Mechanism of the Acid-catalysed Cyclometallation Reaction of Dirhodium(II) Compounds with General Formula $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{P(C_6H_4X)_3\}(OH_2)]$†

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Compounds of general formula $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{P(C_6H_4X)_3\}(OH_2)]$ **2** (X = H, *p*-Me, *p*-Cl, *m*-Me or *m*-Cl) have been prepared by photochemical reaction of the corresponding adduct $[Rh_2(\mu\text{-}O_2CMe)_3\{(C_6H_4)PPh_2\}\{P(C_6H_4X)_3\}(HO_2CMe)]$ **1**. These compounds contain one equatorial phosphine which undergoes a facile cyclometallation reaction, catalysed in the presence of protic acids, to give doubly metallated compounds $[Rh_2(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{(XC_6H_3)\text{-}P(C_6H_4X)_2\}(HO_2CMe)_2]$ **3**. The kinetics and mechanism of this cyclometallation have been studied in chloroform and toluene solutions. A mechanism in which protons facilitate loss of one of the acetate groups in the starting compounds is proposed. Preliminary experiments showed that the addition of phosphines enhances the cyclometallation rate. The mechanism is fully concerted with a highly ordered transition state as seen by the very negative activation entropies. The values obtained for the deuterium kinetic isotopic effect indicate that, for the acid-catalysed path, the transition state lies in a more advanced position on the reaction coordinate than for the thermal process. The gap between the isokinetic plots for the acid-catalysed and thermal reactions is *ca.* 20 kJ mol^{-1}.

Although cyclometallation reactions of mononuclear compounds are well known,[1] the same processes involving two metal centres are much less common.[2] We have been interested in the study of cyclometallation of arylphosphines in dirhodium(II) compounds.[3] The isolation of some reaction intermediates has been achieved, and several mono-[3a–f] and doubly-metallated [3g–j] compounds have been identified by their crystal structures.

In all the reactions studied it has been systematically observed that acetic acid enhances the reaction rate.[3f,g] Studies dealing with mechanistic aspects of cyclometallation reactions are relatively scarce, all of them corresponding to mononuclear compounds.[1c,4] The observation that monometallated dirhodium(II) compounds in the presence of phosphines undergo very clean cyclometallation under relatively mild reaction conditions prompted us to do some kinetic studies involving species **1**–**3** in Scheme 1, aiming to obtain additional information about the role of the acid in this type of reaction. Preliminary estimations of reaction rates for the process **1** ⟶ **3** for several monometallated compounds[3d,j] gave different trends depending on the nature of the starting compound **1**. This behaviour was attributed in principle to the existence of two consecutive reactions **1** ⟶ **2** and **2** ⟶ **3**, giving the overall cyclometallation process. Thus **2** is an intermediate of the process with one equatorial and one metallated phosphine. Owing to the fact that the step **2** ⟶ **3** involves C–H activation, the isolation of intermediate **2** in high yield was pursued.

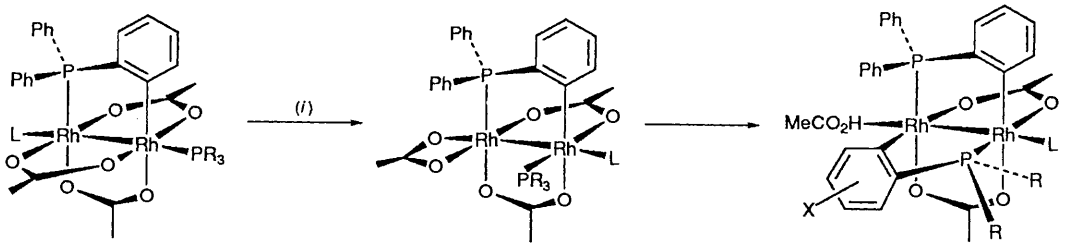
We report in this paper a procedure for the preparation in high yield of several compounds of type **2**. A study of the kinetics and mechanism of the reaction **2** ⟶ **3** (in the presence and absence of protic acid) for several compounds of type **2** is also reported. A mechanism for the C–H bond activation process is proposed.

