Preliminary Communication

Molecular structure of trichloro(η^5-pentamethylcyclopentadienyl)zirconium(IV)

Avelino Martín, Miguel Mena and Federico Palacios

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

(Received April 6, 1994)

Abstract

X-ray analysis of the yellow, air-unstable, crystalline compound Cp^*ZrCl_3 (1) which results from the reaction of $ZrCl_4$ with Cp^*SiMe_3 confirms the presence of two Cp^*ZrCl_3 moieties related by a centre of symmetry with two chlorine atoms bridging the metals. 1 is therefore a dimer, despite the molecular structure of $[CpZrCl_3]$, which was found to be a polymer.

Key words: Zirconium; Dinuclear; X-ray diffraction; Early transition metals; Group 4

The use of Cp^*SiMe_3 as a mild and effective reagent for the preparation of monopentamethylcyclopentadienyl trihalides of the Group 4 elements is well known [1]. It is a noticeable improvement over other reagents [2] for preparing Cp^*ZrCl_3 (**1**). The last step in other preparations was always a tedious sublimation (160°C, 10^{-4} mmHg, 2 days). However, until now we have been unable to obtain suitable single crystals for the study of its molecular structure by X-ray diffraction and there is not much information on similar structures [3]. Here we report the molecular structure of Cp^*ZrCl_3 (**1**).

The molecular structure of compound **1** is shown in Fig. 1, the final atomic coordinates for the non-hydrogen atoms are presented in Table 1 and selected bond distances and angles are given in Table 2. The compound is a dimer in which the two Cp^*ZrCl_3 moieties are related by a centre of symmetry with two chlorine atoms bridging the two metals; the environment around each zirconium atom is the classical four-legged piano-stool structure.

Zr–Cl(terminal) bond distances for compound **1** are 2.385(1) and 2.402(1) Å, while Zr–Cl(bridging) distances are 2.587(1) and 2.589(1) Å respectively, similar to those found for the linear polymer $CpZrCl_3$ [4], Zr–Cl(terminal) 2.419(3) Å and Zr–Cl(bridging) 2.518(3)–2.728(3) Å, and shorter than those reported for the monomeric complex $CpZrCl_3(MeOC_2H_4OMe)$ [5], with average Zr–Cl(terminal) bond distances of 2.464 Å. No bonding distances were found for zirconium atoms from adjacent $[\{Cp^*ZrCl_3\}_2]$ molecules, while the Zr–Zr intramolecular distance for complex **1** is 4.119 Å, close to 4.225 and 4.180 Å, both found for the compound $CpZrCl_3$.

The Zr–Cp*(1) distance, 2.175 Å, is similar to values reported for other Cp*Zr complexes, 2.238(5) Å for $[\{(\eta^5\text{-}C_5Me_5)ZrCl_2(H_2O)(\mu\text{-}OH)\}_2]$ and 2.230 Å (average) for $[\{(\eta^5\text{-}C_5Me_5)ZrCl\}_3(\mu\text{-}Cl)_4(\mu_3\text{-}O)]$ [6]. At the same time, the C_5Me_5 plane is almost parallel to that formed by the four chlorine atoms bonded to each metal, with a dihedral angle of 1.4°.

Hence, the presence of a bulkier ligand, such η^5-C_5Me_5, makes it more difficult for the compound Cp^*ZrCl_3 to be a polymer, but this ligand is not big enough to stabilize a monomeric species such as $[Cp^*TiCl_3]$ [7].

X-Ray Crystallography

A yellow crystal of $[\{Cp^*ZrCl_3\}_2]$ was obtained from toluene (−10°C) and was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed at 20°C using Mo K_α radiation ($\lambda = 0.71065$ Å) and a graphite-orientated monochromator on an Enraf–Nonius CAD4 diffractometer. From the systematic absences and from the

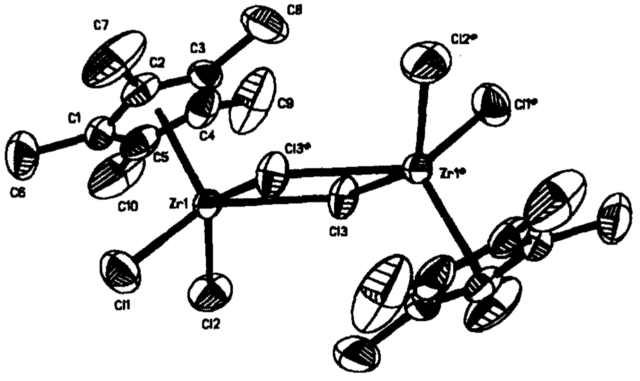

Fig. 1. ORTEP of compound 1 with 50% of probability.

Correspondence to: Dr. M. Mena.

