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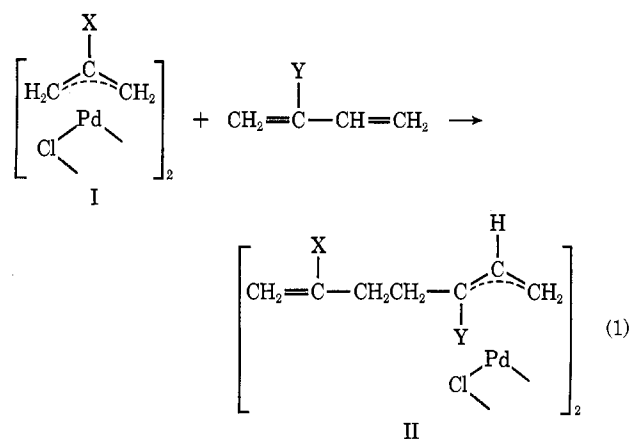
Cationic π -Allylic Palladium Complexes with the Additional Intramolecular Olefin Coordination

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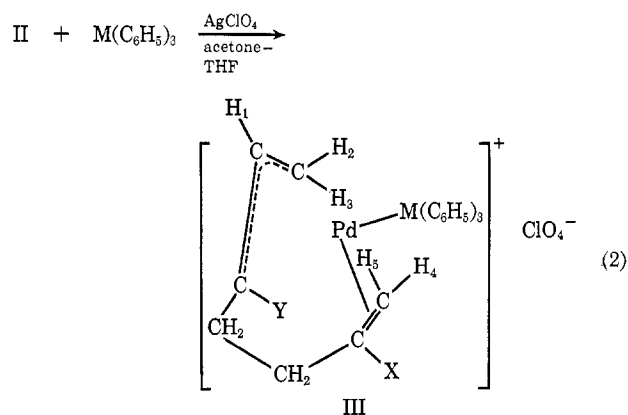
(1,2,3,6,7-Pentahaptoheptadienyl)triphenylphosphinepalladium(II) perchlorate and the homologs were prepared from butenyl- π -allylic palladium complexes. Molar conductivities and nmr and infrared spectra are given and discussed. An attempt to isolate these cationic complexes from the reaction of chloro(π -allylic)triphenylphosphinepalladium(II) with isoprene-AgClO₄ was in vain.

We previously reported the following insertion reactions of conjugated dienes with π -allylic palladium complexes^{1,2} (eq 1). Appearance of $\nu_{C=C}$ absorptions



around the normal region (1640–1645 cm⁻¹) in the insertion products II suggested the absence of the interaction between the terminal double bond and the palladium atom. The high selectivity of a ligand coupling reaction of acetate homologs of II under carbon monoxide could, however, be interpreted as an intramolecular coordination of the relevant olefinic moiety with the palladium atom.^{3,4} In metal-catalyzed reactions of conjugated dienes, a π -allylic complex having an additional intramolecular coordination of the double bond to the metal atom has sometimes been assumed as an intermediate.⁵ However, only a few such π -allylic complexes with the olefin coordination have been isolated.⁶

We have found that new π -allylic cationic complexes III with the additional intramolecular olefin coordination are successfully prepared from the diene-insertion products II according to eq 2, and we report their physical properties in this paper.



	X	Y	M	e	X	Y	M
a	H	H	P		CH ₃	CH ₃	P
b	H	CH ₃	P	f	CH ₃	CH ₃	As
c	H	CH ₃	As	g	C ₆ H ₅	CH ₃	P
d	CH ₃	H	P				

Experimental Section

Infrared spectra were run on a Nippon Bunko Model 403-G double beam grating spectrometer in KBr disks, calibrated by polystyrene. Nuclear magnetic resonance (nmr) spectra were measured in nitrobenzene with TMS as internal standard using a Japan Electron Optics C-60HL spectrometer. Molar conductivities were measured in nitrobenzene at 25°.

Materials.—Common halogen-bridged π -allylic palladium complexes (I) and the monomeric phosphine derivatives were prepared according to the literature methods.⁷⁻⁹ Nitrobenzene was used after purification by washing with aqueous sodium hydroxide, drying over phosphorus pentoxide, and subsequent distillation. All other solvents and conjugated dienes were purified by distillation before use. Triphenylphosphine and -arsine were used without further purification.