Results and Discussion

Our previous spectroscopic studies on the thermal reaction **1** ⟶ **3** (X = H) revealed the existence in solution of compound **2**[3f] as an intermediate which was isolated in *ca.* 1% yield. We therefore first attempted to optimize the yield of compound **2**. By photochemical reaction of compound **1** in chloroform solution we isolated compound **2** in practically quantitative yield. Analogous compounds of type **2** with different equatorial triarylphosphines were obtained by the same procedure. Monitoring of the photochemical reaction **1** ⟶ **2** (X = H) by ^{31}P NMR and UV/VIS spectroscopy shows that no intermediates are detected in solution. Attempts to grow crystals of these compounds of X-ray diffraction quality failed, but ^1H, ^{13}C and ^{31}P NMR spectroscopy (the latter data shown in Table 1) allow us to assign for these intermediates a similar structure to that of the related compound $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(BrC_6H_4)PPh(C_6F_4Br\text{-}o)\}\text{-}\{PPh_2(C_6F_4Br\text{-}o)\}]$ the crystal structure of which is known.[3c]

Compounds of type **2** are moderately stable in the solid state for several weeks, but in chloroform solution at room temperature they evolve very slowly ($t_{\frac{1}{2}}$ > 24 h) to yield the doubly metallated compounds **3**. The stability of these compounds can be increased by replacing the axial molecule of acetic acid by water. Therefore, we have isolated such compounds as water adducts which, in excess of acetic acid generate rapidly and quantitatively the acetic acid adducts.[5] The latter compounds can be isolated as green crystalline

† *Supplementary data available* (No. SUP 56979, 7 pp): first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



1 2 3

Scheme 1 R = XC_6H_4 where X = H, *p*-Me, *m*-Me, *p*-Cl or *m*-Cl; L = H_2O or $MeCO_2H$. (*i*) *hν*

Table 1 Phosphorus-31 NMR data for the compounds $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{P(C_6H_4X)_3\}(OH_2)]$ **2**

X	$\delta_{P_{met}}$	^1J(P–Rh)/Hz	^2J(P–Rh)/Hz	$\delta_{P_{eq}}$	^1J(P–Rh)/Hz	^2J(P–Rh)/Hz
H	15.7	137.6	10.3	41.8	189.0	4.3
p-Me	15.4	137.7	10.1	39.6	188.0	4.2
m-Me	15.6	138.2	10.1	40.3	187.2	4.3
p-Cl	15.6	138.4	9.2	44.2	189.3	3.7
m-Cl	15.3	137.1	9.4	44.0	189.3	3.9

P_{met} = Metallated phosphine phosphorus, P_{eq} = equatorial non-metallated phosphine phosphorus.

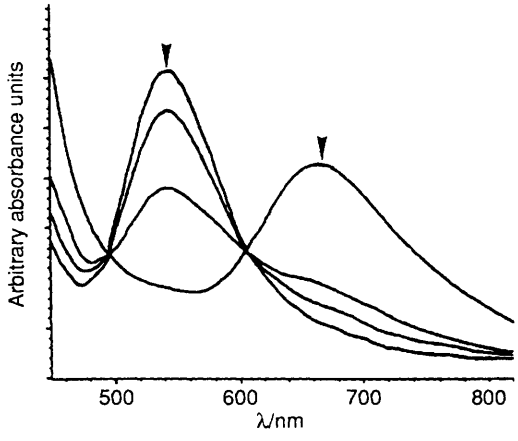


Fig. 1 Repetitive UV/VIS scanning showing the advance of the cyclometallation reaction of compound **2** (X = *m*-Me) in acetic acid–chloroform solution at 40 °C. Arrows indicate the wavelength used for the k_{obs} calculation

powders, and have been characterized by elemental analysis and NMR spectroscopy for some key compounds. No difference in the kinetic results was found when the water or acetic acid adduct was used as the starting material.

The presence of acetic acid makes the reaction **2** ⟶ **3** much faster. Monitoring of this reaction by ^{31}P NMR and UV/VIS spectroscopy (Fig. 1) confirms the absence of any detectable intermediate species.

The kinetics of the cyclometallation reaction **2** ⟶ **3** was followed by UV/VIS spectroscopy at different temperatures, acetic acid, triflic acid (HO_3SCF_3) in acetic acid, and acetic acid–sodium acetate concentrations. The experimental values of k_{obs} at the temperatures and concentrations studied for the different compounds **2** are given in SUP 56979. In the absence of any sort of acid, k_{obs} corresponds directly to the first-order rate constant for each phosphine and temperature. Table 2 collects the kinetic and activation data for experiments run in the absence of acid as a function of temperature and phosphine.

All the non-H^+ catalysed reactions are extremely slow with observed rate constants two to three orders of magnitude smaller than those obtained in the presence of protic acid at the same temperature. Consequently, all the experiments had to be run in toluene solution in order to be able to increase the temperature of the reaction. No dependence on the concentration of the type **2** compound was observed, indicating that the reaction is first order in the concentration of the monometallated species.

