Chirality in Transition-metal Chemistry. The Formation of Diastereomers in the Reaction of the Stereoisomers of Hexa-2,4-diene with Palladium Chloride

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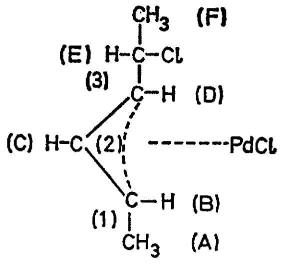
Summary Diastereomeric pairs of enantiomers of 1-(1-chloroethyl)- 3-methyl-π-allylpalladium chloride are formed when either *trans,trans-*, *cis,cis-*, or *cis,trans-*hexa-2,4-diene are allowed to react with palladium chloride at −40° in an aprotic solvent: these reactions can be employed to effect the conversions, *cis,cis* → *trans,trans* ⇄ *cis, trans*-hexa-2,4-diene.

CONJUGATED dienes react with palladium chloride yielding 1-(1-chloroalkyl)-π-allylpalladium complexes.[1,2] In the course of preparation of some of these complexes we found that the geometric isomers of hexa-2,4-diene yield π-allyl complexes with structure (I) in an aprotic solvent at −40°. Remarkably, the products obtained from the *cis,cis-* and the *trans,trans*-isomers on the one hand (Ia) and the *cis, trans*-isomer on the other hand (Ib) show small differences in their n.m.r. spectra (see Table 1).

These complexes, in which the bulky substituents occupy the *syn*-position (thermodynamically the more stable configuration), contain four chiral carbon atoms, three of which are inter-related through the allylic structure. Thus, only two independent chiral centres exist, which can give rise to two diastereomeric complexes. To these we assign the different n.m.r. spectra.



(I)

The mechanism leading to the stereospecific formation

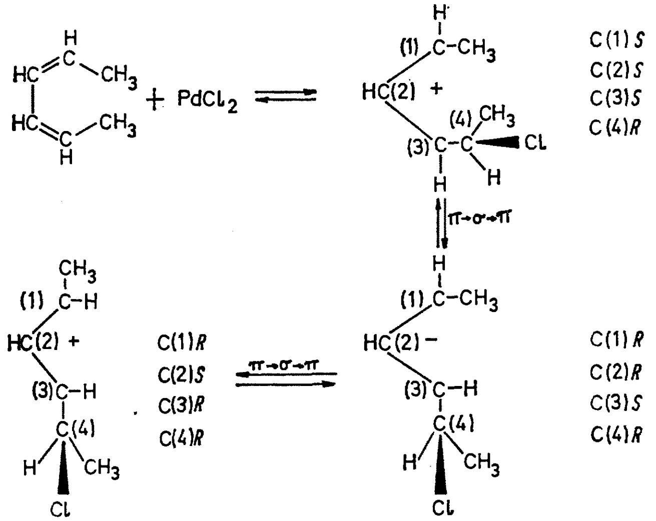
TABLE 1

N.m.r. chemical shifts of diastereomeric 1-*methyl*-3-(1-*chloroethyl*)-π-*allylpalladium chlorides*

		$CH_{3(A)}$	H_B	H_C	H_D	H_E	$CH_{3(F)}$
(Ia)	*cis,cis* *trans,trans*	1·36	4·00	5·47	3·65	4·30	1·78
(Ib)	*cis,trans*	1·41	4·03	5·07	3·80	4·40	1·79

J_{AB} 6, J_{BC} 11, J_{CD} 11, J_{DE} 9, J_{EF} 6·5 Hz.

of the π-allylic complexes will be outlined in detail for the *cis,cis* isomer.† (Scheme):



SCHEME

The addition of palladium chloride to the diene is apparently stereospecific, and most likely concerted. Since *syn*-substituted π-allyl complexes are thermodynamically more stable, substituents which have ended up in an *anti*-position after the first step have to rearrange. This can only occur *via* a π → σ → π rearrangement.[4] By such a rearrangement the chirality of the σ-bonded carbon of the allyl system is retained and that of the other two carbon atoms is inverted. The product will obviously be racemic, since palladium chloride can attack from either side of the diene.

The same operations have been carried out on all conformations of the three isomeric hexa-2,4-dienes. The results are collected in Table 2.

TABLE 2 (for numbering, see Scheme)

Configuration of hexa-2,4-diene	Chirality of carbons in π-allylpalladium chlorides				
	C(1)	C(2)	C(3)	C(4)	
cis,cis	*R*	*S*	*R*	*R*	pair of enantiomers
trans,trans	*S*	*R*	*S*	*R*	
cis,trans	*R*	*S*	*R*	*S*	pair of enantiomers
	S	*R*	*S*	*R*	

It is indeed found that the *cis,cis*- and the *trans,trans*-isomers lead to one, and the *cis,trans*-isomer to another, diastereomeric complex.

Equilibration of the two diastereomers occurs when their solutions are warmed to room temperature. Preliminary kinetic measurements indicate that the rate of this reaction is first-order in the concentration of the complex. The mechanism is as yet unknown. It may consist in racemization on the 1-chloroethyl group or in a flip mode of the allyl plane relative to the palladium atom.[5]

Regeneration of the diene is brought about by coordinating ligands, such as dimethyl sulphoxide, triphenylphosphine, or lithium bromide. This retroreaction is as stereospecific as the formation of the π-allyl complexes and yields exclusively *trans,trans*-hexa-2,4-diene from the diastereomer (Ia) and the *cis,trans*-isomer from (Ib).

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† The absolute configurations are assigned according to Cahn, Ingold, and Prelog.[3] The carbon atoms of the π-allyl system are considered σ-bonded to the metal atom to enable assignment of chirality. The symbols + and − denote the palladium atom above and below the plane of the π-allyl group, respectively.

[1] P. E. Slade and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1957, **79**, 1277.
[2] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1964, 5002 and references therein.
[3] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew Chem.*, **1966**, **78**, 413.
[4] P. W. N. M. van Leeuwen and A. P. Praat, *Chem. Comm.*, 1970, 714.
[5] F. de Candia, G. Maglio, A. Musco, and G. Paiaro, *Inorg. Chim. Acta*, 1968, **2**, 233.