Crystal Structures of Trichloro(η^5-cyclopentadienyl)titanium(IV) and -zirconium(IV)

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The crystal structures of the title compounds have been determined at 295 (1) K by single-crystal X-ray diffraction methods, being refined by full-matrix least-squares methods to residuals of 0.031 and 0.042 for 872 and 1107 independent 'observed' reflections, respectively. Crystals of CpTiCl$_3$ are monoclinic, probable space group $P2_1$, with a = 6.588 (2) Å, b = 10.419 (3) Å, c = 6.680 (2) Å, β = 115.86 (2)°, and Z = 2. The structure is based on that of TiCl$_4$, comprising monomeric species in which a chlorine atom has been replaced by an η^5-Cp ligand. Ti–Cl are 2.201 (5)–2.248 (5) Å, with Cl–Ti–Cl = 102.2 (1)–104.1 (2)°. Crystals of CpZrCl$_3$ are triclinic of space group $P\bar{1}$ with a = 8.629 (8) Å, b = 7.133 (7) Å, c = 6.326 (6) Å, α = 100.68 (7)°, β = 91.67 (7)°, γ = 98.78 (7)°, and Z = 2. The structure is based on that of the solid-state structure of the parent compound ZrCl$_4$, a linear polymer with successive zirconium atoms, related Zr–Cl(terminal) is 2.419 (3) Å, while Zr–C(bridging) is 2.518 (3)–2.728 (3) Å.

Introduction

The structures of a wide range of metal tetrahalides have been established, as is also true for their bis(cyclopentadienyl) (η-C$_5$H$_5$ ≡ Cp) adducts, Cp$_2$MX$_2$, particularly of the early transition metals. As yet, there appear to be no recorded structure determinations of neutral species with the stoichiometry CpMX$_3$. In this report, we record structure determinations of representative compounds for the group 4 elements, CpTiCl$_3$ and CpZrCl$_3$. Both compounds were prepared by the most recent procedures of the numerous methods available,[1] viz., TiCl$_4$ and C$_5$H$_5$SiMe$_3$, and photolytic chlorination of Cp$_2$ZrCl$_2$ for CpTiCl$_3$ and CpZrCl$_3$, respectively. Suitable crystals were obtained by sublimation at 10^{-3} mmHg, at a temperature of 80 °C for CpTiCl$_3$ and 230 °C for CpZrCl$_3$.

Crystallography

Crystal Data. 1: C$_5$H$_5$TiCl$_3$, M_r = 219.4, monoclinic, space group $P2_1$ (C$_2^2$, No. 4), a = 6.588 (2) Å, b = 10.419 (3) Å, c = 6.680 (2) Å, β = 115.86 (2)°; U = 412.6 (2) Å^3; D_{calcd} (Z = 2) = 1.77 g cm^{-3}; $F(000)$ = 216; μ_{Mo} = 19.4 cm^{-1}. Specimen: irregular compact fragment mounted in a capillary (approximated as a sphere 0.25 mm in diameter for absorption correction); $2\theta_{max}$ = 60°; N and N_0 = 1254 and 872; R and R' : 0.031 and 0.040.

2: C$_5$H$_5$ZrCl$_3$, M_r = 262.7, triclinic, space group $P\bar{1}$ (C$_i^1$, No.2), a = 8.629 (8) Å, b = 7.133 (7) Å, c = 6.326 (6) Å, α = 100.68 (7)°, β = 91.67 (7)°, γ = 98.78 (7)°; U = 377.4 (6) Å^3; D_{calcd} (Z = 2) = 2.31 g cm^{-3}; $F(000)$ = 252; μ_{Mo} = 23.8 cm^{-1}. Specimen: 0.1 × 0.2 × 0.3 mm (capillary); $2\theta_{max}$ = 50°; N and N_0 = 1348 and 1107; R and R' = 0.042 and 0.051.

