Molecular structure of ansa-compound $(\eta^5\text{-}C_5H_4)CMe_2(\eta^5\text{-}C_9H_6)TiCl_2$

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The structure of a new ansa compound, $(\eta^5\text{-}C_5H_4)CMe_2(\eta^5\text{-}C_9H_6)TiCl_2$ (**1**), was studied by X-ray analysis: a = 15.00(1), b =15.500(5), c = 13.032(4) Å, β = 92.66°(4), V = 3025.1(1) Å^3, space group $P2_1/\alpha$, R = 0.038. The distorted tetrahedral coordination sphere of the Ti atom is formed by two Cl atoms and two π-ligands. It was proposed that the angle (τ) between the C—M direction and the line normal to M—Cp can be considered as one of the geometric parameters characteristic of the "structure—properties" correlation.*

Key words: structure, ansa-complexes, titanocenes.

The ansa-biscyclopentadienyl derivatives of group IV transition metals have now been extensively investigated due to their unique catalytic activity in polymerization processes, in particular, in the polymerization of olefines.[1] Complexes with substituted cyclopentadienyl rings are used as catalysts for the stereoselective polymerization of olefines.[2—4]

Structures have been established for the simplest complexes of the $B(C_5H_4)_2MX_2$ type, where B = CH_2, $(CH_2)_2$, $C(Me)_2$, $Si(Me)_2$; M = Ti, Zr, Hf; X = H, Me, Cl.[5—7]

The present work reports the results of the X-ray analysis of the complex $(\eta^5\text{-}C_5H_4)CMe_2(\eta^5\text{-}C_9H_6)TiCl_2$ (**1**), which contains the indenylcyclopentadienyldimethylmethane ligand.

Results and Discussion

Unit cell **1** contains two crystallographically independent molecules, **1A** and **1B**, whose geometric parameters are the same within the limits of accuracy (Tables 1, 2).

A general view of molecule **1A** is shown in Fig. 1. The Ti atom has a distorted tetrahedral coordination formed by two Cl atoms and two π-ligands. The centroid C^1—Ti(1)—C^2 and Cl(2)—Ti(1)—Cl(3) angles are 121.8(1)° and 97.0°(1), respectively.**

The tetrahedral coordination of the C(9) bridge atom is significantly distorted. The C(4)—C(9)—C(12) angle is 95.8°. Moreover, the plane-trigonal configuration of the C(4) and C(12) atoms is notably distorted. These atoms are bent from the plane of the neighboring atoms (0.15 and 0.12 Å, respectively, relative to the Ti(1) atom):

Atom	Sum of the bond angles /deg	Deviation of the bond with the bridge atom from the plane of the aromatic ligand /deg
C(4)	356.5(7)	16.4
C(12)	356.9(7)	12.65

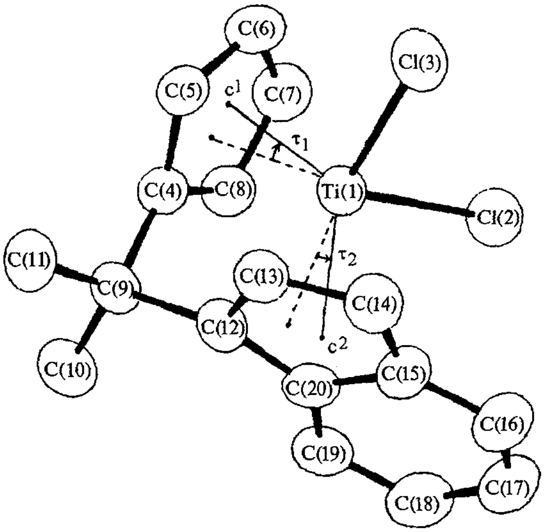

Fig. 1. General view of molecule **1A** (the distances between Ti atom and the centroids (C^1—C^2) of η^5-ligands are shown with thin lines, and the normals to the planes of the five-membered rings are shown with dashed lines).

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* C is the center of gravity of the cyclopentadienyl ring.

** Hereafter, in the analysis of the molecule structures, the geometric parameters for molecule **1A** are given, because these values are the same within the limits of experimental accuracy for both independent molecules.

