chinn Jr., and M.B. Hall, J. Am. Chem. Soc., 105 (1983) 4930.
18 M.D. Rausch, W.H. Boon, and H.G. Alt, J. Organomet. Chem., 141 (1977) 299.
19 R.D. Gorsich, J. Am. Chem. Soc., 82 (1958) 4211.
20 J. Blenkers, H.J. de Liefde Meijer, and J.H. Teuben, J. Organomet. Chem., 218 (1981) 383.
21 International Tables for X-ray Crystallography; Kynoch Press; Birmingham, England, Vol. IV, 1972, pp. 72, 99, 149.
22 See paragraph at the end of paper regarding supplementary material.