Journal of Organometallic Chemistry, 140 (1977) 317—323

REACTION OF 2-t-BUTYL-1,3-BUTADIENE WITH π-ALLYLIC PALLADIUM COMPLEXES. A NOVEL CYCLIZATION OF ALLYLIC LIGANDS

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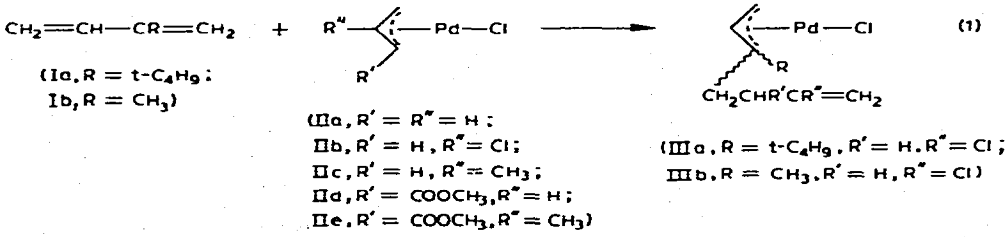
(Received June 6th, 1977)

Summary

The reaction of 2-t-butyl-1,3-butadiene with π-allylic palladium chlorides is described. The 2-chloroallyl complex gives a π-allylic complex with an open chain structure, in which the butenyl group in is the *anti*-position. Allyl-, 1-carbomethoxyallyl-, methallyl-, and 1-carbomethoxymethallyl-palladium chlorides give six-membered cyclic complexes. The product of the former two are π-allylic and those of the latter are σ-bonded complexes.

Introduction

The reaction of π-allylic metal complexes with conjugated dienes, which leads to insertion products and gives butenyl-substituted π-allylic complexes [1—3], is of considerable interest from the view-point of synthetic chemistry and because of its relationship to the mechanism of the stereospecific polymerization of 1,3-butadiene [4,5]. The attack of the dienes occurs at the most highly substituted π-allylic carbon.



(1)

(Ia, R = t-C_4H_9; Ib, R = CH_3)

(IIa, R' = R'' = H;
IIb, R' = H, R'' = Cl;
IIc, R' = H, R'' = CH_3;
IId, R' = $COOCH_3$, R'' = H;
IIe, R' = $COOCH_3$, R'' = CH_3)

(IIIa, R = t-C_4H_9, R' = H, R'' = Cl;
IIIb, R = CH_3, R' = H, R'' = Cl)

In general, the *syn—anti* isomerization (eq. 2) is very facile and the bulkiest substituent on the π-allylic terminal carbon is in the *syn*-position. Therefore, in

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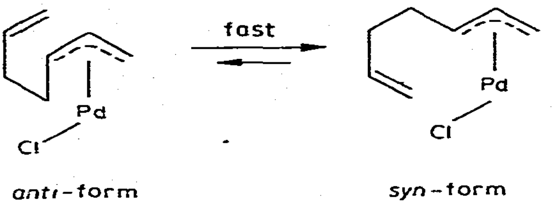
most cases the butenyl substituent is in the *syn*-position. The t-butyl group is very bulky and should occupy the *syn*-position of the π-allylic ligand. Thus the preparation of π-allylic complexes having the *anti*-butenyl substituent is expected to be possible when 2-t-butyl-1,3-butadiene (Ia) is allowed to react with various π-allylic complexes (II). In order to obtain systematic information on the influence of the *anti*-butenyl substituents in the π-allylic ligands, we investigated the insertion of Ia into the Pd—C bond of different π-allylic complexes.



(2)

Results and discussion

All the reactions were carried out in benzene under an atmosphere of argon. The reaction conditions are summarized in Table 1. Electron-withdrawing substituents on the π-allylic ligand facilitate the reaction considerably [3]. Therefore, the reaction of the 2-chloroallyl complex (IIb) was complete within 30 min at room temperature, while those of the other complexes required heating.

Reaction of IIb. The product IIIa was compared with IIIb, which had already been prepared by Medema et al. [2]. The NMR spectra of these complexes are shown in Fig. 1. Complex IIIb is a mixture of the *syn*- and *anti*-isomers, which is shown by the two methyl signals at τ 8.8 and 8.7 ppm, respectively. The absorption due to H_e of the *anti*-butenyl group of IIIb appears at τ 8.16 ppm. The appearance of H_e of III at τ 8.1—8.3 ppm shows that the butenyl group of IIIa is in the *anti*-position. The infrared spectrum shows absorptions at 1636 and 885.7 cm^{-1}, which are assigned to the C=C stretching and C—H out-of-plane

