# The Mechanisms of the Reactions between Hydrido-complexes and Diazonium Salts. Part 1. The Reactions of *trans*-$[PtH(Cl)(PEt_3)_2]$

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The mechanism of the reaction between *trans*-$[PtH(Cl)(PEt_3)_2]$ and $(p\text{-}R'C_6H_4N_2)BF_4$ (R' = $NO_2$, Cl, F, H, Me, or MeO) has been studied in acetonitrile. It has been shown to involve attack of the diazonium cation on the solvento-species *trans*-$[PtH(NCMe)(PEt_3)_2]^+$, which labilises the hydrido-group resulting in its loss as a proton. Subsequent substitution of the solvento-ligand, in the intermediate $[Pt(NCMe)(N_2C_6H_4R'\text{-}p)(PEt_3)_2]^+$, by chloride renders the aryldiazenido-ligand sufficiently basic to be protonated yielding the aryldiazene product, *trans*-$[Pt(NHNC_6H_4R'\text{-}p)Cl(PEt_3)_2]^+$. The relevance of these studies to the formal 'insertion' of unsaturated molecules into the Pt–H bond is discussed.

Both the redox and substitution reactions of diazonium salts with transition-metal complexes have been areas of continuing interest for several years.[1] Such reactions form the basis of the synthetically important Sandmeyer[2] and Meerwein reactions.[3]

Diazonium salts react with a variety of hydrido-complexes to give aryldiazene compounds,[4] as shown in the archetypal reaction (1),[5] which has subsequently been generalised by

$$trans\text{-}[PtH(Cl)(PEt_3)_2] + C_6H_5N_2^+ \longrightarrow trans\text{-}[Pt(NHNC_6H_5)Cl(PEt_3)_2]^+ \quad (1)$$

variation of the substituent on the aryl group and of the co-ligands.[6,7] Indeed this is just one member of the general class of reactions in which an unsaturated molecule [*e.g.* $RN_2^+$ (R = arene), alkene,[8] or alkyne[9]] reacts, apparently, with the Pt–H residue to yield the so-called 'insertion' products. Undoubtedly this classification is stoicheiometrically correct, but mechanistically may cover a range of reaction types. Clearly it is important to understand how the hydrogen moves from the metal to the unsaturated molecule.

In this and the following paper are described detailed kinetic studies on reactions between hydrido-complexes and diazonium salts, which demonstrate, at least for these strongly electron-withdrawing substrates, that the lowest-energy pathway to products involves proton loss from the metal, and then recapture by the 'inserting' ligand. This contrasts to the mechanism, often assumed for these 'insertion' reactions, which involves an intramolecular migration of the hydrogen from metal to ligand.[10] The present paper concentrates on the mechanism of the reactions between *trans*-$[PtH(Cl)(PEt_3)_2]$ and the diazonium salts $(p\text{-}R'C_6H_4N_2)BF_4$ (R' = $NO_2$, Cl, F, H, Me, or MeO) in acetonitrile, as typified by equation (1).

## Results

The reactions between *trans*-$[PtH(Cl)(PEt_3)_2]$ and $p\text{-}R'C_6H_4N_2^+$ (R' = $NO_2$, Cl, F, H, or Me) in acetonitrile were all studied by stopped-flow spectrophotometry. In all cases, at high concentrations of diazonium salt, the absorbance–time traces are biphasic. Both phases exhibit a first-order dependence on the concentration of the complex. The rate of the faster phase exhibits a first-order dependence on the concentration of the diazonium salt over the concentration range amenable to study on the stopped-flow time-scale. Furthermore the rate of this phase is sensitive to the concentration of HCl, the acid having an inhibitory effect. The empirical rate equation for the fast phase is as in (2), where $a = (1.5 \pm 0.2) \times 10^4$, $b = 52.4 \pm 0.5$ (R' = Cl), $a = (5.1 \pm 0.2) \times 10^3$, $b = 77.9 \pm 0.5$ (R' = F), $a = (2.0 \pm 0.3) \times 10^3$, $b = 60.0 \pm 0.8$ (R' = H), and $a = (4.2 \pm 0.5) \times 10^2$ dm³ mol⁻¹ s⁻¹, $b = 12.2 \pm 0.5$ dm³ mol⁻¹ (R' = Me). In contrast, the rate of the slower phase is independent of both the concentration and the nature of the diazonium salt, and independent of the acid concentration. The observed rate equation for the slow phase is thus as in (3).

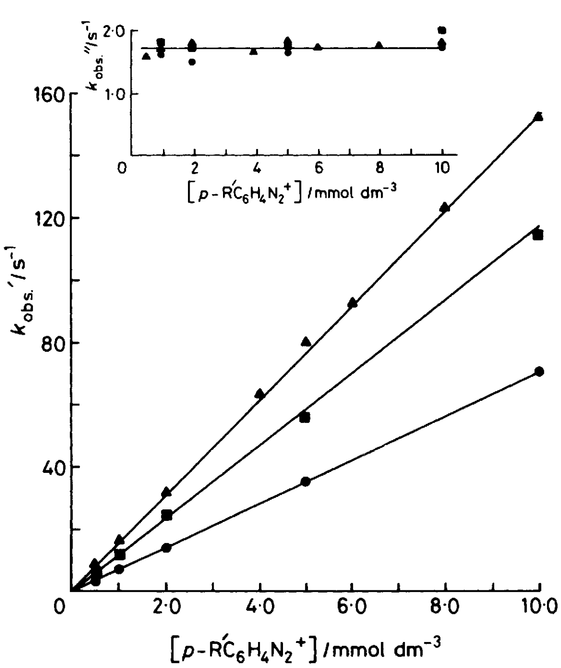


**Figure 1.** Dependence of the observed rate constants, for both the slow phase (insert) and the fast phase, on the concentration of $(p\text{-}ClC_6H_4N_2)BF_4$ for the reaction with *trans*-$[PtH(Cl)(PEt_3)_2]$ in acetonitrile at 25.0 °C. [Pt] = 5 × $10^{-5}$ mol dm$^{-3}$; [HCl] = 0.5 (▲), 5.0 (■), and 20.0 mmol dm$^{-3}$ (●)

$$k_{obs.}' = \frac{a[p\text{-}R'C_6H_4N_2^+]}{1 + b[HCl]} \quad (2)$$

$$k_{obs.}'' = 1.2 \pm 0.2\ s^{-1} \quad (3)$$

The kinetic data for these reactions are shown in Tables 1 and 2. The dependence of the observed rate constants on the

