

JOM 23502

Preparation and structure of bis( $\eta^5$ -methylcyclopentadienyl)titanaindane

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(Received December 14, 1992)

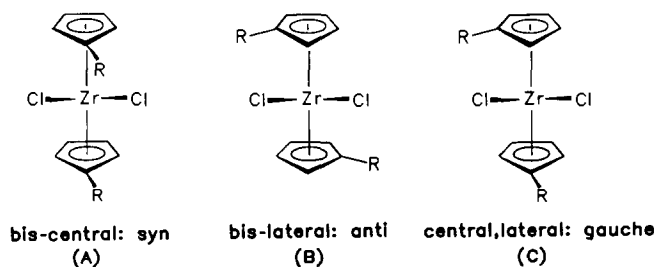
## Abstract

Bis( $\eta^5$ -methylcyclopentadienyl)diphenyltitanium (1) reacts with ethylene (10 bar) at 80°C in toluene solution via the intermediate (MeCp)<sub>2</sub>Ti( $\eta^2$ -1,2-didehydrobenzene) (2) to give 1,1-bis( $\eta$ -methylcyclopentadienyl)titanaindane (3, 71% isolated as crystals from pentane). An X-ray diffraction study has shown that complex 3 adopts a bent metallocene conformation, which has one Cp-bound methyl group in a lateral position and the other oriented towards the narrow back side of the bent metallocene wedge.

## 1. Introduction

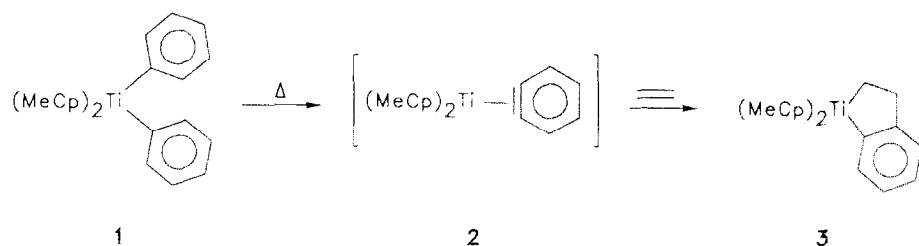
Bent metallocene complexes (RCp)<sub>2</sub>MX<sub>2</sub> bearing one substituent on each cyclopentadienyl ligand often exhibit structures in the crystal which fall into three structural types that differ in respect of the relative rotational arrangement of the monosubstituted  $\eta$ -cyclopentadienyl rings. These most commonly found local conformational isomeric types are those based on the idealized geometries **A** (with both R-groups positioned eclipsed towards the open side of the bent metallocene wedge), **B** (with both groups located towards the lateral sectors), and **C** (one R group arranged centrally and the other oriented laterally). Many examples have been shown experimentally to possess solid state structures which come close to these three geometries, which have been characterized as (i) bis-central: *syn* (**A**), (ii) bis-lateral: *anti* (**B**), and (iii) central, lateral: *gauche* (**C**) metallocene conformers. It appears that (RCp)<sub>2</sub>MX<sub>2</sub> complexes bearing tertiary alkyl substituents R on the Cp-rings favour the bis-lateral: *anti* (**B**) type rotamers [1]. In contrast, all three conformational types seem to be rather close in energy when R is a secondary alkyl group. In one such case, namely bis( $\eta$ -isopropylcyclopentadienyl)zirconium di-

chloride, all three rotamers **A**, **B**, and **C** were found to be present in the unit cell [2].



Primary alkyl substituents R seem to favour a conformational arrangement in which they lie in the central position in the front of the bent metallocene wedge. Typical examples are bis( $\eta$ -methylcyclopentadienyl)-ZrCl<sub>2</sub> or bis( $\eta$ -benzylcyclopentadienyl)TiCl<sub>2</sub>, which both exhibit bis-central: *syn* (**A**) type structures in the crystal [3]. In the course of our work aimed at calibration of a force field molecular mechanics program for bent metallocene complexes we became interested in knowing about cases where these simple rules were no longer obeyed. For calibration of the conformational isomers of primary alkyl-substituted bent metallocenes we had to look for structures in which groups of substituents on the central metal exerted an influence on the RCp-arrangement that result in a deviation from the usually observed bis-central: *syn* structural

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type. The metallaindane system described below turned out to provide such an example.