Preparation of (1,2,3,6,7-Pentahaptoheptadienyl)triphenylphosphinepalladium(II) Perchlorate (IIIa).—After a mixture of 0.478 g of [(π -C₃H₅)PdCl]₂ (Ia), 1.0 ml (-78°) of butadiene, and 5.0 ml of benzene was heated for 1 hr at 70° in a sealed tube, the solvent was evaporated off under reduced pressure. The oily residue was dissolved in acetone, and 0.686 g of triphenylphosphine was added. After stirring for 0.5 hr at room temperature, 10.8 ml of a tetrahydrofuran solution of silver perchlorate (1.00 g/in 20.0 ml of THF) was added and stirred for 10 min. The resultant yellow solution with suspended silver chloride was filtered and evaporated to give a yellow oily residue, which was dissolved in 15 ml of tetrahydrofuran. A colorless crystalline precipitate appeared after a few minutes; it was filtered off and dried *in vacuo* at room temperature, yield 1.00 g (70%).

Preparation of (1,2,3,6,7-Pentahapto-6-methylheptadienyl)triphenylphosphinepalladium(II) Perchlorate (IIIId).—This preparation is the same as that above except that [(π -C₄H₇)PdCl]₂ (Ib) was used instead of Ia.

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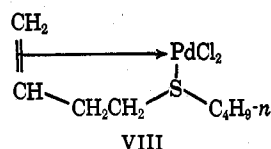
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TABLE I
 CATIONIC π -ALLYLIC PALLADIUM COMPLEXES III

Complex	Yield, %	Mp, ^a °C	Analysis (calcd)			Ir band of coord olefin, cm ⁻¹ ^b	Molar conductivity, ^c ohm ⁻¹ cm ² mol ⁻¹ (concn 10 ⁻³ M)
			% C	% H	% Cl		
IIIa	77	170-175	53.35 (53.31)	4.68 (4.65)		1520 (w)	38.3 (6.73)
IIIb	71	179-183	54.01 (54.09)	4.92 (4.89)		1510 (w)	
IIIc	75	170-173	50.19 (50.27)	4.50 (4.54)	5.60 (5.71)	1520 (w)	37.8 (7.00)
IIId	67	162-164	54.09 (54.09)	4.87 (4.87)		1519 (w)	37.9 (6.78)
IIIe	52	180-182	54.84 (54.92)	5.11 (5.17)	5.96 (5.99)	1560 (bw)	37.9 (7.15)
IIIf	65	176-179	50.98 (51.05)	4.76 (4.76)	5.55 (5.58)	1545 (sh)	38.5 (7.83)
IIIg	55	178-179	58.73 (58.82)	5.06 (4.94)		1537 (w)	

^a With decomposition. ^b Measured in KBr disk; in the complex VIII a band appearing at 1529 cm⁻¹ is also attributed to the coordinated



olefin [D. C. Goodall, *J. Chem. Soc.*, 887 (1968)]. ^c Measured in nitrobenzene at 25°. The conductivity of $[(\pi\text{-C}_4\text{H}_7)\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]\text{ClO}_4$ (Vb) is 38.2 ohm⁻¹ cm² mol⁻¹ at 6.95×10^{-3} M.

Preparation of (1,2,3,6,7-Pentahapto-3-methylheptadienyl)-triphenylphosphinepalladium(II) Perchlorate (IIIb).—From di- μ -chloro-bis[1-(3-butenyl)-1-methyl- π -allyl]dipalladium(II) (IIb), which was prepared by the reaction of 0.522 g of Ia with isoprene (2.0 ml) in a sealed tube at 70° for 2 hr, the title compound was obtained analogously using 0.736 g of triphenylphosphine. Similar isolation and drying procedures were carried out.

Preparation of Other Cationic Complexes (IIIc, IIIe, and IIIf).—These preparations are the same as above except that Ib or triphenylarsine was used instead of Ia or triphenylphosphine, respectively.

