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syn- AND *anti*-(1-ALKYL-π-ALLYL)PALLADIUM CHLORIDES

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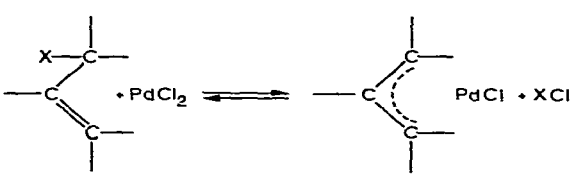
SUMMARY

π-Allylpalladium chlorides with bulky substituents on the terminal carbon atoms are often formed with these substituents in the less stable *anti* configuration. The activation energy of the π–σ–π rearrangement to the *syn* configuration increases with the bulkiness of the substituent. The difference in energy between the *anti* and *syn* configurations decreases with increasing size of the substituents on the terminal and *meso* carbon atoms. The phenomena can best be explained by assuming that there is steric interaction between the substituents on the terminal carbons of the π-allyl ligand and either other ligands on the metal or the substituent on the *meso* carbon of the π-allyl ligand.

INTRODUCTION

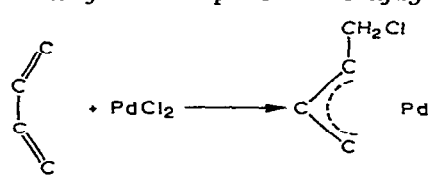
The methods of formation of π-allylpalladium complexes can be separated into two types depending on the π system of the organic reagent:

A. Elimination of a substituent α to an olefinic bond

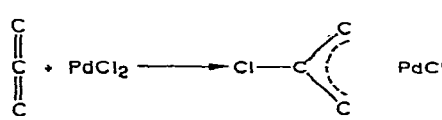


(1)

B. Addition of a nucleophile to a conjugated or cumulated diene system



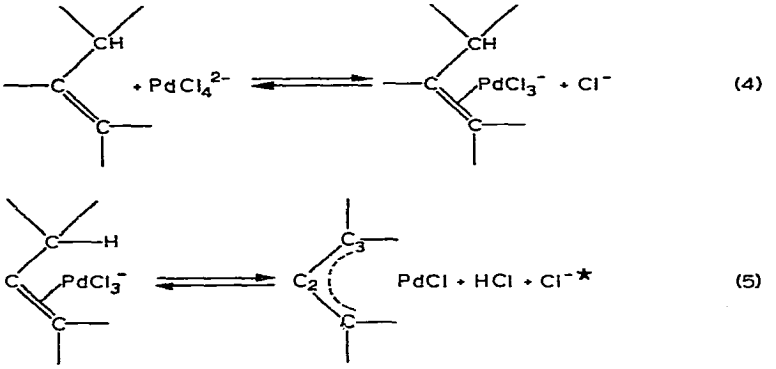
(2)



(3)

We concentrate attention below on reactions of type *A*.

The mechanism of reactions of type *A* with X=H has been discussed by Volger[1], who showed that the reaction proceeds via coordination of the olefin to the metal, followed by elimination of a proton from the allylic carbon atom:



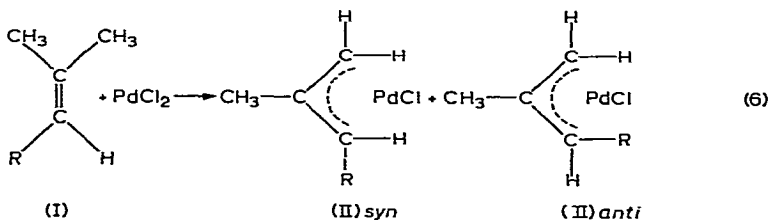
From NMR data (*cis* and *trans* coupling between the hydrogen atoms attached to C_1/C_3 and C_2; shielding of *anti*-H by the metal), it was concluded that of the substituents on C_1/C_3 the bulkier ones would always occupy the *syn* position[1], irrespective of the initial geometry of the olefin. This phenomenon was attributed to isomerization of any incipient *anti* isomer via an autocatalytic π–σ–π rearrangement[2].

Recently we succeeded in preparing a π-allylpalladium complex in which the bulkier substituent on one of the terminal carbon atoms of the π-allyl ligand was present in the *anti* position.

