Journal of Organometallic Chemistry 92 (1975) 329—340
© Elsevier Sequoia S A Lausanne — Printed in The Netherlands

CYCLOOCTATETRAENETITANIUM CHLORIDE AND ITS ADDUCTS WITH THF AND SOME AMINES

H R VAN DER WAL, F OVERZET, H O VAN OVEN, J L DE BOER, H J DE LIEFDE MEIJER and F JELLINEK

Laboratories of Inorganic and Structural Chemistry The University Zernikelaan Groningen, (The Netherlands)

(Received January 13th 1975)

Summary

The syntheses and the results of mass spectrometry and infrared spectroscopy are reported of cyclooctatetraenetitanium chloride and its adducts with the donor molecules THF, diethylamine, pyrrolidine and pyridine Single crystal X-ray diffraction shows the chloride to be tetrameric, $[C_8H_8TiCl]_4$, and the adduct with THF dimeric, $[C_8H_8TiCl \cdot THF]_2$

Introduction

Lehmkuhl and Mehler [1] briefly reported the electrochemical preparation of $C_8H_8TiCl \cdot THF$ and $C_8H_8TiCl \cdot C_5H_5N$ and the formation of C_8H_8TiCl upon heating the pyridine adduct in vacuum In view of our interest in cyclooctatetraenetitanium complexes and the possible use of C_8H_8TiCl as a starting material in their preparation, we have studied the synthesis of C_8H_8TiCl and some adducts $C_8H_8TiCl \cdot L$ (L = donor molecule) and investigated some of their properties The crystal structures of C_8H_8TiCl and $C_8H_8TiCl \cdot THF$ were studied by X-ray diffraction, the compounds were found to consist of tetrameric molecules $[C_8H_8TiCl]_4$ and dimers $[C_8H_8TiCl \cdot THF]_2$, respectively

Results

$C_8H_8TiCl \cdot THF$ was prepared by reaction of $TiCl_3 \cdot 3THF$ and $K_2C_8H_8$ in boiling THF Crystals suitable for X-ray diffraction were obtained by recrystallization from THF

C_8H_8TiCl was obtained by repeated washing of $C_8H_8TiCl \cdot THF$ with ether Crystals suitable for X ray diffraction were obtained by recrystallization from C_6H_5Cl

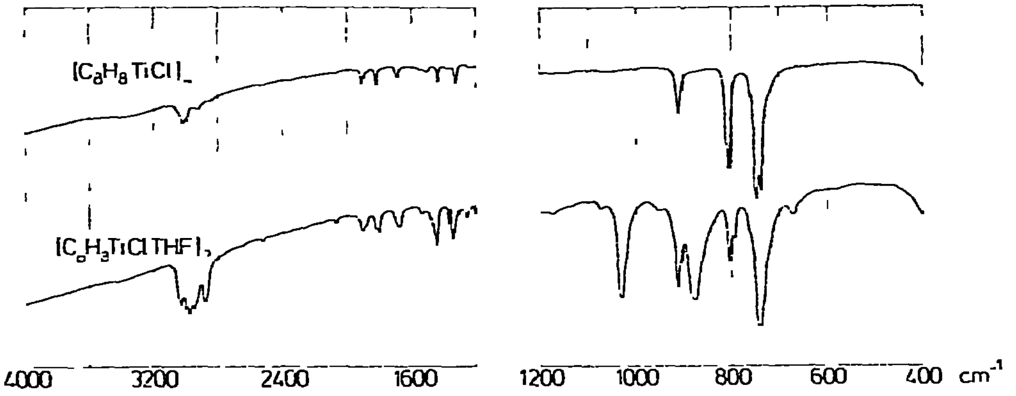

Fig. 1 Infrared absorption spectra of [C_8H_8TiCl]$_x$ and [$C_8H_8TiCl \cdot THF$]$_2$

Adducts $C_8H_8TiCl \cdot L$, where L = diethylamine, pyrrolidine or pyridine, were obtained by reaction of $C_8H_8TiCl \cdot THF$ with the donor L in hexane. The compounds were purified by recrystallization from C_6H_5Cl.

Similar experiments starting from the adducts $C_8H_8TiCl \cdot L$ show an increase in stability of $C_8H_8TiCl \cdot L$ in the sequence L = THF < diethylamine < pyrrolidine < pyridine. The same stability sequence was found in DTA experiments (heating rate 2°C/min), the observed decomposition temperatures are L = THF, 130°C, L = diethylamine, 190°C, L = pyrrolidine, 245°C, L = pyridine, 270°C.

The infrared spectra of the compounds $C_8H_8TiCl \cdot L$ show the absorptions of π-bonded C_8H_8 rings, together with the absorptions of the coordinated donor molecules L (Fig. 1).

