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INSERTION REACTIONS OF CONJUGATED DIENES WITH π-ALLYLIC PALLADIUM COMPLEXES

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SUMMARY

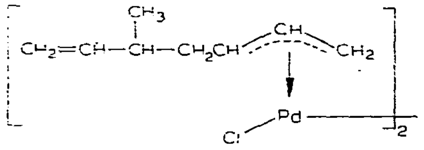
π-Allylic palladium complexes reacted with conjugated dienes to give diene-inserted products. Isoprene gave 1,1-disubstituted allyl complexes rather than 1,2-disubstituted ones. Two types of allylic complexes were studied, and halogen-bridged dimer complexes showed lower reactivity than acetylacetonato complexes. When the allylic group or diene was varied, the reactivity decreased in the order:

allyl > 2-methylallyl > 1-methylallyl > cinnamyl

and

butadiene > isoprene > chloroprene > 2,3-dimethylbutadiene

The crotyl complex reacted with butadiene less readily, to give mainly the product with the structure:



The reactivity variations and the reaction mechanisms are discussed.

INTRODUCTION

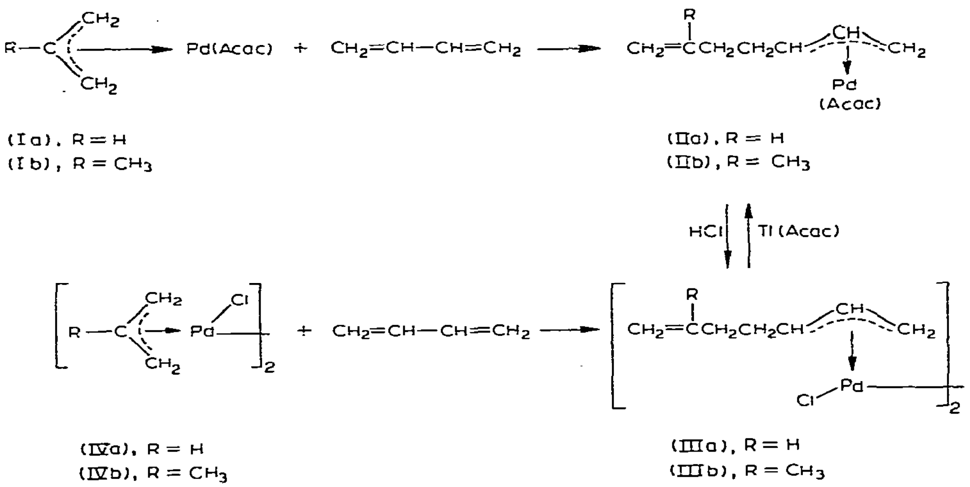
In our previous paper[1] the insertion of butadiene into the allyl–palladium bond of acetylacetonato-π-allylic palladium complexes was reported. This type of insertion has been extended to other allylic palladium complexes and conjugated dienes.

RESULTS AND DISCUSSION

The acetylacetonato-π-allylpalladium complex (Ia) reacted with butadiene at ordinary temperature for 20 h to give a yellow viscous oily product, acetylacetonato-π-(1-butenyl)allylpalladium (IIa). Its infrared spectrum showed absorption bands assigned to a terminal vinyl group (1640, 995 and 910 cm^{-1}) and an acetylacetonato group. (IIa) was treated with hydrogen chloride giving bis[π-(1-butenyl)allylpalladium chloride] (IIIa). Complex (IIIa) was also obtained by direct reaction between butadiene and bis(π-allylpalladium chloride) (IVa) in a sealed tube at 70° for 1 h.

The reaction of the methallyl complex (Ib) with butadiene occurred analogously, the product (IIIb) had infrared bands attributed to a vinylidene type olefin (1655 and 890 cm^{-1}). When (IIIa) and (IIIb) were treated with acetylacetonatothallium, complexes (IIa) and (IIb) were regenerated, respectively. These results suggested that butadiene had inserted to the allyl–palladium bond, and the reaction scheme can be shown as in Scheme 1.