Preliminary results have been published elsewhere[5].

RESULTS

A number of olefins of general structure (I) were treated with palladium chloride in acetic acid/sodium acetate, reaction (6).



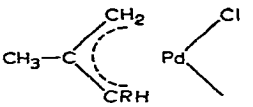
(a) R=C(CH$_3$)$_3$ (d) R=CH$_2$CH$_3$
(b) R=CH(CH$_3$)$_2$ (e) R=CH$_3$
(c) R=CH$_2$C(CH$_3$)$_3$ (f) R=H

In each case the reaction mixture was quenched when the colour had turned from red to yellow, indicating that the reaction was complete. The results are presented in Table 1.

* Good yields are obtained if the hydrogen chloride formed is removed by a base.

TABLE 1

YIELDS OF STRUCTURAL ISOMERS OF π-ALLYLPALLADIUM CHLORIDE COMPLEXES



Compound	*R*	*Reaction time (min)*	*anti* (%)	*syn* (%)	*Structural isomers* (%)	*Total yield* (%)
(IIa)	tert-Butyl	45	85	15		63
(IIb)	Isopropyl	35	56	35		73
(IIc)	Neopentyl	15	37	43	20	80
(IId)	Ethyl	25		100		80
(IIe)	Methyl	15		100		80

TABLE 2

NMR CHEMICAL SHIFTS[a]

Compound	3-*H anti*	3-*H syn*	2-*Me*	1-*H anti*	1-*H syn*	*Alkyl anti*	*Alkyl syn*
(IIa) *anti*	3.47	3.87	2.02		4.44	C_4H_9 1.13	
(IIa) *syn*	2.67	3.62	2.18	3.48			C_4H_9 1.25
(IIb) *anti*	3.16	3.82	2.08		4.26 (*J* 9 Hz)	$CHC(CH_3)_2$ 0.93/1.28 (*J* 7 Hz)	
(IIb) *syn*	2.60	3.66	2.12	3.42 (*J* 9 Hz)			$CHC(CH_3)_2$ 1.09/1.27 (*J* 7 Hz)
(IIc) *anti*	3.12	3.82	2.05		4.42	$CH_2C_4H_9$ 1.6 0.87	
(IIc) *syn*	2.66	3.70	2.07	3.7			$CH_2C_4H_9$ 1.6 0.97 *J* 5/10 Hz
(IId) *syn*	2.67	3.70	2.08	3.65 (*J* 6.5 Hz)			CH_2CH_3 1.67 1.14 (*J* 7.5 Hz)
(VII) *anti*	3.42	3.75			4.50	0.98 or 1.10	2-CH_2–$C(CH_3)_3$ 0.98 or 1.10

[a] Ppm downfield from internal TMS.

It is apparent that the percentage of *anti* form increases with the size of the substituent R in (I)*.

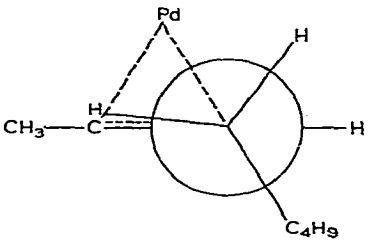
The *syn* and *anti* configurations were identified from their NMR spectra (Table 2). The assignments are based on the spectrum of (IIb), in which the hydrogen geminal to the isopropyl group can be identified unambiguously by its coupling with

* The neopentyl group must be considered "less bulky" than the isopropyl group since it can bend away from the rest of the molecule (metal or vicinal substituent) with which it would interfere (*vide infra*).

the methine hydrogen of the isopropyl group. Since the extent to which a hydrogen atom is shielded by a metal atom is inversely proportional to the distance between the two atoms, and since an *anti* substituent is closer to the metal than a *syn* substituent, the singlet at higher field can be assigned to the *anti* and the remaining singlet at lower field to the *syn* hydrogen at C_3.

It is interesting to note that the configuration (*anti vs. syn*) of the substituents on C_1 has a marked influence on the chemical shifts of the hydrogens on C_3; if C_1 carries an *anti* substituent, the *syn* and *anti* hydrogen atoms at C_3 are shifted by 0.15–0.25 ppm and 0.4–0.8 ppm lower fields, respectively, this shift increasing with the size of the substituent at C_1. The explanation of these downfield shifts must be sought in the elongation of the ligand–palladium bond as a result of interference between the metal and the substituent, this interference being greater with *anti* than with *syn* substituents.

