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Preliminary communication

SYNTHESES OF NEW π-ALLYLPALLADIUM CHLORIDE COMPLEXES CONTAINING A CYCLOPROPANE RING

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Summary

The reaction of thujopsene, and of 2- and 3-carenes with palladium(II) chloride in the presence of potassium acetate in acetic acid afforded the corresponding new π-allylpalladium complexes in good yields without opening of the cyclopropane ring.

The reactions of vinyl- and homoallyl-cyclopropanes with $PdCl_2(MeCN)_2$ or $PdCl_2(PhCN)_2$ are known to proceed with cleavage of the cyclopropane ring, and to give chloropalladium adducts [1—4]. More recently, Bäckvall and coworkers have reported [5,6] on the stereochemistry of palladium(II)-induced ring-opening of the cyclopropane in a vinylcyclopropane. Albelo and Rettig had earlier reported [7,8] that the reaction of bicyclo[6.1.0]non-4-ene with $PdCl_2(PhCN)_2$ in benzene gave the olefinic π-complex, which was so unstable that it rearranged into the chloropalladium complex. However, there has been no report on the synthesis of π-allylpalladium chloride complexes from vinyl- and allylcyclopropane derivatives without opening of the cyclopropane ring. In relation to these studies, it is of interest to prepare a π-allylpalladium complex containing a cyclopropane ring.

We have investigated the stereoselectivity of nucleophilic substitutions on steroidal π-allylpalladium complexes [9]. As a first step in this research project, we reported earlier that reactions of cholestene derivatives with palladium(II) chloride in the presence of potassium acetate in acetic acid afforded the corresponding steroidal palladium complexes [10], and that oxidation of these complexes with chromium(VI) oxide in *N,N*-dimethylformamide readily gave the corresponding α,β-unsaturated ketones in good yields [11]. In these reports, we demonstrated that palladium(II) chloride, containing potassium acetate in acetic acid, is a useful reagent for the syntheses of steroidal π-allylpalladium complexes, and that the reagent shows higher regioselectivity than $PdCl_2(PhCN)_2$.

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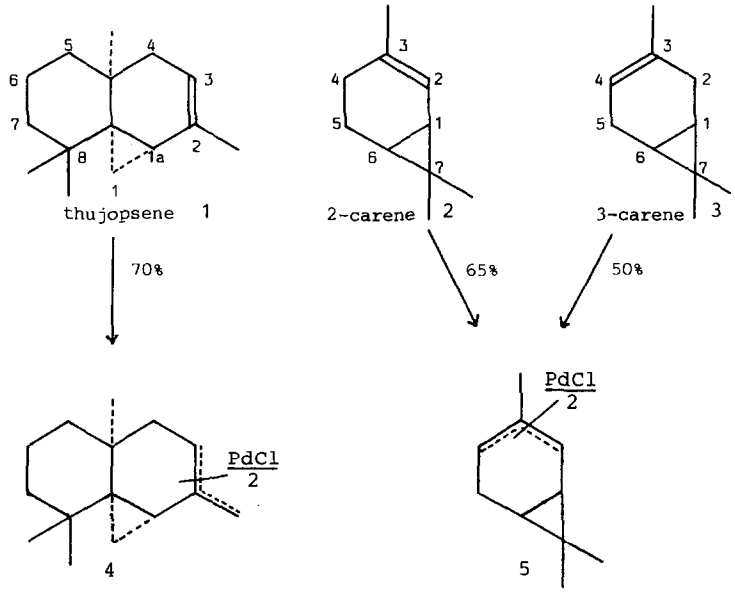
In the present communication, we report the synthesis of π-allylpalladium complexes from compounds containing a vinyl- or allyl-cyclopropane ring, such as thujopsene, and 2- and 3-carenes, which can easily be obtained.

The reaction of thujopsene (1) (3.78×10^{-2} mol) with palladium(II) chloride (1.0 mol. equiv.) and potassium acetate (1.0 mol. equiv.) in acetic acid at 55—60°C for 4 h yielded an exocyclic π-allylpalladium chloride complex (4) (70%) (greenish plates), m.p. 148—151°C, NMR ($CDCl_3$): δ 0.80 (d, 1H, J 5.0 Hz, 1-H), 1.00 (d, 1H, J 5.0 Hz, 1-H), 0.75—0.95 (m, 1H, 1a-H), 2.95 (s, 1H, 2-$\overset{\cdots}{=}CH_2$), 3.87 (s, 1H, 2-$\overset{\cdots}{=}CH_2$), and 3.98 (t, 1H, J 3.0 Hz, 3-H). (Found: C, 52.73; H, 6.90. $C_{30}H_{46}Pd_2Cl_2$ calcd.: C, 52.19; H, 6.72%.) This compound (4) showed absorptions at 3048 and 3025 cm^{-1} assigned to the cyclopropane ring in its IR spectrum. The NMR spectrum showed AB-type signals, doublets at δ 0.80 and 1.00 ppm, assignable to the C(1) protons of the cyclopropane ring.



In the case of 2-carene (2), an endocyclic π-allylpalladium chloride complex (5) was obtained. Yield 65%, orange yellowish plates, m.p. 128—131°C, NMR ($CDCl_3$): δ 1.20 (s, 3H, 7-Me), 1.23 (s, 3H, 7-Me), 1.48 (s, 3H, 3-Me), 1.55—1.90 (m, 2H, 1- and 6-H), 4.80—5.30 (m, 1H, 4-H), and 5.70 (broad s, 1H, 2-H). (Found: C, 43.40; H, 5.59. $C_{20}H_{30}Pd_2Cl_2$ calcd.: C, 43.35; H, 5.46%.) Complex 5 showed IR absorption at 3025 cm^{-1} and the NMR spectrum showed a multiplet at δ 1.55—1.90 ppm due to C(1)-H and C(6)-H. Irradiation at the frequency of C(2)-H (δ 5.70 ppm) gave a doublet (J 6.0 Hz) due to C(1)-H. Similarly, 3-carene (3) gave the same complex (5, 50%, m.p. 128—130°C).

On the basis of the IR and NMR spectral data for 4 and 5, the structures of these complexes were determined to be π-allylpalladium chloride complexes possessing a cyclopropane ring.

This is the first time that synthesis of π-allylpalladium chloride complexes without ring-opening has been successfully accomplished. This success is no

doubt attributable to the special properties of the palladium(II) chloride—potassium acetate system.

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