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THE REACTION OF PLATINUM(II)—OLEFIN COMPLEXES WITH METHOXIDE IONS

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Summary

When platinum(II)—olefin complexes, such as *cis*-[$(PPhEt_2)PtCl_2(C_2H_4)$], are treated with methoxide ions three reactions occur, namely (i) nucleophilic attack on the coordinated olefin to yield an unsaturated methyl ether, (ii) substitution of the olefin by methoxide ion and decomposition of the resulting methoxy complex to formaldehyde and (iii) displacement of the olefin and formation of $[(PPhEt_2)PtCl_2]_2$. The relative importance of these three reactions depends upon the precise experimental conditions. The implications of the present results for mechanistic studies of the reactions of coordinated olefins with nucleophiles are discussed.

Introduction

The attack of nucleophiles on olefins coordinated to metal ions, particularly palladium(II), has been widely investigated and developed into commercial processes such as the Wacker process. Recently there has been considerable interest in the stereochemistry of the nucleophilic attack [2 - 10]. Two approaches have been used to investigate this. In the first [5 - 10] the stereochemistry of catalytic reactions has been investigated, whereas in the second [4,11 - 15] investigations have been carried out using a preformed olefin complex. Most of these preformed olefin complexes have involved olefinic ligands which are chelating ligands containing either a second olefinic group or a different type of group such as a tertiary phosphine group. It has become apparent that the stereochemistry observed with the chelate ligands is not necessarily that observed for unidentate olefins, and tentative explanations have been advanced to account for this [2,3]. Since the olefin complexes of commercial interest all involve simple unidentate olefins and since further, with most catalytic systems there is a high probability of secondary reactions obscuring the stereochemistry of the initial nucleophilic attack, we set out to investigate model systems in which preformed platinum(II) complexes of simple olefins were used. In our initial work we chose methoxide ion as the attacking nucleophile because very few methoxy complexes of platinum(II) have been reported [16] suggesting that, in contrast to many other nucleophiles such as amines, methoxide ions may be poor ligands for platinum(II) and thus coordination of the attacking nucleophile to the metal might not cause too much difficulty.

Experimental

cis-[(PPhEt$_2$)PtCl$_2$(olefin)], where Olefin = C_2H_4 and $CH_3CH=CH_2$, were prepared from [(PPhEt$_2$)PtCl$_2$]$_2$ [17], using the standard procedure [18]. Tetraethylammonium methoxide and tetraphenylarsonium methoxide were prepared by passing methanolic solutions of the corresponding chloride salts down a BioRad AG1-X8 anion exchange column in the methoxide form.

(i). Reactions of cis-[(PPhEt$_2$)PtCl$_2$(C$_2$H$_4$)] with nucleophiles

(a). With an equimolar quantity of NEt$_4$OMe or AsPh$_4$OMe. A solution of *cis*-[(PPhEt$_2$) PtCl$_2$(C$_2$H$_4$)] (0.1 mmole) in dichloromethane (1 ml) was added to a solution of NEt$_4$OMe (0.1 mmole) in methanol (0.5 ml) at 0° and the solution stored in a refrigerator at 5° for 3 days during which no precipitation or decomposition to platinum metal was observed. GLC analysis indicated the presence of free ethylene but no methyl vinyl ether could be detected. The platinum was shown to be present as [(PPhEt$_2$)PtCl$_2$]$_2$ by comparison with an authentic sample of the dimer.

(b). With excess NaOMe. A solution of *cis*-[(PPhEt$_2$)PtCl$_2$(C$_2$H$_4$)] (0.2 mmole) in dichloromethane (1 ml) was added to a vigorously stirred solution of NaOMe (0.6 mmole) in methanol (1.5 ml) at room temperature. Significant decomposition to platinum metal was observed within a few minutes and GLC analysis indicated that the major organic product was ethylene together with a small amount (ca. 5%) of methyl vinyl ether. A small sample (0.5 ml) of the solution was treated with water (0.5 ml) and animal charcoal and, after filtration, this solution was shown to contain formaldehyde by applying the chromotropic acid test [19].

