π-Allylic Palladium Complexes from Methyl Sorbate

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The reaction of sodium chloropalladite with conjugated diolefin in alcohols has been shown to result in the formation of alkoxy-π-allylic palladium complexes.[1,2] Thus, butadiene in methanol gaves the chloro-bridged 4-methoxy-π-butenyl complex, $[Pd_2Cl_2(C_4H_6OCH_3)_2]$,[1] while the reaction of cycloocta-1, 3-diene with sodium chloropalladite in methanol gives rise to di-μ-chlorodi-(4-methoxy-cyclooct-2-enyl)-dipalladium. When this is heated, *in situ,* the methanol is eliminated and an unsaturated complex, di-μ-chlorodi-(cycloocta-2, 4-dienyl)-dipalladium, is formed.[2]

This paper will describe the application of this reaction to methyl 2, 4-hexadienoate (methyl sorbate).

Results and Discussion

The treatment of methyl sorbate with sodium chloropalladite in methanol at room temperature for 20 hr gave two products, $[C_{16}H_{26}O_6Cl_2Pd_2]$ (mp 122—125°C) as the major product and $[C_{14}H_{18}O_4Cl_2Pd_2]$ (mp 116—119°C); the I and IIA structures respectively were assigned to these productes on the basis of their infrared and NMR spectra. The dimeric nature of these compounds was supported by the molecular-weight determinations, and by their reacting with pyridine to give readily-soluble monomeric derivatives (*cf.* Fig. 1).

The infrared spectrum of the major product (I) showed the presence of methoxy group at 2820 and 1097 cm^{-1} and an uncoordinated ester carbonyl group at 1728 cm^{-1}. The allylic structure of this complex was also supported by an examination of its NMR spectrum, which showed a doublet at 8.63 τ (3H, $J=6$ cps) for methyl protons on C_5, a singlet at 6.63 τ (3 H) for methoxy protons on C_4, a multiplet at 6.57 τ (1 H) for the proton on C_4, a doublet at 6.47 τ (1 H, $J_{1,2}=10$ cps) for the allylic proton on C_1, a singlet at 6.31 τ (3 H) for methyl protons of the ester group, a double doublet at 6.00 τ (1 H, $J_{2,3}=10$ cps and $J_{3,4}=2$ cps) for the allylic proton on C_3, and a triplet at 3.90 τ (1 H, $J=10$ cps) for the allylic proton on C_2. These spectral data suggest that

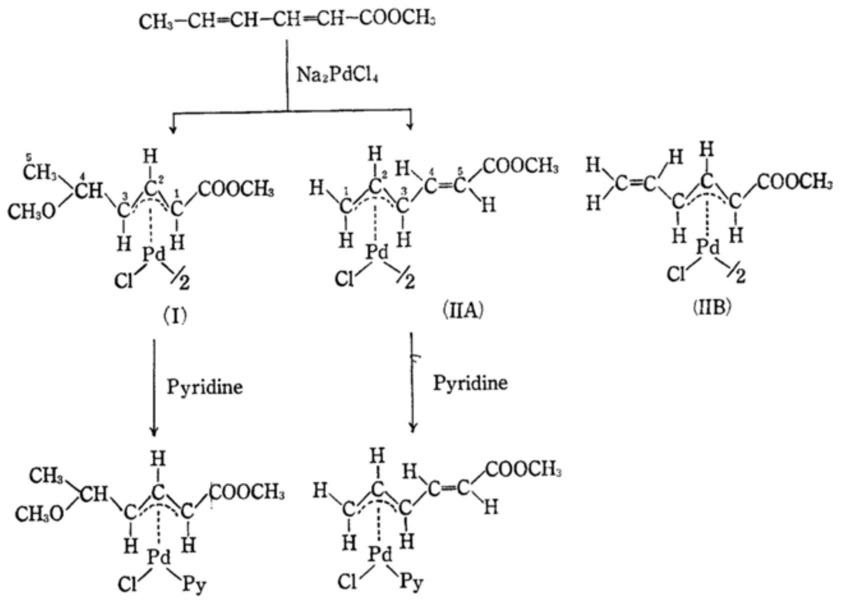

Fig. 1

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[1] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.,* **1963**, 4806.

[2] a) S. D. Robinson and B. L. Shaw, *ibid.,* **1964**, 5002. b) M. R. Churchill, *Chem. Commun.,* **1965**, 625; *Inorg. Chem.,* **5**, 1608 (1966).

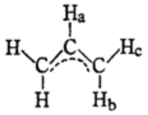

Fig. 2

the major product (I) is di-μ-chlorodi-[1-carbomethoxy-3-(1′-methoxyethyl) -π-allyl]-dipalladium. In addition, the proton on the center carbon atom (C_2) of the π-allyl system couples with the two trans protons on C_1 and C_3; their coupling constants were found to be both 10 cps. In the simple π-allyl complex (*cf.* Fig. 2), the trans coupling constant ($J_{a,b}$) between the proton on the center carbon and the proton on the terminal carbon is 11 cps and the cis coupling constant ($J_{a,c}$) is 7 cps.³⁾ Thus, it may be concluded that the orientation of the methoxyethyl and carbomethoxy groups in I is "*syn.*"

