Journal of Organometallic Chemistry, 47 (1973) 153–163

THE STEREOSPECIFIC ADDITION OF DIENES TO PALLADIUM CHLORIDE

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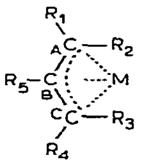
(Received June 19th, 1972)

SUMMARY

Using 2,4-hexadiene as a model compound we have shown that dienes add to palladium chloride in a stereospecific way. The three diene isomers react to give a pair of epimeric π-allylpalladium diastereomers, one of which is formed from the *cis,trans*-diene, the other from either the *trans,trans* or the *cis,cis*-isomer. The mechanisms of the epimerization and solvolysis of the products have been studied, and the reactions found to proceed via a diene–palladium complex.

INTRODUCTION

A carbon atom in the sp^2-hybridization state carrying three different substituents does not constitute a centre of chirality. However, when coordinated to a metal it becomes a chiral centre since there is no longer a plane of symmetry[1]. Accordingly, coordinated π-allyl groups can contain up to three such centres, depending on the degree of substitution of the allyl system.



(Ia) $R_1 = R_2, R_3 = R_4$; Achiral
(Ib) $R_1 \neq R_2$ or $R_3 \neq R_4$; Two chiral centres
(Ic) $R_1 \neq R_2, R_3 \neq R_4, CR_1R_2 \neq CR_3R_4$; Three chiral centres

All the experimental results obtained so far indicate that in the thermodynamically most stable configuration, of the substituents at C_A and C_C, the bulkier groups occupy the *syn* positions**. If the mechanism of the reaction leading to the π-allyl complex is such that the bulkier substituents would end up in the *anti* positions, then the reaction is followed by a rearrangement to the most favoured configuration. There is adequate evidence that these rearrangements proceed via a so-called "π–σ–π" mechanism[3]. The first step in such a mechanism consists of the formation of a σ-allyl ligand or, in other words, in the conversion of the *trihapto* coordination into a σ carbon–metal and an uncoordinated π-bond.

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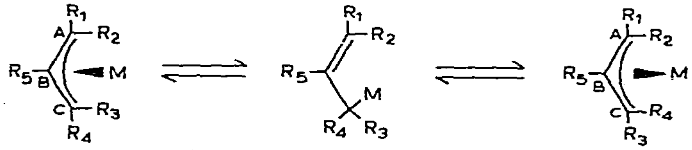
** For exceptions to this rule due to an "oversized" substituent see ref. 2.

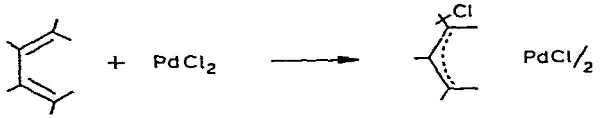
In Scheme 1 this mechanism is illustrated for the exchange of R_3 and R_4.

SCHEME 1

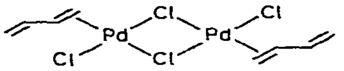


The metal, after rotating on B–C, re-attaches to the other side of the double bond. A consequence of this rearrangement is that inversion of configuration on C_C is accompanied by *inversion of chirality* on C_A, C_B. In general terms, it can be stated that in any π–σ–π rearrangement the *meso*-carbon changes its chirality, while one of the two terminal carbons inverts its configuration and the other its chirality. Thus, the rearrangements take place in a stereospecific manner, and if the formation reaction were also stereospecific, interesting features could be expected.

The addition of conjugated dienes to palladium chloride is a very convenient way of preparing 1(1-chloroalkyl)-π-allylpalladium chlorides[4].

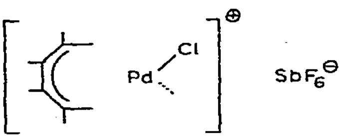


The adducts contain a chiral allyl group, as is shown in structure (Ic). Donati and Conti detected at low temperatures (−40°) an intermediate olefin complex, in which the diene was coordinated as a monodentate ligand[5].



