Journal of Organometallic Chemistry, 340 (1988) 179–185
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Organotitanium chemistry

VIII *. X-Ray crystal structures of bis(cyclopentylcyclopentadienyl)titanium dichloride and bis(cyclohexylcyclopentadienyl)titanium dichloride

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(Received January 26th, 1987; in revised form August 10th, 1987)

Abstract

The crystal structures of bis(cyclopentylcyclopentadienyl)titanium dichloride and bis(cyclohexylcyclopentadienyl)titanium dichloride have been determined by X-ray diffraction and refined to conventional *R* factors of 0.0345 for 1191 reflections and 0.0818 for 1481 reflections, respectively.

Introduction

Transition metal organometallic chemistry is becoming a powerful tool in synthetic organic chemistry. A large number of organometallic compounds containing such metals as Fe, Ni, Cu, Zr and Ti are being used for organic synthesis both as catalysts and stoichiometric reagents. Now chemists pay more attention to organotitanium compounds because they are cheap and relatively easy to prepare. It was found that the low-valent Ti system formed from Cp_2TiCl_2/reducing-agent is an effective catalyst for many reactions [1,2], such as polymerization, oligomeriza-

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* For Part VII, see ref. 7.

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tion, isomerization, hydrogenation of olefins, and N_2 fixation. Recently a series of organotitanium compounds with substituted cyclopentadienyl ligands have been prepared, and the effect of substitution on the catalytic activities and selectivities have been studied by our group [3]. In this paper we wish to report the crystal structures of bis(cyclopentylcyclopentadienyl)titanium dichloride (I), and bis(cyclohexylcyclopentadienyl)titanium dichloride (II).

Experimental

Preparation

(cyclo-$C_5H_9Cp)_2TiCl_2$ (I) was prepared by the reaction of cyclo-$C_5H_9Cp^- Li^+$ and $TiCl_4$ in THF at room temperature, under argon. The lithium salt was prepared from the fulvene, cyclopentylenecyclopentadiene, and $LiAlH_4$.

I : M.p. 197–198°C. (Found: C, 62.32; H, 7.8; Ti, 12.56; Cl, 18.09. $C_{20}H_{26}Cl_2Ti$ calcd.: C, 62.35; H, 6.75; Ti, 12.44; Cl, 18.44%.) [4].

(cyclo-$C_6H_{11}Cp)_2TiCl_2$ (II) was prepared in the same way.

II: M.p. 252–253°C. (Found: C, 64.13; H, 7.25; Ti, 11.51; Cl, 17.77. $C_{22}H_{30}Cl_2Ti$ calcd.: C, 63.94; H, 7.26; Ti, 11.60; Cl, 17.19%.) [4].

Table 1

Crystal data and experimental details

Compound	I	II
Formula	$C_{20}H_{26}Cl_2Ti$	$C_{22}H_{30}Cl_2Ti$
M_r	385.23	413.29
Colour/habit	red/plates	red/plates
Size (mm)	0.15×0.25×0.2	0.15×0.3×0.6
Crystal system	monoclinic	triclinic
Systematic absences	$0k0$; $k=2n+1$	
Space group	$P2_1$	$P1$
a (Å)	6.584(2)	6.679(3)
b (Å)	24.011(7)	6.743(4)
c (Å)	6.713(1)	13.772(8)
α (°)		81.76(5)
β (°)	118.70(2)	76.26(4)
γ (°)		60.15(4)
V (Å^3)	930.9(5)	522.3(5)
Z	2	1
D_c (g/cm^3)	1.37	1.31
μ(Mo-K_α) (cm^{-1})	7.6	6.8
$F(000)$	404	218
Scan method	θ–2θ	θ–2θ
Max. 2θ (°)	50	48
Scan rate (° min^{-1})	4–30	4–30
Number of observed reflections	1191 $I > 1.96\sigma(I)$	1481 $I > 2.50\sigma(I)$
R	0.0345	0.0818
R_w	0.0356	0.0872
$w = 1/\sigma^2(F)$		
GOF	0.790	1.041