**Table 1.** Kinetic data for the reaction of *trans*-[PtH(Cl)(PEt$_3$)$_2$] with ($p$-R'C$_6$H$_4$N$_2$)BF$_4$ (R' = NO$_2$, F, Cl, H, Me, or MeO) in acetonitrile at 25.0 °C, [Pt] = 5 × 10$^{-5}$ mol dm$^{-3}$

| R' | [R'C$_6$H$_4$N$_2^+$] | [HCl] | $k_{obs.}'$ | $k_{obs.}''$ |
|---|---|---|---|---|
| | mmol dm$^{-3}$ | | s$^{-1}$ | |
| Cl | 0.5 | 0.5 | 7.6 | 1.6 |
| | 1.0 | | 19.2 | 1.8 |
| | 2.0 | | 40.0 | 1.8 |
| | 4.0 | | 65.0 | 1.7 |
| | 5.0 | | 81.3 | 1.8 |
| | 6.0 | | 100.6 | 1.8 |
| | 8.0 | | 128.3 | 1.8 |
| | 10.0 | | 145.0 | 1.9 |
| | 1.0 | 5.0 | 13.0 | 1.9 |
| | 2.0 | | 24.2 | 1.8 |
| | 5.0 | | 62.5 | 1.8 |
| | 10.0 | | 120.0 | 2.1 |
| | 1.0 | 20.0 | 7.5 | 1.7 |
| | 2.0 | | 14.4 | 1.6 |
| | 5.0 | | 34.5 | 1.8 |
| | 10.0 | | 71.5 | 1.8 |
| | 20.0 | | 145.0 | 1.8 |
| | 0.5 | 0.5 | 7.3 | 1.2 |
| | | 2.5 | 6.6 | 1.3 |
| | | 5.0 | 5.9 | 1.2 |
| | | 10.0 | 4.6 | 1.4 |
| | | 20.0 | 3.7 | 1.4 |
| | | 40.0 | 2.4[a] | |
| F | 0.5 | 0.5 | 2.2 | 1.2 |
| | 1.0 | | 4.9 | 1.4 |
| | 2.0 | | 10.2 | 1.5 |
| | 4.0 | | 20.1 | 1.6 |
| | 6.0 | | 23.8 | 1.4 |
| | 8.0 | | 40.9 | 1.5 |
| | 10.0 | | 52.3 | 1.3 |
| | 15.0 | | 73.5 | 1.3 |
| | 20.0 | | 96.1 | 1.3 |
| | 0.5 | 5.0 | 1.8[a] | |
| | 1.0 | | 3.6 | 1.2 |
| | 2.0 | | 7.5 | 1.5 |
| | 5.0 | | 17.6 | 1.6 |
| | 10.0 | | 35.8 | 1.6 |
| | 20.0 | | 73.1 | 1.8 |
| F | 0.5 | 20.0 | 1.0[a] | |
| | 1.0 | | 1.7[a] | |
| | 2.0 | | 3.8 | 0.9 |
| | 5.0 | | 8.0 | 1.2 |
| | 10.0 | | 16.5 | 1.4 |
| | 20.0 | | 34.0 | 1.4 |
| | 1.0 | 0.5 | 4.9 | 1.2 |
| | | 2.5 | 4.3 | 1.1 |
| | | 5.0 | 3.7 | 1.2 |
| | | 10.0 | 2.8 | 1.3 |
| | | 20.0 | 1.8[a] | |
| | | 40.0 | 1.2[a] | |
| H | 0.5 | 0.5 | 1.1[a] | |
| | 1.0 | | 1.5[a] | |
| | 2.0 | | 3.5 | 1.4 |
| | 4.0 | | 7.2 | 1.5 |
| | 6.0 | | 11.1 | 1.5 |
| | 8.0 | | 14.4 | 1.6 |
| | 10.0 | | 18.6 | 1.7 |
| | 20.0 | | 36.7 | 1.7 |
| | 4.0 | 0.5 | 7.5 | 1.4 |
| | | 2.5 | 7.0 | 1.5 |
| | | 5.0 | 6.3 | 1.5 |
| | | 10.0 | 5.1 | 1.5 |
| | | 20.0 | 3.6 | 1.5 |
| | | 40.0 | 2.3[a] | |
| Me | 0.5 | 0.5 | 0.26[a] | |
| | 1.0 | | 0.42[a] | |
| | 2.0 | | 0.67[a] | |
| | 4.0 | | 1.2[a] | |
| | 6.0 | | 1.8 | 1.0 |
| | 8.0 | | 3.4 | 1.0 |
| | 10.0 | | 4.6 | 1.3 |
| | 15.0 | | 6.3 | 1.2 |
| | 20.0 | | 8.1 | 1.2 |
| | 20.0 | 0.5 | 8.3 | 1.2 |
| | | 2.5 | 8.1 | 1.3 |
| | | 5.0 | 7.9 | 1.2 |
| | | 10.0 | 7.4 | 1.3 |
| | | 20.0 | 6.8 | 1.2 |
| | | 40.0 | 5.6 | 1.2 |
| MeO[b] | 0.5 | 0.5 | 0.027 | |
| | 1.0 | | 0.037 | |
| | 2.0 | | 0.074 | |
| | 4.0 | | 0.14 | |
| | 6.0 | | 0.19 | |
| | 8.0 | | 0.25 | |
| | 10.0 | | 0.32 | |
| | 15.0 | | 0.46 | |
| | 20.0 | | 0.58 | |
| | 25.0 | | 0.71 | |
| | 30.0 | | 0.85 | 0.9 |
| | 35.0 | | 1.23 | 0.8 |
| | 40.0 | | 1.41 | 0.9 |
| | 45.0 | | 1.62 | 1.1 |
| | 50.0 | | 1.83 | 1.2 |
| | 40.0 | 0.5 | 0.33 | |
| | | 2.5 | 0.31 | |
| | | 5.0 | 0.34 | |
| | | 10.0 | 0.36 | |
| | | 20.0 | 0.36 | |
| | | 40.0 | 0.36 | |
| NO$_2$[c] | 0.5 | 1.0 | 90.0 | 1.9 |
| | 1.0 | | 180.0 | 1.7 |
| | 2.0 | | 360.0 | 1.7 |