Structure Determinations. Unique data sets were measured at 295 K by using Syntex P2$_1$ and P$\bar{1}$ four-circle diffractometers, fitted with monochromatic Mo Kα radiation sources, in conventional $2\theta/\theta$ scan mode within a preset $2\theta_{max}$ limit. N independent reflections were obtained, N_0 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after correction of the data for absorption and solution of the structure (1, direct methods; 2 heavy-atom method). Anisotropic thermal parameters were refined for the non-hydrogen atoms: $(x, y, z,$ and $U_{iso})_H$ were included as constrained estimates in **2**; in **1**, $(x, y, z)_H$ were refined. Residuals at convergence were R and R', reflection weights being $(\sigma^2(F_0) + 0.0005 (F_0)_2)^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anamalous dispersion (f', f'').[2] Com-

putation used the X-RAY 76 program system[3] implemented on a Perkin-Elmer 3240 computer by S. R. Hall.

A further comment is in order about the structure determination of CpTiCl$_3$. It is evident from Figure 1 that the array conforms quite closely in symmetry to space group $P2_1/m$. The initial refinement in that space group led to convergence at R and R' of 0.038 and 0.037, respectively; thermal motion and anisotropy on the Cp ring atoms show very marked irregularities indicative of disorder or incorrect space group, and it was decided, given the quality of the data, to attempt refinement in space group $P2_1$. This effected a significant reduction in R, with diminished vibrational amplitudes and anisotropies in the thermal tensors of the Cp ring atoms; this is achieved by rotation of the Cp ring about its major axis as seen in Figure 1, removing the mirror plane in the process. Accordingly, this model was adopted as "correct", although for chemical purposes the difference is trivial.

Discussion

Surprisingly these represent the first structure determinations reported for species with stoichiometry [CpMCl$_3$]$^{x\pm}$ with the exception of a report of the structure of (LiCpCrCl$_3$·2C$_4$H$_8$O)$_2$·C$_4$H$_8$O$_2$ in which the CpCrCl$_3$ species is found in association with a lithium ion.[4] Moreover, the two structures are of interest since they represent two distinct structural types.

The unit cell contents of CpTiCl$_3$ comprise two distinct molecules of that stoichiometry (one comprising the asymmetric unit) related by the crystallographic twofold screw axis; the molecule contains no crystallographically imposed symmetry. The structure is based on that of the TiCl$_4$ structure in which one chlorine atom has been replaced by the (η^5-C$_5$H$_5$) ligand. In TiCl$_4$ the Ti–Cl distance is 2.170 (2) Å, with tetrahedral stereochemistry; in the present case, Ti–Cl is appreciably longer ranging from 2.201 (5) to 2.248 (5) Å (uncorrected for libration) with Cl–Ti–Cl angles correspondingly reduced below the tetrahedral to range between 102.2 (2) and 104.1 (2)°. In the structure of CpTiCl$_2$,[6] Ti–Cl is much longer (mean 2.36$_4$

(1) (a) A. M. Cardoso, R. J. H. Clark, and S. Moorhouse, *J. Chem. Soc., Dalton Trans.*, 1156 (1980) (CpTiCl$_3$). (b) G. Erker, K. Berg, L. Treschanke, and K. Engel, *Inorg. Chem.*, 21, 1277 (1982) (CpZrCl$_3$).

(2) "International Tables for X-ray Crystallography", J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, 1974, Vol. IV.

(3) "The X-RAY System – Version of March, 1976", Technical Report TR-446, J. M. Stewart, Ed., Computer Science Center, University of Maryland, College Park, MD, 1976.

(4) B. Muller and J. Krausse, *J. Organomet. Chem.*, 44, 141 (1972).

(5) M. F. A. Dove, J. A. Creighton, and L. A. Woodward, *Spectrochim. Acta*, 18, 267 (1962).

