Displacement of 2,2′-Bipyridyl as an Intermediate Step in the Reaction of 2,2′-Bipyridyl(diethyl)platinum(II) with Methyl Acrylate

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2 2′-Bipyridyl(diethyl)platinum(II) reacts with methyl acrylate to give ethylene and [Pt{CH(Me)(CO_2Me)}$_2$(bipy)]. A study of the kinetics of the reaction has shown that it is first order in the concentrations of both the platinum complex and methyl acrylate and is strongly retarded in the presence of free bipy. The mechanism is thought to involve an initial displacement of bipy from platinum by methyl acrylate followed by β elimination of ethylene from the ethylplatinum groups, insertion of methyl acrylate into the resulting Pt–H bonds, and reco-ordination of bipy.

THERE has been considerable interest recently in the mechanism of reaction of alkenes and alkynes with methylplatinum(II) and hydridoplatinum(II) complexes. Thus for insertion of ethylene into the Pt–H bond of *trans*-[PtH(OCMe$_2$)(PEt$_3$)$_2$]$^+$ it has been established[1,2] that reaction takes place *via* a four-co-ordinate intermediate *trans*-[Pt(C_2H_4)H(PEt$_3$)$_2$]X which then gives three-co-ordinate [PtEt(PEt$_3$)$_2$]$^+$. The reverse β-elimination reaction from [PtBu$^n_2$(PPh$_3$)$_2$] also involves formation of a three-co-ordinate intermediate [PtBu$^n_2$(PPh$_3$)] from which β elimination of butene actually occurs.[3] Similarly insertion reactions of alkenes and alkynes with methylplatinum(II) complexes take place most readily if there is a ligand which can dissociate easily, suggesting that co-ordinatively unsaturated intermediates are again formed.[4,5] However, methylplatinum complexes are less reactive than hydridoplatinum complexes towards insertion reactions, and such reactions only take place with alkenes and alkynes with electronegative substituents.[5,6] No kinetic studies on such reactions have yet been reported.

We recently prepared some alkyl- and aryl-platinum(II) complexes stabilised by the ligand 2,2′-bipyridyl (bipy).[7] In many ways these complexes are considerably more reactive than the more usual complexes with tertiary phosphine or arsine ligands. They are highly coloured,[7] which makes kinetic studies convenient since the reaction course can be monitored by the u.v. spectra, and, since similar complexes of Ni^{II} and Pd^{II} are known, it is possible to compare reactivity and mechanism for analogous complexes in the same Group of the Periodic Table.[8] The reactions of [PtMe(X)bipy)] (X = Cl or I) with some acetylenes have been reported earlier,[8,9] and intermediates of the type [PtMe(acetylene)(bipy)]X were identified in some reactions.[9] We considered, however, that dialkyl(2,2′-bipyridyl)platinum(II) complexes probably react with alkenes and alkynes *via* five-co-ordinate intermediates since they contain no ligand which is likely to dissociate readily.[9] In many of these reactions the products have low solubility and are hence difficult to characterise fully, but we found that 2,2′-bipyridyl(diethyl)platinum(II) reacted cleanly with methyl acrylate to give a well characterised platinum complex and ethylene. A five-co-ordinate intermediate of the type proposed earlier should be unable to β-eliminate ethylene, and in order to determine the mechanism we have now studied the kinetics of the reaction. We were surprised to find that the good chelate ligand bipy appears to dissociate from platinum at an intermediate stage of reaction.