SCHEME 1



The structures of (IIIa) and (IIIb) were supported by their NMR spectra shown in Fig. 1. In the spectra of (IIIb) (Fig. 1b) sharp resonance peaks for the protons on

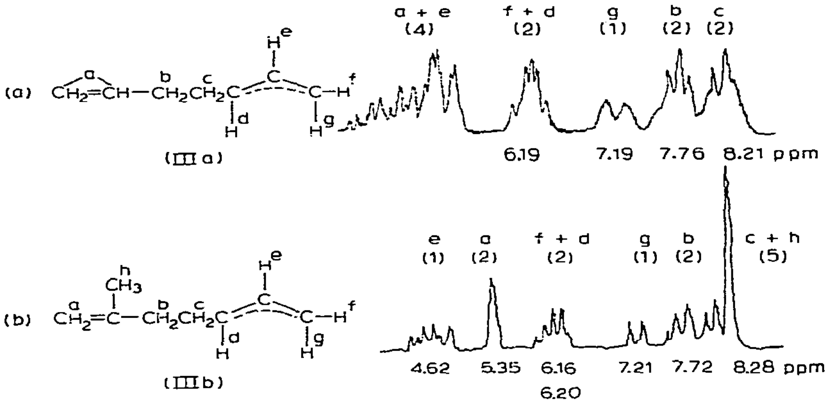


Fig. 1. NMR spectra of compounds (IIIa) and (IIIb) in carbon tetrachloride (internal standard TMS). The values in parentheses show intensity ratios. J_{eg} 12.0 Hz, J_{ef} 6.0 Hz.

π-allylic group were observed and could be assigned unambiguously, while compound (IIIa) showed moderately broad resonance bands. The broadening of the peaks can be explained by intra- or inter-molecular interaction between a vinyl group and a palladium atom[2]. From the comparison of the two spectra (Fig. 1a and 1b), it appears that a terminal vinyl group interacts with the palladium atom more strongly than a vinylidene group.

The chemical shifts and the coupling constants between protons in π-allylic group agreed with those expected for simple π-allylic complexes[3]. All the data are summarized in Fig. 1. A butenyl or isopentenyl group situated on 1-π-allyl group has the *exo*-configuration, the coupling constant J_{ed} being nearly equal to J_{eg}, showing that protons H_d and H_g have the *endo*-configuration.

Isoprene also reacted with (Ia) under the same conditions as butadiene to give a yellow oily product, having infrared bands at 1640, 995 and 910 cm^{-1} assigned to terminal vinyl group. The complex (Ib), however, did not react with isoprene.

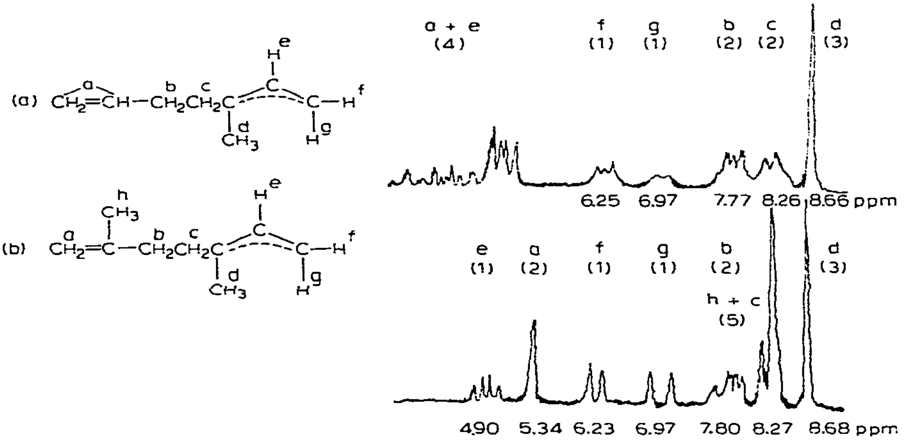
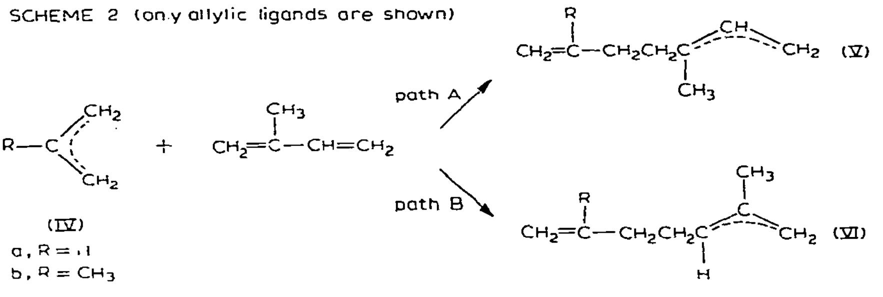


