ELSEVIER

Journal of Organometallic Chemistry 491 (1995) 31–39

Journal of Organometallic Chemistry

Dynamic stereochemistry in the titanocene series with central and planar chirality. X-Ray structure and relative configuration of the racemic form (m.p. 186°C) of $[(\eta^5\text{-1-Me-2-}^i\text{PrC}_5\text{H}_3)(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})\text{Cl}]$

Jack Besançon [a,*], Jan Szymoniak [a], Claude Moïse [a], Loïc Toupet [b], Bernard Trimaille [c]

[a] *Laboratoire de Sythèse et d'Electrosynthèse Organométalliques associé au CNRS (URA 1685), Faculté des Sciences, 6 bd Gabriel, 21000 Dijon, France*
[b] *Groupe Matière Condensée et Matériaux, URA 804 au CNRS, Campus de Beaulieu, Av Géneral Leclerc, bât B11, 35042 F-Rennes-Cédex, France*
[c] *Département de Chimie, 1er cycle, UFR Sciences et Techniques, 25030 Besançon-Cedex, France*

Received 13 June 1994

Abstract

The dynamic stereochemistry of two substitution reactions [(i) and (ii)] for the thiocyanate and isocyanate complexes of titanocene has been reinvestigated.

$$\underset{(1)}{[(\eta^5\text{-Cp})(\eta^5\text{-Cp}')\text{TiOArX}]} \xrightarrow[\text{i}]{\text{Br}^-} \underset{(2)}{[(\eta^5\text{-Cp})(\eta^5\text{-Cp}')\text{TiBrX}]} \xrightarrow[\text{ii}]{\text{SC}_6\text{H}_5^-} \underset{(3)}{[(\eta^5\text{-Cp})(\eta^5\text{-Cp}')\text{Ti}(\text{SC}_6\text{H}_5)\text{X}]}$$

$\left(\text{Cp} = \text{C}_5\text{H}_5;\ \text{Cp}' = \text{1-Me-2-}^i\text{PrC}_5\text{H}_3;\ \text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3;\ \text{X} = \text{NCO, NCS or Cl}\right)$

The metathesis reaction (ii) has been shown to be chemoselective and stereospecific with inversion of the configuration at the titanium for X = NCO and retention for X = NCS. This stereochemical behaviour contrasts with that proposed previously, i.e. inversion of configurations for both X = NCO and X = NCS. The present result is unambiguously supported by the crystallographic structure of the racemic compound **1c′** (X = Cl, m.p. 186°C), which was chosen as the starting stereochemical reference. The complex **1c′** crystallizes in the monoclinic system, space group C_c. Two well-characterized quasi-eclipsed and staggered conformational forms of the complex **1c′** are presented. According to Seebach's nomenclature, this structure corresponds to the **u**(Ti, p) configuration.

Keywords: Titanium; Titanocene; Chirality; X-ray diffraction

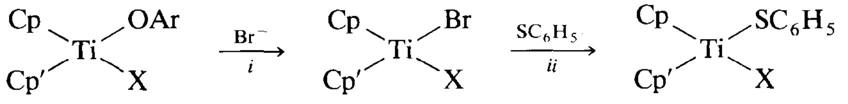
1. Introduction

Our previous work [1] dealt with the dynamic stereochemistry of the two new substitution reactions (i) and (ii) in Scheme 1. These reactions started from pairs of racemic diastereomeric pseudohalogen titanocene complexes **1** (X = NCO or NCS), which have both a central chirality at the metal atom and a planar chirality at the substituted cyclopentadienyl ring. The stereochemical course of the reactions was unequivocally established on the basis of the X-ray of structures **1b** (m.p. 193°C) and **3b′** (m.p. 173°C) (see Fig. 1; only one of two enantiomers is presented here), and ^{1}H NMR (X = NCS or NCO) [2] and photoelectron spectral data [1]. It was rationalised by extended Hückel calculations [1]. Reaction (i) is shown to occur with retention of the configuration at the titanium atom for X = NCS as well as for X = NCO. In contrast, the stereochemical course of reaction (ii) depends on the heteroatom used, giving

---

[*] Corresponding author.

0022-328X/95/$09.50
SSDI 0022-328X(94)05242-5



1 2 3

[Cp: C_5H_5; Cp': 1-Me 2-^iPrC C_5H_3; Ar: 2,6 $Me_2C_6H_3$; X: NCO(a, a'); NCS(b, b'); Cl(c, c')]

1a (m.p. 202°C) $\xrightarrow{RET}$ **2a** (m.p. 172°C) $\xrightarrow{INV}$ **3a'** (m.p. 131°C, 97%) + **3a** (m.p. 126°C, 3%)
1a' (m.p. 180°C) $\longrightarrow$ **2a'** (m.p. 150°C) $\longrightarrow$ **3a** (m.p. 126°C)
1b (m.p. 193°C) $\xrightarrow{RET}$ **2b** (m.p. 143°C) $\xrightarrow{RET}$ **3b** (oil, 90%) + **3b'** (m.p. 173°C, 10%)
1b' (m.p. 148°C) $\longrightarrow$ **2b'** (m.p. 172°C) $\longrightarrow$ **3b'** (m.p. 173°C, 99%) + **3b** (oil, 1%)

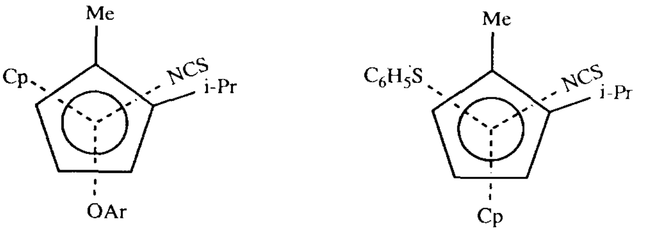
Scheme 1.

retention for X = NCS and inversion of the configuration for X = NCO.

