

**Preliminary communication**

**DYNAMIC STEREOCHEMISTRY OF LIGAND SUBSTITUTION AT A CHIRAL TITANIUM CENTER. SYNTHESIS OF ASYMMETRICAL HALIDOPSEUDOHALIDOTTANOCENE COMPLEXES**

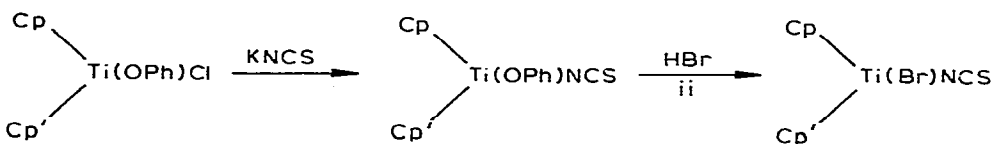
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**Summary**

Two new ligand exchange reactions (i and ii) at a chiral titanium center have been studied:

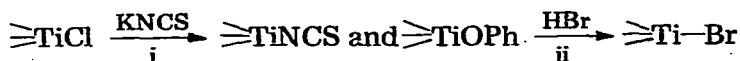


(Cp =  $\eta^5\text{-C}_5\text{H}_5$  ; Cp' =  $\eta^5\text{-C}_5\text{H}_3\text{Me-1CHMe}_2\text{-2}$  or 3 ; OPh =  $-\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6}$ )

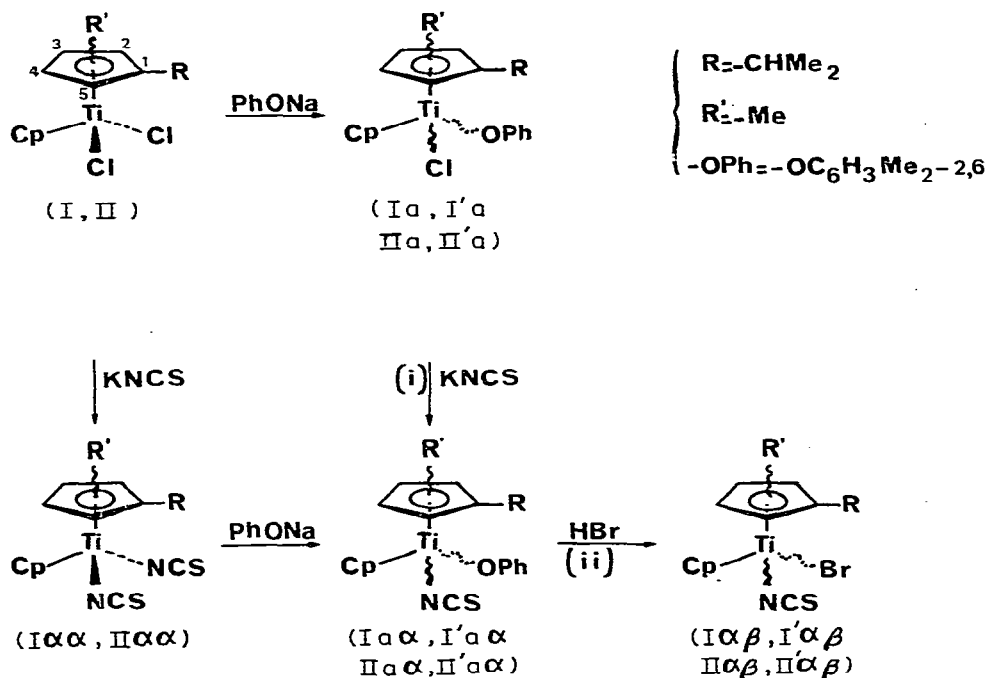
These two reactions are selective but only the second is stereospecific. Reaction ii is shown to involve retention at the titanium atom. By use of these reactions, the first pairs of asymmetrical halidopseudohalido titanocene complexes have been isolated, and their relative configurations are suggested.

In earlier work [1] we obtained dipseudohalido-organometallic titanocene complexes with two different groups attached to a  $\pi$ -bonding cyclopentadienyl ring. We also found that the pseudohalidoaryloxy derivatives of  $\text{Ti}^{\text{IV}}$  are stereostable [2]. In previous studies [3] of the dynamic stereochemistry of ligand substitution reactions in the quasitrahedral titanocene series, it was shown that some processes involve racemisation ( $\rightleftharpoons\text{TiCl} \xrightarrow{\text{RM}'} \rightleftharpoons\text{Ti-R}$ ;  $\rightleftharpoons\text{TiOPh} \xrightarrow{\text{RM}'} \rightleftharpoons\text{TiR}$ ;  $\rightleftharpoons\text{TiCl} \xrightarrow{\text{ROM}'} \rightleftharpoons\text{TiOR}$ ;  $\rightleftharpoons\text{TiR} \xrightarrow{\text{HCl}} \rightleftharpoons\text{TiCl}$ ), while others ( $\rightleftharpoons\text{TiOR} \xrightarrow{\text{HCl}} \rightleftharpoons\text{TiCl}$ ;  $\rightleftharpoons\text{TiOPh} \xrightarrow{\text{HCl}} \rightleftharpoons\text{TiCl}$ ) occur with retention of the configuration at the titanium atom.