Another interesting feature of Table 2 is provided by the different coupling constants of the methylene hydrogen atoms of the neopentyl group in (IIc)-*syn* with the hydrogen at C_1 (5 and 10 Hz). Hindered rotation about the bond R–C_1, in other words unequally populated conformations, seems the most likely explanation. With the aid of the Karplus plot, the bond angles C_4H_9–C(H)H–C_1H–$C_2(CH_3)$–C_3H_2 can be estimated to be roughly 60° and 180°. This means that the C_4H_9 moiety in the neopentyl group is fixed at an angle of ~90° to the plane formed by C_3, C_2, C_1, C_1 CH_2, and it can safely be assumed to lie away from the metal:



The structure of *anti*-2-methyl-(1-tert-butyl-π-allyl)palladium chloride has been determined by X-ray analysis, and the dimer structure is shown in Fig. 1. The

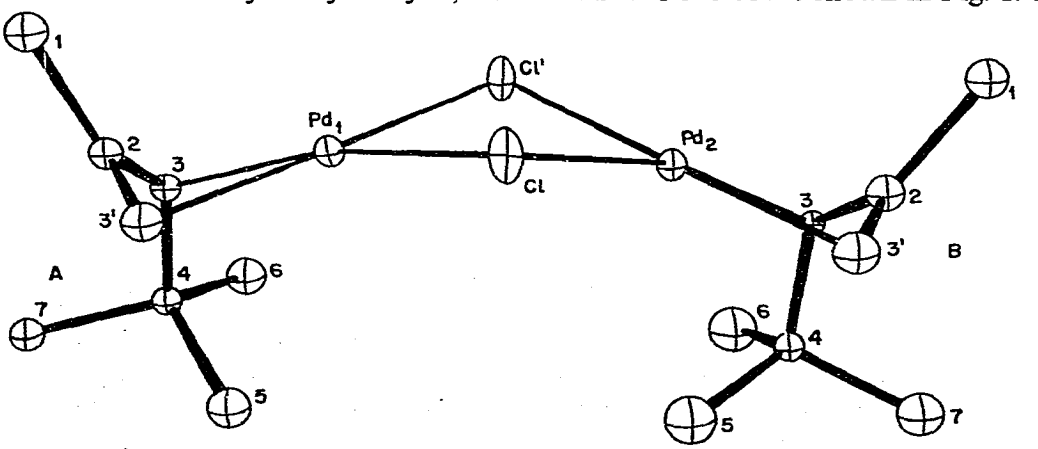


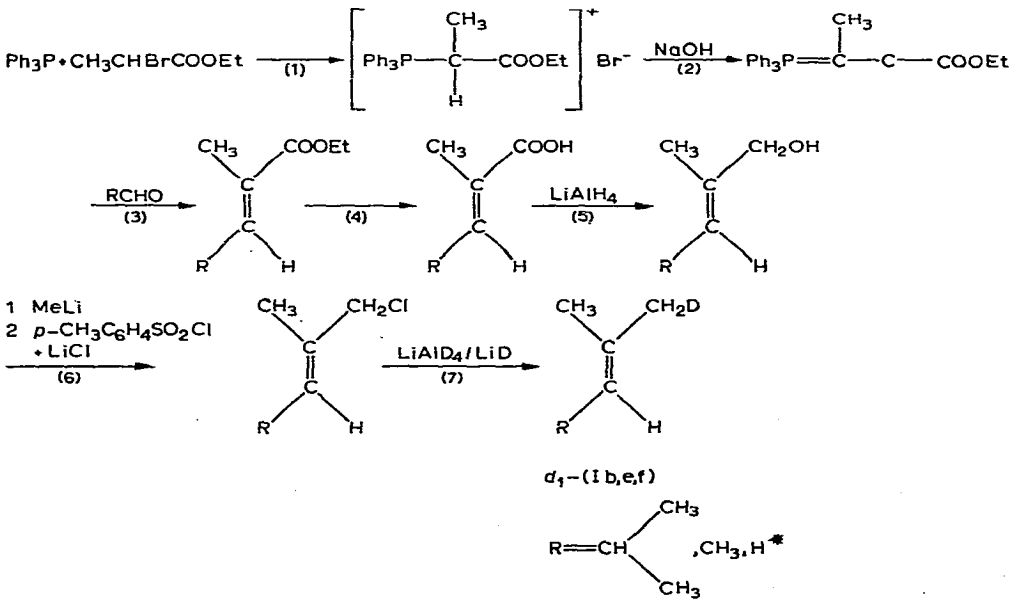
Fig. 1. The (*anti*-2-methyl-1-tert-butyl-π-allyl)palladium chloride dimer (A crystallographic mirror plane passes through A1, A2, Pd1, Pd2, B2 and B1; 3 and 3' are not related by it).