RESULTS

Preparation of [Pt{CH(Me)(CO_2Me)}$_2$(bipy)].—Methyl acrylate (5 cm^3) was condensed into a flask containing [PtEt$_2$(bipy)] (0.089 g, 0.22 mmol) under high vacuum by cooling in liquid nitrogen. The flask was allowed to warm to room temperature and the contents were stirred *in vacuo* for 4 h at room temperature and then at 50 °C for 2 h until no further colour change took place. The colour of the solution changed from red to yellow, and a gas was evolved. The flask was opened to the vacuum line and the volume of gas was measured (*ca.* 0.4 mmol). The gas was then identified as pure ethylene (with no ethane) by its g.l.c. retention time and its mass spectrum. The volume of solvent was reduced from the remaining solution and diethyl ether was added to precipitate the *product* as a yellow powder (0.030 g, 26%). More product was obtained by cooling the filtrate to 0 °C overnight, m.p. 250 °C (decomp.); n.m.r. spectrum in CDCl$_3$ $\delta(CH_3O)$ 3.6 [^5J(PtH) 5], $\delta(CH_3C)$ 1.3 (d) [^3J(HH) 7, ^3J(PtH) 60], and δ(CH) 1.9 (q) p.p.m. [^3J(HH) 7 Hz]; i.r. spectrum ν(CO) at 1 690s and 1 670s cm^{-1} (Found: C, 41.3; H, 4.0; N, 5.5. Calc. for $C_{18}H_{22}N_2O_4Pt$: C, 41.1; H, 4.2; N, 5.3%). The mass spectrum did not give a parent ion but major peaks were at *m/e* 438 [$P - C_4H_7O_2$]$^+$, 407 [$P - C_4H_6O_4$]$^+$, 379 [$P - C_6H_{10}O_4$]$^+$, and 351 [$P - C_8H_{14}O_4$]$^+$. Thermal decomposition of the complex gave methyl propionate and methyl acrylate which were identified by their g.l.c. retention times and mass spectra by comparison with authentic

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[1] H. C. Clark and C. R. Jablonski, *Inorg. Chem.*, 1974, **13**, 2213.

[2] H. C. Clark and C. S. Wong, *J. Amer. Chem. Soc.*, 1974, **96**, 7213.

[3] G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5258.

[4] M. H. Chisholm and H. C. Clark, *Accounts Chem. Res.*, 1973, **6**, 202.

[5] H. C. Clark, C. R. Jablonski, and K. von Werner, *J. Organometallic Chem.*, 1974, **82**, C51.

[6] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1970, **9**, 2670.

[7] N. Chaudhury and R. J. Puddephatt, *J. Organometallic Chem.*, 1975, **84**, 105.

[8] N. Chaudhury, M. G. Kekre, and R. J. Puddephatt, *J. Organometallic Chem.*, 1974, **73**, C17.

[9] N. Chaudhury and R. J. Puddephatt, *J. Organometallic Chem.*, 1975, **87**, C45.

samples. The u.v. spectrum in ethyl acetate solution ($\lambda_{max.}$ 440 nm, ε 1 300 dm^3 mol^{-1} cm^{-1}) was identical with that of the final product in the kinetic runs.

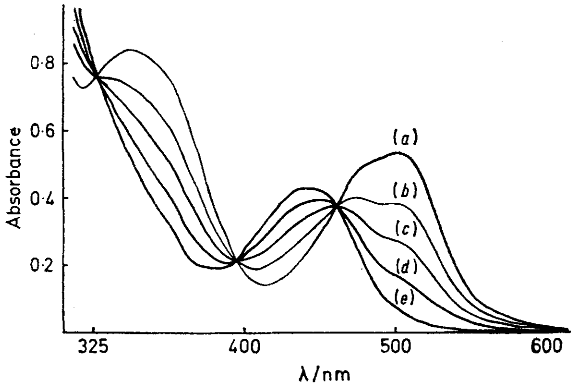


FIGURE 1 Changes in the u.v. spectra during the reaction with methyl acrylate (1.203 mol dm^{-3}) in ethyl acetate at 46 °C. Spectra recorded after: (*a*) 5; (*b*) 25; (*c*) 47; (*d*) 85; and (*e*) 130 min

Kinetic Studies.—The reaction rate was studied by following changes in the u.v. spectrum of the reaction mixture, which was set up in 1-cm quartz cells held in the electrically heated thermostatted cell compartment of a Pye Unicam SP 8000 spectrophotometer. Typical u.v. spectra obtained during the course of reaction are shown in Figure 1. The u.v. spectrum of [PtEt$_2$(bipy)] in ethyl acetate and in methyl acrylate were essentially identical when freshly prepared. Clear isosbestic points were observed at 460, 395, and 325 nm in all cases. The concentration of [PtEt$_2$(bipy)] used was always *ca.* 2 × 10^{-4} mol dm^{-3}. The absorbance values at 500 nm were used to calculate the rate constants. Plots of log($A_t - A_\infty$) against time gave good linear graphs showing a first-order dependence of the rate on the concentration of the platinum complex (Figure 2).

