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PRELIMINARY NOTE

Complexes of vinylcyclopropanes with palladium chloride

Butadiene-1,3 reacts with dichlorobis(benzonitrile) palladium(II) in benzene to give a chloro-bridged π-4-chlorobutenyl palladium complex[1]. This complex is formed by rearrangement of an initially formed butadiene, $PdCl_2$ π-complex which is unstable above $-20°$[2].

Cyclopropane has some olefinic-character and consequently vinylcyclopropanes are analogous, to a degree, to conjugated dienes[3]. For example, polymerization of vinylcyclopropanes yields products with 1,5-enchainment analogous to the 1,4-enchainment commonly found in polymers of conjugated dienes[4,5]. Vinylcyclopropane, therefore, might be expected to form a π-complex through the olefinic bond with palladium chloride which would be more stable than the butadiene π-complex yet would still thermally rearrange at higher temperatures to a chloro-substituted π-allyl complex by opening of the cyclopropane ring.

Some alternative modes of interaction of vinylcyclopropane with palladium chloride also appear to be possible. Thus, vinylcyclopropane and its derivatives smoothly rearrange by a unimolecular path to cyclopentenes at elevated temperatures[6,7]. It is possible, therefore, that attempts to synthesize a vinylcyclopropane–palladium chloride complex would yield the cyclopentene π complex. A Cope-type rearrangement of this kind has recently been observed by Jonassen and co-workers who have shown that the reaction of *cis,trans*-1,5-cyclodecadiene with dichlorobis(benzonitrile) palladium(II) yields *cis*-1,2-divinylcyclohexane palladium chloride[8].

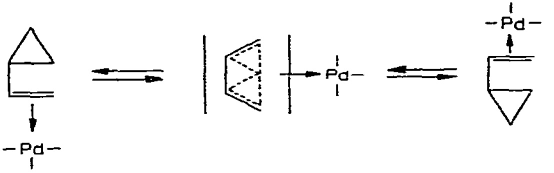
A third, and seemingly rather unlikely, complex which might be formed would be one in which the cyclopropyl group is bonded to palladium. Chatt and co-workers have shown that cyclopropane itself forms a complex with platinum chloride in which the opened ring is believed to be σ-bonded to the metal through the 1 and 3 carbon atoms[9]. A structure with the cyclopropyl group bonded to palladium in this way and with the vinyl group as a non-bonded substituent cannot, therefore, be excluded.

Vinylcyclopropane–$PdCl_2$ complex was prepared by treating 1 g of di-μ-chlorodichlorobis(ethylene)dipalladium suspended in 15 ml of methylene chloride with 1 ml of vinylcyclopropane at 25°. All the complex dissolved. After 30 minutes a precipitate (A) formed which was filtered. Evaporation of the filtrate yielded more complex (B). (*Analysis.* (A): Pd, 43.32; C, 24.45; Cl, 28.72; H, 3.22%. (B): Pd, 43.12; C, 24.51; Cl, 28.80; H, 3.22%. Calcd. for $C_5H_8PdCl_2$: Pd, 43.34; C, 24.46; Cl, 28.92; H, 3.29%.) Both complexes decomposed at approximately 110° and appeared, from subsequent analytical work, to be identical. The yield was quantitative.

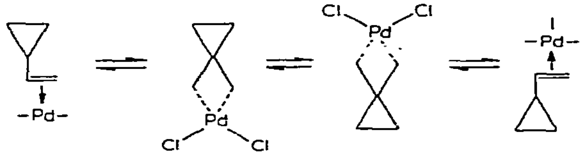
Unlike most olefin π-complexes with $PdCl_2$, the vinylcyclopropane complex is indefinitely stable in water at room temperature. The infrared spectrum shows absorptions at 1515 and 1532 cm^{-1} which can be assigned to the complexed π-bond of the olefin and bands at 1022, 1060 and 3080 cm^{-1} characteristic of the cyclopropyl group. The NMR spectrum in $CDCl_3$, however, shows neither cyclopropyl nor olefinic signals but only one major peak, a singlet at 8.49 τ (area 5.2). A small multiplet at

5.5 τ (area 1.0) is the only other clearly observable signal. However, when dimethyl sulfoxide was added to the complex the spectrum obtained was identical with that of free vinylcyclopropane. Hydrogenation of the complex gave a product which had a retention time in the vapor phase chromatograph corresponding to a branched hexane.

These results indicate that vinylcyclopropane forms a π-complex with $PdCl_2$ through the olefinic bond but that some hydrogen transfer process occurs rapidly enough in the complex so that only a time-averaged spectrum is observed in the NMR. Two possibilities which suggest themselves are (1) a rapid interchange of the vinyl and cyclopropyl systems:

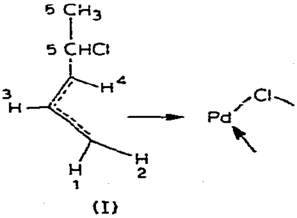


and (2) a similar interchange proceeding by hydrogen migration and the formation of σ-bonded cyclopropane complexes analogous to those described by Chatt for Pt:

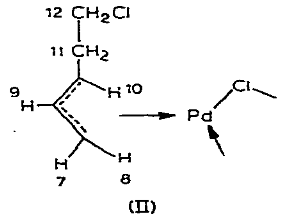


The time-averaged spectrum in either case should show all protons as equivalent. The multiplet at 5.5 τ (which is present consistently in a number of samples we have prepared) suggests, however, that one proton may be exchanging more slowly than the others. As yet, we have not been able to find a solvent in which the complex is sufficiently soluble at low temperatures to allow us to study the NMR spectrum under these conditions.