The Reaction of Chloro(π -allyl)triphenylphosphinepalladium(II) (IVa) with Isoprene in the Presence of Silver Perchlorate.—A mixture of 0.703 g of complex IVa and isoprene (isoprene/IVa = 6) in 20 ml of acetone was treated with silver perchlorate-THF solution (6.6 ml), and the mixture was stirred for 1 hr, filtered, and evaporated to give a yellow oily complex. It was dissolved in 15 ml of THF and kept in a refrigerator overnight. A white precipitate was filtered and dried *in vacuo*. From nmr and infrared spectra, this compound was identified as bis(triphenylphosphine)- π -allylpalladium(II) perchlorate (Va), yield 0.457 g (80.5% based on triphenylphosphine). Methallyl derivative IVb behaved similarly giving bis(triphenylphosphine)- π -methallylpalladium(II) perchlorate (Vb) in 72% yield.

The Reaction of Chloro(π -crotyl)triphenylphosphinepalladium(II) (IVc) with Silver Perchlorate in the Presence of Isoprene.—A similar isolation was carried out to give a white complex. Elemental analyses (found: C, 52.35; H, 5.01) are not consistent with the calculated values for III- and V-type cationic complexes and suggest a mixture of the two. In the infrared spectrum, a band at 1520 cm⁻¹, assignable to a coordinated terminal vinyl group, was observed unlike π -allyl (IVa) and π -methallyl complexes (IVb).

These cationic complexes are fairly stable and can be handled without the necessary precautions needed for explosive perchlorate salts.

Results and Discussion

When butenyl- π -allylic palladium complex IIc (X = Y = CH₃), which was obtained by the insertion reaction of isoprene with di- μ -chloro-di(π -methallyl)dipalladium(II) (Ib), was treated with triphenylphosphine and subsequently with a tetrahydrofuran solution of silver perchlorate, the cationic (1,2,3,6,7-pentahapto-3,6-dimethylheptadienyl)triphenylphosphinepalladium(II) perchlorate¹⁰ (IIIe) was obtained in 52% yield as pale yellow crystals. Other substituted derivatives III were similarly prepared from the corresponding butenyl- π -allylic complexes II. Triphenylarsine analogs of III were also isolated in

(10) According to the nomenclature proposed by F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6320 (1968).

moderate yields. These are white to pale yellow compounds, soluble in nitrobenzene and insoluble in benzene and ether. Analytical data, selected infrared frequencies, and molar conductivities of III are listed in Table I. The molar conductivities ($6\text{--}7 \times 10^{-3}$ M) in nitrobenzene are in the range of 37–39 ohm⁻¹ cm² mol⁻¹, indicative of uni-univalent electrolytes. The observed conductivities of III are in agreement with those of the typical cationic complex, bis(triphenylphosphine)- π -methallylpalladium(II) perchlorate (Vb), and support the proposed structure of the complexes III, in which the olefinic group is coordinated intramolecularly.

The infrared spectra of III have no band due to free olefin, but the weak bands at near 1500 cm⁻¹ are assignable to the coordinated olefin (Table I). Treatment of IIIa with triphenylphosphine gave a white complex, the infrared spectra of which showed a band at 1640 cm⁻¹ due to the free terminal vinyl group, as expected, supporting the structure of III.

The nmr spectra of complexes III were measured in nitrobenzene, and the spectral data obtained are listed in Table II. The spectra show no temperature dependence except a slight variation of the chemical shift, indicating the maintenance of the rigid structure even at higher temperature. The nmr spectrum of IIIe at 80° is illustrated in Figure 1. The coordinated olefinic protons, H₄ and H₅, were observed at τ 5.85 (as a doublet due to the coupling with phosphorus atom, $J_P = 6.0$ Hz) and at τ 5.24 (as a singlet), respectively, both with further fine splitting by geminal and/or allylic coupling. These assignments were supported by the spectrum of the arsine analog IIIf (Figure 2), in which both H₄ and H₅ were found as singlets at τ 5.64 and 5.23, respectively (measurement temperature, 60°).