[a] Exponential absorbance time traces. [b] Traces at high concentration of $p$-MeOC$_6$H$_4$N$_2^+$ fitted by two exponentials (see text). [c] Limited data due to extreme rapidity of reaction.

concentration of ($p$-ClC$_6$H$_4$N$_2$)BF$_4$ for the two phases is shown in Figure 1, and the dependence of the fast phase on the concentration of acid is shown in Figure 2.

The introduction of deuterium labels into either the platinum complex as *trans*-[Pt$^2$H(Cl)(PEt$_3$)$_2$], or in the acid, has no effect on the reaction rates of either phase as shown in Table 3.

The introduction of NEt$_4$Cl into the reaction of *trans*-[PtH(Cl)(PEt$_3$)$_2$] with ($p$-FC$_6$H$_4$N$_2$)BF$_4$ diminishes the extent of the total absorbance change observed, while at the same time leaving the rates of the fast phase and of the slow phase unaffected. Addition of NBu$_4$Br affects the total absorbance change, while leaving the rate of the fast phase essentially unperturbed, but the slow phase is now markedly faster than in the presence of chloride. These data are collected in Table 4.

In contrast to the results described above, the reaction of *trans*-[PtH(Cl)(PEt$_3$)$_2$] with $p$-MeOC$_6$H$_4$N$_2^+$ exhibits a single exponential absorbance–time curve and an apparent non-linear dependence upon the concentration of diazonium salt. As

**Table 2.** Kinetic data for the reaction of *trans*-[PtH(Cl)(PEt$_3$)$_2$] with ($p$-R′C$_6$H$_4$N$_2$)BF$_4$ (R′ = F, H, or Me) in acetonitrile. Dependence on the concentration of *trans*-[PtH(Cl)(PEt$_3$)$_2$]; [HCl] = 0.5, [R′C$_6$H$_4$N$_2$$^+$] = 10.0 mmol dm$^{-3}$

| R′ | [PtH(Cl)(PEt$_3$)$_2$]/ mmol dm$^{-3}$ | $k_{obs.}'$/s$^{-1}$ | $k_{obs.}''$/s$^{-1}$ |
|---|---|---|---|
| F | 0.013 | 54.1 | 1.2 |
| | 0.025 | 52.5 | 1.3 |
| | 0.050 | 52.0 | 1.3 |
| | 0.10 | 52.8 | 1.3 |
| H | 0.013 | 19.6 | 1.8 |
| | 0.025 | 18.8 | 1.5 |
| | 0.050 | 21.0 | 1.7 |
| | 0.10 | 20.5 | 1.9 |
| Me | 0.013 | 4.5 | 1.6 |
| | 0.025 | 4.7 | 1.6 |
| | 0.050 | 4.4 | 1.6 |
| | 0.10 | 4.5 | 1.6 |
| MeO* | 0.013 | 0.35 | |
| | 0.025 | 0.31 | |
| | 0.050 | 0.32 | |
| | 0.10 | 0.31 | |

* Exponential traces obtained with [MeOC$_6$H$_4$N$_2$$^+$] = 10 mmol dm$^{-3}$.

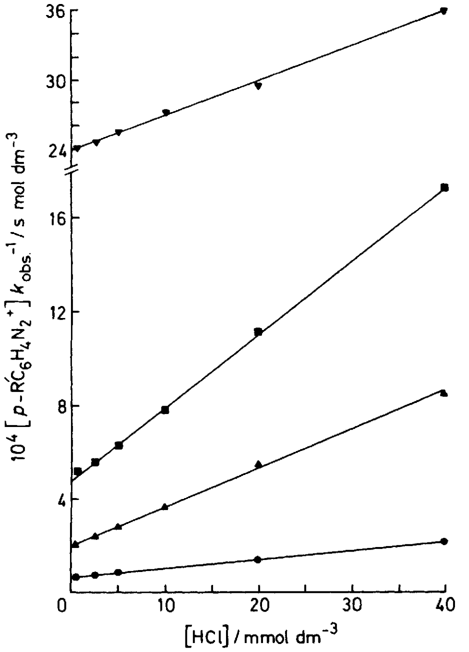


**Figure 2.** Graph of [$p$-R′C$_6$H$_4$N$_2$$^+$]/$k_{obs.}$ against [HCl] for the reactions of *trans*-[PtH(Cl)(PEt$_3$)$_2$] with ($p$-R′C$_6$H$_4$N$_2$)BF$_4$ in acetonitrile at 25.0 °C, where R = Cl (●), F (▲), H (■), and Me (▼). Note change of scale for the R = Me data

was also observed at low concentrations of the other diazonium salts, the exponential curves are a consequence of the reaction with $p$-MeOC$_6$H$_4$N$_2$$^+$ occurring at a rate slower than that observed for the second phase [equation (3)]. The apparent limiting kinetics is a consequence of the biphasic behaviour observed in the previous studies starting to make a contribution to the overall rate at the higher concentrations of $p$-MeOC$_6$H$_4$N$_2$$^+$. The rate of the slow phase augments the faster rate constant in the manner that appears to decrease the observed rate constant. By fitting of the absorbance–time curves obtained