However, retention of configuration in (ii), X = NCS, appears to contrast with the **inversion** previously proposed for this reaction [2b,3]. This is worth noting as it is based on the chemical relation between compounds **1**, **2** and **3** using the racemic diastereomeric precursors (X = Cl), **1c** (m.p. 181°C) and **1c'** (m.p. 186°C) (Scheme 2). The diastereomers **1c** and **1c'** have been especially considered as stereochemical references. Their configurational assignments were based on the close analogy between their ^1H NMR data and those of the racemic compound **4c**, which is representative of the 1–3 series (Cp'' = 1-Me-3-$^iPrC_5H_3$) for which the X-ray structure has already been established (Fig. 2; only one of two enantiomers is shown) [4,5]. Such internal consistency led us to propose structure **I** (X = Cl, Y = OAr) for **1c** and structure **II** for the diastereomeric complex **1c'** (Fig. 3; only one of two enantiomers is shown here). The NMR-based comparison of pairs of diastereomers which possess different planar chiralities (series 1–2 versus 1–3) alone, thus appears to be inadequate.

2. Results and discussion

In order to resolve this contradiction we have determined the X-ray structure of one of the two diastereomers with m.p. 186°C (**1c'**).



1b (m.p.193°C) **3b'**(m.p.173°C)

Fig. 1. X-ray structures of **1b** and **3b'**.

2.1. X-Ray analysis of compound 1c'

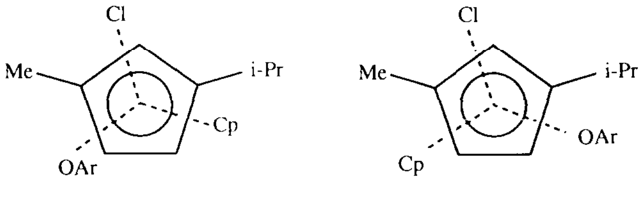
$C_{22}H_{27}ClOTi$: M = 390.82, monoclinic, C_c, $a = 16.291(6)$, $b = 15.702(5)$, $c = 15.719(4)$ Å, $\beta = 92.43(5)°$, V = 4017(4) Å^{-3}, $Z = 8$, $D_x = 1.292$ mg m^{-3}, λ(Mo Kα) = 0.70926 Å, $\mu = 5.61$ cm^{-1}, $F(000) = 1648$, $T = 293$ K. The sample (0.22 × 0.26 × 0.32 mm) was studied on an automatic Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. Data collection: $2\theta_{max} = 50°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range $19 \leqslant h \leqslant 19$, $0 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 18$, intensity controls without appreciable decay (0.4%) gave 3821 reflections of which 2732 were independent ($R_{int} = 0.017$) with $I > \sigma(I)$.

After Lorentz and polarization corrections, the structure was solved by a Patterson map which indicated the position of the two Ti atoms in the structure. The remaining non-hydrogen atoms of the molecule were found after several scale factor and Fourier difference calculations. After isotropic ($R = 0.012$) and anisotropic refinement ($R = 0.063$), many hydrogen atoms were found Fourier difference analysis (between 0.43 and 0.19 e Å^{-3}). The whole structure was refined by a full-matrix least-squares techniques, use of F magnitude; x, y, z, β_{ij} for Ti, Cl, C and O atoms and x, y, z fixed for H atoms; 450 variables and 2732 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$ with the resulting $R = 0.048$, $R_w = 0.039$ and $S_w = 1.72$ (residual $\Delta\rho < 0.22$ e Å^{-3}).

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* [6a]. All the calculations were performed on a Digital MicroVAX 3100 computer using the MOLEN package (Enraf-Nonius, [6b]).

1(X:Cl) $\xrightarrow{NCS^-}$ **1**(X:NCS)
1c (m.p. 181°C) $\longrightarrow$ **1b** 60% + **1b'** 40%
1c' (m.p. 186°C) $\longrightarrow$ **1b** 40% + **1b'** 60%

Scheme 2.



4c (m.p.150°C) **4c'** (m.p.122°C)

Fig. 2. X-ray structures of **4c** and **4c'**.

The racemic form of the compound crystallises with two conformations A and B (Figs. 4 and 5) [6c]. Table 1 lists the atomic coordinates, Tables 2 and 3 list the bond distances and bond angles, and Table 4 gives the least-square planes of the cyclopentadienyl rings, and the distances and angles of the various atoms on the basis of these planes. The whole structure, with its two conformations, is shown in Figs. 6 and 7 [6c].

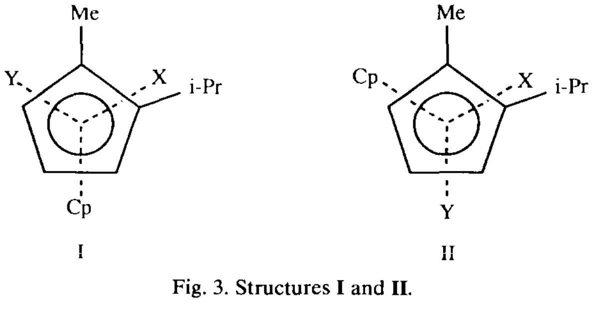
The data show that the configuration and the two conformations are established unambiguously in the solid state. Structure **I** (Fig. 3) represents the complex **1c'**, m.p. 186°C. This structure may be defined by the relative configuration **u**(Ti, p) [7,8]. The results clearly reveal that the configuration previously established by NMR (structure **II**) is erroneous.

Table 5 provides comparative data for **1c'** (m.p. 186°C) and **4c** (m.p. 150°C). The Ti–Cl and Ti–O distances, Ti–O–C and Cl–Ti–O angles are quite similar and the main differences concern the Ti–C* and O–C distances and the relative positions of the cyclopentadienyl planes.

The views of the two molecules show that the cyclopentadienyl rings are eclipsed in one case and staggered in the other. In these two conformations, the Cl atom (which is smaller than —$OC_6H_3Me_2$) lies in the more congested part of the molecule.

The X-ray analysis demonstrates that **1c'** has the same configuration as its positional isomer **4c**. This is not expected from the spectral comparison of the latter and complex **1c**, a diastereomer of **1c'**.