We first describe below the formation of diastereomeric allyl complexes from isomers of 2,4-hexadiene and palladium(II) chloride[6] and indicate a possible pathway for this stereospecific reaction. Then we consider the epimerization of the diastereomers, and discuss the ready solvolysis, which leads to a number of substituted π-allylpalladium complexes[4,7].

We show that the solvolytic reaction involves a stabilized intermediate cation, similar to a long-lived species containing a *cisoid, tetrahapto* diene-like ligand, which one of us reported previously[8]:

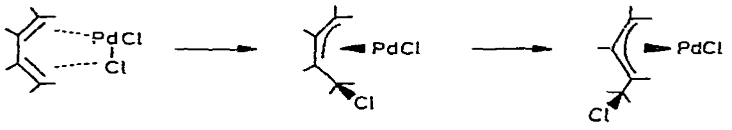


RESULTS AND DISCUSSION

A. Addition

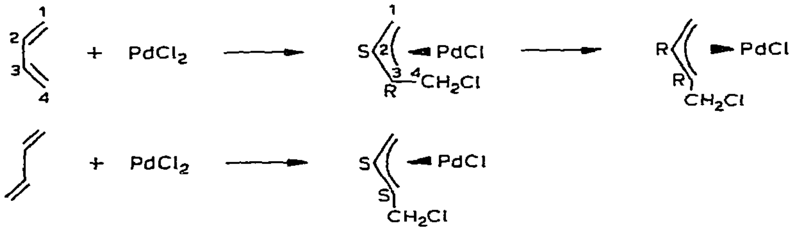
In considering the structures of the π-allylpalladium products we shall for the moment, assume that palladium chloride reacts with the *cisoid* diene via (1,2,3)-4 addition, and that π–σ–π rearrangement(s) will subsequently cause the bigger substituents to move to the *syn* positions (Scheme 2).

SCHEME 2



In view of the fact that bulky groups tend to occupy the *syn* positions, 1,3-butadiene will only form a racemic mixture of two enantiomers (Scheme 3).

SCHEME 3*



This is in agreement with experimental results, NMR indicating the presence of only one product. Substitution on the terminal carbon atoms of the diene changes the situation, however, since the chlorine-bearing carbon atom becomes a chiral centre. In addition, *cis* and *trans* isomers will lead to different diastereomers. Since asymmetric dienes, such as 1,3-pentadiene, give structural isomers, we have chosen the symmetric 2,4-hexadiene (II) as a model compound.

The three geometrical isomers of 2,4-hexadiene (*cis,cis*; *trans,trans and cis, trans*) were brought into reaction with palladium chloride (see Experimental). The *trans,trans* and the *cis,cis* isomers lead to the same compound (III); the *cis,trans* isomer yields complex (IV). Table 1 gives the chemical shifts of the two π-allylpalladium complexes. Compounds (III) and (IV) have the same substituents in the *syn* and *anti* positions, and thus any differences in the spectra can only be due to the formation of diastereomers.

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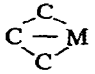
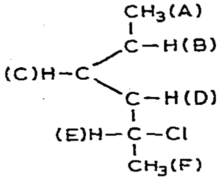
* We previously arrived at the absolute configurations shown in ref. 6 by assuming the metal to be σ-bonded only to the carbon in question. To avoid confusion we will use the connotation of Paiaro *et al.*[9], who for the purpose of this assignment assume all three carbons of the π-allyl system to the σ-bonded to the metal:



