ansa-Metallocene derivatives of Ti^{IV} and Zr^{IV} with the shortest $-C(CH_3)_2-$ bridge

I.E. Nifant'ev, A.V. Churakov

Department of Chemistry, Moscow University, Moscow, 119899 (Russia)

I.F. Urazowski, Sh.G. Mkoyan and L.O. Atovmyan

Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432 (Russia)

(Received January 8, 1992)

Abstract

Novel $-C(CH_3)_2-$ bridged molecules, $(CH_3)_2C(C_5H_4)_2M(CH_3)_2$, M = Ti, Zr, were synthesized. The structures of both molecules were determined by X-ray diffraction analysis. For the Ti compound: crystals, monoclinic; space group, $P2_1/m$, $a = 7.196(4)$, $b = 10.227(1)$, $c = 8.941(3)$ Å, $\gamma = 89.95°$. For Zr compound: crystals, monoclinic; space group $P2_1/m$, $a = 7.333(4)$, $b = 10.429(3)$, $c = 9.031(6)$ Å, $\gamma = 89.98°$. Both molecules are characterized, as expected, by significant intramolecular tension resulting in obvious distortion of the sandwich moiety.

Introduction

ansa-Metallocene derivatives of early transition metals, *i.e.* Ti, Zr, and Hf, are of interest because of their unusual and specific activity as components of Ziegler–Natta polymerization catalysts (see for example ref. 1). Synthesis of particular compounds with the given bridge is a challenge for every practicing organo-metallic chemist. Recently several unusual molecules were obtained and characterized structurally (see ref. 2 and refs. therein).

Insertion of a rigid and/or very short bridge between the Cp-rings of a metallocene moiety will undoubtedly lead to severe distortion of its "normal" geometry. It may result in change of the electronic configuration of the central metal atom and the character of π-bonding of the Cp-ligands. Brintzinger and his co-workers [3] were first to admit the real possibility of a "splitting" of the η^5-system into a combination of η^2- and η^3-bonds within a single CpM moiety, when analysing the structure of a methylene-bridged titanocene dichloride

Correspondence to: Dr. I.E. Nifan'ev, Department of Chemistry, Moscow University, Moscow, 119899, Russia; or Dr. I.F. Urazowski, Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia.
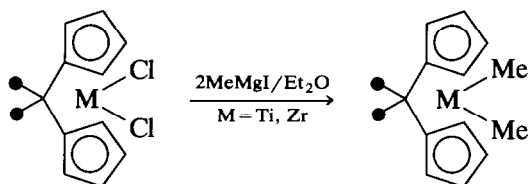
Scheme 1.

molecule, $CH_2(C_5H_4)_2TiCl_2$. The X-ray diffraction data obtained in [3] were not, however, accurate enough to prove such an assumption. The said splitting of the η^5-Cp ligand system was also admitted by the authors in a structural investigation of $-Si(CH_3)_2-$ bridged $(CH_3)_2Si(C_5H_4)_2MCl_2$, M=Ti, Zr [4].

In this paper, we present the synthesis and results of an X-ray diffraction structural study of two $-(CH_3)_2C-$ bridged *ansa*-metallocene derivatives, $(CH_3)_2C(C_5H_4)_2M(CH_3)_2$, M=Ti (I) and M=Zr (II).

Results and discussion

The title compounds were obtained from the corresponding dichloride complexes (see Scheme 1). Synthesis of the dichlorides is described elsewhere [5]. Both dimethyl derivatives are readily soluble in every organic solvent including pentane; they are relatively stable towards water and dry air. In a moist atmosphere, they are slowly degraded. The Ti compound is much more stable than its analog $(C_5H_5)_2Ti(CH_3)_2$ towards natural light and heating. Crystals of I and II suitable for X-ray study were obtained from pentane solution.

