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CRYSTAL STRUCTURE AND REACTIVITY OF $C_4Ph_4TiCl_3 \cdot Mg_2Cl_3(THF)_6$, A NEW TYPE OF ORGANOMETALLIC COMPLEX

MACHTELD E.E. MEIJER-VELDMAN, JAN L. DE BOER and HENK J. DE LIEFDE MEIJER *

Laboratorium voor Anorganische Chemie, University of Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

ANTOINE M.M. SCHREURS, JAN KROON and ANTHONY L. SPEK

Vakgroep Algemene Chemie, afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht (The Netherlands)

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Summary

Reaction of $TiCl_3 \cdot 3THF$, diphenylacetylene and i-PrMgCl yields a blue complex of composition $C_4Ph_4TiMg_2Cl_6 \cdot 6THF$. The complex is very sensitive to moisture. An X-ray diffraction study has shown that it consists of an ion pair $(C_4Ph_4TiCl_3)^-$, containing a planar cyclobutadiene ring, and $(Mg_2Cl_3 \cdot 6THF)^+$, in which the magnesium atoms are octahedrally surrounded by three bridging chlorine atoms and three disordered THF molecules.

Introduction

During studies of the oligomerization of acetylenes in the presence of titanium complexes three organotitanium compounds containing two acetylene units were isolated. Thus the reaction of $(C_8H_8TiCl \cdot THF)_2$ with diphenylacetylene in the presence of i-PrMgCl yielded $(C_8H_8TiPhC_2Ph)_2$ [1], which in turn could be thermally converted into the sandwich complex $C_8H_8TiC_4Ph_4$ [1,2], and the reaction of $TiCl_3 \cdot 3THF$ with i-PrMgCl and diphenylacetylene gave a complex with the composition $C_4Ph_4TiMg_2Cl_6 \cdot 6THF$ [3,4]. The synthesis, properties and crystal structure of this last complex are described in this paper.

Results and discussion

Reaction of $TiCl_3 \cdot 3THF$ with one equivalent of i-PrMgCl and an excess of diphenylacetylene in THF for 5 h under reflux gave a dark brown solution. After evaporation of the THF the crude product was washed with benzene. The brown by-products dissolved, as did the hexaphenylbenzene, which was formed in about

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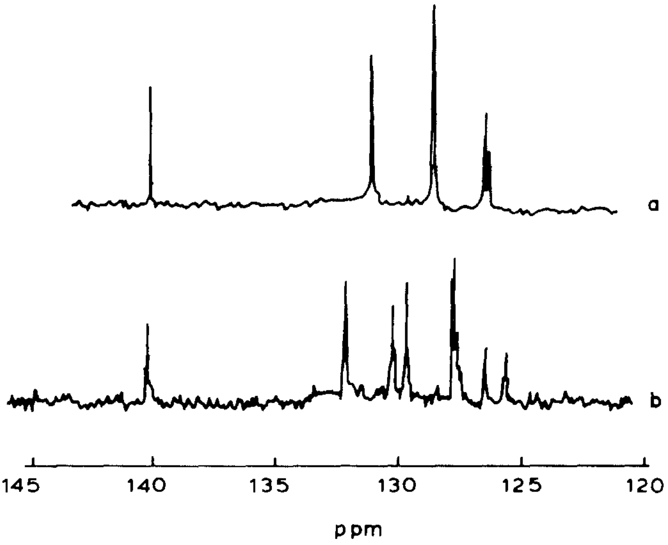

Fig. 1. Decoupled (a) and off-resonance (b) spectrum of $(C_4Ph_4TiCl_3)^-$ $(Mg_2Cl_3 \cdot 6THF)^+$ (120–145 ppm).

15% yield, based on titanium. The blue residue was further purified by two recrystallizations from THF/pentane. Analytical data indicated the composition $C_{52}H_{68}Cl_6Mg_2O_6Ti$, which corresponds to the formula $C_4Ph_4TiMg_2Cl_6 \cdot 6THF$.

The ^1H NMR spectrum in THF-d_8 shows resonances in the aromatic region (δ 6.8–7.8 ppm); the signals of the THF in the complex coincide with the peaks of the solvent (δ 1.8 (m) and 3.6 (m) ppm). No other signals were found.