**Table 3.** Kinetic data for the reactions between *trans*-[Pt$^2$H(Cl)(PEt$_3$)$_2$]* and ($p$-FC$_6$H$_4$N$_2$)BF$_4$ in acetonitrile at 25.0 °C ([Pt] = 0.05 mmol dm$^{-3}$)

| [$p$-FC$_6$H$_4$N$_2$$^+$]/ mmol dm$^{-3}$ | [$^x$HCl]/ mmol dm$^{-3}$ | $k_{obs.}'$/s$^{-1}$ | $k_{obs.}''$/s$^{-1}$ |
|---|---|---|---|
| | $x = 1$ | | |
| 0.5 | 0.5 | 2.5 | 1.2 |
| 1.0 | | 5.0 | 1.3 |
| 2.0 | | 10.4 | 1.4 |
| 5.0 | | 25.6 | 1.5 |
| 10.0 | | 51.5 | 1.3 |
| 20.0 | | 99.2 | 1.3 |
| | $x = 2$ | | |
| 0.5 | 0.5 | 2.1 | 1.2 |
| 1.9 | | 4.8 | 1.3 |
| 2.0 | | 11.0 | 1.3 |
| 5.0 | | 25.0 | 1.2 |
| 10.0 | | 52.0 | 1.3 |
| 20.0 | | 102.3 | 1.3 |

* Isotopic purity *ca.* 70% (see Experimental section).

at the relatively high concentration of diazonium salt it was shown that the data for fast and slow phases obey equations (4) and (5) respectively. The close similarity between the derived

$$k_{obs.}' = (35.2 \pm 0.8)[p\text{-MeOC}_6\text{H}_4\text{N}_2^+] \qquad (4)$$

$$k_{obs.}'' = 0.9 \pm 0.3\ \text{s}^{-1} \qquad (5)$$

value of $k_{obs.}''$ in equation (5) and that in (3) gives further credence to this interpretation. Unlike the studies with the other diazonium salts, the acid concentration has no effect on the rate of the fast phase with $p$-MeOC$_6$H$_4$N$_2$$^+$.

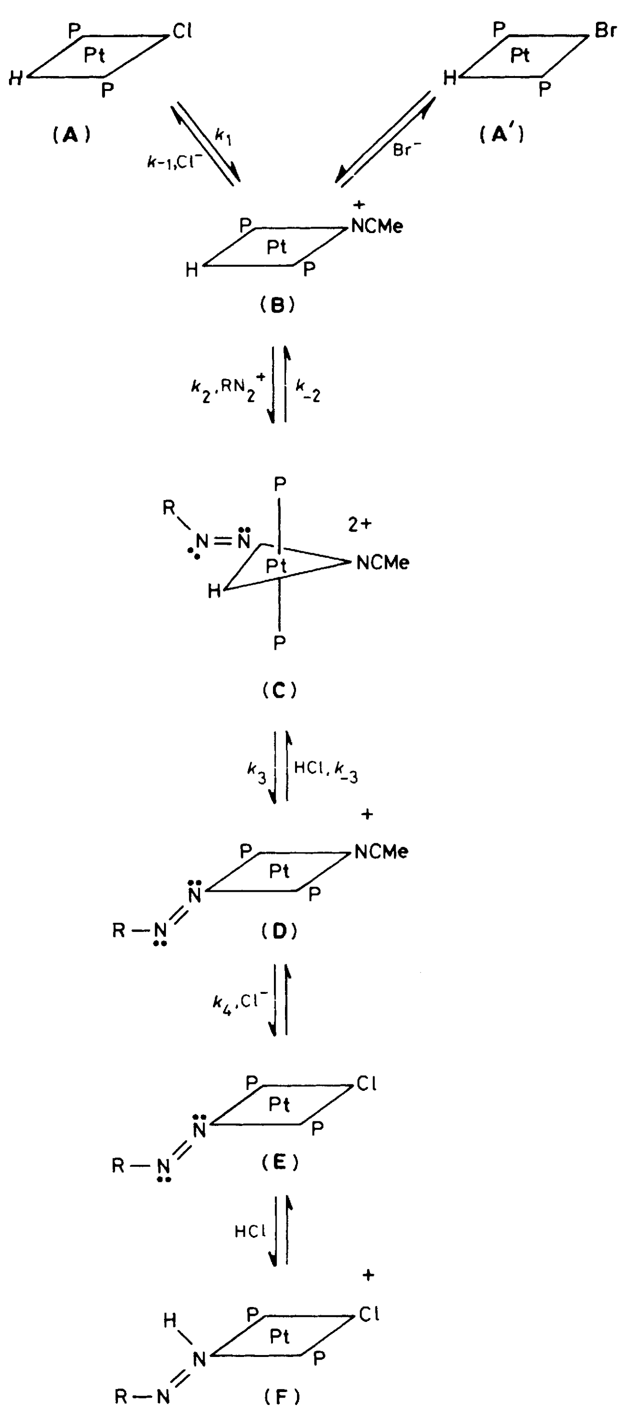
The kinetic data for the reactions with $p$-MeOC$_6$H$_4$N$_2$$^+$ are shown in Tables 1 and 2.