The general view of compound I is given in Fig. 1. The results of the structural study of I and II are indicative of a significant intramolecular tension, characteris-
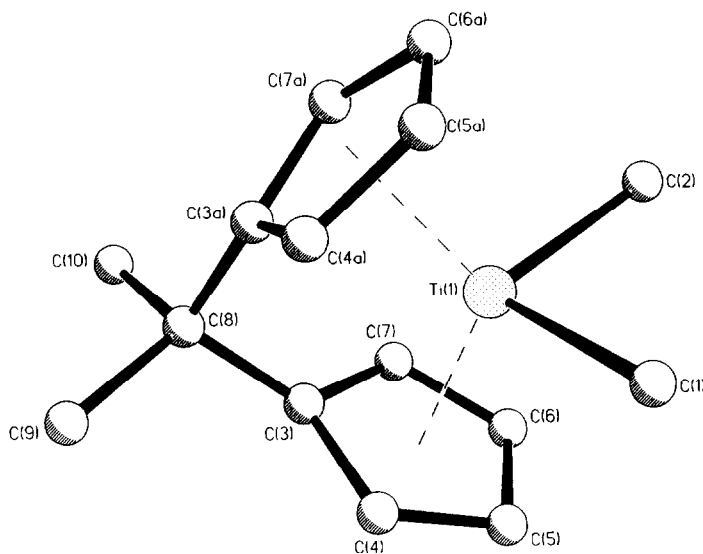

Fig. 1. Molecular structure of I.

Table 1

Atomic coordinates in I

Atom	x	y	z
Ti(1)	0.6938(1)	0.3133(0)	0.2500(0)
C(2)	0.8073(4)	0.5094(4)	0.2500(1)
C(3)	0.4085(5)	0.3798(5)	0.2500(1)
C(4)	0.8142(6)	0.1314(4)	0.1254(4)
C(5)	0.9122(6)	0.2443(5)	0.0702(2)
C(6)	0.7925(5)	0.3264(4)	−0.0081(4)
C(7)	0.6155(5)	0.2654(5)	−0.0069(4)
C(8)	0.6270(5)	0.1491(6)	0.0714(3)
C(9)	0.8709(6)	0.0474(5)	0.2500(1)
C(10)	1.0866(6)	0.0204(4)	0.2500(1)
C(11)	0.7731(6)	−0.0874(5)	0.2500(1)

tic of both complexes, I and II. This is obvious from the distortion of the angle C(4)–C(9)–C(12) by the C(9) bridge atom, normally tetrahedral, which is 99° for I and 99.4° for II (see Table 4). This value coincides with that observed for $CH_2(C_5H_4)_2TiCl_2$ (III), namely 99° (96°) [3]. The deviation of the bridge C–C bond lines from the mean planes of the corresponding Cp rings is also significant. This value is 17.1° for I and 13.7° for II, in comparison with 16° for III (see Table 5).

The displacements of the central metal atoms from the intersection point of two perpendiculars dropped from the centroids of the C_5H_4-ring (the position which may be regarded as ideal and observed for example in $(C_5H_5)_2TiCl_2$ [6]) are substantial: 0.28 Å for I and 0.447 Å for II and accompanied by a change in the M–C ring distances in I and II. Notwithstanding the obvious deformation of the normal bent sandwich geometry of the $(C_5H_4)_2M$ fragments characteristic of complexes Cp_2MX_2 (where Cp are C_5H_5 or a substituted cyclopentadienyl and X is any σ-ligand), the ring geometry is unaffected and quite typical of this structural class. The rings in I and II are practically plane, the standard deviations of the C atoms from the mean planes are in the range of 0.016 Å for I, and 0.0213 Å for II (Table 6).

Table 2

Atomic coordinates in II

Atom	x	y	z
Zr(1)	0.6834(0)	0.3202(0)	0.2500(0)
C(2)	0.3827(4)	0.3756(3)	0.2500(0)
C(3)	0.8155(3)	0.5152(4)	0.2500(1)
C(4)	0.8111(3)	0.1324(3)	0.3791(4)
C(5)	0.6287(5)	0.1480(3)	0.4335(3)
C(6)	0.6196(4)	0.2565(5)	0.5197(5)
C(7)	0.7887(4)	0.3142(3)	0.5212(4)
C(8)	0.9076(3)	0.2376(4)	0.4318(3)
C(9)	0.8699(5)	0.0463(5)	0.2500(1)
C(10)	1.0744(4)	0.0214(5)	0.2496(3)
C(11)	0.7702(6)	−0.0816(6)	0.2500(1)

Table 3

Bond lengths in I and II (in Å)

