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MOLECULAR ASYMMETRY IN THE COORDINATION OF OLEFINS TO TRANSITION METALS : PRELIMINARY STUDIES OF CIS-DICHLORO-OLEFIN-AMINE-PLATINUM(II) COMPLEXES.

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In previous papers (1,2) we have described the preparation and properties of diastereoisomeric complexes of the general type : trans[dichloro-olefin-α-phenethylamine-platinum(II)](i), where the sites of optical isomerism are the asymmetric (R or S) amine and an olefin (of symmetry lower than 2 *m* *m* ; i.e. propylene, styrene, trans-2-butene) complexed to the metal atom.

No stereospecific effects of induction of configuration could be detected in solution. For instance, starting both from the (+)-trans-2-butene-(R)-amine and the (-)-trans-2-butene-(R)-amine complex the same equilibrium value of optical rotation was obtained, which corresponded in both cases to a 1:1 ratio of the two diastereoisomers. In this paper we wish to report some preliminary results concerning the corresponding cis complexes of

the general type : cis-[dichloro-olefin-α-phenethylamine-platinum(II)] (ii).

To an aqueous solution of potassium tetrachloroplatinate (II) two moles of (-)(S)α-phenethylamine (with an optical purity of 97%) were added (3).

Crude (-)[cis dichloro-(S)-α-phenethylamine-platinum(II)], $[Pt<C_8H_{11}N,Cl><C_8H_{11}N,Cl>]$, was recovered after standing one day. After boiling this product in 1 N,HCl, a yellow solution containing $[C_8H_{12}N][PtCl_3C_8H_{11}N]$ was obtained, from which, by shaking with ethylene at 50 psi green-yellow pale needles of (-) cis [dichloro-ethylene-(S)-α-phenethylamine-platinum(II)] separated.

Recrystallization from toluene gave a product having mp. 164°C, $[\alpha]_D^{25}$ - 54.5° (c 1.3, Acetone). Anal : Calcdt for $C_{10}H_{15}NCl_2Pt$; C 28.9 ; H 3.64 ; N.3.38 . Found : C 28.71 ; H 3.84 ; N 3.69.

The IR spectrum of this complex is very similar to that of the trans-isomer (mp. 71°, $[\alpha]_D^{25}$ - 33° (c 1.35, Acetone).

From this compound we obtained the other olefinic complexes through exchange in solution with the corresponding olefin. As already observed in the preparation of the corresponding trans-complexes, the exchange yelds crude mixtures containing the two possible diastereoisomers, (+) and (-) cis-[dichloro-olefin-(S)α-phenethylamine-platinum (II)]. The resolution of the diastereoisomers of the propylene, trans-2-butene and styrene complexes was obtained through crystallization from several different solvent mixtures.

The analyses of these compounds agreed with the assigned formula (ii).

X-Ray and Molecular Weight data of the (-) cis[trans-C_4H_8, $C_8H_{11}N$, Cl_2Pt] are : a = 12.85, b = 8.88, c = 6.65 Å ; γ = 102°38' ; d 2.00 g/cm³ ; space group $P2_1$. The molecular weight of the independent unit is 446 ; mol.wt. (443, calcd.

The X-Ray structure analysis confirms the cis-coordination(4)
The complex with cis-2-butene was not capable of resolution, because the two asymmetric carbon-atoms of the bonded olefin have enantiomorphous configurations, and thus constitute a meso-systems.

The optical rotation of the complexes are reported in Table I. In the trans series (i) the pure diastereoisomers of the complexes with trans-2-butene have values of molecular rotation equidistant from the value of molecular rotation of the corresponding ethylene complex. The activity of both diastereoisomers attain this value by epimerization ; this indicates that the solution at equilibrium containes a 1:1 ratio of the two diastereoisomers.

The diastereoisomeric complexes of the cis-series (ii), on the contrary, exhibit, equilibrium values of rotation signi-

Table I: Data of optical activity [a] of cis-dichloro-olefin-(S)-α-phenethylamine-platinum(II)

Olefin	Diastereoisomers $[\alpha]_D$	$[M]_D$	$[\alpha]_D$ [b]	$[M]_D$ [b]
ethylene			-54.5	-226
cis-2-butene			-59.6	-264
(+)-propylene	+2.5	+10.7	-55.3	-238
(-)-propylene	-113	-485	-55.3	-238
(-)-trans-2-butene	-184	-815	-79.0	-350
(-)-styrene	-197	-967	-62.4	-306

a) In acetone at 25° (c 1.2 - 1.4)

b) Values at equilibrium (after isomerisation) and values not-resoluble complexes.

ficantly different from that of the corresponding ethylene complex.

The effect is particularly noticeable in the case of the trans-butene complex (ii), where the molecular activity at equilibrium is nearly 50% higher than the activity of the ethylene complex.

We take these observations as an indication of a possible induction of asymmetry in the case of cis-complexes, in solution, due probably to a different steric interaction of the R or S complexed olefin in respect to the cis coordinated amine.

Further studies on this point are in progress.

References

1) G.Paiaro, P.Corradini, R.Palumbo and A.Panunzi, Die Makromolekulare Chemie, 71, 184 (1964)

2) G.Paiaro and A.Panunzi, J.Amer.Chem.Soc. 86, 5148 (1964)

3) R.Kramer, J.Amer.Chem.Soc. 86, 217 (1964)

4) C.Pedone, (private comunication).