We have now established the dynamic stereochemistry of two new ligand exchange reactions:



The different sequences obtained starting from the two isomeric dichlorides I or II (I: 1,2 substitution; II: 1,3 substitution [1]) are given in Scheme 1. The following symbols are used: I, I' or II, II' are diastereoisomeric forms;  $\alpha$ ,  $\alpha$  and  $\beta$  refer to the  $\sigma$  ligand:  $\alpha = \text{OC}_6\text{H}_3\text{Me}_2\text{-2,6}$ ;  $\alpha = \text{NCS}$ ;  $\beta = \text{Br}$ .



For the two reactions i and ii, the main starting substrates are the two diastereoisomers I $\alpha\alpha$ , I' $\alpha\alpha$  or II $\alpha\alpha$ , II' $\alpha\alpha$  which have central chirality on the metal atom and a planar chirality.

In each case, the two pairs of diastereoisomers are obtained starting from the corresponding dipseudohalido-complexes I $\alpha\alpha$  or II $\alpha\alpha$  by reaction with phenoxy sodium salt. These pairs of diastereoisomers have been separated by thin layer chromatography (eluant benzene/hexane/ether: 6/4/0.3). This reaction is only partially stereoselective. For instance, the transformation I $\alpha\alpha$   $\rightarrow$  I $\alpha\beta$  + I' $\alpha\beta$  gives the two diastereoisomeric forms in the ratio I $\alpha\beta$ /I' $\alpha\beta$ : 60/40.

The characteristics of all the compounds are given in Table 1.



The action of KNCS on the chloro derivatives I $\alpha$ , I' $\alpha$  or II $\alpha$ , II' $\alpha$ , obtained from the dichlorotitanocene complexes I or II [4] is selective, but it is not stereo-

TABLE 1  
PHYSICAL DATA OF THE COMPOUNDS I AND II ( $\alpha\alpha$ ,  $\alpha\beta$ )

Complexes	M.p. (°C)	IR $\nu(\text{C}\equiv\text{N})$ ( $\text{cm}^{-1}$ )	$^1\text{H NMR}$ (Solvent $\text{CDCl}_3$ , TMS as internal reference)	
			$\text{C}_5\text{H}_5$ <sup>a</sup>	$\text{CH}_3$ <sup>b</sup>
I $\alpha\alpha$	148–150	2047	6.16(s) <sup>c</sup> (5) <sup>d</sup>	1.06(d) <sup>c</sup> (6) <sup>d</sup> 1.16(d)
I' $\alpha\alpha$	193–194	2070	6.11(s) (5)	1.07(d) (6) 1.24(d)
II $\alpha\alpha$	132	2058	6.12(s) (5)	1.06(d) (6) 1.13(d)
II' $\alpha\alpha$	128	2070	6.12(s) (5)	1.21(d) (6) 1.22(d)
I $\alpha\beta$	163	2040	6.51(s) (5)	1.18(d) (6)
I' $\alpha\beta$	146	2038–2040	6.51(s) (5)	1.06(d) (6) 1.15(d)
II $\alpha\beta$	103	2040	6.52(s) (5)	1.13(d) (6) 1.26(d)
II' $\alpha\beta$	122	2038	6.52(s) (5)	1.13(d) (6) 1.26(d)

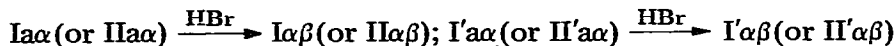
<sup>a</sup> Unsubstituted cyclopentadienyl ring. <sup>b</sup> Methyl group of the isopropyl group. <sup>c</sup> s, singlet; d, doublet.  
<sup>d</sup> Relative intensities of the signal.

specific. In each case, the two pseudohalido diastereoisomers were obtained, for example Ia  $\rightarrow$  I $\alpha\alpha$  (60 %) + I' $\alpha\alpha$  (40%).

Moreover, under our experimental conditions (refluxing in acetone with an excess of KNCS), a partial epimerisation is observed for each pseudohalido diastereoisomer.



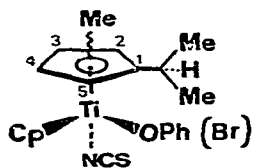
The bromination of the complexes I $\alpha\alpha$ , I' $\alpha\alpha$  and II $\alpha\alpha$ , II' $\alpha\alpha$  is wholly selective and only the splitting of the Ti—O bond is observed. It is also stereospecific, only one halidopseudohalido derivative being obtained:



This reaction enables the isolation of the separate forms of the first pairs of halidopseudohalido diastereoisomers of substituted titanocene complexes.

We suggest that in this reaction the breaking of the titanium—oxygen bond proceeds with retention of the configuration at the titanium atom. This is proposed by analogy with the retention which occurs in the substitution of an aryl-oxy ligand by a chlorine atom [3a]. The proposal is in good agreement with the NMR data. In particular there is an evident morphological analogy for the signals of the methyl of the isopropyl groups between complexes I $\alpha\alpha$  and I $\alpha\beta$  on one hand and complexes I' $\alpha\alpha$  and I' $\alpha\beta$  on the other: the diastereotopy of these methyl groups increases for one type of diastereoisomer (I' $\alpha\alpha$ , I' $\alpha\beta$ ) and decreases for the other (I $\alpha\alpha$ , I $\alpha\beta$ ).

These results, as well as the relative configurations of the complexes Ia and II [4] and the systematic analogy of the NMR data between the complexes Ia and I $\alpha\alpha$  (or IIa and II $\alpha\alpha$ ), indicate the following relative configuration for the compounds under discussion.



(Ia  $\alpha$  (I  $\alpha$   $\beta$ )  
or II  $\alpha$  (II  $\alpha$   $\beta$ ))

Details will be given in the complete paper.

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