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Zr and Hf metallocenes. Study of the structure of a novel mononuclear zirconium trivalent organometallic

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Abstract

$Cp_2^{**}MCl_2$, M = Zr and Hf, were obtained by reaction of MCl_4 with $Cp^{**}Li$, where Cp^{**} = 1,3-di-tertbutylcyclopentadienyl. Reduction of $Cp_2^{**}MCl_2$ with metallic potassium in pentane gave $Cp_2^{**}MCl$. The molecular and crystal structure of $Cp_2^{**}ZrCl$ was established from X-ray diffraction; monoclinic, space group $P2_{1/b}$, $a = 12.722$, $b = 16.336$, $c = 13.426$ Å, $\gamma = 70.68°$, $R = 0.065$; monomeric $Cp_2^{**}ZrCl$ molecules, the average Zr–C bond length is 2.505 Å, that of Zr–Cl is 2.423 Å, and the Cp^{**}centroid–Zr–Cp^{**}centroid angle is 133.3°.

Introduction

We recently reported the synthesis and the structure of $[1,3\text{-}(^tC_4H_9)_2C_5H_3]_2TiCl_2$ and $[1,3\text{-}(^tC_4H_9)_2C_5H_3]_2TiCl$ [1]. Four t-butyl groups introduce significant intramolecular tension in these molecules. Their geometry and other physical properties differ substantially from those of the unsubstituted Cp_2TiCl_2 and $[Cp_2TiCl]_2$. In fact, the 15-electron titanium monochloride $[1,3\text{-}(^tC_4H_9)_2C_5H_3]_2TiCl$ (I) is not able to associate either in solution or in the solid, thus indicating a stable paramagnetic Ti^{III} species.

Here we report the synthesis of 1,3-di-(t-butyl)cyclopentadienyl zirconium and hafnium derivatives, $Cp_2^{**}MCl_2$ and $Cp_2^{**}MCl$*.

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* We have used Cp^{**} to denote (η^5-1,3-di(t-butyl)cyclopentadienyl ligand in order to avoid confusion with commonly used Cp^* symbol for the η^5-pentamethylcyclopentadienyl ligand and Cp' for any other substituted cyclopentadienyl (see e.g. [2]).

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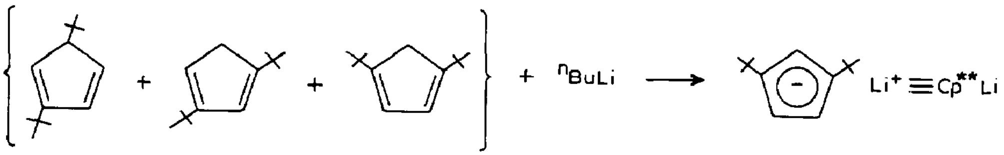
We were curious as to why the 1,3-di(t-butyl)cyclopentadienyl ligand had not been extensively employed in organometallic chemistry, the parent substituted cyclopentadiene having been reported as early as 1963 by Riemschneider [3].

Results and discussion

We prepared $Cp_2^{**}ZrCl_2$ and $Cp_2^{**}HfCl_2$ by a routine technique, namely, reaction of pure anhydrous $ZrCl_4$ or $HfCl_4$ with $Cp^{**}Li$. The initial 1,3-di(t-butyl)cyclopentadiene, obtained as a mixture of the three possible isomers was prepared after the method of Riemschneider [3] in high yield. This mixture is readily metallated with butyllithium, as the 2 *M* hexane solution diluted with a variety of solvents such as benzene, ethers, THF, and DME, to give a clear colourless solution the desired cyclopentadienyllithium derivative.