On the other hand, the minor product, [$C_{14}H_{18}O_4Cl_2Pd_2$], was less stable than the major product (I); it gradually decomposed in a solution to give a palladium mirror. In the infrared spectrum of this complex, there were no bands in the regions between 2810—2840 and 1080—1110 cm^{-1}, suggesting the absence of a methoxy group.²ᵃ⁾ Furthermore, the spectrum did not show the characteristic absorption bands due to a vinyl group. The ultraviolet absorption spectrum in ethanol did, however, show a strong absorption band at 211 mμ, suggesting the presence of a double bond conjugated with the ester group. These spectral data favor the conjugated structure (IIA) rather than the vinylic structure (IIB), formed simply by the loss of methanol from the structure (I). This structure was also supported by an examination of its NMR spectrum, which showed a doublet at 6.98 τ (1 H, $J_{1,2}$=1.05 cps) for the allylic terminal "*anti*" proton on C_1, a double doublet at 6.47 τ (1 H, $J_{3,4}$=13 cps and $J_{2,3}$=10 cps) for the allylic proton on C_3, a singlet at 6.33 τ (3 H) for methyl protons of the ester group, a doublet at 5.83 τ (1 H, $J_{1,2}$=6.5 cps) for the allylic "*syn*" proton on C_1, a multiplet at 4.04 τ (1 H) for the allylic center proton on C_2, a doublet at 3.74 τ (1 H $J_{4,5}$=18 cps) for the olefinic proton on C_5, and a double doublet at 2.60 τ (1 H, $J_{4,5}$=18 cps and $J_{3,4}$=13 cps) for the olefinic proton on C_4. The complex (IIA) seems to be derived from methyl sorbate by the activation of allylic hydrogen at the terminal methyl group, followed by eliminating hydrogen chloride,⁴⁾ rather than from the complex (I) by the loss of methanol, followed by a 1, 3 shift of the palladium atom.

Experimental

All the melting points are uncorrected. The infrared spectra were measured in KBr disks with a Hitachi EPI-S infrared spectrometer, while the ultraviolet absorption spectra were measured with a Hitachi recording spectrophotometer, model EPS-3T. The NMR spectra were recorded by a Varian Model A-60 instrument in deuterochloroform, using tetramethylsilane as an internal standard.

Reaction of Methyl Sorbate with Sodium Chloropalladite. Methyl sorbate (2.52 g) was added to a suspension of sodium chloropalladite trihydrate (7.0 g) in methanol (50 m*l*). After 20 hr, the metallic palladium thus deposited was removed by filtration, and then the brown filtrate was evaporated to dryness under reduced pressure. Chromatography in chloroform on an alumina column gave two complexes. The first complex eluted was di-μ-chlorodi-[1-carbomethoxy-3-(1′-methoxyethyl)-π-allyl]-dipalladium (1.10 g, 16.5 %). Recrystallization from cyclohexane gave yellow needles, mp 122—125°C (decomp.). $\lambda_{max}^{\mathrm{EtOH}}$: 213 m$\mu$ (log ε 2.66). IR spectrum (KBr): 2820 (OCH_3), 1728 (ester), and 1098 cm^{-1} (OCH_3).

Found: C, 32.14; H, 4.77%; mol wt, 595 (in benzene). Calcd for $C_{16}H_{26}O_6Pd_2Cl_2$: C, 32.08; H, 4.67%; mol wt, 598.

The second complex eluted was di-μ-chlorodi-[1-(2′-carbomethoxy-ethenyl)-π-allyl]-dipalladium (0.09 g, 1.7%), yellow needles. Mp 116—119°C (decomp.). $\lambda_{max}^{\mathrm{EtOH}}$ 211 mμ (log ε 4.47). IR spectrum: 1720 cm^{-1} (ester).

Found: C, 31.22; H, 3.41%; mol wt, 529 (in benzene). Calcd for $C_{14}H_{18}O_4Pd_2Cl_2$: C, 31.43; H, 3.36%; mol wt, 534.

The Preparation of Chloro-(π-allyl)-pyridine-palladium Complexes. A solution of the chloro-bridged palladium complex (0.05 g) in dichloromethane (5 m*l*) was treated with a solution of pyridine (5% excess) in ether. After 10 min, the solvent was removed under reduced pressure, after which chromatography on alumina using chloroform afforded the expected product. The complexes below were prepared in this manner.

Chloro-[1-carbomethoxy-3 - (1′-methoxyethyl)-π-allyl]-pyridine-palladium. Yellow crystal. Mp 128—132°C (decomp.).

Found: C, 41.47; H, 4.68; N, 3.81%. Calcd for $C_{13}H_{18}O_3NPdCl$: C, 41.25; H, 4.75; N, 3.70%.

Chloro - [1-(2′ - carbomethoxy - ethenyl) - π - allyl]-pyridine-palladium. Yellow crystal. Decomp. p. 78—84°C (without melting).

Found: C, 41.85; H, 4.22; N, 4.18%. Calcd for $C_{12}H_{14}O_2NPdCl$: C, 41.59; H, 4.07; N, 4.04%.

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3) M. L. Green and P. L. Nagy, "Advances in Organometallic Chemistry," Vol. II, ed by F. G. A. Stone and R. West, Academic Press, New York (1964), p. 331.

4) Recently, the preparations of π-allyl palladium complexes from α, β-conjugated carbonyl compounds have been reported.⁵⁾

5) a) G. W. Parshall and G. Wilkinson, *Chem. & Ind.*, **1962**, 261; *Inorg. Chem.*, **1**, 896 (1962). b) J. Tsuji, S. Imamura and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4491 (1964); J. Tsuji and S. Imamura, This Bulletin, **40**, 197 (1967). c) A. Kasahara, K. Tanaka and K. Asamiya, *ibid.*, **40**, 351 (1967).