TABLE 1

REACTIONS OF II WITH 2-t-BUTYL-1,3-BUTADIENE

π-Allyl	Conditions	Products	Yield (%)	M.p. (decomp) (°C)	Analysis (found (calcd.) (%))	
					C	H
IIb	room temp., 0.5 h	IIIa	57.3	141—142	40.32 (40.33)	5.53 (5.54)
IIc	60°C, 4 days	IVa	53.5	130	46.98 (46.92)	7.10 (6.89)
IIe	60°C, 3 days	IVb	60.0	140	46.32 (46.05)	6.10 (6.35)
IIa	60°C, 4 days	Va	32.7	108—109	44.93 (45.07)	6.65 (6.53)
IId	60°C, 18 h	Vb	38.3	153—154	44.60 (44.47)	6.29 (6.03)

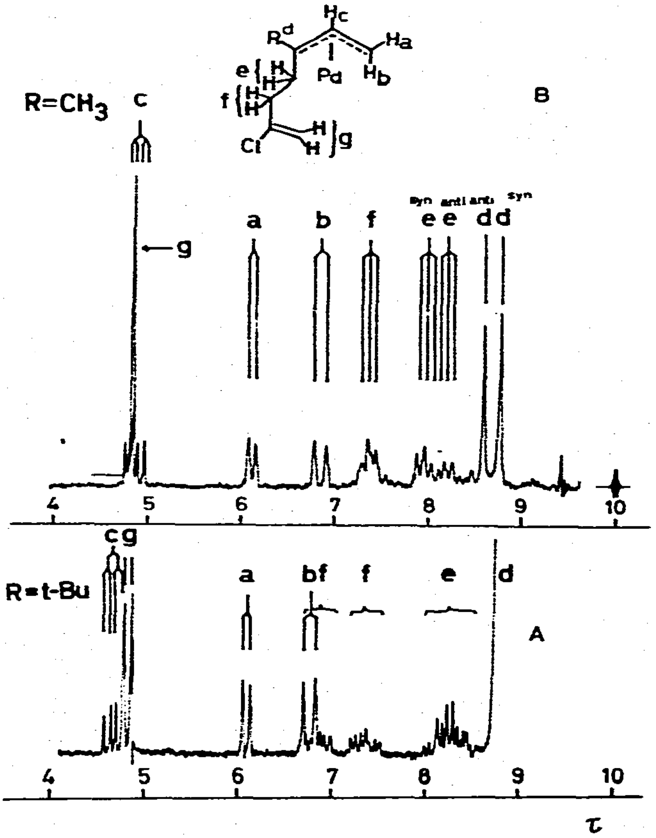


Fig. 1. ^{1}H NMR spectra (100 MHz) of IIIa (A) and IIIb (B) in $CDCl_3$.

vibrations of the terminal double bond, respectively. The far infrared spectrum has a strong absorption at 225 cm^{-1} due to the bridging ν(Pd—Cl). Osmometry showed that IIIa was dimeric.

Reactions of IIc and IIe. In contrast to the reaction decsribed above, IIc and IIe gave cyclic products, which were found to have one olefinic proton by NMR (Fig. 2). Their IR spectra show medium absorptions at 1515 and 1510 cm^{-1}, which are assigned to the coordinated double bonds of IVa and IVb, respectively. The reduction of IVa with $LiAlH_4$ (or $LiAlD_4$) gave 1-t-butyl-4,4-dimethyl-1-cyclohexene, which had an NMR spectrum identical with that reported [6]. Deuterium was incorporated into the methyl group with $LiAlD_4$.

Assignment of the NMR signals was based on decoupling experiment. It is notable that the resonances due to H_8 and H_9 of IVa are split into doublet of doublets. This fact is explained by the assumption that IVa is in the form of a half-chair. The splittings of H_8 and H_9 arise from long-range coupling with H_4 (J 1 Hz) and H_5 (J 2 Hz), respectively. This coupling occurs through the four σ bonds when the five atoms are in the all *trans* relationship [7]. Because of steric requirement, IVb presumably is deformed slightly and this deformation