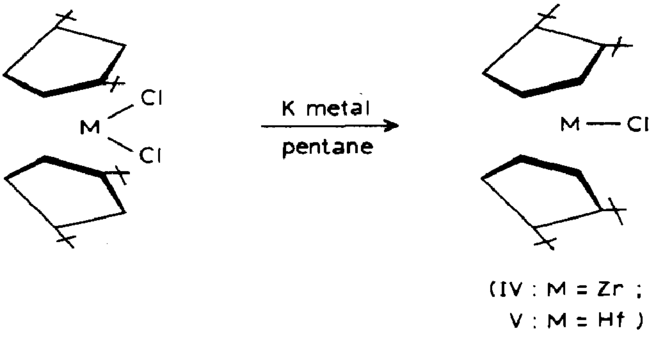


$$2Cp^{**}Li + MCl_3 \xrightarrow{25\,^{\circ}C} Cp^{**}{}_2MCl_2$$
$$(II\colon M = Zr;\ III\colon M = Hf)$$

The synthesis of the metallocene derivatives of Zr and Hf proceeds smoothly, and gives the complexes II and III, respectively, in about 50% yields. Pure samples of II and III were obtained after crystallization from toluene.

We have found that II and III can be reduced with potassium sand in pentane to give a moderate yield of paramagnetic $Cp_2^{**}ZrCl$ (IV) and $Cp_2^{**}HfCl$ (V), respectively, in moderate yields.

The monochlorides IV and V are very sensitive towards air-moisture and oxygen. In pentane solution, IV and V are rapidly oxidized to give the uncharacterized diamagnetic derivatives that are soluble in pentane. However the crystalline samples consisting of large crystals are stable in air for very short periods.



(IV : M = Zr; V : M = Hf)

Although we have designed an effective technique to give di-t-butylsubstituted Cp-sandwich derivatives of Ti, Zr and Hf it is noteworthy that the structure of a

1,1′,3,3′-tetra-t-butylferrocene has been described [4]. The substituted ferrocene was prepared by direct alkylation of ferrocene. The structure of 1,1′,3,3′-tetra-t-butylferrocene is characterized by significant distortion of the regular sandwich configuration owing to the bulky t-butyl substituents. The dihedral angle between the Cp-planes in this case is 7°.

It was of interest to determine the structural features of $Cp_2^{**}MCl$, where M = Zr and Hf. Both molecules appear to be strongly unsaturated which would encourage their association and/or ready solvation. However both trends are eventually hindered by the presence of the four bulky t-butyl groups in the Cp-rings. Moreover the conformational behaviour of IV and V must be strictly determined by the t-butyl substituents. It must be pointed out that the titanium derivative $Cp_2^{**}TiCl$ (I) previously studied by us is monomeric in the solid state, and its Cp-rings are in the hindered conformation. The atomic radii of Zr and Hf are

Table 1

Bond distances (Å) and most of the important bond angles (deg.) in IV

Zr–Cl	2.423(3)				
C1–C2	1.406(10)	C14–C15	1.396(9)	Zr–C1	2.506(8)
C1–C5	1.403(13)	C14–C18	1.408(11)	Zr–C2	2.474(9)
C2–C3	1.394(13)	C15–C16	1.428(11)	Zr–C3	2.526(9)
C3–C4	1.444(11)	C16–C17	1.432(10)	Zr–C4	2.493(8)
C4–C5	1.400(12)	C17–C18	1.394(10)	Zr–C5	2.537(7)
C3–C10	1.523(13)	C16–C23	1.487(10)	Zr–C14	2.497(6)
C5–C6	1.543(11)	C18–C19	1.516(9)	Zr–C15	2.462(8)
C6–C7	1.507(17)	C19–C20	1.516(16)	Zr–C16	2.515(7)
C6–C8	1.481(15)	C19–C21	1.487(22)	Zr–C17	2.496(7)
C6–C9	1.516(18)	C19–C22	1.520(15)	Zr–C18	2.551(6)
C10–C11	1.520(16)	C23–C24	1.546(15)		
C10–C12	1.533(16)	C23–C25	1.564(15)		
C10–C13	1.533(14)	C23–C26	1.528(13)		
C2–C1–C5	108.3(8)	C15–C14–C18	110.2(7)		
C1–C2–C3	109.8(8)	C14–C15–C16	108.6(7)		
C2–C3–C4	105.4(7)	C15–C16–C17	104.3(6)		
C3–C4–C5	109.2(8)	C16–C17–C18	111.6(7)		
C1–C5–C4	107.2(7)	C14–C18–C17	105.3(6)		
C2–C3–C10	129.0(8)	C15–C16–C23	128.5(7)		
C4–C3–C10	125.1(9)	C17–C16–C23	126.3(7)		
C1–C5–C6	127.5(8)	C14–C18–C19	127.8(7)		
C4–C5–C6	124.3(9)	C17–C18–C19	126.1(8)		
C5–C6–C7	110.8(9)	C18–C19–C20	111.3(7)		
C5–C6–C8	108.8(8)	C18–C19–C21	111.1(8)		
C5–C6–C9	110.4(7)	C18–C19–C22	106.8(8)		
C7–C6–C8	108.3(9)	C20–C29–C21	103.8(1.1)		
C7–C6–C9	108.7(1.0)	C20–C19–C22	108.7(9)		
C8–C6–C9	109.8(1.0)	C21–C19–C22	115.1(1.1)		
C3–C10–C11	106.9(7)	C16–C23–C24	108.7(7)		
C3–C10–C12	110.6(9)	C16–C23–C25	111.1(8)		
C3–C10–C13	110.9(9)	C16–C23–C26	110.6(8)		
C11–C10–C12	106.5(1.0)	C24–C23–C25	106.3(9)		
C11–C10–C13	110.6(1.0)	C24–C23–C26	112.2(1.0)		
C12–C10–C13	111.2(8)	C25–C23–C26	107.9(8)		

