Stereochemistry of the Oxidative Addition of Allylic Halides to *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$]

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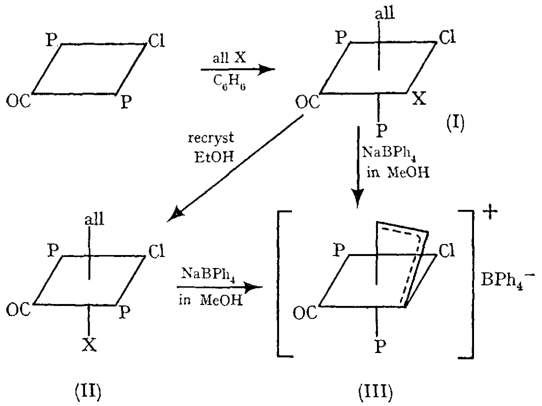
THERE is much interest in the stereochemistry and mechanism of oxidative addition reactions to compounds of the type *trans*-[IrX(CO)L$_2$] (X = halogen, L = tertiary phosphine, tertiary arsine, or olefin).[1–3] Hydrogen (H$_2$) is known to add *cis* to iridium(I) complexes of this type but the addition of halogens, or alkyl halides to *trans*-[IrCl(CO)(PMePh$_2$)$_2$] in a variety of solvents has been shown to give a *trans*-adduct.[1] However, similar additions to *trans*-[IrCl(CO)(PPh$_3$)$_2$] give *cis*-adducts.[2,4] In all these cases the adducts still have the phosphines in mutually *trans*-positions.

We now find that addition of allyl bromide to *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] readily gives a *cis*-adduct of configuration (I; X = Br) in which the two phosphines are in mutually *cis*-positions. The n.m.r. spectrum of this adduct shows all four methyl groups on the phosphines to be non-equivalent, there being no plane of symmetry through either phosphorus–iridium bond,[5,6] and the far-infrared spectrum shows ν(Ir–Cl) = 306 cm.$^{-1}$ indicative of chlorine in a *trans*-position to the carbonyl.[1,2,7] However, in ethanol the adduct of configuration (I) rapidly isomerises to the configuration (II; X = Br) which corresponds to overall *trans*-addition of the allyl bromide (isomerisation also occurs, but more slowly in chloroform solution). This isomer of configuration (II) shows two 1:2:1 ^{1}H n.m.r. triplets due to the phosphine methyls, there being no plane of symmetry through the phosphorus–iridium bonds; and ν(Ir-Cl) = 307 cm.$^{-1}$. Similarly addition of allyl chloride to *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] in benzene gives [IrCl$_2$(C$_3$H$_5$)(CO)(PMe$_2$Ph)$_2$] of configuration (I; X = Cl) [ν(Ir–Cl) = 309 cm.$^{-1}$ (*trans*-CO) and 270 cm.$^{-1}$ (*trans*-PMe$_2$Ph)] which rearranges in ethanol to the isomer of configuration (II; X = Cl) [ν(Ir–Cl) = 304 cm.$^{-1}$ (*trans*-CO) and 249 cm.$^{-1}$ (*trans*-allyl)]. These isomerisations of configuration (I) → (II) could go *via* the π-allylic cation of configuration (III) since complexes of configuration (I) or (II) in methanol in the presence of NaBPh$_4$ or NaPF$_6$ rapidly give salts of this cation (III), and we have shown that this cation when attacked by iodide ion (more strongly bonding than chloride or bromide ion) is converted into a σ-allylic complex [IrICl(allyl)(CO)(PMe$_2$Ph)$_2$] of configuration (II; X = I). When the adduct [IrBrCl(C$_3$H$_5$)(CO)(PMe$_2$Ph)$_2$] of configuration (I) is dissolved in ethanol or methanol, the bromide ligand is solvolysed off (being *trans* to the strongly *trans*-bond weakening PMe$_2$Ph) in preference to the inert chloride ligand (*trans* to CO). Hence the product has configuration (II; X = Br) and is not the corresponding isomer with Cl and Br interchanged. Addition of allyl chloride to *trans*-[IrBr(CO)(PMe$_2$Ph)$_2$] gives mixtures which we could not separate. Similarly addition of allyl bromide to *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] in ethanol gives mixtures {bromide ion liberated by solvolysis would convert some *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] to the corresponding bromide}. We have made 2-methylallyl complexes and also complexes of AsMe$_2$Ph of configurations (I) and (II) corresponding to those mentioned above.



A *cis*-addition similar to those described above could be the initial step in some of the observed overall *trans*-additions of alkyl halides, R′X, or halogens, X$_2$, to iridium complexes of this type.[1] Thus X would initially take up a position *trans* to a phosphine but then be solvolysed leading either to a solvent-containing or a five-co-ordinated intermediate, which when attacked by X$^-$ could give a *trans*-product. Obviously from our work the solvent can play an important part in determining the stereochemistry of oxidative addition reactions and more attention should be paid to the nature of the solvent in future studies.

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