As for the acid-catalysed experiments, the experimental data were fitted to a typical [6] limiting rate equation of type (1) where

$$k_{obs} = \frac{k[H^+]}{K + [H^+]} \quad (1)$$

k is the limiting first-order rate contant and the equilibrium designated by K includes all acid–base equilibria previous to the rate-limiting step. For the plot of the data, the $[H^+]$ value was taken as directly proportional to the values of $[HO_2CMe]$, $[HO_3SCF_3]$, or $[HO_2CMe]/[O_2CMe^-]$ added, where H^+ represents any type of solvated proton present in solution. This assumption is questionable, and an $[H^+] \propto [acid]^{\frac{1}{2}}$ proportionality could also be chemically significant (especially taking into account the weakness of any acid in non-polar media and $K_a = [H^+][A^-]/[HA]$ with $[H^+] = [A^-]$); nevertheless, owing to the fact that the experimental data were fitted to a saturation kinetics rate law, any of these plots will give comparable limiting k values for the systems studied as a whole when the same span of acid concentrations is used.

Fig. 2 shows typical plots of k_{obs} *versus* $[HO_2CMe]_{added}$. No intercept was detected for any of these plots, indicating that the reaction *via* the non-H^+ catalysed path is negligible under these acidity conditions. This was confirmed by the absence of spectral changes for a chloroform solution of complex **2** (X = H) at room temperature over a period of *ca.* 12 h, as well as by the values obtained in the non-catalysed experiments. Additional experiments at different rhodium(II) concentrations showed no changes in the observed rate constants, indicating, again, that the reaction is first order in the concentration of complex **2**.

In order to check the effect of 'non-complexing' acidity in the reactions, runs with various concentrations of triflic acid in chloroform solutions were done; in all cases acetic acid had to be added to the solution to prevent decomposition. At 40 °C these runs gave, again, a clear limiting hyperbolic dependence of k_{obs} on $[H^+]$ (in this case $[H^+] \propto [HO_3SCF_3]_{added}$). No dependence on the amount of acetic acid added was observed,

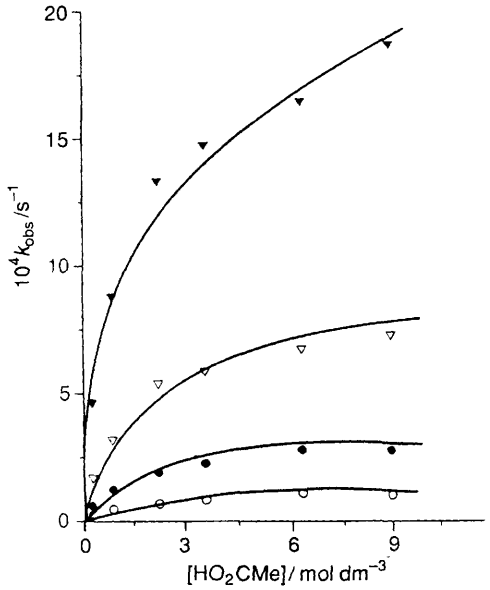


Fig. 2 Plots of k_{obs} *versus* $[HO_2CMe]$ for the cyclometallation reaction of compound **2** (X = H) at different temperatures in chloroform solution: (▼) 40, (▽) 30, (●) 20 and (○) 10 °C

Table 2 First-order rate constants, k, for the different thermal reactions of compounds **2** studied as a function of temperature in toluene solution. A factor of 2 should be applied to the rate constants for the X = *m*-Me and *m*-Cl compounds due to the steric hindrance of one of the two possible metallating positions of the phosphine

X	T/°C	$10^4\ k/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
H	60	0.17	80 ± 5	−105 ± 15
	70	0.30		
	80	1.0		
	90	1.9		
H*	60	0.39	65 ± 7	−140 ± 2
	70	0.62		
	80	0.90		
	90	2.3		
p-Me	70	1.0	91 ± 3	±64 ± 11
	80	2.3		
	90	6.2		
p-Cl	70	2.0	78 ± 12	−99 ± 33
	80	3.6		
	90	9.4		
m-Me	70	0.35	94 ± 8	−66 ± 23
	80	0.77		
	90	2.1		
m-Cl	70	0.7	84 ± 6	−90 ± 17
	80	1.5		
	90	3.9		

* $P(C_6D_5)_3$ ligand.

providing that its concentration was sufficient to prevent decomposition of the type **2** compounds. Fig. 3 shows a plot of k_{obs} *versus* $[HO_3SCF_3]_{added}$, the k value derived being $5.6 \times 10^{-3}\ s^{-1}$. Taking into account the extremely different acid concentration range, this value is of the same magnitude as that obtained for the experiments run in the absence of triflic acid, $2.0 \times 10^{-3}\ s^{-1}$.