Table 2

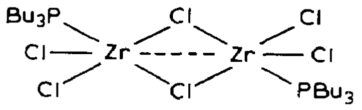
Atomic coordinates for IV ($\times 10^4$) and equivalent isotropic thermal parameters (B_{iso}^{eq})

Atom	x	y	z	B_{iso}^{eq}
Zr	7141(1)	2437(1)	2259(1)	2.5
Cl	6211(3)	3508(2)	2409(3)	6.7
C1	6557(7)	957(5)	1489(7)	3.0
C2	7470(7)	1489(5)	944(7)	3.1
C3	7161(6)	2111(5)	422(7)	2.7
C4	6022(7)	1976(6)	709(7)	2.9
C5	5653(7)	1253(5)	1337(7)	3.0
C6	4422(7)	788(6)	1615(8)	3.6
C7	4323(10)	101(9)	2392(10)	7.3
C8	3813(8)	362(10)	713(10)	7.0
C9	3903(9)	1432(8)	2019(11)	7.3
C10	7794(8)	2731(6)	−395(8)	3.9
C11	7380(12)	2293(8)	−1386(9)	6.1
C12	7504(10)	3570(7)	−379(8)	5.1
C13	9053(9)	2923(8)	−291(9)	5.4
C14	9121(5)	2672(4)	2720(6)	3.1
C15	8465(6)	1900(4)	3165(6)	3.3
C16	7806(5)	2103(4)	3926(5)	2.7
C17	8078(6)	3025(5)	3864(6)	3.3
C18	8895(6)	3383(5)	3148(6)	3.1
C19	9536(6)	4339(5)	3008(7)	4.1
C20	8902(9)	4899(6)	3432(12)	8.8
C21	9657(16)	4574(8)	1934(15)	13.8
C22	10624(9)	4527(6)	3576(13)	11.2
C23	7156(7)	1533(5)	4731(6)	4.0
C24	7826(II)	1762(10)	5712(10)	9.3
C25	6032(9)	1701(8)	4920(10)	7.8
C26	6884(10)	578(6)	4452(9)	7.3

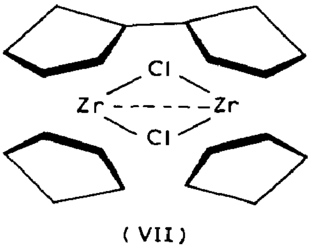
substantially greater than that of Ti so structural studies of the monochlorides IV and V were required to enable comparison.

The molecular and crystal structure of $Cp_2^{**}ZrCl$ has been determined (Fig. 1). The main interatomic distances and bond angles are given in Table 1. The atomic coordinates are listed in Tables 2 and 3.