The ^{13}C NMR spectrum in THF-d_8 exhibits 5 signals due to the C_4Ph_4 group (see Fig. 1), in addition to the THF signals at δ 68.6 and 26.5 ppm. This indicates, that both the four phenyl groups and the four ring-carbons are equivalent, and consequently that the C_4Ph_4 group is present as a tetraphenylcyclobutadiene ring. In

TABLE 1

CARBON-13 CHEMICAL SHIFTS (in δ relative to TMS) OF $(C_4Ph_4TiCl_3)^-(Mg_2Cl_3 \cdot 6THF)^+$ AND SOME OTHER C_4Ph_4Ti COMPLEXES

Compound	Solvent	$\delta C(C_8H_8)$	$\delta C(C_4)$	$\delta C(C_6H_5)$
$C_8H_8TiC_4Ph_4$	THF-d_8	101.0	105.8	139.8 (C(1)) 129.7 } (C(2,6)) and 129.3 } (C(3,5)) 126.1 (C(4))
$(C_4Ph_4TiCl_3)^-$ $(Mg_2Cl_3 \cdot 6THF)^+$	THF-d_8		126.3	140.1 (C(1)) 131.1 (C(3,5)) 128 6 (C(2,6)) 126 5 (C(4))
		$\delta C(C_5H_5)$		
$Cp_2TiC_4Ph_4$	C_6D_6	114.2	136.6, ~128	148.1, 141.1 (C(1)) 131 4, 127.8 (C(3,5)) 127.6, 127.0 (C(2,6)) 124.7, 123.6 (C(4))

Table 1 the ^{13}C NMR spectrum is given, together with those of two other C_4Ph_4Ti complexes. Compared to the ^{13}C spectrum of $C_8H_8TiC_4Ph_4$, the signal of the ring-carbons of the cyclobutadiene unit has shifted to lower field (from 126.3 to 105.8 ppm). This can be attributed to the presence of chlorine atoms coordinated to the titanium atom; these withdraw electrons from the cyclobutadiene ring, and thus the negative charge on the cyclobutadiene ring decreases, causing a downfield shift in the ^{13}C resonance. A similar shift is found in the ^{13}C NMR spectra of $CpTiCl_3$ and $CpTiC_7H_7$ where δ(Cp) is 123.1 and 96.5 ppm, respectively [5,6]. The assignment of the phenyl resonances was carried out using the pattern of the (long range) coupling in the off-resonance spectrum (Fig. 1b).

An X-ray diffraction study showed that the compound consists of two fragments: the anion is made up by $TiCl_3$ and C_4Ph_4, and the cation by six THF molecules and Mg_2Cl_3. Some relevant bond distances and bond angles involving the heavy atoms are listed in Table 2.

The anion (see Fig. 2a) contains the C_4Ph_4 group as a tetraphenylcyclobutadiene ring as was indicated by the NMR data. The distance from the Ti-atom to the cyclobutadiene ring is 2.0 Å and the average Ti–C bond length is 2.24 Å. In comparison with other titanium complexes containing π-bonded rings, the $C(C_4Ph_4)$–Ti bond lengths are rather short. In the isoelectronic complex $CpTiCl_3$ [7] an average Ti–C bond length of 2.31 Å is found, which is quite normal. The distance of the Cp ring from Ti is 2.01 Å, which is the same as the $C(C_4Ph_4)$–Ti distance in our complex. A similar, but even more pronounced, shortening of the Ti–C bond length was found in the sandwich complexes $CpTiC_7H_7$ and $CpTiC_8H_8$ [8]. The $Ti-C(C_7H_7)$ bond length is very short (2.19 Å) while the $Ti-C(C_8H_8)$ bond length is normal (2.32 Å); the distances from the C_7H_7 and the C_8H_8 ring to Ti are about equal, viz. 1.49 and 1.44 Å, respectively. In the complex $(C_4Ph_4)(C_5H_5)Nb(C_2Ph_2)(CO)$ [9] the metal–$C(C_4Ph_4)$ bond length is again shorter than the metal–$C(C_5H_5)$ bond length, viz. 2.38 and 2.44 Å, respectively. When the metal is vanadium, this shortening of the carbon–metal bond does not occur [8,10].

The four-membered carbon ring has an average C–C bond distance of 1.45(6) Å

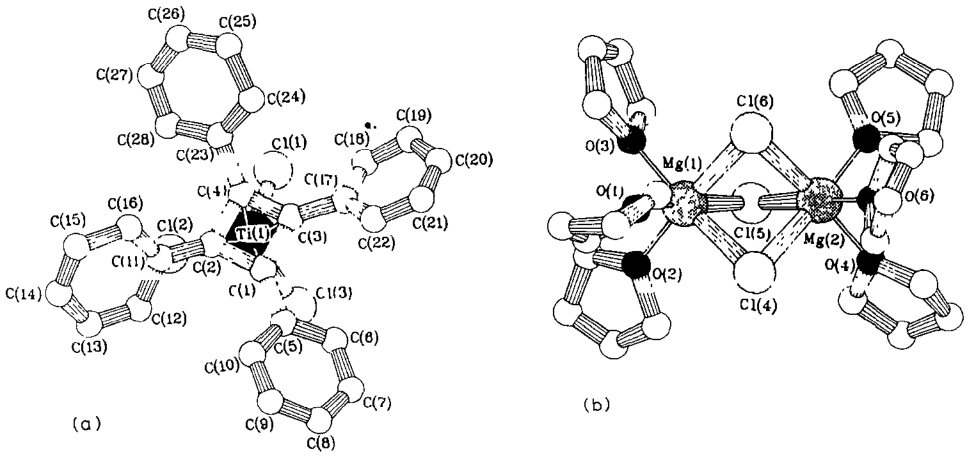

Fig. 2. Drawing of the two ions with the adopted numbering scheme. a: anion $C_4Ph_4TiCl_3$, b: cation $Mg_2Cl_3 \cdot 6THF$.