As for the experiments run in chloroform solutions of acetic acid in the presence of sodium acetate at 40 °C, a clear hyperbolic increase in the observed rate constant upon increasing ratio $[HO_2CMe]/[O_2CMe^-]$ was observed (Fig. 4). This behaviour indicates that the influence of acetate on the reaction rate is solely due to the fact that the $[H^+]$ value diminishes on increasing the acetate concentration. The same data treatment

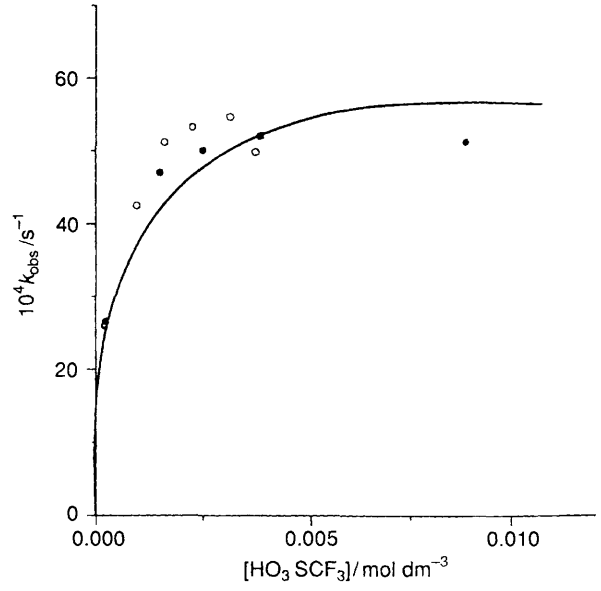


Fig. 3 Plot of k_{obs} *versus* $[HO_3SCF_3]$ for the cyclometallation reaction of compound **2** (X = H) at 40 °C in acetic acid–chloroform solution: (○) 0.045 mol dm^{-3} HO_2CMe, (●) 0.095 mol dm^{-3} HO_2CMe

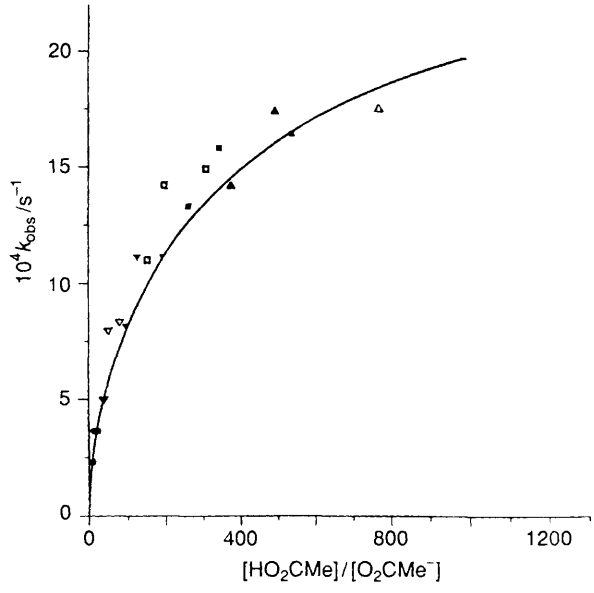


Fig. 4 Plot of k_{obs} *versus* $[HO_2CMe]/[O_2CMe^-]$ for the cyclometallation reaction of compound **2** (X = H) at 40 °C in chloroform solution: $[HO_2CMe]$ = 9.00 (△), 6.30 (●), 3.60 (▽), 2.25 (▼), 0.90 (■) or 0.27 mol dm^{-3} (□)

as for the previous experiments was employed and a k value of $2.0 \times 10^{-3}\ s^{-1}$, the same as that observed in the absence of sodium acetate, was obtained.

Table 3 shows all k values derived from a least-squares fit of equation (1) for the systems studied, as well as the thermal activation parameters derived from standard Eyring plots.

