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## The molecular structure of $\text{Me}_3\text{TiCp}^*$ in the gas phase

R. Blom, K. Rypdal \*

*Department of Chemistry, University of Oslo, Box 1033, Blindern, N-0315 Oslo 3 (Norway)*

M. Mena, P. Royo and R. Serrano

*Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, 28871 Alcalá de Henares Madrid (Spain)*

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### Abstract

The thermal average molecular structure of  $\text{Me}_3\text{TiCp}^*$  has been determined by gas phase electron diffraction (GED). The GED data are consistent with a molecular model in which the  $\text{TiMe}_3$  fragment has  $C_{3v}$  symmetry and the  $\text{TiCp}^*$  fragment has  $C_{5v}$  symmetry. No static tilt of the methyl groups attached to titanium can be detected, although a flattening of the methyl groups with  $\text{Ti-C-H } 103.8(1.2)^\circ$  is obtained. The  $\text{Ti-C(Me)}$  bond distance is  $210.7(5)$  pm, and the  $\text{Ti-C(Cp}^*)$  distance  $238.0(5)$  pm.

### Introduction

Several structures of electronically unsaturated organotitanium compounds have been determined, some of which exhibit an agostic  $\text{Ti} \cdots \text{H}$  interaction and some not [1–7]. The electrons of the C–H bond are partially donated to the metal, with a distortion of the geometry of the organic ligand. The exact geometry of the methyl groups in the title compound was expected to be difficult to determine accurately, but in view of the interest in such compounds we have investigated  $\text{Me}_3\text{TiCp}^*$  by the gas electron diffraction (GED) method.

### Experimental procedure and data processing

$\text{Me}_3\text{TiCp}^*$  was prepared from  $\text{Cl}_3\text{TiCp}^*$  and  $\text{LiMe}$  [1]. The GED data were recorded on a Balzers Eldiograph KD-G2 instrument [8]. The nozzle and reservoir temperature was about  $103^\circ\text{C}$ . A torus shaped nozzle, which allows data to be recorded with a reduced vapour pressure, was used [9]. The electron wavelength was

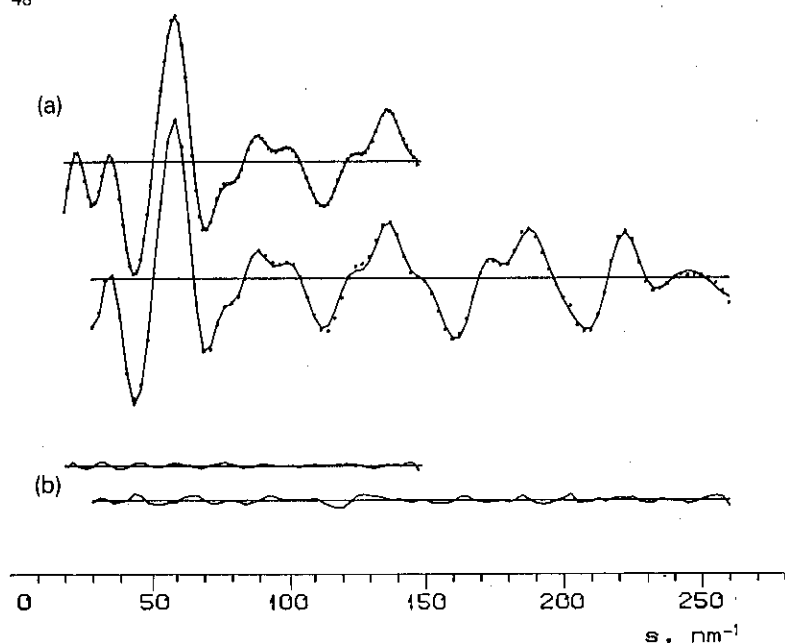


Fig. 1. a) Theoretical (full line) and experimental (dotted line) intensity curves for each nozzle to plate distance; b) Difference curve between experimental and theoretical intensity.

calibrated against the C–C distance ( $r_a$  139.75 pm) in gaseous benzene. Five plates were recorded with a nozzle to plate distance of 50 cm, and four plates with a distance of 25 cm. The  $s$  limits used in the final refinements were  $s$  20.0–148.5 nm<sup>-1</sup> with  $\Delta s$  1.25 nm<sup>-1</sup> (50 cm), and  $s$  30.0–260.0 nm<sup>-1</sup> with  $\Delta s$  25.0 nm<sup>-1</sup> (25 cm). After photometry on a Snoopy densitometer the data were processed by standard procedures [10]. The backgrounds were computer drawn, and the intensity curves were finally averaged within each set of data. Complex atomic scattering factors  $f'(s)$  were taken from Ref. 11. The molecular intensity curves for the best model are shown in Fig. 1.

