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THE SEPARATION OF DIASTEREOISOMERIC (DICYCLOPENTADIENE METHOXIDE)-(S)-α-PHENETHYLAMINECHLOROPLATINUM(II).

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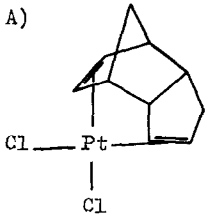
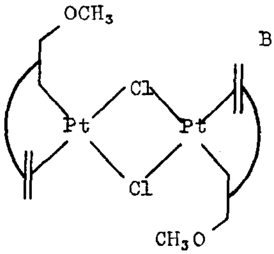
The monomeric complex of platinum(II) with endo - dicyclopentadiene described in 1908 by Hofmann and von Narbutt (1), which has been shown (2) by X-ray crystallography to be (A), reacts with methanol (1,3) to give the dicyclopentadiene methoxy-chloride (B). The reaction of this dimeric product with amines (3) affords

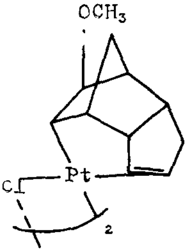
A)



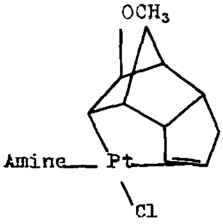
B)



B')



C)

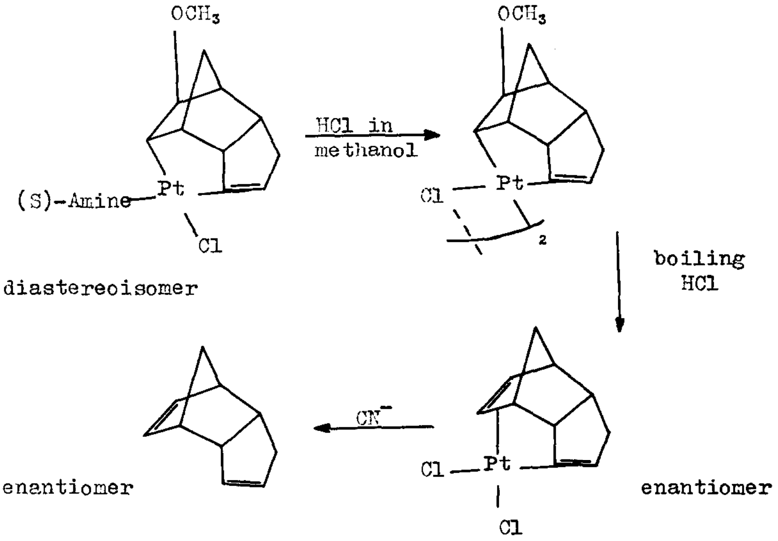


monomeric compounds of the type [dieneOR,amine PtCl] (C). NMR studies of the pyridine derivative have recently shown (4) that the addition of the methoxyl group to (A) is stereospecific: the attack leads to an exo-5-methoxy derivative with the metal in endo position (B').

It clearly appears, therefore, that both (A) and (C) must be resolvable in optical antipodes.

By trying to resolve this type of asymmetry we have obtained by reaction of (B) with (S)-α-phenethylamine ($[\alpha]_D^{19}$-40.3, neat) the diastereoisomeric pair of the type [dieneOR,(S)-α-phenethylamine PtCl]. This product had $[\alpha]_D^{25}$-8.5 (c 0.7, methylene chloride). After fractional crystallization from CCl_4/cyclohexane (1:1) and recrystallizing until constant optical rotation was reached, two fractions were obtained having respectively $[\alpha]_D^{25}$-114 and $[\alpha]_D^{25}$+100. These fractions and the diastereoisomeric pair have very nearly identical IR spectra. From each of these two diastereoisomers the amine was removed by adding HCl to the methanol solution yielding the dimer (B) in an optically active form. The methoxyl group was then eliminated, by boiling concentrated hydrochloric acid, yielding an optically active product which showed IR spectrum and analysis identical with (A).

The optical activity of this product was connected to the presence in it of enantiomeric endo-dicyclopentadiene. The olefin was recovered from the product by shaking it with aqueous sodium cyanide, and, in a preliminary experiment, we obtained, for the first time, optically active endo-dicyclopentadiene, $[\alpha]_D^{25}$ +60 (c 0.8, carbon disulphide)), according to the reported scheme; where the figures clearly don't mean any configurational assignment:



Further studies, tending to establish the optical purity of the olefin and of the resolved complexes are in progress.

Our interest in the separation of enantiomers of the type (A) stems from the possibility of finding evidence of a difference in reactivity of an unsaturated carbon atom in the two opposite configurations that this carbon can achieve when linked to two different groups and coordinated to a transition metal (5). E.g., after reaction of the levorotatory enantiomer (A) with an excess of dl sec. butyl alcohol, we recovered unreacted alcohol as a dextrorotatory product.

This preliminary finding indicates the existence of the possibility of asymmetric induction: this effect is now under quantitative investigation.

REFERENCES

1) K.A.Hofmann and J.V.Narbutt, *Ber*, **41**, 1625 (1908)

2) N.C.Baenziger,J.R.Doyle,G.F.Richards and C.L.Carpenter, *U.S.Dept.Com.,Office Tech.Serv.,PB Rept.*,156, 074 (1961)

3) J.Chatt,L.M.Vallarino and L.M.Venanzi, J.Chem.Soc.,2496 (1957)

4) J.K.Stille,K.A.Morgan,D.D.Whitehurst,J.R.Doyle, *J.Am.Chem. Soc.*, **87** , 3282 (1965)

5)(a) G.Paiaro,P.Corradini,R.Palumbo,and A.Panunzi, *Die Makromoleculare Chemie*, **71**, 184 (1964)

(b) G.Paiaro and A.Panunzi, *J.Am.Chem.Soc.*, **86**, 5148 (1964)