No ions containing the ligands L were found in the mass spectra of $C_8H_8TiCl \cdot L$, indicating elimination of L in the mass spectrometer under the conditions employed (200-250°C, 10^{-6} Torr). The compound C_8H_8TiCl (and the adducts $C_8H_8TiCl \cdot L$) show the following degradation pattern

$$\underset{m\,=\,374}{(C_8H_8TiCl)_2^+} \xrightarrow[m^*\,=\,93.5]{-C_8H_8TiCl} \underset{m\,=\,187}{C_8H_8TiCl^+} \xrightarrow[m^*\,=\,138.6]{-C_2H_2} \underset{m\,=\,161}{C_6H_6TiCl^+} \xrightarrow[m^*\,=\,42.8]{-C_6H_6} \underset{m\,=\,83}{TiCl^+}$$

(above the arrows: $m = 187$, $m = 26$, $m = 78$)

This scheme accounts for the metastable peaks at $m^* = 138.6$, 93.5 and 42.8 observed in the mass spectrum, other metastable peaks were observed at $m^* = 58.5$ (due to $C_8H_8^+ - C_2H_2 \rightarrow C_6H_6^+$) and $m^* = 57.6$ ($C_8H_7^+ - C_2H_2 \rightarrow C_6H_5^+$). The presence of the ions $C_3H_5Ti_2Cl_2^+$ and $C_2H_2Ti_2Cl_2^+$ in the mass spectrum (Table 1) suggests that the C_8H_8Ti groups in the parent molecule are linked by chlorine atoms, similar as in [$(C_5H_5)_2TiCl$]$_2$.

The magnetic susceptibility of C_8H_8TiCl and of $C_8H_8TiCl \cdot L$ with L = THF and diethylamine was determined in the range 100-300 K, after correction for induced diamagnetism a Curie—Weiss behaviour was found with μ = 1.65 B.M. per Ti atom.

TABLE 1

MASS SPECTRUM OF $[C_8H_8TiCl]_4$

Only peaks due to the isotopes ^{48}Ti and ^{35}Cl are given

m/e	Rel int	Ion	m/e	Rel int	Ion
374	8	$C_{16}H_{16}Ti_2Cl_2^+$	91	3	$C_7H_7^+$
231	10	$C_5H_5Ti_2Cl_2^+$	83	18	$TiCl^+$
205	3	$C_2H_2Ti_2Cl_2^+$	78	21	$C_6H_6^+$
187	100	$C_8H_8TiCl^+$	77	11	$C_6H_5^+$
161	20	$C_6H_6TiCl^+$	73	4	C_2HTi^+
152	7	$C_8H_8Ti^+$	65	2	$C_5H_5^+$
150	6	$C_8H_6Ti^+$	63	3	$C_5H_3^+$
126	5	$C_6H_6Ti^+$	52	5	$C_4H_4^+$
124	3	$C_6H\ Ti^+$	51	11	$C_4H_3^+$
113	5	$C_5H_5Ti^+$	50	6	$C_4H_2^+$
104	30	$C_8H_8^+$	48	6	Ti
103	19	$C_8H_7^+$	39	8	$C_3H_3^+$
98	3	$C_4H_2Ti^+$	36	3	HCl

Metastable peaks m^* 138 6 93 5 58 5 57 6 42 8

Structure of cyclooctatetraenetitanium chloride

The crystal structure of cyclooctatetraenetitanium chloride (at 100 K) was determined by single-crystal X ray diffraction methods using a Nonius CAD4 computer controlled diffractometer The compound is tetragonal (a = 10 763 Å, c = 13 657 Å) with space group $I\bar{4}2m$ The unit cell contains four tetrameric molecules $[C_8H_8TiCl]_4$

Central in the tetrameric molecule is a hexahedron of Ti and Cl atoms lying on alternate vertices The symmetry of the hexahedron is close to $\bar{4}3m$, although only symmetry $\bar{4}m$ is required by the space group The hexahedron faces resemble the Ti_2Cl_2 rhombs found in $[C_8H_8TiCl\ \ THF]_2$ (see below) The hexahedron is surrounded by four C_8H_8 rings which are π bonded to the Ti atoms and lie roughly perpendicular to the body diagonals of the hexahedron A stereo view of the molecule is given in Fig 2

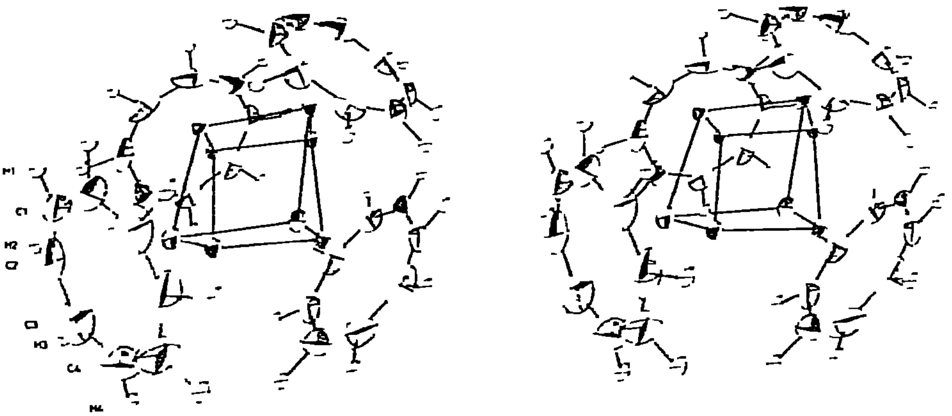

Fig. 2 Stereo view of $[C_8H_8TiCl]_4$ The numbering of the atoms is in accordance with Table 5

TABLE 2

INTERATOMIC DISTANCES (IN Å) AND SOME ANGLES IN $[C_8H_8TiCl]_4$

Standard deviations in units of the last decimal place are given in parentheses.

