Asymmetric Induction by the s-Butyl Group in *cis*- and *trans*-Dichloro(benzylamine)(olefin)platinum(II) Complexes

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Summary In *cis*- and *trans*-dichloro[$CH:CH\cdot(CH_2)_n\cdot\overset{\bullet}{C}H$-(Me)Et](benzylamine)platinum(II) complexes, the asymmetric carbon atom originally present in the olefin induces the opposite absolute configuration in the tertiary carbon atom bound to Pt and, at least in the *cis*-complexes, the extent of asymmetric induction rapidly diminishes with increasing *n*.

NOTHING is known about the asymmetric induction exerted by an s-butyl group present in an olefin when, by complexation of the olefin itself to a transition metal, at least one of the unsaturated carbon atoms becomes asymmetric.

Continuing our studies on platinum(II) complexes involving stereospecific co-ordination of racemic α-olefins,[1] we have synthesized the *trans*-dichloro(benzylamine)[(*S*)-3-methylpent-1-ene]Pt^{II} complex (I) and have investigated the equilibrium between its two possible diastereoisomers (Figure 1) by c.d. and n.m.r. Complex (I) was prepared by the reaction of (*S*)-3-methylpent-1-ene (optical purity ⩾94%) with *trans*-dichloro(benzylamine)(ethylene)Pt^{II}, m.p. 130—131°. Two successive recrystallizations from CH_2Cl_2 gave a product having the same optical rotation $[\alpha]^{25}_{D}$ $-35°$ (*c* 0·23, $CHCl_3$); m.p. 118—119°. Both n.m.r. (Figure 2) and c.d. spectra (Figure 3) of complex (I) change considerably with time. The 220 MHz spectrum (Figure 2) shows initially in the CH_3 region a doublet and a triplet, centred respectively at τ 8·53 and at 9·13. The intensity of the latter resonances rapidly decreases with time and a third complex band centred at τ8·9 appears, the intensity of which is very small if measured immediately after the

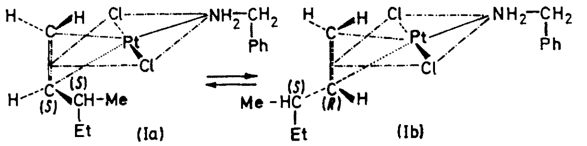

FIGURE 1. *Diastereoisomers of the complex* (I).

preparation of the solution but which increases with time, reaching a constant value after 24 hr.