Fig. 2. NMR spectra of compounds (Va) and (Vb) in carbon tetrachloride (internal standard TMS). The values in parentheses show intensity ratios. J_{eg} 12.5 Hz, J_{ef} 7.8 Hz.

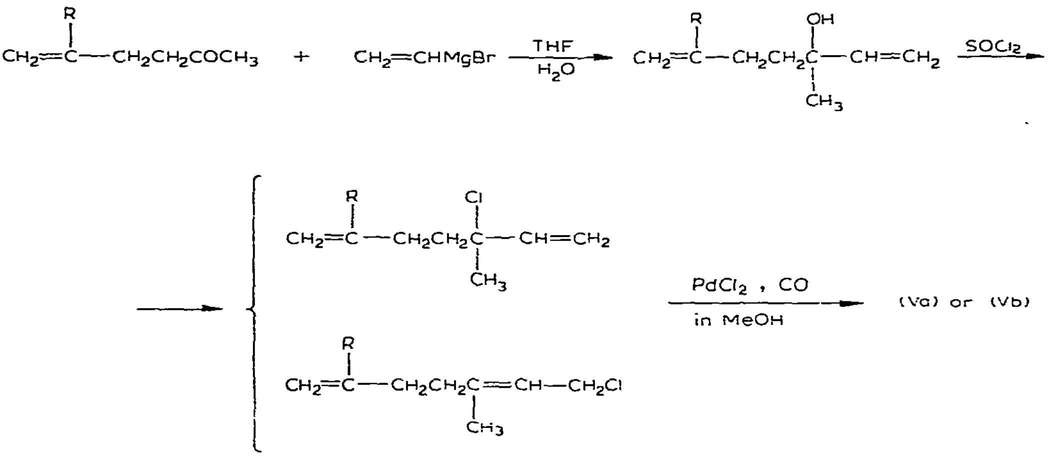
Isoprene reacts similarly with complexes (IVa) and (IVb) in a sealed tube at 70–80°. The NMR spectra showed that (V) is the exclusive product (Scheme 2). This was confirmed by the independent synthesis of (Va) and (Vb) by unambiguous routes as shown in Scheme 3.


SCHEME 2 (only allylic ligands are shown)

The NMR spectra of (Va) and (Vb) showed the expected general features for π-allylic complexes. Complex (Va) also gave broader resonance peaks for the π-allylic protons than complex (Vb), and the interaction of the vinyl group and palladium atom again seems to be stronger than that of vinylidene group.

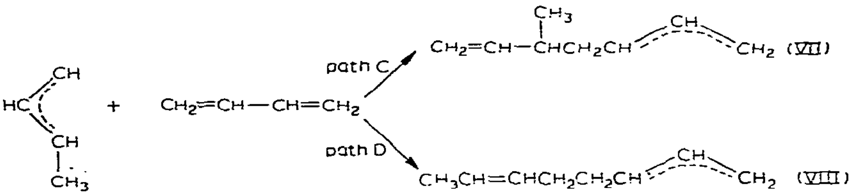
Acetylacetonato-π-crotylpalladium complex (Ic) did not react at all with butadiene and isoprene at room temperature, but bis(π-crotylpalladium chloride)

SCHEME 3



(IVc) reacted with butadiene in sealed tube at 70° for about 10 h to give a yellow oily product, which showed infrared bands at 1640, 995 and 910 cm^{-1} assigned to terminal vinyl group, and which must be (VII), formed by path C in Scheme 4. The NMR spectrum also supported this structure. Bis(π-cinnamylpalladium chloride) behaved like the crotyl complex.