TABLE 2

RELEVANT BOND DISTANCES AND ANGLES

(a) Bond Distances (Å)					
Ti(1)–Cl(1)	2.24(1)	Cl(4)–Mg(1)	2.51(1)	Mg(2)–O(6)	2.11(2)
Ti(1)–Cl(2)	2.25(1)	Cl(5)–Mg(1)	2.51(1)	Mg(2)–O(4)	2.04(2)
Ti(1)–Cl(3)	2.23(1)	Cl(5)–Mg(2)	2.47(1)	Mg(2)–O(5)	2.06(2)
Ti(1)–C(1)	2.25(2)	Cl(6)–Mg(1)	2.48(1)	C(1)–C(2)	1.45(4)
Ti(1)–C(2)	2.23(2)	Cl(6)–Mg(2)	2.51(1)	C(1)–C(3)	1.50(4)
Ti(1)–C(3)	2.27(2)	Mg(1)–O(2)	2.07(2)	C(2)–C(4)	1.47(4)
Ti(1)–C(4)	2.22(2)	Mg(1)–O(3)	2.10(2)	C(3)–C(4)	1.38(4)
Cl(4)–Mg(2)	2.51(1)	Mg(1)–O(1)	2.09(2)	Mg(1)–Mg(2)	3.18(1)
(b) Bond angles (°)					
Cl(1)–Ti(1)–Cl(2)	98.3(7)	Cl(6)–Mg(2)–O(4)	93.9(7)		
Cl(1)–Ti(1)–Cl(3)	103.9(5)	Cl(5)–Mg(2)–O(6)	93.0(7)		
Cl(1)–Ti(1)–C(1)	136.9(7)	O(4)–Mg(2)–O(5)	90.9(9)		
Cl(1)–Ti(1)–C(2)	129.8(8)	O(4)–Mg(2)–O(6)	88.1(9)		
Cl(1)–Ti(1)–C(3)	98.1(7)	O(5)–Mg(2)–O(6)	92.0(9)		
Cl(1)–Ti(1)–C(4)	94.1(7)	Cl(4)–Mg(2)–Cl(5)	84.2(4)		
Cl(2)–Ti(1)–Cl(3)	102.5(8)	Cl(4)–Mg(2)–Cl(6)	83.1(4)		
Cl(2)–Ti(1)–C(1)	116.8(8)	Cl(6)–Mg(2)–O(5)	92.2(7)		
Cl(2)–Ti(1)–C(2)	87.5(7)	Cl(6)–Mg(2)–O(6)	175.4(7)		
Cl(2)–Ti(1)–C(3)	141.9(7)	Cl(4)–Mg(2)–O(6)	92.7(7)		
Cl(2)–Ti(1)–C(4)	108.7(8)	Cl(5)–Mg(2)–Cl(6)	84.7(4)		
Cl(3)–Ti(1)–C(1)	92.6(7)	Cl(5)–Mg(2)–O(4)	175.1(8)		
Cl(3)–Ti(1)–C(2)	123.5(8)	Cl(5)–Mg(2)–O(5)	93.8(8)		
Cl(3)–Ti(1)–C(3)	106.5(8)	Cl(4)–Mg(2)–O(5)	175.0(7)		
Cl(3)–Ti(1)–C(4)	141.1(8)	Cl(4)–Mg(2)–O(4)	91.0(8)		
C(1)–Ti(1)–C(2)	37.6(9)	Ti(1)–C(1)–C(3)	71.(1)		
C(1)–Ti(1)–C(3)	38.8(9)	Ti(1)–C(1)–C(2)	70.(1)		
C(1)–Ti(1)–C(4)	52.8(9)	C(2)–C(1)–C(5)	136.(2)		
C(2)–Ti(1)–C(3)	56.0(9)	C(3)–C(1)–C(5)	132.(2)		
C(2)–Ti(1)–C(4)	38.5(9)	Ti(1)–C(1)–C(5)	125.(1)		
C(3)–Ti(1)–C(4)	35.9(9)	C(2)–C(1)–C(3)	92.(2)		
Mg(1)–Cl(4)–Mg(2)	78.6(4)	Ti(1)–C(2)–C(11)	130.(2)		
Mg(1)–Cl(5)–Mg(2)	79.3(4)	Ti(1)–C(2)–C(1)	72.(1)		
Mg(1)–Cl(6)–Mg(2)	78.9(3)	Ti(1)–C(2)–C(4)	70.(1)		
Cl(5)–Mg(1)–O(2)	174.7(7)	C(4)–C(2)–C(11)	136.(2)		
Cl(6)–Mg(1)–O(3)	96.2(7)	C(1)–C(2)–C(11)	135.(2)		
O(1)–Mg(1)–O(2)	91.1(9)	C(1)–C(2)–C(4)	86.(2)		
O(1)–Mg(1)–O(3)	89.9(9)	Ti(1)–C(3)–C(4)	70.(1)		
O(2)–Mg(1)–O(3)	92.0(8)	Ti(1)–C(3)–C(1)	70.(1)		
Cl(5)–Mg(1)–O(3)	90.9(7)	C(1)–C(3)–C(17)	134.(2)		
Cl(6)–Mg(1)–O(1)	173.5(8)	Ti(1)–C(3)–C(17)	129.(2)		
Cl(6)–Mg(1)–O(2)	91.0(7)	C(1)–C(3)–C(4)	87.(2)		
Cl(4)–Mg(1)–O(1)	90.0(7)	C(4)–C(3)–C(17)	137.(2)		
Cl(4)–Mg(1)–O(2)	93.8(8)	Ti(1)–C(4)–C(3)	74.(1)		
Cl(4)–Mg(1)–O(3)	174.2(8)	Ti(1)–C(4)–C(23)	124.(2)		
Cl(5)–Mg(1)–Cl(6)	84.4(4)	C(2)–C(4)–C(23)	129.(2)		
Cl(5)–Mg(1)–O(1)	93.3(7)	C(3)–C(4)–C(23)	135.(2)		
Cl(4)–Mg(1)–Cl(6)	83.7(4)	C(2)–C(4)–C(3)	96.(2)		
Cl(4)–Mg(1)–Cl(5)	83.3(4)	Ti(1)–C(4)–C(2)	71.(1)		

