Mechanism of the Redox Isomerisation of *af*-Dichloro-*bc*-bis(pyridine)-*de*-trimethyleneplatinum(IV) to the Platinum(II) Complex of Pyridinium Propylide [PtCl$_2$(C$_5$H$_5$NCHEt)(py)]

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Kinetic and other results on the reaction of *af*-dichloro-*bc*-bis(pyridine)-*de*-trimethyleneplatinum(IV) in benzene forming the platinum(II) ylide *trans*-[PtCl$_2$(C$_5$H$_5$NCHEt)(py)] are presented; a dissociative mechanism is suggested.

WHITE *af*-dichloro-*bc*-bis(pyridine)-*de*-trimethyleneplatinum(IV) (I) is formed on reaction of Tipper's compound [1-3] [PtCl$_2$(C$_3$H$_6$)]$_4$ with pyridine. Its crystal and molecular structures have been reported [4] as have those [4a,5] of the yellow platinum(II) ylide complex *trans*-[PtCl$_2$(C$_5$H$_5$NCHEt)(py)] (II) which is formed [2] by isomerisation of (I) in hot benzene. We report here some experiments on this reaction.

EXPERIMENTAL AND RESULTS

Previous Work.[4b]—(i) A saturated solution of (I) in CHBr$_3$ at 80 °C gave (II) in *ca.* 0·5 h, the n.m.r. spectrum

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[4] (*a*) N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *Chem. Comm.*, 1966, 396; (*b*) R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, *J. Organometallic Chem.*, 1971, **33**, 247.

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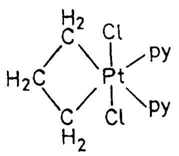
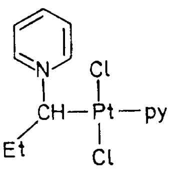
of (I) declining at the same rate as that of (II) grew. (ii) Analogues of (I) containing 3- or 4-picoline, in benzene solution, undergo rearrangement to the ylide species.



(I)



(II)

Products.—Both (I) and (II) were available as pure samples with known spectroscopic properties (n.m.r. and i.r.). Preliminary experiments showed that the yield of yellow (II) was never quantitative. Thus upon heating a solution of (I) in benzene, the concentration of (II) grew, then fell, and the maximum amount of (II) produced $[(\text{II})]_{\text{max.}}$ was, depending on conditions, $65\% < [(\text{II})]_{\text{max.}} < 75\%$ of the initial concentration of (I), $[(\text{I})]_0$. The average value of $[(\text{II})]_{\text{max.}}$ for 6 experiments at differing temperatures was $0{\cdot}71[(\text{I})]_0$; no general trend was observed in $[(\text{II})]_{\text{max.}}$ on varying the temperature. When $[(\text{II})]_{\text{max.}}$ was reached, t.l.c. showed that a small amount of (I) was still present, but this could not be detected in the n.m.r. spectrum (*i.e.* $<5\%$ $[(\text{I})]_0$).

The platinum balance $\{[(\text{I})]_0 - [(\text{II})]_t - [(\text{I})]_t\}$ at time t was made up by the *trans*-isomer of dichlorobis(pyridine)-platinum(II), (III). Solutions in benzene of (I), (II), or of (I) and (II) on prolonged heating formed (III) slowly, but quantitatively; there was no sign of any other long-lived intermediate in the system. In reacting solutions from initially pure (II) in hot benzene, tests by t.l.c. at frequent regular intervals showed that the only platinum-containing bodies present were (II) and (III), no (I) being formed from (II) under these conditions. In acetone, (I) was converted into (III), apparently directly, since there was no observable intermediate formation of (II).

Exchange Studies.—(i) Pyridine inhibited the yellowing of solutions of (I) in benzene. (ii) A solution of (I) in benzene was shaken, at room temperature, with a roughly 5M excess of deuteriopyridine. After 1 day, (I) was recovered; its i.r. spectrum showed that *ca.* $\frac{2}{3}$ of its original pyridine had been replaced by deuteriopyridine. T.l.c. showed some formation of (II) and (III). (iii) When (I) was kept in hot acetone, in the presence of added deuteriopyridine, the recovered 'unreacted' (I) and the (III) formed both contained ligated deuteriopyridine.

