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

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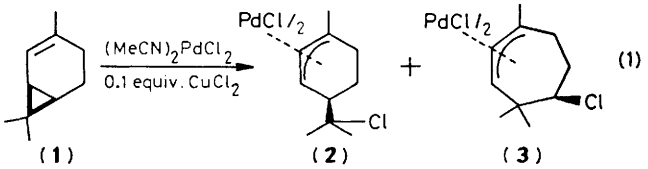
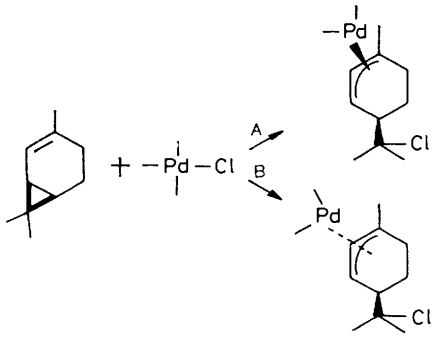
Reaction of (+)-car-2-ene (**1**) with $(MeCN)_2PdCl_2$ produces a mixture of isomeric π-allylpalladium complexes (**2**) and (**3**), where (**2**) was shown to arise from inversion of configuration at the carbon attacked by the metal.

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

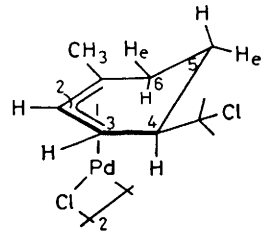
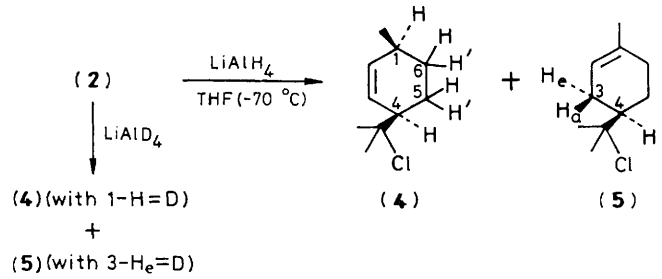


Figure 1



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 $(MeCN)_2PdCl_2$ 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)}[8] in a ratio of 3:1† (equation 1). The complexes were separated by column chromatography (SiO_2, CCl_4:CH_2Cl_2 = 3:2) to give crystalline compounds‡ that were characterized by their ^1H and ^{13}C n.m.r. spectra (200 MHz, $CDCl_3$, Me_4Si) (**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 (^{13}C) 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, C*H*–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 (^{13}C) 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 $(MeCN)_2PdCl_2$ [(**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 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 $LiAlH_4$ 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 $LiAlD_4$ gave [$^2H_1$](**4**) and [$^2H_1$](**5**). The n.m.r. spectrum of [$^2H_1$](**5**) shows the absence of the hydrogen 3-H_e. Since it is known[10] that $LiAlH_4$ 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**) → (**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 known[11] 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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