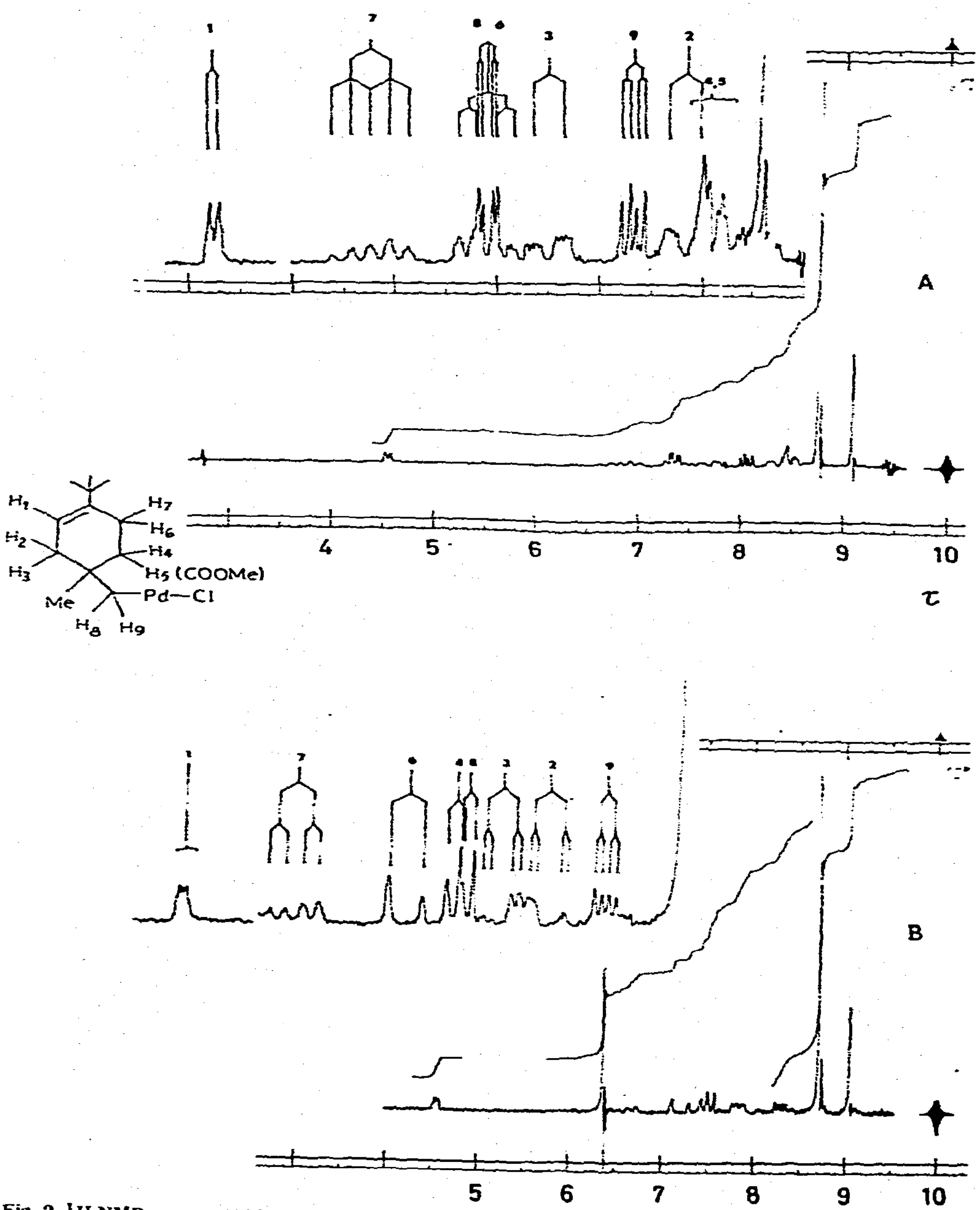
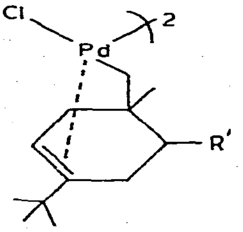
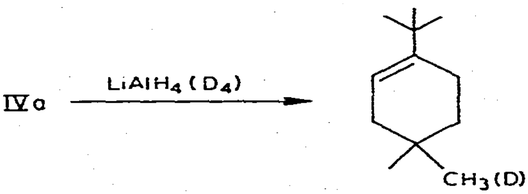


Fig. 2. ^1H NMR spectra (100 MHz) of IVa (A) and IVb (B).

results in the loss of the coupling. Therefore, only the long-range coupling between H_2 and H_9 is observed. This explanation can be well understood by using Dreiding models.

The ^{13}C NMR spectra of IVa and IVb, which are summarized in Table 2, are

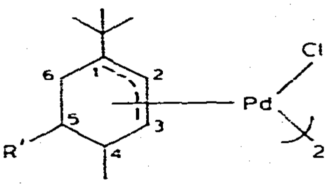




(IVa, R′ = H;
IVb, R′ = $COOCH_3$)

consistent with the proposed structure. There are no appreciable differences in the chemical shifts of the C(2) carbon and the t-butyl group in IVa and IVb.

Reactions of IIa and IId. Complex IId reacted more readily than did IIa, due to the electron-withdrawing substituent on the π-allylic ligand. The products of these reactions were the cyclic π-allylic complexes (V). The identification is based on the IR and NMR spectra. The NMR spectra show the typical resonances of π-allylic protons. The protons on the C(2) and C(3) carbon atoms of Va appear at τ 4.58 and 5.25 ppm (J_{23} 6.8 Hz). Those of Vb appear at τ 4.58 and 5.37 ppm (J_{23} 7 Hz).