On repeating this experiment using 10- and 20-fold excesses of sodium methoxide rapid decomposition the platinum metal together with the formation of formaldehyde was observed, but no significant amounts of methyl vinyl ether could be detected.

(c) With anhydrous sodium carbonate in methanol. Anhydrous sodium carbonate (1 mmole) was stirred in methanol (2 ml) for ½ h. To this was added a solution of *cis*-[(PPhEt$_2$)PtCl$_2$(C$_2$H$_4$)] (0.4 mmole) in dichloromethane (1 ml). After about 5 min there were visible signs of decomposition and within 30 min the solution was black due to the formation of platinum metal. GLC analysis showed the presence of a significant quantity of ethylene and a yield of about 30% of methyl vinyl ether based on the amount of ethylene present in the original complex. Other molar ratios of sodium carbonate to ethylene complex were also used, but the present molar ratio of 1/2.5 (coordinated ethylene/sodium carbonate) gave the maximum yield of methyl vinyl ether.

Treatment of *cis*-[(PPhEt$_2$)PtCl$_2$(CH$_3$CH=CH$_2$)] under the same conditions also led to the formation of platinum metal and formaldehyde. GLC analysis showed that propene was the only organic product, apart for formaldehyde, and that no 2-methoxypropene was formed.

(ii). Reaction of $[PtCl_2(C_2H_4)]_2$ with anhydrous sodium carbonate in methanol

Anhydrous sodium carbonate (1 mmole) was stirred in methanol (2 ml) for ½ h. This solution was added to a flask containing freshly prepared [20] $[PtCl_2(C_2H_4)]_2$ (0.3 mmole). Decomposition to platinum metal was significant after 2 min. GLC indicated that ethylene was liberated but no methyl vinyl ether was formed. The presence of formaldehyde was confirmed using the chromotropic acid test as in (*i b*) above.

(iii). Reaction of cis-$[(PPhEt_2)PtCl_2(C_2H_4)]$ with trans-2-butene

cis-$[(PPhEt_2)PtCl_2(C_2H_4)]$ (1 mmole) was dissolved in dichloromethane (3 ml) in a flask provided with a stopcocked inlet and an acetone/CO_2 condenser. An excess of *trans*-2-butene was admitted through the stopcock and the reaction carried out for 8 h, once at room temperature and once in an acetone/CO_2 bath. In both cases removal of the solvent gave an off-white gummy product which further pumping solidified to yield $[(PPhEt_2)PtCl_2]_2$, which was characterised by comparison with an authentic sample.

GLC analyses

These were performed on a Perkin-Elmer model 452 gas chromatograph fitted with a flame ionisation detector using a gas sampling technique to inject the sample. The products were identified by comparison of their retention times with the retention times of authentic samples of methyl vinyl ether and 2-methoxypropene prepared by pyrolysis of 2,2-dimethoxypropane [21] on two columns, one a 2-metre column packed with diatomite coated with polypropyleneglycol adipate (15%w/w) and the other a 2 m column packed with chromosorb P (60/80) coated with a saturated solution of silver nitrate in ethylene glycol.

