

Structures of bis(cyclopentadienyl) binuclear titanium complexes

Sh. G. Mkoyan,^{a*} Z. G. Aliev,^a I. F. Urazovskii,^a L. O. Atovmyan,^a I. E. Nifant'ev,^b and K. A. Butakov^b

^aInstitute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.

Fax: 007 (096) 515 3588. E-mail: shaen@icp.ac.ru; iu@icp.ac.ru

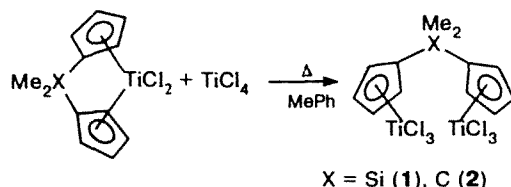
^bDepartment of Chemistry, M. V. Lomonosov Moscow State University,
Vorob'evy Gory, 119899 Moscow, Russian Federation.

Fax: 007 (095) 939 5546

The $(C_5H_4-XMe_2-C_5H_4) \cdot (TiCl_3)_2$ binuclear complexes, where X = Si (1) or C (2), have been studied by X-ray structural analysis. In both structures, the coordination polyhedra about the Ti atoms are distorted tetrahedra formed by three Cl atoms and one Cp ring. The conformations of molecules 1 and 2 and the possibility of the occurrence of secondary Ti—Cp...Cl—Ti interaction are discussed.

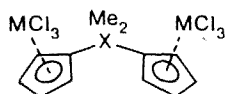
Key words: titanium, cyclopentadienyl binuclear complex, conformation, molecular and crystal structure.

Previously,¹ we have reported the synthesis of binuclear titanium complexes with bis(cyclopentadienyl) ligands, and we have suggested the structure of the $(C_5H_4-SiMe_2-C_5H_4) \cdot (TiCl_3)_2$ compound (1).



With the aim of elucidating the structural features of the binuclear complexes obtained, we have carried out a comparative X-ray structural study of compounds 1 and 2, which differ (taking into account the radii of the Si and C atoms) in the sizes of the bis(cyclopentadienyl) ligands. Crystals of 1 and 2 are isostructural. Overall views of molecules 1 and 2 are shown in Fig. 1.

For complexes 1 and 2, a conformation with metal atoms in *cis* orientations with respect to the bridging fragment (with C_s molecular symmetry) should be, apparently, energetically more favorable as, for instance, in the $SiMe_2[CpMo(CO)_3Cl]_2$ molecule,^{2,3} in which each Mo atom is in an *exo* position with respect to the Cp—Si—Cp fragment.



However, in the crystals the molecules adopt unsymmetrical twist conformations with different orientations of the cyclopentadienyl fragments with respect to the XMe_2 bridge (see Fig. 1).

The orientations of the Cp rings are characterized by the Newman projections along the Si—C(1) and Si—C(6) bonds that are shown in Scheme 1 (*a* and *b*, respectively); the values of the analogous angles for compound 2 are given in brackets.

The dihedral angles between the planes of the Cp rings are 74° and 73° in molecules 1 and 2, respectively. Therefore, the Cp(1) ring, C(1)—C(5), is symmetrically oriented with respect to the two methyl groups, whereas the Cp(2) ring, C(6)—C(10), is twisted about the Si—C(6) bond relative to the $Me_2SiC(11)C(12)$ fragment by ~50°. The two $TiCl_3$ groups are also in different orientations with respect to the Cp rings. The Ti(1) atom lies above the Cp(1) plane on the same side on which the