SCHEME 4 (only allylic ligands are shown)



2,3-Dimethylbutadiene showed the lowest reactivity for all π-allylic complexes, presumably because of the steric factor of methyl group. Our preliminary kinetic studies of the insertion reactions using NMR spectra showed that isoprene was twice as reactive as chloroprene towards bis(π-2-methylallylpalladium chloride), although the methyl group is sterically larger than halogen. Therefore, the electronic effect should not be neglected as a factor determining the reactivity order of conjugated diene.

From these observations, reactivity orders can be derived as follows.

(a) For diene and allylic groups, the reactivity decreases in the order:

allyl > 2-methylallyl > crotyl > cinnamyl

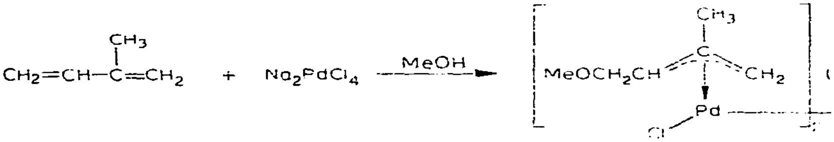
and

butadiene > isoprene > chloroprene > 2,3-dimethylbutadiene.

(b) Acetylacetonato complexes were more reactive than halogen-bridged dimers.

Isoprene reacts with sodium chloropalladate in methanol to give the methoxymethylallyl complex (IX) (ref. 4).

SCHEME 5

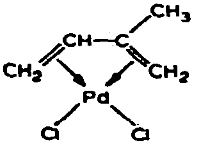


(IX)

This reaction can apparently be formulated as an insertion of isoprene into the Pd–Cl bond[5], and subsequent replacement of halogen by the methoxy group.

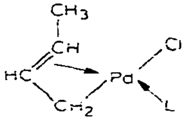
The complex (IX) has a structure in which a methyl group is bonded to the 2-position of the π-allylic group, while in the product (V) in Scheme 2 one methyl group is bound to the 1-position of the π-allylic group, although both reactions include diene-insertion reaction.

In the reaction of Scheme 5, the chelating diene complex (X) may be regarded as an unstable intermediate, with subsequent halogen migration from palladium atom to the terminal carbon atom of isoprene moiety. But, in the reaction with π-allylic complexes (Scheme 2), a part of the diene molecule (probably the terminal vinyl group, but not a vinylidene group) may attack a palladium atom and form an olefin complex.

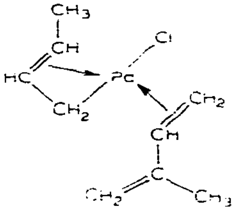


(X)

The attack of olefin on the metal atom of the π-allylic complex will lead to a new π-allylic complex.



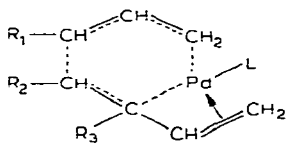
(XI)



(XII)

Bis(crotylpalladium chloride) complex reacts with donor groups, L, in solution to give the product with the structure (XI) (ref. 6). As olefins are good π-accepting ligands, the analogous interaction of π-allylic complexes with the terminal vinyl group of isoprene may be assumed. Therefore, an intermediate (XII) can be postulated for the insertion of conjugated dienes into π-allylic complexes.

A 1-substituted diene, for example, 1-phenylbutadiene, had a lower reactivity than a 2-substituted one, such as isoprene, in spite of the presence of a terminal vinyl group in the former. This decreased reactivity may be explained by assuming the six-membered transition state (XIII). The transition state (XIII) can also account for the fact that crotyl and cinnamyl complexes give the product type (VII) but not (VIII), and that isoprene inserts to give product type (V) exclusively.



(XIII)

(L, the ligand (or ligands) to satisfy the coordination number of the palladium atom).

Porri and co-workers[8] reported that a π-allylnickel complex was a good catalyst for the polymerization of conjugated dienes, but no polymerization of diene occurred in the course of our investigations. It is suggested that the olefinic group in the products formed by the first insertion interacts with the palladium atom and thus inhibits the second insertion of diene. Moreover, large groups in the products may decrease the ease of the second insertion.