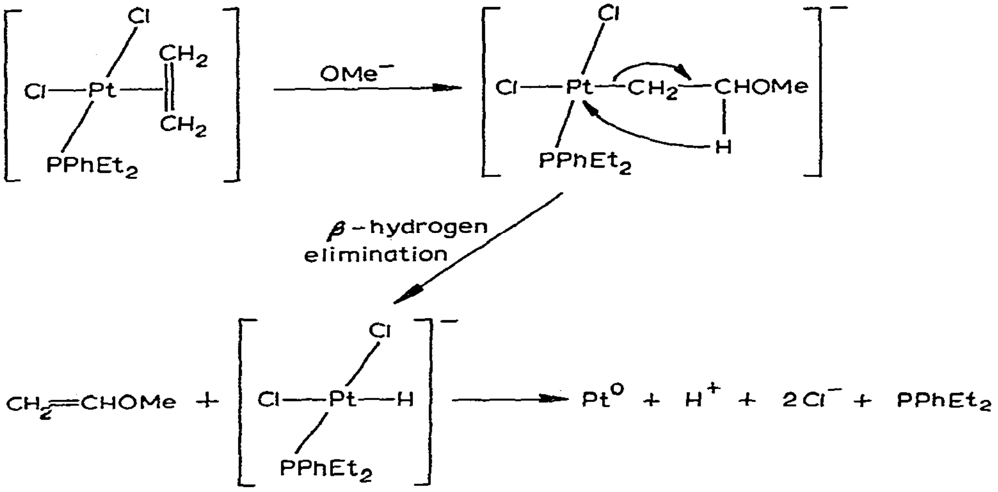
Results

The present results show that when *cis*-$[(PPhEt_2)PtCl_2(C_2H_4)]$ is treated with methoxide ion three reactions can occur simultaneously, the relative importance of the three depending on the precise experimental conditions. These three reactions are:

(i). Nucleophilic attack on the coordinated olefin

Nucleophilic attack of methoxide ion on the coordinated olefin to yield ultimately methyl vinyl ether is in general only a minor reaction, although under suitable conditions it could account for about 30% of the total product. The reaction can be envisaged as occurring as shown in Scheme A, although all attempts to isolate the anionic intermediate containing a platinum(II)—carbon σ-bond, by trapping it with bulky cations such as tetraethylammonium or tetraphenylarsonium, failed. This suggests that its decomposition by a β-hydrogen elimination mechanism, possibly involving the formation of an unstable intermediate hydrido—platinum(II) complex, is a very facile process.

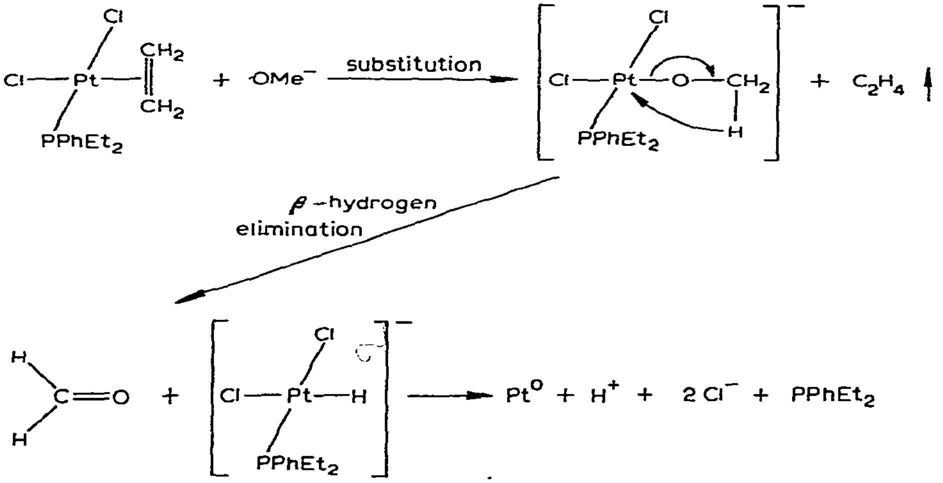
SCHEME A



(ii). Substitution of ethylene by methoxide ion

One of the major reactions appears to be substitution of the ethylene by the methoxide ion. The resulting methoxy—platinum(II) complex is unstable and, as observed previously for alkoxy—palladium(II) complexes [22], decomposes. However, in contrast to the previous work where methoxy—palladium(II) complexes decomposed in methanol to methyl formate, in the present work the oxidation product was found to be formaldehyde. A possible mechanism involving a β-hydrogen elimination mechanism analogous to that suggested in Scheme A for alkyl complexes is shown in Scheme B. Again an intermediate hydrido—platinum(II) complex is shown but this may not actually be formed as such, although the platinum(II) is almost certainly involved in the removal of