$\mathrm{C}\overset{\mathrm{C}}{\underset{\mathrm{C}}{—}}\mathrm{M}$

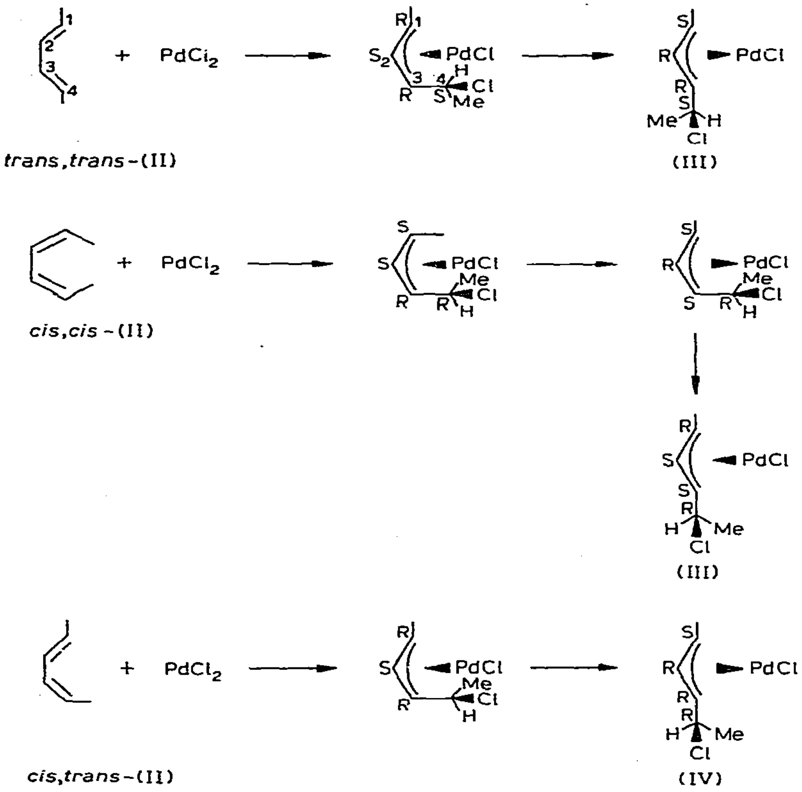
TABLE 1

NMR CHEMICAL SHIFTS (δ ppm) OF (III) AND (IV)



Complex	$CH_3(A)$	H_B	H_C	H_D	H_E	$CH_3(F)$
(III)	1.36	4.00	5.47	3.65	4.30	1.78
(IV)	1.41	4.03	5.47	3.80	4.40	1.79

SCHEME 4



Scheme 4 shows why the *cis,cis*- and *trans,trans*-2,4-hexadienes give the same diastereomer and *cis,trans*-2,4-hexadiene produces another. The absolute configurations of the end products in Scheme 4, collected in Table 2, demonstrate that the two diastereomers are epimeric. The *syn,syn* complexes actually constitute diastereomers with only two independent centres: (*a*) the π-allyl system, and (*b*) the chlorosubstituted carbon.

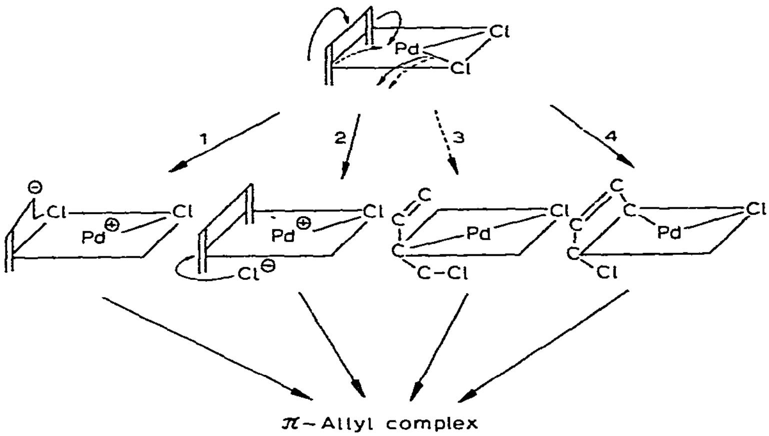
TABLE 2

ABSOLUTE CONFIGURATIONS OF (III) AND (IV)