Ti—Cl	2.557 (2) 1x	C1—C1′	1.355 (10)
Ti—Cl	2.609 (1) 2x	C1—C2	1.358 (11)
<Ti—Cl—Ti	97.16° (5) 2x	C2—C3	1.394 (12)
<Ti—Cl—Ti	102.12° (3) 1x	C3—C4	1.434 (12)
		C4—C4′	1.385 (13)
<Cl—Ti—Cl	81.52° (4) 2x	*Distances from C_8 plane*	
<Cl—Ti—Cl	77.79° (3) 1x	Ti	+1.490
		C1	−0.002
Ti—C1	2.378 (7) 2x	C2	+0.006
Ti—C2	2.345 (6) 2x	C3	+0.011
Ti—C3	2.336 (8) 2x	C4	−0.009
Ti—C4	2.333 (8) 2x		

Interatomic distances and some bond angles are given in Table 2. Each Ti atom has 1 Cl neighbour at a distance of 2.557 Å and 2 Cl at 2.609 Å, moreover, every Ti atom is π-bonded to a C_8H_8 ring. The cyclooctatetraene rings contain a crystallographic mirror plane. The rings are not quite planar (Table 2) and the metal atom does not lie exactly above the centre of the ring, but is displaced away from the C1 (and C1′) atoms. This is evident from the Ti—C distances and is also reflected in the C—C distances, the C—C distances involving C1 being shorter than the other distances. The coordination of the cyclooctatetraene ring at Ti, therefore, is less regular than in $(C_8H_8)Ti(C_5H_5)$ [2]. The hydrogen atoms of the cyclooctatetraene ligands in $[C_8H_8TiCl]_4$ are displaced out of the ring planes, towards the Ti atoms. Although the positions of the hydrogen atoms were not refined, it can definitely be stated that the $Ti(C_8H_8)$ units in the molecule have an umbrella like shape, similar configurations have been found for other $M(\pi\text{-}C_nH_n)$ groups (M = metal) and have recently been discussed by Hodgson and Raymond [3].

A rigid-body analysis by Cruickshank's method [4] shows that the thermal motion of the carbon atoms of $[C_8H_8TiCl]_4$ can be described in rather good approximation in terms of rigid-body libration and translation of the C_8 rings. The largest libration axis is approximately perpendicular to the ring plane, the largest translation axis perpendicular to a mirror plane. The bond lengths given in Table 2 are corrected for the effect of libration, the corrections are 0.022 Å for C—C and 0.023 Å for Ti—C.

Structure of the THF adduct of cyclooctatetraenetitanium chloride

The crystal structure of the adduct of cyclooctatetraenetitanium chloride and THF at about 100 K was also determined by single-crystal X-ray diffraction methods. The compound is monoclinic with space group $P2_1/c$. The structure is found to consist of dimeric molecules $[C_8H_8TiCl \cdot THF]_2$, there are two crystallographically independent dimers, each of which is centrosymmetric. No interatomic distances shorter than the Van der Waals distances are found between different dimeric molecules.

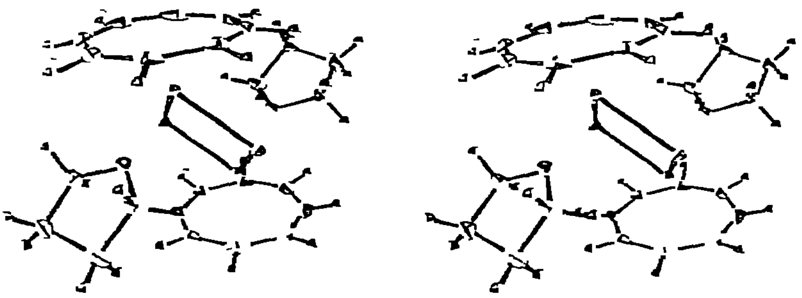

Fig. 3 Stereo view of $[C_8H_8TiCl\ THF]_2$ Only molecule I is shown The numbering is in accordance with Table 7

TABLE 3

INTERATOMIC DISTANCES (IN Å) AND SOME ANGLES IN THE TWO CRYSTALLOGRAPHICALLY INDEPENDENT MOLECULES OF $[C_8H_8TiCl\ THF]_2$