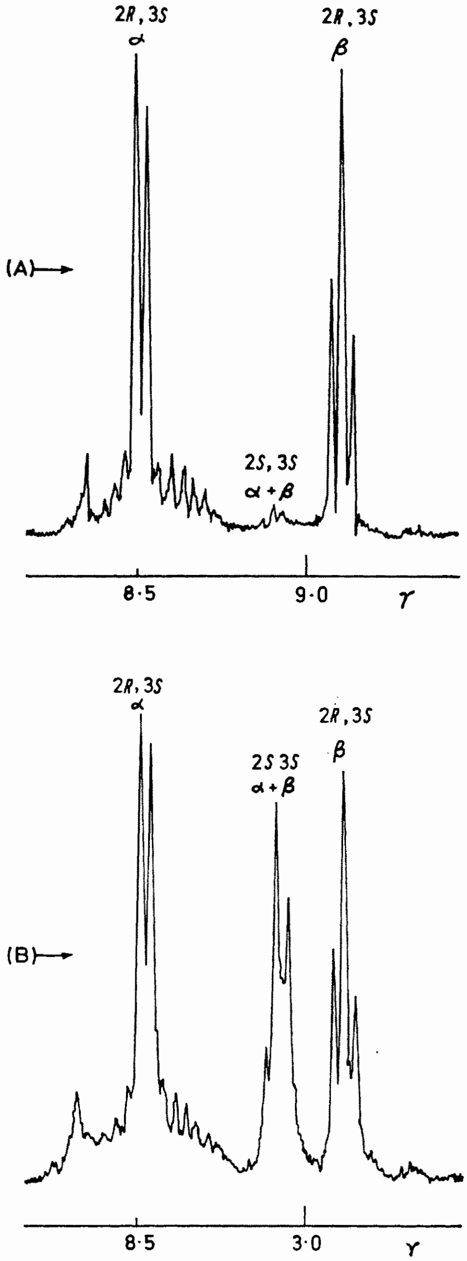

FIGURE 2. *Methyl resonance in the* 220 *MHz n.m.r. spectra of the complex* (I) *in* $CDCl_3$ *at* 20°. A: *Immediately after dissolution.* B: *After* 24 *hr.*

These observations can be interpreted on the basis that the crystalline complex is essentially one diastereoisomer (Ia or Ib) (Figure 1) which undergoes epimerization in solution. A preliminary *X*-ray examination[2] has shown that the diastereoisomer existing in the solid state is the 2*R*,3*S* (Ib).

The epimerization (Ib) to (Ia) is supported by the fact that the negative[3,4] $\Delta\epsilon$ of the c.d. band at 400 nm varies with time while the u.v. spectrum remains unchanged.

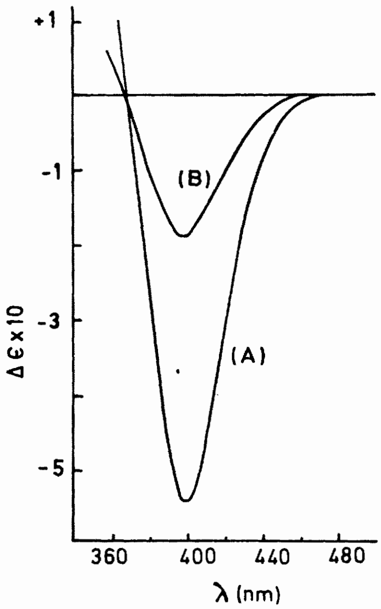

FIGURE 3. *C.d. spectra of complex* (I) *in* CH_2Cl_2 *at* 20°. A: *Immediately after dissolution.* B: *After* 24*hr.*

The sign of the c.d. remains negative when the epimerization equilibrium is reached, indicating that the asymmetric carbon atom in the s-butyl group induces in solution the (*R*) absolute configuration in the tertiary carbon atom bound to the Pt atom. The quantitative evaluations of the diastereoisomeric equilibrium composition, as deduced from n.m.r. and c.d. determinations, are mutually consistent (67 ± 2% of the 2*R*,3*S*-diastereoisomer). This indicates that the asymmetric carbon atom originally present in the olefin contributes only negligibly to the asymmetric environment in which the $d \rightarrow d$ electronic transition of the Pt^{II} complex at 400 nm takes place.

Asymmetric induction phenomena of the same type occur also in the co-ordination of the α-olefins to platinum in the case of *cis*-dichloro(benzylamine)$[CH_2:CH\cdot(CH_2)_n\cdot\overset{*}{C}H(Me)Et]Pt^{II}$ (n = 0, 1, 2) complexes. In fact, according to c.d. measurements on the band at 366 nm,[5] the asymmetric induction† by the s-butyl group occurs to the extent of about 34%, 12%, and 3% when the asymmetric carbon atom is in the α-, β-, or γ-position, respectively. Taking the α-olefin–platinum complex as a very crude model of the first step of the stereospecific polymerization of α-olefins,[6] it appears that the stereospecificity in the complexation of dissymmetric α-olefins to Pt can be taken

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† As % of asymmetric induction we have taken the expression $\frac{c_{RS} - c_{SS}}{c_{RS} + c_{SS}} \times 100$, where c_{RS} and c_{SS} are the concentrations of the two possible diastereoisomers at the equilibrium.

as an indication that the stereospecific polymerization of a racemic α-olefin having the asymmetric carbon atom in the α-position with respect to the double bond must have a certain degree of stereoselectivity.[7]

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