Kurze Mitteilungen

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Asymmetric Catalysis in the Cyclometallation Reaction *

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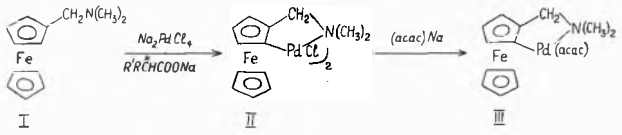
Abstract

The formation of optically active cyclopalladated products starting from dimethylaminomethylferrocene has been observed for the first time using the salts of optically active acids as basic catalysts. This seems to be a unique example for the non-intramolecular asymmetric induction of planar chirality. The maximum enantiomeric excess thus far obtained is nearly 12%.

The direct cyclometallation of benzylic tertiary amines with platinum(II) or palladium(II) salts has first been achieved in the presence of tertiary amines [1]. Yet this type of reaction failed with dimethylaminomethylferrocene I [2], but the desired chelated metallocycle is formed in the presence of sodium acetate as a basic catalyst [3]. This fact suggested the opportunity for asymmetric catalysis in the formation of the resulting planar chiral product if an optically active anion would be used.

Previously, we have studied the diastereoselectivity in the course of the cyclopalladation of the enantiomeric amines $Fc-\overset{*}{C}HR-N(CH_3)_2$, R=$CH_3$ [4], R=D [5]. In the meantime, the planar chiral 2-chloropalladiodimethylaminomethylferrocene II (R=H) has been resolved through the diastereomers with α-phenyl-ethylamine [6], the optical rotation being so high as $[\alpha]_D^{20}$ 400°*. Therefore one could hope to detect even a small extent of asymmetric induction in the products. In practice, it appeared more convenient to measure the optical rotation of the related acetylacetonate complex III which is more soluble and has smaller absorption in UV and the visible region.



I II III

The dimethylaminomethylferrocene I, when treated with Na_2PdCl_4 in methanol in the presence of an equimolar quantity of sodium salts of the representative enantiomeric carboxylic acids, afforded the optically active dimer II in good yield. II was transformed into complex III. The experimental data are shown in the Table. As can be seen, the sodium salts of the two enantiomers of a chiral acid (runs 5 and 6) induced the formation of products in which the enantiomers of opposite planar chirality prevail. The assignment of

* Received December 12, 1977.

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* This is the maximum value experimentally achieved which has been taken as basis for the determination of the degree of asymmetric induction. The dimeric chloride II, $[\alpha]_D^{20}$ − 400° (CH_2Cl_2), afforded the acetylacetonate complex III, $[\alpha]_D^{20}$ − 300° (CH_2Cl_2) of the same optical purity.

Table 1: Enantioselective Synthesis of Planar Chiral Metallocycles II and III.

Run	Type of sodium salt used as chiral catalyst	Its absolute configuration	$[\alpha]_D^{20}$ of dimeric chloride II	$[\alpha]_D^{20}$ of acetylacetonate III	Enantiomeric excess (%)*	Absolute configuration in excess
1	lactic acid	S (+)	**	− 7.6°	2.5	S_p
2	lactic acid	S (+)	**	− 6.3°	2.1	S_p
3	mandelic acid	R (−)	**	+ 17.4°	5.8	R_p
4	mandelic acid	R (−)	**	+ 17.3°	5.8	R_p
5	N-acetyl-L-valine	S (+)	**	+ 25.0°	8.3	R_p
6	N-acetyl-D-valine	R (−)	− 30.0°	− 22.5°	7.5	S_p
7	N-carbo-t-butoxy-L-proline	S (+)	− 40.1°	− 32.6°	10.8	S_p
8	N-carbo-t-butoxy-L-proline	S (+)	− 47.0°	− 36.3°	12.0	S_p

* Calculated taking $[\alpha]_D^{20} \pm 400°$ for II and ± 300° for III as maximum rotations, see [7]. All rotations were taken in dichloromethane, c = 0.4 for II and c = 4.15 for III; c in g/100 ml, l = 1 cm.
** Not measured.

absolute configuration is made using previous results [4] confirmed by the X-ray study of (-)RS_p-1-(1′-dimethylaminoethyl)-2-palladio (acetylacetonate) ferrocene [8].

The present results indicate unambiguously that the acid anion is directly involved in the cyclopalladation reaction (on the stage of either diastereomeric transition states or diastereomeric intermediates). To our knowledge, this is the first example of the introduction of planar chirality into an achiral molecule in enantioselective way. Work is now in progress to achieve a higher enantiomeric excess.

Experimental

The general procedure for cyclopalladation of dimethylaminomethylferrocene in the presence of salts of optically active acids. To the stirred mixture of 0.3 g (1 mMol) of Na_2PdCl_4, 0.040 g of NaOH and 0.160 g of (-)N-acetyl-D-valine (or 0.180 g of solid sodium salt of N-acetyl-D-valine) in 5 ml of methanol was added 0.24 g (1 mMol) of I in 3 ml of methanol. After 2 hrs the chloride complex II was filtered, washed with methanol and dried. Yield: 0.280 g, 70% (generally 60–80%). This product was dissolved in benzene and treated with 0.25 g of sodium acetylacetonate in 3 ml of methanol. The colour turned immediately from red to yellow. The solvent was evaporated and the residue extracted with pentane to give complex III: m.p. 123–124° (from pentane), $[\alpha]_D^{20}$ −22.5° (CH_2Cl_2, c = 4). Found: % C 48.25; H 5.13. $C_{18}H_{23}FeNO_2Pd$ requires % C 48.29; H 5.18.

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