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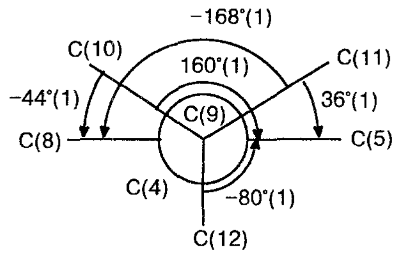
Table 1. Bond lengths (*d*) in molecules **1A** and **1B**

Bond	*d*/Å	
	1A	**1B**
Ti(1)—Cl(2)	2.318(3)	2.322(3)
Ti(1)—Cl(3)	2.345(3)	2.343(3)
Ti(1)—C(4)	2.319(8)	2.320(8)
Ti(1)—C(5)	2.321(8)	2.335(9)
Ti(1)—C(6)	2.426(9)	2.419(9)
Ti(1)—C(7)	2.418(9)	2.416(9)
Ti(1)—C(8)	2.323(8)	2.328(8)
Ti(1)—C(12)	2.315(8)	2.313(8)
Ti(1)—C(13)	2.315(8)	2.333(8)
Ti(1)—C(14)	2.456(9)	2.456(9)
Ti(1)—C(15)	2.560(8)	2.561(8)
Ti(1)—C(20)	2.459(8)	2.431(8)
C(4)—C(5)	1.41(8)	1.41(1)
C(4)—C(8)	1.38(1)	1.41(1)
C(5)—C(6)	1.40(1)	1.42(1)
C(6)—C(7)	1.38(1)	1.37(1)
C(7)—C(8)	1.39(1)	1.43(1)
C(4)—C(9)	1.51(1)	1.52(1)
C(9)—C(10)	1.53(1)	1.52(1)
C(9)—C(11)	1.52(1)	1.53(1)
C(9)—C(12)	1.55(1)	1.54(1)
C(12)—C(13)	1.42(1)	1.41(1)
C(12)—C(20)	1.44(1)	1.42(1)
C(13)—C(14)	1.44(1)	1.42(1)
C(14)—C(15)	1.41(1)	1.37(1)
C(15)—C(16)	1.39(1)	1.42(1)
C(15)—C(20)	1.42(1)	1.45(1)
C(16)—C(17)	1.36(1)	1.34(1)
C(17)—C(18)	1.41(1)	1.41(1)
C(18)—C(19)	1.36(1)	1.37(1)
C(19)—C(20)	1.44(1)	1.46(1)

The observed distortions are, apparently, caused by the tightening effect of the interactions between Ti and the η^5-ligands.

Both π-aryl ligands are coordinated orthogonally to the corresponding bond between the CMe_2-bridge and the neighboring ligand (see the Newman projections):



