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INVESTIGATIONS INTO THE STEREOCHEMISTRY OF NUCLEOPHILIC ATTACK ON OLEFINS COORDINATED TO PALLADIUM(II) AND PLATINUM(II)

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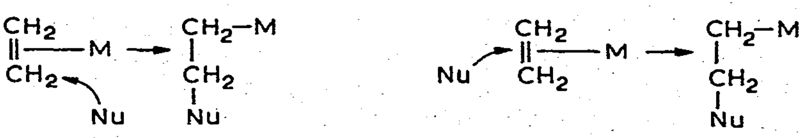
Summary

A study of the oxidative hydrolysis of olefins in the presence of $[Pd(dien)H_2O]^{2+}$ and $[Pd(en)(H_2O)_2]^{2+}$ (dien = diethylenetriamine, en = ethylenediamine) has indicated that where possible nucleophilic attack on the olefin by hydroxide ion involves prior coordination of the hydroxide to palladium(II). However where no coordination site *cis* to the olefin is available, as in $[Pd(dien)(olefin)]^{2+}$ in neutral solution, direct attack on the olefin by hydroxide ion occurs without prior coordination. Such attack is very slow compared to that involving prior *cis*-coordination. Some unsuccessful experiments to establish the stereochemistry of methoxide ion attack on preformed platinum(II)—olefin complexes are reported and reasons for their failure discussed.

Introduction

Nucleophilic attack on olefins coordinated to metal ions, particularly palladium(II), has been widely investigated and developed into commercial processes such as the Wacker process [1]. Recently there has been considerable interest in the stereochemistry of nucleophilic attack [2—20] since the nucleophile can attack the olefin either on the same side as the metal (*cis*-attack, Scheme 1) or on the side remote from the metal (*trans*-attack, Scheme 1).

SCHEME 1



cis-Attack will almost invariably involve prior coordination of the nucleophile

(Nu) to the metal. Two approaches have been used to investigate this stereochemistry.

In the first [4—10], investigations have been carried out using a preformed olefin complex. However most of these preformed complexes have involved olefins that are part of a chelating ligand containing either a second olefinic group or a different type of group such as a tertiary phosphine. It has become apparent that the sterochemistry of nucleophilic attack on chelating olefins is not necessarily the same as that observed for unidentate olefins, and some tentative explanations have been advanced to account for this [2,3]. A successful demonstration that amines attack unidentate olefin ligands, such as 1-butene in *cis*-$[PtCl_2(S\text{-1-butene})\{Ph(CH_3)CHNH_2\}]$, *trans* with respect to the platinum [4] led us to attempt a similar approach with methoxide attack, Scheme 2.

The second approach that has been used to investigate the stereochemistry of nucleophilic attack has involved studying catalytic reactions in which the olefin complex is only formed temporarily in solution [11—20]. Using this approach it has been shown that phenyl [11] and methoxycarbonyl [11] attack *cis*, chloride attacks mainly in a *cis*-manner [12,13], and acetate attacks *trans* [14—18]. Although the hydroxide ion is one of the more interesting and certainly commercially more useful nucleophiles, the stereochemistry of its attack has not been investigated in depth. Henry [19] has deduced from the kinetics of the oxidative hydrolysis of ethylene in the presence of $[PdCl_4]^{2-}$ that the rate was too fast for hydroxide ion to attack the palladium(II)—olefin complex from the opposite side to the palladium (i.e. *trans*-attack), but that it was consistent with prior coordination of the hydroxide ion to the palladium, giving rise to *cis*-attack (Scheme 1). In the present paper we report results using $[Pd(dien)H_2O]^{2+}$ and $[Pd(en)(H_2O)_2]^{2+}$ (dien = diethylenetriamine; en = ethylenediamine) which suggest that whilst *cis*-attack is the preferred mode of reaction, when this is prevented hydroxide ions will attack olefins coordinated to palladium(II) on the side of the olefin remote from the metal.

Results

(i) $[Pd(dien)H_2O]^{2+}$*—olefin reactions in aqueous solution*

A solution of $[Pd(dien)H_2O](ClO_4)_2$ in water was found from its UV spectrum to react within the time of mixing with allyl alcohol and 4-penten-1-ol, the band initially at 316 nm being replaced by a rather more intense band at 312 nm. On allowing these solutions to stand at room temperature slow decomposition occurred with visible formation of palladium metal after about 16 h. 1-Octene was found to react similarly although in this case the solvent used was 50% aqueous methanol which was necessary in order to dissolve the 1-octene; no palladium deposition was observed.