Standard deviations in units of the last decimal place are given in parentheses

(a) MOLECULE I

		C_8H_8 ring		Distances from C_8 plane	
Ti(1)—Cl(1)	2 537(1)	C(1)—C(2)	1 402(5)	Ti(1)	1 518
Ti(1)—Cl(1′)	2 525(1)	C(2)—C(3)	1 399(5)	C(1)	—0 005
<Ti—Cl—Ti	97 6°	C(3)—C(4)	1 408(4)	C(2)	—0 006
<Cl—Ti—Cl	82 4°	C(4)—C(5)	1 400(5)	C(3)	0 005
Ti(1)—O(1)	2 254(2)	C(5)—C(6)	1 412(5)	C(4)	0 011
Ti(1)—C(1)	2 383(3)	C(6)—C(7)	1 415(5)	C(5)	—0 015
—C(2)	2 392(3)	C(7)—C(8)	1 403(6)	C(6)	0 002
—C(3)	2 395(3)	C(8)—C(1)	1 407(6)	C(7)	0 003
—C(4)	2 380(3)			C(8)	0 005
—C(5)	2 384(3)	*THF ligand*		H(1)	0 155
—C(6)	2 377(3)	C(9)—C(10)	1 524(4)	H(2)	0 119
—C(7)	2 375(3)	C(10)—C(11)	1 520(4)	H(3)	0 207
—C(8)	2 373(3)	C(11)—C(12)	1 514(4)	H(4)	0 248
		C(9)—O(1)	1 457(3)	H(5)	0 143
		C(12)—O(1)	1 450(3)	H(6)	0 138
				H(7)	0 270
				H(8)	0 225

(b) MOLECULE II

		C_8H_8 ring		Distances from C_8 plane	
Ti(2)—Cl(2)	2 551(1)	C(13)—C(14)	1 389(4)	Ti(2)	1 530
Ti(2)—Cl(2)	2 547(1)	C(14)—C(15)	1 400(5)	C(13)	0 003
<Ti—Cl—Ti	98 4°	C(15)—C(16)	1 410(6)	C(14)	0 030
<Cl—Ti—Cl	81 6°	C(16)—C(17)	1 418(7)	C(15)	—0 004
		C(17)—C(18)	1 403(6)	C(16)	—0 031
Ti(2)—O(2)	2 258(2)	C(18)—C(19)	1 398(5)	C(17)	0 010
Ti(2)—C(13)	2 389(3)	C(19)—C(20)	1 402(4)	C(18)	0 020
—C(14)	2 382(3)	C(20)—C(13)	1 404(4)	C(19)	0 004
—C(15)	2 387(3)			C(20)	—0 032
—C(16)	2 398(3)	*THF ligand*		H(17)	0 134
—C(17)	2 374(3)	C(23)—C(22)	1 529(5)	H(18)	0 228
—C(18)	2 378(3)	C(22)—C(21)	1 530(5)	H(19)	0 175
—C(19)	2 389(3)	C(21)—C(24)	1 519(4)	H(20)	0 149
—C(20)	2 403(3)	C(23)—O(2)	1 462(4)	H(21)	0 191
		C(24)—O(2)	1 460(4)	H(22)	0 214
				H(23)	0 199
				H(24)	0 107

The central parts of both dimeric molecules are almost planar Ti_2Cl_2 rhombs. In addition to its two Cl neighbours, each Ti atom is coordinated by the oxygen atom of one THF ligand and by a C_8H_8 ring which is π-bonded to the metal. There is no alternation in the C—C bond lengths in a C_8H_8 ring. A stereo view of one molecule of $[C_8H_8TiCl \cdot THF]_2$ is shown in Fig. 3, while interatomic distances and some bond angles are given in Table 3.

While the structures of the two crystallographically independent molecules are closely similar, some minor, but significant differences may be noted. The C_8H_8 rings of dimer II are very slightly buckled to a boat shape (cf. Table 3). The rings of dimer I, on the other hand, are planar (within 0.02 Å), but the Ti atom does not lie exactly above the center of the ring, but is slightly displaced away from the C(2)—C(3) bond; this distortion is similar to that observed in $[C_8H_8TiCl]_4$, but much less pronounced.

In both dimeric molecules the hydrogen atoms are again somewhat displaced out of the ring planes, towards the Ti atom, giving the $Ti(C_8H_8)$ units an umbrella like shape (Fig. 3); the distance of hydrogen from the ring planes is 0.19 Å on average (s.d. 0.05 Å).

Comparing the structure of $[C_8H_8TiCl \cdot THF]_2$ with that of other compounds containing a $(\pi\text{-}C_8H_8)Ti$ group, it is to be remarked that in both independent molecules of $[C_8H_8TiCl \cdot THF]_2$ the distance of the metal from the average ring plane (1.518 and 1.530 Å for molecules I and II, respectively) is somewhat larger than in $[C_8H_8TiCl]_4$ (cf. preceding section) and $(C_8H_8)_3Ti_2$ [5] and much larger than in $(C_8H_8)Ti(C_5H_5)$ [2]. It may finally be remarked that the molecular structure of $[C_8H_8TiCl \cdot THF]_2$ is reminiscent of that of $[C_8H_8CeCl \cdot 2THF]_2$ [6].

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods and freed from oxygen by repeated degassing and saturation with nitrogen. Commercial $TiCl_3$, cyclooctatetraene, diethylamine, pyrrolidine and pyridine were used without further purification.