Fig. 5 shows the isokinetic plot for the reactions studied. It is clear that two different mechanisms are operating, one through an acid-catalysed process and another one through a thermal process. The gap between the two sets of data indicates the energy difference for the two paths involved.

Preliminary experiments run with compound **2** (X = H) and triphenylphosphine in chloroform solution at room temperature indicate that, under these conditions, the reaction is faster than the thermal process. It is well established for mononuclear compounds[1c,7] that steric effects produced by

Table 3 First-order rate constants, k, for the different acid-catalysed systems studied as a function of temperature in chloroform solution. A factor of 2 should be applied to the rate constants for the compounds **2** where X = *m*-Me and *m*-Cl due to the steric hindrance on one of the two possible metallating positions of the phosphine

X	T/°C	$10^3\ k$/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
H	10	0.11	67 ± 1	−86 ± 5
	20	0.34		
	30	0.80		
	40	2.0		
	20[a]	0.20	67 ± 1	−88 ± 3
	30[a]	0.51		
	40[a]	1.3		
	60[a]	6.2		
	60[b]	6.5		
	40[c]	5.6		
	40[d]	2.0		
H[e]	20[a]	0.097	73 ± 2	−75 ± 8
	30[a]	0.30		
	40[a]	0.85		
	50[a]	1.8		
	60[a]	3.9		
p-Me	10	0.13	73 ± 8	−60 ± 27
	20	0.61		
	30	1.2		
	40	3.1		
p-Cl	10	0.15	65 ± 7	−88 ± 22
	20	0.56		
	30	1.1		
	40	2.4		
m-Me	10	0.088	69 ± 2	−85 ± 7
	20	0.22		
	30	0.65		
	40	1.5		−96 ± 6
m-Cl	10	0.067	67 ± 2	
	20	0.19		
	30	0.48		
	40	1.1		

[a] In toluene solution. [b] In deuteriated acetic acid–toluene solution. [c] With triflic acid in chloroform–acetic acid solution. [d] In acetic acid–sodium acetate chloroform solution. [e] $P(C_6D_5)_3$ ligand.

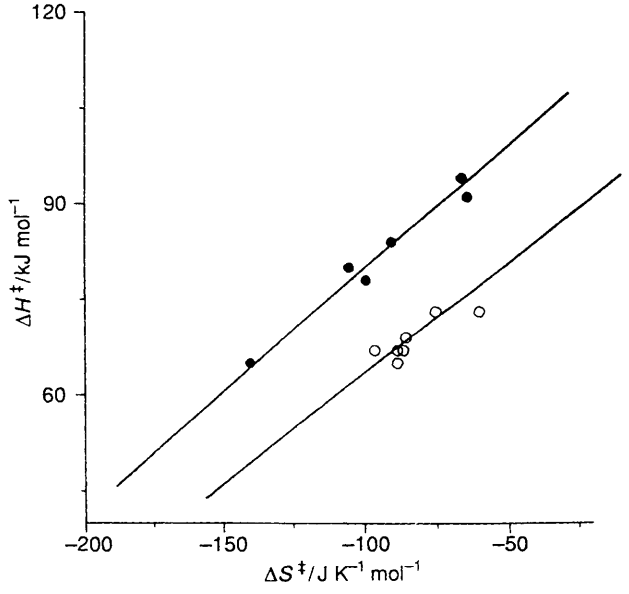


Fig. 5 Isokinetic plots for cyclometallation reactions of the systems studied. Full symbols represent the thermal path, empty symbols the acid-catalysed path. The gap between the lines corresponds to *ca.* 20 kJ mol^{-1}

bulky auxiliary ligands favour cyclometallation reactions. We assume that steric factors are also mainly responsible for the observed activation when an excess of triphenylphosphine is added to **2**. One phosphine can replace the axial ligand in **2** favouring a better interaction between the equatorial phosphine and the metal centre. This result indicates that, by a different path, phosphines also act as a catalyst in these reactions.

Reaction Mechanism.—On the basis of the above-mentioned data, we propose for the thermal cyclometallation the mechanism shown in Scheme 2. A highly ordered transition state should be responsible for the very negative values of the activation entropy. Furthermore, the presence of a deuterium kinetic isotopic effect of *ca.* 0.5–0.8 seems to indicate that in this transition state the C–H bond-breaking process is not very advanced.