The methyl and isopropyl groups on the cyclopentadienyl ring were used as NMR probes. The resonances are shifted downfield or upfield according to the position of aryloxy group. As a result, it is possible to establish the relative configurations of the various pairs



I II

Fig. 3. Structures **I** and **II**.

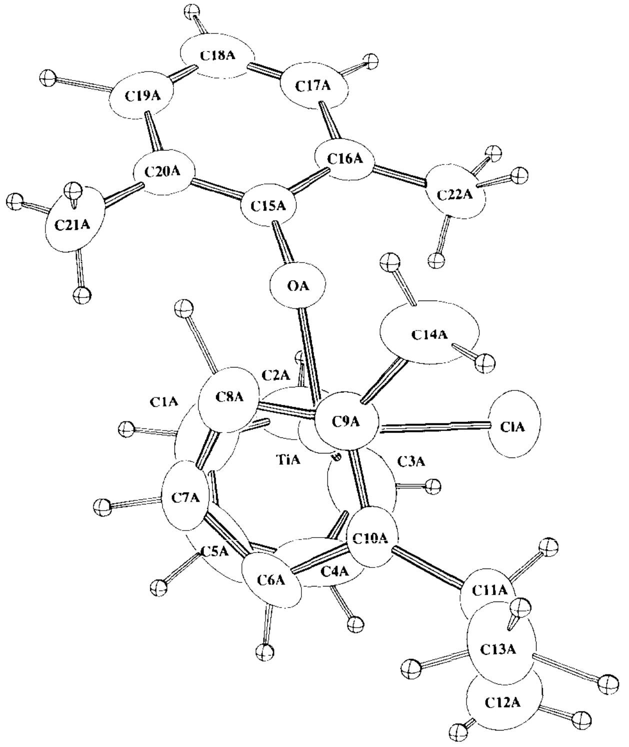


Fig. 4. View of molecule A along the centroid axis.

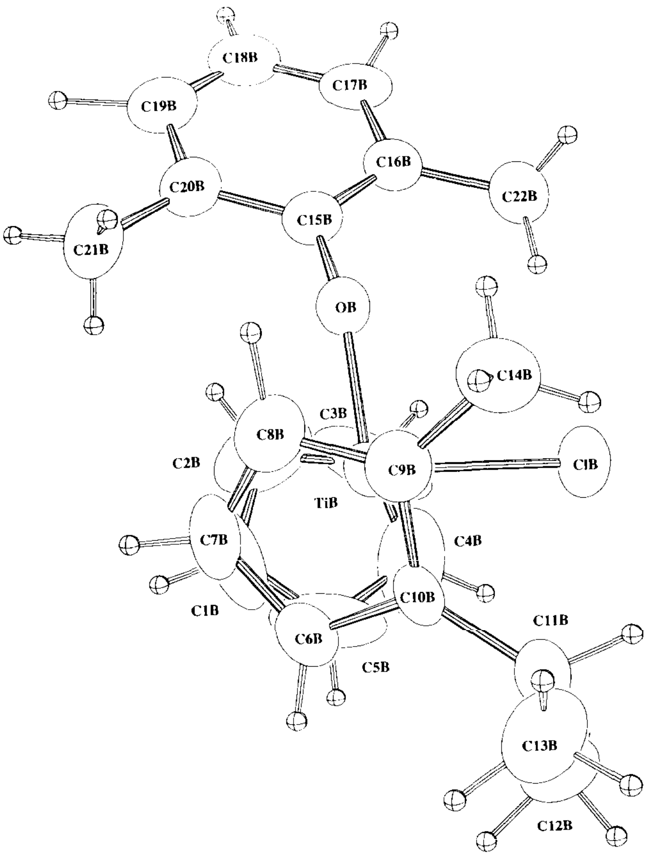


Fig. 5. View of molecule B along the centroid axis.

Table 1
Position parameter and their estimated standard deviations for molecules A and B

