

Stereochemistry of Palladium(II)-induced Ring-opening of the Cyclopropane in a Vinylcyclopropane. Chloropalladation of Car-2-ene

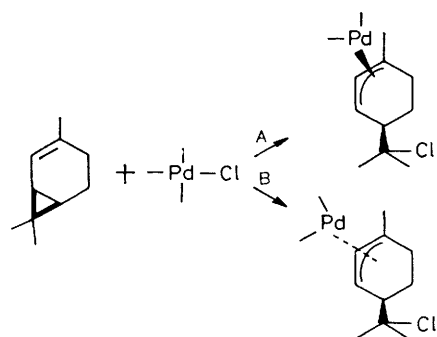
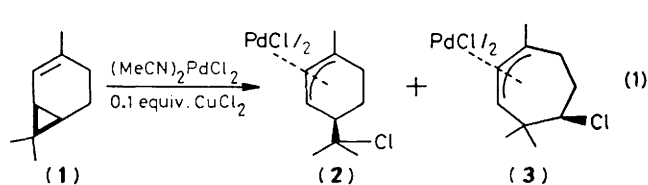
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Reaction of (+)-car-2-ene (**1**) with $(\text{MeCN})_2\text{PdCl}_2$ produces a mixture of isomeric π -allylpalladium complexes (**2**) and (**3**), where (**2**) was shown to arise from inversion of configuration at the carbon attacked by the metal.

Although several studies recently have dealt with the interaction of transition metals with three-membered rings,¹⁻⁷ little is known still about the mechanism of the ring-cleavage reaction. Reactions of cyclopropanes with transition metals

have been suggested to involve oxidative addition of a carbon-carbon bond to the metal to give a metallacyclobutane, which in fact has been isolated in some cases.^{2a,2b,5,6} Vinylcyclopropanes are known to react with palladium



Scheme 1

chloride to give π -allyl complexes *via* a chloropalladation,⁷ but it is not certain whether these reactions involve metallacyclobutane intermediates. In this communication we report our studies on the chloropalladation of the optically active alkenylcyclopropane (+)-car-2-ene (1). We have found that (i) the selectivity for formation of six- and seven-membered ring complexes (2) and (3) can be controlled and (ii) the ring-opened product (2) arises from complete inversion of configuration at the site of palladium attack.

Reaction of (+)-car-2-ene (1) with equimolar amounts of (MeCN)₂PdCl₂ in chloroform at room temperature produced a mixture (crude yield 90%) of the isomeric π -allylpalladium complexes (2) $\{[\alpha]_D^{20} = +130.3$ (tetrahydrofuran) $\}$ and (3) $\{[\alpha]_D^{20} = +164.7$ (tetrahydrofuran) $\}$ in a ratio of 3:1† (equation 1). The complexes were separated by column chromatography (SiO₂, CCl₄:CH₂Cl₂ = 3:2) to give crystalline compounds‡ that were characterized by their ¹H and ¹³C n.m.r. spectra (200 MHz, CDCl₃, Me₄Si) (2), δ (¹H) 5.36 (d, $J_{2,3}$ 6.5 Hz, 2-H), 4.94 (br. d, 3-H), 2.3–2.0 (m, 5-H_e, 6-H), 1.92 (m, $J_{6,6e}$ 17 Hz, $J_{4,6e}$ 2 Hz, $J_{5e,6e} < 0.5$ Hz, 6-H_e), 1.74 (m, $J_{4,5e}$ 6 Hz, 4-H), 1.67 (s, 3 H), 1.54 (s, 3 H), 1.50 (s, 3 H), and 0.92 (m, $J_{5,5e}$ ca. 12 Hz, $J_{5,6}$ ca. 12 Hz, $J_{4,5}$ ca. 12 Hz, $J_{5,6e}$ 6 Hz, 5-H); δ (¹³C) 101.7, 95.8, 73.5, 71.7, 51.6, 34.6, 30.9, 30.3, 24.7, and 21.1 p.p.m.; (3) δ (¹H) 4.65 (d, J 9.0 Hz, 1 H), 4.48 (br. d, J 9 Hz, 1 H, CH-Cl), 4.43 (d, 1 H), 2.34 (m, 1 H), 2.12 (m, 1 H), 2.0–1.8 (m, 2 H), 1.51 (s, 3 H), 1.46 (s, 3 H), and 1.18 (s, 3 H); δ (¹³C) 100.2, 99.7, 85.5, 69.3, 44.1, 37.5, 31.5, 30.3, 28.3, and 24.7 p.p.m. A remarkable change in the ratio of (2) to (3) occurred when chloroform was replaced by benzene as the solvent. Thus in benzene formation of (3) predominates in the reaction of (1) with (MeCN)₂PdCl₂ [(2):(3) = 1:6].