Elementary analyses of Ti, C and H were carried out at the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga. Infrared spectra were recorded with a Hitachi EPI-G spectrophotometer. The samples were examined as mulls in hexachlorobutadiene (4000–1200 cm^{-1}) and Nujol (4000-400 cm^{-1}) between KBr discs. Mass spectra were recorded by Mr. A. Kiewiet with an AEI MS9 instrument. Operating conditions: energy 70eV, resolution 1000, accelerating voltage 8 kV, inlet temperature 200-250°C. The samples were introduced directly into the ion source using a metal probe. The groups of peaks assigned to Ti-containing ions showed the normal isotopic distribution of Ti; only peaks corresponding to ^{48}Ti and to ^{35}Cl are listed in Table 1.

$C_8H_8TiCl \cdot THF$

$TiCl_3$(15.0 g, 97 mmol) was refluxed in 300 ml of THF until the violet compound was converted into the light-blue complex $TiCl_3 \cdot 3THF$. A solution of $K_2C_8H_8$ prepared from 7.6 g of K (195 mmol) and 10.1 g of C_8H_8 (97 mmol) in 400 ml of THF was added dropwise at reflux temperature After refluxing for another two h the reddish-brown mixture was cooled to room temperature Green crystals separated The supernatant solution was decanted and the crude $C_8H_8TiCl \cdot THF$ was dried under reduced pressure at room temperature

Recrystallization from THF gave the pure compound Yield 16 2 g (62 mmol, 64%) (Found C, 55 40, 55 36, H, 6 30, 6 41%, Ti, 18 42, 18 39 $C_{12}H_{16}$-ClOTi calc C, 55 52, H, 6 21, Ti, 18 45)

C_8H_8TiCl

C_8H_8TiCl THF (5 0 g, 19 2 mmol) was stirred in 200 ml of ether for 12 h The supernatant solution was decanted Another portion of 200 ml of ether was added and the procedure repeated

The greyish green compound C_8H_8TiCl was washed three times and dried in vacuum at room temperature Yield 3 0 g (15 9 mmol, 83%) (Found C, 51 52, 51 55, H, 4 44, 4 47, Ti, 25 51, 25 64 C_8H_8TiCl calc C, 51 25, H, 4 30, Ti, 25 55%) Crystals suitable for X-ray determination were obtained by recrystallization from C_6H_5Cl

C_8H_8TiCl $(CH_3CH_2)_2NH$

C_8H_8TiCl THF (0 5 g, 1 9 mmol) was suspended in 50 ml of hexane Diethylamine (0 28 g, 3 8 mmol) was added The mixture was stirred for 20 h at room temperature The supernatant solution was decanted, the crude C_8H_8-TiCl $(CH_3CH_2)_2NH$ washed with 50 ml of hexane and finally dried under reduced pressure at room temperature Recrystallization from C_6H_5Cl gave the pure compound Yield 0 34 g (1 3 mmol 70%) of green crystals (Found C, 55 74, 55 88, H, 7 41, 7 18, N, 5 28, 5 26, Ti, 18 23, 18 18 C_8H_8TiCl $(CH_3CH_2)_2NH$ calcd C, 55 30, H, 7 35, N, 5 37, Ti, 18 38%)

C_8H_8TiCl C_4H_8NH

C_8H_8TiCl C_4H_8NH was prepared by the procedure described for C_8H_8-TiCl $(CH_3CH_2)_2NH$ starting from 0 5 g of C_8H_8TiCl THF (1 9 mmol) and 0 27 g of pyrrolidine (3 8 mmol) Recrystallization from C_6H_5Cl gave green crystals of C_8H_8TiCl C_4H_8NH Yield 0 31 g (1 2 mmol, 65%) (Found C, 55 80, 55 78, H, 6 70, 6 72, N 5 41, 5 68, Ti 18 65, 18 66 C_8H_8TiCl C_4H_8-NH calc C, 55 73 H, 6 63, N, 5 42, Ti, 18 52%) C_8H_8TiCl C_4H_8NH can also be prepared in a similar way starting from $C_8H_8TiCl(CH_3CH_2)_2NH$

C_8H_8TiCl C_5H_5N

C_8H_8TiCl C_5H_5N was prepared by the procedure described for C_8H_8 TiCl $(CH_3CH_2)_2NH$ starting from 0 5 g of C_8H_8TiCl THF (1 9 mmol) and 0 30 g of pyridine (3 8 mmol) Recrystallization from C_6H_5Cl gave brown crystals of $C_8H_8TiCl \cdot C_5H_5N$ Yield 0 16 g (0 6 mmol, 31%) (Found C, 58 75, 59 03, H, 5 06, 5 25, N, 5 26, 4 95, Ti 17 89, 18 01 C_8H_8TiCl C_5H_5N calc C, 58 57, H, 4 91, N, 5 26, Ti, 17 97%) C_8H_8TiCl C_5H_5N can also be prepared in a similar way starting from $C_8H_8Ti(CH_3CH_2)_2NH$ or $C_8H_8TiC_4H_8NH$