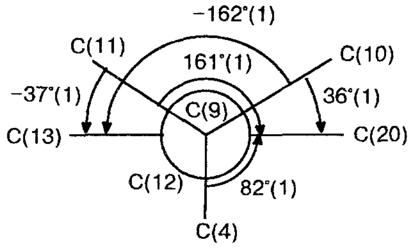


Table 2. Valence angles (ω) in the molecules **1A** and **1B**

Angle	ω/deg	
	1A	**1B**
Cl(2)—Ti(1)—Cl(3)	97.0(1)	96.7(1)
C(4)—C(5)—C(6)	109.5(7)	108.1(8)
C(5)—C(6)—C(7)	106.6(8)	108.6(8)
C(6)—C(7)—C(8)	108.7(8)	108.3(8)
C(4)—C(8)—C(7)	109.6(7)	107.5(7)
C(5)—C(4)—C(8)	105.5(7)	107.4(7)
C(5)—C(4)—C(9)	125.0(7)	124.3(7)
C(8)—C(4)—C(9)	126.0(7)	124.7(7)
C(4)—C(9)—C(10)	112.2(7)	113.3(7)
C(4)—C(9)—C(11)	113.1(7)	112.8(7)
C(4)—C(9)—C(12)	95.8(6)	95.5(6)
C(10)—C(9)—C(11)	108.8(7)	108.4(7)
C(10)—C(9)—C(12)	115.0(7)	111.3(7)
C(11)—C(9)—C(12)	111.5(7)	115.2(7)
C(9)—C(12)—C(13)	121.6(7)	123.4(7)
C(9)—C(12)—C(20)	130.2(7)	129.5(7)
C(12)—C(13)—C(14)	109.1(7)	110.0(8)
C(13)—C(12)—C(20)	106.1(7)	105.2(7)
C(13)—C(14)—C(15)	107.8(7)	108.3(8)
C(14)—C(15)—C(20)	107.4(7)	107.2(7)
C(12)—C(20)—C(15)	109.4(7)	109.1(7)
C(16)—C(15)—C(20)	122.4(8)	121.4(8)
C(14)—C(15)—C(16)	130.2(8)	131.3(8)
C(15)—C(16)—C(17)	117.9(8)	118.9(8)
C(16)—C(17)—C(18)	121.7(9)	121.9(9)
C(17)—C(18)—C(19)	121.7(8)	121.8(9)
C(18)—C(19)—C(20)	118.4(8)	119.3(8)
C(15)—C(20)—C(19)	117.8(7)	116.6(7)
C(12)—C(20)—C(19)	132.7(7)	134.2(7)

The insignificant differences in the torsion angles may be attributed to the spatial non-equivalency of the aryl ligands relative to the CMe_2-bridge due to the steric hindrances produced by the bulky indenyl fragment. The difference between the Ti—Cl bond lengths is worth noting: the Ti(1)—Cl(3) distance, 2.345 Å (3), is within the bounds established for the related compounds (2.33—2.38),[1–5] whereas the Ti(1)—Cl(2) distance, 2.318(3) Å, is notably shorter.

The reason for the shortening of the Ti(1)—Cl(2) bond is obscure. Figure 2 shows that the Cl(2) and Cl(3) atoms are situated unequivalently relative to the indenyl group: the Cl(2) atom is located above this fragment at a distance of 3.06 Å, whereas the Cl(3) is directed outwards.

In molecule **1**, an additional electron interaction between the π-electron system of the indenyl fragment and the Cl(2) atom seems to occur, similarly to that proposed earlier for $Me_2Si(C_5H_4TiCl_3)_2$ (see Ref. 14). The bond lengths in the indenyl rings of **1** fall within the limits determined earlier for complexes with indenyl ligands.[8–9]

The Ti—C distances for the C(4), C(5), and C(8) atoms (2.319(8), 2.321(8), and 2.323(8) Å, respectively) are notably shorter than those for the C(6) and C(7) atoms (2.426(9) and 2.418(9), respectively). In addition,

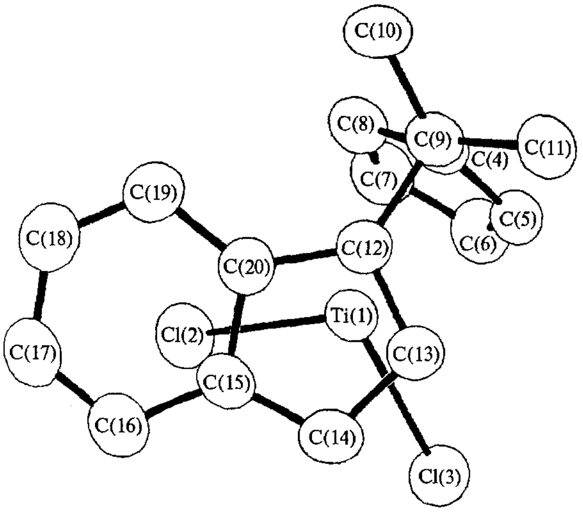


Fig. 2. Proejction of molecule **1A** on the plane of the indenyl fragment.

the C(5)—C(8) line of the pentadienyl ring is inflected in the direction of the Ti(1) atom (the inflection angle is 2.7°), to suggest a $\eta^5 = \eta^3 + \eta^2$ type of coordination. This type of coordination is confirmed by the fact that the C(6)—C(7) bond is the shortest in the ring (1.38(1) Å in **1A** and 1.37(1) Å in **1B**), although the experimental accuracy is not high. The C^1—M—C^2 angle is commonly considered as a main characteristic of metallocene complexes. However, we believe that the angle between the M—*C* direction and the line normal to the ring (the τ angle, Fig. 1) is a more characteristic feature.