final coordinates and the final values of F_o and F_c may be obtained from the authors on request. The bond lengths and angles are listed in Table 4. All bond distances and angles are within the range expected. The dimer has only one unusual feature *viz.* that the chlorine bridge is bent, the dihedral angle between $Cl-Pd_1-Cl'$ and $Cl-Pd_2-Cl'$ being 148°. As far as we know, this is only the third dimer with this property, the other two being bis[(1,2,3-trimethyl-π-allyl)palladium chloride][4] and bis[(1,3-dimethyl-π-allyl)palladium chloride][5], which have dihedral angles of 150° and 155°, respectively.

To establish the ratio of *anti* to *syn* isomers without interference from the *anti*→*syn* rearrangement which accompanies the formation reaction, we deuterated one of the methyl groups in the olefin of general structure (I). For convenience of synthesis we chose the methyl group *anti* to the bulky substituent, and the synthesis was accomplished by the reaction sequence indicated in Scheme 1. From the coupling of the vinylic hydrogen with the methyl group in the product of reaction step 4, it was deduced that these substituents were in the *trans* configuration in at least 97% of this intermediate.

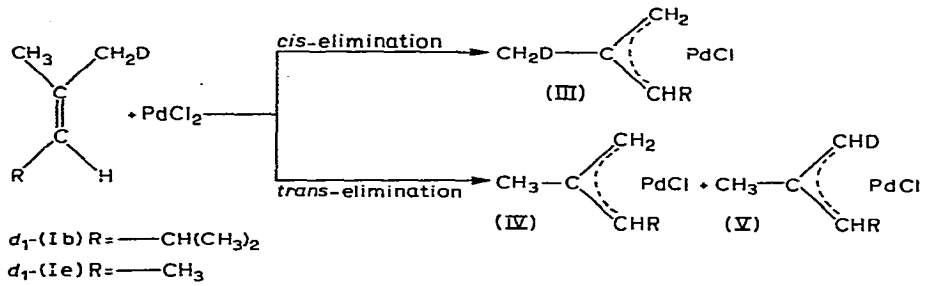
SCHEME 1

SYNTHESIS OF LABELLED ALKENES FOR THE PREPARATION OF π-ALLYLPALLADIUM COMPLEXES



It was expected that in the formation of the π-allylpalladium complexes alkenes d_1-(Ib) and (Ie) would eliminate a hydrogen (or deuterium) atom from either the *cis* or the *trans* methyl group, resulting in a 2-monodeuteromethyl-π-allyl ligand (III) or a 2-methyl-π-allyl (IV) and a 2-methyl-1-deutero-π-allyl ligand (V):

* Reaction step (3) failed in the case of pivaldehyde.



The primary isotope effect influences both the ratio (IV)/(V) and the ratio *cis/trans* [(III)/(IV)+(V)] elimination. We therefore used (If), a compound that is degenerate in *cis–trans* isomerism, to determine this effect; and found it to be 1.3.

The *syn/anti* ratio proved to be 73/27 for the 1-methyl-π-allyl ligand and 33/67 for the 1-isopropyl-π-allyl ligand. [For the methods used to determine the concentrations of (III), (IV) and (V) see Experimental.]

The π–σ–π rearrangement *anti*→*syn* can be catalysed by coordinating compounds such as triphenylphosphine and dimethyl sulfoxide[2]. Table 3 shows that the activation energy increases with the size of the alkyl substituent R in (I); in other words, the tendency to undergo this rearrangement is smaller when R is larger.

