CHEMISTRY LETTERS, pp. 277-280, 1989. 

# Solvent Effects in $^1$H-NMR Spectrum of Steroidal π-Allyl Palladium Chloride Complexes

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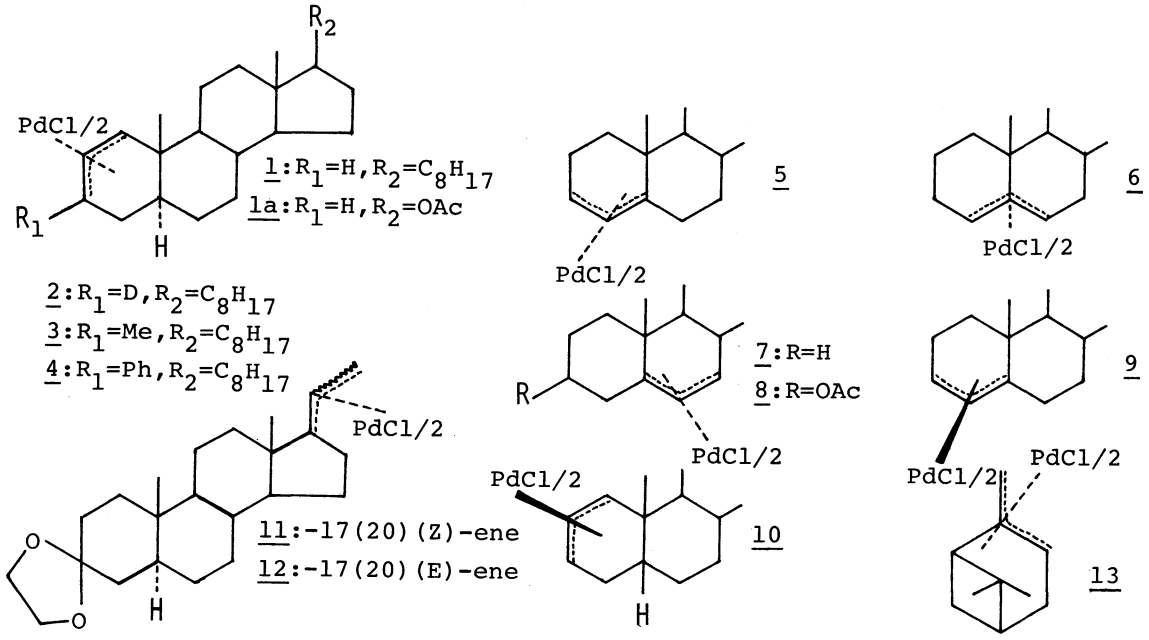
The $^1$H-NMR spectra of the steroidal α-π-allyl palladium complexes in which palladium coordinated at the α-face showed higher field shift of C-19 methyl signal in $C_6D_6$ than in the case of $CDCl_3$. The configuration of palladium in π-allyl palladium complexes was confirmed by this phenomenon.

There has been a considerable amount of work done on the syntheses of π-allyl palladium complexes. On the other hand, with respect to steroids there have been no reports of syntheses except for the case of π-allyl palladium complexes of $\Delta^4$-3-oxo steroids,[1] 5α-cholest-3-ene,[2] cholest-4-ene,[2] cholest-5-ene,[2] 5α-cholest-6-ene,[2] ergosterol,[3] and 3-methoxy-cis-19-norpregna-1,3,5-(10),17(20)-tetraene;[4] and of 3-oxopregn-17(20)(Z)- and 3-oxopregn-17(20)(E)-ene ethylene ketal.[5] We have investigated the stereospecificity of nucleophilic substitutions on steroidal π-allyl palladium complexes.[6] 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,[7] 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.[8] In a previous paper,[9] we reported syntheses of new π-allyl palladium chloride

Table 1. Solvent Effects on Angular Methyl Resonance in Some Steroidal π-Allyl Palladium Complexes ( δ ppm)