Molecule A					Molecule B				
Atom	x	y	z	B_{eq} (Å^2) [a]	Atom	x	y	z	B_{eq} (Å^2)'[a]
TiA	0.754	0.03647(5)	0.445	2.70(2)	TiB	0.75589(7)	−0.45973(5)	0.44145(6)	2.67(2)
ClA	0.6174(1)	0.0445(1)	0.4913(1)	4.68(3)	ClB	0.7631(1)	−0.31549(9)	0.3943(1)	4.21(3)
OA	0.7854(2)	0.1485(2)	0.4737(2)	3.30(8)	OB	0.6451(2)	−0.4764(2)	0.4098(2)	3.17(7)
C1A	0.8763(5)	−0.0065(5)	0.5288(5)	6.9(2)	C1B	0.8318(6)	−0.5824(5)	0.4081(5)	7.6(2)
C2A	0.8192(5)	0.0046(5)	0.5799(4)	6.1(2)	C2B	0.7711(5)	−0.5759(5)	0.3434(6)	8.2(2)
C3A	0.7604(5)	−0.0524(5)	0.5698(5)	7.2(2)	C3B	0.7898(5)	−8.5043(6)	0.3013(4)	8.7(2)
C4A	0.7747(6)	−0.1002(4)	0.5019(5)	7.2(2)	C4B	0.8567(5)	−0.4700(5)	0.3345(5)	7.7(2)
C5A	0.0478(5)	−0.0778(5)	0.4706(5)	7.8(2)	C5B	0.8831(4)	−0.5172(6)	0.4015(5)	7.7(2)
C6A	0.7455(4)	−0.0416(4)	0.3129(4)	3.9(1)	C6B	0.6335(4)	−0.4689(4)	0.5741(4)	3.8(1)
C7A	0.8108(4)	0.0182(5)	0.3116(4)	4.3(1)	C7B	0.7666(5)	−0.5263(4)	0.5726(4)	4.4(1)
C8A	0.7768(4)	0.0994(4)	0.3077(3)	4.1(1)	C8B	0.6940(4)	−0.4774(4)	0.5767(3)	4.2(1)
C9A	0.6911(4)	0.0926(4)	0.3097(3)	3.5(1)	C9B	0.7163(4)	−0.3920(4)	0.5761(3)	3.7(1)
C10A	0.6704(3)	0.0046(4)	0.3105(3)	3.2(1)	C10B	0.0034(3)	−0.3865(3)	0.5756(3)	2.8(1)
C11A	0.5838(4)	−0.0303(4)	0.3030(4)	4.0(1)	C11B	0.8534(4)	−0.3054(4)	0.5840(4)	3.8(1)
C12A	0.5763(5)	−0.1205(5)	0.3334(5)	6.6(2)	C12B	0.9362(4)	−0.3181(5)	0.5482(5)	5.3(2)
C13A	0.5505(4)	−0.0233(5)	0.2120(4)	5.4(2)	C13B	0.8601(5)	−0.2815(5)	0.6788(5)	6.1(2)
C14A	0.6334(6)	0.1673(5)	0.3072(5)	6.2(2)	C14B	0.6564(4)	−0.3189(5)	0.5789(5)	5.2(2)
C15A	0.8294(4)	0.1997(3)	0.5291(4)	3.2(1)	C15B	0.5918(3)	−0.5132(4)	0.3515(4)	3.3(1)
C16A	0.7932(4)	0.2264(3)	0.6050(4)	3.7(1)	C16B	0.5666(4)	−0.4717(4)	0.2784(4)	3.6(1)
C17A	0.8390(5)	0.2777(4)	0.6610(4)	4.8(2)	C17B	0.5142(4)	−0.5142(4)	0.2199(4)	4.3(1)
C18A	0.9169(5)	0.3018(4)	0.6436(5)	5.6(2)	C18B	0.4875(4)	−0.5962(4)	0.2347(4)	4.8(1)
C19A	0.9519(4)	0.2770(4)	0.5687(5)	4.9(2)	C19B	0.5099(4)	−0.6363(4)	0.3092(5)	4.7(1)
C20A	0.9087(4)	0.2243(4)	0.5104(4)	3.9(1)	C20B	0.5630(4)	−0.5971(4)	0.3693(4)	3.9(1)
C21A	0.9468(4)	0.1982(5)	0.4296(5)	5.2(2)	C21B	0.5859(5)	−0.6410(4)	0.4509(5)	5.1(2)
C22A	0.7054(5)	0.2029(4)	0.6204(4)	4.9(1)	C22B	0.5941(4)	−0.3820(4)	0.2602(4)	4.5(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = 4/3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma^2)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

of diastereomers, with the chlorine atom appearing to be located in the region between the two alkyl substituents of the cyclopentadienyl ring (Figs. 2 and 3).

However, the methyl proton resonances may be overlap the resonances of the 2,6-methyl substituents of the aryloxy. This gave a problem previously with **4c**, for which the ^{1}H NMR spectrum was recorded in $CDCl_3$ at 60 MHz [4]. Is this also responsible for the erroneous configurational assignments made for **1c**′? In order to resolve this, we undertook a comparative ^{1}H NMR analysis using a 400 MHz instrument with two more suitable solvents, C_6D_6 and $C_6D_5CD_3$. The ^{1}H NMR data obtained for two pairs of diastereomeric chloro-2,6-dimethylphenoxy titanocenes **1c**,**c**′ and **4c**,**c**′, possessing planar chiralities 1–2 and 1–3 are given in Table 6. Consistent with our previous observations, the methyl resonances are shielded and the isopropyl resonances are deshielded for the same diastereomer of each pair. These results led us at first to propose identical chiralities for **1c** and **4c**.

The present study provides further information. The split in the two well-defined singlets relative to the diastereotopic aryloxy methyl groups contrasts with the single resonance observed in $CDCl_3$. Temperature-variation experiments provide a further insight into the relative characteristics of the two series. Temperature changes had almost the same effect on each of the two

Table 2
Bond distances in angstroms for molecules A and B

Molecule A			Molecule B		
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
TiA	ClA	2.367(2) [a]	TiB	ClB	2.387(1) [a]
TiA	OA	1.883(3)	TiB	OB	1.870(3)
OA	C15A	1.366(5)	OB	C15B	1.363(6)
C1A	C2A	1.355(11)	C1B	C2B	1.392(13)
C1A	C5A	1.436(12)	C1B	C5B	1.328(12)
C2A	C3A	1.316(11)	C2B	C3B	1.347(14)
C3A	C4A	1.334(11)	C3B	C4B	1.305(13)
C4A	C5A	1.354(12)	C4B	C5B	1.343(12)
C6A	C7A	1.418(8)	C6B	C7B	1.414(8)
C6A	C10A	1.421(7)	C6B	C10B	1.385(3)
C7A	C8A	1.392(8)	C8B	C8B	1.413(8)
C8A	C9A	1.402(7)	C8B	C9B	1.389(7)
C9A	C10A	1.423(7)	C9B	C10B	1.422(7)
C9A	C14A	1.502(8)	C9B	C14B	1.509(8)
C10A	C11A	1.513(7)	C10B	C11B	1.514(7)
C11A	C12A	1.502(8)	C11B	C12B	1.485(8)
C11A	C13A	1.513(7)	C11B	C13B	1.536(8)
C15A	C16A	1.417(7)	C15B	C16B	1.368(7)
C15A	C20A	1.391(7)	C15B	C20B	1.430(7)
C16A	C17A	1.388(7)	C16B	C17B	1.398(7)
C16A	C22A	1.506(8)	C16B	C22B	1.508(7)
C17A	C18A	1.363(9)	C17B	C18B	1.382(8)
C18A	C19A	1.386(9)	C18B	C19B	1.364(8)
C19A	C20A	1.402(7)	C19B	C20B	1.397(8)
C20A	C21A	1.495(8)	C20B	C21B	1.490(8)

[a] Numbers in parentheses are estimated standard deviations in least significant digits.

diastereomers within a series. However, significant differences were observed between series. Coalescence takes place at 325 K (C_6D_6) for the pair of diastereomers of the 1–3 series, but at 353 K ($C_6D_5CD_3$) for that of the 1–2 series. Thus the rotational barrier appears to be greater for the latter than for the former. The diastereotopy of the methyls of the isopropyl groups is much more marked for one of the two diastereomers within either series (**1c** for the 1–2 and **4c′** for the 1–3 series). The chemical shifts assignable to protons of the cyclopentadienyl ring tend to confirm correspondence between **1c** and **4c′**. Identical chiralities for **1c** and **4c′** and for **1c′** and **4c** would be still inferred.