Stereoisomers of 2,4-hexadiene	*C*(1)		*C*(2)	*C*(3)	*C*(4)–*Cl*
cis, cis *trans, trans*	(III)	*R*	*S*	*S*	*R*
		S	*R*	*R*	*S*
cis, trans	(IV)	*R*	*S*	*S*	*S*
		S	*R*	*R*	*R*

It is reasonable to assume that the monodentate complex dimer is split up into the bidentate monomers in the first step. Some of the possible subsequent pathways are outlined in Scheme 5: they all lead stereospecifically to one diastereomer only. For route (1) we have to assume that the betaine-like intermediate collapses to the π-allyl complex at a rate which is considerably higher than that of the rotation about one of its allylic C–C bonds[9]. In essence, route (1) is no more than route (3) or (4) broken into steps; it may involve some degree of concertedness. The existence of route(2) was suggested by the identification of the cationic intermediate[8] (*vide infra*), but it is contradicted by the fact that the addition is apparently independent of the nature of the solvent.

SCHEME 5

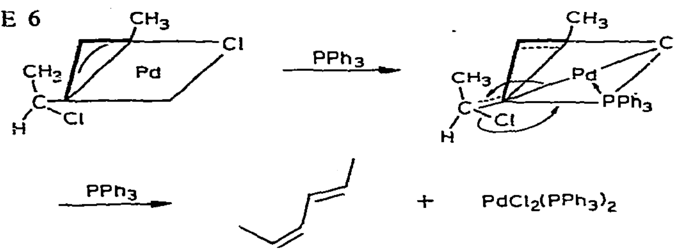


B. Decomposition

The addition reaction of palladium chloride to a diene can be reversed by the addition of an excess of a coordinating compound, such as dimethyl sulphoxide, triphenylphosphine or lithium bromide. This retroreaction is entirely stereospecific, yielding *trans,trans*-(II) from (III) and *cis,trans*-(II) from (IV). Since *cis,cis*-(II) leads to complex (III), the reverse reaction provides a method of converting *cis,cis*-(II) into *trans,trans*-(II).

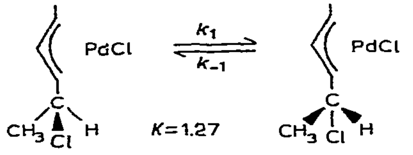
The decomposition probably proceeds in the way depicted in Scheme 6, *i.e.* via conversion to a σ complex, followed by a β-elimination.

SCHEME 6



C. Epimerization

The two diastereomers epimerize when their solutions are warmed to room temperature. One of the two chiral groups, the allyl system or the chloro-substituted carbon, must racemize. The fact that the methoxy analogue does not epimerize in normal conditions, but only under acid catalysis, indicates that racemization occurs at the chloro-substituted carbon.



(IV) (III)

Our finding that the epimerization is first order in the complex excludes the participation of a second complex molecule in the ionization. The values of the activation energy and of the rate constants in various solvents are given in Table 3. Although the solvent effects are small the results indicate that the rates increase with increasing polarity of the solvent, and that they are not influenced by common ions.

