# The Stereochemistry of Addition Reactions to Co-ordinated Olefins

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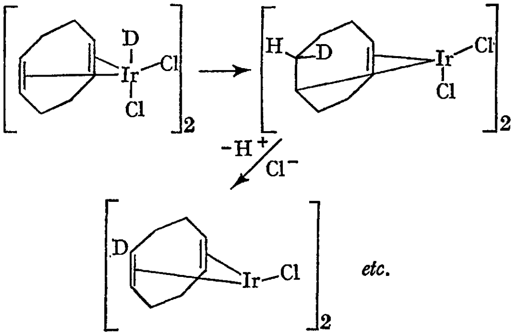
IN the industrially important oxidative hydrolysis of ethylene to acetaldehyde in the presence of palladium(II) halides[1] the kinetic results are only consistent with attack of co-ordinated ethylene by an OH ligand, *i.e.* effectively Pd–OH adds across co-ordinated ethylene in a four-centre *cis*-addition[2]; similarly for other mono-olefins.[3] In contrast, chelating diolefins co-ordinated to $Pd^{II}$ or $Pt^{II}$ in complexes of the type $[MCl_2(C_xH_y)]$ (M = Pd or Pt; $C_xH_y$ = cyclo-octa-1,5-diene, tetraphenylcyclobutadiene, dicyclopentadiene, or bicyclo[2,2,1]heptadiene) react with methoxide or ethoxide ions to give complexes of type $[MCl(C_xH_yOR)]_2$, which have been shown to have the RO group *exo* by *X*-ray[4,5] or n.m.r.[6,7] studies, *i.e.* in effect the addition across the double bond is *trans*. This difference in behaviour between co-ordinated diolefins and mono-olefins has been attributed either to hindrance of attack on the metal (*e.g.* by $OMe^-$) due to the bulky olefin or to the nature of the other ligands on the metal (in some unspecified way).[7] However, the metal, the O and the two C atoms must be coplanar or approximately so, in order to get the four-centre *cis*-addition which has been postulated for the oxidative hydrolysis of ethylene by $Pd^{II}$.[2] This is clearly not possible for a chelating diolefin complex of $Pd^{II}$ or $Pt^{II}$ where the M–OR bond and the C=C bond will be at 90°, *i.e.* a complex of type $(C_xH_y)MCl_2$ (M = Pd or Pt) when treated with $MeO^-$ could readily give some $[(C_xH_y)MCl(OMe)]$ but conversion to [(*endo*-$MeO{\cdot}C_xH_y)MCl]_2$ would not occur for the reason outlined above. However, mono-olefines have been shown to rotate rapidly, around an axis from the metal to the centre of the C–C bond, in $Rh^I$ and $Pt^{II}$ complexes,[8,9] and very probably therefore in mono-olefin–$Pd^{II}$ complexes. During this rotation a C=C and a *cis*-M–OR bond would become coplanar; therefore *cis*-addition to give M–C–C–OR could occur. Clearly the double bond of a chelating diolefin could not rotate in this way and this inability to rotate could be the decisive factor determining the different stereochemistry of attack.

If the octahedral co-ordinating sites of a diolefin complex becomes involved, however, the *cis*-addition to a double bond could occur. Thus the 'planar' iridium(I) cyclo-octa-1,5-diene complex $[IrCl(C_8H_{12})]_2$ in HCl–EtOH readily gives the octahedrally co-ordinated iridium(II) hydrido-complex $[IrHCl_2(C_8H_{12})]_2$.[10,11] In DCl–EtOD some deuteriation of the ring occurs[12]; this could be explained by a *cis*-addition of the Ir–D to a C=C bond, followed by *trans*-elimination of a proton as shown below.



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