| Materials | $^1$H-NMR | $CDCl_3$ | $C_6D_6$ | $\Delta = \delta\ CDCl_3 - \delta\ C_6D_6$ | $^{13}$C-NMR | $CDCl_3$ | $C_6D_6$ |
|---|---|---|---|---|---|---|---|
| 1 | C-19 | 0.79 | 0.48 | 0.31 | | 16.54 | 16.42 |
| | C-18 | 0.63 | 0.61 | 0.02 | | 12.13 | 12.26 |
| 1a | C-19 | 0.77 | 0.41 | 0.36 | | 16.57 | 16.30 |
| | C-18 | 0.81 | 0.73 | 0.08 | | 12.17 | 12.36 |
| 2 | C-19 | 0.79 | 0.48 | 0.31 | | 16.49 | 16.40 |
| | C-18 | 0.63 | 0.61 | 0.02 | | 12.09 | 12.36 |
| 3 | C-19 | 0.75 | 0.49 | 0.26 | | 16.51 | 16.34 |
| | C-18 | 0.63 | 0.63 | 0 | | 12.12 | 12.38 |
| 4 | C-19 | 0.82 | 0.51 | 0.31 | | 16.48 | 16.21 |
| | C-18 | 0.66 | 0.63 | 0.03 | | 12.19 | 12.34 |
| 5 | C-19 | 1.01 | 0.71 | 0.30 | | 22.82 | 23.04 |
| | C-18 | 0.66 | 0.68 | -0.02 | | 11.97 | 12.26 |
| 6 | C-19 | 1.13 | 0.64 | 0.49 | | 20.10 | 20.01 |
| | C-18 | 0.67 | 0.59 | 0.08 | | 11.95 | 12.16 |
| 7 | C-19 | 0.98 | 0.76 | 0.22 | | 19.68 | 19.53 |
| | C-18 | 0.66 | 0.58 | 0.08 | | 12.24 | 12.43 |
| 8 | C-19 | 1.02 | 0.70 | 0.32 | | 20.16 | 20.36 |
| | C-18 | 0.67 | 0.55 | 0.12 | | 12.00 | 12.19 |
| 9 | C-19 | 1.42 | 1.54 | -0.12 | | 20.26 | 20.53 |
| | C-18 | 0.66 | 0.58 | 0.08 | | 11.99 | 12.24 |
| 10 | C-19 | 1.26 | 1.36 | -0.10 | | 20.16 | 20.36 |
| | C-18 | 0.64 | 0.58 | 0.06 | | 12.00 | 12.19 |
| 11[5] | C-18 | 0.98 | 0.64 | 0.34 | | | |
| 12[5] | C-18 | 0.89 | 0.57 | 0.32 | | | |
| 13 | C-8 | 0.98 | 0.64 | 0.34 | | 21.80 | 21.56 |
| | C-8 | 1.35 | 1.01 | 0.34 | | 25.91 | 25.78 |



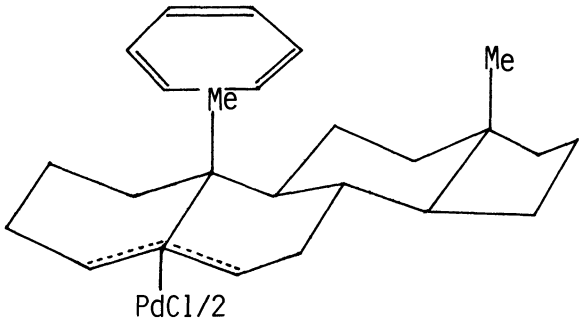
complexes containing a cyclopropane ring. Now, in the present paper, we would like to report solvent effect in $^{1}$H-NMR spectrum of steroidal π-allyl palladium chloride complexes.

A typical procedure is as follows. The π-allyl palladium chloride complexes were synthesized by the methods described in literature.[7] The NMR spectra were measured using JEOL FX 200 Model Spectrometer in $CDCl_3$ and $C_6D_6$, with TMS as internal standard.

The C-18 and C-19 methyl resonances of some steroidal π-allyl palladium complexes in $CDCl_3$ and $C_6D_6$ are summarized in Table 1.

As can be seen in the Table 1, when the α-π-allyl palladium complexes are relatively near C-19 methyl group, as in the α-1-3η-, α-3-5η-, α-4-6η-, and α-5-7η-type complex, the shielding effect from $CDCl_3$ to $C_6D_6$ solution ($\Delta=\delta CDCl_3-\delta C_6D_6$) is greater ($\Delta$0.22-0.49) on the C-19 methyl group. However, in the case of the β-1-3η- and β-3-5η-type complex, the negative value of for the C-19 methyl group shows the deshielding effect causing by benzene ring. It is known that the C-19 methyl resonance of 5α-androstan-1- and -2-one shows a large shielding effect in benzene solution.[10] It is considered that these results are consistent with the formation of a collision complex in which the π-electrons of the benzene ring interact with the partial positive charge on the carbonyl carbon atom.

Therefore, it is possible to consider that in the case of α-π-allyl palladium complexes, benzene ring attacks from the β-face of the complex and then the benzene ring orients in parallel with the palladium by a long range Coulomb's force. Also, this is supported by the fact that the C-19 methyl group of the α-4-6η-type complex (6) shows a large value ($\Delta$ 0.49), and the shielding effect on the C-18 methyl group of two compounds 11 and 12 is larger than of the other complexes (1-10). From these $^{13}$C-NMR spectral data, however, it could not be determined the configuration of palladium in π-allyl palladium



complexes. It is particularly noteworthy that since steroidal π-allyl palladium complexes are rigid ideal molecules, the shift of the angular methyl resonance can be utilized to uncover the geometry of the other complexes.

References

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11) 1a: mp (dec) 178-180 °C; $^{1}$H-NMR($CDCl_3$): δ0.77 (s, 3H, $C_{13}$-Me), 0.81 (s, 3H, $C_{10}$-Me), 2.03 (s, 3H, $C_{17}$ β-OAc), 4.60 (t, 1H, J=6.8Hz, $C_{17}$ α-H), 5.01 (d, 1H, J=6.8 Hz, $C_1$-H), 5.08 (m, 1H, $C_3$-H), and 5.41 (t, 1H, J=6.6 Hz, $C_2$-H); $^{13}$C-NMR($CDCl_3$): δ99.59, 85.32, 83.00, 82.69, 50.56, 49.51, 48.72, 42.69, 41.63, 36.55, 35.39, 31.84, 30.83, 27.60, 27.41, 23.45, 21.14, 20.79, 16.57, and 12.17.

(Received November 1, 1988)