For the acid-catalysed reaction, we propose a variation of this mechanism (Scheme 3). Now a fast protonation equilibrium of species **2** takes place followed by the rate-determining step of the reaction. The K values for this equilibrium derived from the fit of the data by the proposed rate law, although including a large error, indicate that this protonated species exists in low concentration, as expected when one compared acidity constants of co-ordinated species with those of the free acid.[8]

Even though the nature of the protonated species resulting from this equilibrium is not completely clear, we believe that this reaction most probably involves protonation of the chelate acetate group. Recent kinetic results obtained for the exchange of acetate groups by acetic acid in related dirhodium(II) species support this assumption.[9] The transition state produced from there on would be very similar to that shown in Scheme 2 for the thermal process, the difference being the nature of the leaving species. For the acid-catalysed process this should be $H_2O_2CMe^+$ while for the thermal process it should be HO_2CMe, a much poorer leaving group. Consequently, a dramatic increase in the reaction rate constant has to occur when any sort of protons are present in the medium, as is observed.

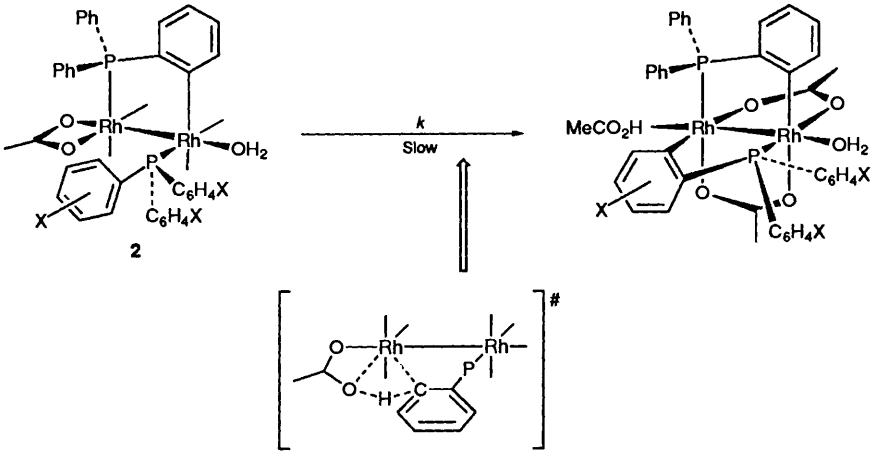
Nevertheless, the exact nature of the protonated species and transition state for this acid-catalysed process is not evident. The presence of acetic acid in the medium results in a simultaneous dynamic process involving exchange of the carboxylate ligands with the acetic acid. This effect has already been observed for other dirhodium(II) compounds.[9]

Data in Tables 2 and 3 show that the activation parameters are only slightly affected by the presence of methyl or chlorine groups in *meta* or *para* positions relative to the phosphorus atom, both for the thermal and acid-catalysed reactions. The negative activation entropies indicate again a highly ordered transition state for the reaction; furthermore, now the deuterium kinetic isotopic effect observed when compound **2** (X = H) has its equatorial phosphine in the deuteriated form, $P(C_6D_5)_3$ (see Tables 2 and 3), is *ca.* 1.5–2.0, indicating that the transition state is happening at a later stage in the reaction coordinate, where the degree of C–H bond breaking is much more important than in the thermal process. On the other hand, the use of deuteriated acetic acid does not give any isotopic effect on the first-order rate constants, but as expected it does affect the reaction rates *via* changes in acidity constants. Changes in the solvent polarity produce the expected effect for a mechanism involving the appearance of a charged intermediate, as shown by the decrease in rate constants observed on substitution of chloroform by toluene in the metallation reaction of compound **2** (X = H). Nevertheless, the overall trend is maintained as shown by the activation parameters.

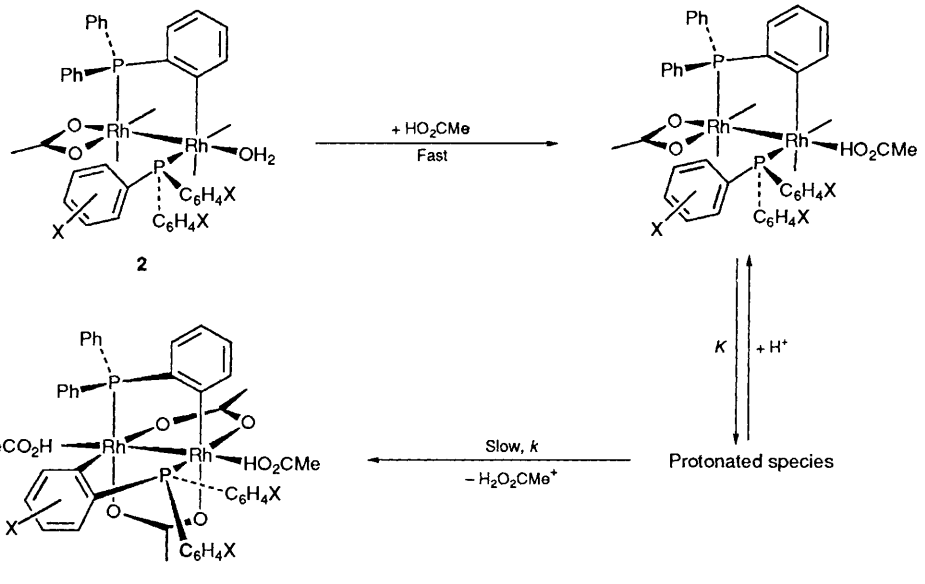
Further studies to clarify additional mechanistic aspects of the metallation reaction are in progress.