The above assignments of H₄ and H₅ were reasonably extended to other derivatives (IIIb and IIIc) (Figure 3). The peaks of H₄ and H₅ in complex IIIc appeared as two overlapping doublets due to the coupling with the internal vinyl proton (X = H). Furthermore, in complex IIIb, the higher field doublet (H₄, $J_{4X} = 8$ Hz) was found to split further by the additional coupling with the phosphorus atom ($J_{4P} = 6.0$ Hz) as shown in Figure 3.

Although these assignments support the structure of

TABLE II
 NMR SPECTRA OF THE CATIONIC COMPLEXES III IN NITROBENZENE^a

Complex	Temp measured, °C	τ_X	τ_Y	τ_2^b	τ_4^c	τ_5^c	J_{4P}	J_{YP}	J_{12}	J_{4X}	J_{5X}
IIIa	60			6.19 (d)	5.55 (dd)	5.12 (d)	6.5		7.0	9	17
IIIb	60		8.18 (d)		5.60 (dd)	5.25 (d)	6.0	4.5		9	16
IIIc	60		8.17 (s)	5.94 (d)	5.43 (d)	5.09 (d)			7.5	8	15
III d	80	8.06 (s)		6.13 (d)	5.79 (d)	5.07 (s)	6.0		7.0		
III e	25	8.06 (s)	8.08 (d)		5.95 (d)	5.22 (s)	6.5	5			
	60	8.04 (s)	8.10 (d)	6.20 (d)	5.88 (d)	5.23 (s)	6.0	5.0	7.5		
	80	8.03 (s)	8.12 (d)	6.18 (d)	5.85 (d)	5.24 (s)	6.0	5.0	7.5		
III f	25	7.98 (s)	8.14 (s)	5.87 (d)	5.72 (s)	5.23 (s)			7.5		
	60	7.97 (s)	8.15 (s)	5.83 (d)	5.64 (s)	5.23 (s)			7.5		
	80	7.97 (s)	8.16 (s)	5.82 (d)	5.62 (s)	5.23 (s)			7.5		
III g	25		8.08 (d)	5.93 (d)	5.33 (d)	4.88 (s)	6.0	5.0	7.5		
	80		8.10 (d)	5.92 (d)	5.29 (d)	4.85 (s)	6.0	4.5	7.5		

^a Notation: s, singlet; d, doublet; dd, double doublet; τ (ppm); J (Hz). ^b Further splitting due to the coupling with geminal proton H_3 ($J_{23} = 2$ Hz). ^c Further splitting due to the coupling with geminal proton ($J_{45} = 2$ Hz) and allylic protons.

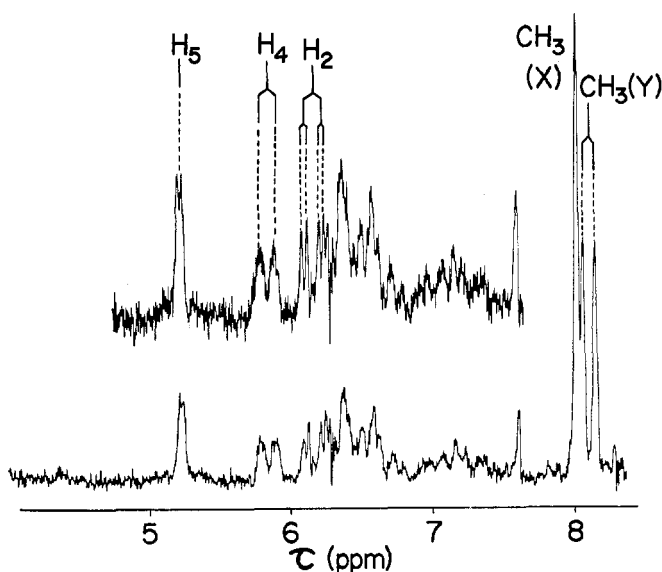


Figure 1.—Nmr spectrum of complex IIIe at 80° in nitrobenzene.