TABLE 3

KINETIC PARAMETERS OF THE REARRANGEMENT *anti*→*syn* AND EQUILIBRIUM CONCENTRATIONS[a]

	Triphenylphosphine		*Dimethyl sulfoxide*		*anti at equilibrium* (%)
	$k(\times 10^4)$ (s^{-1})	E_a(*kcal/mol*)	$k(\times 10^4)$ (s^{-1})	E_a(*kcal/mol*)	
(IIa) *anti*→(IIa) *syn*	1.1 (45°)	19±0.5	3.5 (64°)	15±0.5	12.5
(IIb) *anti*→(IIb) *syn*	7.5 (46°)	18±0.5	14.0 (62°)	15±0.5	17
(IIc) *anti*→(IIc) *syn*	6.2 (45°)	14±0.5	34.6 (55°)	13±0.5	17

[a] Solvent: dichloromethane. Concentration of catalyst: triphenylphosphine: 2.3 %m; dimethyl sulfoxide: 23 %m.

Another noteworthy point in Table 3 is that the π-allyl complexes with a bulky terminal substituent contain an appreciable proportion of the *anti* isomer in equilibrium with the *syn*-isomer, whereas complexes with smaller substituents are largely, if not entirely, converted into the *syn* isomer (*anti* isomer < 3%). [(IId) and (IIe) are not recorded in Table 3, since they can only be obtained in the *syn* configuration; see Table 1]. The results can be summed up as follows:

(a) Under kinetically controlled reaction conditions the percentage of *anti* form increases with increasing size of the alkyl substituent at C_1 (Table 1).

(b) Reaction with specifically deuterated olefins under kinetically controlled conditions gives an *anti/syn* ratio that is not affected by concomitant equilibration. The results for (1-isopropyl-π-allyl)palladium chloride are in line with expectations, but those for the 1-methyl homologue (an excess of *syn* isomer) are at first sight surprising.

(c) The activation energy of the *anti*→*syn* isomerization via a π–σ–π rearrangement increases with the size of the alkyl substituent at C_1.

(d) Under thermodynamically controlled conditions, small C_1-alkyl substituents are found only in the *syn* position, whereas bulky substituents tend to occur in both the *syn* and the *anti* position.

(e) The yield of π-allylpalladium chloride decreases with increasing bulk of the substituent R (Table 1). We were not able to isolate the olefin complex[6] which is the first intermediate in the reaction towards a π-allyl complex for branched R's.

DISCUSSION

The above observations can be rationalized if we take a closer look at eqn. (4), and at the first intermediate, the π-olefin complex. In this complex (Scheme 2) the axis C_1–C_2 of the double bond is approximately orthogonal to and bisected by the square plane formed by the metal and the other ligands. Scale models show that if the size of one of the substituents on the double bond is increased, this substituent will interfere with one of the *cis* ligands (which is reflected in the lower stability of the π-olefin complex in these cases). We assume that to avoid the steric strain the coordinated olefin will deviate from its orthogonal position (Scheme 2). This twisting on the olefin–metal σ bond is part of a rotation of the ligand for which low activation energies have been found in some cases[7]. The next step is a more or less concerted action in which a *cis* ligand ($L = Cl^-$ or OAc^-) leaves the coordination sphere, while the olefin rotates about the bond π–d_{z^2}, with a methyl group approaching the now empty coordination site. An S_N2 reaction of Pd^+ on the methyl group with expulsion of a proton then completes the reaction.

It is now clear why in the case of olefins with bulky substituents it is the *anti* isomer that is formed preferentially. In the π-olefin complex the methyl group *cis* relative to the bulky group R has, by virtue of its twisted configuration (as in Scheme 2) already approached its final position as terminal methylene group in the π-allyl complex, thereby facilitating the subsequent proton removal. Moreover, the alternative route, with the olefin turning towards an empty coordination site *cis* relative to the *trans* methyl group, is rendered unattractive because it further increases the steric crowding between R and "its" *cis* ligand.