Table I. Non-Hydrogen Atom Coordinates for 1 and 2[a]

atom	1, M = Ti			2, M = Zr		
	x	y	z	x	y	z
M	0.53496 (9)	0.89920 (...)[b]	0.16924 (10)	0.34188 (8)	0.42302 (9)	0.22530 (9)
Cl(1)	0.7281 (8)	0.7335 (5)	0.3639 (8)	0.6079 (2)	0.3473 (2)	0.0500 (2)
Cl(2)	0.7365 (7)	1.0658 (5)	0.3731 (7)	0 5633 (2)	0.7063 (2)	0.4583 (2)
Cl(3)	0.6117 (2)	0.8960 (9)	−0.1232 (2)	0.1860 (2)	0.6470 (3)	0.4169 (3)
C(1)	0.248 (3)	0.954 (2)	0.268 (3)	0.2583 (9)	0.1197 (10)	−0.0543 (11)
C(2)	0.231 (3)	0.824 (2)	0.220 (3)	0.2326 (9)	0.0708 (10)	0.1476 (11)
C(3)	0.189 (3)	0.809 (2)	0.008 (3)	0.1136 (9)	0.1689 (11)	0.2380 (11)
C(4)	0.164 (2)	0.930 (2)	−0.083 (2)	0.0657 (9)	0.2758 (12)	0.0960 (14)
C(5)	0.193 (3)	1.013 (2)	0.066 (4)	0.1564 (9)	0.2506 (11)	−0.0866 (11)
C(0)	0.205 (...)	0.906 (...)	0.096 (...)	0.1653 (...)	0.1771 (...)	0.0682 (...)

[a] C(0) is the centroid of the cyclopentadienyl ring.   [b] Defines origin.

Table II. Metal Atom Geometries[a]

1, M = Ti

	r_{Ti-L}	Cl(2)	Cl(3)	C(0)
Cl(1)	2.201 (5)	102.2 (2)	102.3 (3)	117.2 (...)
Cl(2)	2.248 (5)		104.1 (2)	114.3 (...)
Cl(3)	2.221 (2)	104.1 (2)		115.0 (...)
C(1)	2.33 (2)	88.7 (5)	141.0 (4)	30.2 (...)
C(2)	2.31 (2)	119.5 (5)	132.0 (5)	29.9 (...)
C(3)	2.26 (2)	144.7 (6)	98.3 (7)	30.5 (...)
C(4)	2.31 (1)	119.5 (6)	86.2 (3)	29.4 (...)
C(5)	2.36 (2)	91.5 (5)	107.6 (8)	28.4 (...)
C(0)	2.01 (...)	114.3 (...)	115.0 (...)	

2, M = Zr[b]

	r_{Zr-L}	Cl(2)	Cl(3)	Cl(1')	Cl(2'')	C(0)
Cl(1)	2.663 (3)	76.93 (8)	151.00 (5)	74.93 (7)	86.19 (8)	103.9 (...)
Cl(2)	2.728 (3)		77.06 (9)	80.06 (8)	72.78 (8)	173.5 (...)
Cl(3)	2.419 (3)	77.06 (9)		88.15 (9)	98.14 (9)	103.4 (...)
Cl(1')	2.602 (3)	80.06 (8)	88.15 (9)		149.83 (9)	106.5 (...)
Cl(2'')	2.518 (3)	72.78 (8)	98.14 (9)	149.83 (9)		100.8 (...)
C(1)	2.518 (7)	152.7 (2)	130.0 (2)	95.3 (2)	102.7 (2)	28.3 (...)
C(2)	2.491 (7)	145.8 (2)	118.6 (2)	127.5 (2)	74.8 (2)	28.6 (...)
C(3)	2.476 (8)	146.2 (2)	85.9 (2)	128.9 (2)	81.2 (2)	28.5 (...)
C(4)	2.501 (8)	153.3 (2)	76.2 (2)	97.6 (2)	112.6 (2)	28.3 (...)
C(5)	2.506 (7)	158.0 (2)	101.6 (2)	77.9 (2)	128.7 (2)	28.6 (...)
C(0)	2.196 (...)	173.5 (...)	103.4 (...)	106.5 (...)	100.8 (...)	