Hence, according to the type of the NMR analysis used, opposite configurational assignments have been reached. It is therefore unjustified to use NMR data for inferring, for example, the position of a nucleus with respect to the region of diamagnetic anisotropy of the aryloxy fragment.

In order to explain these contradictory conclusions, we first identified marker groups with respect to the centre of gravity and the plane of the phenyl ring. The markers chosen were the methyl groups of **1c′** and of its constitutional isomer **4c**, for which crystallographic data are available. The distances are given in Table 5 and the coordinates of protons concerned are reported in the diagram which represents the model of benzene [9] (Fig. 8). We were thus able to examine the influence of the aromatic system on the chemical shift variations.

The methyl groups of **1c′** and **4c** appear to be located in the same deshielded region. However, the protons concerned are very near the boundary between this region and the shielding region. We assume that the methyl protons, whose coordinates in the diagram are relative to the crystallographic conformations of **1c′** and **4c**, can easily move from one region to another in solution. Therefore, a conformational phenomenon could be responsible for the mistaken correlation of

Table 3
Bond angles in degrees for

Molecule A				Molecule B			
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
ClA	TiA	OA	97.4(1) [a]	ClB	TiB	OB	96.3(1) [a]
TiA	OA	C15A	146.5(3)	TiB	OB	C15B	144.9(3)
C2A	C1A	C5A	105.2(7)	C2B	C1B	C5B	108.4(7)
C1A	C2A	C3A	110.3(7)	C1B	C2B	C3B	104.6(7)
C2A	C3A	C4A	109.2(8)	C2B	C3B	C4B	110.5(8)
C3A	C4A	C5A	109.3(7)	C3B	C4B	C5B	108.6(8)
C1A	C5A	C4A	105.8(6)	C1B	C5B	C4B	107.8(8)
C7A	C6A	C10A	107.9(5)	C7B	C6B	C10B	108.8(5)
C6A	C7A	C8A	108.1(5)	C6B	C7B	C8B	107.4(5)
C7A	C8A	C9A	108.9(5)	C7B	C8B	C9B	107.7(5)
C8A	C9A	C10A	108.1(5)	C8B	C9B	C10B	108.7(5)
C8A	C9A	C14A	124.2(5)	C8B	C9B	C14B	124.4(5)
C10A	C9A	C14A	127.6(5)	C10B	C9B	C14B	126.9(6)
C6A	C10A	C9A	107.0(4)	C6B	C10B	C9B	107.3(7)
C6A	C10A	C11A	128.0(5)	C6B	C10B	C11B	126.7(6)
C9A	C10A	C11A	124.8(5)	C9B	C10B	C11B	125.8(4)
C10A	C11A	C12A	113.9(5)	C10B	C11B	C12B	114.8(4)
C10A	C11A	C13A	110.1(4)	C10B	C11B	C13B	107.8(4)
C12A	C11A	C13A	109.7(5)	C12B	C11B	C13B	110.5(6)
OA	C15A	C16A	119.0(4)	OB	C15B	C16B	121.5(4)
OA	C15A	C20A	119.7(4)	OB	C15B	C20B	117.6(4)
C16A	C15A	C20A	121.3(5)	C16B	C15B	C20B	120.9(5)
C15A	C16A	C17A	118.3(5)	C15B	C16B	C17B	118.6(5)
C15A	C16A	C22A	119.7(4)	C15B	C16B	C22B	121.5(4)
C17A	C16A	C22A	121.9(5)	C17B	C16B	C22B	119.9(6)
C16A	C17A	C18A	120.9(6)	C16B	C17B	C18B	121.4(5)
C17A	C18A	C19A	120.8(5)	C17B	C18B	C19B	120.0(5)
C18A	C19A	C20A	120.5(5)	C18B	C19B	C20B	120.8(5)
C15A	C20A	C19A	118.1(5)	C15B	C20B	C19B	118.2(5)
C15A	C20A	C21A	121.8(5)	C15B	C20B	C21B	121.5(5)
C19A	C20A	C21A	120.1(5)	C19B	C20B	C21B	120.2(6)

[a] Numbers in parentheses are estimated standard deviations in least significant digits.

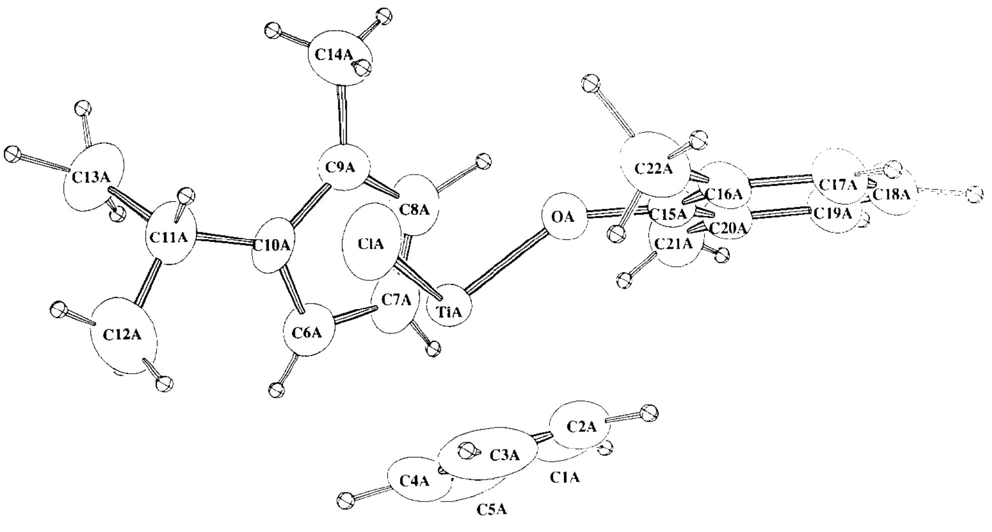


Fig. 6. View of molecule A in the cyclopentadienyl plane.