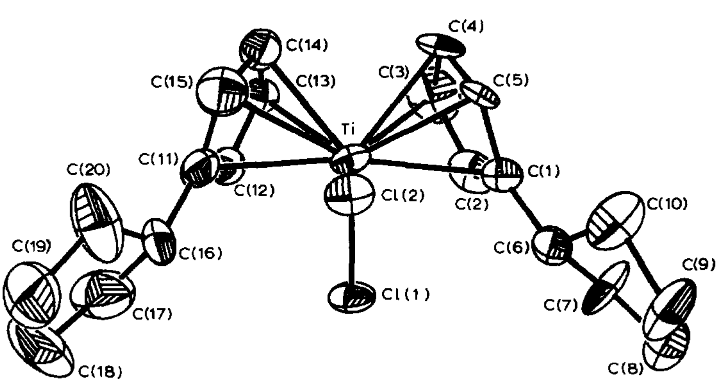
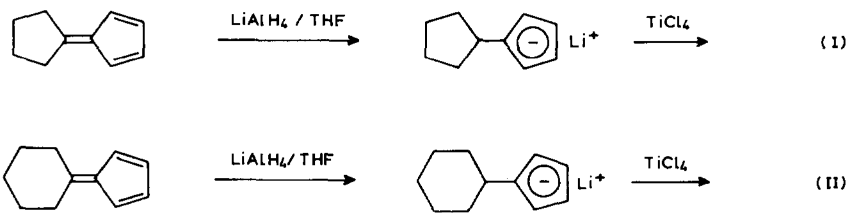


Fig. 1. The molecular structure of I.



Structure solution and refinement

The crystals of both compounds were obtained by recrystallization from $CHCl_3$. Diffraction intensities were recorded with a Syntex P3/R3 four-circle diffractometer, using Mo-K_α radiation with a graphite monochromator, 0.71069 Å. The crystal

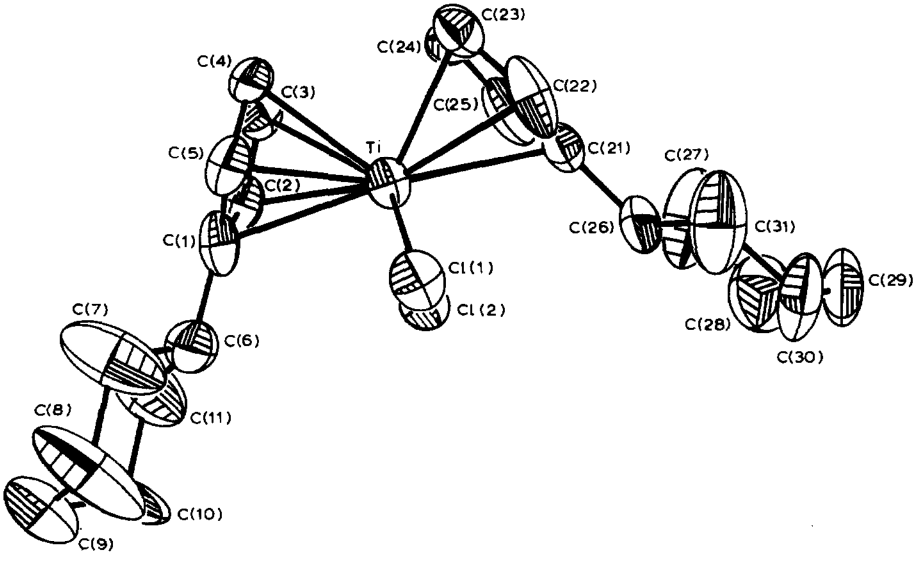


Fig. 2. The molecular structure of II.