A comparison of the rates of formation of palladium metal when solutions of Na_2PdCl_4, $[Pd(en)(H_2O)_2](ClO_4)_2$ and $[Pd(dien)H_2O](ClO_4)_2$ were treated with allyl alcohol, 4-penten-1-ol (both using aqueous solutions), and 1-octene (using 50% aqueous methanolic solution), showed that in all cases Na_2PdCl_4 reacted instantaneously, $[Pd(en)(H_2O)_2](ClO_4)_2$ deposited palladium in 15 sec with 4-penten-1-ol but took about 5 min with both allyl alcohol and 1-octene. $[Pd(dien)H_2O](ClO_4)_2$ took overnight to yield a visible precipitate with both 4-penten-1-ol and allyl alcohol and did not yield palladium metal with

1-octene over a period of 20 days. The much slower reaction of the two cationic aquo-complexes relative to the anionic $[PdCl_4]^{2-}$ is perhaps surprising as the former should be more susceptible to nucleophilic attack. GLC analysis of the solutions after palladium had been deposited showed that the same products were formed in the presence of all three palladium(II) complexes. For allyl alcohol the oxidation product was acrolein; for 4-penten-1-ol all three palladium(II) complexes yielded the same complex mixture of products (at least 4) in approximately the same relative yields. The individual products were not identified, although a complex mixture was expected in view of previous results obtained with higher alcohols [21]. An attempt to oxidise propene by bubbling it directly into a well-shaken flask containing a aqueous solution of $[Pd(dien)H_2O](ClO_4)_2$ yielded acetone.

Since both water and hydroxide ions can act as nucleophiles it was of interest to compare the influence of pH on the rate of oxidation of olefins in the presence of Na_2PdCl_4, $[Pd(en)(H_2O)_2](ClO_4)_2$ and $[Pd(dien)H_2O](ClO_4)_2$. It is well-known that the rate of oxidation of olefins in the presence of Na_2PdCl_4 is inversely proportional to the H^+ concentration [19], indicating that hydroxide ions are the attacking nucleophile. In the present work the initial rate of change of absorbance of the palladium(II)—allyl alcohol solution was measured as a function of acid concentration. Preliminary experiments indicated that both perchloric and sulphuric acids oxidised allyl alcohol to acrolein in the absence of palladium(II) salts and consequently could not be used as a source of protons. Accordingly phosphoric acid was used. When solutions of $[Pd(en)(H_2O)_2](ClO_4)_2$ were treated with allyl alcohol in the presence of phosphoric acid, an immediate change in the absorbance occurred on addition of the allyl alcohol, followed by a subsequent much slower change. An investigation of the initial rate of this subsequent change of absorbance, showed that it decreased steadily with increasing acid concentration in the same way as observed previously for Na_2PdCl_4 (see Table 1). However the acid dependence of the rate of change of absorbance in the presence of $[Pd(dien)H_2O](ClO_4)_2$ was more complex. There was the expected initial decrease in rate with increasing acid concentration up to an H^+ concentration of about 0.3 *M*. However on increasing the acid concentration still further the rate of change of absorbance increased steadily. (See Table 1.)

(ii) Methoxide attack on preformed platinum(II)—olefin complexes

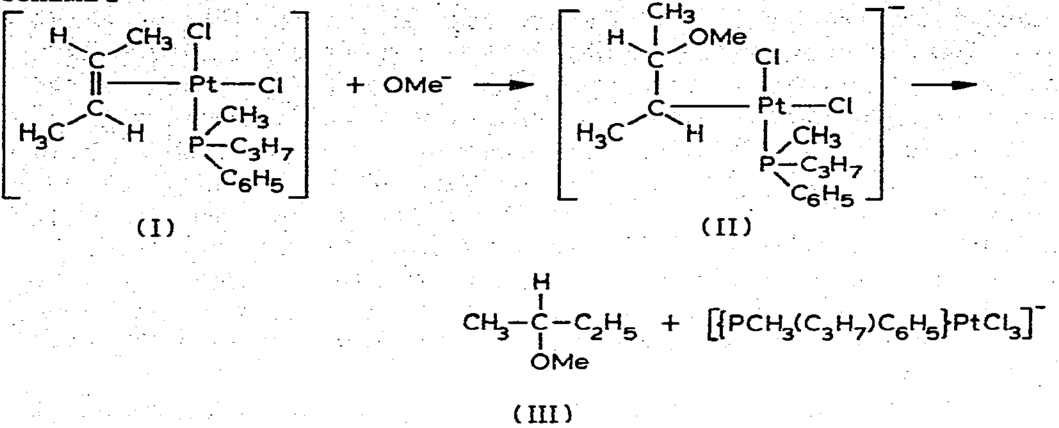
An attempt was made to determine the stereochemistry of methoxide