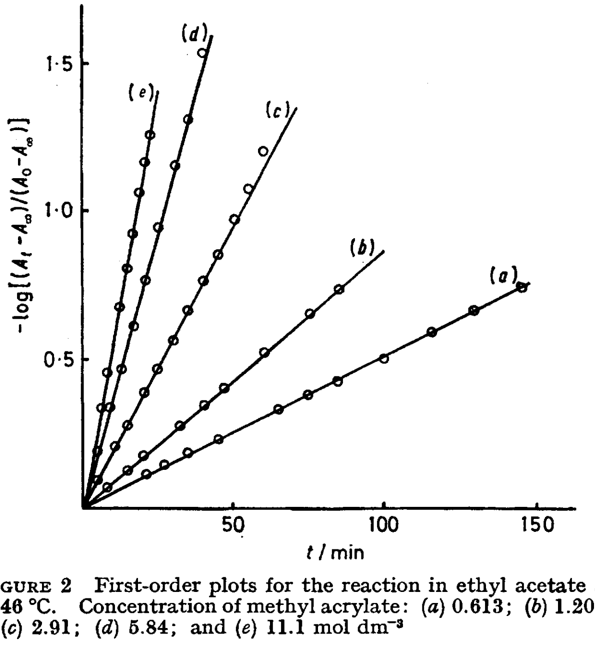


FIGURE 2 First-order plots for the reaction in ethyl acetate at 46 °C. Concentration of methyl acrylate: (*a*) 0.613; (*b*) 1.203; (*c*) 2.91; (*d*) 5.84; and (*e*) 11.1 mol dm^{-3}

Dependence of rate on the concentration of methyl acrylate. Solutions of methyl acrylate in ethyl acetate of known concentration were prepared, and the required quantity of [PtEt$_2$(bipy)] was dissolved immediately before beginning to collect the data. The results are given in Table 1 and are plotted in Figure 3. The observed rate constants were proportional to the concentration of methyl acrylate over the lower concentrations used, but tailed off at higher concentrations. Considering the high concentrations necessary, which are expected to lead to difficulties due to changing the dielectric constant of the solvent as the concentrations are changed, the data are considered satisfactory evidence for a first-order dependence of the rate on the concentration of methyl acrylate.

TABLE 1

Dependence of the pseudo-first-order rate constants on the concentration of methyl acrylate for the reaction in ethyl acetate–methyl acrylate mixtures at 46 °C

[CH$_2$=CHCO$_2$Me]/ mol dm^{-3}	k/min^{-1}
0.613	0.0118
1.203	0.0196
2.91	0.0436
5.84	0.0876
11.1 *	0.1324

* Neat methyl acrylate.

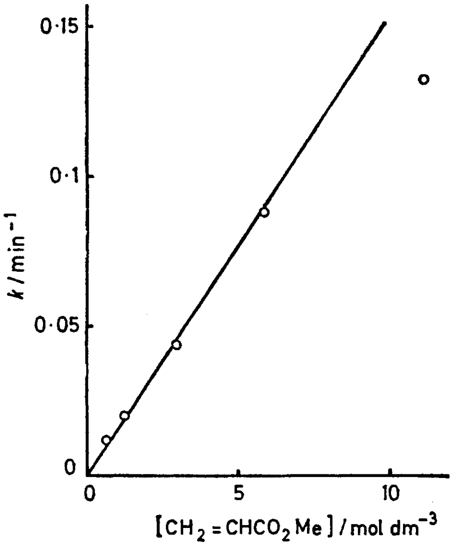


FIGURE 3 Dependence of the pseudo-first-order rate constant (k) on the concentration of methyl acrylate for the reaction in ethyl acetate at 46 °C

Dependence of the rate on the concentration of 2,2′-*bipyridyl.* Preliminary studies showed that bipy did not interact with either [PtEt$_2$(bipy)] or with the reaction product. Thus the u.v. spectra were identical in the presence or absence of bipy, so that the effect of free bipy on the rate of reaction must be due to its reaction with a reaction intermediate rather than with the starting material. The reactions were carried out by preparing solutions of bipy (10^{-2}—10^{-3} mol dm^{-3}) in methyl acrylate and dissolving the required amount of [PtEt$_2$(bipy)] in each solution immediately before starting to collect data. Good pseudo-first-order kinetics were observed in each case. The data are given in Table 2. A plot of $1/k_{obs.}$ (where $k_{obs.}$ is the pseudo-first-order rate constant) against concentration of bipy is shown in Figure 4 and gave a straight line of equation $1/k_{obs.} = 6\,580[\text{bipy}] + 7.5$.