Table 3 shows that one of the largest values of the τ angle is observed for compound **1**. The distances Ti(1)—C(14) 2.456 Å, Ti(1)—C(15) 2.560 Å, and Ti(1)—C(20) 2.469 Å are considerably longer than the distances from Ti(1) to C(5), C(6), and C(7) (2.321, 2.426, and 2.418 Å, respectively). This difference between these distances may be reasonably attributed to the additional steric hindrances that arise between the Cl(2) atom and the benzene fragment of the indenyl ring. Due to the short $(Me_3)_2C$ bridge, the $TiCl_2$ group is shifted from its ideal position towards the bridge (τ = 5.6°). In the compound $(CH_2)_2(C_9H_{10})_2TiCl_2$ (see Ref. 9), destabilization of the metal is caused by the presence of two indene ligands. Owing to this effect, the titanium atom is similarly diplaced from the equilibrium position (τ = 5.8°), even when the $(CH_2)_2$ bridge is relatively flexible (not short). Table 3 also shows that the deviation of the Ti atom from its ideal position (*viz.*, from the intersection point of the lines normal to the Cp-rings) increases as the bridge length shortens and the ligand bulk increases.

Table 3. Angles τ in mononuclear dichlorotitanocens

Compound	τ(mean)/deg[a]
$(C_5H_5)_2TiCl_2$[b]	2.67[10]
$(C_9H_6)_2TiCl_2$[b]	5.14[8]
$(CH_2)_3(C_5H_4)_2TiCl_2$[c]	0.8[11]
$(CH_2)_2(C_5H_4)_2TiCl_2$[c]	1.0[12]
$(CH_2)_3(C_9H_{10})_2TiCl_2$[c]	5.8[9]
$CMe_2(C_5H_4)(C_9H_6)TiCl_2$[c] (**1**)	5.6
$CH_2(C_5H_4)_2TiCl_2$[b]	4.6[12]

[a] τ(mean) between the Ti—centroid Cp vector and the line normal to Ti—Cp.

[b] Compounds without bridges in order of increasing ligand volume.

[c] Compounds containing bridges in order of decreasing bridge length.

It was reported earlier[13] that the catalytic activity of zirconocenes is greater that that of the titanium analogs. We believe that the possible reason for this distinction is the fact that the zirconium atom is larger than the titanium atom, and, therefore, the $ZrCl_2$ group is more strongly drawn from its ideal position.

The proposed τ angle is a useful characteristic of the value of this deviation. It is reasonable to conclude that the value of the τ angle determines the extent of the steric destabilization of the complex and its activity in subsequent reactions with olefins. This point of view allows better understanding of the higher activity of zirconocenes compared to titanocenes, since the values of the τ angle of the former substantially exceed those of the latter.

Experimental

The ^1H NMR spectra of the obtained compound were recorded on a Varian XR-400 instrument at 30 °C.

A dark green plate-like crystal with dimensions 0.05×0.2×0.4 mm was chosen as the specimen for X-ray analysis. The compound crystallizes according to monoclinic syngony with space group $P2_1/\alpha$, a = 15.00(1), b = 15.500(5), c =13.032(4) Å, β = 92.66(4), V = 3025.1(1) Å^3, Z = 8, d_{cal} = 1.49(1) g cm^{-3}. The intensities of 3593 non-zero reflections were measured on a KM-4 four-circle automatic diffractometer (λ(Mo-Kα)-irradiation, graphite monochromator, $\theta/2\theta$-scanning, θ_{max} = 25°).

The structure was established by the direct method. The hydrogen atoms were localized objectively based on the differential Fourier synthesis. Refining the structure in the full matrix anisotropic approximation (isotropic for the H atoms) with 2052 $F \geq 3\sigma(F)$ was completed at R = 0.039. All of the calculations were done on an IBM PC using the AREN-88 set of crystallographic programs (see Ref. 15). Absorption was not taken into account (σ = 8.52 cm^{-1}). The atomic coordinates are given in Table 4.