### Model choice and refinements

The Me<sub>3</sub>TiCp\* was assumed to be formed from C<sub>5</sub>Me<sub>5</sub> and TiMe<sub>3</sub> fragments attached in such a way that the TiCp\* and the TiMe<sub>3</sub> maintain C<sub>5v</sub> and C<sub>3v</sub> symmetries, respectively, and the relative orientation of the two fragments is fixed as shown in Fig. 2b. The methyl groups of the TiMe<sub>3</sub> fragment were allowed to rotate in the initial refinements, but were fixed in the last steps with one C–H bond *anti* to the vector from titanium to the centre of the Cp\* ring. Each methyl group was assumed to have local C<sub>3v</sub> symmetry and was allowed to be tilted (the three fold symmetry axes does not coincidence with the Ti–C bond), but this model did not fit the experimental data. The methyl groups on the pentamethylcyclopentadienyl ring were initially allowed to rotate, but later they were fixed with two hydrogen atoms pointing away (with an equal Ti...H distance) from titanium. They were also allowed to bend out of the cyclopentadienyl plane; a positive bending angle (deviation from planarity) is defined to represent bending towards Ti.

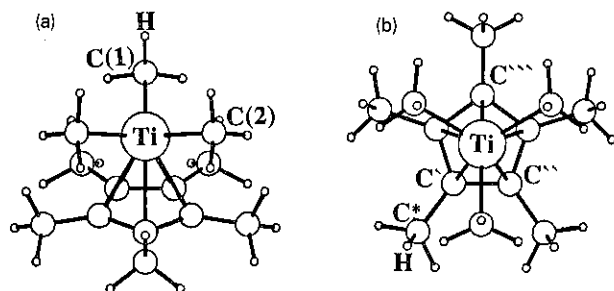


Fig. 2. Molecular model of  $\text{Me}_3\text{TiCp}^*$ .

The adopted model is described by 10 independent parameters: The distance from titanium to the centre of the ring ( $h$ ), the Ti–C(1) bond distance, the two different C–C bond distances in the  $\text{Cp}^*$  ring, the C–H bond distances (all assumed to be equal), the *trans*  $\text{C}^* \cdots \text{C}^*$  non bonded distance of the methyl groups on the  $\text{Cp}^*$  ring, Ti–C(1)–H, ringcentroid–Ti–C(1), the ringcentroid–C'–C\* out of plane bending angle, and tilt of the  $\text{TiMe}_3$  methyl groups. A model of the molecule is shown in Fig. 2. The molecular structure, along with 9 vibrational amplitudes, was refined by a least-squares fit of a theoretical intensity curve to the two experimental curves.

### Results and discussion

The GED data are consistent with the proposed molecular model, and parameters found for the best fitting are listed in Table 1. All least-squares standard errors

Table 1

Geometrical parameters and vibrational amplitudes ( $I$ ) for  $\text{Me}_3\text{TiCp}^*$

<i>The TiMe<sub>3</sub> fragment</i>	$r$ (pm)	$I$ (pm)
Ti–C(1)	210.7(5)	6.5(4)
C–H(average)	111.0(3)	7.4(3)
Ti $\cdots$ H(methyl)	260(2)	12 <sup>a</sup>
C(1) $\cdots$ C(2)	345(2)	7.6(2.1)
<i>Angles (°)</i>		
Ti–C(1)–H	103.8(1.2)	
ringcentroid–Ti–C(1)	108.9(8)	
Tilt	0.0 <sup>a</sup>	
<i>The TiCp* fragment</i>	$r$ (pm)	$I$ (pm)
$h$ (Ti–ringcentroid)	204.9(5)	
Ti–C'	238.0(5)	7.8(4)
C'–C''	142.3(3)	4.9 <sup>a</sup>
C'–C*	149.6(4)	5.5 <sup>a</sup>
C* $\cdots$ C*	517(2)	11.3(2)
Ti $\cdots$ C*	339(1)	15.2(1.0)
C''–C*	260.2(3)	7.0 <sup>a</sup>
C'''–C*	375.4(4)	7.5 <sup>a</sup>
<i>Angles (°)</i>		
C'–C*–H	114.2(1.1)	
ringcentroid–C'–C*	–0.5(6)	

<sup>a</sup> Not refined.