SCHEME 7
THE EPIMERIZATION MECHANISM

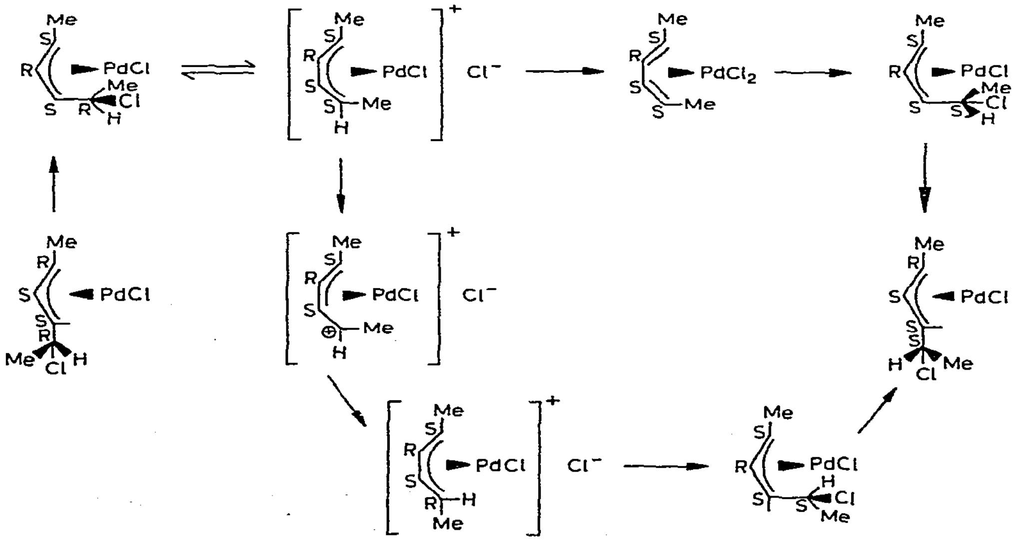


TABLE 3

KINETIC RESULTS OF THE EPIMERIZATION REACTION

Temp. (°*C*)	$k_1 [\times 10^4]$	*Solvent*	$E_a (kcal \cdot mol^{-1})$
35.5	7.42	$CDCl_3$	22.2 ± 0.5
36	7.8	$CDCl_3$	
36	8.0	$CDCl_3$+HCl (1 atm)	
36	9.8	CD_3NO_2	
36	10.0	$CDCl_3 + CH_3COCl$ (molar ratio 1/9)	

A cancellation of common ion and salt effects is probably responsible for the relatively small influence of added hydrogen chloride on the rate constant. These facts are consistent with an S_N1-type mechanism (see Scheme 7).

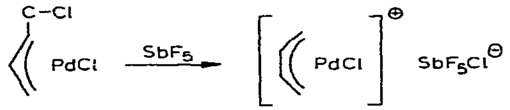
In the first step the chlorine is ionized, while the developing *p* orbital begins to overlap a suitably filled orbital of the metal. Whether elimination occurs from an *anti*- or a *syn*-oriented chloroallyl substituent is immaterial for the chirality of the π-allyl system as long as the two configurations interconvert via a π–σ–π rearrangement.

Two pathways for the collapse of the first intermediate, a metal-stabilized carbonium ion, to the epimer are open:

(*a*) the chlorine ion returns to the metal atom, which carries a partial positive charge. This results in the formation of a neutral *tetrahapto* diene–$PdCl_2$ complex, which collapses to the epimer in the way depicted in Schemes 4 and 5;

(*b*) in the ionic intermediate the metal rotates about the C_3/C_4 bond, *i.e.* the bond between the π-allyl system and the carbon atom which previously bore the chlorine atom. Return of the chloride ion to this carbon atom yields the epimer.

At present we cannot differentiate between paths (*a*) and (*b*). However, previous work of ours[8] offers evidence in support of route (*b*). It was shown that complexes of type (III)/(IV) can be ionized in strongly acidic media to *tetrahapto* dienyl cations:



This reaction is analogous to that involved in route (*b*). It was further evident that with increasing methyl substitution of the terminal carbon atoms, these atoms displayed an increasing tendency towards rotation. Thus, route (*b*) would be favoured, at least in strong acids. It should be emphasized that the conditions of this work differ markedly from those reported in ref. 8.

D. Solvolysis

The diastereomeric complexes (III) and (IV) are stereospecifically solvolysed to a pair of diastereomeric derivatives (for example, alcohols and ethers) by the addition