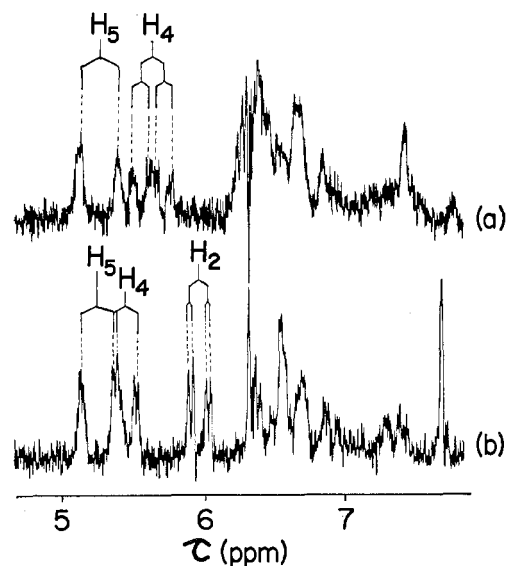


Figure 3.—Nmr spectra of complexes IIIb (a) and IIIc (b) at 60° in nitrobenzene in the range 5–7.5 ppm.

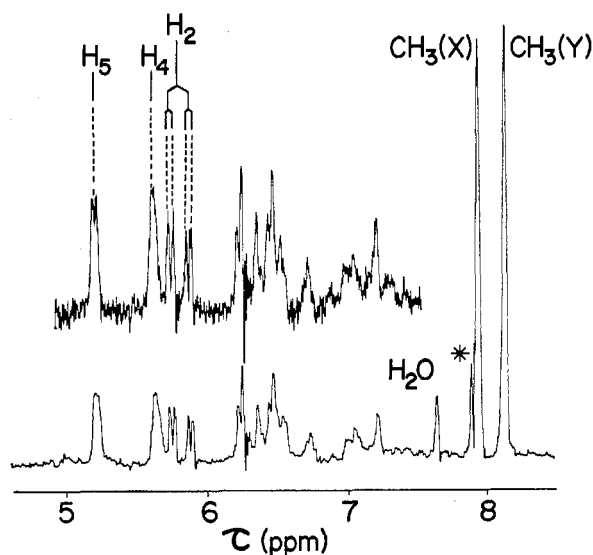


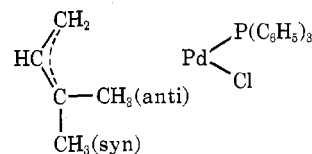
Figure 2.—Nmr spectrum of complex IIIf at 60° in nitrobenzene. An asterisk denotes impurities.

III, it seems surprising that the coupling between H_4 and phosphorus atom located mutually in the *cis* position was observed.¹¹ This is presumably due to a

(11) In $[\text{PdCl}(\pi\text{-}1,3\text{-dimethylallyl})\text{P}(\text{C}_6\text{H}_5)_3]$, a similar *cis* coupling between the methyl group and phosphorus is observed; see ref 7.

direct P–H interaction through space. The absence of the coupling between H_5 and phosphorus atom would support this assumption. It was also found that the coupling between H_4 and phosphorus atom in IIIb disappeared in the presence of excess triphenylphosphine, indicating cleavage of the palladium–olefin bond. These findings are in good accord with the olefin-coordinated structure of III.

In the nmr spectra of complexes IIIb and IIIe, the methyl group situated in the 3 position ($Y = \text{CH}_3$) was observed as a doublet due to the coupling with the phosphorus atom ($J_{PY} = 4.5\text{--}5.0$ Hz). The magnitude of the coupling constant is nearly equal to that observed for the long-range, *trans* spin-spin coupling constant ($J_{P\text{-CH}_3} = 6$ Hz) between the *anti*-methyl and phosphorus atom in the 1,1-dimethylallyltriphenylphosphinepalladium complex which has the structure⁷

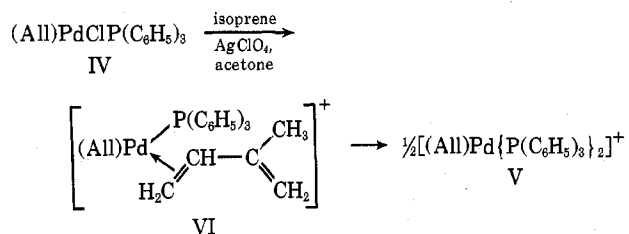


Therefore, it would be reasonable to assume that the methyl group is situated in the 3-*anti* position and *trans*

to phosphine. These features are consistent with the proposed structure of the cationic complexes III.