and an average internal bond angle of 90(4)°. Within experimental error it is a flat square, parallel to the plane through the three chlorine atoms. The phenyl groups are bent out of the plane of the ring, away from the Ti atom. The four phenyl groups make the following acute angles (in degrees) with the four-membered carbon ring C(1)–C(2)–C(3)–C(4): C(5)--C(10) 28(2), C(11)--C(16) 40(2), C(17)--C(22) 44(2) and C(23)--C(28) 30(2).

The average Ti–Cl bond distance is 2.24(1) Å, which is in good agreement with the Ti–Cl bond lengths in $CpTiCl_3$ (2.22 Å) [7] and $[(CpTiCl_2)_2O]$ (2.24 Å) [11]. The average Cl–Ti–Cl angles are 101.6, 102.9 and 102.6°, respectively. These bond distances and angles show the close similarity between the three structures. The thermal motion of the Cl atoms of the anion in our complex (see Fig. 3) indicates the small degree of rotational freedom. The positions of the chlorine atoms with respect to the cyclobutadiene ring are mainly staggered, as is common for this type of complex [12].

The structure of the $Mg_2Cl_3 \cdot 6THF$ cation (Fig. 2b) shows that each magnesium atom is octahedrally surrounded by three chlorine atoms and three disordered (vide infra) THF groups. The three chlorine atoms bridge between the two magnesium atoms. The mean Mg–Cl distance is 2.50(2) Å. A search in the Cambridge Crystallographic Data Base for similar compounds revealed 25 species containing the metal–Cl_3–metal system, but in all of them the metal is a transition metal. Our complex is the first with three bridging chlorines between main group metal atoms. A very recent structure determination of the complex $(V_2Cl_3 \cdot 6THF)^+{}_2(Zn_2Cl_6)^{2-}$ has shown, that it has a cation that is analogous to the one we found, but with vanadium instead of magnesium [13,14].

A stereoview of the packing in the unit cell, viewed along the b-axis, is given in Fig. 4. It shows all the fragments lying in a slab parallel to the ac plane. The packing in the crystal can be described as with an alternating sequence of ionic and non polar layers parallel to the bc plane.

The complex $(C_4Ph_4TiCl_3)^-$ $(Mg_2Cl_3 \cdot 6THF)^+$ is extremely sensitive to moisture, and is insoluble in organic solvents such as pentane, benzene, and toluene. Tetrahydrofuran is the only solvent in which it was found to dissolve without complete decomposition; in acetone it decomposes in a few minutes, to give 1,2,3,4-tetraphenylbutadiene as the main organic product. An attempt to replace

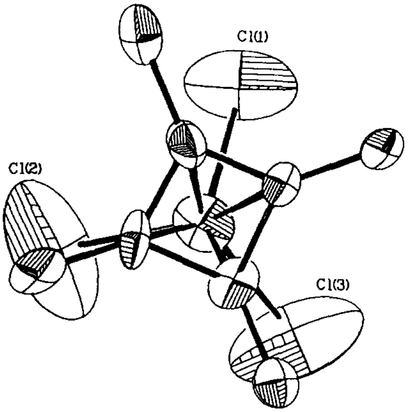

Fig. 3. ORTEP [21] drawing showing 50% probability ellipsoids of the central part of the anion viewed along the axis through Ti and the center of the cyclobutadiene moiety illustrating the degree of freedom of the Cl atoms.