## Discussion

In many ways the reactions of diazonium salts with *trans*-[PtH(Cl)(PEt$_3$)$_2$] (**A**) as exemplifed by equation (1) represent an ideal system to study the mechanism of 'insertion' reactions with this complex. Not only is the stoicheiometry simple and the reactivity of *trans*-[PtH(Cl)(PEt$_3$)$_2$] well studied,[10,11] but also the electronic requirements of the reaction centre can be probed by varying the *para*-substituent on the aryl group.

A persistent feature of the reactions between complex (**A**) and $p$-R′C$_6$H$_4$N$_2$$^+$ (R′ = Cl, F, H, Me, or MeO) is their biphasic behaviour which is observed in all but the lower diazonium salt concentrations. It is thus most convenient to discuss the work in two sections, the first relating to the common slow phase (the initial equilibrium), and the second to the diazonium salt-dependent fast phase (the product-forming reaction). The mechanisms of the reactions are shown in the Scheme.

*The Initial Equilibrium.*—In the time necessary to prepare solutions of complex (**A**) in acetonitrile and load them into the stopped-flow apparatus (*ca.* 5 min) an equilibrium between (**A**) and the solvento-species (**B**) is established. The rapidity of this reaction is a consequence of the *trans* effect of the hydrido-group. Earlier studies on the reactions of (**A**) with nucleophiles are consistent with the substitution lability of this complex.[12] Thus in the reaction with an excess of diazonium salt the biphasic behaviour can be rationalised if species (**B**) reacts with $p$-R′C$_6$H$_4$N$_2$$^+$ (fast phase), but the conversion of (**A**) into (**B**)



**Scheme.** The mechanism of the reaction between *trans*-[PtH(Cl)(PEt$_3$)$_2$] and ($p$-R′C$_6$H$_4$N$_2$)BF$_4$ (R′ = NO$_2$, Cl, F, Me, H, or MeO) in acetonitrile

(slow phase) is unable to keep up with the relatively rapid, product-forming reaction of the latter. At low concentrations of diazonium salt, when the rate of the fast phase falls below that of the slow phase, the former is entirely rate-limiting and a single exponential trace with a rate constant associated with the fast phase is observed. However, the identity of the reactive form is not apparent from these experiments alone. Attempts to disturb the equilibrium between (**A**) and (**B**) in favour of the former by the addition of NEt$_4$Cl results in the complicated behaviour shown in Table 4. As shown by the homoconjugation equilibrium (6), the addition of NEt$_4$Cl introduces a relatively large

$$HCl + Cl^- \overset{K_H}{\rightleftharpoons} HCl_2^- \qquad (6)$$

concentration of two bases, which will influence the protolytic equilibrium involving species (**E**) and (**F**), thus influencing the absorbance change associated with the reaction, but this effect is difficult to quantify.

Furthermore, increasing the concentration of NEt$_4$Cl effectively decreases the concentration of 'free' acid, which will affect the rate of the fast phase. The relatively small value for $K_H$ in acetonitrile (1.58 × 10$^2$ dm$^3$ mol$^{-1}$),[13] together with the low concentrations of acid used, results in the denominator of equation (2) being essentially invariant over the range of NEt$_4$Cl concentrations employed.

Further evidence for the equilibrium between species (**A**) and (**B**) comes from the studies in the presence of NBu$_4$Br (Table 4). The different absorbance changes compared to those observed in the presence of chloride are consistent with the equilibrium process incorporating bromide into the complex, thus establishing a new equilibrium between species (**B**) and (**A′**) shown on the right-hand side of the Scheme. Furthermore although the rate of conversion of (**A′**) into (**B**) is different from that observed in the presence of HCl alone ($k_{obs.}$ = 8.0 ± 0.2 s$^{-1}$), that for the reaction of (**B**) with $p$-FC$_6$H$_4$N$_2^+$ is essentially unchanged $\{k_{obs.} = (4.4 \pm 0.2) \times 10^3[p\text{-FC}_6\text{H}_4\text{N}_2^+]$, $[\text{HCl}] = 0.5 \times 10^{-3}$ mol dm$^{-3}\}$.

Thus it can be concluded that the slow phase is attributable to the solvolysis of (**A**) to (**B**). It seems most probable that this process occurs by a bimolecular substitution mechanism, and the derived second-order rate equation is (7).[14] The ratio of the

$$k_{obs.}'' = k_1[\text{MeCN}] = (6.2 \pm 0.3) \times 10^{-2}\,[\text{MeCN}] \quad (7)$$

absorbance changes (λ = 380 nm) associated with each phase, O.D. (fast)/O.D. (slow), is independent of the nature and concentration of the diazonium salt. Simple analysis shows that when complex (**A**) is colourless this ratio is $K_1$ = [**B**]/[**A**] as shown in Table 5. In addition, it is clear that only species (**B**) can react with diazonium salts to yield the aryldiazene products (**F**).

*The Product-forming Reaction.*—Despite the *para*-substituent on the aryl group being six atoms away from the binding nitrogen atom, the electronic influence of this substituent has a marked effect on the rate of its reaction with complex (**B**) (Table 5). Qualitatively, the more electron-releasing the substituent the slower is the reaction, demonstrating that weakening of the Pt–H bond favours product formation. This, together with the inverse dependence on the concentration of acid [equation (2) and Figure 2] shown by most reactions is consistent only with the mechanism shown in the Scheme.

Binding of the diazonium cation to the metal withdraws electron density from the metal. This, together with the cationic nature of (**B**) renders the hydrido-group in (**C**) sufficiently acidic that it is lost as a proton to yield species (**D**).

The reason that the solvento-species (**B**) is the form that reacts with the diazonium cation, rather than the electrostatically more compatible halogeno-complex (**A**) or (**A′**) is now clear. It is the dicationic nature of species (**C**) which sufficiently weakens the Pt–H bond.