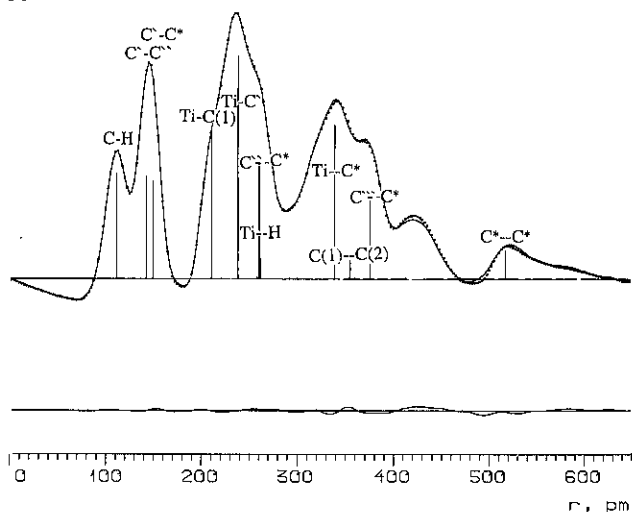


Fig. 3. a) Theoretical (full line) and experimental (dotted line) radial distribution curve. The most important peaks are indicated by bars; b) Difference curve between experimental and theoretical radial distribution curves. Artificial damping is  $30 \text{ pm}^2$ .

are multiplied by a factor of 3 to compensate for the assumptions made in defining the model and the systematic experimental errors. The radial distribution curve, with the most important peaks indicated with bars, are shown in Fig. 3. The  $R$ -factor for the best model was 4.3%\*.

The Ti-C' distance is 238.0(5) pm, the Ti-centroid (Cp\*) distance is 204.9(5) pm and they are within the range found in related pentamethylcyclopentadienyl titanium alkyls [3]. The Ti-C(1) distance of 210.7(5) pm match, within the experimental error, the mean value of all the Ti-C (alkyl) distances reported to date for monopentamethylcyclopentadienyl titanium derivatives (211 pm) [3,13,14], and is somewhat longer than found in the GED investigation of  $\text{Cl}_3\text{TiMe}$  (204.7(6) pm) [6] and slightly shorter than the average distance in  $\text{Benz}_3\text{TiCp}^*$ .

The Ti-C-H angle is unusual ( $103.8(1.2)^\circ$ ) but the  $\text{Ti} \cdots \text{H}$  distance of 260.4 pm does not seem to indicate any anomalous situation. As we have mentioned earlier, tilting of the three methyl groups did not fit the experimental data. An alternative model is that in which only one Me group tilts, a situation similar to that reported for  $\text{TiCp}^*(\text{CH}_2\text{Ph})_3$  in which the presence of one agostic benzyl group is indicated by an X-ray study [1], but this model is too complicated. Moreover, static solid-state agostic situations often become fluxional in solution, as evidenced by  $^1\text{H-NMR}$  spectroscopy [5], and this is case for  $\text{TiCp}^*(\text{CH}_2\text{Ph})_3$ .  $\text{Cl}_3\text{TiMe}$  has been shown by GED, IR spectroscopy, and theoretical calculations to be undistorted in the gas phase [6,7,12]. Calculations by Hall et. al show the methyl group of  $\text{Cl}_3\text{TiMe}$  to have an unusual low degree of methyl group rocking, which is attributed to ready rehybridization of titanium. The exact positions of the hydrogen atoms are difficult to determine accurately by GED, but the observed flattening may be attributed to a large amplitude vibrational mode of the methyl groups, although further studies are needed to clarify this point.

\*  $R = (\sum w(I_{\text{obs}} - I_{\text{exp}})^2 / \sum w I_{\text{obs}}^2)^{1/2}$ .

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