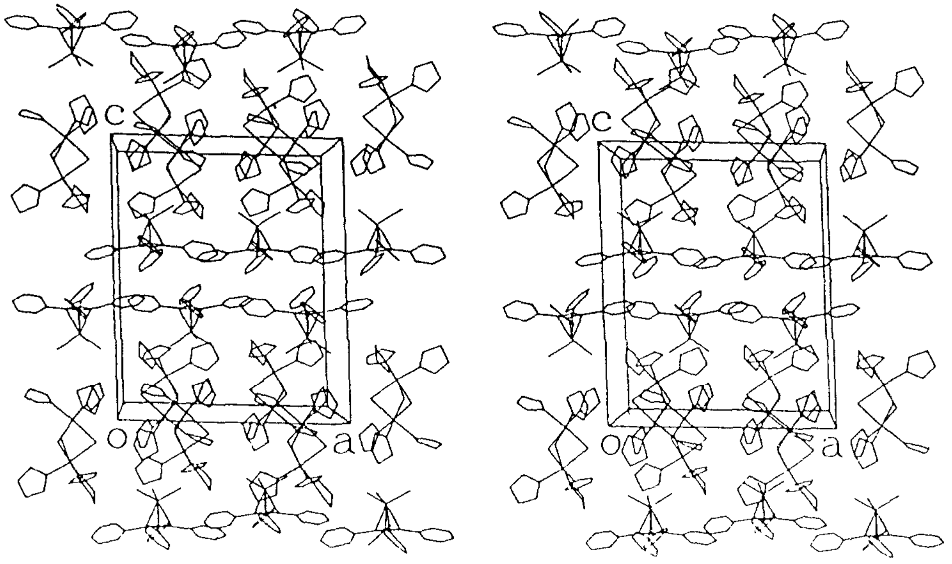

Fig. 4. Stereoscopic drawing of the packing of the unit cell viewed along the b-axis.

some of the THF ligands in the complex by pyridine also resulted in a very rapid decomposition, giving pyridinemagnesium chlorides among other products.

During the synthesis of the complex some hexaphenylbenzene was formed. To check whether the complex is an intermediate in the trimerization, its reactions with diphenylacetylene were examined. Neither after stirring for nine days at room temperature nor after refluxing for 10 h in THF in the presence of excess of diphenylacetylene, was any hexaphenylbenzene detected. (This is in contrast with the previously mentioned cyclobutadieneniobium complex [9], which was claimed to be an intermediate.) The titanium complex is inactive as a catalyst in the hydrogenation of unsaturated hydrocarbons and the polymerization of ethylene and 2-vinylpyridine [15], but it provides a source of other C_4Ph_4Ti compounds, such as $C_8H_8TiC_4Ph_4$, which is readily formed by reaction with cyclooctatetraene disodium. Such reactions are now being investigated.

Experimental

All experiments were carried out under purified nitrogen. Solvents were dried and freed from oxygen before use.

The IR spectrum of the complex, in mulls between KBr windows in Voltalef-3S oil (4000–1200) and Nujol (4000–400 cm^{-1}), was recorded on a Hitachi EPI-G spectrophotometer. The UV-Vis spectrum was recorded on a Perkin-Elmer EPS-3T spectrophotometer. The ^1H NMR spectrum was recorded on a JEOL C-60 HL instrument using TMS as an internal standard ($\delta = 0$ ppm). The ^{13}C NMR spectrum of $C_4Ph_4TiMg_2Cl_6 \cdot 6THF$ was recorded on a Bruker WH270 spectrometer. The other carbon-13 spectra were recorded on a Varian XL-100 spectrometer.

Elemental analyses were performed at the Analytical Department of the Chemical Laboratories of this University under the supervision of Mr. A.F. Hamminga.

The starting materials titanium trichloride (K&K), diphenylacetylene (Aldrich) and the isopropyl chloride (Aldrich) and magnesium (Fluka) used for the preparation of i-PrMgCl in diethyl ether, were used without purification.

Synthesis of $(C_4Ph_4TiCl_3)^-(Mg_2Cl_3 \cdot 6THF)^+$

$TiCl_3$ (2.26 g, 14.6 mmol) was refluxed with THF for 8 h to give $TiCl_3 \cdot 3THF$. One equivalent of i-PrMgCl dissolved in diethyl ether was added dropwise at −30 °C. The mixture turned dark brown upon warming to room temperature. Diphenylacetylene (7.18 g, 43. 8 mmol) was added and the solution was refluxed for 6 h. After evaporation of the solvent the dark tarry product was washed thoroughly with benzene, to leave 4.19 g of a bright blue product. It was recrystallized twice by dissolving it in THF (100 ml), filtering the intensely blue solution obtained and then distilling pentane (100 ml) onto it. Yield 784 mg (= 0.715 mmol, 5%) of $C_4Ph_4TiMg_2Cl_6 \cdot 6THF$. Analysis: Found: C, 56.91, 57.01; H, 6.30, 6.39; Cl, 19.20,