Table 2. Positional $(\times 10^4)$ and thermal $(\times 10^3)$ parameters for I (U_{eq} defined as 1/3 of the trace of the orthogonalized U tensor)

Atom	x	y	z	U_{eq}
Ti	8879(1)	0	12856(1)	31(1)
Cl(1)	5921(3)	−4(3)	3897(3)	44(1)
Cl(2)	1838(2)	4(3)	6696(2)	42(1)
C(1)	8888(10)	−1012(3)	3304(9)	34(2)
C(2)	6884(13)	−852(4)	1268(14)	54(4)
C(3)	7669(19)	−585(4)	−199(13)	75(5)
C(4)	10225(10)	−614(3)	1019(11)	40(3)
C(5)	10774(9)	−853(3)	2967(9)	28(2)
C(6)	8900(20)	−1317(5)	5251(18)	44(5)
C(7)	11051(15)	−1668(4)	6626(14)	68(4)
C(8)	10307(20)	−1990(4)	8203(14)	79(5)
C(9)	7691(28)	−2059(8)	6748(30)	84(8)
C(10)	6954(15)	−1718(4)	4597(16)	71(4)
C(11)	8989(15)	1012(3)	3210(12)	52(4)
C(12)	6996(11)	865(3)	1196(11)	39(3)
C(13)	7595(11)	630(3)	−261(10)	35(3)
C(14)	9849(15)	609(4)	727(13)	53(4)
C(15)	10978(14)	842(4)	3092(14)	62(4)
C(16)	9086(25)	1259(6)	5323(25)	57(7)
C(17)	11160(19)	1598(4)	6769(16)	96(5)
C(18)	10664(32)	1992(10)	8139(31)	110(10)
C(19)	8084(33)	2020(10)	7152(29)	119(10)
C(20)	7194(32)	1668(9)	4974(31)	95(9)

Table 3. Positional $(\times 10^4)$ and thermal $(\times 10^3)$ parameters for II (U_{eq} defined as 1/3 of the trace of the orthogonalized U tensor)

Atom	x	y	z	U_{eq}
Ti	0	0	0	41(1)
Cl(1)	−3894(6)	2949(5)	23(2)	52(1)
Cl(2)	−940(6)	−2942(6)	−25(3)	51(1)
C(1)	389(24)	492(22)	−1835(8)	55(6)
C(2)	636(24)	2115(25)	−1464(9)	53(6)
C(3)	2652(26)	1107(31)	−1037(10)	61(8)
C(4)	3604(20)	−1318(23)	−1106(9)	49(6)
C(5)	2289(22)	−1649(23)	−1587(9)	53(6)
C(6)	−1449(24)	850(25)	−2379(10)	62(8)
C(7)	−2205(39)	3017(28)	−3015(16)	118(13)
C(8)	−4202(45)	3385(38)	−3514(19)	156(18)
C(9)	−3255(37)	1484(27)	−4241(12)	89(10)
C(10)	−2656(50)	−660(43)	−3576(19)	136(19)
C(11)	−581(37)	−1131(29)	−3058(14)	101(12)
C(21)	−940(21)	−461(21)	1844(8)	47(6)
C(22)	1409(31)	−2149(22)	1461(10)	67(8)
C(23)	2738(24)	−1104(25)	1048(10)	57(7)
C(24)	1169(28)	1340(24)	1127(9)	56(7)
C(25)	−974(34)	1602(20)	1621(9)	71(8)
C(26)	−3006(25)	−850(25)	2391(9)	64(8)
C(27)	−2201(39)	−3077(27)	3020(14)	116(11)
C(28)	−4294(40)	−3434(39)	3539(18)	116(15)
C(29)	−6043(35)	−1525(34)	4244(11)	101(12)
C(30)	−6874(33)	696(37)	3633(13)	97(11)
C(31)	−4927(35)	1168(30)	3047(13)	111(11)

