WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS

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α-CHIRAL PLATINUM ALKYLs

P. BERGAMINI - E. COSTA - S. SOSTERO - O. TRAVERSO
P.G. PRINGLE - A.G. ORPEN

A new synthetic route to α-chiral platinum alkyls, recently developed by us\(^1\) and other groups\(^2\), is based on the insertion of a carbene deriving from a diazocompound into a Pt-halogen or a Pt-carbon bond.

\[[Pt] - L + N_2CHR \rightarrow [Pt] - CHRL + N_2\]

\[[Pt] = Pt(II) \text{ complex}\]
\[L = \text{Halogen, } CH_3\]
\[R = COOEt, COpH, COOMenth, SiMe_3\]

The reaction of the sterically hindered \(N_2CHSiMe_3\) with optically active platinum complexes \([PtX_2\text{ (chiral diphosphine)}]\) \((X = Cl, Br, I)\) gives a pair of diastereomeric products \([PtX(CHXSiMe_3)(\text{chiral diphosphine})]\), one being largely predominant (up to 15:1 diastereomeric ratio) in some cases. For both the products \([PtBr(CHBrSiMe_3)(S, S\text{-chiraphos})]\) and \([PtCl(CHClSiMe_3)(S, S\text{-skewphos})]\), the major isomer has been separated in pure form and the absolute configuration at the α carbon has been determined by x-ray crystal structure.
The behaviour of the \( PtCHXSiMe_3 \) group \((X=\text{halogen})\) with respect to epimerization and halogen substitution has been explored.

These compounds are examples of \( \alpha \)-chiral platinum alkyls with a single, assigned and stable configuration at the \( \alpha \) carbon, which is a relevant character for the potential use of this class of compounds to investigate the mechanism of fundamental organometallic reactions and of asymmetric transformations catalysed by transition metals complexes.\(^3\)

During this study, we observed that the group \( Pt - CHXSiMe_3 \) \((X=\text{halogen})\) can easily undergo desilylation in the presence of water, with loss of chirality:

\[
[Pt] - CHXSiMe_3 \xrightarrow{H_2O} [Pt] - CH_2X
\]

This reaction can be used as a convenient alternative synthesis of chloromethylplatinum complexes avoiding the use of \( CH_2N_2 \).

When \( N_2CHSiMe_3 \) reacts with a substrate containing a \( Pt - Me \) bond, both the chiral \( PtCHMe - SiMe_3 \) and the non-chiral \( Pt - CH_2SiMe_3 \) groups can be formed, depending on the reaction conditions.

A mechanism for these transformations will be proposed on the basis of experimental observations.

REFERENCES


P. Bergamini - E. Costa - S. Sostero - O. Traverso
Dipartimento di Chimica
dell’Università di Ferrara e Centro di Studio
su Fotoreattività e Catalisi del C.N.R.
via L. Borsari, 46, 44100 Ferrara
P.G. Pringle - A.G. Orpen
School of Chemistry, Bristol University, U.K.