Interestingly, there is paucity of structural evidence on Zr^{III} derivatives. In a review of the zirconium and hafnium organometallic compounds [2] there is no reference to Zr^{III} organometallic structures. As far as we know the crystal structures of only two diamagnetic Zr^{III} complexes, namely $[ZrCl_3(PBu_3)]_2$ [5] and $(C_{10}H_8)[(C_5H_5)Zr(\mu\text{-}Cl)]_2$ [6] have been determined.



(VI)



(VII)

Table 3

Coordinates of H atoms in IV ($\times 10^3$)

Atom	x	y	z
H1	651(7)	543(6)	309(5)
H2	812(5)	624(5)	399(4)
H3	559(7)	750(6)	449(5)
H4	368(9)	476(7)	246(6)
H5	469(9)	458(8)	290(7)
H6	470(10)	540(8)	207(3)
H7	414(5)	495(5)	470(4)
H8	299(7)	500(7)	425(6)
H9	367(10)	657(9)	366(8)
H10	299(10)	661(9)	256(8)
H11	421(11)	707(9)	272(9)
H12	754(4)	680(4)	649(3)
H13	788(8)	771(7)	722(6)
H14	613(11)	667(9)	671(9)
H15	789(7)	907(7)	494(6)
H16	788(8)	889(8)	586(7)
H17	911(10)	721(9)	530(8)
H18	925(8)	812(7)	455(6)
H19	953(7)	846(7)	585(5)
H20	970(7)	278(7)	205(6)
H21	839(6)	123(6)	301(5)
H22	786(5)	348(5)	429(4)
H23	933(7)	555(7)	363(6)
H24	1088(8)	500(8)	350(7)
H25	1080(14)	403(13)	381(12)
H26	1015(10)	403(9)	151(8)
H27	982(6)	517(6)	181(5)
H28	652(9)	19(7)	488(7)
H29	740(8)	62(7)	476(6)
H30	840(6)	212(5)	555(5)
H31	744(9)	132(8)	626(8)
H32	394(7)	575(6)	488(5)
H33	920(14)	500(12)	447(11)

In addition, the structures of only a few simple inorganic Zr^{III} species are known [5,6]. In both VI and VII, the bridging chlorine atoms cause an effective Zr^{III}–Zr^{III} spin coupling thus making the complexes diamagnetic.

Unfortunately there is no direct structural data on the dimeric compound $[Cp_2ZrCl]_2$, VIII, which is related to complex VII. Two independent η^5-C_5H_5 ligands in VIII correspond to one bridging fulvalene $\eta^5:\eta^5$-$C_{10}H_8$ moiety in VII. But sufficient physical data are available which confirm that the $[Cp_2ZrCl]_2$ is a symmetrical dimer, with two bridging chlorine atoms and a Zr–Zr bond [7,8].

The sterically crowded complex IV is monomeric in the solid state. Compounds IV and V are paramagnetic in solution and in the solid state, and their magnetic susceptibility is not temperature dependent *.

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* The magnetic study was performed by Dr. O.G. Ellert in the Institute of General and Inorganic Chemistry, Academy of Science of the U.S.S.R. Extreme sensitivity of IV and V towards air and moisture leads to underestimated values for IV, $\mu_{eff} = 1.38$ B.m., IV; for V, $\mu_{eff} = 1.42$ B.m., but the observed values are temperature independent.