## 2. Results and discussion

Titanaindanes can easily be prepared by reaction of ( $\eta^2$ -aryne)titanocenes, generated *in situ*, with ethylene. The reactive (benzyne)metallocene is readily available from the corresponding diphenylmetallocene complex

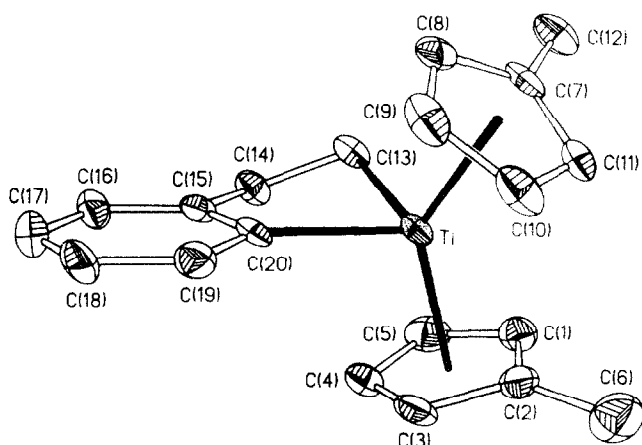


Fig. 1. View of the molecular geometry of **3** (with atom numbering scheme).

TABLE 1. Selected bond distances (Å) and angles (°) in **3**

(a) Bond distances			
Ti–CNT(1) <sup>a</sup>	2.081(5)	C(13)–C(14)	1.532(9)
Ti–CNT(2) <sup>a</sup>	2.073(5)	C(14)–C(15)	1.518(9)
Ti–C(13)	2.199(6)	C(15)–C(20)	1.400(9)
Ti–C(20)	2.183(6)		
(b) Bond angles			
CNT(1)–Ti–CNT(2)	134.4(2)	C(13)–Ti–C(20)	79.1(2)
CNT(1)–Ti–C(13)	107.8(2)	Ti–C(13)–C(14)	107.3(4)
CNT(1)–Ti–C(20)	106.4(2)	C(13)–C(14)–C(15)	110.9(5)
CNT(2)–Ti–C(13)	106.7(2)	C(14)–C(15)–C(20)	118.1(5)
CNT(2)–Ti–C(20)	108.2(2)	C(15)–C(20)–Ti	112.6(4)

<sup>a</sup> CNT(1)-centroid of C(1)–C(5) ring; CNT(2)-centroid of C(7)–C(11) ring.

by means of a thermally induced benzene elimination [4]. Thus 1,1-bis(methylcyclopentadienyl)titanaindane (**3**) was prepared by thermolysis of a toluene solution of ( $\text{Me-C}_5\text{H}_4$ )<sub>2</sub>TiPh<sub>2</sub> (**1**) with ethylene (10 bar) at 80°C, as previously described [5]. The methyl-substituted titanaindane was isolated in > 80% yield from the reaction mixture. Recrystallization from pentane gave crystalline, analytically pure **3** in > 70% overall yield. In solution the metallacycle **3** exhibits <sup>1</sup>H/<sup>13</sup>C NMR signals from the pair of apparently symmetry-equivalent MeCp-ligands at  $\delta$  5.57, 5.62, 5.77, 5.86 (C<sub>5</sub>H<sub>4</sub>–), 1.70 (CH<sub>3</sub>)/ $\delta$  112.0, 113.2, 116.6, 117.7 and 125.5 (C<sub>5</sub>H<sub>4</sub>–), 15.4 (CH<sub>3</sub>). The –CH<sub>2</sub>–CH<sub>3</sub>– moiety of the metallaindane five-membered ring gives rise to signals at  $\delta$  1.36, 3.23 (<sup>1</sup>H NMR, AA'XX') and  $\delta$  38.6 (<sup>1</sup>J<sub>CH</sub> = 127 Hz), 57.5 (<sup>1</sup>J<sub>CH</sub> = 127 Hz)(<sup>13</sup>C NMR).