Rates.—Separation of (I), (II), and (III) was extremely difficult, owing to their similar solubilities, so that evaluation of [(I)] and [(III)] could not be made by a periodic sampling method. The reaction was therefore studied by observations of the electronic spectra of reaction mixtures using a Unicam SP 800 spectrophotometer. The Beer–Lambert law is obeyed by solutions of (II) (at 395 nm, $\varepsilon_{\text{max.}} = 0{\cdot}87 \times 10^3$ l mol^{-1} cm^{-1}) and (I) and (II) in benzene. However, it can be seen from Figure 1 that, in the presence of any measurable amount of (II), no spectrophotometric analysis for [(I)] or [(III)] could be made. Thus all measurements were necessarily of [(II)] as a function of time, temperature, $[(\text{I})]_0$, and [py].

(I) ⟶ (II): *Pyridine absent.* Measurements of the rate of formation of (II), at 10 different temperatures in the range 41—62 °C, were made using 1 cm cells for solutions with $[(\text{I})]_0$ in the range $0{\cdot}5 \times 10^{-3}$—$4{\cdot}0 \times 10^{-3}$M. Values of $A(\text{II})_t$, the absorbance of (II) at a particular time t, were obtained using the total absorbances of reaction mixtures at 395 nm, with corrections for the small absorbances of (I) and (III) at this wavelength; the 'infinity' value $A(\text{II})_\infty = \varepsilon(\text{II}) \times [(\text{I})]_0$. Straight line plots of $\ln\{A(\text{II})_\infty/[A(\text{II})_\infty - A(\text{II})_t]\}$ against time were obtained

We present these results in Figure 2, where they are modified as follows. The formation of (II) is the first stage of a competitive or consecutive reaction. From measurement, the ratio [(II)] : [(III)] *when* (II) *is increasing* is 71 : 29, so that the competitive reactions reduce $[(\text{II})]_t$ below that which would arise if (I) ⟶ (II) were the only reaction in the system. We therefore plot (Figure 2) the function $\ln\{A(\text{II})_\infty/[A(\text{II})_\infty - 1{\cdot}4A(\text{II})_t]$ against time. Straight lines were obtained for all experiments, and least-squares analysis consequently gave values of a rate constant k_f. From the variation of k_f with temperature, the Arrhenius activation energy (E_a) for the rate-determining step of the isomerisation was determined. The plot of ln k_f against $10^3/T$ is shown in Figure 3. These results were also analysed by least-squares treatment to give a value E_a of $31{\cdot}8 \pm 2{\cdot}7$ kcal mol^{-1}.

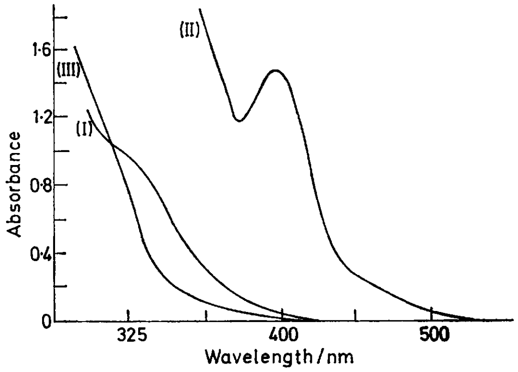


FIGURE 1 Electronic spectra in benzene

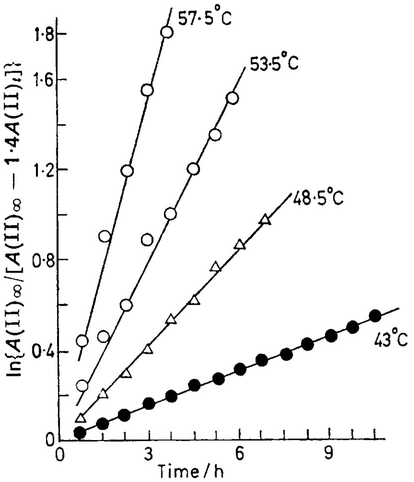


FIGURE 2 Plots of $\ln\{A(\text{II})_\infty/[A(\text{II})_\infty - 1{\cdot}4A(\text{II})_t]$ against time