(Continued on p. 264)

TABLE 3

CRYSTAL DATA AND DETAILS OF THE STRUCTURE DETERMINATION

(a) Crystal Data		
Formula	$C_{52}H_{68}TiMg_2Cl_6O_6$	
Molecular weight	1098.363	
Crystal system	monoclinic	
Space group	$C2$	
Z	4	
$F(000)$ (electrons)	2304	
μ (cm^{-1})	4.5	
Appr. cryst. size (mm)	0.1 × 0.4 × 0.4	
	(I)	(II)
temperature (K)	294	100
a (Å)	17.74(1)	17.58(1)
b (Å)	14.45(1)	14.20(1)
c (Å)	22.03(1)	21.72(1)
β (°)	92.94(6)	92.5(1)
V (Å^3)	5640(6)	5412(6)
$d(x)$ (g cm^{-3})	1.293	1.347
(b) Data collection		
Radiation	Mo-K_α (Zr-filtered)	
θ_{max}	27.5	
$\omega/2\theta$	0.70 + 0.35tg(θ)	
total measured	10621	
total unique	4457	
observed ($I > 2.5\sigma(I)$)	1703	
(c) Refinement		
number of parameters	414	
R	0.095	
R_w	0.103	
weight	1	
Maximum shift/error	0.440	
Residual density (e/Å^3)	−0.350; +0.450	

TABLE 4

POSITIONAL AND THERMAL PARAMETERS AND THEIR e.s.d.'s[a]

Atom	x/a	y/b	z/c	$U_{1,1}$ or U	$U_{2,2}$	$U_{3,3}$	$U_{2,3}$	$U_{1,3}$	$U_{1,2}$
Ti(1)	0.6600(3)	0.641800(0)	−0.2968(2)	0.091(4)	0.085(4)	0.052(3)	0.007(3)	0.007(3)	−0.010(4)
Cl(1)	0.5689(6)	0.570(1)	−0.2480(4)	0.146(7)	0.28(1)	0.066(5)	−0.006(8)	0.018(5)	−0.074(9)
Cl(2)	0.636(1)	0.788(1)	−0.2675(6)	0.53(1)	0.15(1)	0.114(8)	−0.041(8)	0.11(1)	−0.01(1)
Cl(3)	0.7654(6)	0.608(2)	−0.2415(4)	0.136(8)	0.49(1)	0.087(6)	−0.05(1)	−0.017(6)	0.01(1)
Cl(4)	0.2393(5)	0.4712(6)	−0.0765(4)	0.091(6)	0.081(6)	0.092(7)	−0.007(5)	−0.006(5)	−0.013(5)
Cl(5)	0.2381(5)	0.7018(6)	−0.0793(4)	0.117(7)	0.072(6)	0.052(5)	0.001(4)	0.010(5)	0.021(5)
Cl(6)	0.4015(4)	0.5857(8)	−0.0844(3)	0.062(4)	0.126(6)	0.066(4)	0.010(6)	0.001(3)	−0.004(6)
Mg(1)	0.2853(5)	0.5846(9)	−0.1524(4)	0.068(5)	0.091(7)	0.058(5)	0.004(7)	−0.012(4)	−0.016(7)
Mg(2)	0.3009(5)	0.5910(8)	−0.0082(4)	0.082(6)	0.067(6)	0.054(5)	−0.010(6)	0.003(4)	−0.001(6)
O(1)	0.182(1)	0.576(2)	−0.2014(9)	0.088(6)					
O(2)	0.330(1)	0.483(1)	−0.2061(9)	0.084(6)					
O(3)	0.319(1)	0.690(1)	−0.2105(8)	0.084(6)					
O(4)	0.350(1)	0.491(1)	0.0455(9)	0.081(6)					
O(5)	0.357(1)	0.693(1)	0.0417(9)	0.078(6)					
O(6)	0.210(1)	0.591(2)	0.0503(8)	0.087(5)					
C(1)	0.717(1)	0.625(2)	−0.3851(9)	0.06(1)	0.07(1)	0.03(1)	−0.02(1)	−0.030(9)	0.01(1)
C(2)	0.659(2)	0.695(2)	−0.392(1)	0.07(1)	0.04(1)	0.04(1)	−0.00(1)	−0.02(1)	0.03(1)
C(3)	0.659(1)	0.550(2)	−0.380(1)	0.04(1)	0.04(1)	0.06(1)	0.01(1)	−0.00(1)	0.01(1)
C(4)	0.605(1)	0.619(2)	−0.388(1)	0.06(1)	0.04(1)	0.08(1)	0.01(1)	−0.02(1)	−0.00(1)
C(5)	0.800(1)	0.620(2)	−0.391(1)	0.06(1)	0.05(1)	0.04(1)	−0.01(1)	0.00(1)	0.00(1)
C(6)	0.834(2)	0.686(2)	−0.425(1)	0.06(1)	0.07(1)	0.08(1)	0.02(1)	−0.00(1)	0.02(1)
C(7)	0.909(2)	0.682(2)	−0.434(1)	0.08(1)	0.10(1)	0.09(1)	0.02(1)	0.00(1)	−0.04(1)
C(8)	0.955(2)	0.616(3)	−0.410(2)	0.09(1)	0.11(2)	0.14(2)	0.01(1)	0.01(1)	−0.03(1)
C(9)	0.923(2)	0.548(3)	−0.378(2)	0.03(1)	0.11(1)	0.19(2)	−0.06(1)	−0.04(1)	0.02(1)
C(10)	0.847(2)	0.548(2)	−0.369(1)	0.08(1)	0.05(1)	0.09(1)	0.02(1)	−0.03(1)	−0.01(1)
C(11)	0.657(1)	0.787(2)	−0.414(1)	0.04(1)	0.09(1)	0.08(1)	0.05(1)	0.04(1)	0.01(1)
C(12)	0.711(2)	0.855(2)	−0.395(1)	0.10(1)	0.05(1)	0.08(1)	−0.00(1)	0.01(1)	−0.03(1)
C(13)	0.711(2)	0.943(2)	−0.413(1)	0.10(1)	0.05(1)	0.10(1)	0.01(1)	−0.00(1)	−0.05(1)
C(14)	0.660(2)	0.971(2)	−0.455(1)	0.08(1)	0.05(1)	0.10(1)	0.02(1)	0.06(1)	0.01(1)
C(15)	0.609(2)	0.912(2)	−0.479(1)	0.07(1)	0.12(1)	0.08(1)	0.03(1)	0.02(1)	−0.03(1)
C(16)	0.607(1)	0.817(2)	−0.459(1)	0.03(1)	0.12(1)	0.08(1)	0.04(1)	0.02(1)	0.01(1)
C(17)	0.662(1)	0.449(2)	−0.384(1)	0.03(1)	0.05(1)	0.08(1)	−0.02(1)	0.03(1)	0.01(1)