Experimental

Procedures and Materials.—The monometallated compound $[Rh_2(\mu\text{-}O_2CMe)_3\{(C_6H_4)PPh_2\}]\cdot 2HO_2CMe$, was pre-



Scheme 2



Scheme 3 H^+ represents any type of solvated proton present in solution

pared according to literature methods.[3f] Commercially available PPh_3, $P(C_6H_4Me\text{-}p)_3$, $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_4Me\text{-}m)_3$ and $P(C_6H_4Cl\text{-}m)_3$ were used as purchased (Aldrich). All solvents were of analytical grade and were degassed prior to use. Triflic acid was used as purchased. The NMR measurements were made on Bruker AC-200 (^{31}P) and Varian 400 MHz spectrometers (^{13}C and ^1H). The UV/VIS spectra were recorded on Hewlett-Packard 8452A or Shimadzu UV-160A instruments.

Preparation of Compounds $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{P(C_6H_4X)_3\}(OH_2)]$ **2** (X = H, *p*-Me, *p*-Cl, *m*-Me *or m*-Cl).—The complex $[Rh_2(\mu\text{-}O_2CMe)_3\{(C_6H_4)PPh_2\}]\cdot 2HO_2CMe$ (0.13 mmol) and PPh_3 (34 mg) were introduced in a photochemical reactor equipped with a mercury-vapour lamp (Osram-125). The solid mixture was dissolved in $CHCl_3$ (100 cm^3) yielding a brown-orange solution. After 30 min of irradiation the solution became green, and the reaction was stopped after 50 min. The solvent was removed under vacuum and the crude product redissolved in CH_2Cl_2–hexane (5 cm^3 : 5 cm^3). The solution was transferred to a chromatography column (30 × 2 cm) packed with silica gel in hexane. Elution with CH_2Cl_2–hexane (1 : 1) separated one minor yellow band which was discarded. Further elution with hexane–CH_2Cl_2–Me_2CO (10 : 10 : 1) separated a green band which was collected and a minor brown band which was discarded. The green fraction was concentrated to dryness under reduced pressure and dissolved in the minimum amount of CH_2Cl_2. Addition of hexane yielded $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}(PPh_3)(OH_2)]$ **2** (X = H) (yield 81%). ^1H NMR($CDCl_3$), δ 1.12 (CH_3, 3 H, s), 1.18 (CH_3, 3 H, s), 1.72 (CH_3, 3 H, s), 6.39 (aromatic, 1 H, q) and 6.5–7.8 (aromatic, 28 H, m) (Found: C, 54.70; H, 4.40. Calc. for $C_{42}H_{40}O_7P_2Rh_2$: C, 54.55; H, 4.35%).

Addition of a drop of acetic acid to the solution of the above water adduct followed by concentration under reduced pressure gave the corresponding acetic acid adduct $[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}(PPh_3)(HO_2CMe)]$ (yield 79%). NMR ($CDCl_3$): ^1H, δ 1.08 (CH_3, 3 H, s), 1.16 (CH_3, 3 H, s), 1.69 (CH_3, 3 H, s), 2.16 (CH_3, 3 H, s), 6.38 (aromatic, 1 H, q), 6.5–7.8 (aromatic, 27 H, m) and 8.6 (aromatic, 1 H, m); $^{31}P\{^1H\}$ (CH_2Cl_2), δ 14.7 [$^1J(Rh\text{–}P_A)$ = 137.8, $^2J(Rh\text{–}P_A)$ = 10.1], and 41.5 [$^1J(Rh\text{–}P_B)$ = 187.2, $^2J(Rh\text{–}P_B)$ = 4.1 Hz]; $^{13}C\text{-}\{^1H\}$ ($CDCl_3$), δ 21.37 (CH_3, s), 22.58 (CH_3, s), 23.26 (CH_3, s), 23.75 (CH_3, s), 121–143 (aromatic, m), 183.12 (OCO, s), 183.89 (OCO, s), 184.23 (OCO, s) and 187.56 (OCO, s) (Found: C, 54.10; H, 4.50. Calc. for $C_{44}H_{42}O_8P_2Rh_2$: C, 54.60; H, 4.35%).

