Dynamic Stereochemistry of Ligand Substitution in Quasi-tetrahedral Complexes of Bis(η -cyclopentadienyl)titanium. Stereospecific Reaction at Titanium with Retention of Configuration, and X-Ray Structures of $[(\eta^5-C_5H_5)(\eta^5-1-Me, 3-Pr^4-C_5H_3)(2-ClC_6H_4O)ClTi]$ and $[(\eta^5-C_5H_5)(\eta^5-1-Me, 3-Pr^4-C_5H_3)(2-ClC_6H_4O)(2,6-Me_2C_6H_3O)Ti]$

By J. Besançon, S. Top, and J. TIROUFLET*

(Laboratoire de Polarographie Organique, Bld. Gabriel, 21000 Dijon, France)

and J. DUSAUSOY, C. LECOMTE, and J. PROTAS

(Laboratoire de Mineralogie et Cristallographie, Faculté Sciences, 54037 Nancy, France)

Summary Substitution of an OR group by a Cl ligand by the action of HCl on quasi-tetrahedral bis-cyclopentadienyltitanium complexes of the type $[(cp)(cp')Ti(OR^1)-(OR^2)]$ is a stereospecific process which occurs with retention of configuration at titanium; the X-ray crystal structures of chloro- and 2,6-dimethylphenoxy-(2-chlorophenyl)-(η^5 -cyclopentadienyl)-(η^5 -1-methyl-3-isopropylcyclopentadienyl)titanium are reported.

WE have already reported preliminary results on chiral titanium complexes of the type $[(cp)(cp')TiXY](cp=\eta^5-cyclopentadienyl)$ or substituted η^5 -cyclopentadienyl), where the titanium atom is surrounded by four different ligands,¹⁻³ and also the first example of a resolved bis(η -cyclopentadienyl)titanium derivative.⁴ The stereochemistry of ligand substitution has been studied extensively for square-planar and octahedral complexes, but for tetrahedral or quasitetrahedral systems, the known examples are limited to a few complexes of Groups 6, 7, and 8 transition elements.⁵

In the case of quasi-tetrahedral titanium systems, the choice of appropriate compounds is important because the stereochemical reference can be established only by X-ray analysis. We have prepared several suitable types of diastereoisomeric complexes.³,⁶



We report here preliminary results on the following two ligand exchange reactions. Reaction (1): action of phenolate ion on an aryloxy-biscyclopentadienyltitanium chloride to give the diaryloxy-complex; and reaction (2): the action of HCl on this diaryloxy-complex. Both reactions were studied starting from each diastereoisomer of the diastereoisomeric pairs of complexes[†] (1a) and (1a'), (1b) and (1b'), (2a) and (2a'), and (2b) and (2b'). Reaction (1) yields not only the two diaryloxy-compounds (1c) and (1c') and (2c) and (2c'), but also, in some cases, the symmetrical bis(aryloxy)-compound, the diastereoisomer of the starting material, and the diastereoisomeric pair of complexes resulting from exchange of the starting aryloxy-group (see Scheme 1 for examples).

$$\begin{array}{c} \text{(1a)} \xrightarrow{i} (1c) + (1c') + (1d) + (1a) + (1a') \\ (16\%) & (71\%) & (13\%) \end{array} \\ \begin{array}{c} \text{ii} \\ \text{(1b)} \xrightarrow{i} (1a) + (1a') + (1c) + (1c') + (1d) \\ (34\%) & (25\%) & (28\%) \end{array}$$

SCHEME 1. i, NaOC₆H₄Cl-2; ii, NaNH₂-HOC₆H₃Me₂-2,6

Reaction (2) has two main characteristics: (a) it is stereoselective; the leaving group is 2,6-Me₂C₆H₃O; (b) it is stereospecific and involves retention of configuration at titanium.



Crystallographic data supporting this retention of configuration have been obtained for the diastereoisomer of (2b) with m.p. 134 °C, and the diastereoisomer of (2c) with m.p. 171 °C. The other diastereoisomer of (2b) has m.p. 114 °C, and that of (2c) has m.p. 160 °C. The interconversions between these diastereoisomers can be represented by the sequence of reactions in Scheme 2. Crystal data: Complex (2b), C₂₀H₂₂Cl₂OTi, monoclinic, space group P2₁/c; a =14·50(2), $b = 13\cdot03(2)$, $c = 19\cdot38(3)$ Å; $\beta = 98\cdot4(0\cdot4)^\circ$; complex (2c), C₂₈H₃₁ClO₂Ti, orthorhombic, space group Pna2₁; $a = 16\cdot42(3)$, $b = 1245\cdot(2)$, $c = 12\cdot14(2)$ Å. The data were collected on a three-circle diffractometer ($\theta, 2\theta$

† (1a) and (1a'), for example, denote a diastereoisomeric pair of complexes.

scans; Cu- K_{α} radiation. 1840 and 995 reflection intensities with $\sigma(I)/I < 0.25$ and 0.20 for (2b) and (2c) respectively, were used for the structure solutions by statistical methods. The final R factors are 0.095 and 0.078 and the structures are shown in Figures 1 and 2.

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FIGURE 1. Structure of $[(\eta^5-C_5H_5)(\eta^5-1-Me, 3-Pr^iC_5H_3)(2-ClC_6-$ H₄O)ClTi], (2b).

The retention of configuration in reaction (2) must be compared with the stereochemistry of cleavage of α -phenyl ethers by HCl.⁷ We suggest, by analogy with the proposed

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FIGURE 2. Structure of $[(\eta^5-C_5H_5)(\eta^5-1-Me, 3-Pr^iC_5H_3)(2-ClC_6 H_4O)(2,6-Me_2C_6H_3O)Ti], (2c).$

mechanism of cleavage of organomercury compounds⁸ that the reaction occurs by attack of an ion pair or a nondissociated molecule and not by a solvated proton.

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