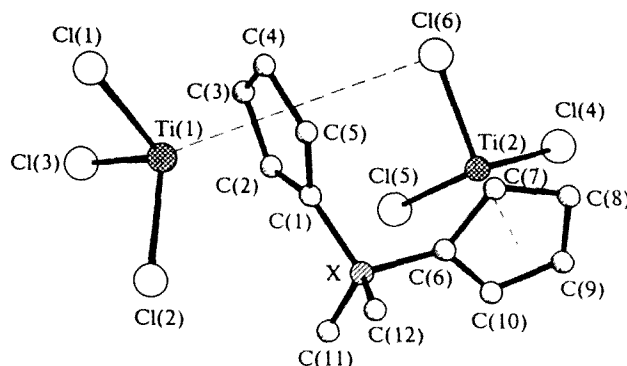
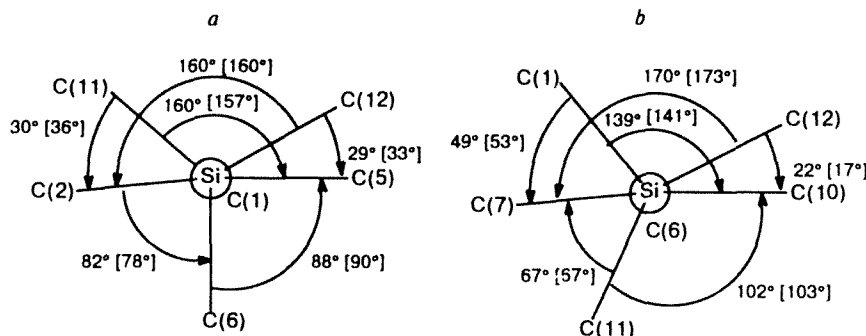


Fig. 1. Structure of the $(C_5H_4-XMe_2-C_5H_4) \cdot (TiCl_3)_2$ molecule, where X = Si (1) or C (2).

Scheme 1

Table 1. Bond lengths (*d*) in the structures of **1** and **2**

Bond	<i>d</i> /Å		Bond	<i>d</i> /Å		Bond	<i>d</i> /Å	
	1	2		1	2		1	2
Ti(1)—Cl(1)	2.217(3)	2.199(9)	Ti(1)—C(5)	2.359(8)	2.42(2)	C(1)—C(2)	1.40(1)	1.40(2)
Ti(1)—Cl(2)	2.220(3)	2.20(1)	Ti(2)—C(6)	2.319(9)	2.42(1)	C(1)—C(5)	1.40(1)	1.36(2)
Ti(1)—Cl(3)	2.196(4)	2.20(1)	Ti(2)—C(7)	2.317(8)	2.36(1)	C(2)—C(3)	1.42(1)	1.43(2)
Ti(2)—Cl(4)	2.238(3)	2.220(5)	Ti(2)—C(8)	2.321(8)	2.32(2)	C(3)—C(4)	1.36(1)	1.41(2)
Ti(2)—Cl(5)	2.229(3)	2.218(5)	Ti(2)—C(9)	2.331(8)	2.30(2)	C(4)—C(5)	1.43(1)	1.39(2)
Ti(2)—Cl(6)	2.161(3)	2.231(5)	Ti(2)—C(10)	2.322(8)	2.33(1)	C(6)—C(7)	1.44(1)	1.42(2)
Ti(1)—C(1)	2.340(9)	2.57(2)	X—C(1)	1.902(5)	1.53(2)	C(6)—C(10)	1.41(1)	1.45(2)
Ti(1)—C(2)	2.340(9)	2.40(2)	X—C(6)	1.876(6)	1.53(2)	C(7)—C(8)	1.38(1)	1.39(2)
Ti(1)—C(3)	2.337(8)	2.26(2)	X—C(11)	1.825(7)	1.59(2)	C(8)—C(9)	1.38(1)	1.43(2)
Ti(1)—C(4)	2.319(9)	2.28(2)	X—C(12)	1.870(6)	1.49(2)	C(9)—C(10)	1.393(3)	1.40(2)