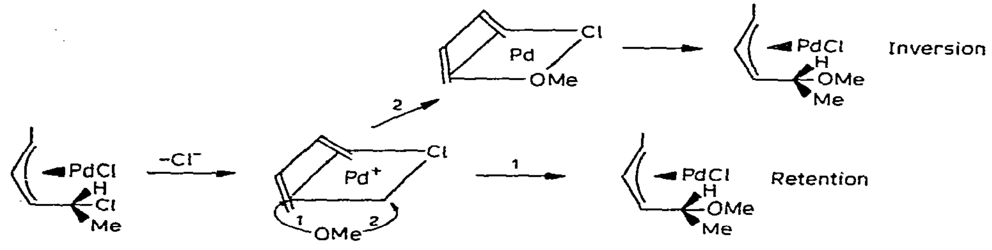
TABLE 4

METHANOLYSIS OF COMPLEX (III)
Molar ratio halide/CD_3OD 1/15, solvent $CDCl_3$

Compound	*Temp.* (°C)	k($\times 10^4$) (sec^{-1})	E_a(*kcal·mol*)
Complex (III)	−7	8.76	14.8 ± 2.5
	−1	15.4	
	+1	23.6	
	+4	27.5	
2-Chloro-1-butene	+120	0.12	

of the appropriate nucleophile to a solution of the complexes in acetone. The question which immediately arises is whether this solvolysis occurs with retention or inversion of configuration. The ease with which the solvolytic reaction proceeds has been regarded as a qualitative indication of the existence of a metal-stabilized carbonium-ion intermediate[8]. Conclusive evidence is now provided by the results shown in Table 4: an increase in temperature by roughly 120° is necessary for 2-chloro-1-butene to solvolyse at the same rate as the complex. The first step of the solvolysis is likely to be similar to that of epimerization (*vide supra*), namely the formation of a cationic intermediate (Scheme 8). The methoxide ion may then attack the intermediate either directly at the ligand (1) or via the metal from which it would be transferred to the ligand (2). The first mode will lead to retention, the second to inversion of configuration*.

SCHEME 8
THE SOLVOLYSIS REACTION



The methanolysis of the adduct of 1,3-cyclohexadiene and $PdCl_2$, (1,2,3-*trihapto*-4-chlorocyclohexenyl)palladium chloride (V), to (1,2,3-*trihapto*-4-methoxycyclohexenyl)palladium chloride (VI) should provide an answer to the question of whether the reaction proceeds via route (1) or route (2). In these complexes, five of the six carbon atoms must lie in a plane; C_5 must be bent out of the plane, either towards or away from the metal. In view of the fact that the palladium chloride reacts with the planar diene via *cis* addition, it is reasonable to assume that in complex (V) carbon atom 5 is bent away from the metal. If the methanolysis proceeds via a planar inter-

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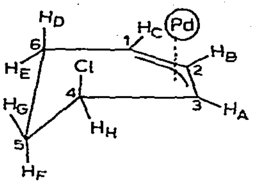
* In epimerization the first pathway is degenerate and therefore not observable.



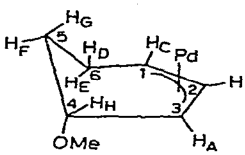


TABLE 5

NMR DATA OF 4-CHLORO- AND 4-METHOXY-1,2,3-*trihapto*-CYCLOHEXENYL PALLADIUM CHLORIDES (V) AND (VI)

	Complex (V)		*Complex (VI)*	
Protons	*Chemical shift (ppm)*	*Coupl. const. (Hz)*	*Chemical shift (ppm)*	*Coupl. const. (Hz)*
A	5.05	6.3	5.05	6.2
B	5.53		5.47	6.2
C	5.26		5.24	
D	2.1–2.4		2.1–1.6	
E				
F				
G	2.68	5.0	1.0	4.8
H	4.46	2.7	3.69	1.0
	A		A	

mediate, direct attack of the nucleophile would result in carbon atom 5 flipping over towards the metal, whereas attack via the metal would occur with retention of the initial bent-away configuration.

The NMR data in Table 5 are indicative of a direct attack on the ligand: hydrogen atoms G and H, which are the most sensitive to metal shielding in structure (VI), are shifted upfield by 1.7 and 0.75 ppm, respectively.