Crystals of complex **3** suited for an X-ray diffraction study were obtained from pentane. The molecular structure of **3** (see Fig. 1) reveals a similar framework to that in the bis(cyclopentadienyl)titanaindane parent compound, whose structure was recently reported [5]. The aromatic six-membered ring of **3** is only slightly distorted (see Table 1). The annulated five-membered metallacycle adopts a distorted twist conformation with C(13) oriented “above” and the titanium atom “below” the mean C(14), C(15), C(20) plane. The bond between the sp<sup>3</sup>-hybridized ring carbon atoms C(13)–C(14) is

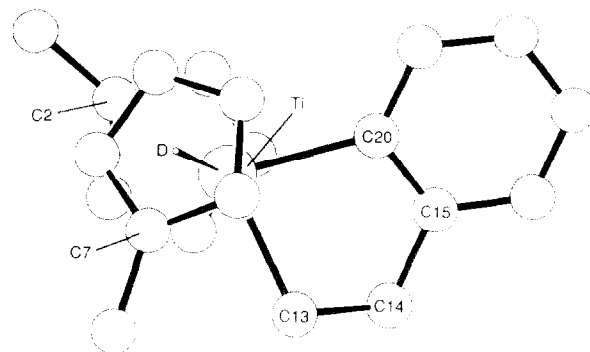


Fig. 2. Projection (top view) of the molecular structure of **3** depicting the conformational situation at the (MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>TiR<sub>2</sub> unit.

TABLE 2. Crystallographic data and details of structure solution of **3**

(a) Crystal parameters			
Formula	C <sub>20</sub> H <sub>22</sub> Ti	V (Å <sup>3</sup> )	1575.9(6)
Formula weight	310.27	Z	4
Crystal system	Orthorhombic	Cryst dimens (mm <sup>3</sup> )	0.25 × 0.25 × 0.40
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Cryst color	Dark red
a (Å)	8.820(2)	D(calcd) (g cm <sup>-3</sup> )	1.308
b (Å)	12.273(3)	μ(Mo Kα) (cm <sup>-1</sup> )	5.46
c (Å)	14.559(3)	Temp (K)	298
(b) Data collection			
Diffractometer	Nicolet R3m	Rflns collected	1274
Monochromator	Graphite	Indpt rflns	1232
Radiation	Mo Kα (λ = 0.71073 Å)	Indpt obsvd rflns	1044
		F <sub>o</sub> ≥ 5σ(F <sub>o</sub> )	
2θ scan range (°)	4–45	Std rflns	3 std/197 rflns
Data collected (h,k,l)	+10, +14, +16	Var. in stds, %	2.82
(c) Refinement			
R(F), %	4.95	Δ(ρ) (e Å <sup>-3</sup> )	0.57
R(wF), %	5.03	N <sub>o</sub> /N <sub>v</sub>	5.49
Δ/σ(max)	0.013	GOF	1.019

1.532(9) Å. The angles at C(13) and C(14) deviate only slightly from the tetrahedral, at 107.3(4)° [Ti–C(13)–C(14)] and 110.9(5)° [C(13)–C(14)–C(15)], respectively. The Ti–C(20) distance is 2.183(6) Å. The σ-ligand angle at titanium [C(20)–Ti–C(13)] is 79.1(2)°.

Two methylcyclopentadienyl ring systems are η<sup>5</sup>-coordinated to titanium. The distance Ti–cent.(1) between the Ti and the centroid of the C(1)–C(5) Cp-ring is 2.081(5) Å; the Ti–cent.(2) separation is only marginally shorter at 2.073(5) Å. However, bonding of

the MeCp-carbons to Ti is somewhat unsymmetrical in that the carbon bearing the methyl substituent is a little further from the metal center than are some of its unsubstituted carbon neighbours [e.g. d(Ti–C(2)) = 2.436(6) Å, d(Ti–C(7)) = 2.436(6) Å, max. Δd = 0.10 Å].