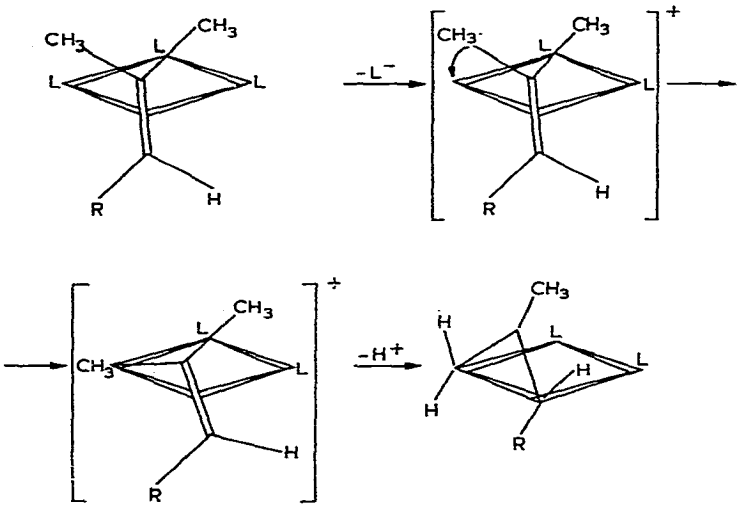
In the light of these considerations it is tempting to assume that the preference for the *anti* configuration decreases with decreasing size of R in (I), until for R = H the reaction becomes non-stereoselective and leads to an equilibrium with 50/50 *anti*/*syn* distribution. In fact, however, for R = Me a ratio of 27/73 was found. Hence, we cannot but conclude that the transition state in the formation of (II) *syn* is energetically slightly more favorable than the one leading to the (II) *anti* species. Since the configuration of the starting material, the olefin complex, will still favour *cis* elimination, resulting in (II) *anti*, in spite of the fact that (II) *syn* is thermodynamically more stable, we may reasonably deduce from the 27/73 *anti*/*syn* ratio that the transition state bears a closer resemblance to the product than to the starting complex.

Surprising as it was to find the *anti* isomer formed under kinetically controlled conditions, the reluctance of bulky groups to undergo the *anti*–*syn* rearrangement was even more unexpected, as was the measurable amount of *anti*-isomer in equilibrium with the *syn* form. Model studies of the π–σ–π transformation reveal two possible steric interferences that may raise the activation energy of this process: when the allyl ligand, σ-bonded at C_1, rotates about the Pd–C_1 bond, the bulky group R

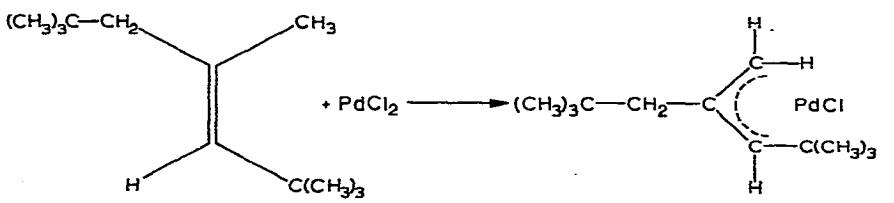
may interfere with the ligand which initiated the rearrangement and/or with the substituent on C_2, after it reached the *syn* position*. In order to determine which of these two interferences is mainly responsible for the observed phenomena, we measured the activation energies of the π–σ–π rearrangement using two different catalyst

SCHEME 2

MECHANISM OF FORMATION OF AN ANTI-1-SUBSTITUTED π-ALLYL COMPLEX
(The central metal atom has been omitted for the sake of clarity.)



ligands, *viz.* triphenylphosphine and dimethyl sulfoxide. The size of the former is much larger than that of the latter. If size is the more important factor, then with decreasing size of the ligand the differences in activation energy between the various alkyl substituents at C_1 should become smaller. This is, indeed, what we found (Table 3). That the size of the alkyl substituent on C_2 also has an influence on the energy difference between the *syn* and *anti* isomers—and, hence, on the position of the equilibrium between these stereoisomers—is demonstrated by the fact that olefin (VI) gives only the *anti*-π-allyl complex (VII). Attempts to isomerize it to the *syn* isomer with triphenylphosphine failed completely.



(VI) (VII)

* Another suggestion, which, although less likely, cannot be rejected, is that the compound necessary as a ligand for initiation of the rearrangement cannot coordinate in the position *cis* relative to C_1.

