Molecular Asymmetry in π-Allylic Complexes of Transition Metals

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IT has been shown that molecular asymmetry is present in olefinic complexes in which a transition-metal atom is bonded to an olefinic compound containing "prochiral" trigonal carbon atoms.[1]

The same kind of asymmetry can be recognized in π-allylic compounds. For example, in 1-substituted allyl complexes, C-1 becomes asymmetric upon co-ordination and can be designated as (*R*) or (*S*) according to the rules of Cahn, Ingold, and Prelog.[2] [See formulae (I) and (IV).] The configurational asymmetry of C-2 is determined by that of C-1 according to the *syn*- or *anti*-nature of the complex.

To demonstrate this kind of molecular asymmetry, studies are in progress on diastereoisomeric compounds in which allylic ligands are π-bonded to metal atoms co-ordinated to an asymmetric ligand (*e.g.*, optically active amines or phosphines).

We report here the results obtained, *inter alia*,[3] on chloro-(1-acetyl-2-methylallyl)(*S*-α-phenethylamine)palladium(II), (A).

A diastereoisomeric mixture was prepared by splitting, in ethyl acetate, the chlorine bridge of $(\pi\text{-}C_6H_9OPdCl)_2$ with (*S*)-α-phenethylamine, $[\alpha]_D^{25}$ $-40{\cdot}3$ (neat), to give (A).

The resolution was achieved by crystallizing the crude diastereoisomeric mixture from CCl_4.[4] Some relevant optical-activity data are listed in the Table. The optical-activity measurements which we could perform in acetone both at very low and

TABLE

Optical rotation of chloro-(1-acetyl-2-methylallyl) (S-α-phenethylamine)palladium(II) *crystallized from* CCl_4 *at several times and at several different temperatures after dissolution.*

Solvent	T(°C)	$[\alpha]_D$	$[\alpha]_{436}$	Time elapsed after dissolution at temp. T(°c)
CH_2Cl_2	25	−19·5	———	25, < 3 minutes
Me_2CO	25	−32·5	———	25, < 3 minutes
,,	−72	−54	−162	Same sample as above cooled to −72°
,,	−72	−465	−1750	−72, ~ 10 minutes
,,	−72	−465	−1750	−72, 1 hour
,,	0	———	−910	−72, (a)
,,	0	———	−620	One minute after (a)
,,	0	———	−330	Three minutes after (a)
,,	25	−31·6	———	−72, (b)
,,	−50	−47	−143	−72, (c)

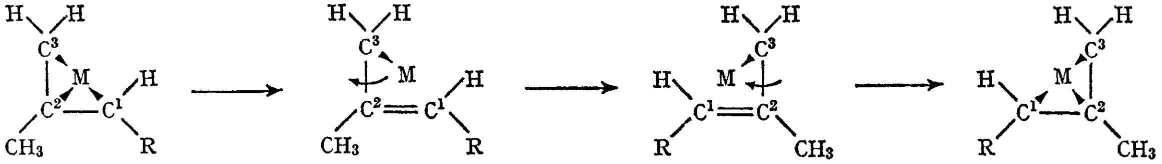
[a] After solution was effected, the sample was warmed to 0° in about 15 minutes. The measurements were taken one minute after temperature of 0° was attained.

[b] The above sample was warmed to 25°.

[c] Sample (b) cooled to −50°. Optical activity did not vary after one hour.

at higher temperatures indicate that: (a) only one of the two possible diastereoisomers was quantitatively obtained in the CCl_4 crystallization through a "second-order asymmetric transformation";[5] (b) epimerization of the pure (−)-diastereoisomer takes place very quickly at temperatures higher than −20°.

The epimerization can occur only through a rotation around the C-2–C-3 bond of the allylic group; accordingly we think that the epimerization occurs through a σ-bonded intermediate, in which the double bond is no longer co-ordinated to the metal atom. Two dissymetric conformers of the σ-intermediate (II, III) are shown as an example in the scheme below:



(I) (II) (III) (IV)

This point of view is supported by recent n.m.r. studies carried out on π-allylic complexes of Pd^{II} in the presence of basic ligands.[6]

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[1] G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, *Makromol. Chem.*, 1964, **71**, 184; G. Paiaro, R. Palumbo, A. Musco, and A. Panunzi, *Tetrahedron Letters*, 1965, 1067; P. Corradini, S. F. Mason, G. Paiaro, A. Panunzi, and G. H, Searle, *J. Amer. Chem. Soc.*, 1966, **88**, 2863; We propose to extend the term "prochiral" as used by K. R. Hanson. *J. Amer. Chem. Soc.*, 1966, **88**, 2731, for tetrahedral carbon atoms having three different substituents (Ca_2bc), to include trigonal carbon atoms of the type (=Cab). More generally, the term "prochiral" could be applied in co-ordination chemistry to molecules in which a non-asymmetric atom becomes asymmetric upon co-ordination.

[2] R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385.

[3] A. Musco and G. Paiaro, *Chimica e Industria*, 1965, **47**, 239; V. Caprio, Doctoral Thesis of University of Naples, 1966.

[4] Yellow, air-stable, crystals were obtained; inclusion compounds containing CCl_4 in 1 : 1 ratio.

[5] E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p. 63.

[6] J. C. W. Chien and H. C. Dehm, *Chem. and Ind.*, 1961, **745**; F. A. Cotton, J. Fuller, and A. Musco, to be published.