C(20)	0.656(2)	0.266(2)	−0.399(1)	0.10(1)	0.07(1)	0.12(1)	0.06(1)	−0.03(1)	0.00(1)
~~C(21)~~	~~0.704(2)~~	~~0.314(2)~~	~~−0.428(1)~~	~~0.12(1)~~	~~0.11(1)~~	~~0.07(1)~~	~~−0.02(1)~~	~~−0.02(1)~~	~~−0.08(1)~~
C(22)	0.707(1)	0.406(2)	−0.420(1)	0.03(1)	0.10(1)	0.05(1)	−0.01(1)	−0.03(1)	0.03(1)
C(23)	0.516(1)	0.620(2)	−0.402(1)	0.09(1)	0.05(1)	0.05(1)	0.01(1)	0.03(1)	0.01(1)
C(24)	0.485(2)	0.543(2)	−0.426(1)	0.13(1)	0.07(1)	0.09(1)	−0.01(1)	0.03(1)	−0.03(1)
C(25)	0.403(2)	0.551(3)	−0.439(1)	0.03(1)	0.18(2)	0.10(1)	0.06(1)	−0.00(1)	−0.02(1)
C(26)	0.367(1)	0.630(3)	−0.425(1)	0.00(1)	0.19(2)	0.13(1)	0.03(2)	0.02(1)	0.03(1)
C(27)	0.402(2)	0.702(3)	−0.400(1)	0.05(1)	0.14(2)	0.12(1)	0.02(1)	−0.03(1)	0.01(1)
C(28)	0.475(2)	0.702(2)	−0.388(2)	0.10(1)	0.07(1)	0.11(1)	0.05(1)	0.01(1)	0.01(1)
C(29)	0.111(3)	0.599(4)	−0.177(2)	0.16(1)					
C(30)	0.057(3)	0.548(3)	−0.220(2)	0.16(1)					
C(31)	0.093(3)	0.547(3)	−0.278(2)	0.17(1)					
C(32)	0.173(2)	0.527(3)	−0.255(2)	0.14(1)					
C(33)	0.376(2)	0.499(3)	−0.259(2)	0.13(1)					
C(34)	0.397(2)	0.406(3)	−0.282(2)	0.13(1)					
C(35)	0.400(2)	0.352(3)	−0.233(2)	0.15(1)					
C(36)	0.345(2)	0.384(3)	−0.186(2)	0.12(1)					
C(37)	0.265(2)	0.748(3)	−0.246(2)	0.13(1)					
C(38)	0.315(3)	0.838(4)	−0.252(3)	0.21(1)					
C(39)	0.382(3)	0.832(4)	−0.226(2)	0.16(1)					
C(40)	0.393(3)	0.737(4)	−0.202(2)	0.17(1)					
C(41)	0.329(2)	0.451(3)	0.103(2)	0.13(1)					
C(42)	0.397(2)	0.398(3)	0.128(2)	0.12(1)					
C(43)	0.432(3)	0.368(3)	0.076(2)	0.14(1)					
C(44)	0.406(3)	0.426(3)	0.024(2)	0.16(1)					
C(45)	0.387(2)	0.686(3)	0.108(2)	0.13(1)					
C(46)	0.413(2)	0.782(3)	0.119(2)	0.12(1)					
C(47)	0.430(2)	0.832(2)	0.064(2)	0.09(1)					
C(48)	0.375(2)	0.782(3)	0.016(2)	0.13(2)					
C(49)	0.185(3)	0.677(4)	0.074(2)	0.17(1)					
C(50)	0.106(3)	0.666(4)	0.095(2)	0.18(1)					
C(51)	0.092(3)	0.590(6)	0.072(3)	0.23(1)					
C(52)	0.148(3)	0.524(4)	0.055(3)	0.21(1)					

