

Preliminary communication

**DYNAMIC STEREOCHEMISTRY OF THE $\text{TiBr} + \text{SPh}^- \rightarrow \text{TiSPh}$,
 CONVERSION WITH ISOCYANATO COMPLEXES OF TITANOCENE**

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B. TRIMAILLE

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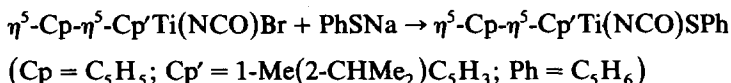
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Summary

The metathesis reaction



has been shown to be selective and stereospecific, with inversion of the configuration at the titanium center. This stereochemical behaviour is in contrast with that observed for the corresponding NCS complexes. The conclusions are based on ¹H NMR data and a crystal structure determination on the complex $\eta^5\text{-Cp-}\eta^5\text{-Cp}'\text{Ti(NCS)O-2,6-Me}_2\text{C}_6\text{H}_3$ (isomer m.p. 193°C), which crystallizes in holohedral form, orthorhombic system, space group *Pbca* with *a* 15.671(3), *b* 15.804(5), *c* 17.478(3) Å. On Seebach's nomenclature this structure corresponds to the *u*(Ti,P) form.

The ligand exchange process at a metallic center is a topic of major importance in modern organometallic chemistry. Information on this process for tetrahedral or pseudo-tetrahedral complexes is scarce, but we have previously described several examples of dynamic stereochemistry at a pseudotetrahedral titanium chiral center [1].

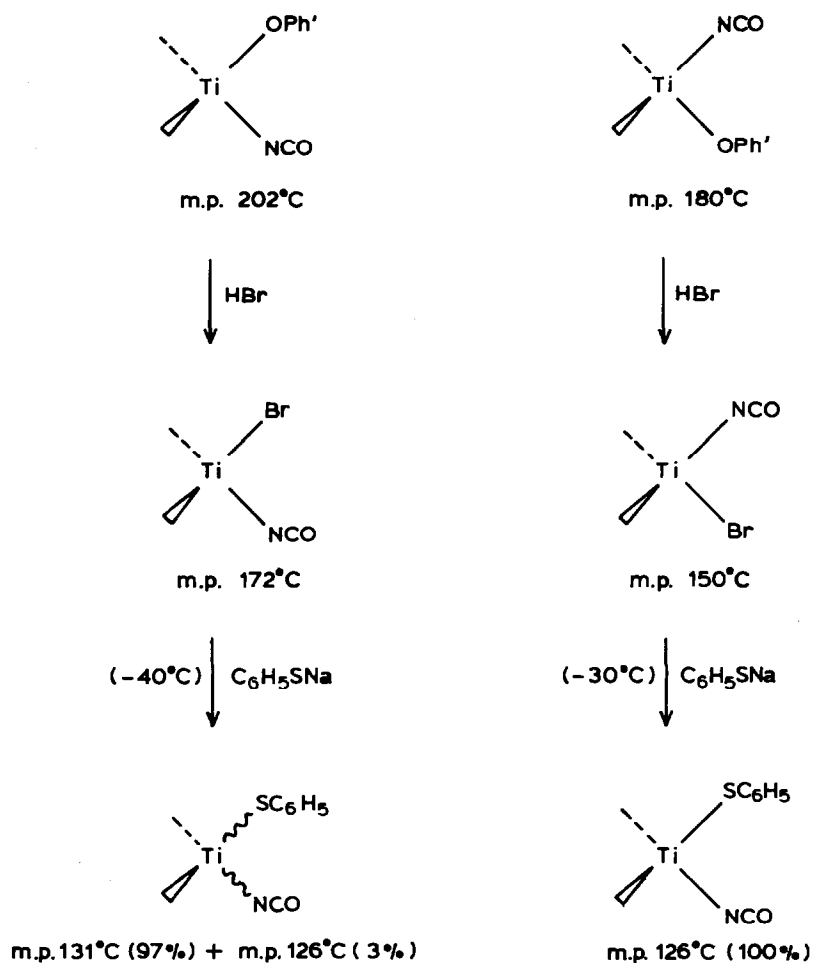
We present here results for complexes of the general formula $\eta^5\text{-Cp-}\eta^5\text{-Cp}'\text{TiXY}$ (Cp = C₅H₅ and Cp' = 1-Me(2-Me₂CH)C₅H₃). These complexes have two chiral

features, namely a central chirality at the titanium atom and a planar chirality for stereochemical reference. The new results concern the two exchange reactions:



The transformations have been studied starting from each of the two diastereoisomeric forms of $\eta^5\text{-Cp-}\eta^5\text{-Cp}'\text{-Ti(NCO)OPh}'$ complexes ($\text{Ph}' = 2,6\text{-Me}_2\text{C}_6\text{H}_3$).

