On the Molecular Structure of Bis(cyclopentadienyl)titanium Borohydride: A Gaseous Electron Diffraction Study

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Metal cyclopentadienyl π-complexes possess a variety of interesting structural features [1]. Some of the questions posed by their structures are the following: the metal–carbon distance, the ring geometry, the relative orientation of the rings, the angle between the ring planes, possible deviation of H atom positions from the ring plane, the variations in the metal–ligand bond configuration of the complex as compared with the uncomplexed molecules.

Metal borohydrides have presented a challenge for structural chemists for some time and the most intriguing question of their structure is the relative orientation of the metal towards the BH_4 tetrahedron (*cf.* [1, 2]).

Bis(cyclopentadienyl)titanium borohydride comprises a cyclopentadienyl π-complex part and a borohydride part and its crystal-phase structure has been investigated by Lippard *et al.* [3] using X-ray diffraction. Among others, they found the (ring centroid)– Ti–(ring centroid) angle (ω) to be 136.7°, r(Ti–B) 2.37(1) Å, r(Ti–C) 2.35(4) and the Ti–(ring centroid) distance 2.03 Å as average parameters, and the carbon atoms of the cyclopentadienyl groups to be disordered.

We decided to perform a gaseous electron diffraction investigation primarily to determine the Ti–C bond length more accurately and to gain more insight into the other structural features if possible. It is of significance to perform vapour-phase structure determinations since the vapour phase is the only phase where the intramolecular interactions solely determine the structure. Weak interactions may be of importance for complex molecules and considerable differences have been observed in structure studied in different phases [1].

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Experimental

The sample was prepared by Drs. B. V. Bulichev and G. L. Soloveichik (Moscow State University). Its purity and vapour composition were checked by elemental analysis and mass spectrometry. The electron diffraction patterns were taken with the Budapest EG-100A apparatus [4, 5] with nozzle temperature of 150 °C. Experimental intensities were used in the following ranges: 50 cm camera distance, $1.75 \le s \le 13.50$ Å^{-1} and 19 cm camera distance $8.50 \le s \le 33.75$ Å^{-1} ($\Delta s = 0.25$ Å^{-1}). The other experimental conditions and the procedure of data reduction were essentially the same as described elsewhere [6–8]. The reduced molecular intensities and experimental radial distribution are shown in Figs. 1 and 2.
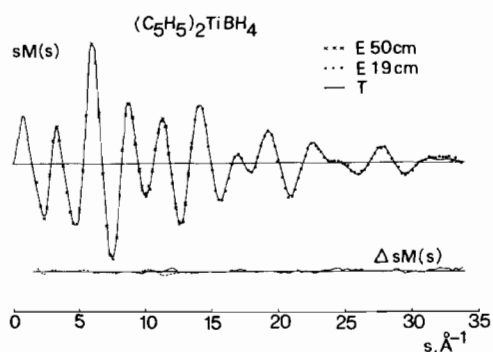

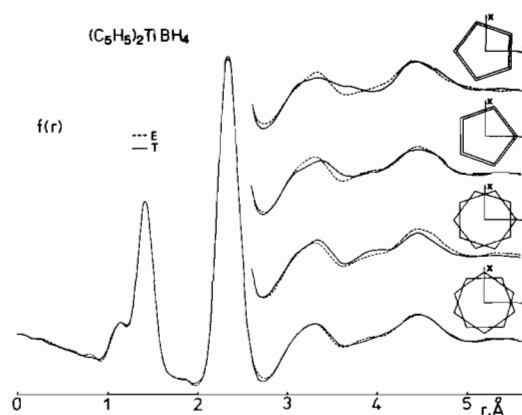Fig. 1. Experimental (E) and theoretical (T) molecular intensities.

Fig. 2. Experimental (E) and theoretical (T) radial distributions.

Structure Analysis

The molecular model used in this analysis can be characterized as follows. The overall configuration is

TABLE I. Molecular Parameters of $(C_5H_5)_2TiBH_4$.

Distances	r (Å)	σ_t (Å)[a]	l (Å)	σ_t (Å)[a]
Ti–C	2.382	0.006	0.091	0.005
C–C	1.423	0.003	0.054	0.002
Ti–B	2.31	0.04	0.062	0.016
Ti–H	1.89	0.05	0.13	0.04
C–H	1.126	0.007	0.067	0.006

Angles	$\angle$ (°)	σ_t (°)[a]
$\angle$Cp–Ti–Cp	137.3	1.4
$\angle P$[b]	18	8
$\angle Q$[b]	–18	8

[a]Total errors calculated in the following way [6]:

distances (r): $\quad \sigma_t = [2\sigma^2 + (0.002\,r)^2]^{1/2}$

amplitudes (l): $\quad \sigma_t = [2\sigma^2 + (0.02\,l)^2]^{1/2}$

angles: $\quad\quad\quad \sigma_t = \sqrt{2}\sigma$.