Substitution of acetonitrile for the more electron-releasing chloro-group in species (**D**) renders the aryldiazenido-group in (**E**) sufficiently basic that it can now be protonated by HCl to yield the aryldiazene product (**F**). The acid plays a further role in the reaction, in which it can convert species (**D**) into (**C**), thus inhibiting the product formation, and this is reflected in the observed rate equation (2). Clearly, for a mechanism involving an intramolecular migration of the hydrogen atom from metal

**Table 4.** The influence of NEt$_4$Cl or NBu$_4$Br on the reaction between *trans*-[PtH(Cl)(PEt$_3$)$_2$] and ($p$-FC$_6$H$_4$N$_2$)BF$_4$ in acetonitrile at 25.0 °C ([Pt] = 0.05, [HCl] = 0.5 mmol dm$^{-3}$)

| X | [NR$_4$X] | [$p$-FC$_6$H$_4$N$_2^+$] | $k_{obs.}'$/s$^{-1}$ | (ΔO.D.)* | $k_{obs.}''$/s$^{-1}$ | (ΔO.D.)* |
|---|---|---|---|---|---|---|
| | mmol dm$^{-3}$ | | | | | |
| Br | 0.5 | 0.5 | 1.7* | 0.31 | | |
| | | 1.0 | 3.2* | 0.31 | | |
| | | 2.5 | 7.5* | 0.31 | | |
| | | 5.0 | 21.0 | 0.20 | 8.0 | 0.11 |
| | | 7.0 | 30.0 | 0.20 | 7.8 | 0.11 |
| | | 10.0 | 45.1 | 0.20 | 8.2 | 0.11 |
| | | 20.0 | 79.5 | 0.20 | 8.2 | 0.11 |
| Cl | 0.0 | 1.0 | 5.1 | 0.12 | 1.2 | 0.11 |
| | 1.0 | | 4.9 | 0.09 | 1.1 | 0.08 |
| | 2.0 | | 5.0 | 0.08 | 1.2 | 0.08 |
| | 4.0 | | 5.1 | 0.06 | 1.2 | 0.08 |
| | 10.0 | | 5.1 | 0.06 | 1.2 | 0.08 |
| | 30.0 | | 4.8 | 0.04 | 1.4 | 0.08 |

* λ = 380 nm.

**Table 5.** Summary of the rate and equilibrium constants for the reactions of *trans*-[PtH(Cl)(PEt$_3$)$_2$] with ($p$-R'C$_6$H$_4$N$_2$)BF$_4$ (R' = NO$_2$, Cl, F, H, Me, or MeO) in acetonitrile at 25 °C

| | | Fast phase[a] | | |
|---|---|---|---|---|
| R' | $K_1$ | $\frac{k_2k_3}{(k_{-2}+k_3)}$ [b] | $\frac{k_{-2}k_{-3}}{k_4(k_{-2}+k_3)}$ [c] | $\frac{k_2k_3k_4}{k_{-2}k_{-3}}$ [d] |
| NO$_2$[e] | 0.73 | 1.8 × 10$^5$ | | |
| Cl | 0.72 | 1.5 × 10$^4$ | 52.4 | 2.89 × 10$^2$ |
| F | 0.75 | 5.1 × 10$^3$ | 77.9 | 0.65 × 10$^2$ |
| H | 0.70 | 2.0 × 10$^3$ | 60.0 | 0.33 × 10$^2$ |
| Me | 0.71 | 4.2 × 10$^2$ | 12.2 | 0.34 × 10$^2$ |
| MeO | | 35.2 | <5 | >0.07 × 10$^2$ |

[a] For slow phase $k_1$ = 6.2 × 10$^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ in each case; calculated using [MeCN] = 19.4 mol dm$^{-3}$. [b] Units are dm$^3$ mol$^{-1}$ s$^{-1}$. [c] Units are dm$^3$ mol$^{-1}$. [d] Units are s$^{-1}$. [e] Limited data due to rapid reaction.

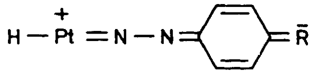
to ligand no such inverse dependence upon the acid concentration would be expected. Indeed the absence of any acid inhibition of the reaction with $p$-MeOC$_6$H$_4$N$_2^+$ precludes any firm conclusion concerning the intimate pathway adopted by this reagent, and we cannot on the kinetic evidence alone rule out a migration pathway. However, it seems unlikely that such a drastic change of mechanism has occurred with $p$-MeOC$_6$H$_4$N$_2^+$. It is to be noted that the acid-inhibition term [equation (6)] becomes progressively less significant with the more electron-releasing substituents, and thus we favour the interpretation that with $p$-MeOC$_6$H$_4$N$_2^+$ this term is negligibly small.

The rate equation (8) associated with the mechanism shown

$$k_{obs.} = \frac{k_2k_3k_4[p\text{-R'C}_6\text{H}_4\text{N}_2^+]}{k_4(k_{-2}+k_3) + k_{-2}k_{-3}[\text{HCl}]} \qquad (8)$$

in the Scheme can be derived by treating species (C) and (D) as steady-state intermediates. This equation is identical in form to that experimentally observed [equation (2)], and the derived parameters for each diazonium salt are shown in Table 5. As is common in this type of treatment, it is impossible to distinguish which of $k_2$, $k_3$, and $k_4$ is rate-limiting. However, studies with *trans*-[Pt$^2$H(Cl)(PEt$_3$)$_2$] and $p$-FC$_6$H$_4$N$_2^+$ exhibited no isotope effect, indicating that the proton-dissociation step ($k_3$) at least is not rate-limiting.