Table 4

Selected bond lengths and angles in I

Bond lengths (Å)			
Ti-Cl(1)	2.364(2)	Ti-Cl(2)	2.370(1)
Ti-C(1)	2.448(6)	Ti-C(11)	2.440(7)
Ti-C(2)	2.387(9)	Ti-C(12)	2.402(7)
Ti-C(3)	2.290(9)	Ti-C(13)	2.384(6)
Ti-C(4)	2.351(8)	Ti-C(14)	2.338(10)
Ti-C(5)	2.381(6)	Ti-C(15)	2.412(9)
C(1)-C(2)	1.423(8)	C(11)-C(12)	1.404(9)
C(2)-C(3)	1.461(16)	C(12)-C(13)	1.342(12)
C(3)-C(4)	1.478(13)	C(13)-C(14)	1.304(11)
C(4)-C(5)	1.310(9)	C(14)-C(15)	1.501(11)
C(5)-C(1)	1.418(10)	C(15)-C(11)	1.410(15)
C(1)-C(6)	1.494(15)	C(11)-C(16)	1.509(20)
C(6)-C(7)	1.521(14)	C(16)-C(17)	1.482(16)
C(7)-C(8)	1.567(17)	C(17)-C(18)	1.462(27)
C(8)-C(9)	1.527(19)	C(18)-C(19)	1.500(28)
C(9)-C(10)	1.523(21)	C(19)-C(20)	1.540(28)
C(10)-C(6)	1.490(16)	C(20)-C(16)	1.515(27)
Ti-Cp(1)	2.043	Ti-Cp(2)	2.080
Bond angles (°)			
Cl(1)-Ti-Cl(2)	92.4(1)	C(7)-C(8)-C(9)	104.1(10)
Cl(1)-Ti-Cp(1)	105.6	C(8)-C(9)-C(10)	107.2(14)
Cl(1)-Ti-Cp(2)	106.6	C(9)-C(10)-C(6)	103.4(9)
Cl(2)-Ti-Cp(1)	105.8	C(11)-C(16)-C(17)	116.2(14)
Cl(2)-Ti-Cp(2)	106.2	C(11)-C(16)-C(20)	116.7(11)
Cp(1)-Ti-Cp(2)	132.9	C(16)-C(17)-C(18)	110.8(14)
C(1)-C(6)-C(7)	114.5(11)	C(17)-C(18)-C(19)	107.4(15)
C(1)-C(6)-C(10)	114.6(7)	C(18)-C(19)-C(20)	103.2(19)
C(7)-C(6)-C(10)	103.8(9)	C(19)-C(20)-C(16)	107.5(13)
C(6)-C(7)-C(8)	100.5(9)	C(17)-C(16)-C(20)	100.1(12)

data and experimental details are listed in Table 1. The intensities were corrected for Lorentz and polarization effects but not for absorption effects.

Both structures were solved readily by the direct method (SOLV instruction of SHELXTL 4.0 program system), and refined by full-matrix block least squares. The hydrogen atoms were introduced into calculated positions (C-H 0.96 Å). Final refinement reduced *R* to 0.0345 for I, and to 0.0818 for II, respectively.

Results and discussion

The molecular structures of compounds I and II are shown in Fig. 1 and 2. Atomic coordinates and temperature factors are listed in Tables 2 and 3 and important bond lengths and angles are listed in Tables 4 and 5, respectively. Hydrogen atomic coordinates and structure factors are available from the authors.

The molecular structure of compound I and II is very similar to that of Cp_2TiCl_2 [5]. For Cp_2TiCl_2, the five carbon atoms in a cyclopentadienyl are equivalent, there is only one single peak, δ 119.7 ppm, in the ^{13}C NMR spectrum. The difference between the longest Ti-C(Cp) bond and the shortest minimum in the same ring is