Analogous procedures were used to obtain compounds with $P(C_6H_4X)_3$ where X = *p*-Me, *p*-Cl, *m*-Me or *m*-Cl.

$[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{P(C_6H_4Me\text{-}p)_3\}$-

(OH_2)]: yield 84%. ^1H NMR ($CDCl_3$), δ 1.16 (CH_3, 3 H, s), 1.24 (CH_3, 3 H, s), 1.82 (CH_3 3 H, s), 2.36 (CH_3, 9 H, s) and 6.4–7.9 (aromatic, 25 H, m).

$[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{P(C_6H_4Me\text{-}m)_3\}(OH_2)]$: yield 78%. ^1H NMR ($CDCl_3$), δ 1.16 (CH_3, 3 H, s), 1.25 (CH_3, 3 H, s), 1.67 (CH_3, 3 H, s), 2.23 (CH_3, 9 H, s) and 6.3–8.2 (aromatic, 25 H, m) (Found: C, 52.60; H, 4.70. Calc. for $C_{45}H_{46}O_7P_2Rh_2{\cdot}CH_2Cl_2$: C, 52.80; H, 4.30%).

$[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{P(C_6H_4Cl\text{-}p)_3\}(OH_2)]$: yield 81%. ^1H NMR ($CDCl_3$), δ 1.17 (CH_3, 3 H, s), 1.25 (CH_3, 3 H, s), 1.81 (CH_3, 3 H, s) and 6.3–8.2 (aromatic, 25 H, m) (Found: C, 46.75; H, 3.65. Calc. for $C_{42}H_{37}Cl_2O_7P_2Rh_2{\cdot}2CH_2Cl_2$: C, 46.70; H, 3.45%).

$[Rh_2(O_2CMe)(\mu\text{-}O_2CMe)_2\{(C_6H_4)PPh_2\}\{P(C_6H_4Cl\text{-}m)_3\}(OH_2)]$: yield 81%. ^1H NMR ($CDCl_3$), δ 1.14 (CH_3, 3 H, s), 1.25 (CH_3, 3 H, s), 1.68 (CH_3, 3 H, s) and 6.4–7.6 (aromatic, 25 H, m) (Found: C, 49.30; H, 3.50. Calc. for $C_{42}H_{37}Cl_2O_7P_2Rh_2{\cdot}CH_2Cl_2$: C, 49.45; H, 3.75%).

Characterization of Type **3** *Products.*—The doubly metallated type **3** products were isolated and characterized by the procedure described.[3f,j]

Kinetic Measurements.—The reactions were followed spectroscopically in the full 750–450 nm range on a Hewlett-Packard 8542A instrument equipped with a multicell transport thermostatted (± 0.1 °C) by use of a circulating bath. Observed rate constants were derived from the absorbance *versus* time traces at the wavelengths where a maximum increase and/or decrease in absorbance was observed. No differences in the values were detected for different wavelengths as expected for reactions where a good retention of isosbestic points is observed.

All runs were performed under psuedo-first-order conditions and rate constants were derived from exponential least-squares fitting by a Marquardt algorithm. Least-squares errors for the rate constants were always in the range of 3–8% of the calculated value. All post-run fittings were done by the standard equipment of the HP8452A instrument. Solutions were prepared by mixing the calculated amounts of thermostatted solutions of the rhodium compound and acetic acid (or acetic–triflic acid and acetic acid–sodium acetate mixtures) in 1 cm optical path spectrophotometric cells. For the reactions in the absence of acid calculated amounts of the rhodium compound were directly dissolved in the cell with thermostatted toluene. The concentration ranges used were (1–5) × 10^{-3} mol dm^{-3} rhodium compound, 0.3–9 mol dm^{-3} acetic acid, (1.5–10) × 10^{-2} mol dm^{-3} triflic acid and (1–2.5) × 10^{-2} mol dm^{-3} sodium acetate.

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