We are now in a position to quantify the influence of the *para*-substituent on the rate of the reaction between complex (**B**) and $p$-R'C$_6$H$_4$N$_2^+$. However, as is clear from equation (8) the parameter involved in the Hammett plot[15] is not a single rate constant but rather the quotient $k_2k_3/(k_{-2} + k_3)$, in which all three elementary rate constants will be affected to varying degrees by the different substituents. The distance between the substituent and the metal precludes an inductive effect, but the intervening delocalised system allows electronic effects to operate at this range. Contributions such as that shown in (**G**) to the structure of (**C**) increase the acidity of the hydrido-group. The contribution of structures such as (**G**) to the ground state of aryldiazenido-complexes has been discussed before,[5–7,16] but not the contribution to an intermediate or transition state.

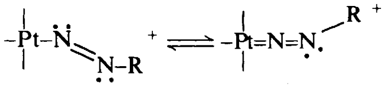


(G)

There is a reasonably good correlation (correlation coefficient = 0.989) between the values of log$_{10}$[$k_2k_3/(k_{-2} + k_3)$] and Hammett $\sigma_p^+$ values as shown in Figure 3. Included on this graph is the point for $p$-NO$_2$C$_6$H$_4$N$_2^+$ collected from relatively limited data, because of the rapidity of the reaction with this substrate. The reaction constant for these reactions (ρ) is +2.31.

A further feature of equation (8) is that the acid-inhibition term in equation (2) is clearly a complicated function, $k_{-2}k_{-3}/k_4(k_{-2} + k_3)$, and thus the minor inconsistencies in the overall trend of this value (Table 5) are a consequence of the various electronic influences of the aryl substituent on the contributory elementary rate constants.

An interesting aspect of the conversion of species (**D**) into (**E**) is the apparent unimolecular nature of this process, as defined by equation (8). Although associative mechanisms often operate in sixteen-electron square-planar complexes, dissociative pathways have also been demonstrated.[17] This dissociative pathway may be favoured by a potential labilising effect of the diazenido-ligand whereby it can change from a formal one-electron donor to a formal three-electron donor as shown in equation (9). This proposed labilising capability in sixteen-electron square-planar complexes is similar in type to that used



(9)

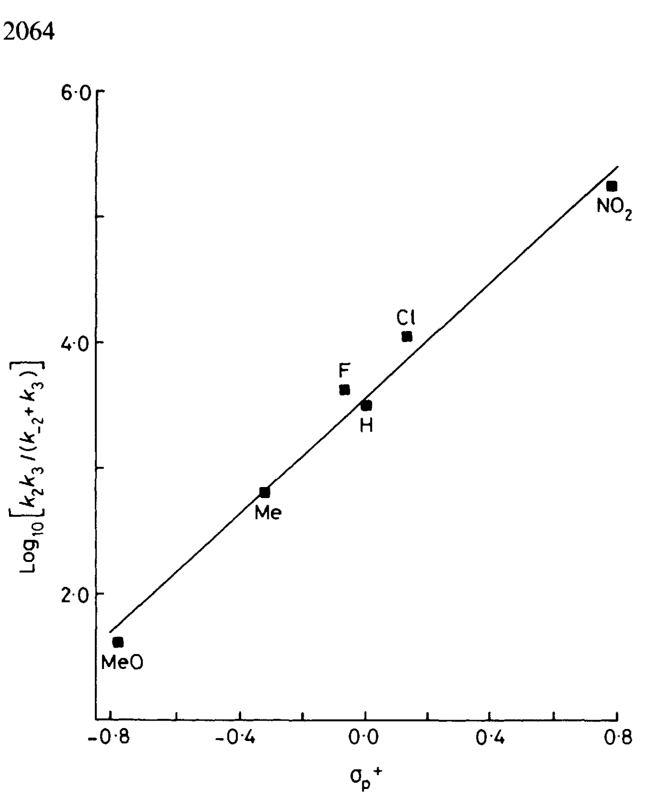


**Figure 3.** Graph of Hammett $\sigma_p^+$ values for the reactions of *trans*-$[PtH(Cl)(PEt_3)_2]$ with $(p\text{-}R'C_6H_4N_2)BF_4$ (R′ = $NO_2$, Cl, F, H, Me, or MeO) in acetonitrile at 25.0 °C

to rationalise the associative mechanisms of eighteen-electron complexes containing polyhapto-ligands.[18] However, it is important to distinguish between this transition-state effect and the ground-state structures shown in the Scheme. The aryldiazenido-residue in species (**D**) and (**E**) is confined to the doubly bent configuration. Theoretical calculations,[19] *X*-ray photoelectron spectroscopy,[20] and practical experience[4] indicate that of the two lone pairs on a doubly bent diazenido-ligand the nitrogen atom adjacent to the metal is the most basic. Thus protonation of the aryldiazenido-ligand in (**E**) results naturally in the aryldiazene product (**F**) rather than the isomeric arylhydrazido(2−)-species, *trans*-$[Pt\{NN(H)C_6H_4R'\text{-}p\}Cl(PEt_3)_2]^+$.

*The Product Equilibrium.*—The sensitivity of the final absorbance to the concentration of $NEt_4Cl$ (Table 4) can be attributed qualitatively to the basic chloride ion disturbing the equilibrium between species (**E**) and (**F**). No doubt it is a consequence of this facile equilibrium which results in the occasional isolation of aryl complexes from the reactions of *trans*-$[PtH(Cl)(PEt_3)_2]$ and $(p\text{-}R'C_6H_4N_2)BF_4$[6,7,16] as shown in equation (10).

$$trans\text{-}[Pt(N_2R)Cl(PEt_3)_2] \longrightarrow trans\text{-}[PtR(Cl)(PEt_3)_2] + N_2 \quad (10)$$

However, the present study does not allow the delineation of the factors influencing this reaction. On the preparative timescale the reaction between *trans*-$[PtH(Cl)(PEt_3)_2]$ and $p\text{-}MeOC_6H_4N_2^+$ yields the corresponding aryl product; however, the kinetics of this reaction indicate that it is very similar to that observed with the other diazonium salts (Table 5). This, together with the linearity of the Hammett plot (Figure 3), indicates that the pathway for the formation of the aryl complexes is identical to that for the formation of (**F**), the aryl complex resulting, presumably, from subsequent decomposition of (**E**).