TABLE 2

Dependence of the pseudo-first-order rate constants on the concentration of added bipy for the reaction in pure methyl acrylate at 46 °C

10^3[bipy]/mol dm^{-3}	k/min^{-1}
0	0.1324
1.02	0.0672
2.08	0.0398
4.16	0.0230
4.38	0.0260
6.24	0.0217
8.75	0.0154
10.3	0.0138
8.92 *	0.11

* Concentration of added pyridine. Deviations from first-order kinetics were observed beyond 50% completion of reaction.

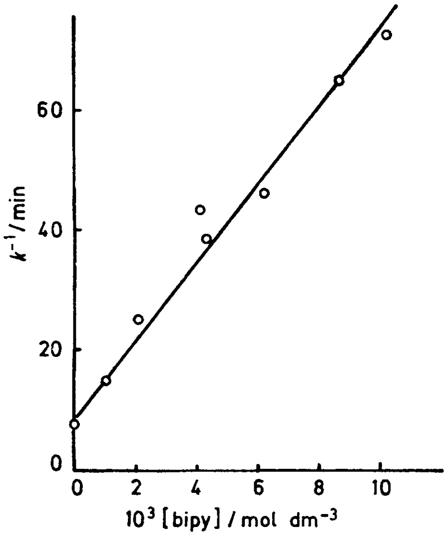


FIGURE 4 Dependence of the pseudo-first-order rate constant (k) on the concentration of added bipy for the reaction in pure methyl acrylate at 46 °C

TABLE 3

Temperature dependence of the pseudo-first-order rate constants for the reaction in pure methyl acrylate

θ_c/°C	k/min^{-1}
32.5	0.0304
34.5	0.0389
43.5	0.1002
46.0	0.1324
51.2	0.2280

Temperature dependence of the rate of reaction. The rate constants were determined in pure methyl acrylate over the temperature range 32.5—51.2 °C. The results are given in Table 3 and an Arrhenius plot is shown in Figure 5. The activation parameters $E^{\ddagger} = 91.9$ kJ mol^{-1} and $\Delta S_{300}^{\ddagger} = -30.7$ J K^{-1} mol^{-1} were calculated, based on the second-order rate constants and taking the concentration of methyl acrylate as 11.1 mol dm^{-3}.

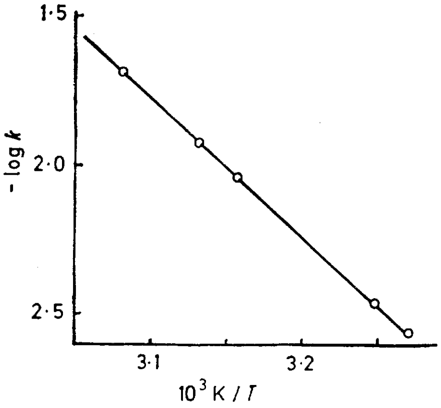
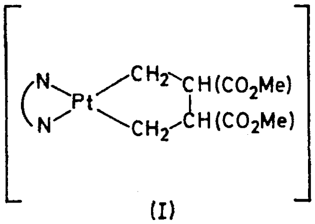


FIGURE 5 Arrhenius plot for the reaction in pure methyl acrylate

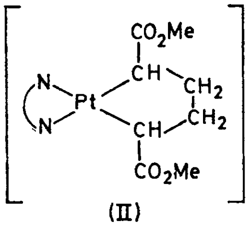
DISCUSSION

Methyl acrylate reacted with [PtEt$_2$(bipy)] [7] to give ethylene and [Pt{CH(Me)(CO$_2$Me)}$_2$(bipy)] according to equation (i). The ethylene formed was free from ethane as shown by gas chromatography, so that a mechanism involving formation of ethyl radicals [10] can be discounted. The product was characterised by elemental analysis and by its spectroscopic properties. Possible structures which were considered are shown in (I)—(IV) where N–N = 2,2′-bipyridyl.

