

Stereochemistry of Chloropalladation of a Vinylcyclopropane. X-Ray Crystal Structure of $\text{Pd}_2\text{Cl}_2(\text{C}_{10}\text{H}_{16}\text{Cl})_2$

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An X-ray crystal structure of $\text{Pd}_2\text{Cl}_2(\text{C}_{10}\text{H}_{16}\text{Cl})_2$ (**3**), obtained by chloropalladation of (+)-car-2-ene (**1**), shows that overall *trans*-addition of Pd-Cl across the cyclopropane moiety has occurred.

Palladium chloride complexes are known to react with cyclopropanes to give chloropalladation adducts,¹⁻⁴ e.g., vinylcyclopropanes give 5-chloro-1,2,3- η^3 -alkenylpalladium complexes.^{1,2} There are two important questions concerning the mechanism of these chloropalladation reactions: (i) how is the ring activated by the metal, and (ii) what is the overall stereochemistry of the chloropalladation?

It has been reported that chloropalladation of a homoallylic cyclopropane (bicyclo[6.1.0.]non-4-ene) occurs with *cis* stereochemistry,^{3a} but that chloropalladation of an allylic cyclopropane (bicyclo[5.1.0.]oct-3-ene) takes place with *trans* stereochemistry.^{3b} Recently *cis*-chloropalladation of methyl-ene-cyclopropanes was established by X-ray crystallography.⁴

In a previous communication² we reported studies of the reaction of the vinylcyclopropane (**1**) [(+)-car-2-ene] with $(\text{MeCN})_2\text{PdCl}_2$ (equation 1). From the configuration of (**2**) we found that cyclopropane ring-opening by the metal takes place with inversion of configuration at carbon. We now report an X-ray crystal structure of the chloropalladation adduct (**3**), which shows that *trans*-chloropalladation of the cyclopropane has occurred.

The product (**3**) was purified by column chromatography and crystallized from hexane-chloroform.

Crystal data: $\text{Pd}_2\text{Cl}_4\text{C}_{20}\text{H}_{32}$, $M = 627.08$, orthorhombic, $a = 10.556(6)$, $b = 16.984(10)$, $c = 13.229(4)$ Å, $U = 2371.6$ Å³, $D_c = 1.76$ g cm⁻³, $Z = 4$, space group $P2_12_12_1$, $F(000) = 1248$. Single crystal X-ray data between the limits $0 < 2\theta < 50^\circ$ were collected with a Syntex P21 diffractometer, using the

ω -scan technique with graphite monochromated Mo- K_α radiation; 2423 unique reflections [$I > 1.96\sigma(I)$] were recorded. The structure was solved by Patterson and Fourier techniques and refined using full-matrix least-square methods with anisotropic thermal parameters for all atoms, except for hydrogen atoms. The final R -value was 0.045.†

The structure of (**3**), given in Figure 1, shows that the allyl groups adopt a *cis* arrangement to one another. Although a *trans* conformation is usually observed for dimeric π -allylpalladium complexes,⁶ a *cis* conformation has been reported for η^3 -cycloheptenylpalladium bromide^{7a} and η^3 -(2,3,4)-