(I) ⟶ (II): *Pyridine present.* The rates of formation of (II) from (I) in the presence of different concentrations of pyridine in the range 3×10^{-4}—17×10^{-4}M were measured at constant temperature (48·5 °C) with solutions of constant $[(\mathrm{I})]_0$ ($2{\cdot}117 \times 10^{-3}$M). As shown in Figure 4,

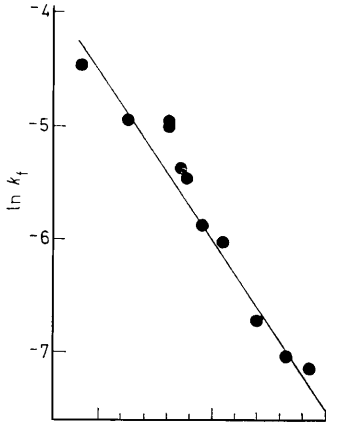


FIGURE 3 Arrhenius plot for the isomerisation of (I) to (II); values of k_f are in min^{-1}

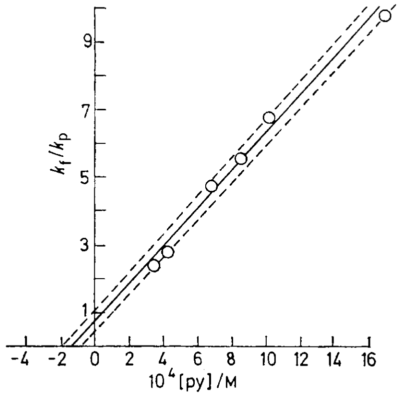


FIGURE 4 Plot of k_f/k_p against pyridine concentration for reactions at 48·5 °C. Standard deviations are indicated by dashed lines

values of k_f/k_p plotted against [py], give a straight line.

(II) ⟶ (III). Approximate values for the rate of conversion of (II) into (III) have been determined at three temperatures by measuring the rate of disappearance of (II) from solutions of pure (II) (initially $1{\cdot}292 \times 10^{-1}$M) in benzene. First-order rate constants k_4 are 5·3 (334), 1·5 (324), and 0·26 (313 K) $\times 10^{-4}$ min^{-1}. This slow reaction is also inhibited by pyridine.

DISCUSSION

In considering possible mechanisms, we may, from the non-kinetic experiments, apply certain boundary conditions at once. For example, the conversion of (I)

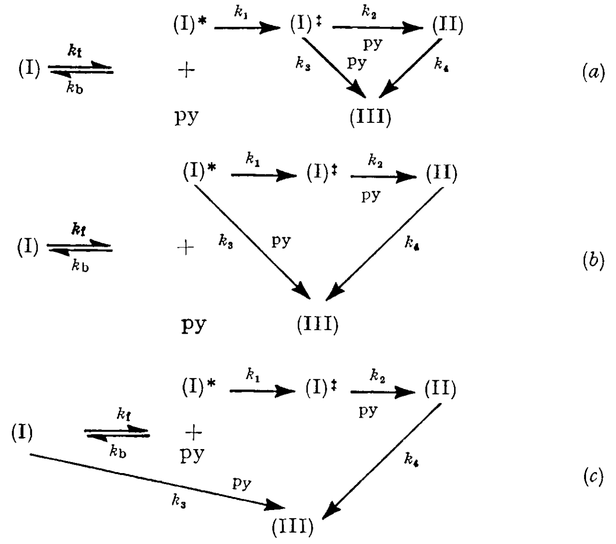
$$\begin{tikzcd}
(\mathrm{I}) \arrow[rr] \arrow[dr] & & (\mathrm{II}) \arrow[dl] \\
& (\mathrm{III}) &
\end{tikzcd} \qquad (1)$$

into (II) is, under our conditions, not reversible [since starting from pure (II) no (I) was formed, only (III)]. We are left with possible mechanisms based on the competitive scheme (1) and its variants, or the consecutive scheme (2). The latter we rule out on the ground

$$(\mathrm{I}) \longrightarrow (\mathrm{II}) \longrightarrow (\mathrm{III}) \qquad (2)$$

that the direct transformation of (II) into (III) is too slow to account for the measured ratio (III) : (II) = 0·4 : 1. We must also have direct formation of (III) from (I).