EXPERIMENTAL

General procedure for the preparation of π-allylpalladium chloride complexes from alkenes and palladium chloride:

Reagents

1 g (5.6 mmol) $PdCl_2$, 0.66 g (11.3 mmol) NaCl, 0.93 g (11.3 mmol) $NaOOC-CH_3$, 1.1 ml (10 mmol) alkene.

Sodium acetate was dried by melting it to allow the absorbed water to evaporate. A procedure for removing crystal water is described in Vogel's "Text-book of practical organic chemistry", 225 Ed., page 192.

Solvent

100 ml glacial acetic acid.

Procedure

$PdCl_2$, NaCl and $NaOOCCH_3$ were dissolved in the glacial acetic acid at 85°. The solution was filtered through a fluted filter paper and the alkene was added to the stirred filtrate. The mixture was kept at 85° until the colour had completely changed from red to yellow (approx. 30 min). The solution was then poured into 500 ml H_2O and extracted four times with 50 ml portions of CH_2Cl_2. The combined extracts were consecutively washed with H_2O, $H_2O+NaHCO_3$, H_2O, and then dried over Na_2SO_4. Evaporation of the solvent and drying under vacuum yielded 1 g (80%) of the yellow, crystalline product. The product could be recrystallized by dissolving it in methylene chloride, adding n-pentane until the solution becomes turbid, and cooling to −80° in a dry ice/acetone bath.

Kinetic measurements (*Table* 3)

The reaction rates were followed by NMR; the experiments were conducted in the NMR tube.

Preparative sequence of Scheme 1

Reaction conditions are described only for (IIc). The other two d_1-alkenes were prepared analogously: (IIa) starting with step 7, from methallyl chloride and (IIb) starting with step 5, from tiglic acid (*trans*-2-methyl-2-butenoic acid).

Ethyl ester of 2,4-dimethyl-2-pentenoic acid

A solution of 30 g (α-carbethoxyethylidene)triphenylphosphorane[8] and 12 ml isobutyraldehyde in dichloromethane was refluxed under nitrogen for 3 h, during which time the colour changed from yellow to cream. The solution was concentrated and n-pentane was added to precipitate triphenylphosphine oxide. The solid was filtered off and the filtrate again concentrated (on a rotary evaporator) and finally distilled to yield 10.5 g (80%) product, b.p. 72.5–73.5°/17 mmHg.

2,4-Dimethyl-2-penten-1-ol

A quantity of 1.9 g (0.09 mol) $LiAlH_4$ was dissolved in 75 ml dry tetrahydrofuran (THF) and the solution cooled in an ice bath. Next, 12.3 g 2,4-dimethylpentenoic

ethyl ester (0.08 mol) in 50 ml dry THF was added dropwise during 1 h. After being stirred for another hour the solution was warmed to room temperature. The excess of $LiAlH_4$ was decomposed by the addition of THF with 10% H_2O. The solution was then poured into ice water, 10% H_2SO_4 was added and subsequently NaCl to separate the THF layer. The water layer was extracted with ether. The combined organic layers were neutralized, dried and finally concentrated in a rotary evaporator. Distillation yielded 5.2 g (58%) of product, b.p. 69°/16 mmHg; n_D^{22} 1.4420.

2,4-Dimethyl-2-pentenyl chloride

The title compound was prepared by the method described in ref. 9, because unlike other methods it does not involve an allylic rearrangement.

A quantity of 24 ml (48 mmol) of a 2 *M* solution of LiMe in ether was added dropwise to a solution of 5 g 2,4-dimethyl-2-penten-1-ol (44 mmol) in 10 ml dry ether and 5 ml HMPTA. The reaction occurs with the evolution of methane. Subsequently, a solution of 13.5 g *p*-toluylsulfonyl chloride (71 mmol) and 8.2 g lithium chloride (193 mmol) in 34 ml dry ether and 17 ml HMPTA was added dropwise in 15 min. A slightly exothermal reaction occurred. Stirring was continued overnight, during which time a white precipitate formed. Ether was added, and the solution extracted with water/$NaHCO_3$. After having been dried over anhydrous sodium sulfate, the ether was evaporated and the residue distilled to yield 3.6 g (62%) product, b.p. 53°/28 mmHg.