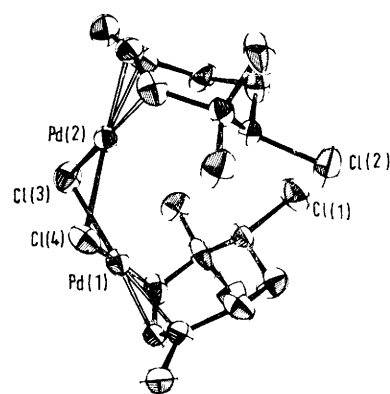
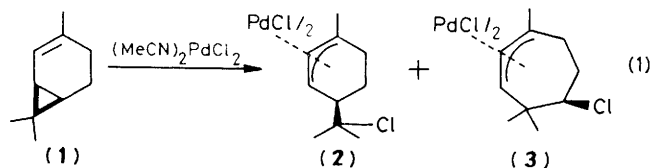
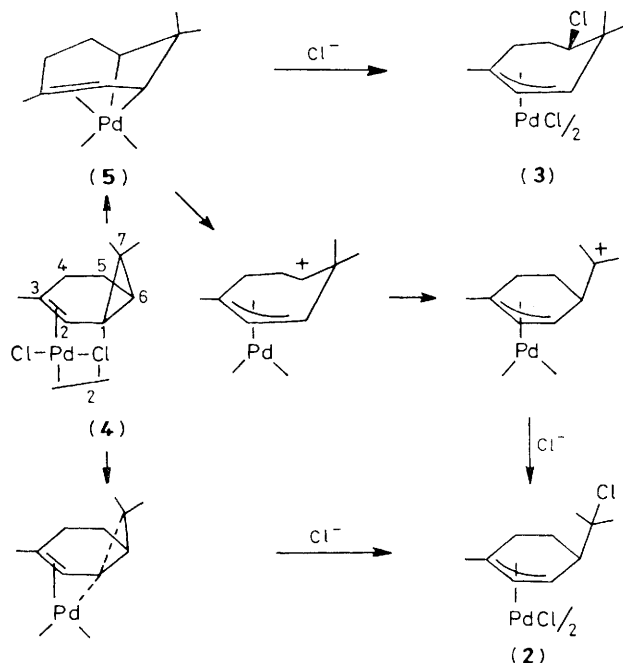


Figure 1. ORTEP drawing of $\text{Pd}_2\text{Cl}_2(\text{C}_{10}\text{H}_{16}\text{Cl})_2$ (**3**).



† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

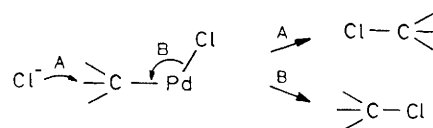


pentenylpalladium chloride.^{7b} Figure 1 also shows that the palladium atom and the chloro-group on the ring are *trans* to one another. Because of the optically pure starting material the absolute configuration of the two rings will be the same, provided the chloropalladation is stereospecific. This results in a C_2 axis as can be seen in Figure 1.

The *trans* relationship between the palladium atom and the chloro-group on the ring shows that chloropalladation of the cyclopropane ring has occurred with overall *trans* stereochemistry. We were not able to establish the absolute configuration of (3), with the present data, but most likely the *trans*-chloropalladation is a result of retention of configuration at the site of metal attack and inversion at the site of chloride attack. Thus, a metallacyclobutane (5) is a likely intermediate in the formation of (3) (Scheme 1). The ring-opening of a cyclopropane with platinum(II) to give a metallacyclobutane has been shown to take place with retention at both carbon atoms.⁹

Our previous results on the chloropalladation of (1) together with the present results could be explained by the mechanism shown in Scheme 1. Thus, formation of a π -olefin complex (4), which could be observed, is most likely to take place from the *exo*-face of (1). Now, cleavage of the 1-6 bond, which gives the seven-membered ring, must take place with retention at carbon, whereas cleavage of the 1-7 bond, which gives (2), occurs with inversion at carbon. Another possible pathway for the formation of (2) would be *via* a metallacyclobutane followed by a rearrangement.

The mechanism of chloropalladation of cyclopropane systems needs some comment. There are many examples reported where a chloride ion attacks a carbon atom bound to palladium with inversion of configuration (path A, Scheme 2).^{‡3b,8-11} On the other hand, examples of the alternative pathway (path B), migration of a co-ordinated chloride from



palladium to carbon, are rare.^{§11,12} As shown by our present and previous work,² ring-opening of cyclopropanes by palladium(II) may take place with either retention or inversion at carbon. It is therefore quite possible and likely that *cis*-chloropalladation of a cyclopropane is a result of inversion at the two carbon atoms attacked by the metal and the chloride, rather than retention at both carbon atoms. Accordingly, overall *cis*-oxymercuration of substituted cyclopropanes has been shown to be a result of inversion at both carbon atoms.¹³

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‡ The carbon atom may be σ -alkyl or part of a π -system.

§ *cis*-Chloropalladation of *t*-butylacetylene was inferred from the stereochemistry of an oligomerization product,^{12a} and *cis*-chloropalladation of cyclohexa-1,3-diene was suggested on the basis of n.m.r. spectra, but no conclusive evidence for such an attack was given.^{12b}