Table 4
Geometrical comparison of the two molecules A and B
Bonds and angles involving C'A, C"A, C'B and C"B cyclopentadienyl rings

Ring	*x*	*y*	*z*	Centre of gravity of rings specified
C'A	0.8157	−0.0465	0.5286	C1A C2A C3A C4A C5A
C"A	0.7389	0.0346	0.3105	C6A C7A C8A C9A C10A
C'B	0.8265	−0.5299	0.3578	C1B C2B C3B C4B C5B
C"B	0.7628	−0.4502	0.5750	C6B C7B C8B C9B C10B

Molecule A

Atom 1	Atom 2	Bond (Å)	Atom 1	Atom 2	Atom 3	Angle (°)
TiA	C1A	2.381(6)	C1A	TiA	OA	97.4
TiA	C2A	2.388(6)	C1A	TiA	C'A	106.0
TiA	C3A	2.406(5)	C1A	TiA	C"A	103.9
TiA	C4A	2.345(6)	OA	TiA	C'A	108.1
TiA	C5A	2.384(6)	OA	TiA	C"A	105.7
TiA	C6A	2.410(5)	C'A	TiA	C"A	130.8
TiA	C7A	2.349(5)				
TiA	C8A	2.418(6)				
TiA	C9A	2.481(6)				
TiA	C10A	2.502(6)				
TiA	C'A	2.082				
TiA	C"A	2.118				

Molecule B

Atom 1	Atom 2	Bond (Å)	Atom 1	Atom 2	Atom 3	Angle (°)
TiB	C1B	2.360(6)	C1B	TiB	OB	96.3
TiB	C2B	2.408(6)	C1B	TiB	C'B	105.6
TiB	C3B	2.398(6)	C1B	TiB	C"B	104.0
TiB	C4B	2.405(6)	OB	TiB	C'B	108.0
TiB	C5B	2.369(6)	OB	TiB	C"B	106.6
TiB	C6B	2.396(5)	C'B	TiB	C"B	131.0
TiB	C7B	2.311(5)				
TiB	C8B	2.407(5)				
TiB	C9B	2.479(5)				
TiB	C10B	2.495(5)				
TiB	C'B	2.097				
TiB	C'B	2.103				

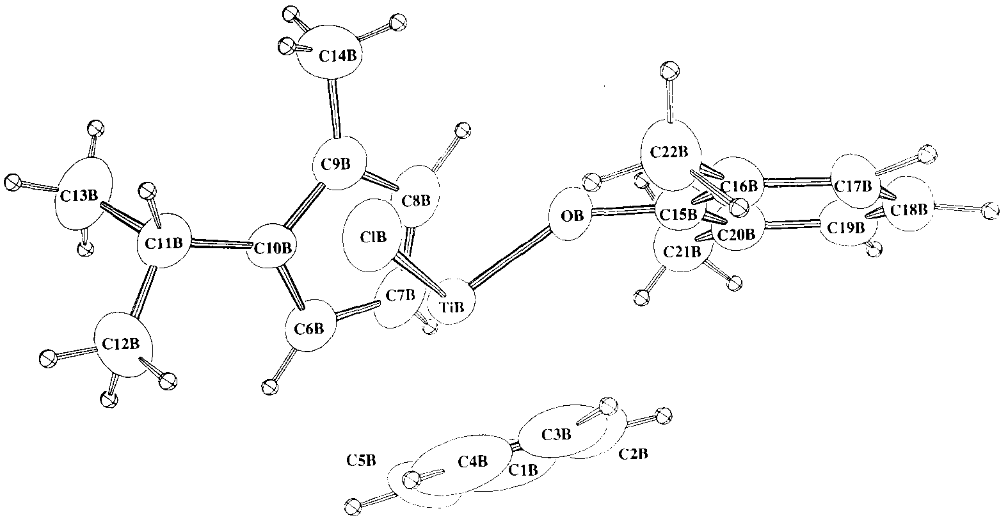


Fig. 7. View of molecule B in the cyclopentadienyl plane.

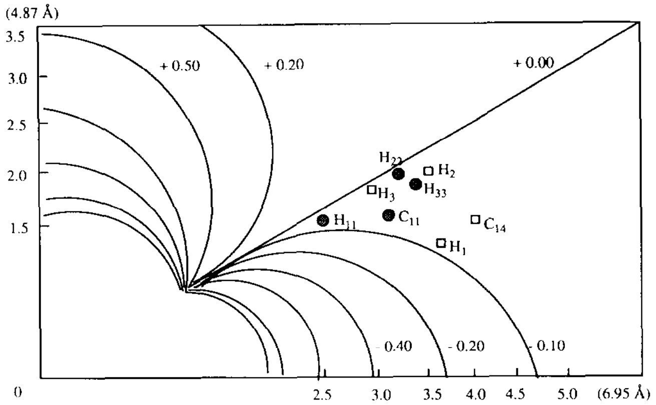


Fig. 8. The diagnostic methyl groups of complexes **1c′** and **4c** in the shielding–deshielding regions around a benzene ring. □, Complex **1c′** (m.p. 186°C); ▨, complex **4c** (m.p. 150°C [5]).

chiralities. Such a hypothesis is all the more plausible because of the easy rotation of the aryloxy group (temperature-variation experiments) as well as the different conformational features for **1c′** (Figs. 4 and 5) even in the solid state.