C₁₅H₂₀Ti (I)		C₁₅H₂₀Zr (II)	
Ti(1)–C(2)	2.166(2)	Zr(1)–C(2)	2.270(1)
Ti(1)–C(3)	2.162(2)	Zr(1)–C(3)	2.667(2)
Ti(1)–C(4)	2.334(2)	Zr(1)–C(4)	2.452(2)
Ti(1)–C(5)	2.356(3)	Zr(1)–C(5)	2.482(2)
Ti(1)–C(6)	2.418(2)	Zr(1)–C(6)	2.570(3)
Ti(1)–C(7)	2.415(3)	Zr(1)–C(7)	2.568(4)
Ti(1)–C(8)	2.367(2)	Zr(1)–C(8)	2.467(4)
C(4)–C(5)	1.441(5)	C(4)–C(5)	1.431(5)
C(4)–C(8)	1.442(8)	C(4)–C(8)	1.400(5)
C(5)–C(6)	1.391(6)	C(5)–C(6)	1.374(6)
C(6)–C(7)	1.419(6)	C(6)–C(7)	1.388(6)
C(7)–C(8)	1.383(5)	C(7)–C(8)	1.423(5)
C(9)–C(4)	1.465(6)	C(9)–C(4)	1.441(6)
C(9)–C(10)	1.576(6)	C(9)–C(10)	1.441(4)
C(9)–C(11)	1.548(6)	C(9)–C(11)	1.441(6)

Table 4

Valency angles in I and II (in °)

C₁₅H₂₀Ti (I)		C₁₅H₂₀Zr (II)	
gc Cp–Ti(1)–gc Cp*	120.9(1)	gc Cp Zr(1)–gc Cp*	115.9(1)
C(2)–Ti(1)–C(3)	93.9(4)	C(2)–Zr(1)–C(3)	101.6(4)
C(4)–C(5)–C(6)	110.7(5)	C(4)–C(5)–C(6)	108.6(5)
C(5)–C(6)–C(7)	106.6(6)	C(5)–C(6)–C(7)	109.4(6)
C(6)–C(7)–C(8)	109.2(6)	C(6)–C(7)–C(8)	107.1(6)
C(7)–C(8)–C(4)	109.4(5)	C(7)–C(8)–C(4)	108.7(5)
C(8)–C(4)–C(5)	104.0(5)	C(8)–C(4)–C(5)	106.2(5)
C(10)–C(9)–C(4)	112.1(5)	C(10)–C(9)–C(4)	111.5(5)
C(10)–C(9)–C(11)	107.0(6)	C(10)–C(9)–C(11)	109.7(6)
C(11)–C(9)–C(12)	113.3(6)	C(11)–C(9)–C(12)	112.1(6)
C(4)–C(9)–C(12)	99.0(6)	C(4)–C(9)–C(12)	99.4(6)

Table 5

The geometry of the sandwiches I and II

C₁₅H₂₀Ti (I)		C₁₅H₂₀Zr (II)	
Cp–Ti(1)–Cp gc	7.5(2)	Cp–Zr(1)–Cp gc	9.3(2)
Cp–Cp*	64.9(2)	Cp–Cp*	72.14(2)
C(9)–C(4)–Cp	17.1(2)	C(9)–C(4)–Cp	13.65(2)

The ring bond distances are 1.38–1.44 Å for I and 1.37–1.43 Å for II (see Tables 3 and 4). Only the angle C(8)–C(4)–C(5) by the C(4) atom of the ring bound to the bridge in I is somewhat smaller than the other ring angles, which may be due to an increase of the *p*-character of the C(4)–C(8) and C(4)–C(5) bonds. This is corroborated by lengthening of the C(4)–C(8) and C(4)–C(5) bond distances and shortening of the C(4)–C(9) bond distance of the bridge; the last is

Table 6

Deviations of the carbon atoms from the ring plane (in Å)

$C_{15}H_{20}Ti$ (I)		$C_{15}H_{20}Zr$ (II)	
C(4)	0.0080(2)	C(4)	−0.0117(2)
C(5)	−0.0080(2)	C(5)	0.0096(1)
C(6)	0.0048(2)	C(6)	−0.0038(2)
C(7)	0.0005(2)	C(7)	−0.0037(1)
C(8)	−0.0053(2)	C(8)	0.0096(2)

Table 7

Crystallographic data for I and II

	$C_{15}H_{20}Ti$ (I)	$C_{15}H_{20}Zr$ (II)
a (Å)	7.196(4)	7.333(4)
b (Å)	10.227(7)	10.429(3)
c (Å)	8.941(3)	9.031(6)
γ (°)	89.95(2)	89.98(2)
V (Å^3)	657.8	690.5
MW	247.9	291.2
d (g/cm^3)	1.36	1.41
Z	2	2
Spatial group	$P2_1/m$	$P2_1/m$
Independent reflections with $I > 3\sigma$	1236	862
Diffractometer	DAR-UM	KM-4
Radiation	Cu-K_α	Mo-K_α graphite
Scan	$5° < \theta < 50°$	$8° < \theta < 43°$
Solution method	Direct	Direct
Refinement	Full-matrix anisotropic	Full-matrix anisotropic
Program	Roentgen-75 [8]	AREN-85 [9]
R_f	0.06	0.04