*The 'Insertion' Mechanism.*—For the reactions of *trans*-$[PtH(Cl)(PEt_3)_2]$ with $p\text{-}R'C_6H_4N_2^+$ (R′ = $NO_2$, F, Cl, H, Me, or MeO) in acetonitrile, the lowest-energy pathway to accomplish the 'insertion' reaction is not a migration mechanism but the proton dissociation/recombination shown in the Scheme. The labilisation of the Pt–H bond by other strong electron acceptors has been observed before. Tetracyanoethylene (tcne) reacts with *trans*-$[PtH(Cl)(PEt_3)_2]$ to yield $[Pt(tcne)(PEt_3)_2]$.[21] Furthermore the reactions of acetylenes containing electron-withdrawing substituents (*e.g.* $MeO_2CC{\equiv}CCO_2Me$ or $F_3CC{\equiv}CCF_3$) have been shown to involve proton dissociation.[9,22] However, these studies are based entirely on the isolation of the intermediate species *trans*-[Pt(alkyne)(solvent)$(PEt_3)_2$] (**H**), and isotope-labelling product analyses. On these grounds alone one cannot determine whether species (**H**) is on the product-forming pathway or on a non-productive side pathway.[9] It has also been claimed that the reaction of $MeO_2CC{\equiv}CCO_2Me$ with *trans*-$[PtH(Cl)(PEt_3)_2]$ proceeds *via* a free-radical mechanism.[23]

The 'insertion' reactions of *trans*-$[PtH(Cl)(PEt_3)_2]$ are thus accomplished by a spectrum of mechanisms, ranging from the intramolecular migration process[10] to the acid–base pathway described in this paper. Clearly, several factors influence the product obtained, the most important being the acidity of the 'insertion' product, irrespective of the mechanism, but an essential criterion for the mechanism described herein to operate is that the ligand must subsequently become sufficiently basic to be protonated. Only detailed kinetic studies and product analyses of the reaction between, for instance, the deuterido-complex and substrate in the presence of a large excess of unlabelled acid, to establish the fate of the isotopic label, are sufficient criteria for defining the mechanism. This last criterion may be unavailable for some systems (including the present one) because of rapid proton exchange in the product.

## Experimental

All manipulations in both the preparative and kinetic aspects of the work were performed routinely under dinitrogen using standard Schlenk and syringe techniques as applicable.

The complex *trans*-$[PtH(Cl)(PEt_3)_2]$ was prepared by the method described in the literature,[24] and recrystallised from hexane (Found: C, 30.7; H, 6.2. $C_{12}H_{11}ClP_2Pt$ requires C, 30.8; H, 6.6%). The corresponding deuterido-complex, *trans*-$[Pt^2H(Cl)(PEt_3)_2]$, having an isotopic purity of *ca.* 70% (as evidenced by i.r. spectroscopy), was prepared by three exchanges of the hydrido-compound in $MeO^2H$–$^2H_2O$ (2:1) with $^2HCl$ present as catalyst.[21] Further successive treatments apparently did not increase the isotopic purity.

The diazonium tetrafluoroborates, $(R'C_6H_4N_2)BF_4$ (R′ = $NO_2$, F, Cl, H, Me, or MeO), were synthesised by the diazotisation of the corresponding aniline in dilute aqueous fluoroboric acid,[25] recrystallised from acetone–diethyl ether, and stored at −20 °C.

*Kinetic Measurements.*—All kinetic measurements were performed on a Aminco-Morrow stopped-flow apparatus, modified for work on air-sensitive compounds as described earlier.[26] The data were collected and analysed on a B.B.C. Microcomputer.

The stopped-flow experiments were routinely performed at $\lambda$ = 380 nm, where for *trans*-$[PtH(Cl)(PEt_3)_2]$, $\varepsilon = 3.8 \times 10^2$ $dm^3$ $mol^{-1}$ $cm^{-1}$, and for *trans*-$[Pt(NHNC_6H_4R'\text{-}p)Cl(PEt_3)_2]^+$, $\varepsilon = 4.6 \times 10^3$ (R′ = F), $4.8 \times 10^3$ (R′ = Cl), $3.4 \times 10^3$ (R′ = H), $7.0 \times 10^3$ (R′ = Me), and $1.0 \times 10^4$ $dm^3$

$mol^{-1}$ $cm^{-1}$ (R′ = MeO). However for R′ = F, H, or MeO the stopped-flow studies were performed at 5-nm intervals over the range 340—440 nm. The rate constants were independent of the monitoring wavelength.

The biphasic kinetics were analysed using a least-squares program fitting to two exponentials, NAG subroutine EO4ABF.

Acetonitrile was dried and freshly distilled from calcium hydride immediately prior to use. Anhydrous solutions of HCl were prepared by the addition of equimolar concentrations of $SiMe_3Cl$ and MeOH. Anhydrous solutions of $^2HCl$ were prepared analogously using $MeO^2H$. Although stock solutions of HCl, $NBu_4Br$ (Lancaster Synthesis), and $NEt_4Cl$ (Aldrich) were prepared and used to make the more dilute solutions used in the kinetics studies, the diazonium tetrafluoroborate salts were weighed directly into the volumetric flasks and then stored at −20 °C until immediately prior to the kinetic study, in order to minimise any decomposition. All solutions containing diazonium salts were used within 15 min of adding the solvent.

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