The synthesis and crystallization of **1** was carried out in an argon atmosphere or in evacuated systems of the Shlenk type. The solvents used were prepared according to the known procedures.[16] Compound **1** was obtained in 21 % yield as fine bright green crystals. The crystals suitable for X-ray experiments were prepared by slow evaporation of a solution of the complex in a toluene-chloroform (1 : 3) mixture. ^1H NMR ($CDCl_3$), δ: 1.948 (5.3H—Me_3); 2.234 (5.3H—Me_3); 5.638 (m, 2 H, cyclopentadienyl); 9.754 (d, 1 H, H(2—3)); 6.672 (m, 1 H, Cp); 6.730 (m, 1 H, Cp); 7.005 (m, 1 H, H(5)

Table 4. Atomic coordinates in molecules **1A** and **1B**

Atom	**1A**			**1B**		
	x	*y*	*z*	*x*	*y*	*z*
Ti(1)	0.9926(1)	0.2325(1)	0.0014(1)	1.0119(1)	0.2657(1)	0.5011(1)
Cl(2)	0.9475(1)	0.1441(2)	0.1328(2)	1.0617(1)	0.3542(2)	0.6356(2)
Cl(3)	0.8917(2)	0.1805(2)	−0.1268(2)	1.1110(2)	0.3158(2)	0.3808(2)
C(4)	1.0371(5)	0.3753(5)	0.0181(6)	0.9659(5)	0.1233(5)	0.5129(7)
C(5)	0.9655(5)	0.3723(5)	−0.0557(6)	1.0015(5)	0.1472(6)	0.6106(7)
C(6)	0.8868(5)	0.3509(6)	−0.0076(7)	1.0944(6)	0.1598(6)	0.6034(7)
C(7)	0.9101(5)	0.3384(6)	0.0948(7)	1.1159(6)	0.1467(6)	0.5033(7)
C(8)	1.0014(5)	0.3514(5)	0.1099(7)	1.0363(5)	0.1255(5)	0.4447(7)
C(9)	1.1346(5)	0.3723(5)	−0.0059(7)	0.8672(5)	0.1279(5)	0.4803(7)
C(10)	1.1947(5)	0.4080(6)	0.0818(7)	0.8443(6)	0.0810(6)	0.3798(7)
C(11)	1.1549(6)	0.4198(6)	−0.1045(7)	0.8070(6)	0.0933(6)	0.5623(7)
C(12)	1.1389(5)	0.2734(5)	−0.0201(6)	0.8650(5)	0.2264(5)	0.4656(6)
C(13)	1.1068(5)	0.2331(5)	−0.1121(6)	0.8947(5)	0.2681(6)	0.3771(7)
C(14)	1.0953(5)	0.1425(6)	−0.0936(7)	0.9087(6)	0.3570(6)	0.3975(7)
C(15)	1.1229(5)	0.1258(5)	0.0098(7)	0.8829(5)	0.3740(5)	0.4953(7)
C(16)	1.1270(6)	0.0484(6)	0.0640(7)	0.8821(6)	0.4520(6)	0.5527(7)
C(17)	1.1559(6)	0.0509(6)	0.1641(7)	0.8551(6)	0.4498(8)	0.6496(8)
C(18)	1.1830(6)	0.1288(6)	0.2124(7)	0.8292(6)	0.3722(6)	0.6964(7)
C(19)	1.1791(5)	0.2056(6)	0.1616(7)	0.8294(5)	0.2952(6)	0.6453(7)
C(20)	1.1494(5)	0.2058(5)	0.0551(6)	0.8575(5)	0.2927(5)	0.5398(7)

indenyl); 7.168 (d.d, 1 H, H(2—3)); 7.451 (m, 1 H, H(4)); 7.543 (m, 1 H, H(7)); 7.543 (m, 1 H, H(6)). The ^{1}H signals of the indenyl and cyclopentadienyl rings were assigned by a double resonance experiment.

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