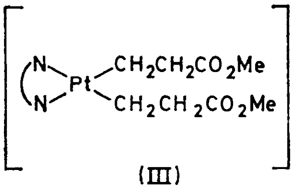
$$[\text{PtEt}_2(\text{bipy})] + 2\text{CH}_2{=}\text{CHCO}_2\text{Me} \longrightarrow [\text{Pt}\{\text{CH(Me)(CO}_2\text{Me)}\}_2(\text{bipy})] + 2\text{C}_2\text{H}_4 \quad \text{(i)}$$



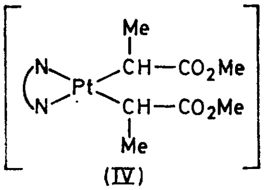
(I)



(II)



(III)



(IV)

Structures (I) and (II) can be excluded because their formation would be expected to be accompanied by equal quantities of ethylene and ethane rather than by ethylene alone and are also inconsistent with the n.m.r. data. Structures (III) and (IV) would each be given in a mechanism involving β elimination of ethylene

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[10] N. G. Hargreaves, R. J. Puddephatt, L. H. Sutcliffe, and P. J. Thompson, *J.C.S. Chem. Comm.*, 1973, 861.

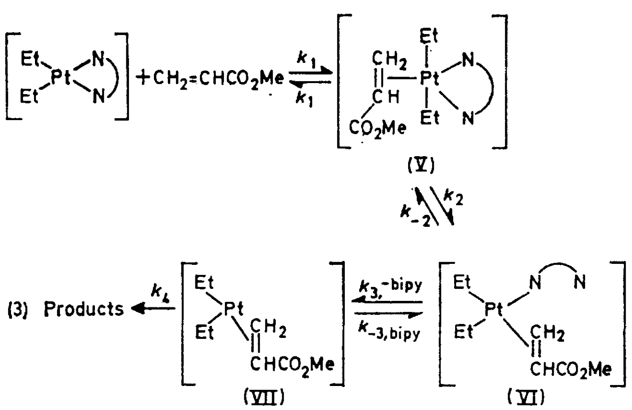
followed by insertion of methyl acrylate into the Pt–H bonds so formed. It has been suggested[2] that the product of insertion of methyl acrylate into the Pt–H bond of *trans*-$[PtH(NO_3)(PEt_3)_2]$ contains the $PtCH_2CH_2CO_2Me$ group, but the evidence given was not compelling and the spectral and chemical properties of our complex show that it contains the $PtCH(Me)(CO_2Me)$ group. The evidence is as follows. (*i*) The complex has high thermal stability, decomposing to give methyl acrylate and methyl propionate only at 250 °C, whereas $[PtEt_2(bipy)]$ decomposes very rapidly at >100 °C. It is well known that transition-metal alkyls are stabilised if there are electronegative substituents (such as CO_2Me) on the α-carbon atom of the alkyl group, so that complex (IV) is expected to be considerably more thermally stable than (III). (*ii*) The lowest-energy band in the u.v. spectra of complexes $[PtR_2(bipy)]$ is due to metal to ligand charge transfer, and its energy has been found to be dependent on the Hammett σ-value of the group R.[7] The band energy for the above complex in ethyl acetate is at 440 nm, which is at somewhat higher energy than for $[PtPh_2(bipy)]$ (450 nm) and considerably higher energy than for $[PtEt_2(bipy)]$ (500 nm). Thus the alkyl group should have a σ_p value slightly higher than that of the phenyl group, suggesting the structure $CH(Me)(CO_2Me)$ rather than $CH_2CH_2CO_2Me$. (*iii*) The n.m.r. spectrum of the complex which crystallised from solution showed a doublet at δ 1.3 p.p.m. and a quartet at δ 1.9 p.p.m. with relative areas *ca.* 3 : 1, confirming the presence of the $PtCH(Me)(CO_2Me)$ group. The peak due to the CO_2CH_3 protons showed clear satellites due to coupling with ^{195}Pt, and such coupling to CO_2Me protons has only been observed previously when the CO_2Me group is attached to a carbon atom bound directly to platinum,[11] again supporting structure (IV). Since structure (IV) contains two asymmetric carbon atoms bonded to platinum, it would be expected to exist as a mixture of *meso* and *rac* diastereoisomers having different physical properties. The observation of only one CH_3O singlet and one CH_3C doublet (the quartet due to the CH proton was partially obscured by the low-field ^{195}Pt satellite of the CH_3C doublet) suggested that only one of the possible isomers was formed. However, the n.m.r. spectrum of the crude product obtained by evaporation of the solvent from the reaction mixture did give an extra singlet (δ 3.5 p.p.m.) and an extra doublet [δ 1.25 p.p.m., *J*(HH) 7 Hz] with intensities about one quarter of those of the corresponding peaks due to the other isomer, so that it appears that the product does exist as a mixture of isomers with the major product crystallising out preferentially. The u.v. spectra of the samples were identical suggesting very similar structures for the two complexes, but we have been unable to separate the minor product in pure form and we do not know if the *meso* or the *rac* isomer is the major product.

