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Preliminary communication

THE MECHANISM OF HYDROXYPALLADATION IN ACYCLIC AND CYCLIC η^2-DIENE COMPLEXES

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Summary

Cyclic dienes in aqueous acetone mixtures do not reduce palladium(II) complexes to palladium as readily as do acyclic ones. It is suggested that the difference arises because of conformational effects in the (η^2-diene)palladium(II) complexes, that nucleophilic attack on the coordinated C=C bond by H_2O (or OH^-) is intermolecular, and that this process only occurs when this bond is nearly perpendicular to the X—Pd—X axis (where the ligands X are *cis* to the C=C group).

In water-containing media, alkenes reduce palladium(II) ions to colloidal metal, as for example occurs in the Wacker process, see eq. 1 to 4 [1]:

$$CH_2{=}CH_2 + PdCl_4{}^{2-} \rightleftharpoons (\eta^2\text{-}CH_2{=}CH_2)PdCl_3{}^- + Cl^- \qquad (1)$$

$$(\eta^2\text{-}CH_2{=}CH_2)PdCl_3{}^- + H_2O \rightleftharpoons (\eta^2\text{-}CH_2{=}CH_2)PdCl_2(OH_2) + Cl^- \qquad (2)$$

$$(\eta^2\text{-}CH_2{=}CH_2)PdCl_2(OH_2) + H_2O \rightleftharpoons HOCH_2CH_2PdCl_2(OH_2)^- + H^+ \qquad (3)$$

$$HOCH_2CH_2PdCl_2(OH_2)^- \to\to CH_3CHO + Pd^0 \qquad (4)$$

However the colloidal metal appears much less quickly, if at all, when the reducing agent is a cyclic diene rather than an acyclic one or a monoene. (Cyclic and acyclic are used in the sense of whether or not both C=C bonds lie within the same ring.) This leads us to suggest that the stereochemistry of the nucleophilic attack in eq. 3 is important.

$[PdCl_3(OH_2)]^-$ reacts with many dienes in water/acetone mixtures by a two step process, eq. 5 and 6 (excluding possible further reactions in which colloidal palladium is produced) [2]:

$$PdCl_3(OH_2)^- + \text{diene} \rightarrow Pd(\eta^2\text{-diene})Cl_3^- + H_2O \qquad (5)$$

$$Pd(\eta^2\text{-diene})Cl_3^- \rightarrow Pd(\eta^4\text{-diene})Cl_2 + Cl^- \qquad (6)$$

For 1,5-cyclononadiene, 1,4-cyclooctadiene, 3-methyl-1,4-cyclooctadiene, tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene, 1,5-hexadiene, 1,7-octadiene, 4-vinylcyclohexene and bicycloocta-2-ene in water/acetone 1/49 (v/v), the first step has a rate constant which is of the order of 1 M^{-1} s^{-1} at 25° C, the value varying only slightly with change in the diene or in the ratio of co-solvents [2a,b]. Thus eq. 5 is normally complete in the order of minutes. In contrast eq. 6 takes several hours.

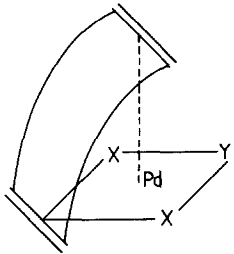
As the water content of the solvent is raised, in the case of some dienes there is an increasing tendency for the colloidal palladium indicative of hydroxypalladation to appear. If this occurs, it takes place when the rate constants signify that the main species present is $[Pd(\eta^2\text{-diene})Cl_3]^-$ and not $[Pd(\eta^4\text{-diene})Cl_2]$. For example, a 1/1 water/acetone solution ca. 10^{-2} M in Pd^{II} and saturated with 1,5-hexadiene turns black within two minutes. Provided the water content is sufficiently high for hydroxypalladation to occur, the phenomenon is exhibited by all the acyclic dienes tested here (that is including 4-vinylcyclohexene). In contrast the cyclic dienes yield no colloidal palladium over periods of several hours.

From the point of view of formation of palladium, monoenes appear at first sight to behave similarly to the dienes; the reactions of 1-hexene and 1-octene are over within two minutes as above, while that of cyclohexene takes only slightly longer.