0022-328X/94/$7.00
SSDI 0022-328X(94)24759-C

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[\{Cp^*ZrCl_3\}_2]$

	x	y	z	U_{eq}
Zr(1)	2668(1)	1919(1)	4104(1)	32(1)
Cl(1)	1592(1)	−41(1)	3598(1)	63(1)
Cl(2)	3917(1)	151(2)	4101(1)	67(1)
Cl(3)	3559(1)	2643(1)	5222(1)	44(1)
C(1)	2341(3)	3207(5)	3047(2)	43(1)
C(2)	1879(3)	4099(5)	3438(2)	44(1)
C(3)	2538(3)	4838(5)	3900(2)	51(1)
C(4)	3396(3)	4396(5)	3803(2)	53(1)
C(5)	3275(3)	3384(5)	3276(2)	50(1)
C(6)	1912(5)	2382(8)	2448(2)	89(2)
C(7)	871(3)	4313(9)	3343(3)	94(2)
C(8)	2366(6)	6019(6)	4386(3)	102(2)
C(9)	4290(5)	5022(10)	4149(3)	120(3)
C(10)	4021(4)	2775(9)	2968(3)	103(3)

subsequent least-squares refinement, the space group was determined to be monoclinic $C2/c$. Unit cell dimensions: $a = 14.987(3)$, $b = 8.350(2)$, $c = 21.598(4)$ Å, $\beta = 101.55(3)°$; $Z = 4$, $D_{calc} = 1.669$ g cm^{-3}.

A total of 2497 reflections in the unique set was collected in the $+h$, $+k$, $\pm l$ octants in the range $6° \leq 2\theta \leq 50°$, ω scan mode, with 2316 independent reflections ($R_{int} = 0.0525$). Two representative check reflection standards were measured after every two h and remained constant within experimental error throughout data collection, so no decay correction was required. Intensities were corrected for Lorentz and polarization effects in the normal manner. No absorption or extinction corrections were made. The structure was solved by direct methods and refined by blocked full-matrix least-squares analysis. All non-hydrogen atoms were anisotropically refined and methyl hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atoms.

TABLE 2. Selected bond lengths (Å) and angles (°) for $[\{Cp^*ZrCl_3\}_2]$

Zr(1)–Cl(2)	2.385(1)	Zr(1)–Cl(1)	2.402(1)
Zr(1)–C(2)	2.469(4)	Zr(1)–C(3)	2.477(4)
Zr(1)–C(1)	2.482(3)	Zr(1)–C(4)	2.484(4)
Zr(1)–C(5)	2.484(4)	Zr(1)–Cl(3)	2.587(1)
Zr(1)–Cl(3)#	2.589(1)	Cl(3)–Zr(1)#	2.589(1)
Zr(1)–Cp*(1)	2.175		
Cl(2)–Zr(1)–Cl(1)	91.87(5)	Cl(2)–Zr(1)–Cl(3)	83.57(5)
Cl(1)–Zr(1)–Cl(3)	139.26(4)	Cl(2)–Zr(1)–Cl(3)#	137.26(4)
Cl(1)–Zr(1)–Cl(3)#	82.21(4)	Cl(3)–Zr(1)–Cl(3)#	74.54(4)
Zr(1)–Cl(3)–Zr(1)#	105.46(4)	Cp*(1)–Zr(1)–Cl(1)	110.7
Cp*(1)–Zr(1)–Cl(2)	112.6	Cp*(1)–Zr(1)–Cl(3)	108.3
Cp*(1)–Zr(1)–Cl(3)#	109.0		

Cp*(1) is the centroid of the C_5-ring.

No solvent molecules were found, the largest peak in the final electron density difference map being 0.660 eÅ^{-3}. Final values of $R = 0.034$ and $R_w = 0.086$ were obtained. The programs SHELX-86 [8] and SHELXL-93 [9] were used to perform all the calculations with an ALPHA AXP Digital Workstation.

Full lists of bond distances, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

Financial support from the Comunidad Autónoma de Madrid (CAM C198/91), the Universidad de Alcalá de Henares, and the Ministerio de Educación y Ciencia (DGICYT PB90-0294) is gratefully acknowledged.

References

1 G. Hidalgo Llinás, M. Mena, F. Palacios, P. Royo and R. Serrano, *J. Organomet. Chem., 340* (1988) 37.

2 (a) J.H. Wengrovius and R.R. Schrock, *J. Organomet. Chem., 205* (1981) 319; (b) P.T. Wolczanski and J.E. Bercaw, *Organometallics, 1* (1982) 793.

3 C. Ting and L. Messerle, *Inorg. Chem., 28* (1989) 173.

4 L.M. Engelhardt, R.I. Papasergio, C.L. Raston and A.H. White, *Organometallics, 3* (1984) 18.

5 D. Seyferth, R.S. Henderson, J.P. Fackler, Jr. and A.M. Mazany, *J. Organomet. Chem., 213* (1981) C21.

6 G. Hidalgo, M.A. Pellinghelli, P. Royo, R. Serrano and A. Tiripicchio, *J. Chem. Soc., Chem. Commun.,* (1990) 1118.

7 R. Poli, *Chem. Rev., 91* (1991) 509.

8 G.M. Sheldrick, *Acta Crystallographica, A46* (1990) 467.

9 G.M. Sheldrick, SHELXL-93, *Program for the refinement of crystal structures,* VMS Version, Universität Göttingen, Germany, 1993.