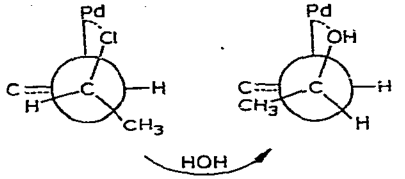
Another, more speculative indication of inversion can be found in the vicinal coupling constants of the hydrogen atoms on C_3 and C_4 in complex (III)/(IV) and its solvolysis products. Table 6 gives the vicinal coupling constants of the heterosubstituted complexes (IV), (III) and their solvolysis products.

TABLE 6

VICINAL COUPLING CONSTANTS $J_{H_3\,H_4}$ IN COMPLEXES (III) AND (IV) AND THEIR SOLVOLYSIS PRODUCTS

	C_3–H | Cl–C_4–H | CH_3	C–H | HO–C–H | CH_3	C–H | CH_3OC–H | CH_3
(III)	9	2.7	3.7
(IV)	4	3.7	3.7

If we assume that the Cl and OH substituents are locked into a particular configuration by interaction with the metal atom, then the change in coupling constant, *i.e.* in bond angle, can be explained by assuming inversion of configuration. For the methoxy derivatives we did not find any difference between the coupling constants of the two diastereomers, which indicates free rotation about the C_3–C_4 bond.



EXPERIMENTAL

Preparation of 1(1-*chloroethyl*)-3-*methyl-π-allylpalladium chlorides* (*III*) *and* (*IV*)

Bis(benzonitrile)palladium chloride (8 g) is dissolved in 50 ml methylene chloride. The solution is filtered and cooled to −20°, after which 4 ml 2,4-hexadiene is added. At this stage, the *trans,trans*-2,4-hexadiene gives a precipitate, whereas the complex from *cis,trans*-2,4-hexadiene remains in solution. After two hours the solution is poured into 200 ml of n-pentane at −80°. The precipitate is collected, washed with n-pentane, and dried under vacuum. Yield: 3.5 g (65% of theory).

Reactions of complexes (*III*) *and* (*IV*) *with triphenylphosphine, dimethyl sulphoxide or lithium bromide*

The reactants are separately dissolved in chloroform and cooled to −80°. An excess of the solution of the coordinating compound is added to the solution of the complex. The mixture is then allowed to warm up to room temperature. GLC and NMR indicate complete liberation of the respective 2,4-hexadienes.

Preparation of the hydroxy and methoxy derivatives of complexes (*III*) *and* (*IV*)

The hydroxy and methoxy derivatives of complexes (III) and (IV) can be prepared by solvolysis of these complexes. Relatively large amounts are most suitably prepared directly from the respective 2,4-hexadiene, palladium chloride and the nucleophile.

1(1-*Methoxyethyl*)-3-*methyl-π-allylpalladium chloride*

A quantity of 2.5 g bis(benzonitrile)palladium chloride is dissolved in 50 ml methanol. The solution is filtered, and 1.5 ml 2,4-hexadiene are added to the filtrate. After 1.5 h the mixture is poured into 500 ml water, which is subsequently extracted in three times with 25 ml portions of methylene chloride. The combined extracts are dried over magnesium sulphate, after which most of the solvent is removed by evaporation. Pentane is added and the solution is left to stand overnight. The mother liquor is decanted and the crystalline precipitate washed several times with n-pentane, before being dried in high vacuum. Yield: 1.7 g (75%).

1(1-*Hydroxyethyl*)-3-*methyl-π-allylpalladium chloride*

A mixture of 2.5 g bis(benzonitrile)palladium chloride, 1.5 ml 2,4-hexadiene and 40 ml water in 50 ml acetone is allowed to react for 5 h. The oily residue obtained after evaporation of the solvent is taken up in a small amount of methylene chloride. This solution is poured into n-pentane at −80° and the precipitate suction-filtered to yield a solid, yellow product. Yield: 1.5 g (95%).

Kinetic measurements

The reaction rates were determined by following the concentrations of the reactants by NMR (Varian A-60 or HA-100).

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