indicative of the greater *s*-character of this bond on the part of the C(4) atom in I. In molecule II, the corresponding shortening is not observed, and the ring angle value by the C(4) atom is nearer to the average than in I. In contrast to the data obtained for $CH_2(C_5H_4)_2TiCl_2$ [3] and $(CH_3)_2Si(C_5H_4)_2MCl_2$, M = Ti, Zr [4], we did not observe shortening of the C(5)–C(7) bond distances in the rings of both I and II, although there was a substantial lengthening of the M–C(6) and M–C(7) bonds, compared to the average M–C_{ring} distances in I and II. This effect can be accounted for if we compare the σ-donating capacity of –Cl and –CH$_3$ ligands. Substitution of –Cl for –CH$_3$ by the central metal atoms undoubtedly led to an increase in electron density on the Cp-rings in I and II compared with that in the dichloride complexes III and $(CH_3)_2Si(C_5H_4)_2MCl_2$ which resulted in an increase in the ionic character of the metal–ring bond and inevitably led to a more obvious likeness of the ring geometry to the geometry of cyclopentadienyl anion.

Experimental

The reactions were performed in sealed glass evacuated vessels of the Schlenk type. The complexes $(CH_3)_2C(C_5H_4)_2MCl_2$ (M = Ti, Zr) were prepared from

MCl$_4$ and dicyclopentadienyldimethylmethane [7] as described in the literature [5]. The ^{1}H NMR spectra were recorded on a Varian VXR-400 spectrometer. The elemental analysis was performed on a Carlo–Erba analyzer. The crystallographic data for I and II are given in Table 7. Hydrogen atom coordinates in I were found from differential Fourier synthesis and only their positional parameters were refined. For II all the hydrogen atoms were included with fixed positional and isotropic thermal parameters in the refinement.

Synthesis of (CH$_3$)$_2$C(C$_5$H$_4$)$_2$M(CH$_3$)$_2$, M = Ti (I) Zr (II)

One millimole of corresponding dichloride compound in 20 ml of dry ether was vigorously stirred under reflux with a 2-fold excess of CH$_3$MgI. After dissolving all the dichloride complex, the solvent was removed and the residue extracted with pentane. The product was recrystallized from pentane. The yield of dark yellow I was 81% and of yellowish II 73% of theoretical.

I: ^{1}H(toluene-d_8): δ 6.5(m, 4H); 4.5(m, 4H); 1.1(s, 6H); 0.3(s, 6H). Anal. Found: C, 72.52; H, 7.91. Calc.: C, 72.59; H, 8.12%.

II: ^{1}H(toluene-d_8): δ 6.7(m, 4H); 4.6(m, 4H); 1.1(s, 6H); 0.2(s, 6H). Anal. Found: C, 61.85; H, 6.96. Calc.: C, 61.81; H, 6.91%.

References

1 J.A. Ewen, R.L. Jones and A. Razavi, J. Am. Chem. Soc., 110 (1988) 6255; T. Mise, S. Miaya and H. Yamazaki, Chem. Lett., (1989) 1853; W. Röll, H.H. Brintzinger, B. Rieger and R. Zolk, Angew. Chem., 102 (1990) 339.
2 P. Burger and H.H. Brintzinger, J. Organomet. Chem., 407 (1991) 207.
3 J.A. Smith, J. von Seyerl, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 173 (1979) 175.
4 C. Bajgur, W.R. Tikkanen and J.L. Petersen, Inorg. Chem., 24 (1985) 2539.
5 I.E. Nifant'ev, K.A. Butakov, Z.G. Aliev and I.F. Urazowski, Metalloorg. Khim., 4 (1991) 1265.
6 V.V. Tkachov and L.O. Atovmyan, Zh. Struct. Khim., 13 (1972) 287.
7 I.E. Nifant'ev, V.L. Yarnykh, M.V. Borzov, B.A. Mazurchic, V.I. Mstislavsky, V.A. Roznyatovsky and Yu.A. Ustynyuk, Organometallics, 10 (1991) 3739.
8 V.I. Andrianov, Z.Sh. Safina and B.L. Tarnopolskii, Zh. Struct. Khim., 15 (1974) 911.
9 V.I. Andrianov, Crystallographia, 32 (1987) 228.