β-Hydrogen Elimination from Oxidative Addition Product of Straight-chain Alkyl Chloride to Vaska's Complex

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Oxidative additions and reductive eliminations are recognized as important steps of many catalytic processes involving low-oxidation state of metal complexes, and considerable interest has been recently devoted to the mechanistic features of these reactions [1–7]. Of particular significance is the β-hydrogen elimination process owing to the determining role played by the reaction in the transition metal catalyzed dimerization and polymerization of olefins [8–13].

In this paper we present the reactions of Vaska's complex with chloroalkyls containing straight-chains of carbon atoms, $Cl\text{-}(CH_2)_nCH_3$ ($n = 5–8$); the reactions occur only using the chloroalkyl as solvent and refluxing the reaction mixture for some hours, the time of the reaction depending on the boiling point of the chloroalkyl. The iridium(III) complex, $[IrHCl_2(PPh_3)_2(CO)]$ [14], with the hydride ligand *trans* to a chloride, was isolated as the only product of the reactions; the formation of the corresponding 1-alkene was evidenced by gas-chromatography.

The chloroalkyl was distilled and purified before use. It was proved that the formation of the reaction product was not attributable to the presence of traces of HCl in the reaction mixture. The formation of the hydride–iridium(III) product probably takes place through β-hydrogen elimination from the iridium(III) σ-alkyl derivative following the oxidative addition of the chloroalkyl to the iridium(I) substrate.

I.R. spectra recorded during the course of the reactions indicate that hydride formation takes place in a single detectable kinetic stage without intermediate accumulation, so it seems reasonable that the β-hydrogen elimination from the intermediate σ-alkyl derivative is a fast stage. Unfortunately the drastic conditions required did not allow a kinetic study of the oxidative addition. Besides, experiments using duroquinone on galvinoxyl seem to indicate that a radical mechanism is not operating, although the high temperatures used do not permit definitive conclusions.

An interesting aspect of the β-hydrogen elimination concerns the interaction of the β-hydrogen with the metal [8–10]. In the reactions reported in this paper the β-hydrogen elimination can either require the formation of a seven coordinate metal hydride directly from the oxidative addition product, or preliminary dissociation of the triphenylphosphine with consequent better availability of the metal center to interact with β-hydrogen. Even though some stable seven-coordinated iridium(III) derivatives, *viz.* $[IrH_5L_2]$ ($L = PEt_2Ph, PEt_3$) have been isolated [15], the latter kind of interaction, which has been shown to occur in many β-elimination processes *viz.* $[(CH_3CH_2CD_2CH_2)_2Pt(PPh_3)_2]$, $[(CH_3)_3CAu(CH_3)_2PPh_3]$ and $[(CH_3(CH_2CH_2)Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)_2]$ [11, 16, 17] is, in our opinion, more reasonable.

Dissociation of neutral ligands is now recognized as a common feature of many reductive elimination reactions yielding hydrocarbons [16, 18–20]; moreover, it has been recently shown that dissociation of tertiary phosphine occurs prior to oxidative addition of aryl halides to iridium(I) substrates [4]. In order to establish if a similar process has to be invoked for the present oxidative addition we carried out the reactions of staight-chain alkyl halides to Vaska's complex in the presence of an excess of free triphenylphosphine. Even in the absence of accurate values of rate constants, the presence of an excess of triphenylphosphine clearly causes increased rates of hydride formation (with a ten-fold excess of PPh_3 the reaction is about 4 times faster).

In our reactions the preliminary dissociation of triphenylphosphine, which the high temperatures required should favor, involves either the formation of three-coordinated or of a square-planar solvento-intermediate. Both these species, in principle, should be less basic than Vaska's complex (starting material); therefore the ability of the substrate to undergo oxidative addition should be decreased by the dissociation process. On the basis of these considerations it seems likely that the increased rate of oxidative addition observed in the presence of added phosphine has to be attributed to the shift of the dissociation equilibrium toward the more reactive Vaska's complex.

A recent report [4] has shown that oxidative additions of aryl iodides to Vaska's type complexes are governed by a two-term rate law and that the dissociation of tertiary phosphine occurs prior to the oxidative addition; in this case the excess of phosphine lowers the second-order rate constants. This argument is not in keeping with our findings, suggesting further investigation on the effects of neutral ligands in the rate of the oxidative addition.

Weinberg and Baird [21] have recently reported that free triphenylphosphine exerts an accelerating

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effect on the reductive elimination of methyl chloride from $[RhMeCl_2(CO)(PPh_3)_2]$; this effect has been attributed to an S_N2 attack on the methyl group by the free triphenylphosphine yielding $[PMePh_3]Cl$ and *trans*-$[RhCl(CO)(PPh_3)_2]$. In our case the nature of the reaction products, $[IrHCl_2(CO)(PPh_3)_2]$ and 1-alkene, and the absence of the phosphonium salt from the reaction mixture, rules out that a similar mechanism could be operating. In conclusion our results indicate that every generalization concerning the effect of the neutral ligand on the rate of oxidative addition and reductive elimination is unwarranted. In fact, very small electronic and steric alterations in the environment of the metal can tip the balance toward different mechanisms of reaction.

Experimental

The *trans*-$[Ir(CO)(PPh_3)_2Cl]$ was prepared according to Collman's method [22]. The chloroalkyls were purified before use as described in the literature [23]. Infrared spectra were recorded with a Perkin-Elmer 457 Spectrometer. A Gas-Chromatograph Carlo Erba Fractovap 2150 with S.E. 30 column was used for the detection of the chloroalkyls and of the 1-alkene.

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