(Va, R′ = H;
Vb, R′ = $COOCH_3$)

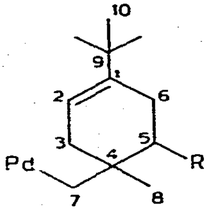
Reduction of Va with $LiAlH_4$ or $LiAlD_4$ further supports the structure of the six-membered cyclic ligand. The organic product of this reduction was 1-t-butyl-4-methyl-1-cyclohexene, which was identified by comparison with an authentic sample. The reduction product with $LiAlD_4$ had deuterium on the C(3) atom.

Reaction mechanism. This type of cyclization of π-allylic ligands on palladium, which leads to six-membered rings, has not been reported previously, although some cyclizations forming five-membered rings have been observed in the oligomerization of acetylenic compounds on palladium [8,9].

The three types of reactions described above are believed to proceed through the same intermediate as shown in Scheme 1. The insertion of 2-butyl-1,3-butadiene occurs at the more substituted carbon of the π-allylic ligand. Therefore, the direction of this insertion (electrolytic reaction on palladium [4]) seems to be determined electronically. The butenyl group, which is formed by the reaction with Ia, is in the *anti*-position and can interact with the palladium. This stereochemical requirement seems to be essential for the internal cycliza-

TABLE 2

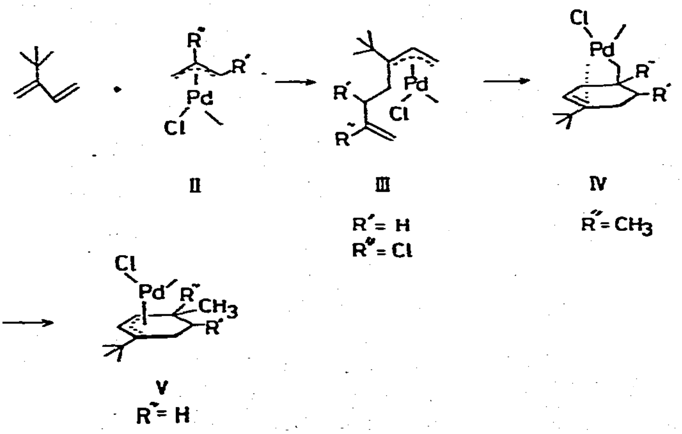
^{13}C NMR SPECTRA OF IV IN $CDCl_3$



(IVa, R′ = H ;
IVb, R′ = $COOCH_3$)

	Chemical shift (ppm from TMS)	
	IVa	IVb
C(1)	131.3	130.8
C(2)	95.6	95.3
C(3)	25.7	29.2
C(4)	37.9	38.7
C(5)	40.9	46.5
C(6)	33.9	36.7
C(7)	52.5	50.8
C(8)	25.3	23.8
C(9)	38.5	38.5
C(10)	29.2	29.2
C(11)		175.4
C(12)		51.2

tion. In fact, the insertion product of isoprene, which has the butenyl group in the *syn*-position, could not be cyclized. When R′ is chlorine, the open chain structure is stable; i.e., coordination of the double bond of C(6)—C(7) in III is not enough to cause insertion into the C(1)—Pd bond. Therefore, no cyclization occurred at 60°C in 4 days. Chlorine, because of its electron-withdrawing nature, decreases the reactivity of the complex toward insertion of the terminal double



SCHEME 1

bond. Complex III was confirmed to be a precursor of IV by observing the IR spectrum of the reaction mixture at an early stage in the reaction. The spectrum showed absorptions at 890 or 990 and 910 cm^{-1} due to the terminal methylene group. The intensities of these absorptions decreased with reaction time. The reaction product from III results from an internal insertion of the double bond (C(6)—C(7)) into the Pd—C(1) bond to form C(1)—C(6) and Pd—C(7) bonds. When R is hydrogen, a H shift from C(1) to C(7) occurs and the six-membered π-allylic ligand of V is formed.

Experimental

Materials. 2-Chloro-π-allyl- [10], 1-carbomethoxy-π-allyl- [11], and 1-carbomethoxy-π-methallyl-palladium [11] chlorides were prepared by the reported methods. 2-t-Butyl-1,3-butadiene was prepared by the reaction of t-butyllithium with pinacol, followed by dehydration, bromination and dehydrobromination in quinoline [12].

Reactions. All of the reactions of the π-allylic palladium complexes (1 mmol) with 2-t-butyl-1,3-butadiene (0.35 ml) were carried out in dried benzene (1 ml) under an atmosphere of argon. After evaporating the benzene, the resulting solid was recrystallized from benzene/petroleum ether. The reaction conditions and the yields are summarized in Table 1. The yields are based on the amount of the complexes obtained after recrystallization.

Acknowledgement

The authors are indebted to the Japan Electronic Optical Laboratory Co. Ltd. for the measurement of ^{13}C NMR spectra.

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