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[a] The temperature factor has the form of $\exp(-T)$ where $T = 8\pi^2 U(\sin\theta/\lambda)^2$ for isotropic atoms and $T = 2\pi^2 \Sigma_{ij} h_i h_j U_{ij} i^* j^*$ for anisotropic atoms. i^* and j^* are reciprocal axial lengths and h_i are Miller indices.

19.51; Mg, 4.28, 4.35; Ti, 4.35, 4.37. $C_{52}H_{68}Cl_6Mg_2O_6Ti$ calcd.: C, 56.86; H, 6.24; Cl, 19.36; Mg, 4.43; Ti, 4.36%.

When the complex was made from $TiCl_4$, diphenylacetylene and two equivalents of i-PrMgCl, it was obtained in more than 50% yield.

The VIS-NIR spectrum (400–2600 nm), recorded in THF, shows one absorption maximum at 630 nm with $\epsilon = 1.6 \times 10^3$ cm^2 mmol^{-1}; the spectrum in the UV range (210–400 nm) could not be obtained because of decomposition at high dilutions.

The IR spectrum shows absorptions at 3040(w), 3020(w), 2880(w), 2840(w), 1590(s), 1490(s), 1440(m), 1180(w,br), 1065(w), 1020(s,br), 915(m,br), 870(s,br), 779(m), 772(m), 764(m), 746(m), 739(m), 708(s), 700(s), 675(w,sh), 540(w), 511(m), 503(m) and 446(m) cm^{-1}.

X-ray structure determination

Pertinent data on the structure determination of the title compound are given in Table 3. The room temperature data set I was collected on a dark blue crystal, sealed under nitrogen in a Lindemann glass capillary. Triclinic symmetry was assumed. Subsequent analysis of the symmetry of the resulting data set revealed that it had a C-centered monoclinic lattice (averaging index 5.7%), but this could be only approximately confirmed by the values of the transformed lattice dimensions due to the relatively poor quality of the crystal. Preliminary attempts to solve the structure with set I did not lead to interpretable results. A few years later a low temperature data set II was collected on the same crystal in an attempt to obtain a higher resolution data set. Although the resolution was not improved very much, as can be understood in retrospect in terms of the presumably static disorder of the tetrahydrofuran (THF) molecules, the structure could be solved in the case of data set II to yield a recognizable heavy atom fragment using MULTAN80 [16] and subsequently completed by DIRDIF81 [17] and standard Fourier techniques. However, since subsequent anisotropic refinement with II was not satisfactory, possibly due to aging of the crystal, the final refinements were carried out with data set I. Scattering factors were those of Cromer and Mann [18]. Data were corrected for Lorentz and polarisation effects. Correction for absorption was considered to be unnecessary in view of a less than 5% variation in the intensity of a psi-scan of a near to axial reflection. All six THFs turned out to be disordered to some degree. Further investigation suggested that the disorder of the THFs can approximately be described in terms of the three pseudo 2-fold rotational axes through the center of gravity of the two Mg atoms and each of the Cl atoms. In view of the limited amount of data available and the purpose of this study, the characterisation of the previously unknown structure of the title compound, it was not considered worthwhile to investigate the disorder in detail. Only the major components were introduced in the final refinement. Figure 2 shows the complete molecule with the numbering scheme used. Hydrogen atoms attached to the phenyl carbon atoms were placed at calculated positions with an overall temperature factor (U) of 0.1 Å^2. All non-hydrogen atoms were refined anisotropically except for those in the THF groups, which were refined isotropically. Table 4 lists all final refined parameters except those of the hydrogen atoms. The calculations were carried out on either the CDC CYBER 175 of the University of Utrecht or on the inhouse ECLIPSE S/230 minicomputer with the ILIAS package (a minicomputer version of SHELX76 [19] by A.L.S.). The illustrations and geometrical calculations were done with the programs of the EUCLID-package [20].

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