TABLE 1

INITIAL RATE OF CHANGE OF ABSORBANCE ($\Delta A/\Delta t$) OF PALLADIUM(II) SOLUTIONS ON ADDING ALLYL ALCOHOL IN THE PRESENCE OF PHOSPHORIC ACID

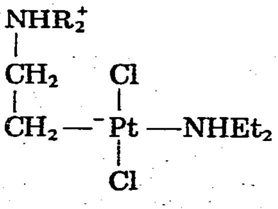
$[Pd(en)(H_2O)_2]^{2+}$		$[Pd(dien)H_2O]^{2+}$	
$[H^+]$ (*M*)	$\Delta A/\Delta t$ at 310 nm (abs. units/min)	$[H^+]$ (*M*)	$\Delta A/\Delta t$ at 300 nm (abs. units/min)
0	26.2×10^{-2}	0	39.5×10^{-4}
0.1	4.68×10^{-2}	0.1	2.92×10^{-4}
0.2	4.05×10^{-2}	0.3	2.42×10^{-4}
1.0	2.95×10^{-2}	1.0	2.45×10^{-4}
2.0	2.52×10^{-2}	1.2	3.72×10^{-4}

SCHEME 2



attack on platinum(II)—olefin complexes via Scheme 2. In this scheme *cis*-[$PtCl_2$(*trans*-2-butene)(PMePrPh)] (I) is prepared using optically pure PMePrPh. The two diastereoisomers of I are separated and the absolute configuration of one of these is determined by X-ray diffraction. This is then treated with methoxide ion to yield initially a platinum(II)—alkyl derivative II which on subsequent treatment with hydrogen chloride should yield an optically pure ether III whose absolute configuration depends on the stereochemistry of the methoxide attack.

This approach failed because in addition to nucleophilic attack, methoxide ion reacts with complexes such as I to give both substitution of the olefin by methoxide ion and displacement of the olefin followed by dimerisation to give $[(PR_3)PtCl_2]_2$ [22]. Both these reactions lead to the presence of free olefin in solution which may react with the $[(PR_3)PtCl_2]_2$ that is formed to give $[(PR_3)PtCl_2(\text{olefin})]$. However, an approximately 1/1 mixture of the two possible diastereoisomers (PR_3 is an optically active tertiary phosphine) will be formed so that a mixture *d*- and *l*-ethers III will result. In addition we were unable to find conditions under which the intermediate alkyl II could be formed and was stable. In all cases where II was formed it underwent a rapid β-hydrogen elimination to yield a vinyl ether. This is perhaps not surprising in view of a recent report [23] that even alkyls such as IV, which are stabilized by internal zwitterion formation, are only stable when the amine is a secondary amine (not primary or tertiary), highly basic and relatively free from steric hindrance.



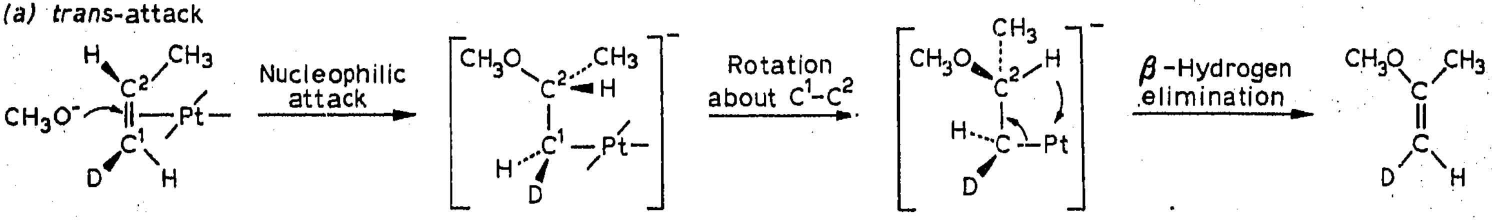
$$\begin{array}{lcl} NHR_2^+ & & \\ | & & \\ CH_2 & Cl & \\ | & | & \\ CH_2 — & {}^-Pt & —NHEt_2 \\ & | & \\ & Cl & \end{array}$$