Table 2. Bond angles (ω) in the structures of **1** and **2**

Angle	ω /deg	
	1	2
Cl(1)—Ti(1)—Cl(2)	100.4(1)	105.0(4)
Cl(1)—Ti(1)—Cl(3)	103.9(2)	99.1(4)
Cl(2)—Ti(1)—Cl(3)	102.6(2)	103.3(5)
Cl(4)—Ti(2)—Cl(5)	101.9(2)	101.8(2)
Cl(4)—Ti(2)—Cl(6)	104.3(2)	102.5(2)
Cl(5)—Ti(2)—Cl(6)	103.5(2)	103.7(2)
C(1)—X—C(6)	104.4(2)	108(1)
C(1)—X—C(11)	113.7(2)	110(1)
C(1)—X—C(12)	109.5(2)	113(1)
C(6)—X—C(11)	103.6(2)	105(1)
C(6)—X—C(12)	109.7(2)	111(1)
C(11)—X—C(12)	115.6(2)	110(1)
C(2)—C(1)—C(5)	109.6(7)	103(1)
C(1)—C(2)—C(3)	106.0(7)	110(1)
C(2)—C(3)—C(4)	109.8(7)	107(2)
C(3)—C(4)—C(5)	108.1(7)	104(2)
C(4)—C(5)—C(1)	106.4(7)	116(2)
C(7)—C(6)—C(10)	106.6(7)	106(1)
C(6)—C(7)—C(8)	107.5(7)	109(1)
C(7)—C(8)—C(9)	109.7(7)	109(1)
C(8)—C(9)—C(10)	108.4(7)	107(1)
C(9)—C(10)—C(6)	108.2(7)	116(2)

Table 3. Crystallographic data for complexes **1** and **2**

Parameter	Me ₂ Si(Cl ₃ TiC ₅ H ₄) ₂ (1)	Me ₂ C(Cl ₃ TiC ₅ H ₄) ₂ (2)
<i>T</i> /K	173	299
<i>a</i> /Å	13.530(9)	13.719(8)
<i>b</i> /Å	23.940(7)	23.450(8)
<i>c</i> /Å	11.780(6)	11.665(6)
<i>V</i> /Å ³	3815.6(2)	3752.6(2)
Space group	<i>Pbca</i>	<i>Pbca</i>
<i>Z</i>	8	8
<i>d</i> _{calc} /g cm ⁻³	1.72(1)	1.69(1)
Radiation	λ(Cu-Kα)	λ(Mo-Kα)
2θ _{max} /deg	82	50
μ/mm ⁻¹	15.6	1.70
<i>N'</i> *	1955	2189
<i>N''</i> *	1184	1262
<i>R</i>	0.062	0.053

* *N'* and *N''* are the numbers of independent and observed (*I* > 3σ(*I*)) reflections, respectively.

two methyl groups are located. The TiCl₃ group bonded to the Cp(2) ring is located between the two Cp rings. The positions of the Cl(6) atom on the line normal to the Cp(1) ring is unusual: the Ti(1) and Cl(6) atoms lie on a

line passing through the center of the Cp(1) ring on opposite sides of this ring. The Ti(1)—Cp(1)—Cl(6) angles are 177° in molecule **1** and 173° in molecule **2**. The distances between the Cl(6) atom and the center of the Cp(1) ring are 3.57 and 3.53 Å in the structures of **1** and **2**, respectively; these distances are close to the sum of the corresponding van der Waals radii (3.5 Å). Generally, the bond lengths and bond angles (Tables 1 and 2) in the TiCl₃ unit agree with the analogous values for other studied titanium complexes.^{4,5} However, in the molecule