An important question concerning the mechanism of the formation of (2) is whether the palladium(II)-induced ring-opening takes place with retention (path A) or inversion (path B) of configuration at the carbon attacked by the metal (Scheme 1). The ¹H n.m.r. spectrum of (2) is consistent with a *trans* configuration of the palladium and the chloroisopropyl moieties with the conformation shown in Figure 1. Thus, the coupling constants $J_{4,5} =$ ca. $J_{5,6} =$ ca. 12 Hz

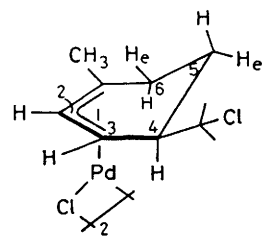
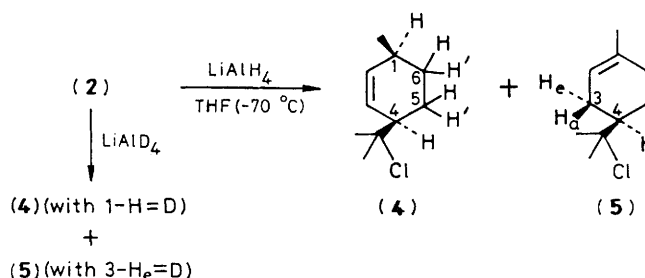


Figure 1



require that the protons 4-H, 5-H and 6-H be axial. Furthermore, the high field shift of 5-H (0.92 p.p.m.) is also in agreement with the structure shown in Figure 1.

The n.m.r. data do not completely exclude the possibility that palladium is on the opposite side of the π -allyl face with retained conformation of the hydrocarbon ligand. Complex (2) was therefore reduced with LiAlH₄ to give a 1:4 mixture of compounds (4) and (5).§ The coupling constants of (4), $J_{1,6}$ 2.7, $J_{1,6'}$ 5.4, $J_{4,5}$ 4.5, and $J_{4,5'}$ 9.3 Hz are consistent only with the methyl and chloroisopropyl groups being *cis* to one another in a conformation where the former group is axial and the latter is equatorial. The n.m.r. spectrum of (5)⁹ shows a broad doublet at 2.16 p.p.m., which we were able to assign as 3-H_e from the n.m.r. data ($J_{3e,3a}$ ca. 16 Hz, $J_{3e,4} < 5$ Hz). Reduction of (2) with LiAlD₄ gave [²H₁](4) and [²H₁](5). The n.m.r. spectrum of [²H₁](5) shows the absence of the hydrogen 3-H_e. Since it is known¹⁰ that LiAlH₄ cleaves π -allylpalladium bonds with retention of configuration at carbon, the results of the above mentioned reductions require the palladium and the chloroisopropyl group in (2) to be *trans* to one another.

The fact that (2) has the *trans* configuration shows that the ring-opening (1) \rightarrow (2) by palladium has occurred with inversion of configuration at the carbon that becomes attached to the metal. This is incompatible with an oxidative addition of a carbon-carbon bond to the metal, which would require retention of configuration. A likely pathway is that palladium becomes co-ordinated to the double bond *trans* to the cyclopropane ring. Complex (3) may now be formed *via* an oxidative addition and complex (2) *via* an electrophilic cleavage with inversion at the site of attack by the metal. Such a mechanism would account for the solvent effect observed. Electrophilic ring-openings of tetrasubstituted cyclopropanes by mercury(II) are known¹¹ to take place with inversion at the site of mercury attack. In general, electrophilic ring-openings of cyclopropanes have been observed to occur with either retention or inversion depending on the substitution pattern and the electrophile.¹²

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† Determined by ¹H n.m.r. spectroscopy on the crude product mixture.

‡ M.p.'s (2), 148–150 °C decomp.; (3), 144–146 °C decomp.

§ In order to avoid hydrogenation of the double bond in (4) and (5), the reaction was worked up by bubbling ethene into the reaction mixture.

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