(IV)

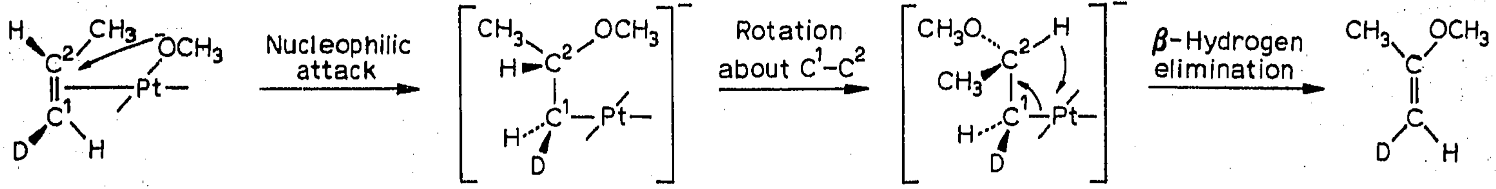
A second approach for investigating the stereochemistry of nucleophilic attack on preformed platinum(II)—olefin complexes is illustrated in Scheme 3. When a *trans*-1-deuteropropeneplatinum(II) complex is treated with a nucleo-

SCHEME 3

(a) *trans*-attack



(b) *cis*-attack



phile such as methoxide the initial product formed will be *cis*-1-deutero-2-methoxypropene if the nucleophilic attack occurs *trans* with respect to the platinum atom, but *trans*-1-deutero-2-methoxypropene if the attack is *cis*. In deducing these products we have made the reasonable assumption that the β-hydrogen elimination process takes place in a concerted reaction involving intermediate coordination to platinum, so that step 3 involves rotation about C_1—C_2 to enable this hydrogen to lie close to the platinum. When Zeise's dimer was treated with a solution of sodium carbonate in methanol no vinylic product could be detected. The only reactions that could be detected were displacement of the olefin and decomposition to give platinum metal, together with the formation of formaldehyde, the latter being formed by β-hydrogen elimination from an intermediate methoxy—platinum(II) complex. Since *cis*-[$(PPhEt_2)PtCl_2(C_2H_4)$] was known to react with methoxide ion to give about 30% yield of methyl vinyl ether, the propene analogue was similarly treated with methoxide ion. However the only detectable product was propene. It appears that the weaker platinum(II)—olefin bond in the propene complex has made the displacement reaction more facile than nucleophilic attack.

Discussion

In [Pd(dien)X] complexes three of the coordination sites around the palladium are blocked by the diethylenetriamine ligand. This leaves only one free site so that when X is an olefin it is impossible for nucleophilic attack on the olefin to take place in a *cis*-manner by prior coordination of the nucleophile to palladium(II). By contrast, of course, $[Pd(en)(olefin)X]^{2+}$ complexes have a vacant site suitable for the nucleophile to coordinate to. Furthermore, as a consequence of the bidentate nature of the ethylenediamine, this site is necessarily *cis* to the olefin. Accordingly, the observation that olefins are oxidised much more rapidly in the presence of $[Pd(en)(H_2O)_2]^{2+}$ than $[Pd(dien)H_2O]^{2+}$, both of which carry the same charge, can be readily understood. The fact that olefins are oxidised, albeit slowly, in the presence of $[Pd(dien)H_2O]^{2+}$ strongly suggests that if the favoured *cis*-attack is prevented then hydroxide ion attack on the olefin will occur on the side remote from palladium. The apparently anomalous proton concentration dependence of the rate of oxidation of olefins in the presence of $[Pd(dien)H_2O]^{2+}$ provides further support for this. Thus at acid concentrations of less than 0.3 *M* slow *trans*-attack of the double-bond occurs. When the acid concentration is increased above 0.3 *M* then, as has been shown previously [24], the protons begin to attack the diethylemetriamine ligand, initially displacing one of the nitrogen atoms to yield $[Pd(NH_2CH_2CH_2NHCH_2CH_2NH_3)(olefin)(H_2O)]^{3+}$ in which diethylenetriamine is bidentate and a water ligand is coordinated *cis* to the olefin. *cis*-Attack can now take place on the olefin and consequently the rate of oxidation rises.