We will look at possible explanations for the contrasting behaviour of the acyclic and cyclic dienes. Some years ago Shaw [3] suggested that intramolecular nucleophilic attack from a metal centre in a square planar complex on to a coordinated alkene could only occur if the C=C bond involved were co-planar with the metal and the other three ligands and recent calculations [4] are based on this supposition. However, if in the $[Pd(\eta^2\text{-diene})Cl_3]^-$ ion, the coordinated C=C group rotates about the axis from its center to the palladium, as occurs in η^2-alkeneplatinum(II) and presumably η^2-alkenepalladium(II) [4,6] systems, then co-planar geometry can be achieved so that intramolecular attack should be possible. Therefore let us suppose that the second C=C group, which is technically non-bonded, in fact coordinates weakly to the palladium to give a complex which is either shaped like a square-based pyramid **1** or possibly a trigonal bipyramid, as **2** or **3**. Rotation is now impossible. In the cyclic diene complexes the two C=C links are approximately parallel. Thus the fully bonded group will be nearly co-planar with Pd—X, and so intramolecular attack ought to occur on the basis of Shaw's hypothesis.

However, experimental evidence [1,7,8] indicates that the nucleophilic attack by H_2O (or OH^-) on alkenes π-bonded to palladium is intermolecular, as in reaction 3. Intramolecular migration of an H_2O or OH^- ligand does not occur. Calculations by Bäckvall et al. indicate that nucleophiles with HOMO of low energy will attack by the intermolecular mechanism [4]; OH^- is shown to be in this category, and presumably H_2O is also.

We propose the following modification to Shaw's suggestion: in the H_2O/OH^- system the attack is intermolecular, and it is easiest if the dihedral angle between



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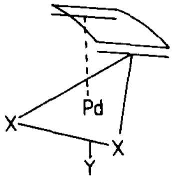

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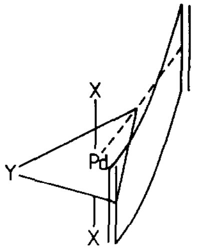

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the C=C and Pd—X axes is 90° becoming impossible as these groups move to co-planarity. Thus attack would be impossible in 1, 2 and 3 since the dihedral angle is zero. In the cyclic systems, geometry will constrain the dienes to a shape somewhat like that depicted in these three figures. In addition oscillation of the fully bonded C=C group will be restricted so that the average dihedral angle will be small. In the acyclic complexes neither of these constraints will apply to such an extent; hence the average dihedral angle will be closer to 90°. Thus attack by the nucleophile will be easier in the acyclic than the cyclic systems.

The hypothesis put forward here can be rationalized simply by postulating that there is through-space donation from the lone pairs of X which is sufficiently effective to de-activate the C=C group to attack by another nucleophile when the X are close to the C atoms as occurs when the C=C and Pd—X bonds are co-planar.

Commercial samples were used of Na_2PdCl_4, 1,5-hexadiene, 1,7-octadiene, and 4-vinylcyclohexene.

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References

1 See, for example, J.-E. Bäckvall, B. Åkermark and S.O. Ljuggren, J. Am. Chem. Soc., 101 (1979) 2411.
2 (a) J.K.K. Sarhan, S.-W. Foong Murray, H.M. Asfour, M. Green, R.M. Wing, and M. Parra-Haake, submitted for publication; (b) H.M. Asfour, and M. Green, unpublished work.
3 B.L. Shaw, J. Chem. Soc., Chem. Commun., (1968) 464.
4 J.-E. Bäckvall, E.E. Björkman, L. Pettersson, and P. Siegbahn, J. Am. Chem. Soc., 106 (1984) 4369.
5 M. Sinya, and J. Saito, Inorg. Chem., 20 (1979) 287 and ref. therein.
6 P.J. Hay, J. Am. Chem. Soc., 103 (1981) 1390.
7 J.K. Stille, and R. Divakaruni, J. Organomet. Chem., 169 (1979) 239.
8 J.K. Stille, and D.E. James, J. Organomet. Chem., 108 (1976) 401.