3. Experimental details

All manipulations of air-sensitive products were under purified argon using Schlenk techniques. Solvents were distilled under argon from sodium benzophenone immediately before use. Preparative thin-layer chromatography used silica gel 7732 G Merck (0.5 mm diameter) and silica gel 9285 Merck was used for column chromatography. Spectra were recorded with the following instruments. IR, Perkin-Elmer 580B; ^{1}H NMR, JEOL FX-100 and Bruker WM-400 spectrometers (δ ppm/TMS); mass spectra, Finnigan 3002. The syntheses of [CpCp′Ti(OAr)Cl](**1c,c′**) and (**4c,c′**) are described in Ref. [4].

3.1. Syntheses of [CpCp′Ti(OAr)X] (1a,a′) and (1b,b′)

1a,a′: X = NCO

In a typical experiment, a solution of [CpCp′-Ti(NCO)$_2$] [10] (555 mg, 1.75 mmol) in 25 cm^3 of dry benzene was warmed at reflux. Excess NaNH$_2$ was then added. To the resulting material, a solution of 2,6-Me$_2$C$_6$H$_3$OH (213 mg, 1.75 mmol) in 20 cm^3 of benzene was added dropwise. The mixture was stirred 30 min at 80°C the progress of this reaction was monitored by TLC; eluent: benzene/hexane/diethyl ether, 6:4:0.3). After filtration through Celite, the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by thin layer chromatography followed by crystallisation from diethyl ether/pentane. This purification afforded successively, in order of decreasing R$_f$: 295 mg of red crystals of **1a′** in 43% yield, m.p. 180°C, and 130 mg of deep-red crystals of **1a** in 18% yield, m.p. 202°C.

1b,b′: X = NCS

[CpCp′Ti(NCS)$_2$] [11] using analogous reaction conditions afforded the following compounds in order of decreasing R$_f$: **1b′** as red crystals (yield 21%), m.p. 148°C, and **1b** as red crystals (yield 14%), m.p. 193°C.

3.2. Synthesis of [CpCp′TiBrX] (2a,a′) and (2b,b′)

2a,a′: X = NCO

In a typical reaction, a solution of HBr in benzene was added slowly to a solution of complex **1a**, m.p. 202°C (123.3 mg, 0.310 mmol) in 5 cm^3 of benzene

Table 5
Selected bond distances (Å) and angles (°) of the chloroaryloxy isomers **4c** and **1c′**

Complex	Ti–Cp [a]	Ti–Cl	Ti–O	Ti–C [b]	O–C	Ti–O–C	C′–Ti–C″	Cl–Ti–O
4c (m.p. 150°C)	2.11	2.38	1.88	2.44	1.38	145	129	97
1c′ (m.p. 186°C)	2.082 (C′A) 2.118 (C″A)	2.367	1.883	2.406	1.366	146.5	130.8	97.4
	2.097 (C′B) 2.103 (C″B)	2.387	1.87	2.402	1.363	144.9	131.0	96.3

[a] Average distance between the metal and the centre of gravity of the cyclopentadienyl ring.
[b] Average distance between the metal and the carbon atoms of the cyclopentadienyl rings.

Table 6
^{1}H NMR (C$_6$D$_6$) data (δ, ppm) for the complexes [CpCp′TiClOAr] (**1c**), (**1c′**), (**4c**) and (**4c′**)

Complex	Cp	Cp′	Me	CH(^{i}Pr)	(Me)$_2$(^{i}Pr)	Me$_2$(Ar)	Ar
1c (m.p. 181°C)	5.75 (s)	5.93 (t); 5.61 (t); 5.20 (t)	1.90 (s)	3.41 (sp)	1.29–1.00 (d–d)	2.44 (s); 1.91 (s)	7.01 (d); 6.80 (t)
1c′ (m.p. 186°C)	5.84 (s)	5.80 (t); 5.73 (t); 5.21 (t)	2.15 (s)	3.16 (sp)	0.90 (d–d)	2.43 (s); 1.92 (s)	7.01 (d); 6.81 (t)
4c (m.p. 150°C)	5.85 (s)	6.16 (t); 5.87 (t); 5.19 (t)	1.82 (s)	2.93 (sp)	1.11–1.02 (d–d)	2.49 (s); 1.92 (s)	7.03 (d); 6.80 (t)
4c′ (m.p. 122°C)	5.80 (s)	6.49 (t); 5.62 (t); 5.23 (t)	1.91 (s)	2.70 (sp)	1.13–0.96 (d–d)	2.49 (s); 1.91 (s)	7.03 (d); 6.80 (t)

s: singlet; d: doublet; t: triplet; sp: septuplet.

while stirring at room temperature. The progress of this reaction was monitored by TLC; eluent: benzene. Once the characteristic red starting material had disappeared, the addition of hydrobromic acid was stopped to limit the formation of the symmetric [CpCp'TiBr$_2$]. Removal of the solvent gave a residue which was washed repeatedly with pentane to eliminate the 2,6-$Me_2C_6H_3OH$ formed during the reaction. This purification afforded complex **2a** (96 mg; yield 86.5%) as red–brown crystals m.p. 172°C.

Treatment of **1a'** m.p. 180°C, according to the above procedure yielded 65% of the expected complex **2a'** as deep-red crystals.

2b,b': X = NCS

These were obtained as brown crystals in the same manner as **2a,a'**; and starting from **1b**, m.p. 193°C, **2b**, m.p. 143°C (yield 37%), was isolated, whereas starting from **1b**, m.p. 148°C, **2b**, m.p. 172°C (yield 78%) was isolated.

3.3. Synthesis of [CpCp'Ti(SC$_6$H$_5$X)] (3a,a') and (3b,b')

3a,a': X = NCO

In a dropping funnel containing 5.5 cm^3 of a solution of C_6H_5SH in 20 cm^3 of dry THF, a stoichiometric quantity of Na wire was added under argon. The white suspension obtained after 12 h was added dropwise to a well stirred THF solution (10 cm^3) of [CpCp'TiNCOBr] (**2a'**), m.p. 150°C (150 mg, 0.421 mmol), cooled to −30°C. After the starting titanium complex had been consumed (TLC; eluent: hexane/diethyl ether, 70:30), the reaction was stopped to avoid the formation of [CpCp'Ti(SPh)$_2$] [1], which was detected by TLC as a purple material in front of the eluent.