EXPERIMENTAL

Infrared spectra were run on Nippon Bunko Type IR-S, and nuclear magnetic resonance spectra were measured using Japan Electron Optics C-60 spectrometer in carbon tetrachloride (internal standard, TMS)

Materials

All conjugated dienes were purified by distillation before use. Solvents were purified by the usual methods. π-Allylic palladium complexes were prepared according to Dent, Long and Wilkinson[9], and Robinson and Shaw[4]. All complexes were used after recrystallization from suitable solvents.

Reaction with conjugated diene

Two methods were used. Typical examples are given.

(1) *Acetylacetonato-π-allylpalladium* (*Ia*). Through a benzene solution of (Ia) (complex, 500 mg, and benzene, 30 ml) butadiene was bubbled for a few minutes. A very small amount of metallic palladium was precipitated. After palladium metal was separated off and the solvent was removed at reduced pressure, a yellow oil was obtained. The product (IIa) had strong infrared bands assigned to the acetylacetonato group (1580, 1510, 1400, 1250, 1190, 1020, 923, and 775 cm^{-1}) and the terminal vinyl group (1640, 995 and 910 cm^{-1}), and could be distilled in high vacuum at 50° with slight decomposition without any change of infrared spectrum. The complex obtained was reacted with hydrogen chloride at room temperature to give a yellow viscous oil (IIIa), which was soluble in n-hexane and carbon tetrachloride and had no infrared bands attributable to a chelating acetylacetonato group. Even when reprecipitated from n-hexane at $-40°$, no crystalline (IIIa) was obtained. (Found: C, 36.66; H, 5.09; Cl, 14.4; Pd, 44.8; mol.wt., 445. $C_{14}H_{22}Cl_2Pd_2$ calcd.: C, 35.47; H, 4.68; Cl, 15.0; Pd, 44.9%; mol.wt., 474.)

(IIIa) was treated with a slight excess of acetylacetonatothallium and complex (IIa) was regenerated. (IIIa) and infrared bands at 1640, 995 and 910 cm^{-1} assigned to the terminal vinyl group, and at 1500 cm^{-1} characteristic to the 1-position of the substituted π-allylic group.

The reaction of (Ia) and isoprene, and of (Ib) and butadiene were performed analogously to give products (Va) and (IIIb), respectively. (IIIb) was analyzed. (Found: C, 37.68; H, 5.25; Cl, 15.0; Pd, 42.9. $C_{16}H_{26}Cl_2Pd_2$ calcd.: C, 38.27; H, 5.22; Cl, 14.2; Pd, 42.4%.) The structure of (Va) was confirmed by comparison with the product obtained from another route. Infrared and NMR spectra of both complexes could be superimposed in each other.

(2) *Bis(methallylpalladium chloride)* (*IVb*). A benzene solution of (IVb) (complex, 500 mg, and benzene, 5.0 ml) and isoprene (2.0 ml) was maintained at 70° in a sealed tube. After evaporation of the solvents a yellow oily complex resulted. The complex (Vb) precipitated at −40° from n-hexane was analyzed. (Found: C, 41.95; H, 5.42. $C_{18}H_{30}Cl_2Pd_2$ calcd.: C, 40.77; H, 5.80%.)

Bis(allylpalladium chloride) (IVa) and bis(crotylpalladium chloride) (IVc) were treated analogously. The complex (Va) obtained from (IVa) was analogous to complex (IIIa). In this case also we could not obtain a crystalline product. (Found: C, 39.58; H, 5.61. $C_{16}H_{26}Cl_2Pd_2$ calcd.: C, 38.28; H, 5.22%.)

Mass spectra of the complexes (Va) and (Vb) showed molecular ion peaks corresponding to each molecular weight at 30 eV.

Synthesis of the complex (Va) and (Vb) by the other route

3-Chloro-3-methyl-1,6-heptadiene was prepared from the reaction of allylacetone and vinylmagnesium bromide and thionyl chloride. Complex (Va) was prepared from the halide according to the method of synthesis of π-allylic palladium complexes.

Complex (Vb) was prepared analogously from methallylacetone. These complexes were yellow viscous oils, and purified by reprecipitation from n-hexane at −40°.

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