It is the conformational arrangement of the methylcyclopentadienyl ligands that makes the structure of this titanocene complex in the solid state somewhat remarkable. Complex **3** exhibits a bent metallocene

TABLE 3. Atomic coordinates (×10<sup>4</sup>) and isotropic thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) for **3**

	x	y	z	U <sup>a</sup>
Ti	2875(1)	149.4(8)	4924.5(7)	29.6(3)
C(1)	2867(8)	–70(6)	3299(4)	43(2)
C(2)	3764(7)	863(6)	3459(4)	41(2)
C(3)	5047(7)	499(6)	3959(5)	48(2)
C(4)	4927(8)	–625(6)	4070(4)	49(2)
C(5)	3574(9)	–972(6)	3676(5)	52(3)
C(6)	3570(10)	1988(7)	3050(5)	68(3)
C(7)	274(7)	720(5)	5218(4)	40(2)
C(8)	1031(7)	760(6)	6071(4)	43(2)
C(9)	2220(8)	1523(5)	6009(5)	48(2)
C(10)	2203(8)	1976(5)	5128(5)	49(2)
C(11)	986(7)	1482(5)	4634(5)	45(2)
C(12)	–1062(7)	15(6)	4985(5)	57(2)
C(13)	2043(7)	–1456(5)	5369(4)	38(2)
C(14)	3407(7)	–2090(5)	5741(4)	39(2)
C(15)	4485(7)	–1338(5)	6250(4)	35(2)
C(16)	5484(7)	–1733(6)	6924(4)	44(2)
C(17)	6506(8)	–1041(6)	7365(5)	53(3)
C(18)	6528(7)	43(6)	7132(4)	48(2)
C(19)	5545(7)	453(6)	6476(4)	39(2)
C(20)	4482(6)	–231(5)	6019(4)	33(2)

<sup>a</sup> Equivalent isotropic U defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

conformation that deviates markedly from those of its known acyclic analogues such as  $(\text{MeCp})_2\text{ZrX}_2$  or  $(\text{PhCH}_2\text{Cp})_2\text{TiX}_2$ . In **3** the methyl substituents at Cp are not oriented towards the front side of the bent metallocene wedge but arranged in a rather different way (for a projection of the molecular structure of **3** see Fig. 2).

The methyl group attached to the Cp carbon atom C(7) avoids the front side of the metallocene and is oriented towards the lateral sector. We assume that the observed twist conformation of the five-membered metallacycle, part of which the  $(\text{MeC}_5\text{H}_4)_2\text{Ti}$  unit is, would create some unfavorable steric interaction with the Cp-bonded methyl substituents lying above this tightly-bonded ring system. Thus it is not too surprising that the Cp-bonded methyl groups tend to avoid their "natural" front position and are rotated away towards the back. Surprisingly, the C(2) bonded methyl group is not found in the other available lateral sector (oriented anti to C(12)), and it seems that there is increased steric crowding in this sector (perhaps brought about by interaction with the C(10)–H linkage) [6]. An unexpected energetic compromise seems to be represented by this unusual conformational situation: the C(6) methyl group has moved all the way back and lies directly at the crowded back-side of the bent metallocene wedge. We conclude from this and related structures [7] that a delicate balance of steric effects seems to control the conformational properties of substituted bent metallocene complexes. This must be taken into account during the continuing efforts to calibrate and parameterize force field molecular mechanics programs aimed at carrying out reliable molecular modelling of Group 4 metallocene complexes and catalyst systems.

### 3. Experimental details

Complex **3** was prepared as previously described [5], and suitable crystals were grown from pentane. Crystallographic data are listed in Table 2. The unit-cell parameters were obtained from the least-squares fit of 25 reflections ( $20^\circ \leq 2\theta \leq 25^\circ$ ). Systematic absences in the diffraction data pointed uniquely to the orthorhombic space group  $P2_12_12_1$ . No correction for absorption was required (low  $\mu$ ).

The structure was solved by direct methods, which located the Ti atom. The remaining non-hydrogen atoms were located by subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were treated as idealized isotropic contributions ( $d(\text{CH}) = 0.960 \text{ \AA}$ ,  $U = 1.2 \text{ U}$  for attached C). All software is contained in SHELXTL (5.1, 1983) program li-

brary (G. Sheldrick, Siemens (Nicolet) XRD, Madison, WI). Atomic coordinates are given in Table 3, and selected bond distances and angles in Table 1.

### Acknowledgements

Financial support from the Fonds der Chemischen Industrie and the Alfred Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

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