1-D_1-2,4-Dimethyl-2-pentene

A 100 ml flask, equipped with a cooler and a magnetic stirrer, was flushed with argon and charged with 0.28 g LiD (31 mmol), 0.4 g $LiAlD_4$ (9.5 mmol) and 10 ml dry THF. A solution of 2 g 2,4-dimethyl-2-pentenyl chloride (15 mmol) in 10 ml dry THF was added dropwise over a period of 20 min. The mixture was allowed to reflux for two hours, after which time a total of 20 ml H_2O was added to destroy any residual metal hydride. Subsequently, the solution was neutralized with 20 ml 0.5 *N* HCl. The organic layer, consisting of product and THF, was separated (yield 1 g=66%) and used as such for the synthesis of the π-allyl complex.

Analysis of deuterated products

The determination of deuterium labelling in the products from (IIb) and (IIc) was done by NMR measurements. The 1-methyl and 1-isopropyl groups were used as internal standards to measure the relative intensities of hydrogens on C_3 and of the methyl group on C_2, respectively.

The latter, when monodeuterated [(IIIb) and (IIIc)], contains two magnetically non-equivalent hydrogens, one of which has a chemical shift slightly different from that of the undeuterated methyl group so that it could be measured directly.

Structure determination of anti-(2-methyl-1-tert-butyl-π-allyl)palladium chloride

The (*anti*-2-methyl-1-*tert*-butyl-π-allyl)palladium chloride dimer crystallizes from methanol as yellow cubes in the orthorhombic system. The cell dimensions are $a=14.82(2)$ Å, $b=12.69(1)$ Å, $c=10.57(1)$ Å, $V=1989$ Å^3, $D_x=1.69$ g/cm^3 with four dimer units in the cell. The extinction rules are: $0kl$: $k+l=2n$, $h0l$: $h=2n$, denoting $Pna2_1$ (C_{2v}^9, No. 33) or $Pnam$ (D_{2h}^{16}, No. 62)[10].

Complete three-dimensional data up to $\sin\theta/\lambda = 0.54$ Å^{-1} were collected on a three-circle diffractometer, using zirconium-filtered Mo-$K\alpha$ radiation and a θ, 2θ scan technique.

The three-dimensional Patterson function showed the palladium and chlorine positions, the Pd1–Pd2 vector being parallel to (001), *i.e.* the mirror plane of the heavy atom and allyl part of the molecule is parallel to (001). Since the difference between $Pna2_1$ and *Pnam* is a mirror plane $z = \frac{1}{4}$, no choice between the space groups could be made at this stage.

Refinement in $Pna2_1$ did not give reliable results, but refinement in *Pnam* gave a final R value (based on F) of 5.7%, with $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w(|F_o|)^2]^{\frac{1}{2}} \times 100\% = 6.0\%$. Here, we introduced the tertiary butyl groups (including CA3 and CB3) as rigid groups.

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) FOR NON-GROUP ATOMS

Pd1–C1	2.41(1)	Pd2–C1	2.41(2)
Pd1–CA3	2.05(5)	Pd2–CB3	2.13(2)
Pd1–CA3′	2.13(4)	Pd2–CB3′	2.16(6)
Pd1–CA2	2.12(2)	Pd2–CB2	2.09(3)
CA2–CA1	1.49(4)	CB2–CB1	1.56(4)
CA2–CA3	1.25(6)	CB2–CB3	1.41(6)
CA2–CA3′	1.42(6)	CB2–CB3′	1.43(6)
Pd1–C1–Pd2	86.3(2)		
C1–Pd1–C1′	89.0(2)	C1–Pd2–C1	89.3(2)
C1′–Pd1–CA3	106(2)	C1′–Pd2–CB3	102(2)
C1–Pd1–CA3′	98(2)	C1–Pd2–CB3′	97(2)
CA3–Pd1–CA3′	66(2)	CB3–Pd2–CB3′	70(2)
CA1–CA2–CA3	128(3)	CB1–CB2–CB3	127(3)
CA1–CA2–CA3′	112(3)	CB1–CB2–CB3′	109(3)
CA3–CA2–CA3′	117(3)	CB3–CB2–CB3′	121(3)
CA2–CA3–CA4	135(3)	CB2–CB3–CB4	127(3)

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