Table 4. Coordinates of nonhydrogen atoms in the structures of **1** and **2**

Atom	1			2		
	x	y	z	x	y	z
Ti(1)	0.3521(1)	0.2534(1)	0.3892(1)	0.3610(4)	0.2563(2)	0.3909(5)
Ti(2)	0.3461(1)	0.0239(2)	0.1360(2)	0.3460(2)	0.0257(1)	0.1431(2)
Cl(1)	0.2488(2)	0.3030(2)	0.4949(2)	0.2647(6)	0.2993(3)	0.5144(6)
Cl(2)	0.4776(2)	0.2437(5)	0.5090(6)	0.5055(6)	0.2561(5)	0.4730(1)
Cl(3)	0.4095(5)	0.3141(5)	0.2659(6)	0.373(1)	0.3246(4)	0.2624(8)
Cl(4)	0.3058(5)	-0.0441(6)	0.0141(7)	0.3059(3)	-0.0462(2)	0.0287(4)
Cl(5)	0.4151(5)	0.0886(6)	0.0256(7)	0.4093(3)	0.0876(2)	0.0201(1)
Cl(6)	0.2066(5)	0.0625(5)	0.1786(7)	0.2013(3)	0.0633(2)	0.1868(4)
X*	0.4878(5)	0.1162(5)	0.3403(7)	0.396(1)	0.1522(7)	0.337(1)
C(1)	0.3718(5)	0.1608(6)	0.3298(7)	0.363(1)	0.1848(7)	0.244(1)
C(2)	0.2965(6)	0.1615(6)	0.4115(7)	0.268(1)	0.2064(7)	0.267(2)
C(3)	0.2181(5)	0.1931(5)	0.3634(7)	0.242(1)	0.1887(7)	0.378(2)
C(4)	0.2454(5)	0.2126(5)	0.2593(7)	0.321(1)	0.1564(7)	0.413(2)
C(5)	0.3420(5)	0.1913(6)	0.2342(7)	0.4527(9)	0.0545(7)	0.297(1)
C(6)	0.4483(6)	0.0457(5)	0.2877(7)	0.504(1)	0.0166(6)	0.223(1)
C(7)	0.3642(5)	0.0155(6)	0.3308(7)	0.458(1)	-0.0364(7)	0.226(1)
C(8)	0.3687(6)	-0.0378(6)	0.2858(7)	0.373(1)	-0.0329(7)	0.298(1)
C(9)	0.4507(6)	-0.0425(6)	0.2167(7)	0.370(1)	0.0230(6)	0.341(1)
C(10)	0.5003(5)	-0.0085(6)	0.2166(7)	0.486(1)	0.1137(7)	0.336(1)
C(11)	0.5274(5)	0.1027(5)	0.4858(7)	0.523(1)	0.1047(8)	0.464(1)
C(12)	0.5853(1)	0.1453(1)	0.2446(7)	0.566(1)	0.1360(9)	0.262(2)

* X = Si (**1**) or C (**2**).

of compound **1**, which was studied by X-ray structural analysis at a low temperature (the accuracy of measurements was thus enhanced), the average value of the Ti(2)—Cl bond lengths is 0.02 Å larger than that of the Ti(1)—Cl bond lengths. The average value of the distances between the Ti(1) atom and the C atoms of the coordinated Cp(1) ring is also larger than the Ti(2)—C[Cp(2)] distance by 0.02 Å. This difference is even more pronounced in the crystal of **2** (0.04 Å). In addition, the Cp(2) ring is "open" on the side opposite the Ti(2) atom because there are no intramolecular contacts within the sums of the van der Waals radii and no intermolecular contacts shorter than 4.5 Å. Therefore, all the data on the structures of molecules **1** and **2** suggest that the twist conformation is stabilized through the Ti(1)—Cp(1)...Cl(6)—Ti(2) interaction, whose nature is not clear.

Apparently, this interaction also affects the geometry of the bridging tetrahedral unit. Thus, the C(1)—Si—C(6) angle in molecule **1** is 104.4°, while the C(1)—C—C(6) angle in **2** is close to tetrahedral (108°).

In the absence of any additional interaction, the larger separation between the TiCl₃Cp groups and the elimination of steric effects should make the C(1)—Si—C(6) angle in molecule **1** close to tetrahedral, whereas by the same reasoning, the C(1)—C—C(6) angle in **2** should be larger than tetrahedral. In fact, the reverse situation is observed. Evidently, this is due to the effect of the attractive Ti(1)—Cp(1)...Cl(6)—Ti(2) interaction. Other reasons for this substantial distortion of the tetrahedral configuration of the Si atom are not evident.

Experimental

X-ray diffraction studies were carried out on an automated three-circle DAR-UM diffractometer (Cu-Kα radiation, graphite monochromator, $\omega/2\theta$ scanning technique, $\theta_{\max} = 41^\circ$) and on an automated four-circle KM-4 diffractometer (Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $\theta_{\max} = 25^\circ$) for compounds **1** and **2**, respectively. All calculations were carried out on an IBM PC computer with the use of the AREN-88 crystallographic program package.⁶

Crystallographic parameters and details of the experiments and the refinement are given in Table 3. Both structures were solved by the direct method; all nonhydrogen atoms were refined anisotropically by the least-squares method. All H atoms were located from difference Fourier syntheses. Atomic coordinates are given in Table 4.

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