Structure determination of $[C_8H_8TiCl]_4$

Because of the sensitivity of $[C_8H_8TiCl]_4$ to air, the green crystals had to

TABLE 4

DATA AND EXPERIMENTALS DETAILS OF THE STRUCTURE DETERMINATION OF $[C_8H_8TiCl]_4$

Tetragonal Space group $I\bar{4}2m$	Weissenberg photographs of zero and higher layer lines supplemented by information from three-dimensional Patterson synthesis
$a = b = 10\ 763$ Å $c = 13\ 657$ Å $T = 100$ K	Least squares refinement on observed optimalised diffractometer angles Θ ϕ and χ of 15 reflections, with $\lambda(\text{Mo } K_{\alpha 1}) = 0\ 70926$ and $\lambda(\text{Mo } K_{\alpha 2}) = 0\ 71354$ Å
$D_M = 1\ 4$ g/cm^3 $Z = 2\ [C_8H_8TiCl]_4$ $D_X = 1\ 573$ g/cm^3	Specific gravity by flotation method (crystal coated with grease)
Intensities of one octant of reciprocal space	Computer operated Nonius diffractometer (CAD-4) Zr filtered Mo-radiation Θ 2Θ scan all indices $hkl \geqslant 0$ $\sin \Theta/\lambda \leqslant 0\ 80706$ Å^{-1} Reflections with $I(\text{net}) \leqslant 0$ were discarded
1011 independent $F(hkl)$ values, $h \geqslant k$	Corrections for L P and for absorption according to Busing & Levy [8] crystal bounded by 8 planes $\mu = 13\ 6$ cm^{-1} Equivalent reflections were averaged

be coated with a thin layer of grease As an additional safeguard towards oxidation of the crystal, the X-ray intensities were collected at about 100 K [7] Details of the experimental work are listed in Table 4

From several space-group possibilities left after Weissenberg inspections, space group $I\bar{4}2m$ unambiguously turned out to be the correct one, after studying a three-dimensional Patterson synthesis When the (special) positions of the one independent Ti and Cl atom were anisotropically refined, the four independent C atoms could be found in two subsequent difference maps After further refinement, the hydrogen atoms could be located from a difference map They were isotropically refined and later fixed at 1 08 Å from the C atoms, without changing the observed C—H directions The index $R = [\Sigma(\Delta F)^2/\Sigma F_0^2]^{1/2}$ decreased to 0 068 and $R_w = [\Sigma w(\Delta F)^2/\Sigma w F_0^2]^{1/2}$ to 0 057, w being the weight due to counting statistics

All calculations were performed on a Cyber 74-16 with the X RAY system, version June 1972, of the University of Maryland The final parameters and standard deviations as found by the least-squares program are listed in Table 5 A list of observed structure factors is available on request

Structure determination of $[C_8H_8TiCl\ THF]_2$

A crystal of maximum dimension 0 4 mm was selected for the intensity measurements which were carried out at about 100 K Because of the sensitivity of the compound to oxygen and moisture, the crystal was coated with grease Details of the data collection are listed in Table 6, together with cell parameters The solution of the crystal structure was straightforward, starting with the location of the Ti and Cl atoms from a three-dimensional Patterson map In the

TABLE 5

CRYSTAL STRUCTURE OF $[C_8H_8TiCl]_4$

Final parameters and standard deviations (in units of the last decimal place)

(a) COORDINATES AND TEMPERATURE PARAMETERS B OF THE HYDROGEN ATOMS

	x/a	y/b	z/c	B(Å^2)
Ti	0 63333(8)	0 63333(8)	0 40472(0)	
Cl	0 60763(10)	0 60763(10)	0 58976(13)	
C(1)	0 8216(6)	0 7326(7)	0 4514(5)	
C(2)	0 8507(6)	0 6347(7)	0 3931(6)	
C(3)	0 8042(8)	0 5813(6)	0 3076(6)	
C(4)	0 7029(9)	0 6119(8)	0 2438(5)	
H(1)	0 8486	0 7498	0 5227	5 2
H(2)	0 9074	0 5584	0 4184	8 1
H(4)	0 6786	0 5415	0 1908	9 2
H(3)	0 8088	0 4857	0 2840	6 9

(b) PARAMETERS U_{ij} (IN 10^{-4} Å^2) OF THE TEMPERATURE FACTOR $\exp[-2\pi^2(h^2a^{*2}U_{11} + \quad + 2ha^*kb^*U_{12} + \quad)]$

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Ti	157(3)	157(3)	199(5)	−8(8)	32(7)	32(7)
Cl	161(4)	161(4)	200(7)	−8(9)	−16(8)	−16(8)
C(1)	263(29)	514(41)	442(35)	−328(54)	202(62)	15(54)
C(2)	214(26)	486(39)	853(55)	−10(50)	645(90)	354(68)
C(3)	591(47)	301(33)	736(55)	−261(63)	−338(71)	1000(88)
C(4)	1153(81)	739(63)	340(30)	−1366(126)	−444(78)	661(84)