Mechanism of Reaction.—The u.v. spectra show that no long-lived intermediates are formed in the reaction, and the simplest mechanism which is consistent with the kinetic data, which indicate that the reaction is first order in the concentration of both $[PtEt_2(bipy)]$ and methyl acrylate and is retarded by free bipy, is shown in equations (1) and (2). If the stationary-state approximation is made for $[PtEt_2(CH_2{=}CHCO_2Me)]$, the rate expression is $-d[PtEt_2(bipy)]/dt = k_1k_2[PtEt_2(bipy)][CH_2{=}CHCO_2Me]/(k_{-1}[bipy] + k_2)$, agreeing with the observed expression, and for the reaction at 46 °C in neat methyl acrylate would give $k_1[CH_2{=}CHCO_2Me] = 0.13\ min^{-1}$ and $k_{-1}/k_2 = 870\ dm^3\ mol^{-1}$.

$$[PtEt_2(bipy)] + CH_2{=}CHCO_2Me \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PtEt_2(CH_2{=}CHCO_2Me)] + bipy \quad (1)$$

$$[PtEt_2(CH_2{=}CHCO_2Me)] \xrightarrow{k_2} \text{Products} \quad (2)$$

The important step is the displacement of the stabilising ligand bipy from platinum by methyl acrylate. By analogy with the known mechanism of displacement of chelate ligands from other square-planar complexes,[12,13] it is likely that this displacement occurs in several steps as shown in equation (3) (N–N = bipy).* Provided that all intermediates are short-lived, this scheme is again consistent with the data but none of the rate constants can be determined. In equation (3) it is suggested that (VI) decomposes by simple dissociation of the unidentate bipy, but it is also possible that this ligand is displaced by the ester group of the solvent mixture or by the carbonyl group of the co-ordinated methyl acrylate.



An alternative explanation of the retarding effect of bipy is that it might interact by an associative mechanism

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* A trigonal-bipyramidal rather than a square-pyramidal structure for (V) is suggested by analogy with known structures of five-co-ordinate platinum–acetylene complexes.[14]

[11] T. G. Appleton, M. H. Chisholm, H. C. Clark, and K. Yasufuku, *J. Amer. Chem. Soc.*, 1974, **96**, 6600.

[12] G. Annibale, L. Cattalini, A. A. El-Awady, and G. Natile, *J.C.S. Dalton*, 1974, 802.

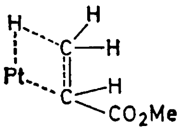
[13] G. Annibale, L. Cattalini, and G. Natile, *J.C.S. Dalton*, 1975, 188.

[14] B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Canad. J. Chem.*, 1972, **50**, 2276; T. Theophanides and P. C. Kong, *ibid.*, 1970, **48**, 1084; J. Hubert and T. Theophanides, *Inorg. Chim. Acta*, 1969, **3**, 391.

with the intermediate (VI) to give an unreactive complex with two unidentate bipy ligands. This possibility is however inconsistent with the observation that no long-lived intermediates are formed in the reaction, as established earlier, and is also inconsistent with the observed kinetic expression. If this mechanism operated one would expect pyridine (py) to be similar to bipy in retarding the reaction but we find that py has only a small effect on the rate (Table 2). We conclude therefore that the mechanism in equation (3) operates and that bipy is completely dissociated from platinum in the reactive intermediate.