In conclusion it would appear that hydroxide ions can react with olefins cooordinated to palladium(II) by either a *cis*- or a *trans*-mechanism (Scheme 1). The *cis*-mechanism, which involves prior coordination of the hydroxide to the palladium, has a significantly lower activation energy than *trans*-attack so that the latter will only be observed when *cis*-attack has been prevented by the nature of the complex. Somewhat similar results have been observed for chloride attack on coordinated olefins where *cis*-attack is the preferred route but some *trans*-attack does also occur [12,13].

Our failure to find routes by which preformed metal—olefin complexes could be used to determine the stereochemistry of nucleophilic attack is disappointing as the results of such work ought to be more clear-cut than the results of reactions in which the actual metal—olefin complex is never isolated from solution and consequently never fully characterised.

Experimental

Preparation of complexes

[Pd(dien)I]I. $PdCl_2$ (5 g, 27.5 mmole) was suspended in water (25 ml) and diethylenetriamine (5 ml; 50 mmole) added. After vigorously swirling on a boiling water-bath for 5 min, the greenish-yellow solution was treated with animal charcoal and filtered to give a clear yellow filtrate. The pH of the solution was reduced to 6 by dropwise addition of 6 *N* hydrochloric acid. After cooling, excess sodium iodide (10 g) was added and a yellow precipitate was formed. This was filtered off, washed with ice-cold water, ethanol and ether and recrystallised from water. Yield 6.0 g, 46%. (Found: C, 10.45; H, 2.79; N, 9.04. $C_4H_{13}I_2N_3Pd$ calcd.: C, 10.37; H, 2.83; N, 9.07%.) Previous workers have noted difficulties in recording the UV-visible spectrum of this compound. One group [25] reported a peak at 370 nm with an extinction coefficient of 500 l mole^{-1} cm^{-1}; a second group [26] reported a peak at 370 nm with an extinction coefficient that was dependent on concentration reaching a maximum value of 680 l mole^{-1} cm^{-1}. The present sample exhibited a maximum absorbance at 372 nm and had an extinction coefficient that was independent of concentration (ϵ 605 at 2.74 10^{-3} moles/l and ϵ 604 at 2.74 10^{-4} moles/l).

[Pd(dien)H$_2$O](ClO$_4$)$_2$. A suspension of [Pd(dien)I]I (2.18 g; 4.7 mmole) in water (10 ml) was treated with silver perchlorate (1.95 g; 9.4 mmole). A rapid precipitation of silver iodide occurred. The solution was heated for 15 min on a boiling water-bath to ensure complete reaction before filtering off the silver iodide precipitate. After washing the precipitate with hot water the combined filtrates were evaporated to 5 ml on a boiling water-bath before placing the solution in a desiccator over phosphorus pentoxide. Yellow crystals deposited which were filtered off and dried over phosphorus pentoxide in vacuo. Yield 1.17 g, i.e. 58%. (Found: C, 10.82; H, 3.25; N, 9.67. $C_4H_{15}Cl_2N_3O_9Pd$ calcd.: C, 11.27; H, 3.55; N, 9.85%.) The UV-visible spectrum (700—220 nm) showed only a single peak at 316 nm (ϵ 665 l mole^{-1} cm^{-1}).

[Pd(en)Cl$_2$]. This was prepared by the literature method [27]. (Found: C, 10.23; H, 3.28; N, 11.61. $C_2H_8Cl_2N_2Pd$ calcd.: C, 10.12; H, 3.40; N, 11.80%.)

[Pd(en)(H$_2$O)$_2$](ClO$_4$)$_2$. This was prepared in solution by treating [Pd(en)Cl$_2$] with two equivalents of silver perchlorate. After warming to coagulate the precipitate the solution was filtered through a Whatman 42 fine grade filter paper.

Platinum complexes

Zeise's dimer was prepared as described previously [28] from Zeise's salt [29]. *cis*-[(PR$_3$)PtCl$_2$(olefin)] was prepared from [(PR$_3$)PtCl$_2$]$_2$ [30] using the standard procedure [31].