The vinylcyclopropane complex is insoluble in benzene at room temperature. When the temperature is raised to 40°, however, the complex dissolves rapidly to form a wine-red solution. Addition of heptane to this solution precipitates a complex whose infrared spectrum no longer has absorptions characteristic of either the π-bond or the cyclopropyl group. The NMR spectrum in benzene shows a doublet centered at 9.12 (area 2.7), a triplet at 8.5 (area 1.0), a complex multiplet centered at 6.65, which partially obscures two doublets centered at 6.48 and 6.75 (total area 4.0) and a multiplet centered at 5.52 τ (area 1.1). Both the infrared and NMR spectra of this new complex are identical with the corresponding spectra of the complex derived



(I)



(II)

from the reaction of 1,3-pentadiene with di-μ-chloro-dichlorobis(ethylene)dipalladium. On treatment with dimethyl sulfoxide, both complexes yield NMR spectra identical to that of an authentic sample of 1,3-pentadiene (*cis,trans*-mixture).

The rearrangement product of the vinylcyclopropane complex is believed to be a mixture of complex (I) and (II). Shaw has prepared the 1,3-pentadiene complex[1] but did not characterize it. NMR assignments are shown in Table 1 together with observed integral ratios and the calculated integral ratios based on the assumption that complexes (I) and (II) are present in a mole ratio of 5 : 3.

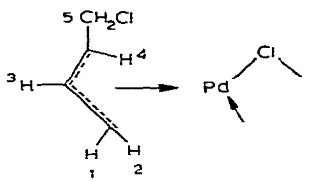
TABLE 1

NMR ASSIGNMENTS FOR REARRANGED VINYLCYCLOPROPANE–$PdCl_2$ COMPLEX[a]

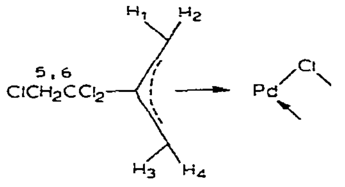
NMR signal (τ)	9.12	8.5	6.65	5.52
Assignment (Proton number)	6	11	1, 2, 4, 5, 7, 8, 10, 12	3, 9
Area ratio (observed)	2.7	1.0	4.0	1.1
Area ratio (calculated)	2.5	1.0	4.0	1.3

[a] Solvent, hexadeuterobenzene. Temp. 36°.

Complexes 1 and 2 do not appear to be separable by conventional techniques. It should be noted that differences in NMR assignments given here and those given by Shaw[1] for 4-chlorobutenylpalladium chloride are due to the fact that the latter data were obtained in $CDCl_3$ solvent. When this compound (III) is dissolved in benzene, the NMR spectrum shows a multiplet centered at 5.50 τ for proton 3 while part of the π-allylic system and protons 5 give a complex absorption centered at 6.67 τ.



(III)



(IV)

The ease with which 1,3-pentadiene is displaced by dimethyl sulfoxide from these complexes is surprising since π-allylic palladium complexes normally undergo structural changes but do not decompose with this reagent[10]. The 4-chlorobutenyl palladium chloride was also found to liberate the diene when treated with dimethyl sulfoxide. The mechanism of this decomposition probably involves the transitory formation of a species in which the allylic group is σ-bonded to palladium[10].

When 1,1-dichloro-2-vinylcyclopropane is allowed to react with di-μ-chloro-dichlorobis(ethylene)dipalladium a tan complex is formed. (*Analysis.* Found: Pd, 44.36; C, 18.42; Cl, 33.12; H, 1.98%. Calcd. for $C_5H_6Cl_4Pd$: Pd, 45.30; C, 19.15; Cl, 33.94; H, 1.61%.) This complex appears to react with atmospheric moisture since the total analysis for the above elements falls slowly from 100% when it is stored without special precautions to exclude moisture. The infrared spectrum of the complex has an olefinic carbon-carbon stretching band at 1610 cm^{-1}. The NMR spectrum in $CDCl_3$ consists of a multiplet from 4.2–5.0 and a multiplet from 7.5–8.6 τ. This spectrum does not differ significantly from that of 1,1-dichloro-2-vinylcyclopropane itself. Furthermore, addition of dimethylsulfoxide to the solution of the complex produces no change in the spectrum. This complex, therefore, appears to be a π-complex of the olefin with $PdCl_2$. It shows no tendency to rearrange under the same conditions as the unsubstituted vinylcyclopropane complex. However, when the $CDCl_3$ solution of the complex is heated at 55°C for 30 minutes a profound change occurs in the NMR spectrum. Three narrow groups of signals are observed at 5.77, 5.80 and 5.90, at 4.59 and at 3.70, 3.63 and 3.60 τ. The integral ratios for these three sets of signals is 1 : 1 : 1. We were not able to isolate satisfactorily this rearranged complex. A reasonable, though not compelling, structure based on the NMR data is IV where H_1 H_3 give the signals centered at τ 3.65, H_2 H_4 those centered at τ 5.84 and H_5 H_6 the signal at τ 4.59. A 1 : 1 complex of 1-cyclopropyl-1-phenylethylene and $PdCl_2$ was also prepared. Both NMR and infrared spectra of this complex showed that the cyclopropyl group was no longer present. However, the spectra appear to arise from a mixture of several structures and are extremely difficult to interpret.

Experimental

Vinylcyclopropane was prepared by dehydration of 1-cyclopropyl ethanol over basic alumina as described by Slabey[11]. The preparations of 1,1-dichloro-2-vinylcyclopropane and 1-cyclopropyl-1-phenylethylene have been described elsewhere[12,13]. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee. NMR spectra were obtained on a Varian A60A instrument and infrared spectra on a Beckman IR 12.

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