[a] The first column in each matrix, r_{M-L}, is the metal–ligand atom distance in Å. Other entries are the angles (deg) subtended at the metal by the relevant ligand atoms.   [b] A prime denotes the transformation $(1 - x, 1 - y, z)$ and a double prime the transformation $(1 - x, 1 - y, 1 - z)$.

Å) with Cl–Ti–Cl = 94.53°. In the latter structure, the mean Ti–Cp(centroid) distance is 2.05$_8$ Å; cp in the present structure is symmetrically bonded with Ti–C(0) = 2.01 Å, and C(0)–Ti–Cl ranging from 114.3 to 117.2°. The structure of [(CpTiCl)$_2$O][7] possesses a similar metal coordination environment to the present structure: Ti–Cl = 2.239 (2) Å (Ti–O = 1.777 (1) Å, Ti–C(0) = 2.01 Å; Cl–Ti–O = 102.3 (1), 103.1 (1)°, Cl–Ti–Cl = 102.6 (1), C(0)–Ti–Cl = 114.9, 115.0°, and C(0)–Ti–O = 117.0°).

In the vapor phase, ZrCl$_4$ is tetrahedral (Zr–Cl = 2.32 Å).[8] In the solid phase however, it has been shown to be a one-dimensional polymeric species.[9] It crystallizes in the space group $P2/c$ with a = 6.361 (4) Å, b = 7.407 Å, c = 6.256 (4) Å, β = 109.30 (4)°, U = 278.2 Å^3, and Z = 2. The polymer comprises edge-shared pseudooctahedral

ZrCl$_6$ units and is generated along c by the combination of inversion centers and twofold axes of the space group:

Zr–Cl(terminal) is 2.30$_7$ Å and the bridging Zr–Cl distances are 2.49 and 2.65$_5$ Å. Zr···Zr is 3.96$_2$ Å.

Just as the structure of CpTiCl$_3$ described above may be reasonably described in terms of the replacement of one of the chloride ligands of the usual TiCl$_4$ array by an (η-C$_5$H$_5$) species, so too it is reasonable to describe the present CpZrCl$_3$ structure in terms of the ZrCl$_4$ structure, not this time as the tetrahedral gas-phase species, but the μ,μ'-dichloro-bridged polymer (Cl$_2$(ZrCl$_2$)Cl$_2$) etc. The cell dimensions of the present structure are not dissimilar to those given above for solid ZrCl$_4$, although U has increased to 377.4 (6) Å by virtue of the bulk of the cyclopentadienyl ligand which has replaced one of the terminal chloride ligands. In consequence of this, although the generator of successive units of the polymer, now (Cl$_2$(ZrCpCl)Cl$_2$), remains the inversion center, the twofold axis passing through the zirconium is lost. The repeat cell distance of

(6) A. Clearfield, D. K. Warner, C. H. Saldarniaga-Molina, R. Ropal, and I. Bernal, *Can. J. Chem.*, **53**, 1622 (1975).

(7) U. Thewat and D. Schomburg, *J. Organomet. Chem.*, **127**, 169 (1977).

(8) (a) V. P. Spiridonov, P. A. Akishin, and V. I. Tsirelnikov, *Zh. Strukt. Khim.*, **3**, 329 (1962). (b) M. Kimura, K. Kimura, M. Aoki, and S. Shibata, *Bull. Chem. Soc. Jpn.*, **29**, 95 (1956).