The action of HBr on the m.p. 202°C form of the $\text{CpCp}'\text{Ti(NCO)OPh}'$ complex gives exclusively the m.p. 172°C form of the $\text{CpCp}'\text{Ti(NCO)Br}$. When this form is treated with PhSNa at -40°C in THF the two $\text{CpCp}'\text{Ti(NCO)SPh}$ diastereoisomers are obtained but one predominates. Similarly the m.p. 180°C form of the $\text{CpCp}'\text{Ti(NCO)OPh}'$ complex gives the m.p. 150°C form of the bromo complex, which is converted at -30°C exclusively into one of the $\text{CpCp}'\text{Ti(NCO)SPh}$ complexes (m.p. 126°C form) (Scheme 1).



SCHEME 1

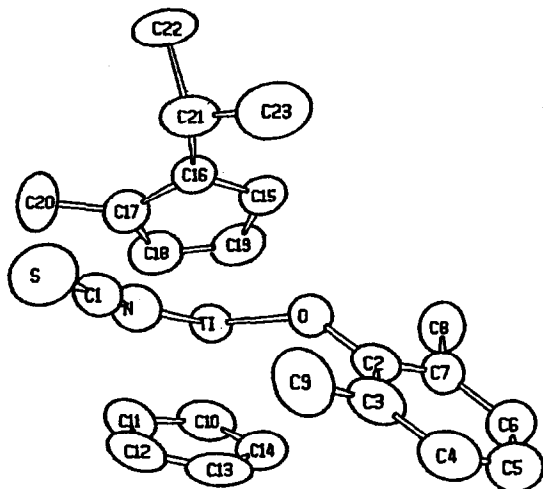


Fig. 1. A perspective ORTEP view of the molecular structure of the complex $\text{CpCp}'\text{Ti}(\text{NCS})\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3$ (isomer m.p. 193°C)

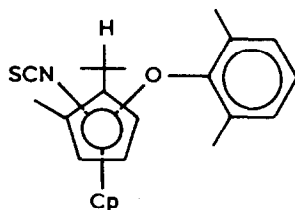


Fig. 2. Complex $\text{CpCp}'\text{Ti}(\text{NCS})\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3$; $\mu(\text{Ti},\text{P})$ (m.p. 193°C)

TABLE 1

^1H NMR DATA ^a

Complexes	CH_3 ^b	$\text{CH}(\text{CH}_3)_2$	$\text{CH}(\text{CH}_3)_2$
$\text{NCO}(\text{OPh})$ m.p. 202	2.03(s) ^c	3.08(hp) ^c	1.06(d) ^c 1.22(d)
$\text{NCO}(\text{OPh})$ m.p. 180	2.09(s)	2.97(hp)	1.05(d) 1.12(d)
$\text{NCS}(\text{OPh})$ m.p. 193	2.09(s)	3.18(hp)	1.07(d) [1b] 1.24(d)
$\text{NCS}(\text{OPh})$ m.p. 148	2.14(s)	3.09(hp)	1.06(d) [1b] 1.11(d)
$\text{NCO}(\text{SC}_6\text{H}_5)$ m.p. 131	2.38(s)	2.86(hp)	1.03(d) 1.10(d)
$\text{NCO}(\text{SC}_6\text{H}_5)$ m.p. 126	2.08(s)	3.07(hp)	1.16(d) 1.42(d)
$\text{NCS}(\text{SC}_6\text{H}_5)$ m.p. 173	2.44(s)	2.97(hp)	1.05(d) [1c] 1.12(d)
$\text{NCS}(\text{SC}_6\text{H}_5)$ oil	2.16(s)	3.12(hp)	1.17(d) [1c] 1.39(d)

^a 100 MHz, CDCl_3 ; TMS as internal reference; δ (ppm). ^b Methyl group of the unsubstituted cyclopentadienyl ring. ^c s, singlet; hp, heptuplet; d, doublet.