[b]This angle is 0° when an apex of the five-membered ring is on the y-axis of the projection (drawing of Fig. 3).
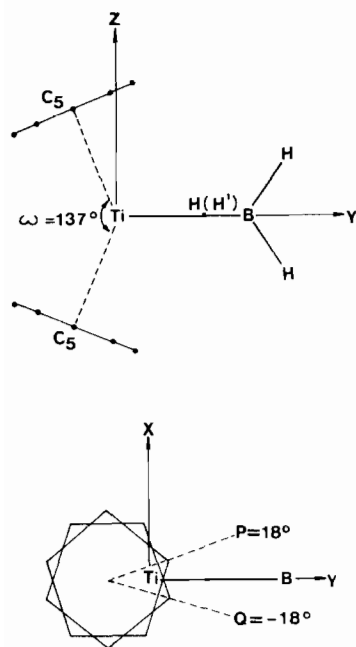
Fig. 3. Schematic drawing of the molecular model as projections in two planes. The angles ω, P, and Q are indicated. P = 0° and Q = 0° when the apexes of the rings are projected onto the Ti–B bond. These angles are positive when the ring is rotated anticlockwise.

shown in Fig. 3. The C_5H_5 rings are of penta*hapto* type, all Ti–C bonds and the intraring C–C bonds are of equal lengths. The Ti atom is situated in the intersection of the two fivefold symmetry axes and the continuation of the Ti...B line bisects the angle ω. In addition to the model with two bridging hydrogen atoms (Fig. 3), a model with three bridging hydrogen atoms has also been tested. Each C_5H_5 ring was characterized by an independent angle of rotation around their respective symmetry axes.

The experimental radial distribution (Fig. 2) contained several features. The maximum at around 1.1 Å and 1.4 could be identified primarily with the contributions from the C–H and C–C bonds of the rings. The sharpness of the C–C bond distance maximum is an indication that all carbon atoms occupy equivalent positions in the ring. The very small individual hump at about 1.8–1.9 Å was thought to correspond to the Ti–H distances. The main contribution to the largest maximum at around 2.4 came from the Ti–C bonds and C...C nonbonding intraring distances. The outer part of the radial distribution is due to ring-rotation dependent C...C, B...C, C...H, and B...H interactions.

The analysis was based on the molecular intensities using a least-squares procedure. For references on programs and scattering factors see [6–8]. Most refinement schemes have been constructed for both models with two and three bridging hydrogen atoms

and the agreement with the two bridge model was always somewhat better than with the three bridge model. Accordingly, the results presented in Table I refer to the preferred two bridge model.

The Ti–C bond length is especially well determined. On the other hand, the contribution from the Ti–B is much smaller, and the closeness of the two distances produced strong correlation between them and their mean vibrational amplitudes as well. Various combinations of the starting values for the latter resulted always in essentially the same results as given in Table I. A refinement scheme was also constructed in which the weighted mean distance of the Ti–C and Ti–B bonds and their differences were used as independent parameters. r(Ti–C) – r(Ti–B) was then determined to be 0.053 ± 0.017 (standard deviation from the least-squares refinement), and a Hamilton test [9] indicated that r(Ti–C) was larger than r(Ti–B) even on a 99.5% significance level.

As for the relative orientation of the two rings with regard to each other, various staggered and eclipsed conformations were tested. Different rotation forms were also tried as regards the relative orientation of the rings towards the Ti...B axis. The best agreement (lowest R factor) was achieved for a form shown in projection in Fig. 3 while we cannot reject other rotational forms.

The deviation of the H atom positions from the plane of the respective C_5 ring did not exceed the value of its standard deviation.

Discussion

The length of the C–C bonds is in excellent agreement with those observed in other cyclopenta-

dienyl complexes (for data and references see [1]). This indicates that the C_5H_5 rings are hardly influenced by participation in different complexes. The Ti–C distances agree very well with analogous distances, *e.g.*, in gaseous $Ti(C_5H_5)_2Cl_2$ (2.372 ± 0.006) [10] and crystalline $C_{10}H_8(C_5H_5)_2Ti_2Cl_2$ (average value 2.376 Å for the cyclopentadienyl ligand) [11], $[(CH_3C_5H_4)_2TiCl]_2$ (average value for the ring carbon atoms 2.380 Å, σ 0.024 Å) [12], $[(CH_3C_5H_4)_2TiBr]_2$ (average value for the ring carbon atoms 2.383 Å, σ 0.037 Å) [12], $[(C_5H_5)TiCl]_2MnCl_2 \cdot 2(OC_4H_8)$ (average value 2.369 Å, σ 0.018 Å) [13]. Note also that the (ring centroid)–Ti–(ring centroid) angles vary in a relatively narrow range, around 130–140°, in the cyclopentadienyltitanium derivatives (see *e.g.* [11–15]). In the vapour phase the cyclopentadienyl rings of $(C_5H_5)_2TiBH_4$ molecules seem to take an orientation of relatively high symmetry with regard to each other and the Ti...B axis.

Acknowledgements

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