The detailed possibilities within (1) are shown in the Scheme, which also takes account of the kinetic findings. For example, the isomerisation of (I) to (II) is first order in [(I)] and inverse in [py]; this is consistent with a mechanism in which the rate-determining step is loss of pyridine to form a five-co-ordinate intermediate (I)* which then undergoes a further series of reactions to give the products (II) and (III). The three mechanisms 1(*a*—*c*) are kinetically indistinguishable and all can be shown to follow a rate equation of the general form (3).



SCHEME

Possible reaction pathways: (I)* and (I)‡ are five- and four-co-ordinated intermediates respectively.

$$d[(\mathrm{II})]/dt = \frac{k_f[(\mathrm{I})]}{(k'[\mathrm{py}] + 1)} - k_4[(\mathrm{II})] \qquad (3)$$

The only significant difference in the three rate equations is that for mechanisms (*b*) and (*c*) the k_f term includes the factor of 1·4 (discussed above).

Mechanism (*c*) seems a less likely path than that of (*a*) since on heating (I) in acetone in the presence of added deuteriopyridine, the (III) formed and the 'unreacted' (I) both contain deuteriopyridine ligand, indicating that the direct route from (I) to (III) (at least in acetone) goes *via* the pre-equilibrium (4). It is thus probable

$$(\mathrm{I}) \rightleftharpoons (\mathrm{I})^* + \mathrm{py} \qquad (4)$$

that the major reaction path is (*a*) or (*b*). The former is discussed in detail only because it is simpler. The k_f values derived from this treatment in terms of (*a*) are 1·4 times greater than those that result from treatments in terms of mechanisms (*b*) or (*c*). The E_a value is unaffected, as are the results of the pyridine inhibitions.

A number of approximations were used in the derivation of equation (5), the rate equation for mechanism (*a*).

$$\frac{d[(\mathrm{II})]}{dt} = \frac{k_1 k_f[(\mathrm{I})]_0}{1{\cdot}4(k_b[\mathrm{py}] + k_1)} - \left\{\frac{k_1 k_f}{(k_b[\mathrm{py}] + k_1)} + k_4\right\} [(\mathrm{II})] \quad (5)$$

$[(\mathrm{I})]_0$ = initial concentration of (I); $[(\mathrm{II})]$ = concentration of (II) at time t

(i) $k_4 \ll k_2$ and k_3 [k_2 and k_3 are specified as very large rate constants, relating to the reaction between pyridine and the short-lived reactive intermediate $(\mathrm{I})^\ddagger$]. (ii) The [(I)] present when [(II)] is maximal is small and has been neglected in setting $k_3 = 0{\cdot}4k_2$ and $[(\mathrm{III})] = 0{\cdot}4[(\mathrm{I})]$ {since $[(\mathrm{II})]:[(\mathrm{III})]$ at $[(\mathrm{II})]_{\max} = 71:29$ and $k_4 \ll k_2$ and k_3, this is also the ratio $k_2 : k_3$. Thus the ratios are valid at all times when [(II)] is increasing}. (iii) $d[(\mathrm{I})^*]/dt = 0 = d[(\mathrm{II})^\ddagger]/dt$ (steady-state approximation). (iv) The pyridine which arises from equation (4) has a negligibly small concentration compared with that added as an inhibitor.