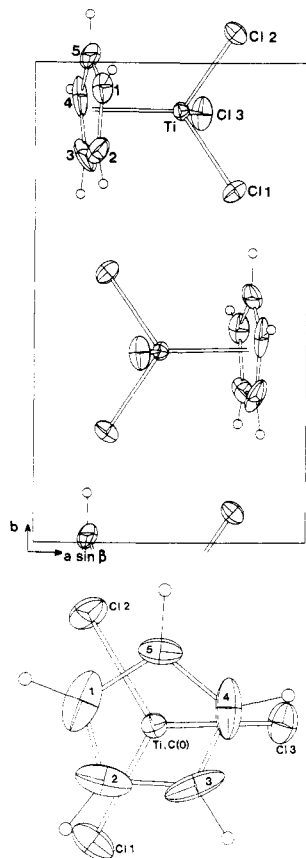(9) B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **8**, 146 (1969).

Figure 1. Unit cell contents of 1, projected down c. The 20% thermal ellipsoids and atom numbering are shown for the non-hydrogen atoms.
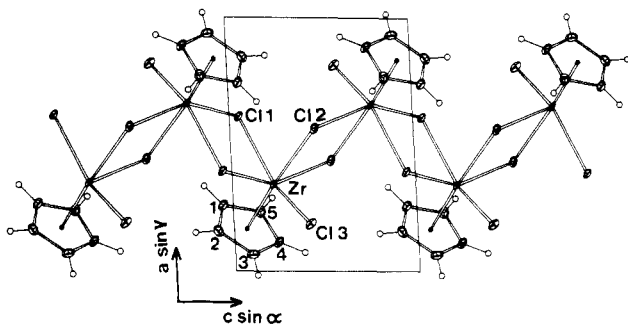

Figure 2. Unit cell contents of 2, projected down b.

the polymer, c in each case, remains remarkably similar in both structures.

In the present structure, Zr–Cl(terminal) at 2.419 (3) Å is considerably longer than its counterparts in $ZrCl_4$ (see

above). Briding Zr–Cl distances are also longer and remain unequivalent (2.663 (3), 2.728 (3) Å). The Zr···Zr repeat distances are 4.225 (4) and 4.180 (4) Å. Zr–Cp(centroid), 2.19$_6$ Å, may be compared with the mean value of 2.20 Å for Cp_2ZrCl_2;[10] here, however, the analogy cannot be extended, since presumably in consequence of the increase in bulk of the ligands about the central metal atom, the structure has reverted to the monomeric type. Interestingly the larger polyhapto ligand, cyclooctatetraenyl (COT), containing complex, as a tetrahydrofuran (THF) adduct, $(COT)ZrCl_2·THF$, is monomeric.[11]

In conclusion, both metal centers are best described as distorted tetrahedra and octahedra for $CpTiCl_3$ and $CpZrCl_3$, respectively, with angular distortions from the ideal polyhedra a consequence of the bulk of the cyclopentadienyl ligand. In $CpTiCl_3$ the centroid–Ti–Cl angles are all greater than the tetrahedral value while in $CpZrCl_3$ the centroid–Zr–Cl angles associated with the four cis chlorine atoms are 100.8–106.5° such that the zirconium resides out of the plane defined by these chlorine atoms. The centroid–Zr–Cl(trans) angle is 173.5°. Expansion of the zirconium coordination sphere for $CpZrCl_3$ occurs also in the presence of various coordinating solvents, exemplified by the 1:1 1,2-dimethoxyethane derivative which has been structurally characterized. There, a similar octahedral distortion is evident.[12] Replacing halides by bidentate ligands such as dithiocarbamates is associated with the formation of distorted pentagonal-bipyramidal structures with the Cp ligand in an apical position and the equatorial atoms distorted away from it[13] in a similar manner to the octehedral complexes described above.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, thermal parameters, hydrogen atom parameters, ring planes, and ligand geometries (12 pages). Ordering information is given on any current masthead page.

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(13) A. H. Bruder, R. C. Fay, D. F. Lewis, and A. A. Sayler, *J. Am. Chem. Soc.*, **98**, 6932 (1976).