Kinetic studies

The kinetics of the oxidation of allyl alcohol to acrolein in the presence of $[Pd(dien)H_2O](ClO_4)_2$ were studied as follows: 2 ml of a solution of $[Pd(dien)H_2O](ClO_4)_2$ (0.0387 g in 10 ml of water i.e. 9.05 10^{-3} *M*) was pipetted into a 10 ml flask. The appropriate volume of a 5 *M* solution of phosphoric acid was added and the volume made up to about 8 ml. 1 ml of twice redistilled allyl alcohol (b.p. 97.5—97.75°) was added, the volume made up to 10 ml as rapidly as possible and the absorbance recorded against time. It took about 90 sec from the time the allyl alcohol was added until the first absorbance reading was obtained. In the case of $[Pd(dien)H_2O](ClO_4)_2$ the reaction was relatively slow, and so four solutions were placed in the spectrophotometer at once and their absorbances recorded every two minutes using the programme controller and digital printer. For $[Pd(en)(H_2O)_2](ClO_4)_2$ the reaction was faster and so the absorbance of each solution at 310 nm was plotted on a chart recorder. Since palladium metal was deposited on the cell windows after some time it was impossible to carry out a traditional kinetic analysis [32] since the absorbance at infinite time could not be measured, nor, because of the nature of the products formed, could it be calculated with any accuracy. Accordingly plots of absorbance against time were prepared and their initial slopes measured by drawing a suitable tangent.

GLC analysis

GLC analyses were performed on a Perkin—Elmer model 452 gas chromatograph fitted with a flame ionisation detector. The oven was maintained at 150° and a 2-metre column, packed with diatomite coated with polypropyleneglycoladipate (15% w/w), was used. The products were identified by comparison of their retention times with those of authentic samples. During the course of confirming that one of the products was acetone we made the interesting observation that although very dilute aqueous solutions of acetone in water gave rise to a single broad GLC peak, more concentrated solutions gave rise to a second sharper peak with a lower retention time (see Fig. 1). This result, which was independent of the source of the acetone [3 sources of analytical grade $(CH_3)_2CO$ and 1 of $(CD_3)_2CO$ were used] was explained by suggesting that the first sharp peak was due to acetone alone (this was confirmed by its coincidence with the

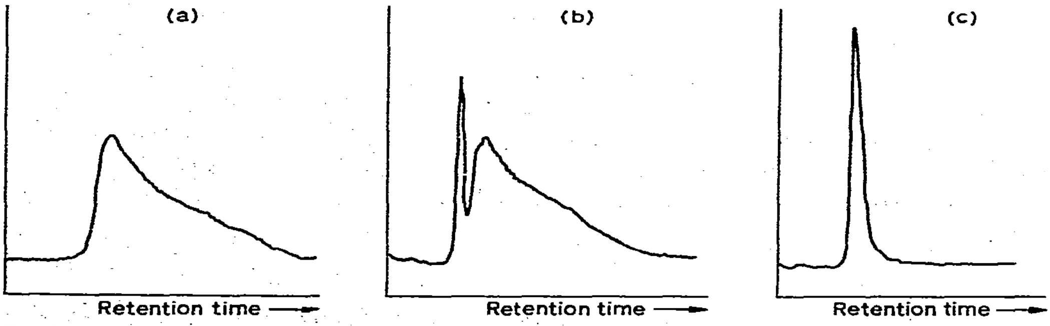


Fig. 1. GLC traces for (a) very dilute aqueous acetone (sensitivity 1), (b) more concentrated solution of acetone in water (sensitivity 1/6) and (c) neat acetone (sensitivity 1/400).

position of the peak obtained from neat acetone) and the second broader peak was due to aquated acetone. The observation of the free acetone peak only in the more concentrated samples is consistent with this explanation.

UV-visible spectra

A Unicam SP1700A spectrophotometer, provided with an SP1805 programme controller, SP1803 wavelength selector and DR10 printer was used. The cell compartment was thermostatted at 25° using a Tecam Tempunit.

Microanalyses

Microanalyses were carried out in the Chemistry Department at University College, London.

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Note added in proof

Since the completion of the methoxide section of this work J.K. Stille, D.E. James and L.F. Hines (J. Amer. Chem. Soc., 95 (1973) 5062) have used a catalytic system to show that methoxide ion attack on 2-butene coordinated to palladium(II) occurs *trans* with respect to the metal.