No assignment of protons other than those listed in Table II, such as H_1 , H_3 , and methylene protons of the side chain, has been made owing to the overlapping of each other or with solvent side bands. But, the 1-syn proton H_2 was clearly observed as a double doublet probably due to the coupling with meso proton H_1 and the geminal coupling with antiproton H_3 ($J_{12} = 7.0-7.5$ Hz, $J_{23} = 2$ Hz). The observed cis coupling ($J_{12} = 7$ Hz) is in the range of that for common π -allylic palladium complexes.¹²

Direct preparations of cationic species IIIb and IIIc by the reaction of monomeric chloro(π -allylic)triphenylphosphinepalladium(II) (IV) with isoprene in the presence of silver perchlorate gave only (π -allylic)-bis(triphenylphosphine)palladium(II) perchlorate (V), and no sign of insertion reaction of isoprene was observed. However, the π -crotyl derivative IVc gave

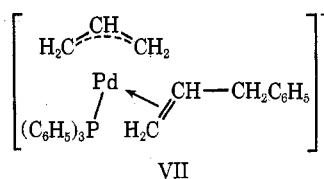


a, All = π -allyl; b, All = π -methyllyl; c, All = π -crotyl

(12) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).

partly the diene-inserted cationic complex, which had an infrared band at 1520 cm^{-1} due to a coordinated terminal vinyl group, but unfortunately the pure III-type complex could not be isolated. We cannot give a clear explanation for the different behavior between π -crotyl (IVc) and π -allyl (IVa) or π -methyllyl analogs (IVb). However, it seems possible that the intermediate VI (an intermolecular olefin-metal complex), which was formed from IV and a conjugated diene, is so unstable that it has a tendency to disproportionate to the cationic complex V. This finding also supports the view that a cationic olefin complex III obtained from II should have a chelated structure, namely, intramolecular coordination of the double bond to the palladium atom.

An attempt to isolate cationic complex VII by the reaction of complex IVa with allylbenzene in the presence of silver perchlorate or fluoroborate was also in vain, and the recovered olefin was found to be converted completely to propenylbenzene. It is interesting,



however, that the terminal olefin structure in complexes III was retained, although $[(\pi\text{-allylic)PdP(C}_6\text{H}_5)_3]^+$ catalyzes olefin isomerization.

CONTRIBUTION FROM THE FACOLTÀ DI CHIMICA INDUSTRIALE, UNIVERSITY OF VENICE, VENICE, ITALY, AND LABORATORIO DEI COMPOSTI DEL CARBONIO CONTENENTI ETREATOMI DEL CNR, OZZANO E., BOLOGNA, ITALY

Some Reactions of Palladium(II)-Thiol Complexes with Organic Halides

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New palladium(II) complexes of 1,2-ethanedithiol and 1,3-propanedithiol are reported. These complexes, which are probably polymers with S bridges, react under relatively mild conditions with certain organic halides. The products of some of these reactions have been identified. Corresponding reactions of the known polymer $[\text{Pd}(\text{SPH})_2]_n$ have been carried out for comparison, and reasons for the varied reactivity of metal-thiol complexes are discussed.

Introduction

Considerable interest has been shown recently in the properties and reactions of metal complexes of ligands containing sulfur donors.²⁻⁹ Several complexes of palladium with aliphatic and aromatic monothiols (RSH) were prepared by Mann and Purdie,¹⁰ who considered them to be S-bridged high polymers of general

formula $[\text{Pd}(\text{SR})_2]_n$. A similar formulation was adopted by Jensen¹¹ for the corresponding nickel compounds. Hayter and Humiec¹² concluded that the palladium complexes of higher aliphatic thiols (e.g., for $\text{R} = n\text{-Pr}$) were probably S-bridged hexamers. Other examples of hexameric units in nickel- and palladium-thiol complexes have since been reported.^{13,14} The complexes of Pt and Pd with $\text{C}_6\text{F}_5\text{SH}$ also appear to be polymeric.¹⁵

A mercaptide ion often retains its tendency to form S bridges even in the presence of other groups capable of coordination, but in these cases the extent of polym-

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