The main problem was to assign the exact stereochemistry to the two diastereoisomeric forms of each couple.

It was not possible to obtain crystallographic data for the TiNCO complexes, but we have previously presented such data for a CpCp'Ti(NCS)SPh diastereomeric form [1c] and we report here the structure of a CpCp'Ti(NCS)OPh' form. This structure, represented in Fig. 1, reveals the relative configurations of the two asymmetric centres of the m.p. 193°C form; on Seebach's nomenclature [2,3] this structure corresponds to the *u*(Ti,P) form (Fig. 2) *.

The N-Ti-O plane practically bisects the two cyclopentadienyl planes. The five atoms TiNC(1)SO are in the same plane; the N-Ti-O angle is 95° and the Ti-N-C(1)-S' atoms are nearly aligned.

Starting from these data it is possible to assign structures to the corresponding Ti-NCO complexes on the basis of analogy in the NMR spectral patterns, which are shown in Table 1.

On the other hand, the retention stereochemistry of the ligand exchange Ti-OPh' → TiBr is well established [6]. If the arguments we have used to establish the stereochemical similarity between the NCO complexes and the NCS complexes through RMN data are correct, the TiBr → TiSPh substitution appears to involve a predominant inversion process.

The detailed knowledge of the structure of the complex CpCp'Ti(NCS)OPh' form reported here has another important consequence, in that it shows that the TiBr → TiSPh substitution gives a major product which is formed by a retention process and not by an inversion process as was previously postulated [1c]. These two results appear to be in conflict. It is possible that NMR correlation we have used may be in error, but our conclusion has some theoretical support, analysis of photoelectronic spectra having revealed a strong interaction through the bonds between the orbitals of ligands X (NCS, Br and OC₆H₅) and the two cyclopentadienyl rings [7]. There is an inversion of the highest occupied molecular orbitals on going from the isocyanato to the isothiocyanato complexes. Moreover, the lowest unoccupied molecular orbital (LUMO) of the CpCp'Ti(Br)NCZ complexes is different for Z = 0 and Z = S; this orbital is localized on Br for NCO complexes and on NCS for NCS complexes. Such a difference must lead to a marked change from a stereochemical point of view of the transition state of the substitution process [7].

References

- 1 (a) J. Besançon, H. Tan, F. Huq and J. Tirouflet, *Bull. Soc. Chim. France II*, (1978) 465; (b) J. Besançon, D. Camboli and J. Tirouflet, *J. Organomet. Chem.*, 186 (1980) C15 and ref. therein; (c) J. Besançon, D. Camboli, B. Trimaille and Y. Dusausoy, *C.R. Acad. Sci. Paris, Ser. II*, 301 (1985) 83.
- 2 D. Seebach and V. Prelog, *Angew. Chem. Int. Ed.*, (1982) 654.
- 3 J. Tirouflet, A. Dormond, C. Lecomte, Y. Dusausoy and J. Protas, *J. Organomet. Chem.*, 73 (1974) 67.

* The complex $\eta^5\text{-Cp-}\eta^5\text{-Cp'Ti(NCS)O-(2,6-Me}_2\text{)C}_6\text{H}_3$ (isomer m.p. 193°C) crystallizes in holohedral form, orthorhombic system, space group *Pbca*: *a* 15.671(3), *b* 15.804(5), *c* 17.478(3) Å; *V* = 4328 Å³; *d*_{calc} = 1.264, *Z* = 8. The structure was solved by direct methods of phase determination [4] using 2516 observed ($\sigma(I)/I < 1$) reflexions (4097 measured), and refined to a final residual *R* = 0.074 with the CAD₄-SDP program [5] (automatic diffractometer Enraf-Nonius CAD₄ F).

- 4 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq and M.M. Woolfson. MULTAN 80A. System of computer programs for the Automatic solution of Crystal structures from X-Ray Diffraction data. Univ. York, England and Louvain, Belgium, 1980.
- 5 B.A. Frenz, Computing in Crystallography edited by H. Schenk, R. Olthof-Hazekamp, H. Van Koningsveld and G.C. Bassi, Delft. Univ. Press (1978) pp. 44-71.
- 6 Ref. 3c of 1b.
- 7 C. Guimon, G. Pfister-Guillouzo, J. Besançon and Ph. Meunier, J. Chem. Soc. Dalton Trans., (1986) in press.