SCHEME B



the β-hydrogen atom. The only stable methoxy complexes of platinum(II) and palladium(II) reported so far, namely $[(Ph_2PCH_2CH_2PPh_2)Pt(OCH_3)$-$(\overline{-C{=}CH-(CH_2)_4})]$ [16] and *trans*-$[(PEt_3)_2Pd(OCH_3)CN]$ [23], will not, according to Wilkinson's interpretation of the β-hydrogen elimination mechaanism for metal-carbon σ-bonded complexes [24], readily undergo β-hydrogen elimination. This is because they both contain ligands with a high affinity for the metal that are not readily lost, so preventing the formation of a vacant site to which the hydride group that is lost from the methoxy ligand may coordinate to. Accordingly, these complexes are stable whereas the present methoxy complex, $[(PPhEt_2)PtCl_2(OMe)]^-$ is anionic and contains relatively weakly bonded chloride ligands so that it readily undergoes a β-hydrogen elimination reaction to yield formaldehyde.

(iii). Loss of ethylene and formation of a dimeric platinum(II) complex

The principal reaction of *cis*-$[(PPhEt_2)PtCl_2(C_2H_4)]$ in the presence of an equimolar quantity of methoxide involve loss of ethylene and formation of the dimeric complex $[(PPhEt_2)PtCl_2]_2$ (reaction 1).

$$cis\text{-}[(PPhEt_2)PtCl_2(C_2H_4)] \xrightarrow{1\text{ mole }OMe^-} \tfrac{1}{2}[(PPhEt_2)PtCl_2]_2 + \uparrow 2C_2H_4 \qquad (1)$$

Whether the methoxide ion itself, or the methanol that is also present, is responsible for this reaction is uncertain since treatment of a solution of *cis*-$[(PPhEt_2)PtCl_2(C_2H_4)]$ in dichloromethane with methanol does result in the slow liberation of ethylene and the formation of yellow $[(PPhEt_2)PtCl_2]_2$. Reaction (1) can also be effected by treating *cis*-$[(PPhEt_2)PtCl_2(C_2H_4)]$ with *trans*-2-butene. This suggests that 2-butene is such a weak ligand for platinum(II) that, although it can displace ethylene, it is fairly readily lost from the resulting complex (reaction 2).

$$cis\text{-}[(PPhEt_2)PtCl_2(C_2H_4)] + trans\text{-2-butene} \rightarrow$$
$$cis\text{-}[(PPhEt_2)PtCl_2(trans\text{-2-butene})] + \uparrow C_2H_4 \rightarrow$$
$$\tfrac{1}{2}[(PPhEt_2)PtCl_2]_2 + trans\text{-2-butene} \qquad (2)$$

It is possible that two molecules of either the methoxy complex $[(PPhEt_2)$-$PtCl_2(OMe)]^-$, or the methanol complex $[(PPhEt_2)PtCl_2(MeOH)]$, may react similarly with loss of methoxide ion, or methanol, to form the dimeric tertiary phosphine—platinum(II) complex.

Conclusion

The present work has shown that the main reaction between methoxide ions and preformed platinum(II)—olefin complexes is displacement of the olefin from coordination to platinum(II) rather than nucleophilic attack on the olefin. Thus attempts to investigate the details of the mechanism of the nucleophilic attack reaction using preformed olefin complexes are unlikely to be successful, except in the rather special case of amines as the attacking group where a complex stablised by internal zwitterion formation is involved [25].

Furthermore the present work suggests that, since olefins coordinate more weakly to palladium(II) than to platinum(II) [26], nucleophilic attack on olefins coordinated to palladium(II), which is, of course, the basis of many catalytic reactions especially the Wacker Process, is probably a relatively inefficient process, since most encounters between the complex and the nucleophile are likely to lead to displacement of the olefin rather than to nucleophilic attack upon it.

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