The final product is likely to be formed from the intermediate (VII) by the following series of steps: (*i*) β elimination of ethylene from an ethylplatinum group to give a platinum hydride (the ethylene would be quickly displaced from platinum by methyl acrylate); (*ii*) insertion of a co-ordinated methyl acrylate into the Pt–H bond to give the PtCH(Me)(CO$_2$Me) group; (*iii*) repetition of steps (*i*) and (*ii*) for the second ethylplatinum group to give [Pt{CH(Me)(CO$_2$Me)}$_2$(CH$_2$=CHCO$_2$Me)]; and (*iv*) co-ordination of bipy with displacement of methyl acrylate to give the final product.

The intermediate (VII), having a vacant co-ordination site on platinum in the square plane, is expected to undergo β elimination of ethylene readily,[3] whereas [PtEt$_2$(bipy)] is less reactive to β elimination and the intermediate (V), being co-ordinatively saturated, could not undergo β elimination. It is clear therefore why it is necessary for the bipy to be displaced before β elimination takes place. Similarly insertion reactions into the Pt–H bond take place *via* co-ordinatively unsaturated alkene(hydrido)platinum(II) complexes, so that the insertion of methyl acrylate into the Pt–H bond formed is also expected to be rapid.[5] The insertion step is likely to involve a transition state (VIII) in which some Pt–C σ-bond character has developed. The preferred stereochemistry of the insertion reaction may therefore be due to the greater strength of the incipient Pt–C bond when the PtCH(Me)(CO$_2$Me) group rather than the PtCH$_2$CH$_2$CO$_2$Me group is formed.



(VIII)

The more general conclusion from this work is that co-ordinatively unsaturated intermediates or intermediates in which one or more of the co-ordination sites in a square-planar complex is occupied by weakly bound solvent molecules must be expected in insertion reactions of alkenes and alkynes with hydrido- and alkylplatinum(II) complexes even in those cases where one would not normally expect ligand dissociation to occur readily. We reported earlier that the reactivity of the alkyl derivatives of Ni^{II}, Pd^{II}, and Pt^{II} towards alkenes and alkynes is largely determined by the energy of the *d* orbitals on the metal,[8] and interpreted this in terms of the rate-determining step being formation of a five-co-ordinate intermediate in which the bonding between the metal and olefin or acetylene was due largely to donation of electron density from the metal to the unsaturated ligand. Since a dissociative mechanism is now established in many cases, this correlation cannot be expected to hold in all cases, and the reactivity may depend on the ease of ligand loss. However, since substitution reactions at square-planar metal centres usually take place by an associative mechanism, it is still possible that formation of the five-co-ordinate intermediate is rate determining in many cases. The activation parameters for the reaction of [PtEt$_2$(bipy)] with methyl acrylate (in the absence of bipy) refer to the displacement of bipy from platinum [equation (3)]. Since the entropy of activation is negative, it seems that the initial step to give the five-co-ordinate intermediate (V) may in fact be largely responsible since the k_2 and k_3 steps (being dissociative) would be expected to give positive contributions to $\Delta S^\ddagger$.

It is interesting to compare the product of this reaction with those from the corresponding reaction[15] of [NiEt$_2$(bipy)] which are butane and a mixture of [Ni(CH$_2$=CHCO$_2$Me)(bipy)] and [Ni(CH$_2$=CHCO$_2$Me)$_2$(bipy)]. In this case it seems that the intermediate five-co-ordinate complex [NiEt$_2$(CH$_2$=CHCO$_2$Me)(bipy)] undergoes reductive elimination of butane by coupling of the ethyl groups rather than dissociation of bipy followed by β elimination and insertion reactions. The factors responsible for this difference in behaviour are not yet understood.

Finally we note that the final product [Pt{CH(Me)(CO$_2$Me)}$_2$bipy)] has two asymmetric carbon atoms bound to platinum and so can exist as *meso* and *rac* isomers. The isomers are formed in unequal amounts, presumably as a result of asymmetric induction, with the chirality of the second asymmetric carbon atom formed being largely determined by the chirality of the first. Similar effects have been established previously in the asymmetric hydrogenation of alkenes using transition-metal catalysts with optically active ligands.[16]

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[5/1848 *Received, 25th September*, 1975]

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[15] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1971, **93**, 3350.

[16] W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J.C.S. Chem. Comm.*, 1972, 10.