After filtration and removal of the solvent under reduced pressure, a brown–violet solid resulted which was purified by thin-layer chromatography. This, followed by crystallization from hexane, afforded 62 mg of orange crystals of **3a** in 62% yield, m.p. 126°C.

Treatment of **2a**, m.p. 172°C according to the above procedure, but at −50°C, yielded 41% of the expected mixture of complexes **3a'** + **3a**. Chromatographic separation afforded 43 mg of **3a'**, m.p. 131°C, and 2 mg of **3a**, m.p. 126°C, in order of decreasing R$_f$ value.

3b,b': X = NCS

These were prepared as above, except that the reactions were performed at −40°C and −15°C, starting from **2b** and **2b'**, respectively. After thin layer chromatographic purification (eluent: hexane/diethyl ether, 7:3), with **2b'** as the starting material, **3b'**, m.p. 173°C was obtained as red needles and **3b** as an oil in the ratio of 99:1 (total yield 75%). Starting from **2b**, the products were **3b'**, m.p. 173°C, and **3b** as an oil in the ratio of 1:9 (total yield 60%).

Table 7
Complexes corresponding to the general structure **I** (see Fig. 3)

Complex	X	Y	Configuration
1c' (m.p. 186°C)	Cl	OAr	u(Ti, p)
1b' (m.p. 148°C)	NCS	OAr	l(Ti, p)
2b' (m.p. 172°C)	NCS	Br	u(Ti, p)
3b' (m.p. 173°C)	NCS	SC_6H_5	l(Ti, p)
1a' (m.p. 180°C)	NCO	OAr	l(Ti, p)
2a' (m.p. 150°C)	NCO	Br	u(Ti, p)
3a' (m.p. 131°C)	NCO	SC_6H_5	l(Ti, p)

4. Conclusions

The crystal structure should be considered as an essential support for dynamic stereochemistry studies. The results presented here clearly indicate the limits of the NMR data-based correlations. The assignment of chirality is generally accurate within the same series, notably 1–2 in this work or 1–3 in Ref. [5]. Caution is advised, however, in correlating structures which belong to different series, especially when a planar chirality is concerned. We recall here the erroneous correlation of the planar chirality reported for the benchrotrenic compounds. The configurations 1*S* and 1*R* were proposed for the isomeric (+)-*o*-methylbenchrotrenic and (−)-*m*-methylbenchrotrenic acids on the basis of the quasi-symmetric curves of the rotatory dispersion and circular dichroism [12]. However, the same chirality was demonstrated for these compounds by X-ray analysis [13].

Finally, we list the complexes corresponding to the general structure **I** (Fig. 3, Table 7) to facilitate the examination of the stereochemistry of the diastereomers. Structure **I** also corresponds to the structures of all major diastereomers **I** of the 1–2 series [4], for which X = Cl and Y = OAr (2-ClC$_6$H$_4$O or 3-Me-6-^{i}PrC$_6$H$_3$O). Faster chromatographic elution of the minor diastereomers of each series was always observed. This behaviour is reversed for complexes of the 1–3 series.

Coordinates and temperature factors for the hydrogen atoms, anisotropic temperature factors for non-hydrogen atoms and a table of observed and calculated structure factors are available from the authors and have been deposited with the Cambridge Crystallographic Data Centre.

---

[1] This complex was identified by comparison with an authentic sample prepared from [CpCp'TiI$_2$] [10]. After removal of solvent, the crude product was purified by flash chromatography (eluent: benzene). The benzene was evaporated to afford [CpCp'Ti(SPh)$_2$] (yield 62%) as purple crystals, m.p. 180°C.

References

[1] C. Guimon, G. Pfister-Guillouzo, J. Besançon and P. Meunier, *J. Chem. Soc., Dalton Trans.*, (1987) 107.

[2] (a) J. Besançon, J. Tirouflet, B. Trimaille and Y. Dusausoy, *J. Organomet. Chem., 314* (1986) C12; (b) J. Besançon, D. Camboli, B. Trimaille and Y. Dusausoy, *C.R. Acad. Sci., Paris, Ser. II, 301* (1985) 83.

[3] J. Besançon, D. Camboli and J. Tirouflet, *J. Organomet. Chem., 186* (1980) C15.

[4] J. Besançon and S. Top, *J. Organomet. Chem., 127* (1977) 139.

[5] J. Besançon, S. Top, J. Tirouflet, Y. Dusausoy, C. Lecomte and J. Protas, *J. Organomet. Chem., 127* (1977) 153.

[6] (a) *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham (present distributer D. Reidel, Dordrecht), 1974; (b) *Enraf-Nonius Molecular Structure Determination Package; MOLEN Version 1990*, Enraf-Nonius, Delft, 1990; (c) C.K. Johnson, *ORTEP*, *Report ORNL-3794*, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

[7] D. Seebach and V. Prelog, *Angew. Chem., Int. Ed. Engl., 21* (1982) 654.

[8] J. Tirouflet, A. Dormond, C. Lecomte, Y. Dusausoy and J. Protas, *J. Organomet. Chem., 73* (1974) 67.

[9] F.A. Bovey (ed.), *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1969, p. 65.

[10] D. Camboli, J. Besançon and B. Trimaille, *C.R. Acad. Sci. Paris, Ser. C, 290* (1980) 365.

[11] D. Camboli, *Thesis*, 1980.

[12] N.L. Alinger and E.L. Eliel (eds), *Topics in Stereochemistry*, Interscience Publishers, New York, 1967, p. 77.

[13] M.A. Bush, T.A. Dullforce and G.A. Sim, *J. Chem. Soc., Chem Commun.*, (1969) 1491.