Terms in k_4 [the rate constant for the formation of (III) from (II)] are assumed to be negligibly small; direct measurements of k_4 show it to be *ca.* 25 times smaller than k_f so that it falls outside the 10% reliability factor of the results. The integrated rate equation thus becomes that of (6). When [py] = 0,

$$\ln \frac{[(\mathrm{I})]_0}{[(\mathrm{I})]_0 - 1{\cdot}4[(\mathrm{II})]} = \frac{k_f}{(1 - k_b[\mathrm{py}]/k_1)}\, t \quad (6)$$

i.e. no pyridine is added to the solution, equation (6) simplifies to that of (7). Thus the rate-determining

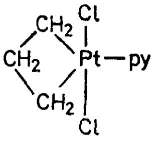
$$\ln \frac{[(\mathrm{I})]_0}{[(\mathrm{I})]_0 - 1{\cdot}4[(\mathrm{II})]} = k_f t \quad (7)$$

step is the forward step in equation (4). Experimental results have been successfully interpreted on this basis, as shown in Figure 2.

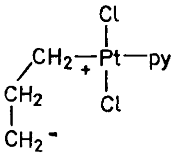
In the presence of inhibiting pyridine the observed rate constant k_p is related to k_f by equation (8). As

$$k_p \frac{k_f}{(1 + k_b[\mathrm{py}]/k_1)} \text{ or } \frac{k_f}{k_p} = 1 + \frac{k_b}{k_1}[\mathrm{py}] \quad (8)$$

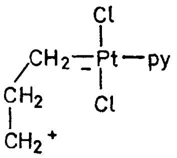
shown in Figure 4, the results agree with this. From equation (8), the gradient g is k_b/k_1 and the extrapolated line should cross the negative [py] axis at k_1/k_b (P). Thus, in theory, $g = 1/P$. Least-squares analysis of the experimental results gives a line with $g = (5{\cdot}46 \pm 0{\cdot}28) \times 10^3$ and $1/P = (7{\cdot}19 \pm 2{\cdot}83) \times 10^3$. The line should pass through the point 1·00 on the k_f/k_p axis and experimentally passes through 0·82 ± 0·26.



I*

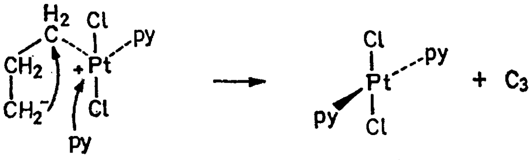


$\mathrm{I}^\ddagger$ (IV)



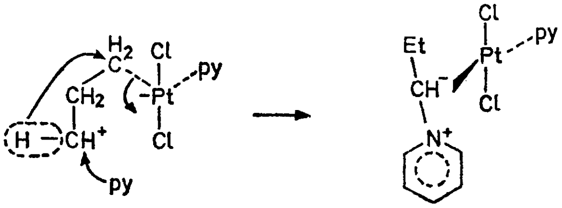
$\mathrm{I}^\ddagger$(V)

It is proposed that $(\mathrm{I})^*$ is a five-co-ordinate intermediate which can either reform (I) with pyridine (k_b) or rearrange (k_1) to $(\mathrm{I})^\ddagger$ [formulated as (IV) or (V)] by heterolytic cleavage of a Pt–C bond. Pyridine could attack (IV) at the Pt^+ site or (V) at the C^+ site. Thus, the k_3 route can be explained by a concerted mechanism,



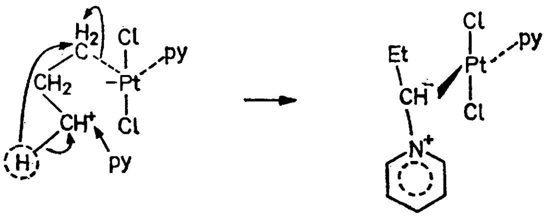
(IV) (III)

and route k_2 by



(V) (II)

involving hydride shift, or



(V) (II)

involving proton shift. Such mechanisms involve the release of cyclopropane in the direct formation of (III) from (I). This has been postulated on the basis of the known reaction of (I) with strong nucleophiles, *e.g.* cyanide and phosphine.[2]

In the intramolecular redox isomerisation described here, the two electrons required to pass from the higher stable oxidation state [platinum(IV), d^6] of the metal ion to the lower [platinum(II), d^8] are removed from a ligand which is itself retained and transformed within the co-ordination sphere. This is an example of what may be expected (for $d^6 \rightleftharpoons d^8$ in rhodium, iridium, cobalt, and platinum) to be a large and interesting class of intramolecular reactions.

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