TABLE 6

DATA AND EXPERIMENTAL METHODS ON THE STRUCTURE DETERMINATION OF $[C_8H_8TiCl \cdot THF]_2$

Monoclinic	Weissenberg photographs
Space group $P2_1/c$	
a = 10 779(1) b = 14 304(1) c = 15 478(3) Å β = 100 84(2)° T = 100K	Least-squares refinement of $\sin^2\Theta$ values of $0kl$ $h0l$ and $hk0$ reflections with $\lambda(\text{Mo } K_{\alpha 1})$ = 0 70926 $\lambda(\text{Mo } K_{\alpha 2})$ = 0 71354 Å
D_M = 1 40 g/cm^3 Z = 4 $[C_8H_8TiCl \cdot THF]_2$ D_X = 1 447 g/cm^3	Specific gravity by flotation method
10307 independent intensities	Automatic Nonius diffractometer Zr filtered Mo radiation, Θ 2Θ scan $\sin\Theta/\lambda \leqslant$ 0 80[illegible]1 Å^{-1} Reflections with I(net) $\leqslant$ 0 were discarded
9206 $F(hkl)$ values	Corrections for L P and for absorption according to Busing & Levy [8] crystal bounded by 12 planes μ = 9 5 cm^{-1}

TABLE 7

CRYSTAL STRUCTURE OF $[C_8H_8TiCl \cdot THF]_2$

Final parameters and standard deviations (in units of the last decimal place) as calculated by the least-squares program

(a) COORDINATES AND TEMPERATURE PARAMETERS *B* OF THE HYDROGEN ATOMS

	x/a	*y/b*	*z/c*	*B*(Å²)
Molecule I				
Ti(1)	0 50132(4)	0 53353(3)	0 11921(3)	
Cl(1)	0 49066(6)	0 38725(4)	0 02542(4)	
O(1)	0 7089(2)	0 5159(1)	0 1183(1)	
C(1)	0 2827(3)	0 5596(3)	0 1182(2)	
C(2)	0 3405(3)	0 6477(2)	0 1238(2)	
C(3)	0 4537(3)	0 6853(2)	0 1696(2)	
C(4)	0 5566(3)	0 6493(2)	0 2302(2)	
C(5)	0 5868(3)	0 5624(2)	0 2704(2)	
C(6)	0 5303(3)	0 4730(2)	0 2647(2)	
C(7)	0 4160(4)	0 4355(2)	0 2173(2)	
C(8)	0 3141(3)	0 4715(3)	0 1565(2)	
C(9)	0 7966(3)	0 5941(2)	0 1229(2)	
C(10)	0 9137(3)	0 5514(2)	0 0968(2)	
C(11)	0 9144(3)	0 4515(2)	0 1303(3)	
C(12)	0 7826(3)	0 4330(2)	0 1469(2)	
H(1)	0 2013	0 5595	0 0653	3 4
H(2)	0 2910	0 6967	0 0764	2 6
H(3)	0 4731	0 7538	0 1458	4 2
H(4)	0 6366	0 6962	0 2398	2 5
H(5)	0 6824	0 5588	0 3073	1 9
H(6)	0 5934	0 4212	0 2997	2 6
H(7)	0 4132	0 3600	0 2158	3 2
H(8)	0 2571	0 4137	0 1267	3 7
H(9)	0 7512	0 6472	0 0783	3 7
H(10)	0 8149	0 6168	0 1906	1 7
H(11)	0 9015	0 5542	0 0259	1 5
H(12)	0 9992	0 5867	0 1276	2 5
H(13)	0 9440	0 4015	0 0859	5 5
H(14)	0 9907	0 4378	0 1849	6 3
H(15)	0 7362	0 3701	0 1189	4 1
H(16)	0 7824	0 4319	0 2165	6 2
Molecule II				
Ti(2)	0 09722(4)	0 40416(3)	0 45553(3)	
Cl(2)	0 09994(6)	0 49768(4)	0 59619(4)	
O(2)	0 1883(2)	0 5372(1)	0 4197(1)	
C(13)	−0 0379(3)	0 2806(2)	0 3905(2)	
C(14)	−0 0146(3)	0 2663(2)	0 4809(2)	
C(15)	0 0937(4)	0 2701(2)	0 5468(2)	
C(16)	0 2218(4)	0 2927(2)	0 5501(2)	
C(17)	0 2935(3)	0 3243(2)	0 4878(3)	
C(18)	0 2679(3)	0 3410(2)	0 3969(3)	
C(19)	0 1605(3)	0 3338(2)	0 3307(2)	
C(20)	0 0349(3)	0 3069(2)	0 3282(2)	
C(21)	0 2336(3)	0 6710(2)	0 3422(2)	
C(22)	0 3513(3)	0 6477(2)	0 4108(3)	
C(23)	0 3002(3)	0 5805(2)	0 4725(2)	
C(24)	0 1641(3)	0 5781(2)	0 3317(2)	
H(17)	−0 1369	0 2774	0 3609	2 7
H(18)	−0 0983	0 2577	0 5092	3 7
H(19)	0 0717	0 2638	0 6119	4 4
H(20)	0 2779	0 3020	0 6152	3 1

(continued)