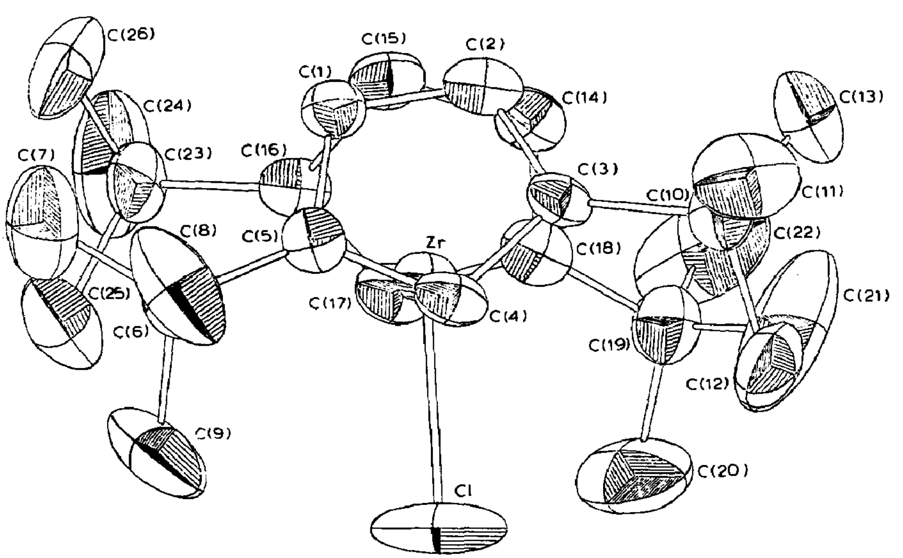

Fig. 1. Molecular structure of $Cp_2^{**}ZrCl$ (IV). Hydrogen atoms are omitted.

The most important geometric parameters of IV are as follows: an average Zr–C bond length of 2.505 Å (2.47–2.55 Å), a Zr–Cl distance of 2.423 Å, a Cp^{**}centroid–Zr–Cp^{**}centroid angle of 133.3°, the angle between the normals to the least squares planes of the Cp^{**} ligands 131.4°.

Complex IV is the first example of a coordinatively and electronically unsaturated Zr^{III} sandwich compound. There are no close valent analogs to be compared with. The average $Zr–C_{Cp}$ distance in IV does not differ from that of many other bis-cyclopentadienyl Zr derivatives, with Zr in different oxidation states [2], but because of the greater atomic radius of Zr far less significant derivations from the planar geometry of Cp^{**} ligands in IV are observed, as compared with the Ti analog $Cp_2^{**}TiCl$ [1]. The quaternary carbon atoms of the t-butyl groups in IV deviate only slightly from the least squares planes of the Cp^{**} rings, the relevant values being: C6, 0.29; C10, 0.25; C23, 0.28; and C19, 0.24 Å (see Table 4).

The Zr–Cl bond distance in IV, 2.423 Å, is the shortest of the known values for the large diversity of Zr organometallics [2]. The shortening of the Zr–Cl distance in IV may be caused by the bonding overlapping of *np*-electron density of the Cl with the vacant AO of the Zr^{III} atom. A similar shortening of the M–Cl distance is also observed in $Cp_2^{**}TiCl$ as compared with $Cp_2^{**}TiCl_2$ [1].

A unique feature of the molecule of IV is the lack of a C_2 axis coinciding with the line Zr–Cl. The Ti compound I does have this symmetry operation. This difference between Zr and Ti compounds can be accounted for in terms of the difference between the atomic radii of Zr and Ti. The Zr molecule is less strained and its t-butyl groups can rotate independently, and the orientation of four t-butyl groups is not symmetrical, as determined from the equilibrium conformation by X-ray diffraction in solid IV. Moreover the Zr–Cp^{**} centroid distances for the two Cp^{**} rings are not equal, 2.202 and 2.198 Å.

In general it is obvious that the use of two η^5-di-t-butylcyclopentadienyl ligands ($= Cp^{**}$) provides sufficient steric bulk to render $Cp_2^{**}MCl$, M = Zr or Hf, monomeric and thus stable in the non-typical oxidation state of +3 for both metals.

Table 4

Deviations of atoms from mean square planes of the Cp rings: (Δ (Å)): a (C1–C5 ring; $1.253x + 8.918y + 10.525z = 3.244$) and b (C14–C18 ring; $9.297x - 2.465y + 9.073z = 10.285$)

a		*b*	
Atom	Δ	Atom	Δ
C1	0.002	C14	−0.004
C2	−0.014	C15	0.012
C3	0.020	C16	−0.016
C4	−0.020	C17	0.014
C5	0.012	C18	−0.007
Zr	−2.202		2.197
Cl	−3.198		3.190
C6	0.29	C23	−0.28
C10	0.25	C19	−0.24
C7	0.09	C26	−0.01
C8	1.69	C24	1.74
C9	−0.65	C25	0.63
C11	1.73	C21	0.68
C12	−0.48	C20	0.10
C13	−0.19	C22	−1.72