Table 5

Selected bond lengths and angles in II

Bond lengths (Å)			
Ti–Cl(1)	2.356(3)	Ti–Cl(2)	2.367(5)
Ti–C(1)	2.469(11)	Ti–C(21)	2.481(10)
Ti–C(2)	2.377(14)	Ti–C(22)	2.396(14)
Ti–C(3)	2.354(19)	Ti–C(23)	2.360(16)
Ti–C(4)	2.328(11)	Ti–C(24)	2.349(19)
Ti–C(5)	2.391(12)	Ti–C(25)	2.424(13)
C(1)–C(2)	1.366(26)	C(21)–C(22)	1.427(17)
C(2)–C(3)	1.404(22)	C(22)–C(23)	1.368(28)
C(3)–C(4)	1.438(24)	C(23)–C(24)	1.450(19)
C(4)–C(5)	1.323(24)	C(24)–C(25)	1.365(27)
C(5)–C(1)	1.436(16)	C(25)–C(21)	1.371(22)
C(1)–C(6)	1.489(24)	C(21)–C(26)	1.532(23)
C(6)–C(7)	1.506(23)	C(26)–C(27)	1.530(22)
C(7)–C(8)	1.539(43)	C(27)–C(28)	1.528(38)
C(8)–C(9)	1.519(32)	C(28)–C(29)	1.512(27)
C(9)–C(10)	1.519(30)	C(29)–C(30)	1.514(27)
C(10)–C(11)	1.581(44)	C(30)–C(31)	1.511(33)
C(11)–C(6)	1.525(26)	C(31)–C(26)	1.542(19)
Ti–Cp(1)	2.069	Ti–Cp(2)	2.088
Bond angles (°)			
Cl(1)–Ti–Cl(2)	93.8(1)	C(7)–C(8)–C(9)	109.0(17)
Cl(1)–Ti–Cp(1)	106.7	C(8)–C(9)–C(10)	104.1(17)
Cl(1)–Ti–Cp(2)	106.4	C(9)–C(10)–C(11)	109.1(26)
Cl(2)–Ti–Cp(1)	106.6	C(10)–C(11)–C(6)	108.3(15)
Cl(2)–Ti–Cp(2)	106.6	C(21)–C(26)–C(27)	112.1(13)
Cp(1)–Ti–Cp(2)	130.6	C(21)–C(26)–C(31)	112.7(16)
C(1)–C(6)–C(7)	111.9(18)	C(27)–C(26)–C(31)	109.9(12)
C(1)–C(6)–C(11)	111.5(12)	C(26)–C(27)–C(28)	110.8(16)
C(7)–C(6)–C(11)	107.8(14)	C(27)–C(28)–C(29)	111.3(23)
C(6)–C(7)–C(8)	110.0(21)	C(29)–C(30)–C(31)	114.6(15)
C(30)–C(31)–C(26)	112.1(18)	C(28)–C(29)–C(30)	107.6(14)

small, 0.05 Å. But for $(RCp)_2TiCl_2$, the substituent destroys the symmetry of the cyclopentadienyl ring, and the five carbon atoms in it become unequal, so that its extent of bonding to the titanium atom also becomes unequal. This inequivalence must reduce the bonding strength between the whole cyclopentadienyl ring and the titanium atom. Inequivalence becomes more pronounced the larger the size of the substituent, and the weaker the bonding strength. This inequivalence property is manifested by the unequal chemical shifts in the ^{13}C NMR spectrum, or from the difference between the longest Ti–C(Cp) bond and the shortest in the same cyclopentadienyl ring. This difference is 0.13 for I, and 0.14 Å for II, respectively. The chemical shifts in ^{13}C NMR are δ 143.34, 120.45, 115.72 for I, and 145.05, 119.52, 115.67 ppm ($CDCl_3$, 90 MHz) for II. It has been observed that the compound with a bulky substituent, such as bis(menthylcyclopentadienyl)titanium dichloride or bis(neomenthylcyclopentadienyl)titanium dichloride, has low stability in the reaction system and its ligands are reduced and are readily dissociated by the reducing-agent cocatalyst. This is the main reason why low enantiomeric excesses of $(menCp)_2TiCl_2$ or $(neomenCp)_2TiCl_2$ are used as the catalyst [6].

Acknowledgements

Financial assistance from the National Science Fund of China is gratefully accepted.

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