TABLE 7 (continued)

	x/a	y/b	z/c	
H(21)	0.3859	0.3486	0.5194	3.8
H(22)	0.3472	0.3755	0.3768	4.9
H(23)	0.1751	0.3650	0.2698	1.4
H(24)	−0.0220	0.3205	0.2642	2.1
H(25)	0.0630	0.5848	0.3111	3.4
H(26)	0.1974	0.5298	0.2876	3.1
H(27)	0.1831	0.7248	0.3702	2.7
H(28)	0.2538	0.6971	0.2807	2.1
H(29)	0.4005	0.7052	0.4472	3.4
H(30)	0.4177	0.6121	0.3779	4.7
H(31)	0.3674	0.5261	0.4966	3.0
H(32)	0.2751	0.6164	0.5282	3.6

(b) PARAMETERS U_{ij} (IN 10^{-4} Å^2) OF THE TEMPERATURE FACTOR $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2ha^*kb^*U_{12} + \ldots)]$

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Molecule I						
Ti(1)	113(2)	145(2)	141(2)	26(3)	−34(3)	48(3)
Cl(1)	172(3)	120(2)	180(3)	6(4)	12(4)	61(4)
O(1)	131(8)	121(8)	282(10)	15(12)	41(14)	43(14)
C(1)	159(12)	631(24)	262(15)	68(28)	−262(31)	114(22)
C(2)	244(14)	405(18)	277(15)	353(26)	−71(26)	140(24)
C(3)	336(16)	240(14)	232(14)	199(24)	−52(22)	150(24)
C(4)	252(14)	299(15)	217(13)	43(23)	−170(23)	73(22)
C(5)	242(13)	381(17)	180(12)	192(24)	−96(23)	3(21)
C(6)	411(18)	305(15)	191(13)	225(27)	153(23)	199(24)
C(7)	447(19)	303(16)	315(16)	−146(29)	−35(26)	446(30)
C(8)	276(15)	489(20)	351(17)	−314(29)	−327(31)	379(27)
C(9)	162(11)	155(11)	405(17)	−52(19)	20(23)	−4(22)
C(10)	182(12)	222(13)	313(15)	−42(20)	59(22)	120(21)
C(11)	217(14)	224(14)	622(23)	170(23)	294(29)	332(29)
C(12)	172(12)	184(12)	460(18)	132(20)	239(25)	59(24)
Molecule II						
Ti(2)	133(2)	104(2)	176(2)	12(3)	0(3)	15(3)
Cl(2)	154(3)	166(3)	181(3)	63(4)	−11(4)	−26(4)
O(2)	205(9)	164(9)	244(10)	−87(15)	−6(15)	83(15)
C(13)	186(12)	145(11)	311(15)	−80(18)	−56(20)	44(21)
C(14)	411(17)	145(12)	320(16)	−105(23)	−27(22)	330(28)
C(15)	714(25)	153(13)	193(14)	130(29)	69(21)	156(30)
C(16)	579(23)	182(14)	345(17)	278(29)	−77(25)	−486(32)
C(17)	206(14)	192(14)	784(28)	129(23)	−318(32)	−274(31)
C(18)	218(14)	163(13)	693(25)	4(21)	−163(28)	368(30)
C(19)	385(17)	158(12)	345(16)	26(23)	−38(23)	395(27)
C(20)	319(15)	154(12)	205(13)	36(21)	−38(19)	20(22)
C(21)	398(17)	201(13)	348(17)	−135(24)	−30(24)	435(28)
C(22)	257(15)	329(17)	518(21)	−265(26)	−88(31)	322(29)
C(23)	211(13)	244(14)	439(19)	−152(22)	−34(26)	18(25)
C(24)	354(16)	222(13)	239(14)	−121(23)	25(22)	182(24)

later stages of the (anisotropic) refinement, a difference Fourier map F_0-F_c (Ti, Cl, O, C) for low-angle reflections only, clearly showed all hydrogen atoms. Their positions were at first isotropically refined and in the final stages fixed at 1.08 Å from the C atoms, without changing the observed C—H directions. During the final refinement cycles, the weighing scheme used was $w = [w_c^{-1} +$

0 0004 $F^2]^{-1}$, w_c being the weight based on counting statistics The index $R = [\Sigma(\Delta F)^2/\Sigma F_0^2]^{1/2}$ decreased to 0 0588 and $R_w = [\Sigma w(\Delta F)^2/\Sigma w F_0^2]^{1/2}$ to 0 0544 The final coordinates and standard deviations as calculated by the least-squares program are listed in Table 7 A list of observed and calculated structure factors is available on request All calculations were performed on a Cyber 74-16 computer.

References

1 H Lehmkuhl and K Mehler J Organometal Chem 25 (1970) C44
2 P A Kroon and R B Helmholdt J Organometal. Chem 25 (1970) 451
3 *K O Hodgson and K N Raymond Inorg. Chem 12 (1973) 458*
4 D W J Cruickshank Acta Crystallogr 9 (1956) 754
5 H Dierks and H Dietrich Acta Crystallogr Sect B 24 (1968) 58
6 K O Hodgson and K N Raymond Inorg Chem 11 (1972) 171
7 F van Bolhuis, J Appl Crystallogr 4 (1971) 263
8 W R Busing and H A Levy Acta Crystallogr 10 (1957) 180