Non-bonded intramolecular distances in IV (Å)

C1 ··· C15	3.29
C2 ··· C13	3.03
C2 ··· C14	3.32
C2 ··· C15	3.21

Experimental

X-ray study of IV. The X-ray diffraction study was carried out by use of a DURRUM automatic, Cu-K_λ radiation, graphite monochromator, at room temperature. The structure was determined by direct methods using the "Roentgen 75" program.

Crystals of IV are monoclinic, space group $P2_{1/b}$, $a = 12.722(2)$; $b = 16.336(2)$; $c = 13.426(4)$ Å; $\gamma = 70.68°$; $V = 2633$ Å^3. 2721 unique reflections with $I \geqslant 2\sigma(I)$ were measured up to $\sin\theta/\lambda = 0.626$, no absorption correction was applied. The difference synthesis revealed 33 of the 42 independent hydrogen atoms. The structure was refined anisotropically by full-matrix least squares to $R = 0.065$ for non-hydrogen atoms. Hydrogen atoms were included in the refinement with fixed positional and isotropic thermal parameters.

In Table 1 are listed the most important interatomic distances and bond angles. The atomic coordinates are listed in Tables 2 and 3.

Preparation of complexes II and III

$Cp_2^{**}ZrCl_2$. 110 ml of 2.0 *N* hexane solution of nBuLi (0.22 mol) was added to 30.8 g (0.2 mol) di-t-butylcyclopentadiene in 200 ml benzene. The mixture was cooled to 0 °C,and 100 ml ether was added dropwise with vigorous stirring. Then 23.3 g (0.1 mol) powdered $ZrCl_4$ was added in small portions, and the mixture was stirred for 30 min. The solid residue was separated off, washed with 500 ml cold

pentane and then extracted with boiling toluene. $Cp_2^{**}ZrCl_2$ was obtained as pale greenish-yellow needles. The mother liquor from the reaction slowly gives another crop of the compound after pentane sedimentation. The general yield was 28 g (60%) of II. Found: C, 58.62; H, 7.89; Cl, 13.64. $C_{26}H_{42}ZrCl_2$ calcd.: C, 60.47; H, 8.14; Cl, 13.76%.

^1H NMR (δ, ppm, $CDCl_3$): 1.29 s (36H); 6.02 d (4H); 6.64 t (2H); $J = 2.50$ Hz.

$Cp_2^{**}HfCl_2$. Complex III was obtained as described above for II. The general yield 52%. Found: C, 51.20; H, 6.55; Cl, 11.92; $C_{26}H_{42}HfCl_2$ calcd.: C, 51.74; H, 6.99; Cl, 11.77%.

^1H NMR (δ, ppm, $CDCl_3$): 1.30 s (36H); 5.90 d (4H); 6.42 t (2H); $J = 2.50$ Hz.

Preparation of complexes IV and V

$Cp_2^{**}ZrCl$. A suspension of 4.7 g (10 mmol) of $Cp_2^{**}ZrCl_2$ and 0.40 g (10.3 mmol) of finely divided potassium in 50 ml pentane was stirred vigorously in a sealed Schlenk-type apparatus until the potassium disappeared (15–20 h). The clear solution was separated off, the solvent was evaporated to 10 ml and the solution cooled to −78 °C. The large orange crystals were separated off, washed with cold pentane and dried in vacuo to give IV. Yield 1.2 g (28%). Found: C, 64.22; H, 8.51; Cl, 6.92. $C_{26}H_{42}ZrCl$ calcd.: C, 64.89; H, 8.80; Cl, 7.37%.

$Cp_2^{**}HfCl$. Complex V was obtained as described above for IV. Yield, 34%, as bright yellow crystals. Found: C, 53.50; H, 7.15; Cl, 5.72. $C_{26}H_{42}HfCl$ calcd.: C, 54.93; H, 7.45; Cl, 6.24%.

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